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U.S. DEPARTMENT OF ENERGY

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

FINAL PROCEEDINGS

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Department of Energy
Washington, DC 20585

May 30, 1996

Dear Colleague:

Enclosed are the final proceedings for the Plutonium Stabilization & Immobilization Workshop held in December 1995. The Workshop's purpose was to foster communication within the technical community on issues surrounding stabilization and immobilization technologies for the Department of Energy's surplus plutonium and plutonium-contaminated wastes. An additional objective of the Workshop was to build a common understanding of the performance, economics, and the maturity of stabilization and immobilization technologies. The Workshop brought together individuals and groups with differing interests and viewpoints. We believe that the Workshop successfully served as an initial step toward accomplishing these objectives.

The proceedings include the papers presented at the sessions, the major discussions, and summaries of the breakout sessions.

I'd like to extend my wholehearted thanks and appreciation to all of you who attended and participated in the Workshop, and who helped to make the Workshop a success.

Sincerely,

Richard J. Guimond

Richard J. Guimond
Assistant Surgeon General, USPHS
Principal Deputy Assistant Secretary
for Environmental Management

Enclosure

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

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DECEMBER 12-14, 1995

WORKSHOP PURPOSE AND OBJECTIVES

WORKSHOP PURPOSE...

TO FOSTER COMMUNICATION WITHIN THE TECHNICAL COMMUNITY ON ISSUES SURROUNDING STABILIZATION AND IMMOBILIZATION OF THE DEPARTMENT'S SURPLUS PLUTONIUM AND PLUTONIUM-CONTAMINATED WASTES.

WORKSHOP OBJECTIVES...

TO BUILD A COMMON UNDERSTANDING OF THE PERFORMANCE, ECONOMICS AND MATURITY OF STABILIZATION AND IMMOBILIZATION TECHNOLOGIES...

TO PROVIDE A SYSTEM PERSPECTIVE ON STABILIZATION AND IMMOBILIZATION TECHNOLOGY OPTIONS...

TO ADDRESS THE TECHNICAL ISSUES ASSOCIATED WITH TECHNOLOGIES FOR STABILIZATION AND IMMOBILIZATION OF SURPLUS PLUTONIUM AND PLUTONIUM-CONTAMINATED WASTE.

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

SESSION PURPOSES AND OUTCOMES

HIGHLIGHTS OF WORKSHOP SESSIONS

SESSION	PURPOSE	OUTCOME
Introductory	State the purpose of the workshop. Provide overviews of the stabilization and immobilization programs as well as stakeholder views.	Sets the stage for the following sessions, provides background information, shows broadly how the DOE Office of Environmental Management (EM) and Office of Fissile Materials Disposition (MD) program complement each other.
Materials and Conditions	Provide information as to the types and quantities of materials that must be stabilized with emphasis on their chemical nature and the status of technologies for characterization.	Sets the stage for the following session on how stabilization will be addressed by defining our under-standing of the current status of materials.
Stabilization Standards and Applications	Provide information as to the materials condition expected after stabilization (i.e. standards), the technologies that could be used for stabilization, and how the stabilization technologies could be applied to the materials described in the previous session.	Better understanding of stabilization requirements. Better understanding of the match between residue types and technologies. Better understanding of technology limits and development needs. Description of feed materials for the immobilization process.
Immobilization Waste Forms	Provide historical perspective. Discuss the principal waste forms (glass and ceramic) in terms of composition, plutonium solubility, radiation spiking, poison addition, problems and development needs.	Better understanding of match between immobilization feeds and waste forms. Provides a clear picture as to what is known and what must still be studied.
Immobilization Facilities	Discuss engineering aspects of technologies including feed treatment, design, flowsheets, offgas, waste streams, technology maturity, economics, safeguards and security.	Provides a description and status of the principal technologies under study and identifies the development needs.
Long Term Performance	Provide discussion of leaching, safeguards and security, and retrievability from a longterm perspective.	Describe long term issues that require resolution.
Breakouts	Provide for more in-depth technical discussion of key issues. Allow for continued discussion of items from the invited paper sessions. Allow for alternative technical points of view and technical items not covered by the papers.	Better understanding of DOE technical strategy.
Summary		Reports from breakout sessions, synthesis of breakout sessions. Overall workshop summary.

WORKSHOP PERSPECTIVES

Workshop Perspectives

Jeffrey N. Kass, Lawrence Livermore National Laboratory and
Randy Erickson, Los Alamos National Laboratory
Workshop Technical Leads

This workshop was designed to allow discussion of the full range of technological activities that must occur in order to (1) chemically stabilize plutonium containing scraps and residues and then (2) convert the scraps and residues as well as other forms such as excess pits into an immobilized form that is not suitable for subsequent weapons use. The latter effort is termed disposition. Immobilization, along with reactor burning and burial in a deep borehole are being considered for the disposition effort. We also included a discussion of some issues associated with eventual entombment of the immobilized forms in a mined geological repository. The time frames for these activities differ. The chemical stabilization effort has a relatively near term focus of about 6 years. The disposition effort has an intermediate time frame of 10 to 20 years, and the potential entombment in a mined geological repository has a very long time frame. The workshop was, of course, also intended to provide a broad range of technical views as to how this complex process might be accomplished. We are very grateful for the constructive participation by many non government officers, and are very pleased by the participation of scientists from universities as well as scientists from overseas, particularly those from Russia. The papers presented by the Russian team were of high quality and added significantly to the quality of the workshop. Staying abreast of technology developments outside the United States is recognized as an important element of the overall effort. We have learned several important items from the results of this conference, especially about the interfaces between the important stages in the overall process for dealing with these materials.

We have found that there is a variety of plutonium forms. These range from fabricated metallic weapons components, to metal and oxide, and also to a varied group of scraps and residues. Many of the scrap and residue forms are currently in a condition that requires treatment to assure long term chemical stability. While chemical characterization of all scraps and residues is not yet complete, there is enough information to begin conceptual design and development activities along with stabilization operations for some of the material forms. Studies at each site have resulted in identification of the materials for which chemical stabilization is most time urgent. The complexity associated with the broad range of plutonium scrap and residue chemical forms results in the need for careful examination of each type of form to assure the proper stabilization techniques are selected and applied. The Department of Energy, along with its supporting labs and plants have surveyed the materials that must be treated and have identified a broad range of treatments that can be used. It is likely that no single treatment technology will be adequate for the full range of scraps and residues. Instead, varying treatments will be selected for individual types of residues based on technical and economic considerations. A research program has been started to develop some new stabilization approaches. There are a number of interesting and useful immobilization technologies that are available for the chemical stabilization work. While these immobilization for stabilization techniques are promising, some additional development work is needed before application to plutonium bearing scraps and residues. Our Russian colleagues described some additional techniques that may also be useful.

Immobilization is also being developed as one of the principal options for disposition of excess fissile materials - the process that will render these materials unsuitable for subsequent weapons use. In this sense, the chemical stabilization processing provides part of the feed to the immobilization for disposition work. Therefore, the chemical stabilization processing must be done in a manner that does not prevent or unduly complicate subsequent disposition. Both ceramic and glass forms are being considered for the immobilization disposition work but the overall technology is not yet as mature as that of reactor burning. This is not surprising, given the extensive experience in reactor technology throughout the world and the European experience in burning mixed oxide fuel. There is considerable experience in immobilization of high level waste using glass and, to a lessor extent, ceramics, but there is very little experience in immobilization of plutonium. Nevertheless, considerable progress has recently been made in identifying suitable glass and ceramic materials as well as processing approaches. These studies have shown that plutonium can be immobilized and that practical processing appears to be feasible. Specifications for immobilization have not yet been established. There is a general understanding that leach rates in a repository environment must be acceptable and that a radiation field that would be lethal to a potential terrorist must be present until repository employment to assure the plutonium cannot be readily extracted but considerably more work must be conducted to establish the needed specifications. It is hoped that as these studies progress to an extent suitable to justify investment of significant funds, a pilot plant or prototype processing facility can be established. Some technologies presented by our Russian colleagues are very interesting and may provide significant advantages.

The last part of the workshop was devoted to discussion of some issues associated with the possible eventual entombment of immobilized forms in a geological repository. Safeguards and security, with particular emphasis on retrievability was discussed. This discussion was important because, if the end goal is to render the excess plutonium not suitable for subsequent weapons use, then retrieval from a mined geological repository must be less attractive than alternative means of obtaining plutonium for weapons use.

In summary, this conference was very useful because it served as a forum for discussion of technologies and technological issues associated with the overall process of converting excess weapons plutonium in its current form to a form that is no longer suitable for subsequent weapons use. Important programmatic interfaces were identified and progress was made in international cooperation on this crucial issue.

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

INTRODUCTORY SESSION

SESSION CHAIR: JILL LYTLE, US DEPARTMENT OF ENERGY,
OFFICE OF ENVIRONMENTAL MANAGEMENT

Introductory Session Opening Remarks
Jill Lytle, US DOE Office of Environmental Management

I am Jill Lytle and I am the Deputy Assistant Secretary for Nuclear Materials and Facilities Stabilization in the Department of Energy. I want to welcome all of you to this Plutonium Stabilization & Immobilization Workshop.

The purpose of the meeting is to foster communications within the technical community on issues surrounding both the stabilization and immobilization of the Department's surplus plutonium and plutonium-contaminated waste. This is a technical meeting, not a policy meeting. Since the Office of Material Disposition in the Department, is preparing a programmatic environmental impact statement, the Department and its contractors are necessarily constrained on discussing a preference for one technology over another for immobilization. However, I believe we can discuss the technical issues thoroughly about each of the technologies. We tried to design the workshop to have a very productive technical discussion. What I'd like to do is just briefly review the outline of the plenary sessions. These are the topics we are going to be covering in the plenary sessions today, tomorrow, and Thursday.

I want to mention that these plenary sessions will be audio taped so that we will be able to have the benefit of a translation.

Second, I would like to show you the outline of the breakout sessions. These are the various specific topics that we will be doing in breakout sessions. Before we go on with our main meeting, I would like to ask Elaine Powell, however, to come up and give you some logistics information.

Introductory Session:
Plutonium Stabilization and Immobilization Workshop Objectives

Thomas P. Grumbly
Assistant Secretary for Environmental Management

INTRODUCTION

Good Morning. Thank you all for coming to this workshop on the stabilization and immobilization of the Department s surplus plutonium and plutonium-contaminated materials. I would like to extend a special welcome to our Russian friends who have made such a long trek to attend this workshop. I think your participation speaks exceptionally well of the kind of cooperation required between our two nations to assist each other in the profoundly vexing problems of dealing with plutonium, to invest in better solutions to common problems. I understand that we also have people here from other countries including Australia, France and Germany. And we thank you for participating.

It is precisely this theme of cooperation and teamwork that I hope permeates the next three days at this workshop and beyond. Henry Ford had a formula for it: Coming together is a beginning; keeping together is progress; working together is success. Today, we have come together to work on these issues, although it did take much longer than I envisioned when we committed to conducting such a meeting. For plutonium stabilization and immobilization, we are at steps two and three in Mr. Ford s formula: progress and success is dialogue and working together.

Purpose of the Workshop

During this workshop, I hope that the scientific community can achieve a meaningful dialogue on the scientific issues and technologies for the stabilization and immobilization of surplus plutonium and plutonium contaminated waste. There has been a great deal of public discussion and debate on policy questions involving plutonium stabilization and immobilization. That is not why we have gathered here today. We have structured this workshop so we can have a productive **technical** not policy discussion about the various plutonium-related technical issues and technologies. And I believe this forum will build a common understanding of the performance, economics, and maturity of stabilization and immobilization technologies.

As many of you know, this workshop was originally intended to focus on vitrification and other immobilization options. We quickly broadened the focus to include both Immobilization and Stabilization. Immobilization is our word for a range of technologies, including vitrification, that we can use to meet the spent fuel standard for the disposition of surplus plutonium. Stabilization is more about preparing plutonium scrap and residues for storage until final disposition can take place. We felt it was important to include the aspect of stabilization that must interface with the long term activities of immobilization. The stabilization activities are the near term activities that Environmental Management is conducting to address to address the more immediate safety problems such as repackaging Plutonium Metal and placing our liquid waste into a safer configuration.

All of us at DOE are trying to make the best technology choices for stabilizing and dispositioning plutonium and plutonium-contaminated materials. Mr. Greg Rudy, Director of the Office of Fissile Materials Disposition, will outline the process being used to evaluate the reasonable disposition alternatives against the disposition criteria. My colleagues are doing a wonderful job at answering some tough questions, and we re making similar progress against the plutonium stabilization problems. However, our choices are limited by history. Since DOE has never before wanted or needed to stabilize, immobilize or otherwise disposition plutonium, we have never made an effort to develop the technologies to do it. We can do a lot to piggyback onto technologies developed for other uses, but the sad fact is that innovative ideas like immobilization have not had the benefit of decades of research, development and demonstration. That is one reason why we sponsored this workshop: to help strengthen the technical side of what may be some very attractive policy options, and to try, if we can, to level the playing field.

This conference comes at a propitious moment in this historic transition from plutonium extraction to plutonium stabilization emphasis. As you know, the Department is currently preparing an EIS on plutonium disposition. Whether or not direct immobilization is chosen in that EIS for the bulk of plutonium, it is clear that more research in this area will be needed because of the other forms of plutonium such as residues, which will need stabilization. As many of you know, Senator Helms last week agreed to allow the START II treaty to be voted on in the Senate where we are expecting ratification. This treaty, initially signed by a previous administration, would dramatically reduce the size of the nuclear weapons arsenal. This action simply codifies the reality of the end of the Cold War.

So we are poised at the brink of a new era. This new era challenges us to think in new ways, act in new ways, and to develop new tools to help in these endeavors. During the Cold War we valued separated pure plutonium, and we developed extraordinary machines to help us do this. We built some of the largest industrial operations the world has ever known, resulting in some of the most daunting environmental challenges we have ever grappled with. Now our national priority has turned from the purity of the plutonium to the safety and the proliferation resistance of plutonium. The National Academy of Science has set the benchmark that has been well accepted now -the spent fuel standards -- for nonproliferation. We now need a similar standard for the safety of plutonium. Perhaps this and other workshops will contribute to fulfilling that ambition.

I don t expect this workshop will be able to resolve or even fully address all the technical issues facing us. I do hope, however, that we today are starting a process for resolving the issues, and that there will be other technical workshops in the future. We need to understand how the various aspects of plutonium storage, treatment, and disposal fit together. We need to gain an understanding of the risks and benefits of various technologies. While the focus is on technical aspects of our program, I want to assure you that we fully appreciate the need to consider non-technical aspects of acceptance of technology and have tried to encourage interaction with stakeholders and regulators. To provide some perspective on plutonium, let me briefly give some background.

Background: Long Term vs. Short Term

Plutonium began as, and has remained, a controversial subject. When it was first discovered, right after the discovery of the element Neptunium, it seemed appropriate to name it after the next planet, Pluto. Pluto was the Roman God of the underworld, but the name comes from the Greek word *ploutos,* which means wealth. Clearly, the scientists working on the Manhattan project appreciated the double meaning of Pu. One can see that, even before the first nuclear chain reaction was achieved, there has been tension between the energy value of nuclear power and the destructive potential of nuclear weapons.

Plutonium has done its first job-- nuclear weapons were built to help keep the peace in the post-World War II era-- but now, to assure peace, safety, and national security for decades (even centuries) to come, we need to earnestly debate and discuss what to do with it. In the **short term**, we need to stabilize these fissile materials and ensure adequate physical security against terrorist theft or sabotage, safeguards against proliferation, and protection against environmental and health risks, such as those outlined in Defense Nuclear Facilities Safety Board Recommendation 94-1. This is the responsibility of the Office of Environmental Management. Over the **long term**, we need viable disposition. In a rough division of labor, that is the responsibility of the Office of Fissile Materials Disposition. One can plainly see that the cooperation between our offices needs to be absolutely exceptional.

The short term and long term issues associated with plutonium are inextricably linked-- they have more of a 'chicken and egg' twist than some of our other problems. We have to establish a sound long term protocol in order to make good short term decisions in stabilizing these materials. But it will take us years to implement that long term policy, and we can't wait that long to stabilize and safely store the plutonium bearing materials around the complex. Many of them are in 'temporary' storage situations, at best; and the definition of 'temporary' has turned out to be longer than was intended in many cases, so we have to act quickly to control urgent environmental, safety and health risks. At the same time, we have to be careful that our short term solutions don't work against viable long term options-- and through it all, we need to coordinate our environmental, safety and health concerns with our nuclear nonproliferation objectives. Ideally, it would be desirable to treat materials once and maximize the cost effectiveness of all the operations throughout DOE. Thus, it is critical that we establish technical understanding of the activities and bring together the researchers all around the Department to insure that our efforts are coordinated.

So, acknowledging that we can't have totally separate discussions of short term versus long term, and recognizing that in this whole area we have to be simultaneously pragmatic and visionary, I hope that the technical discussions of the following sessions lead to a greater understanding of and greater integration and focus between the long term and short term activities.

Where is it, Whose is it and What Form?

Let me give an rough overview of the different forms, locations, and ownership of the Department s unclassified plutonium. Not counting classified amounts of plutonium at the Pantex site, the Department currently has more than 33 metric tons of plutonium in various forms at 13 'major sites' and 22 'other sites' throughout the complex. This plutonium falls into three general categories: plutonium metal, in the form of pits, buttons and ingots; plutonium oxides, either plutonium dioxide or plutonium trioxide of weapons grade specification; and plutonium residues, defined as materials excess to the Department's needs that require significant processing in order to separate the plutonium. These residues exist in both liquid and solid form, and generally contain less than 28% plutonium.

The bureaucratic custodians of all of this material include:

- Defense Programs, which is responsible for "strategic reserves" of plutonium, and for nuclear warhead stockpile maintenance;

- The Office of Fissile Materials Disposition, which is responsible for the Department's technical and management activities to provide for the disposition of fissile materials declared surplus to national defense; and

- Environmental Management, which is responsible for plutonium-contaminated waste, ranging from lightly dusted booties to heavily laden sludge. We are also responsible for facilities. We operate many storage vaults for plutonium scrap, including hemishells intended for pits. A single plutonium vault at Hanford costs $30 million per year to maintain and keep secure. We are responsible for stabilization facilities, such as the F- and H-Canyons at the Savannah River Site, which contain considerable amounts of plutonium in different forms.

"Who owns what" within the Department of Energy can be hard to keep track of at times. Let me describe the responsibilities by describing the situation at three "EM landlord" sites, that is sites where the budget comes out of the Environmental Management account. These sites contain significant amounts of plutonium materials. At Rocky Flats, there are a total of about 13 metric tons of plutonium in the form of metals, plutonium oxides, and plutonium residues. At Hanford, there are 4 metric tons of plutonium oxides in addition to 7.2 metric tons of reactor fuels. During past transfers of responsibilities at various sites, the "ownership" of non-waste special nuclear materials has remained with Defense Programs with the exception of the plutonium residues at Rocky Flats. While Defense Programs continues to retain "ownership" of these materials, it is in name only. Environmental Management is responsible for the buildings the material is stored in as well as the security, inspection, stabilization, repackaging and consolidation of these materials to provide safe and efficient storage. I hope this quick background in plutonium sets the stage for more detailed discussions.

Workshop Papers

The agenda includes many good scientific papers, but it doesn t include all the papers you volunteered to provide at the originally scheduled August workshop. It s simply an embarrassment of riches. My announcement for this meeting and the call for papers resulted in far greater interest than we had anticipated. I regret that we could not include all of the excellent papers that were submitted. Due to time constraints, we had to make difficult decisions on the use of papers that represented the principal thrusts of the science and policy advice that we are receiving. I encourage all of you who prepared papers, whether or not you are presenting them at this meeting, to seek out peer reviewed journals and have your papers circulated as widely as possible to invite thought and discussion. How we dispose of these materials will be a science and policy issue for years to come. The more discussion we encourage at the outset, the easier our job will be in the long run.

CONCLUSION

This workshop is structured to help promote the exchange of information among the various organizations. For the most part we ll work in plenary sessions to maximize the exchange of information across program lines. This introductory session is designed to provide an overview of various activities within the Department, and external to the Department, to place the more technical information into context. I want to thank Dr. Anderson, the head of the Russian Delegation and Dr. Kushnikov, a member of this panel; Dr. Paul Leventhal from the Nuclear Control Institute; Mr. Davis Hurt from the Defense Board; Mr. LeRoy Moore from the Rocky Mountain Peace Center; Mr. Hank Dalton who heads the Department s Plutonium Stabilization Task Force; and Dr. Leonard Gray from Lawrence Livermore National Lab, for working with Greg Rudy and my staff and participating in this workshop.

Let me repeat that we do not expect to resolve all the issues at this workshop. Many of them will require additional study, and the Department must follow the NEPA process before we make decisions. But this workshop should be a significant step in our journey towards the optimal combination of *intelligent* and *publicly acceptable* behavior with respect indeed, with a lot of respect! to Plutonium.

To conclude, let me reaffirm my belief that principles of democracy can best be fulfilled by providing opportunities such as this for exchange of technical information and working cooperatively in solving complex problems. I recall what Thomas Jefferson said: I know of no safe depository of the ultimate powers of society but the people themselves; and if we think them not enlightened enough to exercise their control with a wholesome discretion, the remedy is not to take it from them, but to inform their discretion. I thank you for attending. I trust that as we listen to each other, we will be better informed; and that as we become better informed, our behavior will steadily approach the ideal of wholesome discretion.

DISCLAIMER

The views expressed in this paper are those of the author and do not necessarily reflect any views, proposed actions, or decisions of the United States Government or any agency thereof.

Overview of Surplus Weapons Plutonium Disposition

Greg Rudy
Acting Director
Office of Fissile Materials Disposition

Thank you, and good morning. The safe disposition of surplus weapons useable plutonium is a very important and urgent task with profound environmental, national and international security implications. We can all be proud to be a part of a group of concerned and capable professionals that are working to contribute to success in reducing the global nuclear danger.

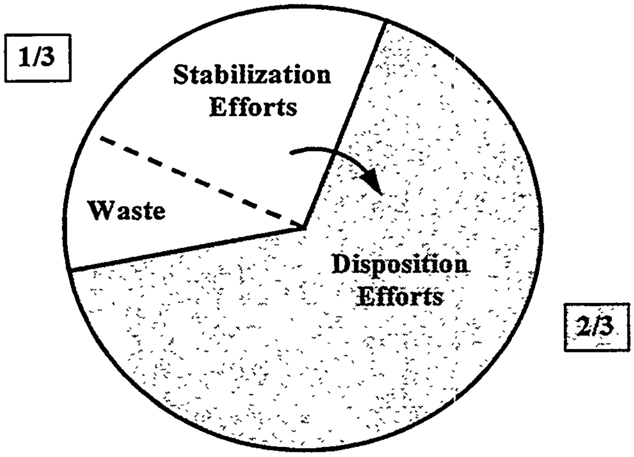
By way of quick background, the end of the Cold War, Presidential Policy Directive 13, and various thoughtful analyses by renown scientific, technical and international policy organizations have brought about a focused effort within the Department to identify and implement paths forward for the long term storage and disposition of surplus weapons useable highly enriched uranium and plutonium.

Within the Department, the organizational focus on this issue was started in early 1994 by the Secretary's formation of a small cross-cutting project organization. Subsequently, in October, 1994, a permanent office was formed by statute, reflecting the importance that Congress places on this task.

While the functions of long-term storage and disposition directly relate to the Department's weapons program and the environmental management program, the focus of this effort is particularly national security and nonproliferation. In the very near term, additional specific information on the quantities, forms and locations of the surplus highly enriched uranium and plutonium will be declassified and made publicly available. In the interim, the figure below provides a summary breakdown of the surplus plutonium inventories being addressed by the Department.

As we move forward in our efforts to evaluate technologies for disposition of the surplus plutonium, we are also working jointly with Russian counterparts on a joint study of plutonium disposition options. This joint study, initiated by President's Clinton and Yeltsin in 1994, will provide a consistent comparison of a range of technology options for plutonium disposition. It will address nuclear nonproliferation, safety, environmental, technical and economic factors. It is important to note that the particular technology paths eventually chosen by the United States and Russia need not be necessarily identical. The central, overarching goal is to render surplus weapons plutonium as inaccessible and unattractive for reuse in nuclear weapons, as the much larger and growing stock of plutonium contained in civilian spent reactor fuel. The technology options under study will be evaluated against a set of common criteria. I'll briefly discuss some of the criteria a bit later.

The joint study is well underway and the working groups recently completed a productive meeting in Oak Ridge last week. Follow-on meetings are planned for January and the final joint study effort should be completed this coming summer.



Nominal 50 Metric Tons Planning Basis

Figure 1: Of the nominal 50 MT plutonium declared surplus, roughly one-third requires some stabilization to address near-term health and safety concerns. Some of that stabilized plutonium will join the remaining two-thirds of stable plutonium forms in safe, secure storage until disposition efforts commence.

Our efforts to arrive at a decision for the disposition of surplus U.S. plutonium include environmental analyses, as required by the National Environmental Policy Act, and technical, schedule, cost and policy considerations. As part of this decision process, the Department participates in the Interagency Working Group on Plutonium Disposition that is co-chaired by the President's Office of Science and Technology Policy and the National Security Council. Taken together, the environmental and technical, schedule, cost, and nonproliferation policy analyses will enable a record of decision on the long-term storage and disposition of surplus weapons useable plutonium late next year.

We started this process in mid 1994 with a Notice of Intent to prepare a Programmatic Environmental Impact Statement (PEIS) on the Long-term Storage and Disposition of Surplus Plutonium. This was followed by a series of public scoping meetings late last year and separate technical information sessions. At the start, there were some 37 technology options, many with numerous subsets or variants. Later in the course of this workshop, Leonard Grey of LLNL will be talking about many of the 70+ vitrification variants initially identified within the immobilization family of options.

During the scoping sessions, we received public and industry comment on a set of criteria against which the various technology options would be initially screened to determine those most appropriate for further review. The criteria are similar to those from the National Academy of Sciences Report:

- Resistance to theft or diversion by unauthorized parties
- Resistance to retrieval, extraction, and reuse by the host nation
- Technical viability
- Environmental, safety and health compliance
- Cost effectiveness
- Timeliness
- Fostering progress and cooperation with Russia and other countries
- Public and institutional acceptance

Based on an assessment of the options against these criteria, we have arrived at the following core set of technology options for surplus plutonium disposition:

- Immobilization options in which plutonium is emplaced in glass, ceramic or glass-bonded zeolite waste forms.
- Reactors options in which surplus plutonium is fabricated into mixed-oxide fuel for use in domestic or Canadian nuclear reactors.
- Deep geologic disposal options in which plutonium in an appropriate form would be emplaced in a deep borehole (roughly 2 - 4 km deep) and sealed for isolation from the accessible environment.

We are currently scheduled to publish the Draft PEIS for long-term storage and plutonium disposition early in 1996 and host another series of public meetings. In parallel, during FY 1996, we are performing R&D and we are planning limited technical demonstrations on the various disposition technology options. Our efforts in these regards include close coordination with Tom Grumbly's office, the field activities and National Labs. An example of a planned demonstration that is most germane to this workshop, is the planned demonstration next week, of a cold test of the "can-in-canister" concept for plutonium disposition utilizing the Defense Waste Processing Facility at Savannah River. One of the sessions tomorrow will be addressing this idea. This "can-in-canister" demonstration is not only an example of how we work together within the Department, but also how we can remain open to suggestions and ideas from our stakeholders.

I am confident that much will be learned and shared during this workshop on the scientific issues and technologies for stabilization and immobilization of surplus plutonium. As Tom noted in his introductory comments, " Progress and success is *dialogue and working together*". Thank you for contributing to progress and success in this important effort.

DISCLAIMER

The views expressed in this paper are those of the author and do not necessarily reflect any views, proposed actions, or decisions of the United States Government or any agency thereof.

Radioactive Waste Management and Plutonium Recovery Within the Context of the Development of Nuclear Energy in Russia

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The Russian strategy for radioactive waste and plutonium management is based on the concept of the closed fuel cycle that has been adopted in Russia and, to a great degree, falls under the jurisdiction of the existing Russian nuclear energy structures.

From its very beginning, Russian atomic energy policy was based on finding the most effective method of developing the new fuel direction with the maximum possible utilization of the energy potential from the fission of heavy atoms and the achievement of fuel self-sufficiency through the recycling of secondary fuel. This also guided Russia's choice between the available options, the reprocessing of spent fuel from nuclear power plants (the "closed" cycle) and the burial of spent fuel without reprocessing (the "open" cycle).

Although there can be no doubt about the importance of economic considerations (for the future), concerns for the safety of the environment are currently of the utmost importance. In this context, spent NPP fuel can be viewed as a waste to be buried only if there is persuasive evidence that such an approach is both economically and environmentally sound.

The production of I GW of energy per year is accompanied by the accumulation of up to 800 - 1000 kg of highly radioactive fission products and approximately 250 kg of plutonium. Currently, spent fuel from the VVER 100 and the RBMK reactors contains approximately 25 tons of plutonium. There is an additional 30 tons of fuel-grade plutonium in the form of purified oxide, separated from spent fuels used in VVER 440 reactors and other power production facilities, as well as approximately 100 tons of weapons-grade plutonium from dismantled warheads. The spent fuel accumulates significant amounts of small actinoids - neptunium, americium, and curium. Science and technology have not yet found technical solutions for safe and secure burial of non-reprocessed spent fuel with such a broad range of products, which are typically highly radioactive and will continue to pose a threat for hundreds of thousands of years.

Figure 1 shows the current situation and near term development plans for the nuclear fuel cycle in Russia.

Implementation of the closed fuel cycle approach to nuclear energy was begun with the start up of the first Russian regenerating facility (1997, Mayak production facility in Chelaybinsk). This plant (RT-1) is a multipurpose facility for the regeneration of spent fuel from VVER 440 reactors, from BN 350 and BN 600 fast breeder reactors, as well as spent fuel from reactors and propulsion systems on icebreakers, submarines, and research reactors. The capacity of the plant for the regeneration of the primary fuel to be reprocessed at this plant, the spent fuel from the VVER 440 reactors, is 400 tons per year. This means that the plant has the capacity to regenerate fuels not only from Russian reactors, but from reactors of the same type in other countries. So far the plant has processed approximately 3000 tons of spent fuel. The recycling of regenerated uranium (conditioning of the fuel for U-235 content is done by mixing) for use in fuel for RBMK and production reactors was begun in 1980, and shortly afterwards a pilot scale program was started for the BN and VVER reactors.

Construction has begun on a new radiochemical plant, the RT-2 complex, which will begin operations in the Krasnoyarsk region. Upon completion of the first phase of the project (plant operations are slated to begin before 2005), the facility will have the capacity to regenerate 1500 tons of spent fuel per year. The already completed storage pond at the new facility contains 1100 tons of spent fuel from VVER 1000 reactors, while another 1000 tons of spent fuel is currently stored at the NPP sites. The spent fuel from the RBMK 1000 and RBMK 1500 reactors is also in interim storage at the NPP storage sites. There are existing regulations governing the long-term (decades) monitored storage of spent fuel.

The guiding principle for the management of radioactive waste from the nuclear fuel cycle is to provide for the isolation of the radioactive waste from the biosphere for the total period that it presents a threat to the environment.

The program of the Russian Federation for radioactive waste and nuclear material management is directed at providing a comprehensive solution. It includes the development of the appropriate legislative and normative basis for regulating radioactive waste management, the development of corresponding technologies, and technical means for the collection, reprocessing, interim storage, recovery and transportation of radioactive waste and spent nuclear materials, as well as the creation of facilities for the assured isolation of these materials from the biosphere during long-term storage and burial.

At the beginning of the nuclear age, the operation of nuclear facilities was accompanied by a "passive" period of accumulation and temporary storage of waste products.

The production of weapons grade nuclear materials at the Mayak production facility, the Siberian Chemical Complex, and the Chemical Mining Facility of Minatom has resulted in the accumulation of radioactive waste with approximately 1.3 billion cu. Approximately 250,000 m^3 of liquid radioactive waste with 570 million cu is held in special storage tanks, while another 400 million m^3 with 700 million cu is stored in open ponds and special pools. Surface plant storage facilities contain radionuclide contaminated materials, equipment, and structures with total radioactivity levels of 12 billion cu.

At the present time, after completion of extensive research and development activities, the nuclear complex facilities have begun the reprocessing and conditioning of accumulated waste for its final burial.

The reprocessing of liquid radioactive waste, especially high level liquid waste, is a complex and costly process. Consequently, at a reprocessing plant the relatively small volume of high level waste (5m^3/t of spent fuel for reprocessing) contains more than 99% of the radioactivity of the spent fuel. Regardless of the level of radioactivity, the general approach to liquid waste processing is in the direction of its solidification, which is closest to the concept of safe burial (see Figure 2, schematic diagram for liquid radioactive waste management at the RT-1 facility).

Research in solidification of liquid radioactive waste began in Russia in the fifties. The first large-scale samples of vitrified high level waste were produced in 1959. The first pilot vitrification plant began operating at Mayak at the RT-1 site in 1987. The technology was based on a direct heating electrical furnace that produces phosphate glass.

The vitrification plant processed over 9100 m^3 of high level liquid waste, producing more than 1800 tons of phosphate glass containing approximately 220 million cu. A second production line for vitrification is currently under construction. At the same time, we are pursuing the development of alternative solidification technologies for high level waste based on a two-stage process. A pilot facility for this technology is under construction. It will use an induction melter with a cold crucible for the immobilization of radionuclides on glass and mineral type matrices.

Vitrified waste is placed in special facilities for safe storage until a final decision is made on its burial in geological formations.

Research is also continuing in the area of matrix material characteristics (glass and mineral type materials for radioactive waste immobilization), in our search for matrices with greater chemical, thermal and radiation stability than phosphate glass.

A series of investigations is being conducted to determine the behavior of vitrified radioactive waste under long-term storage and burial conditions. These studies allow us to determine the processes that take place when vitrified waste comes in contact with a specific geological environment and to develop requirements for environmentally safe management of waste.

Construction is under way of a facility for the vitrification of medium and low level waste. The completion of this facility will make it possible to solidify all types of radioactive waste at the RT-1 site.

The RT-1 vitrification plant immobilizes all radionuclides with the exception of plutonium, uranium and to some extent neptunium, including highly radioactive actinoids and other components, on phosphate glass. Research and development in high level waste separation is also very promising because separation technologies would make it possible to separate the radionuclides in the solutions of the reprocessing facilities taking into account such factors as their half-life, toxicity, as well as the possibility for further utilization of some radionuclides.

Perfection of such technologies will make it possible to choose the optimum and most reliable approach: "incineration", nuclear transmutation in fast reactors or in special electro-nuclear facilities of some radionuclides, while others would be placed in monitored long-term storage and still others could be buried. These promising directions are presented in Figure 3.

Burial of highly radioactive waste requires isolation for hundreds and thousands of years, will be in deep geological formations, in thick rock with low permeability below the level of active water-exchange, in regions of tectonic stability and low seismic activity for the total time that the waste poses a threat. The presence of all possible dangerous biological components will also be taken into account.

In accordance with current plans, by the year 2000 approximately 3 billion curies of radioactive components will be converted into forms that satisfy safety criteria for storage and burial.

The handling of plutonium, its production, separation, storage and utilization, requires the resolution of a very complex series of problems. All of these issues - the utilization of plutonium for nuclear energy production, the further development of the mixed uranium-plutonium fuel cycle and the associated technologies, the role of fast and thermal-neutron reactors and other aspects of plutonium utilization, are intensively studied at the Ministry facilities (the All-Russian Research Institute of Mechanical Engineering, the Institute of Physics and Energy, the Mayak Production Facility, the All-Russian Research Institute for Atomic Reactors, and others).

Research and pilot programs on the utilization of plutonium for energy production and in particular in fast breeder reactors began in the fifties. In the sixties, pilot research reactor cores - BR-5, IBR-2', IBR-30 - as well as experimental fuel assemblies for the BOR-60 reactor were created. The scope of research increased significantly in the 80's. Pilot plants at the Mayak facility, working with different technologies, manufacture uranium-plutonium fuel as well as full-scale fuel assemblies for testing in the BN-350 and BN-600 reactors.

In Obninsk at the Institute of Physics and Energy, tests have been completed on two cores in the fast breeder BR-10 reactor. The plutonium dioxide fuel was manufactured from weapons-grade plutonium.

The BOR-60 research reactor (at the Research Institute for Atomic Reactors in Dimitrovgrad) was used to test and analyze large batches of fuel elements made from uranium-plutonium oxides with different plutonium isotope compositions, manufactured with different technologies. This reactor has been operating for an extended period of time with plutonium fuel (80% Pu-239 and 20% Pu-240).

Tests have been completed of the pilot BN-350 reactor and were followed by research and experiments of chemical reprocessing of mixed U-Pu fuel manufactured from weapons-grade materials. Over 2000 fuel elements of the U-Pu type have been manufactured and tested in the BN-350 and BN-600 reactors. Not one of the fuel elements failed with burn-out reaching 10%, with heat release rates of 490 W/cm and cladding temperatures of 690°C.

The base design for the fast breeder production reactor is the BN 800. There are plans for the construction of a nuclear power complex in the Urals with 3 to 4 fast breeder reactors of this type. The BN 800 design has gone through all required expert analysis, including an economic assessment, and approval has been given by the local regional authorities. The design calls for an initial fueling of 2.3 tons of plutonium with yearly replenishment of 1.6 tons of plutonium. In support of the fast breeder reactor programs, there are plans for the construction at the Mayak production facility of a special plant for the manufacture of uranium-plutonium fuel (plant 300) with a production capacity of 900 fuel assemblies per year. Financial problems have led to a stoppage of construction at the plant, with work completed to 50%. This is also the reason for the slow pace of construction of reactors at the Chelyabinsk and Beloyarsk sites.

Against this background of encountered difficulties, work, is proceeding on fast reactors at small pilot production facilities for the manufacture of new fuel elements and assemblies (the "Granat" and "Paket" facilities, the Mayak production facility and the Scientific Research Institute for Nuclear Reactors) with an increase in the scope of tests conducted and the utilization U-Pu fuel in the BN 600 reactors. Efforts are also being made to continue construction of the BN 800 reactors and plant "300" (and this could be of interest to foreign investors) so that the fast reactors would be ready for large scale utilization of the plutonium for energy production by the beginning of the next decade.

A complex program on U-Pu fuel development falls within the overall program for utilizing plutonium in fast reactors. However, this does not preclude the possibility of plutonium utilization in light water reactors. We have been conducting research and development in this area from the beginning of the decade. This particular program is designed to recycle plutonium from regenerated VVER 1000 spent fuel and is based at the RT-2 facility.

The new problems that have arisen as a result of arms reduction programs are treated within the context of the conversion of weapons-grade materials for use in energy production. However, it is proposed that the utilization of weapons-grade plutonium in the fuel cycle of fast and thermal reactors would for the most part not begin till the existing supplies of fuel-grade plutonium are exhausted. The priority tasks in this area are those dealing with the removal of materials from warheads and safe storage of spent nuclear materials, as well as demonstrating the feasibility of converting weapons-grade plutonium for use in the fuel cycle.

Immobilization of plutonium in glass and mineral type materials, in accordance with standards set for spent fuel, is one of the possible options for conversion of weapons-grade materials. This is one of the directions that needs be pursued in the area of handling highly radioactive waste, which has unique aspects because of the increased concentrations of fissile materials in the end product. The question of safety during the processing of weapons-grade plutonium for the immobilization of the materials on glass or mineral type matrices is one of the main areas to be pursued and requires detailed investigations. In order to be able to determine the feasibility of applying such technologies for the conversion of weapons-grade plutonium, research should be conducted on the following questions:

- the acceptability of existing equipment and technology for the vitrification of liquid highly radioactive waste for the virtification of weapons grade plutonium; analyses and measurement of the process parameters, as well as the equipment, must be carried out for the purpose of increasing safety and reliability;

- the amount of plutonium that can be safely immobilized in glass type materials without changing the physio-chemical properties and structure of the material with the eventual goal of burial;

- development of requirements for physical safety barriers at all stages of the technological process for the immobilization of plutonium;

- determination of the amount of other radionuclides that could and must be included in the glass so that it satisfies standards set for spent fuel;

- determination of the geometric configurations of the vitrified products, the packaging requirements,and development of transportation containers for the transfer of the vitrified materials for burial;

- investigation of safety from the standpoint of criticality at all stages of the vitrification process for weapons grade plutonium, including packaging, temporary storage and transfer for burial;

- investigation of long-term safety issues in order to determine whether in some distant future criticality problems could arise at the plutonium burial sites;

- development of physical measurement techniques for monitoring plutonium content in the containers; development of an MPC&A system; and development of safeguards for the non-proliferation of plutonium at all stages of the immobilization process and burial;

- analysis of all issues connected to burial sites selection, design and construction;

- assessment, analysis and regulation of safety at all stages of the immobilization process for weapons-grade plutonium, including the development of licensing procedures for such technologies;

- development of the normative documentation for regulating the handling of vitrified products that contain significant concentrations of fissile materials.

The search for answers to questions dealing with the handling of spent fuel, plutonium and radioactive wastes is guided by a single principle, i.e., to provide for maximum safety at all stages of the nuclear fuel cycle, in accordance with a special program developed for this industry. Our many years of experience in operating nuclear facilities and the fact that the industry has highly qualified scientific and technical personnel gives us confidence that we can maintain acceptable levels of safety (nuclear, fire, explosion) and provide constant surveillance to monitor all deviations in accordance with international criteria.

DISCLAIMER

SCHEMATIC DIAGRAM OF THE RUSSIAN NUCLEAR FUEL CYCLE

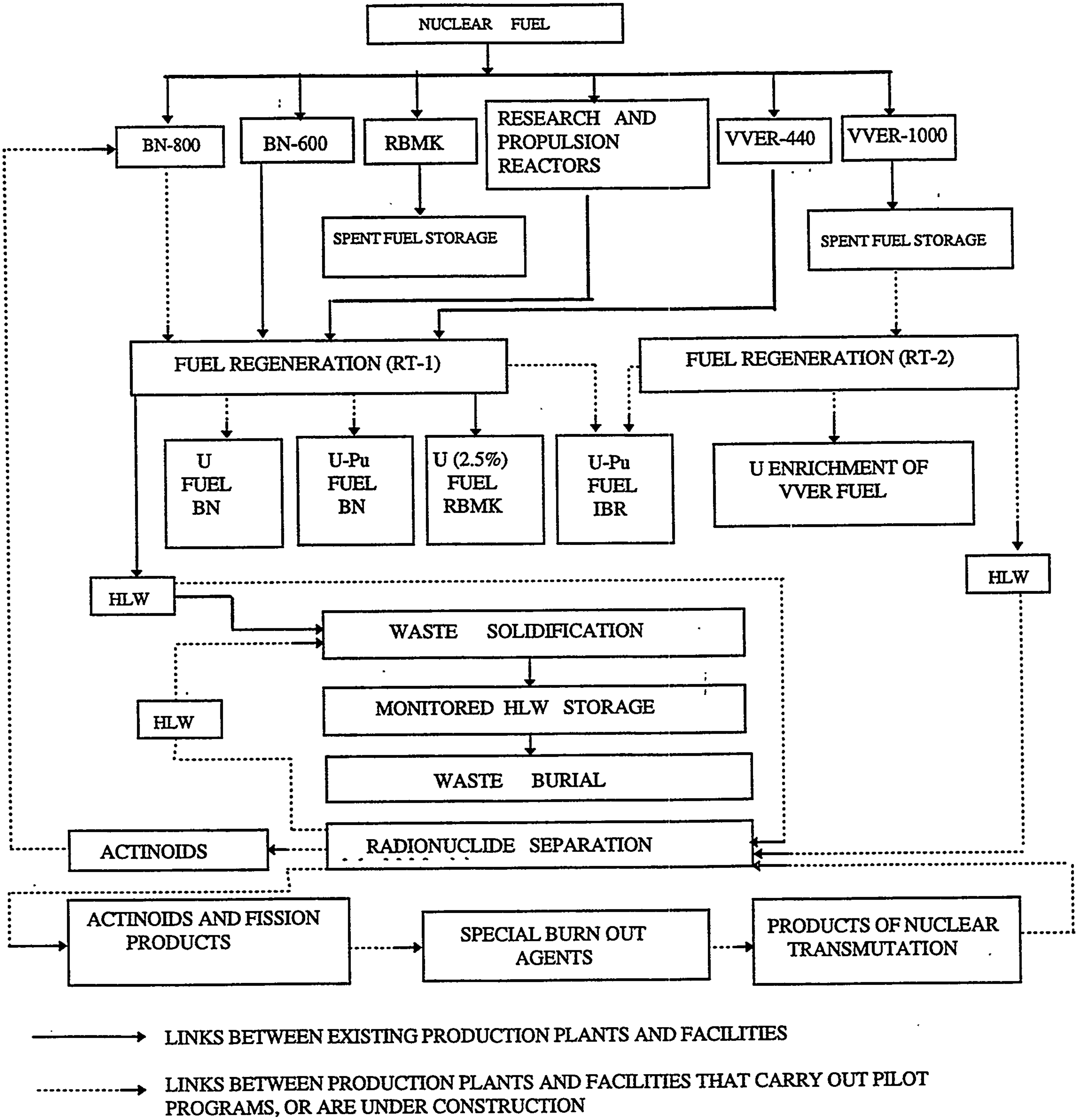

FIG. 1

LIQUID RADIOACTIVE WASTE MANAGEMENT AT THE RT-1 FACILITY

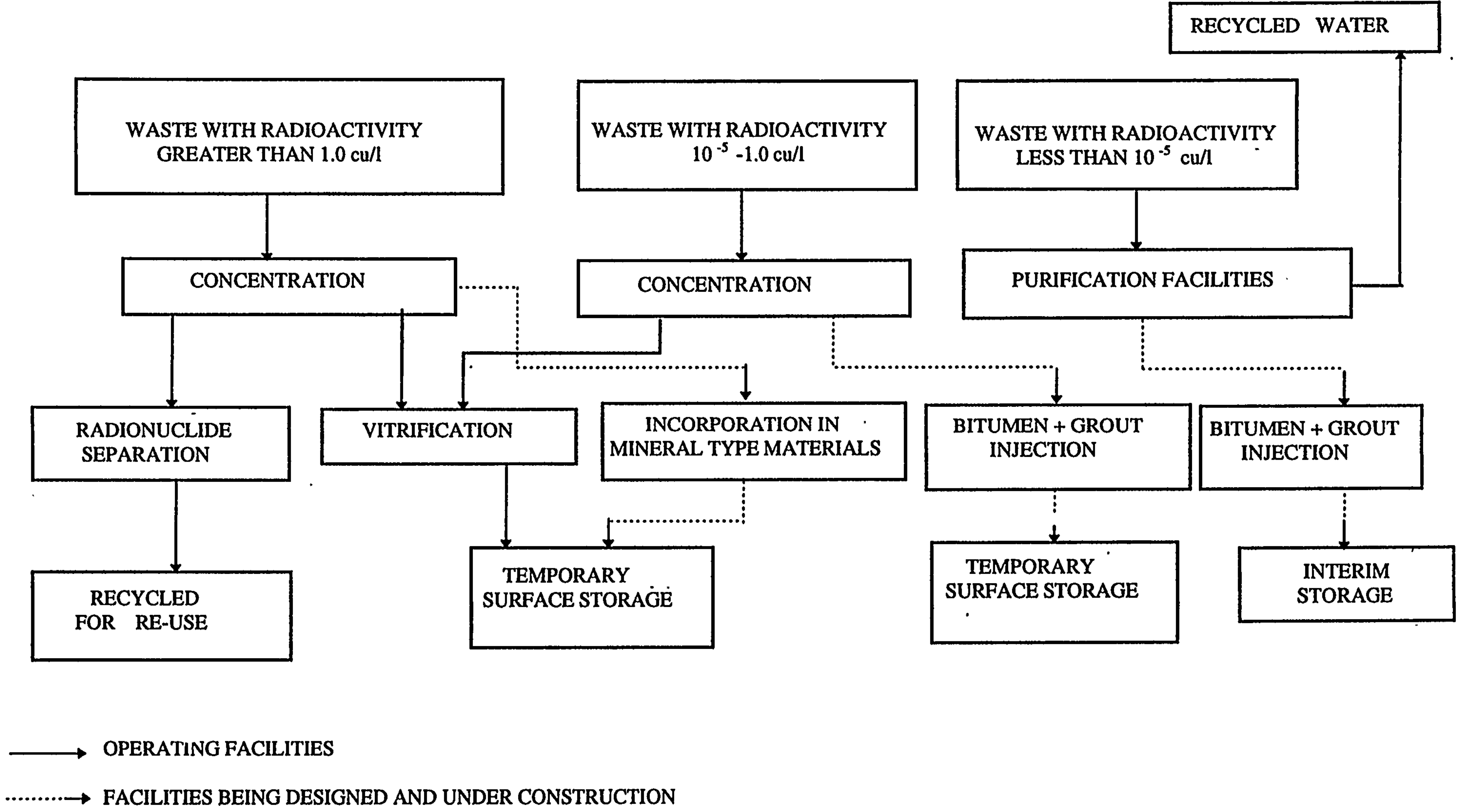

FIG. 2

PROPOSED REPROCESSING DIAGRAM FOR WEAPONS GRADE PLUTONIUM

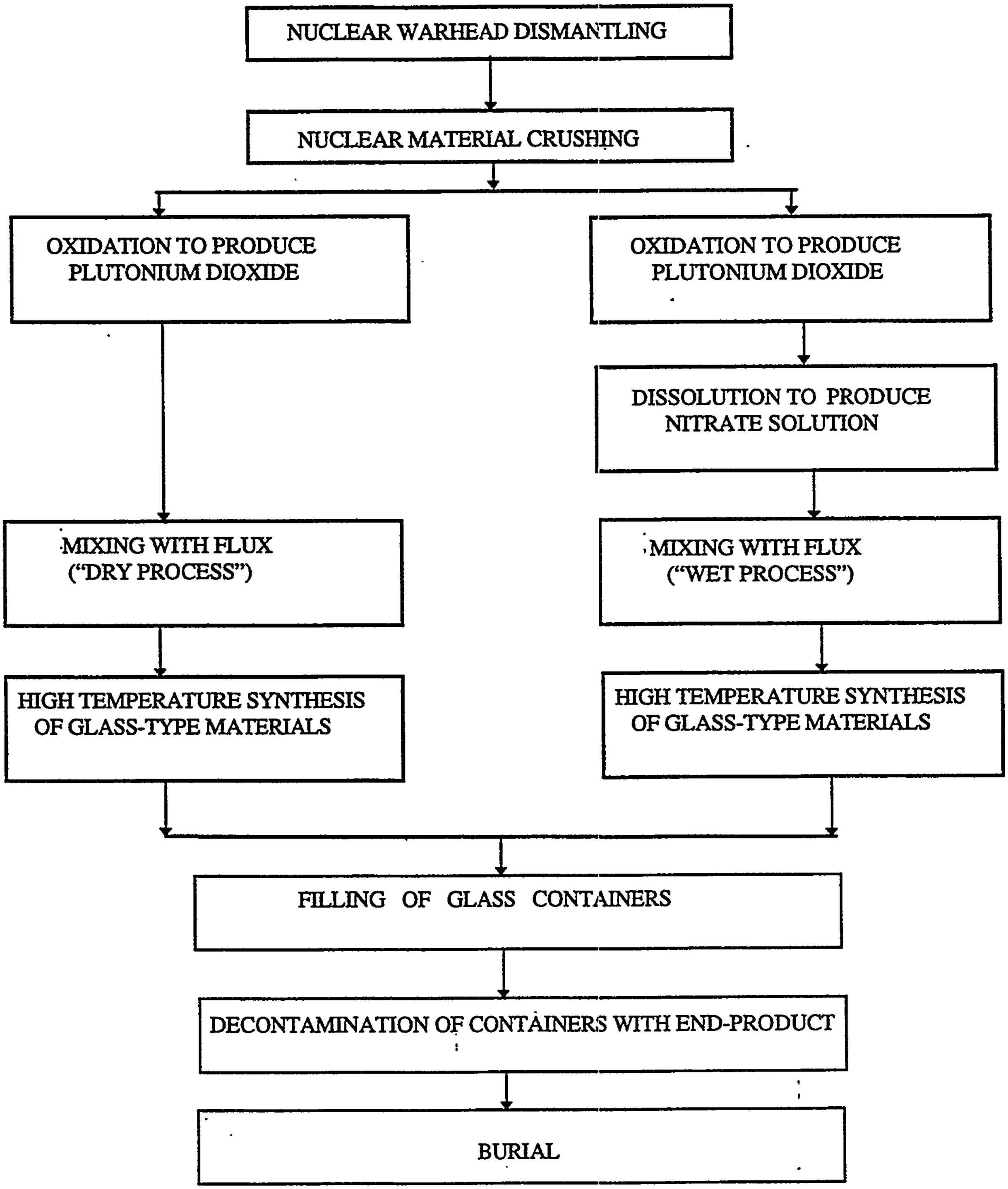

FIG.3

Progress on Plutonium Stabilization

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INTRODUCTION

The Defense Nuclear Facilities Safety Board has safety oversight responsibility for most of the facilities where unstable forms of plutonium are being processed and packaged for interim storage. The Board has issued recommendations on plutonium stabilization and has had a considerable influence on DOE's stabilization schedules and priorities. The Board has not made any recommendations on long-term plutonium disposition, although it may get more involved in the future if DOE develops plans to use defense nuclear facilities for disposition activities.

POSITIVE DEVELOPMENTS

There has been significant improvement in DOE's plutonium stabilization programs over the last two years. Two years ago the Board was coming to the conclusion that there were significant safety risks posed by surplus plutonium stored in unstable forms or inappropriate containers at several DOE facilities.[1] By early 1994, the Board decided that an official recommendation was warranted, and the result was Recommendation 94-1, which called for specific timetables for stabilizing surplus nuclear materials within the Weapons Complex.[2] The Board recommended that DOE assign high priority to stabilization programs for the most hazardous plutonium materials, such as unstable residues at Rocky Flats, tanks of solutions at Rocky Flats and the Savannah River Site, and plutonium metal packaged in close proximity to plastic, which turned out to be a problem mainly at Rocky Flats. The recommendation included timetables for processing or otherwise stabilizing those materials, as well as spent fuel at the Savannah River Site and Hanford.

The Board had concluded in 1994 that many DOE managers did not recognize the seriousness and immediacy of the stabilization problems. There has been considerable improvement in that respect since the recommendation was issued. In late 1994 DOE completed a large-scale study, popularly known as the Plutonium Vulnerability Study, of plutonium safety within the Complex. The Vulnerability Study came to the same conclusions as the Board regarding the seriousness of risks posed by unstable plutonium inventories.[3] The Study agreed that Rocky Flats is the site with the most severe plutonium storage problems, and that there are serious problems at other sites as well. All parties now agree that the situation requires intense, near-term corrective action.

The Secretary of Energy accepted Recommendation 94-1 and appointed a task force to prepare an Implementation Plan. It took several months, but a good Implementation Plan was eventually developed. The 94-1 Implementation Plan sets specific milestones for stabilization of all the materials cited in Recommendation 94-1, plus some related types of materials not named by the Board. The Plan is a serious commitment by DOE to make rapid, measurable progress on stabilizing these materials.[4]

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*The views expressed in this paper are those of the author and do not necessarily reflect any views, proposed actions, or decisions of the Defense Nuclear Facilities Safety Board or any other government agency.

The Assistant Secretary for Environmental Management has responsibility for the majority of the programs involved in implementation of Recommendation 94-1. During the first year and a half of the recommendation's life, the Assistant Secretary has consistently provided the funding and institutional support needed to begin the stabilization programs. The aggressive programs called for in the recommendation have had a big impact on previously established DOE programs, and only strong support from the Assistant Secretary and the efforts of DOE's Nuclear Materials Stabilization Task Group have made it possible for this ambitious program to get off to a strong start in most areas.

There is generally a high level of enthusiasm at the plutonium sites for the Recommendation 94-1 stabilization program. Most of the scientists and engineers at the plutonium sites are as concerned as the Board about the safety of unstable or poorly packaged plutonium, spent fuel, and other hazardous materials. Responsible people in the technical community are eager to accelerate the stabilization work, and are confident that it can be done safely and effectively. There has, of course, been a significant loss of experienced workers at the sites. While that is a general source of concern to the Board, it does not appear to be a limiting factor for 94-1 programs. There are still personnel at plutonium sites with the experience and technical expertise to conduct the 94-1 stabilization work if adequate funding and necessary authorizations are made available.

STANDARDS

There is a new DOE standard for plutonium storage with important implications for Recommendation 94-1, and plutonium stabilization in general.[4] The Board has a statutory obligation to review all DOE safety standards. In light of its importance to Recommendation 94-1, the Board has taken a particular interest in the plutonium metal-and-oxide storage standard. It would be difficult to make progress in stabilization, or even to agree on what constitutes progress, without defining forms of plutonium and types of packages that can be stored for long periods with little need for remedial action. The new standard for safe 50-year storage of plutonium metals and oxides provides that definition.

DOE is scheduled to issue another plutonium standard, covering 20-year storage of plutonium residues and low-grade oxides. The merits of that standard are somewhat more debatable. On the one hand, it may be necessary to store some residues for several years, and there is no standard now that covers residue storage, so the new standard should fill a gap. On the other hand, it would probably be best for long-term safety to process most residues to remove plutonium and other actinides. Then the separated plutonium, which need not be highly pure, could be stored in accordance with the metal-and-oxide storage standard, and the mostly-plutonium-free residual material could be stored or disposed as radioactive waste. The ideal course of action would be to use a process that would produce a residual material with sufficiently low actinide concentrations to qualify as a low-level waste. There are processes available for treating pyrochemical salt residues that could achieve such effective separation.[5] Even if a high degree of separation is not possible in all cases, removal of most of the plutonium and other alpha-emitters will greatly reduce the radiation-driven evolution of gases and unstable radiolysis products, making the residual waste material easier and safer to store.

PROBLEM AREAS

This touches on a general problem. The plutonium that needs stabilizing is all part of the approximately 50 metric tons that have been declared surplus to the country's needs. There is no identified need at present for this plutonium; it has no assignable value in any conventional sense. Why incur the expense of plutonium separation when the plutonium is by current definition a waste material?

The answer is that plutonium is generally safer to store in a pure form than when mixed with other materials. Plutonium weapon components, which are basically pure metal, have been stored safely for decades, and a great deal is known about how to prepare and package plutonium metal for long-term stability in storage. The behavior of purified plutonium oxide in long-term storage is not quite as well understood, but there is still a fairly substantial base of experience.[6] The general consensus of the technical community is that plutonium oxide can be safely stored for long periods if it is stabilized at a high temperature, certified to be free of potentially volatile contaminants, and stored in very robust containers.[5]

With plutonium residues, which are mixtures of plutonium with many other substances, there is little long-term storage experience, and what there is is problematic.[1,3] Off-gassing, corrosion of containers, and radiation-driven formation of reactive compounds are serious risks if residues are stored in unseparated form. The better approach, even if initial expense is greater, would be to remove most of the plutonium from the residue, store the plutonium as a relatively pure metal or oxide, and dispose of the contaminated leftovers as transuranic or low-level waste.

A substantial amount of processing will have to be done for residues, and it will mostly have to be done in old facilities. That raises a host of problems. It is not easy to restart old processing facilities that have been allowed to atrophy; it is not easy to make old equipment work correctly; it is not easy to find enough trained workers to operate old facilities safely; it is not easy to meet modern standards of safety analysis for these plants. But old facilities are all DOE has, with one or two exceptions, and it is unlikely that new facilities can be built in the required time. The old facilities must be used if the surplus materials are to be placed in safe, storable forms. One reason for issuing Recommendation 94-1, which urged DOE to move much faster on stabilization, was that the old facilities are continuing to age, and will be even more difficult to use in the future than they are now.

This bears on an important part of Recommendation 94-1 that is sometimes overlooked: the need to maintain facilities in operable condition until all surplus materials are stabilized. Premature shutdown of facilities can have severe consequences. Between 1989 and 1994, Rocky Flats lost a great deal of processing capability through failure to maintain facilities and retain skilled workers. Capabilities were lost before the full extent of the site's plutonium stabilization needs was widely appreciated, leading to the very difficult situation Rocky Flats faces today. Badly deteriorated process lines now have to be restarted as quickly as possible for short stabilization processing campaigns. DOE also shut down some facilities at Hanford and the Savannah River Site without taking inventories of unstable plutonium materials into proper account.

The Board has urged DOE not to make a hasty decision on shutting down either of the reprocessing canyons at the Savannah River Site. Stabilization facilities are rare commodities today; when one is shut down, stabilization options for plutonium and other hazardous materials may be significantly reduced. DOE's commitments under Recommendation 94-1 include keeping in operable condition those facilities that may be needed for future stabilization work. Which facilities are needed and what constitutes operable condition will certainly be debated for many specific cases, but the basic commitment has been made and is binding on shutdown decisions such as the one facing the Savannah River Site.

CONCLUSIONS

DOE is laying sound plans for plutonium stabilization, and doing so with a more appropriate sense of urgency than two or three years ago. Actual physical progress on stabilization has been modest so far. Continued effort is needed to fund and execute the actual work. The goal is a surplus plutonium inventory that is well-characterized, processed into stable forms, and correctly packaged for long-term storage.

DISCLAIMER

The views expressed in this paper are those of the author and do not necessarily reflect any views, proposed actions, or decisions of the Defense Nuclear Facilities Safety Board or any other government agency.

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Vitrification of Plutonium at Rocky Flats
The Argument for a Pilot Plant

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ABSTRACT

The local danger posed by large quantities of plutonium at Rocky Flats and the global threat of theft or diversion of plutonium and thus of further nuclear weapons proliferation can both be addressed by vitrification of plutonium. Current plans for stabilizing and storing the plutonium at Rocky Flats fail to put the material in a form suitable for disposition and resistant to proliferation. Vitrification should be considered as an alternate technology. To resolve questions regarding the viability of this technology, plutonium vitrification at Rocky Flats should begin with a small-scale pilot plant. There are numerous questions to which the public requires satisfactory answers before this technology can move to a larger scale at Rocky Flats.

INTRODUCTION

The most serious danger to people who live in the vicinity of Rocky Flats stems from large quantities of plutonium now stored on site in hazardous forms. This local danger -- one not limited to Rocky Flats -- is paralleled by global threats that some of the huge amounts of plutonium extant at various locations on the planet may wind up as a global black market commodity leading to further proliferation of nuclear weapons. Vitrification of plutonium could help alleviate both of these urgent problems.[1] My presentation begins with a brief look at plutonium conditions at Rocky Flats, criticizes current plans for resolving onsite problems, and proposes a pilot project for plutonium vitrification as an alternative. The paper concludes with questions to which the public requires satisfactory answers before this technology can move to a larger scale.

A COMMENT ON PUBLIC PARTICIPATION

For some time people in Colorado have been urging management at Rocky Flats to consider creating a small-scale pilot plant for vitrification of the plutonium at Rocky Flats. We have felt like prophets crying in the wilderness. Until I read abstracts of papers circulated before this workshop[2] I thought the topic of plutonium vitrification was as neglected elsewhere in the DOE complex as it has been at Rocky Flats. This workshop encourages me to think the concept is alive and well and may have a future after all. I myself address the topic of vitrification of plutonium not as a technical specialist but as one who lives near Rocky Flats and is concerned about both the local danger and the global threat previously mentioned. I am grateful to be part of this workshop but am sorry to see that public participation is scant. DOE can gain the trust of affected citizens only if it involves them at the earliest possible moment and in the fullest possible way in any consideration of matters that impact them. If local communities are to endorse vitrification, it is essential that they have access to technical information and that they have full opportunity to work directly with technical people. This workshop is, at best, only a beginning.

CONDITIONS AT THE SITE

Rocky Flats currently contains the largest known store of plutonium at any facility within the U.S. DOE nuclear weapons complex (quantities at Pantex are greater, but the amounts remain classified). Plutonium on site at Rocky Flats exists in the following forms and quantities:

- Metals: 6,600 KG
- Compounds: 3,200 KG
- Residues: 3,100 KG
- Solutions (the most dangerous material on site): 140 KG
- Holdups (in ductwork, equipment, buildings): 320 KG (rough estimate)

Metals, compounds, and residues add up to the 12.9 metric tons of plutonium usually referred to as the total inventory of plutonium on site. Including solutions and holdups brings the estimated total to 13.36 metric tons. Some of this total -- a classified amount -- belongs to Defense Programs and thus will be retained for the nuclear weapons stockpile. Most of the total, however, is no longer part of the weapons stockpile and therefore is destined for disposition. My paper focuses on this portion.

Much of the large quantity of plutonium at Rocky Flats is stored in unsafe form within unsafe buildings. DOE's plutonium vulnerability study singled out Rocky Flats as having the most severe vulnerabilities of any facility nationwide. Here are a few highlights from the vulnerabilities report:

- The two potentially most dangerous buildings within the DOE complex are at Rocky Flats.
- Five of the nine most vulnerable buildings nationwide are located at Rocky Flats.
- The report identified 27,679 separate packages of unstable plutonium at Rocky Flats.
- "Current packaging and facilities . . . are not designed for extended storage."[3]
- Thousands of containers of plutonium scrap are stored in work areas, compromising safety.
- "The exact magnitude of the problem [at Rocky Flats] is uncertain because of missed or incomplete inspections and the difficulty of ascertaining the status of the degraded materials and packaging."[4]

CURRENT PLANS FOR DEALING WITH THE PLUTONIUM ON SITE

In the face of this critical situation at Rocky Flats, Herculean efforts are now underway to stabilize unstable material and to put it in form suitable for safe long-term storage.[5] Essentially, two separate options are now preferred at the site. For the **stabilized plutonium** -- the solids, compounds, solutions, and larger amounts recovered from holdups -- the operable plan is to place stabilized material in the "fifty year can" now being developed at Los Alamos.[6] This is the preferred option for all Rocky Flats plutonium except the residues. **Residues** were traditionally production byproducts that would have been discarded as waste except that they contained "recoverable" amounts of plutonium. By the nature of the case, residues are diverse in form, with some forms being quite unstable. The plan for the residues is to put the material in "a form and container that is safe for a period of twenty years,"[7] in the expectation that within this period this material can be disposed of at WIPP as TRU-mixed waste.

CONCERNS ABOUT THE FIFTY YEAR CAN

There are many concerns about the fifty year can, including the following:

- To prepare material for the fifty year can entails the oxidation of plutonium as well as the processing that would be required beforehand, such as dissolution of plutonium in acid. These activities extend the threat of accidents and routine environmental problems of the type that have plagued Rocky Flats for decades?
- Is the package safe? The idea of a "fifty year can" for long-term storage and disposition of plutonium seems ludicrous. Can DOE design a container that could go through a certification process to guarantee its half-century durability? If so, how long will the can hold up? With the accumulation of gas from the plutonium decay, will the can eventually rupture, leading to possible dispersion of the contents, particularly if the contents are in oxide form?
- Will plutonium stored in the fifty year can require further processing at some future date to prepare it for permanent disposition? Is the fifty year can a suitable container for permanent disposition?
- Is this package sufficiently proliferation-resistant? As a cylinder ten inches long and five inches wide, the fifty year can is wonderfully portable and therefore subject to diversion or theft. The contents, of course, will be plutonium in near weapons-grade form. Who can provide absolute assurance that security will remain adequate to offset the danger of theft or diversion for as long as required?
- Is DOE's fifty-year can in reality less a method for plutonium disposition than one for indefinite retention of plutonium in near weapons-grade form? Why leave plutonium in a form that can too easily be converted back into weapons-usable material when the U.S. has no need for more weapons-usable plutonium?
- For the U.S. to keep its own plutonium in easily usable form will prevent it from persuading Russia to convert its plutonium into non-weapons-usable forms -- a prime U.S. security goal.

PROBLEMS WITH THE PLAN FOR RESIDUE DISPOSITION

Problems with the plan for disposition of plutonium residues include the following:

- Why does management at Rocky Flats assume it is safe to dispose of unstable plutonium residues underground? Won't this particular disposition plan further galvanize the already significant opposition to the opening of WIPP?
- Is it wise to rely on availability of WIPP? And will WIPP, even if it opens, be able to accommodate the quantities of TRU waste expected to be disposed of there?
- If WIPP isn't available, how wise is the twenty-year-container plan for ongoing storage of plutonium residues at Rocky Flats? Wouldn't a good management strategy dictate development of a viable alternative, one that would stabilize the material in a form suitable for long-term storage and disposition?

VITRIFICATION AS AN ALTERNATIVE

Vitrification of plutonium could avoid all these problems at Rocky Flats, especially if a new technology invented by DOE's Oak Ridge National Laboratory can be utilized.[8]

- The Oak Ridge technology streamlines processing by combining oxidation with the vitrification step, replacing extensive chemical treatment of plutonium compounds and residues. Plutonium materials in various chemical forms are put into molten glass containing lead oxide. The plutonium combines with the oxygen in the lead oxide, creating plutonium oxide and lead metal. The lead metal, insoluble in glass, drops to the bottom of the glass melter, whence it can be extracted, re-oxidized and re-used.
- After vitrification the plutonium would end up dispersed and embedded in glass logs, posing lower risks than if stored as plutonium oxide.
- The logs would be too large for easy theft or diversion, while the plutonium content per log would be so small that several logs would be required to obtain enough plutonium to make a bomb.
- The plutonium logs could be poisoned with radionuclides or a rare-earth element to make theft or diversion even less likely.
- Extensive processing would be necessary to recover the plutonium.
- Direct vitrification of some residues, particularly combustibles, may not be possible; if so, this material would require some processing prior to the vitrication step.

VITRIFICATION SHOULD BEGIN WITH A SMALL-SCALE PILOT PLANT

The Oak Ridge direct vitrification technology evidently could handle many different types of plutonium residues and scraps. Other vitrification technologies should also be considered for the situation at Rocky Flats. Whatever technology is used must be taken from the laboratory to an industrial scale. Its operating and environmental characteristics need to be studied. The best approach for doing this at Rocky Flats would be to build a small pilot plant for testing various aspects of the technology, demonstrating its feasibility, and working out problems. Operating a vitrification pilot plant first would help DOE acquire experience that it sorely lacks. If a pilot project shows that it would not be feasible to move to full-scale operations, little would have been expended and much would have been learned.

RATIONALE FOR VITRIFICATION AND FOR A PILOT PLANT

- Vitrification may streamline processing of plutonium, bypassing a separate oxidation step.
- Vitrification embeds plutonium in a form that minimizes or eliminates dispersibility.
- The end result is a stable, proliferation-resistant form suitable for long-term storage or disposition.
- A small-scale pilot plant would cost little, could be begun soon, and would provide an opportunity to test the technology to determine the feasibility of vitrification on a larger scale.

IS PUBLIC ACCEPTANCE POSSIBLE?

If in other respects Rocky Flats seems a logical location for a plutonium vitrification pilot plant, can such a project gain public acceptance? DOE spokespersons now say a requisite condition for future operations at any site is public acceptance. At Rocky Flats, however, as well as elsewhere DOE personnel face a cautious, sometimes angry public. In this context, is substantive public acceptance for a plutonium vitrification facility even possible? If so, what must be done to gain such acceptance? This workshop, as I stated earlier, sets a poor standard for public participation. On behalf of members of the affected public who are not here I shall next provide a long list of questions posed by some of them. Full and careful written answers to these questions can help the absent public begin to know how to assess vitrification. Of course, answers on paper are no substitute for the open exchange that must happen if there is to be any forward movement.

QUESTIONS WHICH NEED TO BE ANSWERED

What follows are some of the questions to which positive answers are required in order to proceed with vitrification of plutonium at Rocky Flats or elsewhere:

- If plutonium vitrification is initiated at Rocky Flats or elsewhere, what must be done to assure regulation by an agency outside DOE? What agency will regulate and according to what standards ?
- For any site that takes on the responsibility of plutonium vitrification, what commitment is being made? What amount of plutonium will be vitrified over what period? What assurances can be given that the resources necessary to do the task safely will be provided?
- What would be the chief environmental, safety, and health problems associated with vitrification of plutonium, particularly in the kind of smelter pioneered at Oak Ridge?
- On the principle that plutonium should be handled as little as possible, what assurance can be given that vitrification operations will entail less processing than other approaches to stabilization and immobilizaion?
- Can the U.S. create a vitrification model with minimum handling of plutonium and mimimum possible waste streams that can be replicated in other countriees?
- What steps will the U.S. take to encourage other countries to commit to non-proliferation by vitrifying their plutonium in preparation for disposition?
- What types of skills are needed for workers engaged in plutonium vitrification?
- What problem does the addition of plutonium pose in "making good glass"?
- What measures are taken to see that plutonium diffuses uniformly throughout the glass?
- What is the appropriate ratio of plutonium to glass?
- What safeguards can protect against criticality both in processing and in storage?
- At what temperature would the glass melter operate?
- What is the risk of molten glass leaking from the melter?
- What would be the result of water leaking into the melter? Can this be prevented?
- What pollution control devices would be used?
- What kind of storage would be required for vitrified logs of plutonium?
- How would vitrified logs hold up to a fire? an explosion? a building collapse?
- What hazards do the vitrified logs pose to workers? to the public?
- What is the effect on glass of bombardment by alpha, beta, and neutron radiation?
- Is it possible that glass logs might shatter or flake over years for any reason? If so, what would be the result? Could this contribute to plutonium dispersion?
- Should vitrified logs be encased in another container?
- Could plutonium leach out of glass logs over time? If so, at what rate and for how long?
- Can all the residue forms present at Rocky Flats be used as feed material for vitrification? If so, are any special measures required for the processing? If not, what additional processing would be required before the material could be vitrified?

- What additives might be used to poison logs of vitrified plutonium? What dangers are associated with specific additives, and what precautions would be required to protect workers, the public, and the environment?
- Does plutonium in glass logs pose problems for international verification of plutonium inventories? How might such problems be solved?
- How does vitrification of plutonium compare to other disposition options in terms of cost, risk, and proliferation-resistance?
- What would be the appropriate size of a pilot facility at Rocky Flats? of a full-scale facility to handle all the plutonium on site?
- What assurance can be given that vitrification operations at Rocky Flats would be used only for plutonium on site?
- To what extent would plutonium contaminate the vitrification facility by the time it is done operating? What problems might this pose?

A CAVEAT REGARDING PLUTONIUM DISPOSAL

In the long-term, plutonium glass logs would need to be disposed of as waste. This disposal problem has not been solved. Moreover, military surplus plutonium constitutes a considerably smaller portion of global plutonium inventories than the plutonium from civilian nuclear power reactors. Currently the latter (plutonium in spent fuel as well as separated plutonium) amounts to almost three times the quantity of military plutonium produced globally over five decades.[9] Creating a sound, proliferation-proof waste management plan for civilian plutonium is a major problem needing early attention.

CONCLUSION

The problems of plutonium immobilization and disposition are urgent and serious, nowhere more so than at Rocky Flats, with more than 13 metric tons on site, much of it in unsafe form. There are no perfect, risk-free solutions. DOE has made progress by identifying the hazards of existing storage practices. It needs now to give up the urge to hang on to plutonium in close to weapons-usable forms. In keeping with the facility's new name -- Rocky Flats Environmental Technology Site -- DOE needs to take the bold steps required to develop plutonium vitrification technology at the site as soon as possible in a manner consistent with public involvement, openness, and environmental protection.

Vitrification of plutonium at Rocky Flats should begin on a small scale with a pilot plant. Then if the technology proves feasible, the project can be scaled up to an appropriate size for handling the large quantities of plutonium materials and residues on site. While numerous questions await answering, vitrification of plutonium at Rocky Flats seems a promising alternative to the other options being considered at the facility. As shown, vitrification may entail less processing, while its end-product will be a proliferation-resistant form suitable for long-term storage or permanent disposition.

DISCLAIMER

The views expressed in this paper are those of the author(s) and do not necessarily reflect any biases, proposed action, or decisions of the United States Government or any agency thereof.

NOTES

1. I wish to acknowledge the important work done on this topic by Arjun Makhijani of the Institute for Energy and Environmental Research. See Arjun Makhijani and Annie Makhijani, Fissile Materials in a Glass Darkly: Technical and Policy Aspects of the Disposition of Plutonium and Highly Enriched Uranium (Takoma Park, MD: IEER Press, 1995).

2. U.S. DOE, Plutonium Stabilization and Immobilization Workshop, Washington, DC, December 12-14, 1995.

3. Plutonium Working Group Report on Environmental, Safety and Health Vulnerabilities Associated with the Department's Plutonium Storage, vol. I: Summary (Washington, DC: U.S. Department of Energy, November 1994 [DOE/EH-0415]), p. 18.

4. Ibid., I, p. 26.

5. See Rocky Flats Environmental Technology Site, Site Integrated Stabilization Management Plan (SISMP), Version 3.0, October 10, 1995.

6. In keeping with DOE Standard Criteria for Safe Storage of Plutonium Metals and Oxides, DOE-STD-3013-94.

7. SISMP, p. 35.

8. See Charles W. Forsberg and E. C. Beahm, "Direct Conversion of Plutonium-Containing Materials to Borosilicate Glass for Storage or Disposal" (June 27, 1995), for Thirty-Sixth Annual Meeting, Institute for Nuclear Maerials Management Conference, Palm Desert, CA, July 9-12, 1995; and Forsberg, "What Is Plutonium Stabilization, and What is Safe Storage of Plutonium?" (June 29, 1995), Discussion Paper for the U.S. DOE Research Committee for the Stabilization of Nuclear Materials. Both papers are available from Forsberg at the Oak Ridge National Laboratory, Box 2008, Oak Ridge, TN 37831.

9. See Makhijani, Fissile Materials in a Glass Darkly, p. 11.

Stabilization and Immobilization of Military Plutonium: A Non-Proliferation Perspective

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INTRODUCTION

The Nuclear Control Institute welcomes this DOE-sponsored technical workshop on stabilization and immobilization of weapons plutonium (W Pu) because of the significant contribution it can make toward the ultimate non-proliferation objective of eliminating weapons-usable nuclear material, plutonium and highly enriched uranium (HEU), from world commerce. The risk of theft or diversion of these materials warrants concern, as only a few kilograms in the hands of terrorists or threshold states would give them the capability to build nuclear weapons. [1]

Military plutonium disposition questions cannot be addressed in isolation from civilian plutonium issues. The National Academy of Sciences has urged that "further steps should be taken to reduce the proliferation risks posed by <u>all</u> of the world's plutonium stocks. military and civilian, separated and unseparated...." [2] A similar point was made in a Rand Corporation report: "It is critical that countries pay attention to the proliferation threat from the civilian side if they want to maximize the non-proliferation value of dismantling U.S. nuclear weapons and those of the FSRs [former Soviet republics]. If countries ignore the civilian threat, they can compound the problem by making wrong choices in how to deal with military materials." [3]

The Clinton Administration has correctly identified the minimizing of civilian plutonium stocks worldwide as a major non-proliferation objective:

> The United States believes that growing quantities of plutonium in international commerce present a threat to the nonproliferation regime. In countries where material control and accountancy or physical protection systems are not sufficiently rigorous, there is a risk of diversion or theft of such materials. In addition, even in countries with effective nonproliferation commitments, the presence of unneeded stocks of plutonium could raise security concerns on the part of neighboring countries. Accordingly, United States policy is not to encourage the civil use of plutonium. [4]

Decisions on the disposition of W Pu will have major effects on the future of plutonium use in civilian nuclear power programs. These decisions are being watched closely by plutonium fuel cycle advocates around the world. The nuclear industry has launched a full-court press, with nearly every major vendor re-designing its reactor system for potential use as a weapons-plutonium burner. In 1993, Congress mandated that the Department of Energy conduct several studies of various MOX options, including a review of reactor options and an assessment of the so-called triple-play reactor that would use weapons-plutonium MOX fuel to generate electricity and produce tritium for the nuclear arsenal.

Comparable attention and resources were not directed toward consideration of vitrification and other immobilization options. This situation led the National Academy of Sciences to make the following recommendation in its study this year of disposal options:

> Since it is crucial that at least one of these options [MOX or vitrification] succeed, since time is of the essence, and since the costs of pursuing both in parallel are modest in relation to the security stakes, we recommend that project-oriented activities be initiated

> on both options, in parallel, at once. DOE should assign sufficient resources (both funding and personnel) to manage pursuit of both options in parallel.[5] [emphasis in original]

One of the main goals of this workshop, therefore, should be to fulfill the NAS mandate by righting the imbalance between the MOX and vitrification disposal options and creating a more level playing field that will help give equal consideration to the viability of non-reactor alternatives.

Vitrification and MOX as the Lead Disposition Options

Most experts agree with the conclusion of this year s NAS study that the two most viable options for disposing of plutonium recovered from retired nuclear warheads are the irradiation in reactors of mixed-oxide fuel made from this plutonium (the MOX option), and direct disposal of warhead plutonium by means of vitrifying it with high-level radioactive waste (the VHLW option). The Nuclear Control Institute regards the vitrification approach as posing fewer risks than the MOX approach with regard to diversion or theft of warhead material, reversal of the disarmament process, and other adverse effects on international arms control and non-proliferation efforts. Proposals for transferring warhead plutonium MOX fuel to third countries not now possessing nuclear weapons pose additional risks.[6]

To minimize proliferation and terrorism risks in the post Cold War world, we advocate that a symmetrical regime be developed to address the dual threat of military and civilian plutonium. Such a regime would place comparable obligations on nuclear-weapon and non-nuclear weapon states to meet the spent-fuel standard and to avoid production and use of separated plutonium in any form. A decision to dispose of warhead plutonium by means of vitrification or other immobilization technology would be an essential step toward achievement of such a regime.

Proponents of MOX disposition claim that vitrification technology is immature, speculative, and cannot be ready soon enough.[7] This view is nearly universal in the nuclear power industry, despite being flatly contradicted by this year s NAS study on disposal options, which concluded that [i]n terms of the crucial timing aspect of security, the current-reactor/spent-fuel options and the vitrification-with-wastes options are roughly comparable to each other (as well as superior to all other options). Under the most optimistic assumptions that are defensible, loading of W Pu into current-reactor types could begin between 2002 and 2004 and be completed between 2015 and 2025; loading of W Pu into waste-bearing glass logs could begin around 2005 and be completed as early as 2013."[8] Accordingly, this workshop can summarize and begin to assess the range of outstanding technical issues related to VHLW options, in order to provide direction for a concerted R&D effort.

Effects of Disposition Choices on Civilian Plutonium Fuel Cycles

The 1994 NAS study emphasized the importance of the "Fuel Cycle Policy Signal":

> [P]olicymakers will have to take into account the fact that choosing to use weapons plutonium in reactors would be perceived by some as representing generalized U.S. approval of separated plutonium fuel cycles, thereby compromising the ability of the U.S. government to oppose such fuel cycles elsewhere. Conversely, choosing to dispose of weapons plutonium without extracting any energy from it could be interpreted as reflecting a generalized U.S. government opposition to plutonium recycle. Either choice could have an impact on fuel cycle debates now underway in Japan, Europe, and Russia.[9]

The Nuclear Control Institute believes that the vitrification option would send the <u>right</u> fuel cycle policy signal to the civilian nuclear sector and would be fully consistent with the Clinton Administration's September 1993 non-proliferation policy statement. The statement declared that "the United States does not encourage the civil use of plutonium and, accordingly, does not itself engage in plutonium reprocessing for either nuclear power or nuclear explosive purposes."[10]

On the other hand, the MOX option, though it does not necessarily involve further reprocessing, would clearly encourage civilian use of plutonium, which in some countries like Japan even includes plans for reprocessing irradiated MOX fuel. The U.S. Government would be engaging in or sponsoring MOX activities for the first time on a commercial scale, legitimizing the use of MOX in civil nuclear power programs. Such a sea change in U.S. policy would confuse and complicate U.S. non-proliferation diplomacy. It would send the <u>wrong</u> fuel-cycle policy signal to Western Europe, Japan, and other non-nuclear-weapon state members of the Non-Proliferation Treaty (NPT).

In our view, the MOX option sends the wrong signal in three ways. First, this option effectively declares that plutonium has an asset value, and that the energy contained within it should be viewed as a "national asset" (as the U.S. DOE expressed it) or even "national treasure" (as the Russians put it), when in fact plutonium fuel has been shown to be an economic liability. [11]

Second, the MOX option suggests that a commercial plutonium fuel cycle can be effectively safeguarded, when, in fact, it is becoming obvious that large-throughput plutonium plants face daunting safeguards problems. [12]

Third, the MOX option would be portrayed as giving credibility to the claim that plutonium recycle in light water reactors (LWRs) is essential to nuclear waste management at a time when direct disposal of spent fuel is looking increasingly attractive to utilities. [13]

Finally, the MOX option undercuts U.S. non-proliferation diplomacy directed at so-called "rogue states." If the U.S. actively pursues the MOX option, it will become far more difficult to deny nations of proliferation concern, such as North Korea and Iran, their "right" to civil use of plutonium. In our view, the only credible way to oppose the separation and use of plutonium in nations of proliferation concern is to oppose it comprehensively---that is, to oppose its separation and use in *any* nation for *any* purpose. Such an approach is effectively precluded if the U.S. insists upon retaining the right to use MOX fuel in civilian reactors, albeit for the purpose of weapons plutonium disposition.

Important Workshop Goals

This workshop should help point the way forward to near-term demonstration of technically viable vitrification/immobilization processes. Some technologies, such as Oak Ridge s GMODS, are at risk of being dismissed as smoke and mirrors without first being allowed the kind of detailed assessment that has been devoted to the various reactor options. A number of promising technologies are to be outlined in presentations at this workshop, and deserve a fair chance in the disposition decision-making process.

This workshop also can provide the catalyst for closer cooperation with our Russian colleagues. Plutonium exists in enormous amounts and, in many cases, in the form of dangerous residues in both U.S. and Russian weapons production facilities. Though our attitudes on commercial use and final disposition of plutonium vary widely, stabilization of these particular military wastes is a pressing problem for both nations, and cooperation on technical solutions is in our mutual interest. For reasons of economy and safety, certain waste forms may lend themselves to stabilization and immobilization without partitioning of plutonium and other actinides, and could provide the basis for initial cooperation between the United States and Russia on non-reactor disposal options.

The Department of Energy is to be commended for convening this ground-breaking technical workshop, and Russian participation is most welcome and important. I look forward to the discussions of the next two days.

DISCLAIMER

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END NOTES

1. J. Carson Mark et al., "Can Terrorists Build Nuclear Weapons?," in Preventing Nuclear Terrorism: Report and Papers of the International Task Force on Prevention of Nuclear Terrorism, Paul Leventhal & Yonah Alexander, Eds., New York: D.C. Heath, 1987, pp. 55-65; J. Carson Mark, "Some Remarks on Iraq's Possible Nuclear Weapon Capability in Light of Some of the Known Facts Concerning Nuclear Weapons," Nuclear Control Institute, May 16, 1991.

2. Committee on International Security and Arms Control, National Academy of Sciences, Management and Disposition of Excess Weapons Plutonium [NAS 1994], p. 34.

3. Brian Chow and Kenneth Solomon, Limiting the Spread of Weapon-Usable Fissile Materials, Rand Corporation Report, November 1993, p. xii.

4. U.S. Department of Energy, Environmental Assessment of Urgent-Relief Acceptance of Foreign Research Reactor Spent Nuclear Fuel, DOE/EA-0912, April 1994, p. 1-4.

5. Panel on Reactor-Related Options for the Disposition of Excess Weapons Plutonium, Committee on International Security and Arms Control, National Academy of Sciences, Management and Disposition of Excess Weapons Plutonium: Reactor-Related Options, 1995 [NAS 1995], p. 417

6. Paul Leventhal and Steven Dolley, "The MOX and Vitrification Options Compared: A Non-Proliferation Perspective," Proceedings of the Fifth International Conference on Waste Management and Environmental Remediation: ICEM '95, Berlin, Germany, September 3-7, 1995, pp. 535-539; Paul Leventhal, "What Should Be the Fundamental Basis of a National Plutonium Policy?," presented to the International Policy Forum on Management and Disposition of Nuclear Weapons Materials, Leesburg, Virginia, March 8, 1994.

7. Typical of such assertions is the claim by Pierre Goldschmitt, general manager with Synatom SA in Belgium, that "[p]lutonium vitrification and disposal is only conceptual at this time: it must first be demonstrated technically and followed by practical industrial application reaching the same safety level as presently achieved by the mixed oxide industry. Its cost and feasibility remain to be assessed from a number of standpoints: criticality, long-term stability, radiation protection, environmental impact, economics and nonproliferation." Pierre Goldschmitt, "Plutonium and Peace, the Point of View of a European," Paper Presented at the Nuclear Energy Institute International Uranium Seminar, Beaver Creek, Colorado, September 25-28, 1994, p. 5. Similar claims were posited by the American Nuclear Society in its recent report on plutonium policy: ANS Special Panel on the Protection and Management of Plutonium, "Key Conclusions and Recommendations," 1995, p. 2.

8. NAS 1995, p. 413. The NAS study also noted that "W Pu immobilization by vitrification in borosilicate glass represents a feasible technology that could meet the spent fuel standard, could be available in the relatively near future (within about a decade hence), and could potentially immobilize all of the nominal 50 tons of U.S. excess W Pu in glass in a relatively short time once the vitrification campaign had begun (i.e., in a few years, very likely less than 10)." Ibid., p. 410.

9. NAS 1994, p. 149.

10. White House Fact Sheet, "Nonproliferation and Export Control Policy," September 27, 1993, p. 2

11. Paul Leventhal and Steven Dolley, "A Japanese Strategic Uranium Reserve: A Safe and Economic Alternative to Plutonium," Science and Global Security, 1994, Volume 5, pp. 1-31; Brian Chow and Kenneth Solomon, Limiting the Spread of Weapon-Usable Fissile Material, Rand Corporation, November 1993.

12. Marvin Miller, "Are IAEA Safeguards on Plutonium Bulk-Handling Facilities Adequate?," Nuclear Control Institute, August 1990; "'Astounding' Discrepancy of 70 Kilograms of Plutonium Warrants Shutdown of Troubled Nuclear Fuel Plant in Japan," Nuclear Control Institute, May 9, 1994; Mark Hibbs, "Rebuild at PNC's PFPF Plant Will Cost Japan $100 Million," NuclearFuel, October 9, 1995, p. 11.

13. "Germans Likely to Terminate Two-Thirds of Their Post-2000 Reprocessing Deals," NuclearFuel, June 5, 1995, p. 4.

Integrating the Stabilization of Nuclear Materials

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In response to Recommendation 94-1 of the Defense Nuclear Facilities Safety Board, the Department of Energy committed to stabilizing specific nuclear materials within 3 and 8 years. These efforts are underway. The Department has already repackaged the plutonium at Rocky Flats and metal turnings at Savannah River that had been in contact with plastic. As this effort proceeds, we begin to look at activities beyond stabilization and prepare for the final disposition of these materials.

To describe the plutonium materials being stabilized, Figure 1 illustrates the quantities of plutonium in various forms that will be stabilized. Plutonium as metal comprises 8.5 metric tons. Plutonium oxide contains 5.5 metric tons of plutonium. Plutonium residues and solutions, together, contain 7 metric tons of plutonium. Figure 2 shows the quantity of plutonium-bearing material in these four categories. In this depiction, 200 metric tons of plutonium residues and 400 metric tons of solutions containing plutonium constitute most of the material in the stabilization program. So, it is not surprising that much of the work in stabilization is directed toward the residues and solutions, even though they contain less of the plutonium.

Figure 3 sketches the stabilization paths for these materials. Plutonium metal and oxide are packaged according to the departmental standard, DOE-STD-3013-94. The materials will then be suitable for 50-year storage, although we expect that the materials will be dispositioned well before 50 years. Residues and solutions show two paths. One path is to concentrate plutonium suitable for packaging. This requires that the plutonium be concentrated to greater than fifty percent, and be low in water and organic content, as prescribed by the standard. No purity requirements above that specified in the standard are required. So, for example, at Savannah River, plutonium will be prepared as a metal after being precipitated from solutions. The plutonium will not be purified by anion exchange, however, and would not be weapons grade.

The other path is to dispose of residues as transuranic waste. The maximum average concentration, following anticipated Waste Acceptance Criteria for the Waste Isolation Pilot Plant (WIPP), are below 0.5 gram per kilogram of material. This limit establishes the need for the path in which plutonium is packaged for disposition other than as waste. With this limit, the plutonium in residues and solutions would require 30,000 drums for disposal. Given an estimated disposal cost of $10,000 per drum in WIPP, disposal of all residues and solutions would require $300 million. We expect that we can experience considerable savings by disposing of some of the plutonium as other than waste in WIPP. The decision as to the path for the residues will depend on projected costs.

In the stabilization program, we welcome immobilization as a viable option to the treatment of residues. Preparation of the residues for disposition (such as in vitrified form) would reduce the amount of materials in intermediate form and would thus reduce the cost of disposing to WIPP. In any case, we are committed to putting material that will not be disposed as waste into a form that will be compatible with the disposition decision reached through the Office of Fissile Materials Disposition determines through the National Environmental Protection Act (NEPA) process.

Figure 4 shows the amount of plutonium metal and oxide that we will package in the stabilization program through May 2002. You can see we have a very aggressive program for the plutonium that will be stabilized and are excited about the progress we anticipate at the Department's sites.

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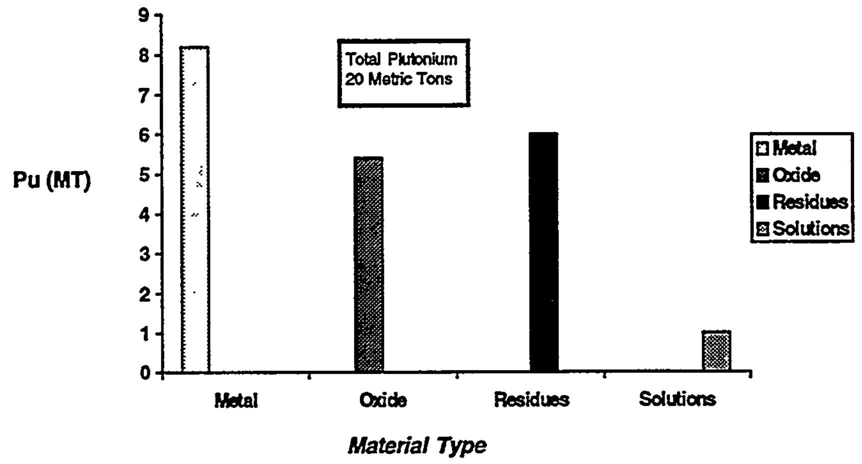
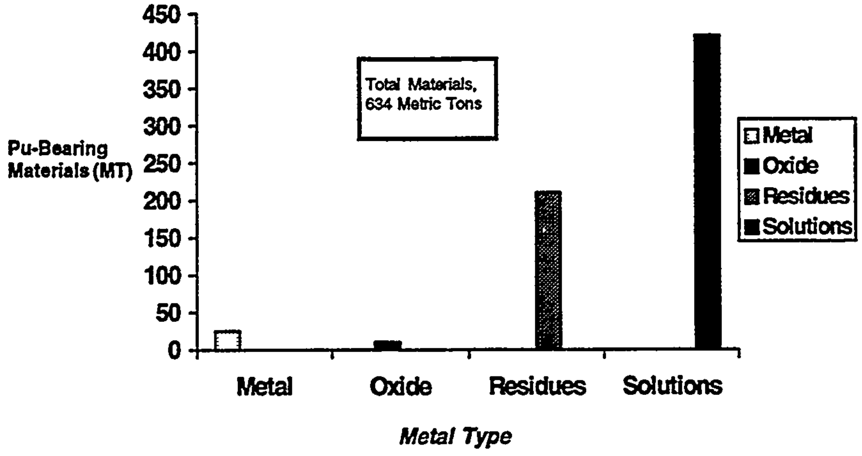
Figure 1
Quantity of Plutonium



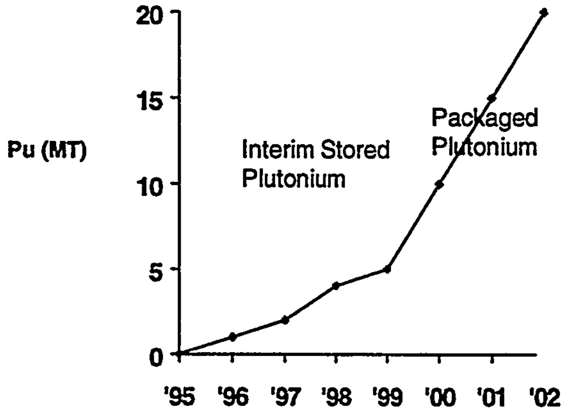
Plutonium Stabilization & Immobilization Workshop

Figure 2
Quantity of Plutonium-Bearing Material



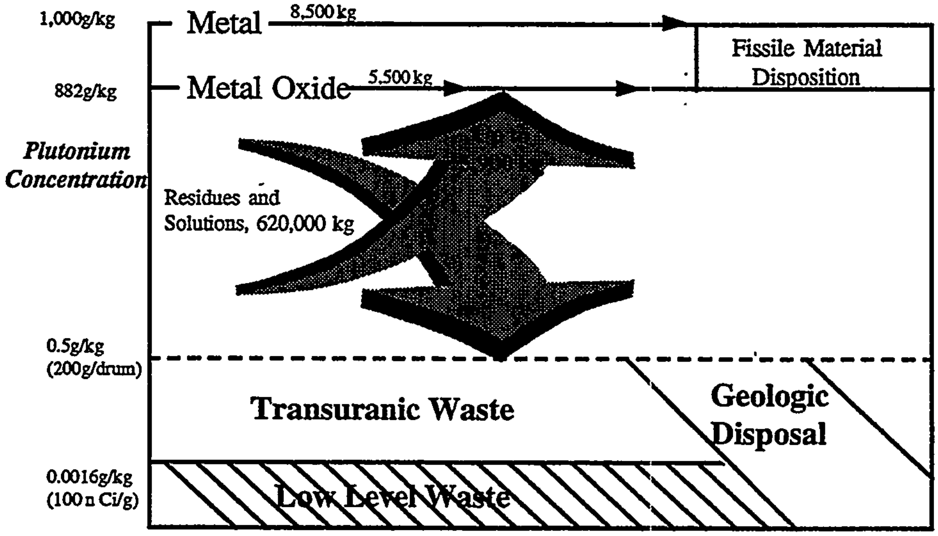
Plutonium Stabilization & Immobilization Workshop

Figure 3
Plutonium Metal and Oxides will be Packaged, Suitable for 50-year Storage by May 2002.



Plutonium Stabilization & Immobilization Workshop

Figure 4
Stabilized Plutonium is Destined for Disposition or Geologic Disposal



Immobilization Needs and Technology Programs

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ABSTRACT

In the aftermath of the Cold War, the U. S. and Russia agreed to large reductions in nuclear weapons. To aid in the selection of long-term management options, DOE has undertaken a multifaceted study to select options for storage and disposition of plutonium in keeping with U. S. policy that plutonium must be subjected to the highest standards of safety, security, and accountability. One alternative being considered is immobilization. To arrive at a suitable immobilization form, we first reviewed published information on high-level waste immobilization technologies and identified 72 possible plutonium immobilization forms to be prescreened. Surviving forms were further screened using multi-attribute utility analysis to determine the most promising technology families. Promising immobilization families were further evaluated to identify chemical, engineering, environmental, safety, and health problems that remain to be solved prior to making technical decisions as to the viability of using the form for long-term disposition of plutonium. From this evaluation, a detailed research and development plan has been developed and initiated to provide answers to these remaining questions.

INTRODUCTION

In the Cold War aftermath, significant quantities of enriched uranium and weapons-grade plutonium have become surplus to national defense needs in both the U. S. and Russia. Nuclear powers are now faced with management of tonnes of Pu in excess to national security needs. These excess stockpiles pose a danger to national and international security, not only in the potential proliferation of nuclear weapons but also in the potential for environmental, safety, and health consequences if these fissile materials (FMs) are not properly managed.

If agreed reductions are implemented, perhaps 100 tonnes of Pu will no longer be needed for military purposes by Nuclear Weapons States. Continued implementation of arms reduction agreements will result in further dismantling of weapons and increasing stockpiles of surplus weapons-usable materials.

There is a serious risk of nuclear proliferation from the resulting growing stockpiles. Nuclear weapons or fissile materials could fall into the hands of terrorists or rogue non-nuclear nations through theft or diversion of FMs. The U.S. National Academy of Sciences (NAS) report[1] on the management and disposition of excess weapons plutonium characterized this as a "clear and present danger." This nuclear danger is, in many ways, more diffuse, harder to manage, and more dangerous than the nuclear tensions of the Cold War era.

On January 24, 1994, in response to the President's nonproliferation policy, Secretary O'Leary created a Department of Energy (DOE)-wide project for control and disposition of surplus fissile materials which later became the Office of Fissile Materials Disposition (MD). MD, through task teams composed of experts from national laboratories, production sites, universities, industry, and other DOE programs, e.g. Civilian Radioactive Waste Management, (RW), have used a process that considered potential long-term storage and disposition options, evaluated them against screening criteria, and identified alternatives reasonable for continued evaluation in a Programmatic Environmental Impact Statement (PEIS) process. Screening criteria, which were developed with input from the public, reflect the President's Nonproliferation and Export Control Policy of September 1993, the January 1994 Joint Statement by Presidents Clinton and Yeltsin on Nonproliferation of Weapons of Mass Destruction and the Means of Their Delivery and the analytical framework established by the NAS.

To aid in selecting long-term management options for surplus weapons Pu, DOE has undertaken a multi-faceted study to select options for storage and disposition in keeping with U. S. policy that excess Pu must be subjected to the highest standards of safety, security, and international accountability. The primary goal is to render weapons-usable fissile materials as inaccessible and unattractive for weapons fabrication as that in commercial reactor spent fuel (i.e. meet the "spent fuel standard") while protecting human health and the environment. Disposition is defined as a process of use or disposal of materials that results in the remaining material being converted to a form substantially and inherently more proliferation-resistant than the original form. Disposition options must take into account technical, nonproliferation, environmental, and economic considerations.

Disposition can be divided into three distinct but overlapping phases—dismantling, intermediate storage, and long-term disposition (Fig. 1). Dismantling of U.S. and Former Soviet Union weapons and storage of resulting surplus fissile materials (SFM) are already under way. Conversion of residue materials and long-term disposition of all FM will take far longer to accomplish.

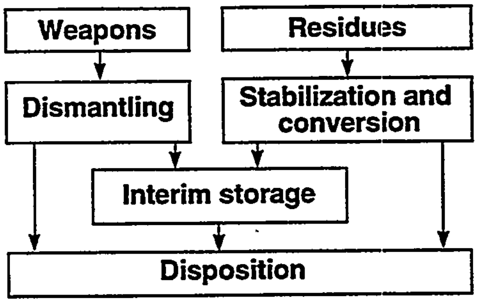


Figure 1. Steps in control and disposition of surplus fissile materials.

Immobilization Program

One class of disposition alternatives is immobilization. In these alternatives, surplus Pu would be immobilized in an acceptable matrix to create a chemically stable form for disposal in a high-level waste repository. The radiation level of the immobilized form would also meet the "spent fuel standard" in that fissile material would be mixed with high-level wastes or other radioactive isotopes and immobilized to create a radiation field that could serve as a proliferation deterrent comparable to commercial spent nuclear fuel.

MD selected the Lawrence Livermore National Laboratory as Lead Laboratory to study and recommend methods for transformation of SFM into long-term immobilized forms meeting environmental, safety, and security objectives; to provide appropriate input to other Disposition Tasks Teams so as to assess technical feasibility of immobilization as a long-term disposition option; and describe infrastructures required to conduct disposition of SFM. Support laboratories include Savannah River Technology Center, Argonne National Laboratory, Oak Ridge National Laboratory, and Pacific Northwest Laboratory. The team also includes support from US universities and industries.

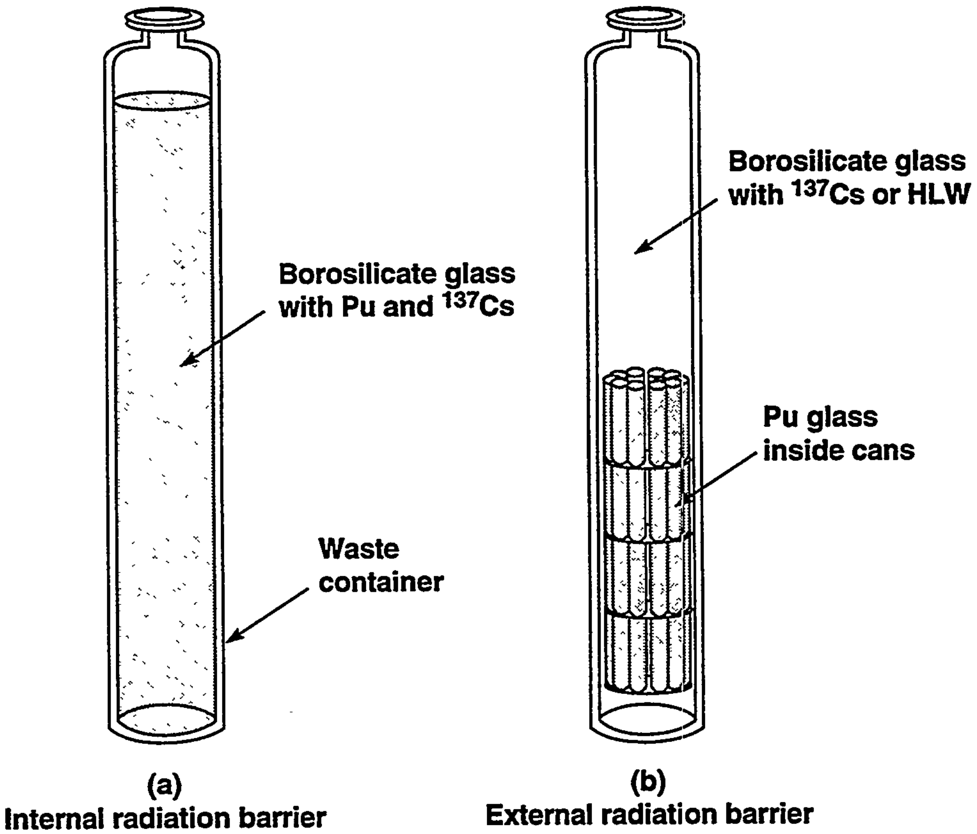
As part of the disposition program, other nations with relevant interests and experience have been invited to participate in the disposition study. Australia, the United Kingdom, France and Russia are participants in the Immobilization Program.

Immobilization would embed Pu in a tailored ceramic, glass, or other suitable material, alone or mixed with radioactive fission products to produce a suitable disposal form. To be viable, the Pu concentration of the form must be in the range of 1.0 to 10 wt% range. To arrive at suitable forms, published information on HLW immobilization technologies was reviewed; 72 uniquely named forms were identified.[2-5] After prescreening, the 16 surviving forms were screened using multi-attribute utility analysis (MAUA) to determine the more promising technologies. Promising immobilization families (glass, ceramics and metals) were further evaluated to identify and seek solutions for chemical, engineering, environmental, safety, and health (ES&H) problems remaining to be solved prior to making technical decisions as to their viability for long-term disposition of Pu. We are also assessing modifications required to existing U.S. high-level waste immobilization approaches, and modifications required to the DOE response to the Defense Nuclear Facilities Safety Board's Recommendation 94-1, ES&H implications, costs, and schedule.

Processing Options

Five immobilization base case options comprising glass and ceramic forms are being evaluated in the PEIS/ROD process:

- Vitrification
    - Internal radiation barrier (Fig 2)



(a) Internal radiation barrier

(b) External radiation barrier

Figure 2. Two options for vitrification of Pu

(1) a new greenfield facility that produces a borosilicate glass containing Pu, neutron absorbers, and ^{137}Cs (as a radiological barrier), and then encapsulates this glass in a storage canister;

(2) an adjunct melter to the existing Defense Waste Processing Facility (DWPF) that produces a glass containing Pu, neutron absorbers, and high level waste (HLW), and then encapsulates this glass in a storage canister;

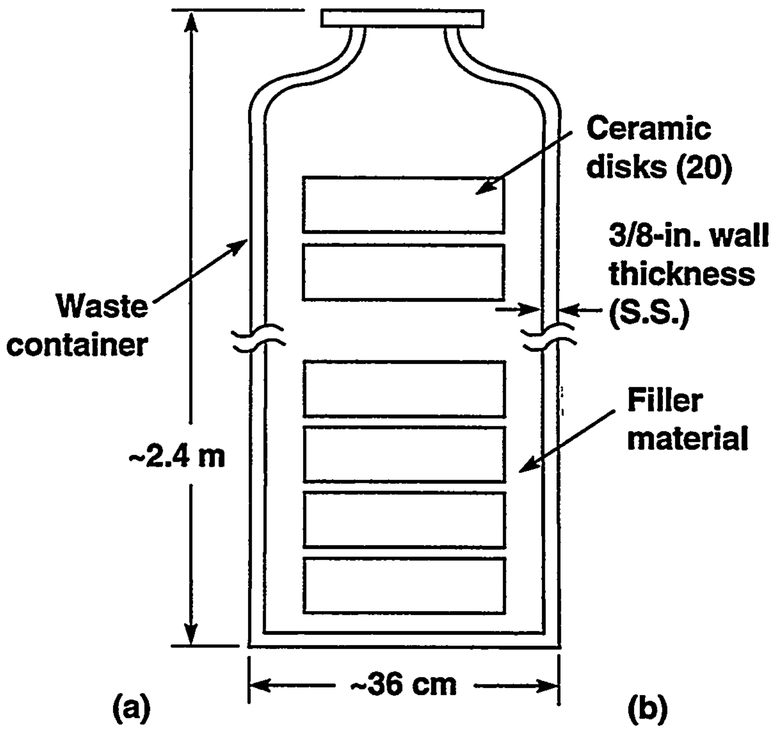
- External radiation barrier (Fig 2)

  (3) a "can-in-canister" variant, in which an inner can containing a Pu- and neutron-absorber-bearing glass is surrounded by a glass containing a radiological barrier, which, in turn is contained in an outer storage canister.

- Ceramics
  - Internal radiation barrier (Fig 3)

    (4) a new ("greenfield") facility that produces a ceramic containing Pu, neutron absorbers, and ^{137}Cs and then encapsulates the ceramic in a storage canister;

- External radiation barrier (Fig 3)
  (5) a "can-in-canister" alternative in which an inner can of a ceramic containing Pu and neutron absorbers is surrounded by a ceramic or glass that contains a radiological barrier, which is in turn contained in an outer storage canister.



	Internal radiation barrier	External radiation barrier
Ceramic	Ceramic with Pu and ^{137}Cs	Ceramic with Pu
Filler	Inert material (TiO_2 powder)	Solidified $Na_2Ti_3O_7$ with ^{137}Cs

Figure 3. Two options for immobilizing Pu in a ceramic

Several variants to the base cases are also being examined. These include use of either plutonium oxide (base case) or plutonium nitrate solution as the feed to the melters. The base case for the ceramics is plutonium nitrate feed; the variant is the use of plutonium oxide feed.

Feed Stocks

When the Cold War unexpectedly and abruptly ended in 1991, DOE stopped production of plutonium for nuclear weapons —it had already in effect stopped production of the warheads themselves in 1988. Facility missions were abruptly changed and budgets were dramatically reduced.

Tonnes of plutonium, previously slated for warheads, were left in place, much of it in forms and facilities not suited to long term storage. There are approximately 26 tonnes of Pu, not including amounts contained in assembled and disassembled weapons, located throughout the weapons complex. The alpha decay of Pu results in formation of free radicals which induce chemical reactions within stored solutions and solids containing organics (plastics, paper, cloth, etc.) that make behavior of these solutions and solids difficult to predict. The Defense Nuclear Facilities Safety Board (DNFSB) recognized this when they issued their recommendation 94-1, in May 1994, calling on DOE to:

- bring stored plutonium metal and oxide into conformance with the DOE storage standard
- process the plutonium solutions into forms safer for interim storage
- process possibly unstable plutonium residues into forms suitable for interim storage
- establish a research program to help choose among candidate processes for conversion to interim forms and longer-term disposition.

Under the assumption that long term storage and ultimate disposition of plutonium are not considered to be technologically feasible during this century, current DOE programmatic efforts are focusing corrective actions on stabilizing stored materials in response to the DNFSB recommendations. Materials returning from the nuclear stockpile, together with these existing inventories of fissile materials, which may easily be converted to a weapon usable form, define the scope of materials that have generated a concern for international security. It is assumed that corrective actions will be completed prior to the start of large scale disposition activities and that the source of plutonium for disposition will include weapons-usable materials stored in stabilized forms defined by DNFSB 94-1 recommendations.

Only the very top level of the DOE corrective action plan has been completed. Since the lower level corrective actions have not yet been planned or executed, it is not possible to specify the exact form, quantity, or location of the plutonium contained in the stabilized scrap or irradiated materials which may be available for disposition.

At the end of the cold war, there was also a considerable quantity of material which contained amounts of Pu which were considered to be economically recoverable but which were not considered primary manufacturing feed stocks. These residues, largely in storage at the Rocky Flats site, represent a concern since the fissile inventory is sufficiently large to be of proliferation concern. However, the Pu content for all residues, which is always less than 50%, is only on the order of about 1% on the average overall. The chemical and physical form of these residues presents difficulties for long term storage or use in the weapons complex. As a consequence, these have been declared as waste with the intent to discard them at WIPP when WIPP becomes operational.

Several of the immobilization options, however, may well present a more cost effective approach for the elimination of these residues rather than just placing them in WIPP. In order to consider this question, calculations were done at LLNL which estimated the cost associated with various options for either discarding the Pu directly, or for immobilizing the Pu for disposition as part of the Fissile Materials Disposition Program. These cost calculations considered the cost of packaging and disposing of the residues in WIPP versus the cost of processing the residues, dissolving them in glass, and adding the radiation spike prior to repository emplacement. In doing these calculations, parameters considered included the average Pu cutoff for processing (with the leaner residues always going to WIPP) and the average Pu loading per barrel which could be reasonably expected for WIPP disposition.

Figure 4, shown below, indicates the cost estimates for disposition for the nation's excess Pu using glass immobilization where various quantities of the residues are either included or excluded (based on the Pu cutoff percentage for processing).

As can be seen, there may well be cost advantages in processing a significant portion of the residues for immobilization disposition given the WIPP limits of 200 grams/barrel. Average WIPP loading values will likely be less than 200 grams/barrel (Fig 5). A reasonable value is probably on the order of 100 grams Pu per barrel

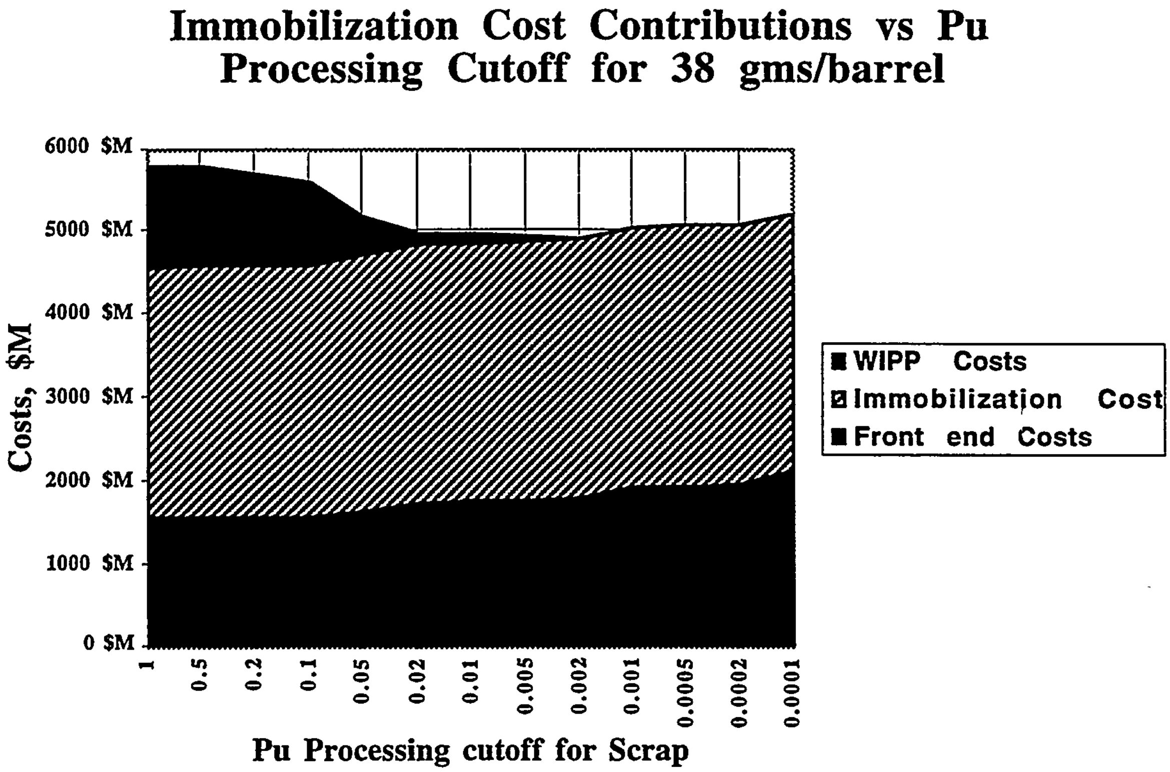
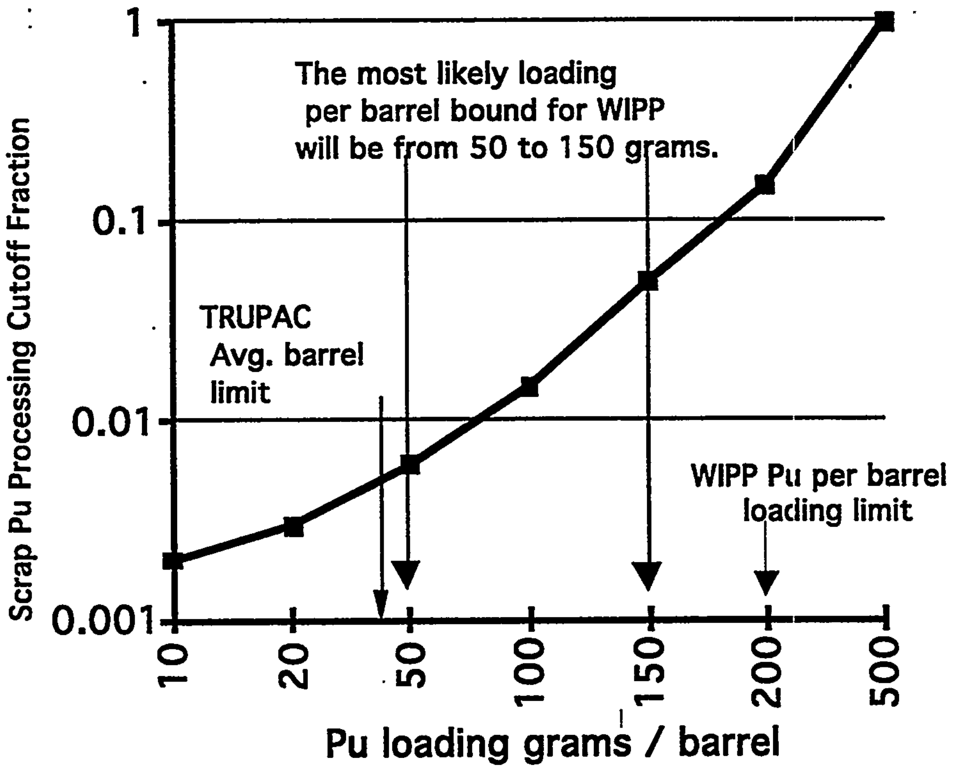


Figure 4. Cost Estimates

Figure 5. "Optimum" Scrap Processing Cutoff Points Vs. Average WIPP Loading Limits



OVERALL R&D KEY FEATURES

Each of these technologies require further research and development to:

1. identify a material formulation that optimizes processability and long term performance;
2. develop processing equipment, material flow and process controls, operational strategies, and material accountability while minimizing impacts on workers, the environment, cost, and the ability to maintain an acceptable implementation schedule;
   demonstrate on a pilot scale that individual operations or processing steps fit together seamlessly;
3. demonstrate that the specific disposal forms meet the spent fuel standard for proliferation resistance.

The fundamental features of the overall long term research and development (R&D) plan for plutonium disposition using immobilization technologies include:

- Full understanding of criticality safety margins at every stage of plutonium handling and processing

- Practical limits of plutonium concentration from both solubility and kinetic considerations
- Incorporation of ^{137}Cs and its effects on both process operations and final waste form performance and proliferation resistance
- Sensitivity of immobilization process formulation and product performance to impurity concentrations in the feed
- Process optimization to minimize waste, costs, and time of disposition
- Pilot scale demonstrations with transuranics to confirm viability of the process
- Evolving and characterizing equipment designs and compositions that reliably and safely handle plutonium weight loadings that result in economically effective operations
- Properties that influence performance, reliability, and safety considerations—such as nuclear criticality—must be determined
- Assessment of the impact of plutonium volatility
- Assessment of the impact of the presence of neutron absorbers
- Assessments of the physical durability of the product and the plutonium product phases. Relative durability and leach rate determination
- Assessments of Pu recovery and proliferation resistance of the immobilized plutonium form
- Development of predictive material control and accountability and process controls and models for plutonium immobilization operations.

Analytical tools and techniques will need to be properly validated. These issues have a large effect on process complexity and limitations on throughput, so it is imperative that a consistent set of baseline data be carefully and fully determined. The experimental work and other assessments identified in the R&D plan are intended to address these issues.

SUMMARY

An International Team was assembled for the purpose of selecting suitable immobilization forms and processing technologies for the Fissile Materials Disposition Program Office. The Task Team use the NAS Study as a reference point for starting the study but was not limited to recommendations of the NAS.

Three basic forms have been selected and the processing options to provide those three forms have been defined. As this conference is for the discussion of glass and ceramics only, metal forms were not discussed. Environmental Data has been supplied to the DOE contractor writing the PEIS for the Disposition Program. The Task Team is now developing cost data for the Record of Decision—which is anticipated in the Fall of 1996. The Task Team is also evaluating these options to determine if they indeed meet the security standard and goals set up by the NAS Study.

APPENDIX
LONG RANGE RESEARCH AND DEVELOPMENT PLAN

The Long Range Research and Development Plan, Immobilization Technologies, summarizes the long term research and development (R&D) requirements for plutonium disposition using immobilization technologies.

In this overview, a brief summary of the status of the immobilization options and the emphasis of the required research and development is presented for each of the immobilization options being considered. The fundamental features of the overall long term research and development (R&D) plan for plutonium disposition using immobilization technologies are presented.

Vitrification Technology

The plan consists of individual stand-alone plans for each immobilization options. Three alternatives based on vitrification technology are under consideration:

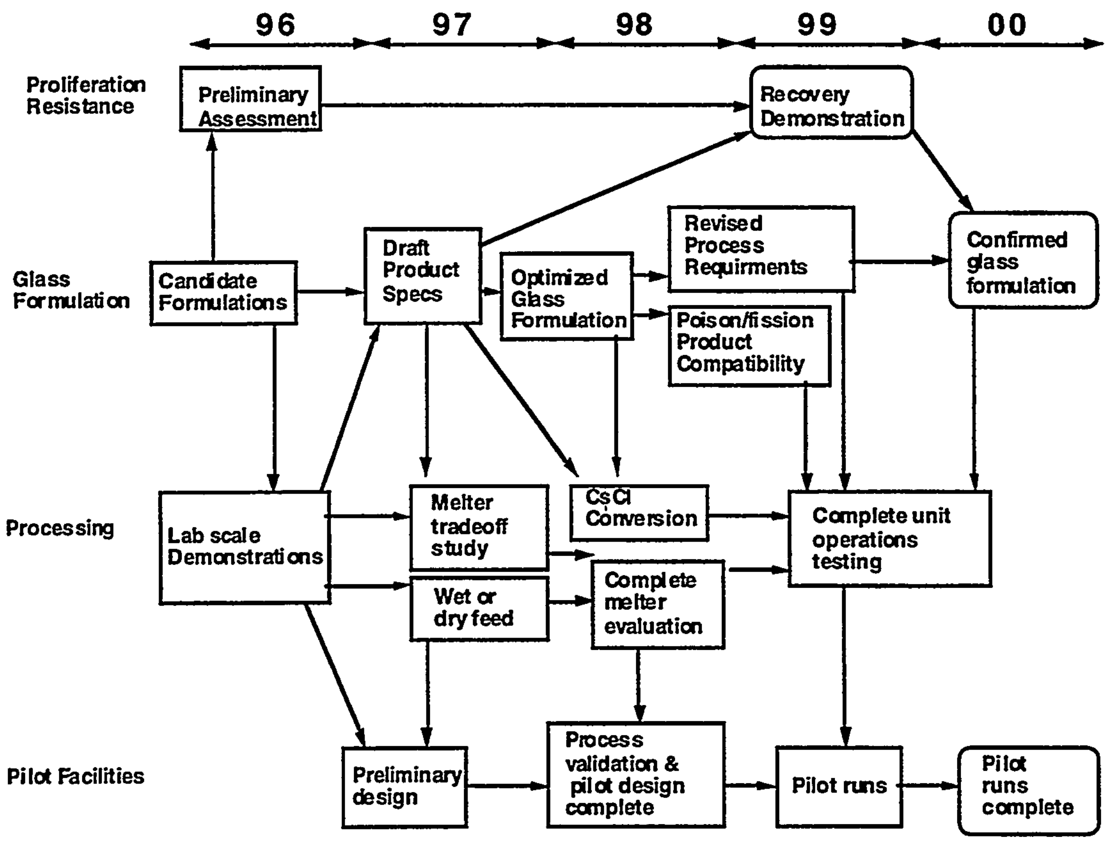
1. Vitrification at a Greenfield site (Internal Radiation Barrier)
2. Vitrification using an External radiation barrier (Can-in-Canister)
3. Vitrification using a DWPF Adjunct melter (Internal Radiation Barrier)

The logical relationship of key milestones for the vitrification alternatives are shown in diagram form in Figure 6. A critical concern relates to whether a glass for each of the alternatives can be formulated to meet the processability and performance requirements.

Development and Characterization of Optimized Glass Formulations for Plutonium Immobilization

The specific glass formulation selected will strongly influence the design and cost of the immobilization facility, as well as the extent of characterization, necessary for facility and immobilization form licensing, with a direct impact on implementation schedule. For example, the maximum allowable plutonium loading, which will be set by the limits of process safety and long term performance of the immobilization form may determine facility size and throughput.

Figure 6. Glass Immobilization - Key Milestones



Project Objective

To formulate, through testing and analysis, a Pu-containing glass optimized for safety, performance, processability, and cost effectiveness. To achieve adequate understanding of the glass behavior, both during processing and at long times, so that Title 1 design can be initiated.

Project Description

Detailed glass requirements for both processing and long term performance will be documented. Guided by existing data and analysis, a range of glass formulations will be prepared and characterized for Pu solubility, the influence of required additives such as neutron absorbers, tolerance for process and compositional variations, processability, resistance to radiation damage, and long-term chemical durability. Models for Pu processing parameters and release rates will be developed and used to optimize the formulations. These formulations will be characterized, material response models modified as necessary, and long term performance testing initiated. This effort will be closely coupled with the Processing and Equipment Technologies effort to insure that candidate formulations meet processability and process safety requirements. Completion of this task is not required prior to beginning Title 1 design.

Key Information Generated/Key Issues Resolved

- Pu solubility as a function of glass composition
- neutron absorber solubility as a function of glass composition
- physical and chemical requirements for feedstocks
- effect of radiation damage on stability of immobilization form
- composition of final immobilization form
- information needed for long-term degradation/radionuclide release models
- relative release rates of fissile materials and neutron absorbers.

Process Development, Controls, and Equipment Technologies

Immobilization with large weight fractions Pu has never been implemented in a production setting. Optimization of the facility for safety, performance, ES&H and cost effectiveness will require background development for feed stock preparation, process flow, melter design, material accountability, and process and criticality control. These efforts will work in close concert with the Glass Formulation R&D tasks.

Project Objective

To understand facility unit processes and production flow well enough to optimize facility and equipment design, performance, and cost effectiveness (while maintaining adequate safety and performance margins) during Title 1 and 2 design.

Project Description

Glove box scale operations will be set up, evaluated and modeled for each unit operation. Process schemes will be developed, analyzed and, tested comparing wet and dry melter feed streams. For the greenfield alternative, the process for converting ^{137}CsCl from Hanford to a form suitable for a glass feed will be demonstrated and off-gas handling approaches developed. In combination with glass formulation efforts and nuclear criticality analysis, glass melter designs will be evaluated and modifications proposed. Prototype melter performance will be documented. A Process/Product Control System will be developed consistent with the glass processability models determined in the formulation effort. The technology for tracking accountable materials will be demonstrated.

Key Information Generated/Key Issues Resolved

- determination of whether to use a wet or dry feed for melter
- demonstration of the process for converting CsCl and other potentially incompatible feed materials to suitable form
- establishment of processing requirements on glass formulation
- development of process criticality control, process quality, and materials accountability systems
- processing equipment and melter design

Pilot Facility for Plutonium Vitrification

Prior to completing detailed facility design, it is essential to demonstrate that full scale (glove box) processes and control strategies work together seamlessly and predictably. For these operations surrogates will be used in place of radiation barrier (e.g., ^{137}Cs) materials.

Project Objective

Demonstrate processes for making Pu-containing glass logs using realistic equipment and procedures.

Project Description

Using facilities, melter and procedures developed in other tasks, demonstrate full scale operations, initially using surrogates and later using Pu-containing glass but no radiological barrier. Demonstrate process control and monitoring systems. Develop operational experience, characterize product and compare to model, and modify unit operations and Process Control System as appropriate.

Key Information Generated/Key Issues Resolved

- demonstration of compatibility of unit processes
- demonstration of lack of Pu or neutron absorber segregation in product glasses

Determination of Proliferation Resistance of Plutonium Glasses

Prior to implementation, it is important to demonstrate that Pu glasses meet the spent fuel standard.

Project Objective

To document the proliferation resistance of candidate Pu glasses.

Project Description

Process flow sheets for dissolution and recovery of Pu from vitrified immobilization forms will be determined. Time and cost estimates will be made. Limited validation testing will be performed.

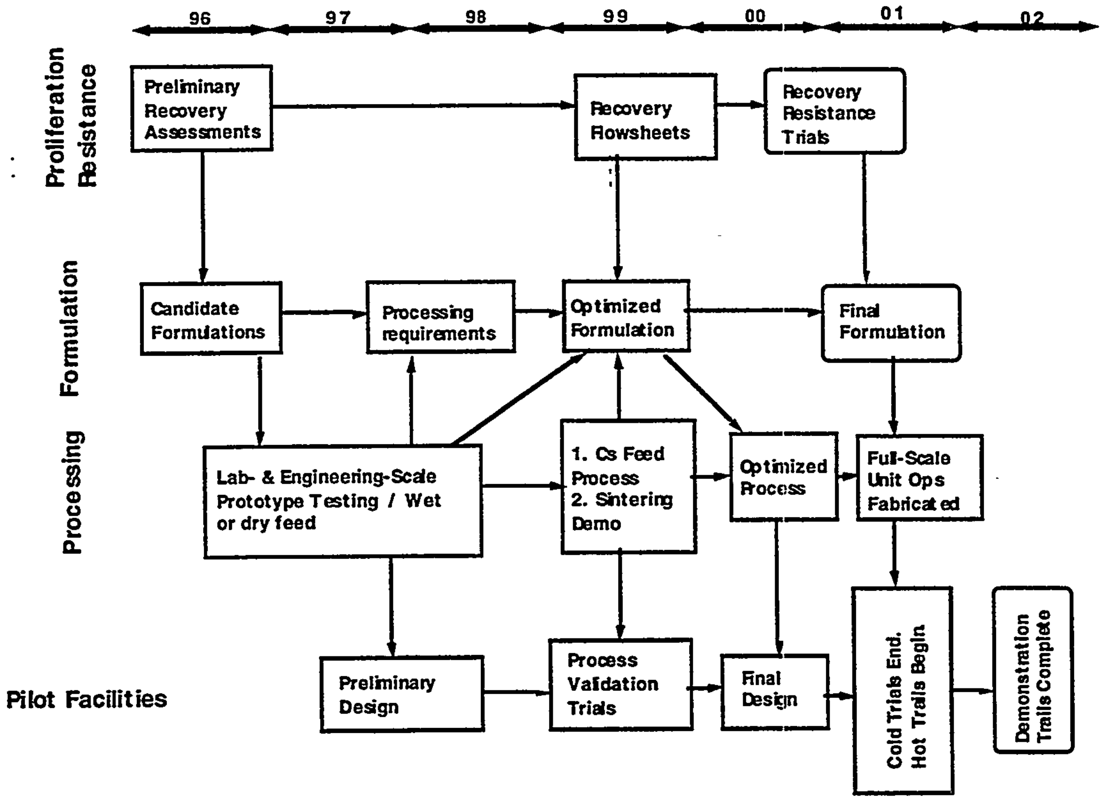
CERAMICS TECHNOLOGY

Two different immobilization alternatives based on ceramics technology are under consideration:

1.	Ceramics	Greenfield site (Internal Radiation Barrier)
2.	Ceramics	External radiation barrier (Can-in-Canister)

The logical relationships of key milestones for the ceramic alternatives are shown in diagrammatic form in Figure 7. A critical concern relates to whether a ceramic can be formulated that meets the processability and performance requirements

Figure 7. Ceramic Immobilization - Key Milestones



Development and Characterization of Optimized Ceramic Formulations for Plutonium Immobilization

The specific ceramic formulation selected will strongly influence the design and cost of the immobilization facility, as well as the extent of characterization necessary for facility and immobilization form licensing, with a direct impact on implementation schedule. For example, the maximum allowable Pu loading, which will be set by the limits of process safety and long term performance, may determine facility size and throughput.

Project Objective

To formulate, through testing and analysis, a Pu-containing ceramic optimized for safety, performance, processability, and cost effectiveness. To achieve adequate understanding of the ceramic's behavior, both during processing and at long times, so that Title 1 design can be initiated.

Project Description

Detailed ceramic requirements for both processing and long term performance will be documented with all relevant agencies and departments Guided by existing data and analysis, a range of ceramic formulations will be prepared and characterized for Pu solubility, the influence of required additives such as neutron absorbers, tolerance for process and compositional variations, processability, resistance to radiation damage, and long-term chemical durability. Models for Pu processing parameters and release rates will be developed and used to optimize the formulations.

These formulations will be characterized, material response models modified as necessary, and long-term performance testing initiated. This effort will be closely coupled with the Processing and Equipment Technologies effort to insure that candidate formulations meet processability and process safety requirements. Completion of this task is not required prior to beginning Title 1 design.

Key Information Generated/Key Issues Resolved

- Pu solubility as a function of ceramic composition
- neutron poison solubility as a function of ceramic composition
- physical and chemical requirements for feedstocks
- effect of radiation damage on stability of immobilization form
- composition of final immobilization form information needed for long-term degradation/radionuclide release models
- relative release rates of fissile materials and neutron poisons

Process Development, Controls, and Equipment Technologies

Immobilization using ceramics with large weight fractions of Pu has never been implemented in a production setting. Optimization of the facility for safety, performance, ES&H, and cost effectiveness will require background development for feed stock preparation, process flow, calciner and press design, material accountability, and process and criticality control. These efforts will work in close concert with the Ceramic Formulation R&D task.

Project Objective

To understand facility unit processes and production flow well enough to optimize facility and equipment design, performance, and cost effectiveness (while maintaining adequate safety and performance margins) during Title 1 and 2 design.

Project Description

Glove box scale operations will be set up, evaluated and modeled for each unit operation. Process schemes will be developed, analyzed and, possibly, tested comparing wet and dry melter feed streams. The effect of impurities in feed materials on ceramic processability will be evaluated, and if needed, preprocessing procedures established. For the greenfield alternative, the process for converting ^{137}CsCl from Hanford to an acceptable feed for ceramics will be demonstrated and off-gas handling approaches developed. In combination with ceramic formulation efforts and nuclear criticality analysis, calciner and press designs will be evaluated and modifications proposed. A Process/Product Control System will be developed consistent with the ceramic processability models determined in the formulation effort. The technology for tracking accountable materials will be demonstrated.

Key Information Generated/Key Issues Resolved

- determination of whether to use a wet or dry Pu feed
- demonstration of process for converting ^{137}CsCl and other potentially incompatible feed materials to suitable form
- establishment of processing requirements on ceramic formulation development of process criticality control, process quality, and materials accountability systems
- processing equipment (e.g., hot press, calciner, slurry tank) design

Pilot Facility for Immobilization of Plutonium Using Ceramics

Prior to completing detailed facility design, it is essential to demonstrate that the full scale (glove box) processes and control strategies work together seamlessly and predictably. For these operations will culminate in the pilot-scale production of Pu-containing ceramics with surrogates used in place of the radiation barrier materials.

Project Objective

Demonstrate the integration of the slurrying, calcining, and hot-pressing operations needed to make Pu-containing ceramic immobilization forms using realistic equipment and procedures.

Project Description

Using facilities and procedures developed in other task demonstrate full scale operations, initially using all surrogates and later using Pu and non-radioactive surrogates for the radiation-barrier. Demonstrate process control and monitoring systems. Develop operational experience, characterize product, compare to models, and modify unit operations and Process Control System as appropriate.

Key Information Generated/Key Issues Resolved

- demonstration of compatibility of unit processes
- demonstration of homogeneity of materials in the slurrying and calcination processes

Proliferation Resistance of Plutonium Ceramics

Prior to implementation, it is important to demonstrate that Pu ceramics meet the spent fuel standard.

Project Objective

To document the proliferation resistance of candidate Pu ceramics.

Project Description

Process flow sheets for recovery of Pu from ceramic immobilization forms will be determined. Time and cost estimates will be made. Limited validation testing will be performed.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

DISCLAIMER

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5. L. W. Gray, T. Kan, W.G. Sutcliff, J. M. McKibben, W. Danker, "Disposition of Surplus Fissile Materials via Immobilization," Vol. XXIV,413, Institute of Nuclear Materials Management 36th Annual Meeting Proceedings, Palm Desert, CA, July 9 -12, 1995

Session Chair for Introductory Session:
Jill Lytle, US DOE, Office of Environmental Management
Tuesday, December 12, 1995; 8:30 am

Question / Comment 1:
Rob Einziger, Pacific Northwest Nat'l Lab
You mentioned in your talk the need to develop new tools to handle the plutonium. Does the Department have the funds to develop these new tools and what methodology will the Department employ to encourage the development of these tools?

Answer:
Tom Grumbly, US DOE, Office of Environmental Management
Good question. In our 97 budget request, which will be the tightest budget request that has gone to the hill in a long time, you'll see an initial emphasis on the development of some new technologies to help us deal with plutonium. As we speak, we're working on moving forward to stabilize some of the material at Savannah River and to include in that stabilization process, the development of a small pilot scale vitrification plant. I think we're going to have to make larger investments over the next three or four years. The nature of those investments, I might add, will come out of meetings like this over the next year as we develop the rest of our budget for the rest of the century.

Question / Comment 2:
Arjun Makhijani, Institute for Energy and Environmental Research
This question is for Mr. Hurt. You outlined a daunting set of problems at the Savannah River Reprocessing Plant: they are aging facilities that will need a lot of training, and may be prone to accidents and so on. You recognize there are some problems. But I would like to know what safety studies the DNFSB did, or commissioned, to come to the conclusion that operating the canyon at Savannah River would be safer than storing the fuel as it is, or even better, putting it in cans the way they did at Hanford in 1980? Also, why you thought it would be quicker and safer? Finally, would you be willing to share these studies with us?

Answer:
Davis Hurt, Defense Nuclear Facilities Safety Board
We have published a technical report on that subject that's available, called DNFSB/TECH 7. This report focused on the question of what we thought the problems would be with continued wet storage of the fuel. Have you seen that report?

Makhijani:
I know the problems with continued wet storage, but did you (DNFSB) compare them with problems of (red-oil) explosions in reprocessing or a fire in the island storage tanks, from degrading high-level waste?

Hurt:
I think the report made some high level comparisons like that similar to those you described. It's available, and if you give me your address, someone on our staff will send it to you. I don't think the board has claimed to know what is the absolute right answer. When the DOE implementation plan for the DNFSB recommendation 94-1 was made about a year ago, DOE proposed to use both canyons at Savannah River to deal with the variety of fuels and other materials that required stabilization. Now, that's my understanding of DOE's plan as of today, unless something happens.

Makhijani:
Are you satisfied with the DNFSB recommendation that to operate the reprocessing plant is really unequivocally a safer option than the others? Have you thoroughly studied this question before making a recommendation?

Hurt:
Well, the DNFSB did not specifically recommend operating the plants. We recommended stabilizing these fuel materials within 2 - 3 years. The Department told us that they would do that by operating these plants and we said okay. Those plants, if they're restarted, will be subject to other board recommendations on safe restart of the facilities, on authorization basis, and on other things. Now, you probably know, as well as I do, that there is change in the air about what facilities at Savannah River might be restarted. I don't know which, but, we could ask Mr. Grumbly, if he were still here. [Editor's Note: Tom Grumbly had to leave early for another engagement] I don't know what his plans are, but the Board, when they heard about the possible changes, said we still feel that it's not safe to leave that fuel in wet storage, and we feel as strongly about that as before.

Makhijani:
I just want to make a comment that I didn't read the report you referenced.

Question / Comment 3:
Larry Penberthy, Penberthy Vitrification, Inc.
I have been working with vitrification technology for a long time since my days with Eastman Kodak in the Optical Division. I first started melting glass electrically, in 1949. I now process it world wide, 16 million tons of glass a year. Grumbly mentioned "Public" participation. What I want to emphasize is that there should be "Industry" participation. Industry has a great deal of information about vitrification glass and the processing technology based on it. What I have here is some glass made with Hanford sand, basaltic sand, and it has in it 2% samarium oxides as the surrogate for Pu, and 1% cadmium oxide as a neutron absorber. It's got a little bit of uranium in it so that people can't say, "Well, that's just black glass that came from the hardware store." This is fresh glass made only a couple of weeks ago. The point is, that we need to have a stable glass, and industry knows very well, based on my publications in 1973, that boric oxide in glass makes it soluble. Boric oxide makes a glass, and so does silica, but silica is four valent and the boric is three valent and it does not make a continuous network. The alkali borate separates out as phases and is very well illustrated in chapter 4 of that book. There is no reason for us to continue to think that borosilicate glass is a stable form for Pu. Thank you.

Question / Comment 4:
Marilyn Meigs, BNFL
I thought this was going to be a technical workshop on methods of immobilizing plutonium, but so long as the debate has been opened up to immobilization and MOX use, I'll open it up to policy issues such as nonproliferation objectives. I just wanted to comment that I really don't think that the U.S. decision on disposition of U.S. plutonium (excess weapons plutonium) has any effect on nonproliferation objectives world wide. There are ways that the U.S. can and is influencing non-proliferation objectives, but I don't think this is one of them. I think no matter what the U.S. does with its material, the civilian nuclear fuel industry will continue doing a good job and doing things as they see fit. I think the Russians will make their decisions based on their own perceptions and may or may not, hopefully will not, be influenced by the what the U.S. decides. In any event, whatever the U.S. decides, BNFL is willing to help in any way it can. It has a mature industry, thank God, that the rest of the world will stop reprocessing in this country and we have a lot of technologies both for MOX and in immobilization. We are helping, as Leonard Gray said, in that we will do whatever we can to support the decision, but immobilization makes sense from many perspectives. Thank you.

Answer:
Jill Lytle, US DOE, Office of Environmental Managment
I do want to emphasize that although there are obviously some strong feelings among both the participants here and outside, on the policy issues, we are trying to concentrate on the technical issues at this conference and to focus on what we can do collectively as technical people to contribute, in a positive way, to these decisions. Obviously, there are going to be policy aspects to the decisions, but we want to make sure that the technical side is robust and that we have good technical information on the table when we're debating the policy decisions. This is not going to be the venue for that debate: the policy debate.

Question / Comment 5:
Paul, Pacific Northwest Laboratories
Besides the Pu issue, there is also another big problem out there, and that is the area of DOE spent fuel that's in storage basins in all sorts of forms. Studies have shown a lot of that fuel may have to be processed in order to be economically disposed. What is being done to integrate these 2 programs so we can handle these issues and not reinvent the wheel?

Answer:
Jill Lytle, US DOE, Office of Environmental Managment
I think I'll take that one on since I have the pleasure now of being in charge of the program that manages both of those issues. I recently moved from the position of directing the waste management program including Spent Nuclear Fuel (SNF) to this new position in Nuclear Materials and Facility Stabilization. I brought the SNF with me. So now these two programs are together. They are also together in the DNFSB 94-1 recommendation. They wisely saw this as part of a larger picture of the various materials that need to get stabilized in the short term and also dealt with in the long term. So I appreciate your comment. We are trying to get these two pieces much more integrated in our technology programs, and also in our analysis and strategic planning.

Questions / Comment 6:
<Questioner not identified>
Dr. Moore, when you mentioned lack of public participation, I was wondering, what ideas do you have in enhancing and encouraging public participation, and also, in extending invitations to the public and the Agencies responsible for deciding technical issues?

Answer:
Leroy Moore, Rocky Mountain Peace Center
I have the impression that DOE is an organization that hardly knows what its doing inside itself. The left hand doesn't know what the right hand is doing. I'm glad to hear the response to the last question, which indicates that there's some integration. I think that DOE needs to take seriously its commitment to public participation and to make sure that when an event like this happens, that members of affected publics from all around the sites are present. These people are wise, because they are affected and have many questions, only some of which I can begin to get up here today. I don't think a meeting like this should happen without some of these people being present. I know several people really wanted to be here and there was no means for them to do so. As for other kinds of things, I think that the principal vehicle we have at Rocky Flats for public participation is the Rocky Flats Citizens Advisory Board. It is only one medium that we have there. There are others and those need to be taken full advantage of. It's not simply a matter of being in the room. That's new of having conversations between people that not so long ago weren't talking to each other, hardly knew each other, and were often speaking past each other. It's also a matter of paying attention. I could give you numerous examples from Rocky Flats of the things that the public said that were not being paid attention to and that's bothersome, because that's inefficiency of the worst possible sort. When the public responds again and again and isn't heard, it's not going away and even the problems are not going to go away. We're in the situation that we are in today because a technical freeze craft in the U.S. that brought us to this place. I know I'm speaking to the religious group right here right now. This is the most religious meeting I have been to in a long time. I am speaking to the priesthood. Now, I admire your technical competence enormously, and I really want to learn from you and I enjoy very much the opportunity to get to do so, but its very important that the non technical persons that carry within their bodies the effects of your work are constantly paid attention to so that they get to be heard and that they have at least some participation in the decisions that are being made. I knew that question was going to come up and I'm not sure that my answer is very good, except we need more of it. Thank you.

Jill Lytle, US DOE, Office of Environmental Managment
Thank your very much, we obviously have a challenge both to rise to the occasion both on the technical side and on the issue of making sure our decision making includes the public interests groups and everyone who really has a lot to contribute to these decisions. We will try to do better in the future. I want to thank you, all of you, for your participation, in particular to the members of the panel for a very good introduction to this conference and in the next three days.

DISCLAIMER

The views expressed in this report are those of the author(s) or the individuals identified as making the remarks, and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP
DECEMBER 12-14, 1995

MATERIALS AND CONDITIONS

SESSION CHAIRS: RICHARD HAHN, US DEPARTMENT OF ENERGY,
OFFICE OF DEFENSE PROGRAMS, DP-22 AND
KEN SCHEFFTER, WESTINGHOUSE SAVANNAH RIVER COMPANY

Materials and Conditions Opening Remarks
Ken Scheffter, Westinghouse Savannah River

This is the first technical session in the conference. The conference talks this morning were non-technical, but this is what we came for, these sessions. I am employed by Westinghouse Savannah River Company, but I am on temporary assignment with DOE here at Headquarters in Germantown in DP-22, which is the Office of Materials Management. I am also sharing time with EM-63, which is the Office of Material & Facility Transition, that governs and watches over the Savannah River Plant. My role here, this afternoon, will be to introduce the speakers; and we have three of them.

The Materials and Conditions session is the topic at hand, and what I would like to do first is to give you a starting point, so to speak, on the amounts of plutonium that are at sites in the U.S. that we are going to be considering here. This slide is the same basic map of the US that one of the speakers Dr. Gray, I believe, displayed. It gives you an idea, just an idea of the unclassified inventory as of September 1994, the last reconciled inventory that we have, and gives you a flavor of the types of materials about and the amounts we are talking about. The technical talks won't necessarily go into detail on the amounts. These numbers are just to orient your minds to what we are talking about with plutonium.

Next, I want to state a disclaimer about any positions that the speakers might be taking, or are apparently taking, or you perceive them taking. This is a technical workshop, as has been stated before, and especially for any Department of Energy speakers or DOE contractors, it is especially important to realize that nothing that they say should be taken as a Department of Energy position on any of the issues at hand at this point. There is another process out there the NEPA process, that is in progress to rigorously make decisions and that is not the intent of this forum. I want to make sure that is clear. There is nothing that is said that will indicate that a particular option has already been chosen or a decision has been made. Also, the expressed views of the individual speakers do not necessarily represent the DOE positions

Next are some agenda changes. The final conference schedule that you have in your hand shows four presentations. However, we only have three papers. The paper "14 Tons and Deeper in Debt" will not be presented. So, we are going to allow the Russian gentleman to extend his talk a few minutes because of the translation. Then, we will just move up the whole rest of the day, as we can, by these speakers doing their job and the timer doing her job to keep this rolling. We might be able to get to the break a little sooner.

Finally, the objectives of this session--Materials and Conditions presentations. The papers will relate to the following topics, and the question and answer session afterwards will also be addressing these topics. The first paper will discuss chemical and physical forms of materials that have been in storage, and will cite both normal examples of the materials and their conditions in storage, and exceptions to the norm. There will also be application of the lessons that we have learned from storing these materials in the past years, and up to and including the present. We are going to review the present state of technology for stabilization of residues. That will be the second paper. The final paper will be the handling of some of those residues from the perspective of the Russian contingent.

During the question and answer session, make sure that as you walk up to the microphone, you identify yourself clearly, and also speak your question clearly and slowly for both the translations and for me, the session chair. I have to summarize the question and answer session into a one-page sheet that we can put into the published proceedings for this Workshop. Thank you very much for your attention.

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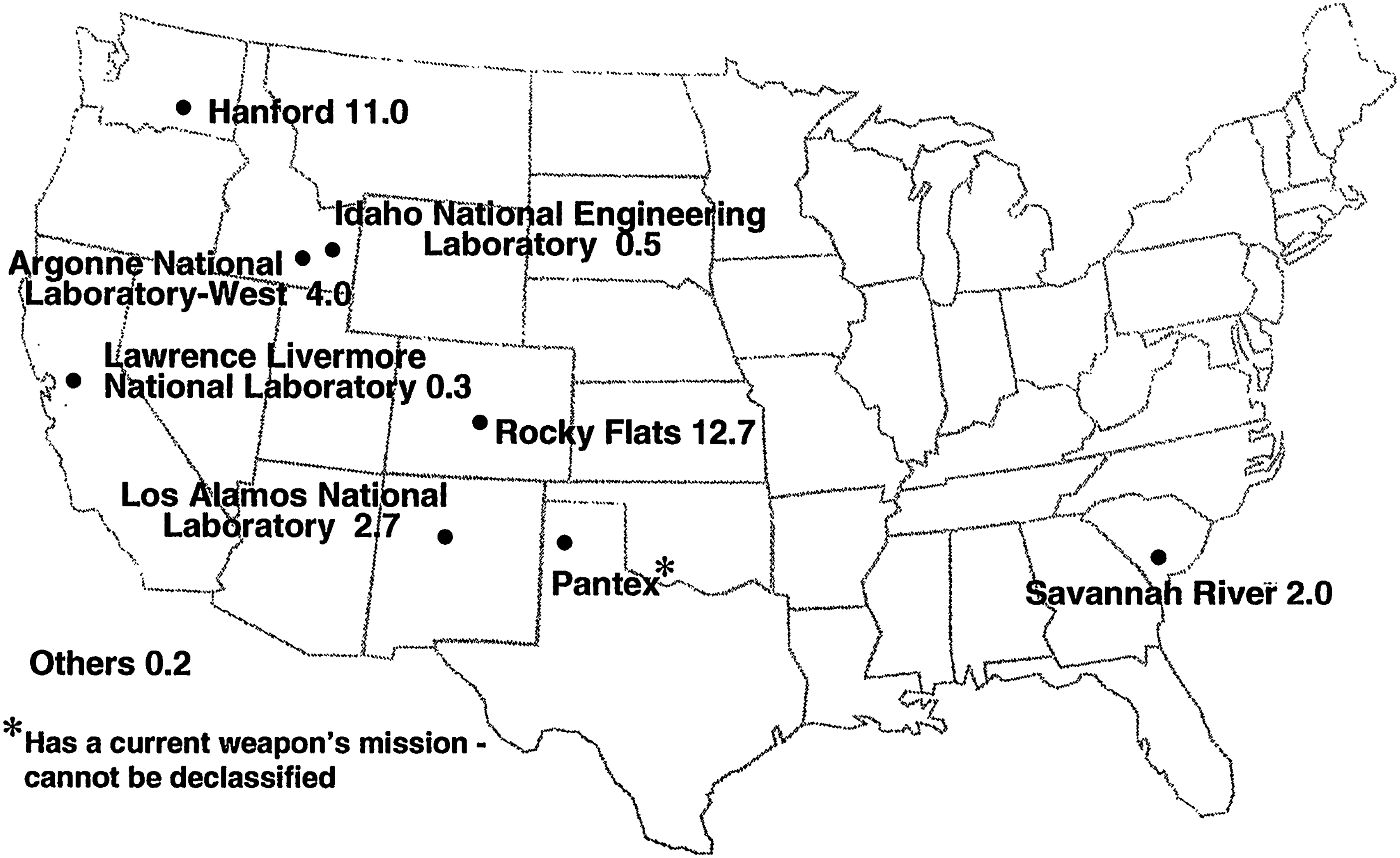
Plutonium Inventory
(Metric Tons Through September 1994)



Others 0.2

*Has a current weapon's mission - cannot be declassified

Plutonium Storage Phenomenology

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ABSTRACT

Plutonium has been produced, handled, and stored at Department of Energy (DOE) facilities since the 1940s. Many changes have occurred during the last 40 years in the sources, production demands, and end uses of plutonium. These have resulted in corresponding changes in the isotopic composition as well as the chemical and physical forms of the processed and stored plutonium. Thousands of ordinary food pack tin cans have been used successfully for many years to handle and store plutonium. Other containers have been used with equal success. This paper addresses the chemical and physical forms of plutonium in storage and presents examples of the norm and exceptions to this satisfactory experience. To aid in understanding the challenges of handling plutonium for storage or immobilization the lessons learned from past storage experience and the necessary countermeasures to improve storage performance are discussed.

HISTORY OF PLUTONIUM PROCESSING AND STORAGE AT THE DOE SITES

The original mission of the DOE plutonium sites was to supply plutonium metal for national defense. Plutonium was produced by uranium irradiation in nuclear reactors and irradiated fuel elements were processed in chemical separations facilities at Hanford and Savannah River to separate the plutonium from fission products and remaining uranium. The plutonium portion or product of the separation facility was a nitric acid solution of plutonium. Direct pipe transfer or heavy-wall stainless steel containers were used to handle and transport this solution to other facilities where the plutonium solution was converted to metallic plutonium. Urgent demands for large quantities of plutonium metal during the 1940s and 1950s limited amount and time plutonium was held in storage. Food pack type tin cans and other containers saw relatively short-term (i.e., weeks or months) use as a package for plutonium transport and short term storage of metal product. Production residues stored in such containers, however, were typically stored for longer periods.

In the 1960s, plutonium processing started to change in several ways. Demands for plutonium metal declined while research in power reactor technology indicated that plutonium in the form of plutonium dioxide could be used in place of fissionable ^{235}U in power reactor fuel. Later, breeder reactor research showed how to utilize plutonium oxide as a fuel for breeder reactors. A new product form, a fine powdery oxide, joined the traditional product form of a single metallic piece weighing about 2 kilograms. Demands for the oxide powder form increased from grams to kilograms to thousands of kilograms. In the late 1960s and 1970s the Hanford plutonium facilities provided almost all of the plutonium oxide used in this country. This included thousands of kilograms for several Fast Flux Test Facility (FFTF) cores.

The declining demand for metallic plutonium initiated interim and finally long-term storage of the metal. Some metal has been in storage over 25 years. Production strategies for the oxide dictated scheduling production between metal production campaigns and a degree of overproduction to allow for process losses, out of specification product, and ability to fulfill unanticipated requests for kilogram quantities of plutonium oxide for research efforts. Storage of oxide product prior to shipment as well as production overrun material became common.

In the 1960s the Hanford plutonium facility was provided with plutonium scrap recovery capability. Plutonium scrap from military application research and virtually all from commercial and breeder reactor research was returned to Hanford for recovery of the plutonium. This scrap, which had a wide variety of chemical and physical forms, was added to the growing inventory of plutonium metal and oxide being stored at Hanford and other sites. Cans stored soon numbered in the thousands. Radiation levels and ambient temperatures in storage vaults increased.

Vaults such as the typical pedestal storage vault shown in Figure 1 were used to store these cans. Fundamentally, it is an open room with floor-to-ceiling vertical pedestals to which steel storage cups have been welded. Cans of plutonium are placed in the cups for storage. A large storage vault contains over a thousand storage positions. A later version of pedestal storage incorporated concrete shielding around small groups of pedestals for radiation shielding of personnel is shown in Figure 2.

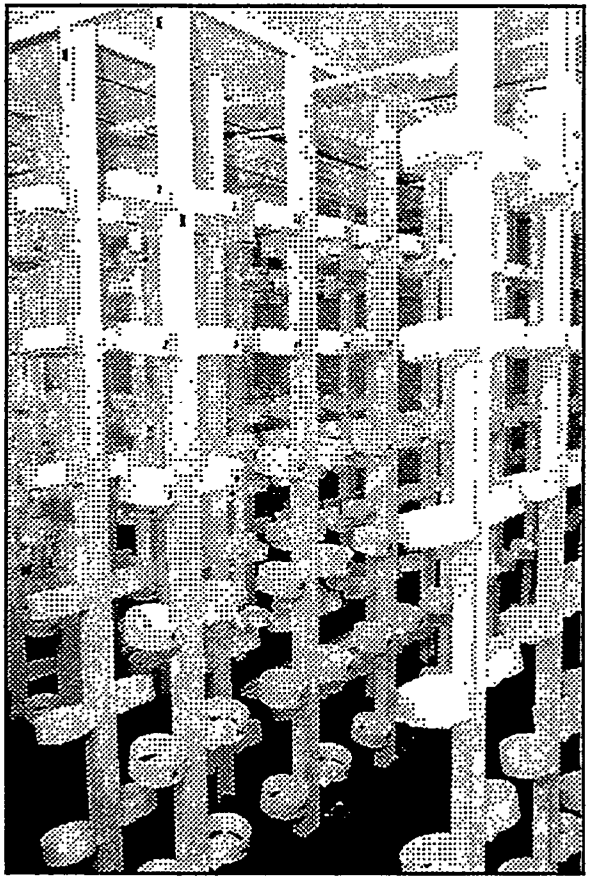

Figure 1 Open room storage vault contains hundreds of storage positions for food pack type cans. Personnel entering this room are directly exposed to radiation from every can.

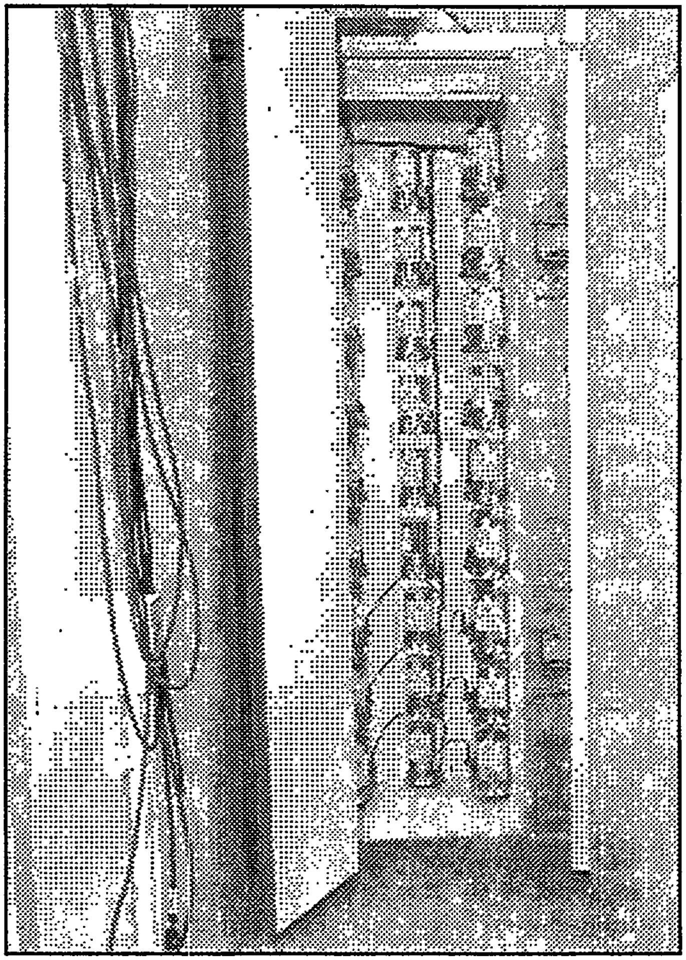

Figure 2 Newer storage vault design utilizes concrete cubicles with concrete shielding doors to reduce personnel radiation exposures.

During the 1960s and 1970s other changes were taking place which would ultimately impact the plutonium storage. The isotopic composition of much of the plutonium changed. The declining demand for plutonium metal caused N Reactor production to be changed from nominal 6% ^{240}Pu weapons-grade plutonium to nominal 12% ^{240}Pu. The 12% ^{240}Pu material as used for breeder reactor research and in the FFTF cores. Commercial nuclear reactors and some government experimental reactors produced plutonium with higher ^{240}Pu content which was commonly referred to as fuels-grade plutonium. Much of this material has been stored in Hanford plutonium storage vaults as metal, oxide, or scrap. Since the late 1980s many of the defense related plutonium activities in the DOE have been shut down and the number of nuclear warheads reduced. This has resulted in a buildup of large inventories of excess weapons grade plutonium metal and other forms at Rocky Flats, Pantex and to lesser degrees at other sites.

PLUTONIUM CHARACTERISTICS

Plutonium is a mixture of isotopes with varying important physical properties (i.e,, those relating to storage). The exact mixture of isotopes produced is the result of many complex physical characteristics of nuclear reactor hardware and operation as well as fuel cycle operations. Reactor power level, length of fuel exposure, neutron flux energy spectrum and other factors influence the production rates of the individual plutonium isotopes. Table 1 shows some plutonium isotopic distributions which may be considered typical and illustrates the wide distribution of plutonium isotopes.

TABLE 1. Plutonium Isotopic Mixtures.

Plutonium Type	Weight Percent				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Weapons Grade	0.004	92.84	6.48	0.61	0.23
12 %	0.04	86.20	11.80	1.70	0.15
Fuels Grade	1.40	70.12	15.67	10.70	2.10
High Exposure or Reactor Grade	0.57	65.08	23.36	7.66	3.34

The mixtures shown in Table 1 are listed in order of increasing ^{240}Pu content. The ^{240}Pu content is the usual way that the general pedigree of the plutonium is characterized. Technically, no precise line separates the types although certain ^{240}Pu levels have been administratively designated as cut-off points.

Table 2 presents properties of the individual isotopes that are of interest in plutonium handling and storage.

TABLE 2. Properties of Plutonium Isotopes.

Property	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Half-life (years)	89.6	24,000	6,600	13.2	380,000
Principal means of decay	Alpha	Alpha	Spontaneous Fission	Beta	Spontaneous Fission
Significant daughters of decay	None	None	None	^{241}Am	None
Curies per gram	17.0	0.061	0.22	112	0.004
Decay heat (watts/gram)	0.56	0.002	0.007	0.003	0.001

Except for ^{242}Pu, each isotope has some attribute that is of concern in plutonium handling and storage:

- ^{238}Pu--high decay heat (0.56 watts/gram) must be dissipated
- ^{239}Pu--fissionable material requires nuclear criticality prevention considerations
- ^{240}Pu--relatively high spontaneous fission rate results in neutron exposures
- ^{241}Pu--short half-life decay to ^{241}Am which has high decay heat (0.12 watts/gram) and high gamma radiation.

In addition to the nuclear properties outlined, the physical and chemical forms of plutonium have characteristics that also affect plutonium handling and storage. Based on experience gained in successfully storing ton quantities of various forms of plutonium for decades and the lessons learned from the relatively few incidents of less than adequate storage conditions, the behavior of plutonium in storage is predictable. The following discussion and illustrations are intended to display the breadth of plutonium characteristics that must be dealt with whether the plutonium will be stored, stabilized or immobilized.

PLUTONIUM METAL

- Very high density (about 19.4 g/cc) material.
- Chemically stable in most finished product forms.
- Somewhat pyrophoric if impurity content or decay heat is high. Can combine with oxygen at ambient temperature to form plutonium oxide.
- When reacted with hydrogen or carbon, unstable compounds can result.

Figure 3 Two kilogram plutonium metal button shown shortly after being produced in 1988.

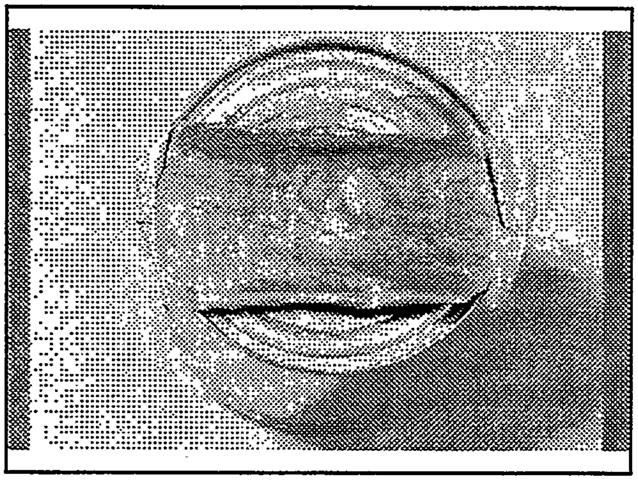

Figure 4 High decay heat of fuels grade plutonium can result in high temperatures as evidenced by this charred label.

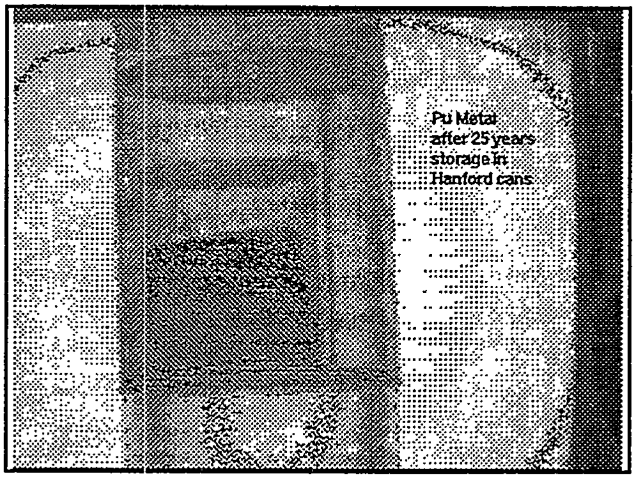

Figure 5 Radiograph of 2 kilogram metal ingot stored for 25 years in sealed food pack cans shows little indication of corrosion.

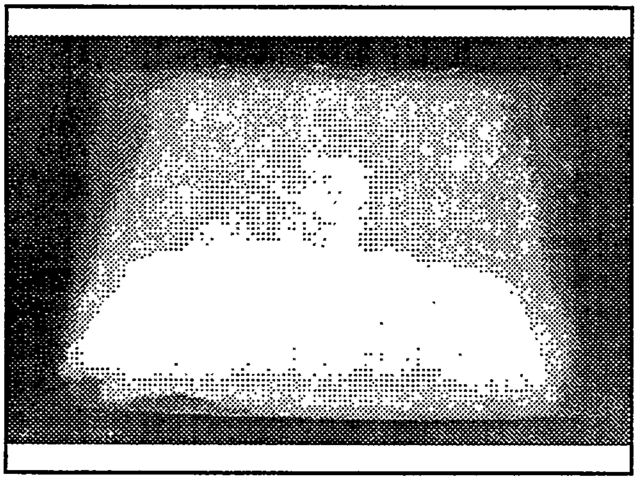

Figure 6 Radiograph shows inner can filled with oxide from corrosion of this metal piece. Note irregularity of top surface of metal.

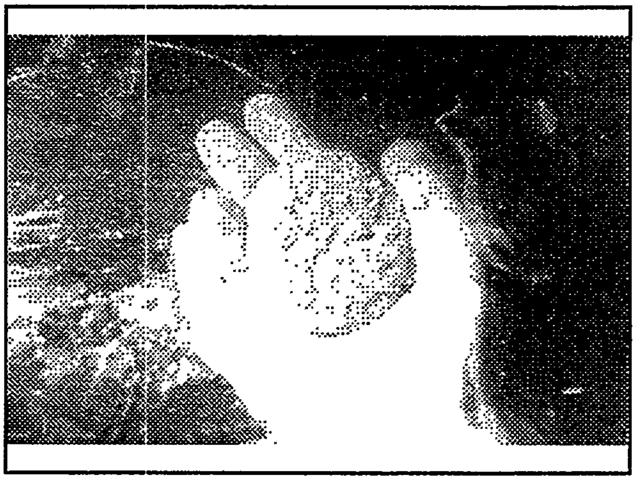

Figure 7 Metal piece removed from can shown in Figure 6. The cans were not properly sealed allowing air to enter and oxidize nearly 25% of the metal in 4 years.

PLUTONIUM OXIDE

- Density typically about 2 gm/cc (theoretical 10.3 g/cc).
- Dispersibility spans a wide range from fine powders to pressed pellets
- Hygroscopic.
- Impurities may result in generation of gases due to radiolysis.

Figure 8 Product and some scrap plutonium oxide is typically a fine dry appearing powder. Hundreds of cans of product oxide produced at Hanford and other sites have been stored for over a decade without incident.

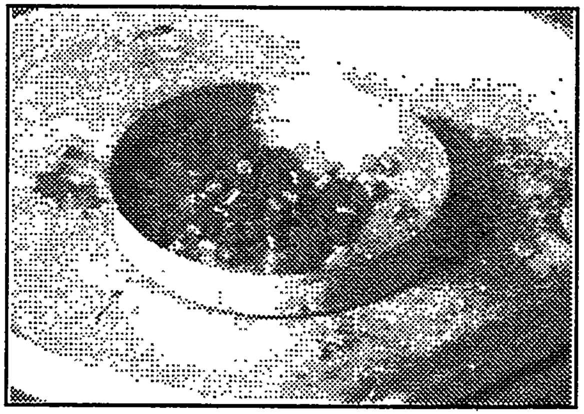

Figure 9 Some oxide is in the form of pellets of varying quality depending on previous fabrication or testing steps.

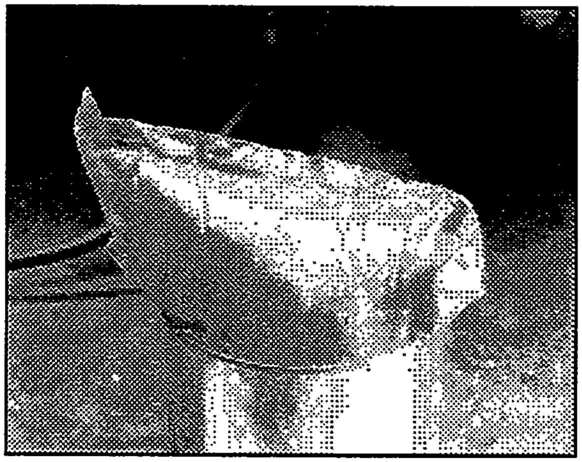

Figure 10 Slight bulging of can end plates indicated internal pressure of about 3 psig prompting this can to be opened. After several years in storage the plastic bag still holds pressure.

PLUTONIUM SCRAP AND RESIDUES

- Properties span the range of plutonium metal and oxide identified above.
- May include foreign matter which may be chemically inert or chemically reactive. This can lead to container corrosion or pressurization.
- Exact chemical composition or impurities sometimes not known.
- Chemical reactivity of scrap can cause the material to be pyrophoric or release flammable or explosive gases, such as hydrogen and oxygen.

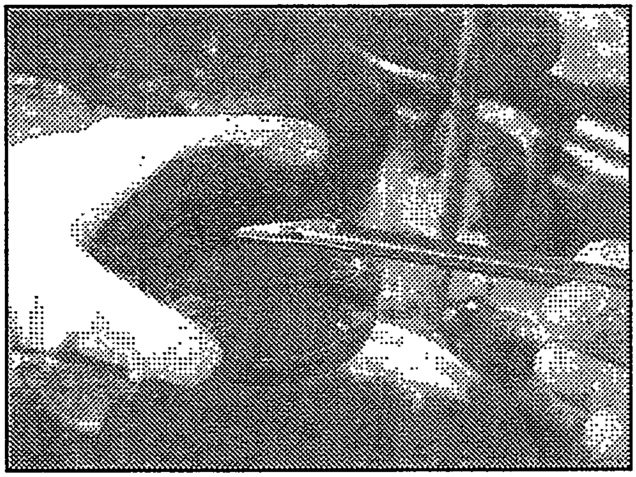

Figure 11 Some oxide scrap may contain powders, pellets or other physical forms. In this container pellets were found in the powder oxide.

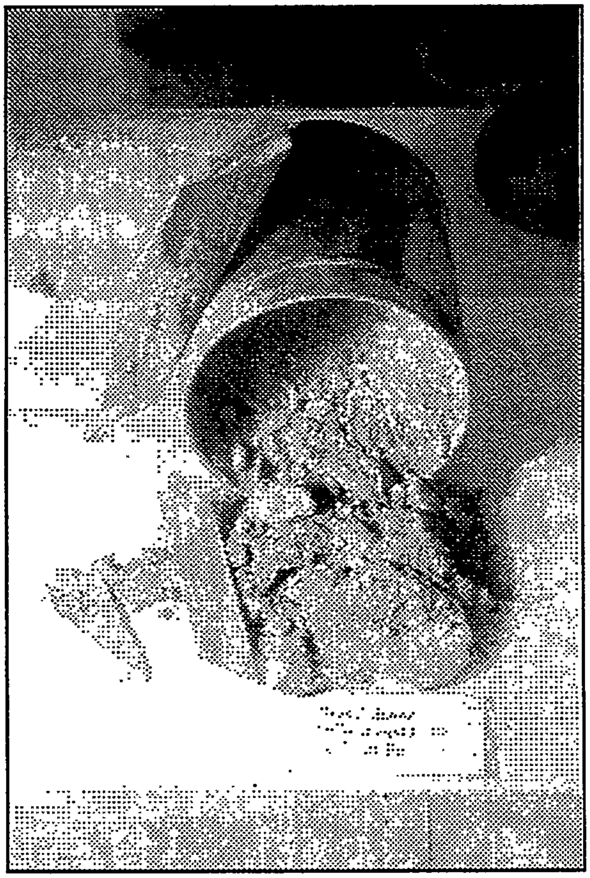

Figure 13 Tools, in this case a broken hacksaw blade, used in gloveboxes sometimes are found in residue containers.

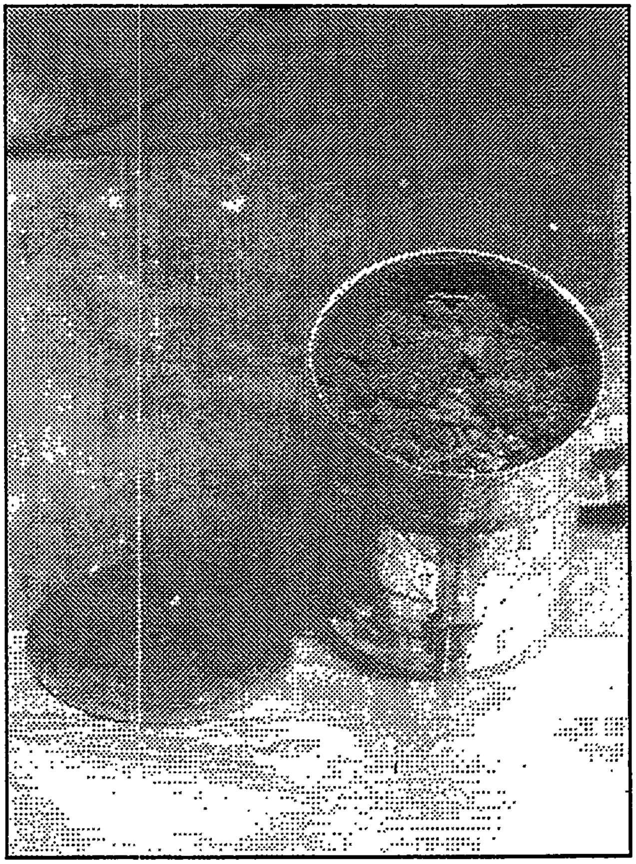

Figure 12 The phyical form of residues may be clumps of a wide range of sizes and brittleness.

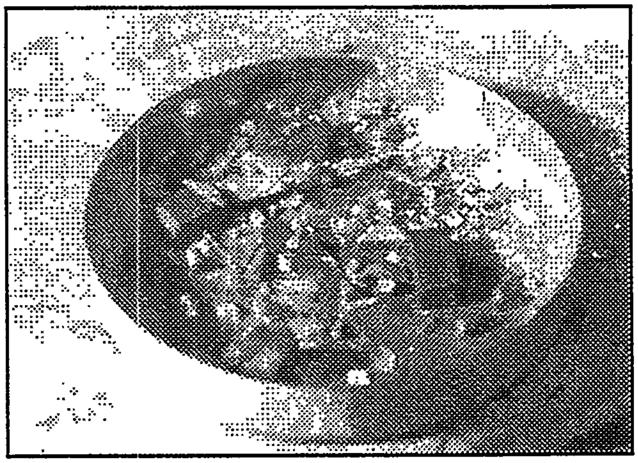

Figure 14 Non plutonium materials are sometimes found in glovebox residues. This material was screened from about a kilogram of oxide powder.

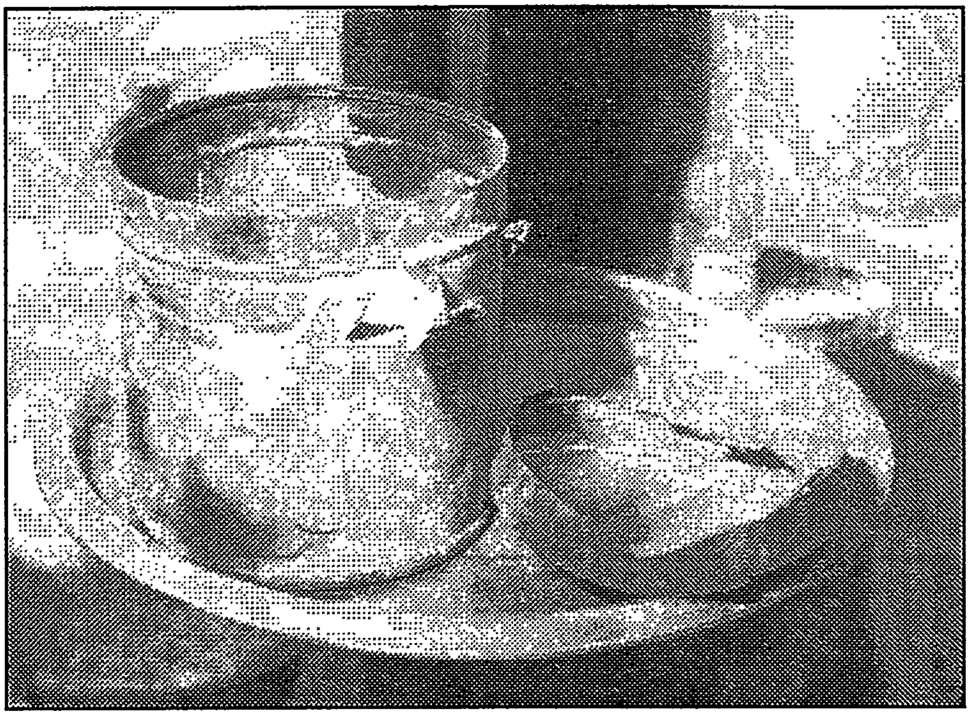

Figure 15 The contents of this container started burning minutes after it was repackaged and removed from a glovebox in 1980.

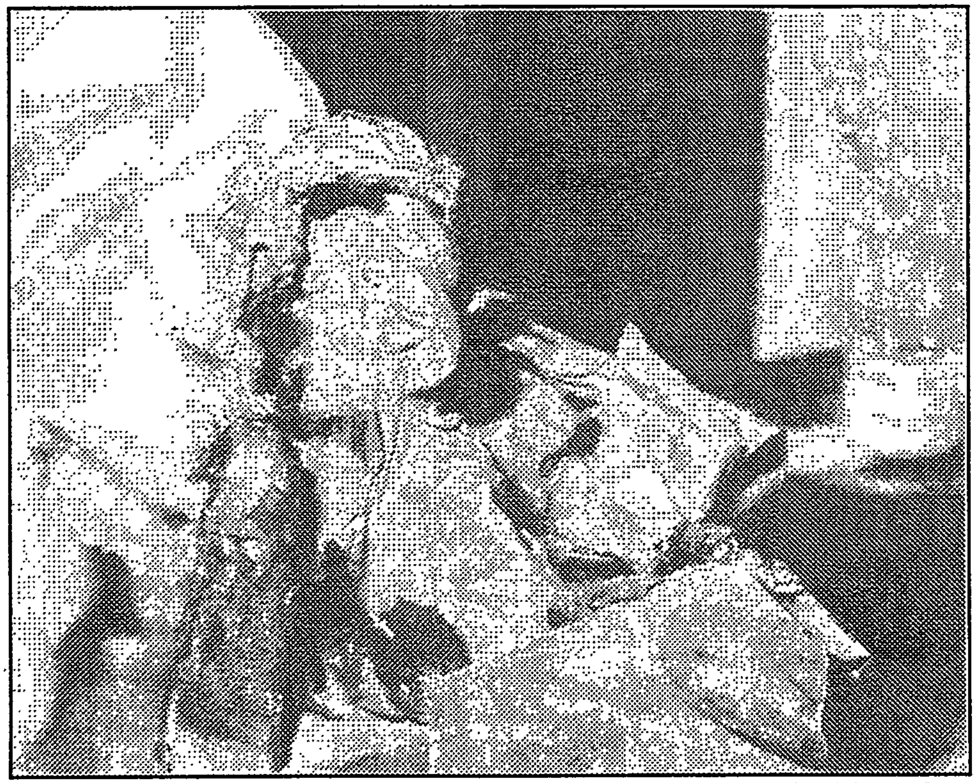

Figure 16 This burned bag was the result of spontaneous ignition of residue materials that occurred minutes after the can containing the plutonium residues was bagged out of a glovebox in 1980.

LESSONS LEARNED AND CORRECTIVE ACTIONS

Table 3 is a summary of the lessons learned from unsatisfactory storage or packaging conditions. Implementation of the corrective actions have been successful in precluding similar occurrences.

TABLE 3. Summary of Lessons Learned and Corrective Actions

Lessons Learned	Corrective Action
Size increase of oxidizing plutonium metal can be sufficient to rupture cans.	Plutonium metal overpacked in can large enough to accommodate complete oxidation of largest metal piece handled.
Personnel can become contaminated by walking into a vault where a can has ruptured.	Storage vaults equipped with continuous air monitors.
Poor can seals will allow oxidation of plutonium metal to continue to completion.	Can seal inspection procedure and canning machine preventative maintenance implemented.
When plutonium metal oxidizes, inner containers can rupture without an outer container appearance change.	Periodic weighing instituted to detect oxidation.
If properly sealed, tin cans will bulge when pressure builds up.	Straight-edge bulge test instituted to detect pressurizing containers well in advance of dangerous can deformation.
Plutonium oxide containing moisture or impurities can pressurize cans to the point of rupture.	Glovebox storage mandated for all materials suspected of being capable of causing pressurization. Thermal stabilization and weight loss on ignition testing criteria established.
High decay heat can degrade plastic bags and can seals allowing oxygen to enter to sustain oxidation of plutonium metal.	Limits established on decay heat of plutonium stored in tin cans. Plastic bags are not relied on to exclude oxygen.
Misidentification of material can allow storage in cans incompatible with the material.	Rigid material identification requirements have been imposed. Monthly visual container inspection program instituted.

DISCLAIMER

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REFERENCES

1. Szempruch, R.W., "The Effectiveness of Corrective Actions Taken to Preclude Events Involving Tin Cans and Plutonium," RHO-HS-SA-59 P, in *DOE/ANL Training Course on Prevention of Significant Nuclear Events,* Kennewick, Washington, May, 1984.

Technical Considerations And Policy Requirements For Plutonium Management

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ABSTRACT

The goals for plutonium management have changed dramatically over the past few years. Today, the challenge is focused on isolating plutonium from the environment and preparing it for permanent disposition. In parallel, the requirements for managing plutonium are rapidly changing. For example, there is a significant increase in public awareness on how facilities are operated, increased attention to environmental, safety and health (ES&H) concerns, greater interest in minimizing waste, more emphasis on protecting material from theft, providing materials for international inspection, and a resurgence of interest in using plutonium as an energy source. Of highest concern, in the immediate future, is protecting plutonium from theft or diversion, while the national policy on disposition is debated. These expanded requirements are causing a broadening of responsibilities within the Department of Energy (DOE) to include at least seven organizations. An unavoidable consequence is the divergence in approach and short-term goals for managing similar materials within each organization. The technology base does exist, properly, safely, and cost effectively to extract plutonium from excess weapons, residues, waste, and contaminated equipment and facilities, and to properly stabilize it. Extracting the plutonium enables it to be easily inventoried, packaged, and managed to minimize the risk of theft and diversion. Discarding excess plutonium does not sufficiently reduce the risk of diversion, and as a result, long-term containment of plutonium from the environment may not be able to be proven to the satisfaction of the public.

INTRODUCTION

As a result of the Strategic Arms Reduction Treaties and unilateral offers and agreements made by Presidents Bush, Gorbachev, and Yeltsin, the United States and Russia will retire many thousands of nuclear weapons within the next decade. This will remove many metric tons of plutonium from military control. Plutonium is one of the essential elements of nuclear weapons, and physical controls on the access to plutonium historically have been the primary barrier to theft and proliferation of nuclear weapon material. Not so obvious today is the fact that surplus plutonium also exists in the form of raw metal and oxide, residues, transuranic (TRU) and low level waste (LLW), contaminated facilities and equipment, and spent nuclear fuel (SNF), each of which also represents a significant source for diversion. With the end of the cold war, the management of these categories of materials is fragmented; and, consequently, they are at increasing risk for loss of management control.

A recent National Academy of Sciences study on the "Management and Disposition of Excess Weapons Plutonium"[1] is quoted as saying that, with regard to the weapon-related materials: "The existence of this surplus material constitutes a clear and present danger to national and international security." This report defines the need to safeguard and more comprehensively manage surplus inventories until permanent disposition options can be selected. The state of technology to address this inventory will be explored.

DISCUSSION

Recently, numerous studies have been published concerning the management of plutonium.[1-4] This fact indicates the keen interest that the international community places on managing this material safely and properly. Over the 50 years since its discovery, the main use for plutonium in the U.S. has been in national defense. A second major use has been as an energy source in advanced fuel programs. At the time of the discovery, all plutonium work was conducted under self-imposed secrecy, as a result of the recognition that it was possible to produce a powerful explosive through the rapid fissioning of plutonium by neutron bombardment. This precedent was maintained during the cold war, and very little actual information concerning the use and inventories of weapons plutonium was published. Numerous physical security measures were deployed to protect against the diversion of either information or the actual material outside the nuclear weapon community. This was accomplished fairly easily because all the material was handled under the jurisdiction of the Department of Energy Office of Defense Programs (DOE/DP), and Office of Nuclear Energy (DOE/NE).

The New Requirements

The end of the cold war has brought about a significant change in how plutonium inventories are managed. First, the Secretary of Energy began an initiative to increase the quality of ES&H management within Department facilities.[5] This step exposed the nuclear defense community to a broader range of oversight organizations, most of which are outside the Department. At the same time, Congress established the Defense Nuclear Facilities Safety Board (DNFSB), with the charter to evaluate the performance of the Department of Energy (DOE) in the execution of its safety and health obligations.[6] This became a very public vehicle for bringing scrutiny on the Department's nuclear operations. Congress and the Department established the Office of Environmental Remediation and Waste Management (DOE/EM) with the charter to clean up excess cold war nuclear facilities and sites.[7] This resulted in the transfer of a significant amount of plutonium to the new DOE/EM in the form of residues, waste, and contaminated equipment and facilities. The DOE/EM Office is heavily involved in the privitization of facility clean up functions, and most of the new contractors are unaware of the historical basis of nuclear material management. The Secretary announced the "Openness Initiative" wherein previously classified information was released for public consumption. This included the disclosure of quantities of plutonium that exist in the defense inventories.[8] Congress recognized the fact that plutonium would become an inventory challenge and initiated the DOE Office of Material Disposition (DOE/MD) to evaluate permanent disposition options for excess weapons materials. An additional dimension to the charter of DOE/MD was the opening of relations with the Russian Federation and the discussion of plutonium management.[9] In 1995, the President announced that the U.S. would place 200 metric tons of special nuclear material under the International Atomic Energy Agency (IAEA) safeguards program.[10] This action exposed the DOE facilities to the potential for international safeguard controls over material. During 1994, two weapons DOE Complex-wide plutonium safety assessments were made; one by the DNFSB and the other by the Assistant Secretary for Environmental Safety and Health.[11, 12] The latter assessment resulted from a 1993 Presidential initiative on nuclear nonproliferation and DOE's effort to develop strategies for the eventual disposition of excess fissile materials.[12,13] Both of these assessments identified the imminent dangers to workers, environment, and the public associated with the ever-deteriorating state of nuclear material packages, infrastructure, and nuclear facilities. This list of significant changes and actions has generated an increasingly more complex list of requirements for material management and facility operations. Globally, the new requirements include:

1. Theft protection of materials -- The DOE published a minimum set of requirements and procedures for the control and accountability of nuclear materials.[14] In addition, a set of international standards has been proposed concerning storage, protection, and accountability of spent nuclear fuels in surface and geologic storage.

2. Long-term ES&H management -- The DOE strengthened the role of its Office of Envirnoment, Safety and Health (DOE/EH) in performing its self-assessment responsibilities and has engaged other government organizations in jointly performing ES&H oversight to include the Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), and others.

3. Cost of Material Management -- The Department is embarking on the development of a uniform approach for the packaging and storage of excess nuclear materials and has published a standard for the handling of materials that have a plutonium content of >50%.[15] The Department is also working on a packaging and storage standard for lower-concentration materials.

4. Waste Management -- The responsibility for the management and minimization of waste is distributed among a number of offices. Managing the source-term for materials considered for discard is the key to controlling the release of plutonium to the environment. The EPA, as well as state and local agencies, also have a role in the management, handling, transportation, and disposal of mixed waste.

5. Military Applications and Nonproliferation -- Nuclear weapons continue to represent an aspect of national defense. The control of nuclear weapon technology and information, as well as the identification of the spread of such technology, is essential.

6. Energy Production -- Countries having nuclear capability are evaluating the use of excess plutonium and enriched uranium in future power production. A number of national studies have evaluated this approach and support it.[1,2,3] The current policy of the U.S. is not to reprocess and recycle spent nuclear fuels.

7. National Policy -- The national policies concerning the use of plutonium in the fuel cycle, disposal of plutonium, control of weapon information, and other aspects of the problem, are being considered and debated. Understanding and managing these policy changes is an essential requirement.

These requirements are the major issues that are changing the organizations involved with and the approaches to managing nuclear materials. Establishing a uniform basis for managing these materials must take into account these requirements. Whereas in the past, plutonium was managed by the

DOE/DP and DOE/NE, the significant changes discussed above have caused a rapid distribution of responsibility to include as many as seven DOE organizations, thus exacerbating the problem. Figure 1 shows the various organizations who have responsibility over materials, technology, information, and/or operations involving nuclear materials. The *X*s in the table indicate where each organization plays a role in implementing the various requirements. The very fact that so many *X*s occur indicates the need to develop a uniform policy and approach for nuclear material management.

Program Requirements for Nuclear Material Management

Organization	Theft	ES&H	Waste	Cost	Military	Energy	Policy
DOE/DP	*X*	*X*	*X*	*X*	*X*		*X*
DOE/NE	*X*	*X*			*X*	*X*	*X*
DOE/EM	*X*	*X*	*X*	*X*			*X*
DOE/MD	*X*	*X*	*X*			*X*	*X*
DOE/NN	*X*			*X*	*X*	*X*	*X*
DOE/EH		*X*	*X*				*X*
DOE/PO	*X*	*X*	*X*	*X*	*X*	*X*	*X*

Figure 1. Department of Energy organizational relationship versus program requirements for nuclear material management.

Of the new categories of requirements, the one involving the greatest concern is the Theft (anti-theft) requirement. In an effort properly to evaluate this category, the DOE Order on the Control and Accountability of Nuclear Materials[14] can be used to express the forms of plutonium according to their theft attractiveness. Figure 2 is extracted from the DOE Order in terms of the Attractiveness Categories and the materials categories. On the far right side of the figure are listed the typical materials existing within inventories and how they are categorized within the definitions of the DOE Order. From a theft and proliferation standpoint, weapon assemblies and components are the highest and are therefore noted at level A in the figure. Plutonium pits, freshly separated plutonium metal and oxide, and recycled metal and oxide are slightly lower in attractiveness, and therefore fall into attractiveness level B. Residues, unirradiated fuel and some TRU wastes fall into attractiveness level C. SNF and most (TRU) waste both fall into attractiveness level D. Finally, HLW and LLW fall into the lowest level of attractiveness, level E. Added at the bottom of the figure, although not specifically noted in the DOE Order is a category titled "other". Within this category exists material such as Nevada Test Site Debris. Although this is relatively difficult to obtain, never the less, it represents a source of plutonium for theft or diversion. In fact, in the old test locations, materials have cooled sufficiently such that nuclear materials are relatively desireable.

The plutonium weapon components, separated metal and oxide, and small portions of the residues are currently under the jurisdiction of the DOE/DP and are managed in a fashion consistent with national defense security guidelines. Similarly, the storage, protection, and accountability of SNF falls under the jurisdiction of the IAEA and the DOE, and is managed in a consistent fashion. It is the materials that fall in the categories of residues, TRU waste, and LLW that are managed in a number of organizations and that have less of an integrated focus. Of particular concern is the fact that the American Nuclear Society Special Panel on Protection and Management of Plutonium[3] reported that SNF is a continuing proliferation risk, that burial of SNF is not adequate to protect it from proliferation, and that SNF becomes more attractive over time because of the die-out of short-lived daughter products. These facts were reinforced by Dr. Glenn T. Seaborg in his plenary talk to the American Nuclear Society on October 30, 1995.[16] In looking at Figure 2 and in reading reference 3, one clearly concludes that if SNF represents a continuing proliferation risk, then residues and waste (TRU and LLW) also represent a continuing proliferation risk. Therefore, consistency in nuclear materials management is becoming increasingly important.

Attractiveness Level [14]	Materials Categories [14]	Typical International and DOE Materials
A	Weapons: assemblies and test devices	Weapon assemblies and some components such as some pits.
B	Pure Products: Pits, major components, buttons, ingots, recastable metal, directly convertible materials	Most pits, freshly separated metal and oxide (IAEA) and recycled metal and some oxide (DOE)
C	High-Grade Materials: Carbides, oxides; solutions >25 g/l, nitrates, fuel elements, alloys.	Unirradiated fuel, Oxide, Weapon Manufacturing Residues, Some TRU Waste
D	Low Grade Materials: Solutions 1-25 g/l, process residues requiring extensive reprocessing, moderately irradiated materials	Old Spent Nuclear Fuel, Some Weapon Manufacturing Residues, Most TRU Waste
E	All Other Materials: Highly irradiated forms, solutions <1 g/l,	New Spent Nuclear Fuel, High Level Waste, Low Level Waste.
Other *	Difficult to access materials	Nevada Test Site Debris

Figure 2. Nuclear Material Safeguards Categories. (* The 'Other" category is not specifically an aspect of reference 14)

Consequently, it is worthwhile to look at the history of categorization of these materials. During the cold war period, the United States hosted a program of nuclear weapon fabrication that included the making of new plutonium in reactors and, simultaneously, the recycle of manufacturing residues. The value of new plutonium was calculated based on the cost of nuclear reactor and separation canyon operations. The cost of recycle was then compared to the cost of new plutonium, and a decision was made concerning the discard of residues. Those with a cost of recovery that exceeded the cost of new plutonium were categorized as waste and packaged for disposal. Those with a cost of recovery less than new plutonium were saved for recycle. This concept was referred to as the "Economic Discard Limit." In addressing the priority for residue recycle, the residues with large plutonium content, and therefore most easily recovered, were selected for recycle first. The lower-concentration residues were stored for future recovery. This approach was referred to as "High-Grading." The decisions were based on available budget and not limited based on whether appropriate technology was available for processing. Clearly this approach was flawed in that it is the lower-concentration residues that contain undesirable characteristics and constituents that are today causing storage difficulties. These difficulties include container failures, corrosion, pressurization, and general loss of containment.[17]

Of special interest is the fact that the basis for discard of nuclear materials was based on an economic evaluation and did not take into account the cost of waste management nor did it take into account the cost of future safeguards. This means that the basis for Material Accountability and Safeguards and the basis for discarding the material as waste were not coordinated. Therefore, some materials having a realtively high attractiveness were not deemed recyclable and were discarded.

The New Goals, Taking Into Account The New Requirements

Clearly today, the goals for plutonium handling have changed dramatically. The focus of the past was on the use of plutonium in nuclear weapons and advanced fuels, while the emerging needs revolve more around the elimination of the current packaging hazards, as well as around the safe isolation and stabilization of material. With regard to the excess residues, waste, facilities, and equipment, figure 3 illustrates this change in paradigm and, therefore, states the basis for the new goals.

Old Paradigm	New Paradigm
• Pu had great value.	• Pu is a liability.
• Pu was purified.	• Bulk residue is purified.
• Pu is the product.	• Bulk residue is the product.
• "Economic Discard Limit" Economy is practiced	• "Zero" Hazard Discharge Economy is practiced
• TRU waste was accepted.	• Benign discharge is most desired.
• Exceptions were granted to rules.	• Full compliance to rules is expected.

Figure 3. The paradigm shift in the management of plutonium.

In recognition of this new paradigm, DOE has abandoned the concept of "Economic Discard Limits"[18] and is in the process of preparing an approach referred to as the "Plutonium Discard Methodology" (PDM), which takes into account a number of criteria including technology availability, waste minimization, diversion risk, health and safety of processing, and cost.[19] In addtion, the DOE is preparing an approach for defining when safeguards provisions are to be terminated on discardable nuclear materials.[26] It is a concentration based criteria and provides for an absolute concentration calculation for safeguards termination. In order to evaluate the impact of this new paradigm, and both the PDM and termination criteria, it is essential to evaluate the status of plutonium inventories and then to evaluate the status of technology needed properly to address isolation and stabilization requirements.

Status of the Residues (The First Problem Area)

Many plutonium residues are complicated mixtures of different compounds. This means that establishing and validating accurate accountability records and proper safeguards is difficult. In many residues, there is little fissile content in large-bulk inventories of material. Therefore, handling and packaging strategies are not obvious. Although the problems associated with plutonium residues were recognized by the sites, there is now a heightened awareness within the DOE and a basis for action, addressing the problems associated with the legacy plutonium residues within U.S. Defense Complex, has been prepared.[20,21] The significance of the residue problem is illustrated by the recently completed plutonium ES&H vulnerability study[12] which revealed that there are more than 50,000 at-risk packages of plutonium stored in various configurations throughout the DOE Complex. Of the 26 metric tons (MT) of plutonium identified as potentially at-risk during this assessment, most exist in a variety of unstable and reactive solid matrices with varying degrees of ES&H vulnerabilities. For example, at three major locations within the DOE Complex, there are large quantities (more than 100,000 gal. total) of solutions containing plutonium and other transuranics having high likelihood for causing environmental contamination and worker safety problems. Figure 4 indicates the distribution of residues around the DOE Complex.

Facility	Total Number of Items
Rocky Flats Environmental Test Site	27,679
Hanford Reservation	8,404 *
Los Alamos National Laboratory	9,470
Savannah River Plant	3,794
Argonne National Laboratory (West)	2,360
Lawrence Livermore Nat'l Laboratory	2,299
Mound Facility	236
Argonne Nat'l Lab. East/New Brunswick	9,898
Oak Ridge National Laboratory	622
Sandia National Laboratories	117
Lawrence Berkeley Nat'l Laboratory	473
Total	**65,352**

*Does not include equipment holdup and in-process solutions

Figure 4. The number of residue items located at various DOE facilities.[12]

Declaring these items as waste and directly disposing of them is being considered.[27] None of the current fissile material is in a form that could be packaged directly for waste disposal and the U.S. has not yet opened a TRU or HLW repository, despite decades of effort. Recent studies[1] conclude that direct disposal does not adequately address the theft and diversion problems. These constraints suggest that it could be prudent and economically attractive to separate the radioactive material from the bulk materials and thereby provide a robust long-term storage form. To meet the standards that will be required for long-term storage, current technologies[22, 23] will need to be adapted and, in some cases, new technologies will need to be developed to isolate plutonium. In addition, these technologies must be in total compliance with the 1992 Federal Facilities Compliance Act and the 1993 Executive Order mandating major waste reductions at all federal facilities[25, 26], particularly with regard to TRU and mixed waste generation. To ensure success, a technology base has to be maintained and new technologies have to be developed and demonstrated to manage the inventories of fissile materials. Consequently, actinide processing and handling technology, in conjunction with enhanced waste treatment technology, is essential to the successful development of a national strategy for fissile material disposal. In particular, developing criteria for suitable material storage forms and processes to produce these forms will enable the proper decisions to be made.

1. **Status of Technologies for Addressing the Residue Problem:** There are demonstrated technologies that can be immediately applied to reduce the short-term safety concerns resulting from inadequately stored residues. Approaches must be considered for ultimate disposal of excess fissile material. Fabrication into reactor fuel or immobilization in glass are two possibilities. No schedule for implementation of fissile material disposition has been set by either Congress or by the Clinton Administration. Because a national policy has yet to be formulated, long-term retrievability is required.

Since much of the material is in solution form and in dilute degradable matrices, processing/stabilization is required to prepare it for safe storage.

2. **TRU Residue Processing:** On the basis of our current knowledge of residues, only properly prepared oxide and metal are considered suitable for long-term storage. Because oxide and metal are a relatively small portion of the residue holdings in terms of net weight, an assessment was completed of the entire residue inventory to identify vulnerabilities. The overall priorities for stabilization were assigned as follows:

- Items that present an unusual radiation or release hazard;
- Items that are corrosive and can breach their current containers;
- Items that are combustible or can easily form combustible mixtures;
- Reactive/unstable mixtures such as organics in contact with radioactive material, calcium metal, or solutions in interim containers.

At Los Alamos, a multistaged sampling program, for vault holdings, was designed in an effort to assess the status of packaging against the above criteria. Every container was visually inspected and handled in order to evaluate container integrity. Suspect packages were removed from the vault shelves and repackaged. In a second phase, 160 items were selected at random and totally unpackaged in order to evaluate package integrity. In phase three, 220 old packages were selected in an effort specifically to evaluate the effect of age on package integrity. Finally, every item that is brought up for processing undergoes an evaluation for package integrity simultaneous with the actual residue stabilization effort.

All vault items are categorized, based on hazard reduction, for processing as shown in figure 5. Therefore, the risk-reduction approach will be to process and stabilize these items so that they can be properly converted to stable oxides for long-term storage.

Residue Category	Identified Hazards	Remediation Approach
Solutions	Containment, Radiolysis, Criticality, Control of Solution Chemistry	Ion Exchange, Solvent Extraction, Precipitation, Direct Calcination
Salts		
Pyrochemical	Reactive Metals, Corrosion, Gas Generation	Oxidation, Reduction, Distillation
Sand, Slag, and Crucible	Reactive Metals, Corrosion	Size Reduction, Pu Separation
Ash	Radiolysis, Gas Generation	Calcination, Pu Separation
Metals	Oxidation, Radiolysis	Repackaging
Oxides	Radiolysis, Pyrophoricity, Dispersibility	Calcination, Repackaging
Combustibles	Radiolysis, Gas Generation, Flammability	Volume Reduction, Matrix Destruction, Pu Separation
Noncombustibles	Radiolysis of Packaging Materials, Gas Generation	Volume Reduction, Pu Separation

Figure 5. Processing approach by general category.

The goal is ultimately to isolate radioactive materials and other hazards from the bulk matrix; produce only a LLW (or better) during processing; and to store the radioactive material in a safe, acceptable form pending final disposition. To accomplish this goal, we must be able to treat effectively the spectrum of radioactive residues and to continue to develop and demonstrate enhanced recovery, stabilization, and assay capabilities. As examples of the type of capability improvement, we continue to lower detection limits for assay instruments and to develop residue processing operations for the improvement of the actinide recovery efficiencies, using better separation and waste treatment technologies.

To eliminate these immediate corrosive and reactive hazards, several existing technologies have been identified and can be implemented to reduce the risk involved with these residues. In order to reduce the life-cycle cost of radioactive material management and the long-term liability of handling and storing energetic materials, the final state of material must meet the storage criteria. The only proven method to achieve this stability is to separate the plutonium or other radioactive material from the bulk matrix, discard the bulk material as a certified waste form, and store the radioactive material as a metal or oxide. In essentially all cases, methods exist for remediating residues. However, these methods were developed and optimized to purify plutonium, rather than to produce a safe storage form with minimium waste. Consequently, in order to meet the new goals, it will be desirable to adapt proven technologies for plutonium separation and advanced waste treatment. These modified and new methods should be implemented to ensure that the processing of plutonium residues has the least impact on the environment and worker safety as is technically and economically possible.

3. Separation Techniques

- **Salts** -- Pyrochemical salts and sand, slag, & crucible represent a signficant fraction of the residue inventory in the DOE Complex. Potential hazards associated with these salts include corrosion of the container, gas generation from radiolysis of moisture with the salt or the packaging materials, and the presence of reactive metals.

  Processing techniques have been developed that use carbonate to oxidize the reactive metals in pyrochemical salts. Tests for water decomposition by reactive metals have been conducted to document the efficiency of this process. In all cases using this chemical oxidation procedure, no hydrogen evolution above the baseline was observed. Chemical oxidation alone would meet the stabilization requirements, but plutonium separation is required to facilitate the safe disposal of these salts as waste. A distillation process is under development that will extensively reduce the need to use aqueous processing flowsheets to remove plutonium from this matrix. A recent trade study commissioned by the Department of Energy's Nuclear Material Stabilization Task Group, taking into account waste minimization, radiation exposure, disposal costs, and schedule, found that salt distillation would be the most efficient process to facilitate the disposal of the majority of the pyrochemical salt inventory.

- **Solutions** -- Plutonium nitrate and chloride solutions are currently being stored in configurations that were not designed for extended storage. The solutions are stored in plastic bottles, stainless steel and plastic-lined tanks, and process piping. These solutions, which range from 0.25 to 300 gm Pu/*l*, represent some of the most significant vulnerabilities to the worker. Control of the solution chemistry to prevent unanticipated concentration or precipitation of neutron absorbers, such as boron, is required. There is no question that solutions are not suitable for safe interim storage and must, therefore, be solidified as expeditiously as possible. Several processing techniques have been or are under development within the DOE Complex to meet specific site requirements for the stabilization of these solutions. Well-demonstrated precipitation techniques may be the most efficient. A flowsheet involving the Pu (III) oxalate precipitation followed by magnesium hydroxide precipitation of the filtrate has been demonstrated for the stabilization of Rocky Flats nitrate solutions containing high levels of plutonium (> 6 gPu/*l*). This technology effectively stabilizes the solution, while minimizing processing exposure and the generation of waste.

A vertical calciner is being developed by Hanford personnel for the direct conversion of plutonium nitrate solutions to a stable, storable solid. In this process, small amounts of plutonium-bearing solutions are metered into a continuously heated and stirred bed of solids. Calcination proceeds through rapid evaporation of liquid, slowly drying to solids, denitration, and initial heat treatment of stable plutonium dioxide. This process is known to work on solution concentrations ranging from 15 to 500 gm/*l*.

- **Combustibles and Noncombustibles --** Currently, pyrolysis, electrochemical oxidation, and hydrothermal processing are being tested as advanced methods of processing combustible wastes. As an example, a pilot-scale pyrolysis experimental setup was designed and constructed to test the viability of this approach. Materials commonly used in glovebox applications were pyrolyzed. All of the materials were reduced significantly in mass to dry, solid, black materials. Introducing a few conventional technologies (e.g., a cold trap and an activated carbon filter to capture the organics, and a catalytic converter to oxidize carbon monoxide to carbon dioxide), will allow pyrolysis to be readily deployed in a manner compliant with environmental regulations.

In addition, it is possible, with a select variety of combustible and noncombustible items to remove the plutonium by first freezing the material and then crushing it to increase surface area. The plutonium on the surface can then be removed by simple washing. Therefore, safety concerns about potential fire or explosion hazards due to radiolytic-hydrogen generation or high flammability can be reduced. Bench scale tests on polypropylene filters, which were used as pre-filters in the rich-residue ion-exchange process line at the Los Alamos Plutonium Facility were performed using ultrasonics, and advanced dissolution agents as a method for dislodging particulates. Batch experiments were run on crushed filter material in order to determine the amount of Pu removed by stirring, stirring and sonication, and stirring and sonication with the introduction of Pu-chelating water-soluable polymers or surfactants. Significantly more Pu is removed using sonication and sonication with chelators than is removed with mechanical stirring alone.

As leaner residues are scheduled for processing, improved solid treatment methods will be required to reduce the volume of TRU (>100 nCi/g) waste. This is important because of the large cost difference between TRU and LLW. Also, physical solid-solid separation methods, such as magnetic separation, are being implemented to reduce the initial volumes of the low-level residues, such as ash and graphite.

Status of Waste Treatment (The Second Problem Area)

Waste exists in solid, liquid, and gaseous forms. For the most part, gaseous forms are treated via scrubbing and filtering, and are therefore not considered a problem in waste management. The principal issues include treating liquid and solid wastes as well as certifying waste products.

1. **Liquid Waste:** This treatment effort must meet all applicable state and federal regulations for radioactive and hazardous waste. Generally, the most pressing issues involve characteristics other than radioactive materials, such as nitrate content or heavy metal content. In addition, there are considerable cost savings incurred by minimizing waste wherever possible. At Los Alamos, for example, it is planned to implement acid recycle in order to lower the volume of solid waste produced at the TA-50: Low-Level Waste Treatment Plant. Also, chelating extractants will be deployed to reduce the radioactivity discharges from the liquid waste stream in order to comply with the proposed 0.5 µCi/*l* discard limits being considered for the Liquid Waste Treatment Facility.

2. **Solid Waste:** Improved methods, such as advanced soaps, plasma-based, and electrochemical decontamination techniques will be tested and implemented to remove plutonium from the solid residues, such as plastic filters, dirt and blacktop, tools and supplies, and other items that do not meet the current waste acceptance criteria. These technologies can also be used to reduce the volume of secondary radioactive solutions that are inevitable during processing operations.

Nondestructive Assay (NDA) Methods

Because of the nonhomogeneous and dilute nature of the residues and waste, better assay methods are required to ensure good accountability of fissile material. Improved NDA techniques, including the preparation of certified reference materials for calibration and measurement control, will also ensure that the waste forms can be properly certified for final disposal. NDA methods are attractive because they can be done in-line and do not require chemical sampling of the matrix. Furthermore, they can be computerized to ensure repeatability and improve safety by reducing operator exposure.

CONCLUSIONS

With the end of the cold war, the goals for plutonium management have changed dramatically. The focus seems to be on the immobilization of plutonium via vitrification, mixing into ceramic based materials, or mixing with high level waste. In addition, direct packaging and disposal at Waste Isolation Pilot Plant, of Rocky Flats residues, is being planned for.[27] It is imperative that plutonium be safeguarded against theft and diversion. Recent studies have asserted that materials, such as SNF, may represent an unacceptable diversion risk if disposed of in its present form. By using the DOE Order on Nuclear Material Safeguards, it is clear that plutonium bearing residues, and many waste materials (TRU and LLW) are at least as attractive as SNF, and, therefore, must be safeguarded in as rigorous a fashion. This implies that direct discharge of residues and some waste items into repositories is likely unacceptable.

With regard to the storage of plutonium materials, experts know most about the long term stability of relatively pure plutonium oxide and metal. The storage of plutonium in all other forms, such as residues, has resulted in the loss of containment within relatively short periods of time, via corrosion and pressurization mechanisms. In addition, the country has been unable to open and operate a long term repository for storage of waste and excess materials, presumably a result of the inability to assure containment of radioactive materials.

Therefore, it is prudent to consider a fourth approach for plutonium management, that of separations. Separation of plutonium from the bulk matrices, discard the bulk as certified waste, and storing plutonium as a storable oxide, provides the option to safely manage plutonium until such time as disposition approaches can be evaluated and ultimate disposition can be selected. The oxide would not be highly purified as in the "Cold War" past. The necessary separations technology base exists to handle essentially all forms of plutonium residues and can be quickly deployed. Some research and development is approapriate to properly tailor process flowsheets to meet this new challenge. Separating and storing the plutonium meets safeguards needs, protects against escape of plutonium into the enviroment, eliminates identified vulnerabilities, and preserves <u>all</u> options currently being considered for ultimate disposition, whether they be vitrification, cementation, deep bore hole discharge, spent fuel standard, or transmutation.

DISCLAIMER

The views expressed in this paper are solely those of the authors. The views are based on the evaluation of numerous references concerning the management of plutonium, most of which are DOE citations. Despite this, the views do not necessarily reflect the views of the U.S. government or any of its agencies.

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Handling of Non-Stable Forms of Plutonium

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In accordance with Russian-American agreements on investigating the problem of the conversion of weapons grade plutonium, the following directions for plutonium utilization have been defined:

- utilization of the plutonium in fuels for light-water and fast reactors;
- long-term storage of the plutonium;
- burial off the plutonium in geological formations;
- immobilization and stabilization of solutions and other forms of plutonium.

It is well known that plutonium, in the form of metal, is used in weapons. Therefore, before we reprocess this type of plutonium into-MOX-fuel, the plutonium metal must first be converted into a solution from which americium and other ballast admixtures have been removed, and then in the form of plutonium nitrate (IV) or dioxide, it becomes raw material for the manufacture of MOX-fuel.

Regardless of the option that is chosen from those mentioned above, the most difficult problem in the utilization of weapons grade plutonium is to provide for the preservation of the environment, its protection from the harmful effects of the highly toxic plutonium and its compounds, because the threat that it presents does not diminish for millions of years in view of its long half-life. It is extremely important, while studying processes for plutonium utilization, to address questions dealing with radiation and nuclear safety and the prevention of accidental fires and explosions.

Non-stable forms of plutonium include the following:

- plutonium corrosion products in atmospheres with different levels of humidity and low temperatures ($<100^0$C). In terms of their chemical composition, the products of metal corrosion are non-stoichiometric compounds of plutonium and oxygen, hydrides, oxo- and hydrooxohydrides of plutonium;
- plutonium corrosion products that are formed when plutonium metal is dissolved in acids with low levels of dissociation, for example, sulfamine and formic acids and other organic acids, as well as highly diluted solutions of mineral acids (with the exception of nitric acid). The composition of the products is practically identical to the composition of corrosion products formed in humid atmospheres under low temperatures;
- finely crushed plutonium metal.

Non-stable forms of Plutonium require careful handling since they may contain plutonium compounds that are flammable or have pyrophoric properties under certain conditions.

Handling Plutonium Metal In The Presence Of Corrosion Products In The Atmosphere
During warhead dismantling, preparation of plutonium solutions, temporary storage in transport containers if the plutonium metal is exposed to a humid atmosphere, it is subject to corrosion /1,2,3/with the resultant formation of plutonium dioxide mixed with non-stoichiometric plutonium oxides. Investigations have shown that the plutonium-oxygen system is not ideal.

When plutonium is exposed to air, the surface oxidizes forming an easily detachable oxide film, which in turn easily turns into an aerosol. A similar powder, yellow in color, is formed when plutonium corrodes in very humid environments in temperatures below 50^0C, while oxides that are formed in an atmosphere of humid argon or helium are green /1/.

Under certain conditions the powder that is formed is black in color.

The properties of products from the oxidation of plutonium metal in the air and in an inert atmosphere change significantly in response to oxidation conditions. The oxides that are formed when the metal is oxidized at room temperature are for the most part in the form of small particles (97% of the mass of the particles is 5 microns in size), with high specific surface values (10 - 20 m^2/g) and typically are pre-stoichiometric compounds of PuO_x, with $1.8 < x < 1.9$. Oxides formed on the surface of the plutonium metal at high temperatures and in a reduction atmosphere have values nearing 1.5/3/.

Plutonium oxides formed when the plutonium is exposed to air and high temperatures (approximately 500^0C) have larger particles. Particles that are greater than 1mm in size comprise 20% of the mass, while those that are smaller than 10 microns account for no more than 0.1 % of the mass. The particles have well defined crystallinity and are almost stoichiometric, thereby precluding the possibility of self-heating of the oxidizing metal in contrast to the situation that exists when the metal is oxidized at low temperatures. The reaction between metallic plutonium and plutonium dioxide with pre-stoichiometric oxides in the presence of oxygen is spontaneous and exothermic and that is why plutonium oxides play an important role in determining plutonium pyrophorosity.

Several factors determine the fire point of plutonium metal /3/:

- specific surface;
- particle size;
- oxygen concentration in the reaction zone;
- surface conditions at the metal-gas interface;
- composition of the metallic plutonium; carbon reduces the ignition temperature, while uranium has no impact.

However, the most important parameter is particle size.

When plutonium ignites, plutonium oxide particles are dispersed as aerosol and are then deposited on the surfaces of the chamber, the piping and ventilation ducts. This means, that plutonium dismantling operations, preparation of solutions and temporary storage of plutonium in the transportation containers should be of short duration. Although specific studies have not been carried out, there is ample evidence to conclude that the duration of such operations should not exceed 50 hours. Unfortunately, we do not have instrumentation that makes it possible to monitor plutonium corrosion during the plutonium solution preparation process, and safety relies on organizational measures.

Handling Of Plutonium Metal Corrosion Products In Acid Solutions

During the process of preparing plutonium solutions, not all of the plutonium is completely dissolved in dilute solutions of mineral or organic acids and part of the plutonium (1.0 - 20% of the mass) is transformed into pyrophoric compounds of plutonium. The amount of pyrophoric precipitant formed depends to a great extent on the concentration of hydrogen ions in the solution. When plutonium is dissolved in hydrochloric acid and the final solution has a concentration of hydrochloric acid >3.0 mole/l, no pyrophoric precipitants are formed. With concentrations in the 1.2 - 3.0 mole/l range , pyrophoric precipitants are measured in tenths of a percent. The precipitant in these cases is mostly plutonium dioxide. When hydrochloric acid concentrations drop below 1.2 mole/l, the amount of pyrophoric precipitant increases from tenths of one percent to 10 - 20 % /4/, while the amount of acid in the final solution decreases. A fine, black precipitant is deposited on the walls of the vessel when the solution is removed. The sedimentation rate of the particles in solution is extremely low. There is no danger in handling them while they are wet, but during the drying, calcination and transfer operations, when the material is in a dry form, the particles can spontaneously ignite and even explode, depending on the thickness of the residue layer. The smallest particles remaining on the walls of the vessel, after drying on the surface, will ignite from the slightest touch with any object. The fireworks will continue for several seconds until the particles burn up.

Such fires are accompanied by the dispersion of particles and as a rule leads to contamination of the piping and ventilation ducts. If the particles are heated in a muffle, an explosion occurs within several seconds.

Similar precipitants form when plutonium is dissolved in a dilute solution of mineral acids or in weak dissociated acids. They have the same properties as precipitants in weak hydrochloric acid solutions.

Handling Metallic Plutonium In The Form Of Fine Powder

Powders are formed during the following processes:

- conditioning of the surface of plutonium samples. The powders are a mixture of metallic plutonium and oxides of various compositions.
- cutting compact blocks of plutonium into pieces in the preparation of solutions;
- decay of plutonium hydroxides.

Powders require special care in handling and strict adherence to operational safety instructions.

Currently there are no surveillance systems for monitoring the accumulation of non-stable forms of plutonium and safe handling is assured through organizational measures.

DISCLAIMER

The views expressed in this paper are those of the author(s) and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Discussion Summary of Materials and Conditions Session
Ken Scheffter, Westinghouse Savannah River Company

After completion of the Materials and Conditions Session technical presentations, the Session Chairman opened the floor to questions. The first of two questions dealt with the photograph of a plutonium button shown by Mr. Richard Szempruch (from Westinghouse Hanford Company) in the first presentation. It was asked whether the materials causing the oxidation visible in the photograph had been identified, and whether the plastic bag was decomposed. Mr. Szempruch responded that he did not know if the exact mechanism for the oxidation had been determined, but it was obvious that the exposure of the plutonium to air and to the plastic bag both contributed to oxidation. There was air leakage through the external can, the inner plastic bag, the inner can, and to the material itself for several years, and there was no real expectation that the bag would be an effective barrier to the oxygen. There was evidence of radiolytic decomposition of the plastic bag, but the specifics of the bag s condition were not known by the speaker.

The second question was asked of Dr. Leonid Borisov (from the Institute of Inorganic Materials) and concerned process instrumentation. Specifically, Dr. Borisov was asked what functions or characteristics were needed in stabilization process measurement instrumentation. Dr. Borisov responded, Plutonium separation processes should be controlled to prevent the formation of pyrophoric precipitants. However, actions of the operator can at times lead to various violations (process upsets) which in turn may result in the formation of these precipitants. These processes must be controlled to some degree by technical means. Unfortunately, at this time we do not have the devices needed to recognize the accumulation of such precipitants during the metal dissolution process.

Following this discussion, Mr. Scheffter concluded the technical session.

Session Chair for Materials and Conditions:
Ken Scheffter, Westinghouse Savannah River Company
Tuesday, Dec 12, 1995; 1:00 pm

Question / Comment 1: << inaudible >>

Answer:
Richard Szempruch, Westinghouse Hanford Company
Actually, a 1/4 of it, yes. The container that it was stored in was a multi-sealed container. I don't know that the exact mechanism was actually determined. It's quite obvious, from experience, when you expose plutonium to air, such as that, you will form the oxide. Evidence of radiolytic decay of the bag and hydrogen generated from that might have caused the reaction to go. The bag was on the outside of the container that you were looking at. The packaging mechanism, if you will, or packaging configuration, was the button, the can, bag and then an external can to that. There was air leakage through the entire pathway under the conditions of storage for several years. There was no real expectation that the bag would be an effective barrier to the oxygen. You would have to rely on the can seals.

Questioner:
Did you say the bag was decomposed?

Szempruch:
I don't know the specifics of the bag. What I said was that it was generally not expected that the bag would not be an effective barrier after an extensive period of time in storage.

Question / Comment 2:
Ken Scheffter, Westinghouse Savannah River Company
Dr. Borisov mentioned several times that there was instrumentation that needed development or implementation. I was wondering what functions or characteristics you were looking for in terms of measurement of instrumentation? What exactly are we trying to measure with this desired instrumentation?

Answer:
Leonid Borisov, Institute of Inorganic Materials
Plutonium separation processes should be controlled to prevent the formation of these pyrophoric precipitants. However, actions of the operator can at times lead to various violations (process upsets) which in turn may result in the formation of these precipitants. These (processes) must be controlled to some degree by technical means. Unfortunately, at this time, we do not have the necessary devices needed to recognize the accumulation of such precipitants, during the metal dissolution process.

DISCLAIMER

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

STABILIZATION STANDARDS, TECHNOLOGIES AND APPLICATIONS

SESSION CHAIRS: MARTIN SEITZ, US DEPARTMENT OF ENERGY,
OFFICE OF ENVIRONMENTAL MANAGEMENT, EM-64,
AND ALAN WILLIAMS, SCIENCE APPLICATIONS INTERNATIONAL CORPORATION

Stabilization Standards, Technologies and Applications Opening Remarks
Dr. Martin G. Seitz, US Department of Energy, Office of Environmental Management

My name is Martin Seitz. I am a physical scientist with the Stabilization Task Group with a specific responsibility in the area of stabilizing plutonium liquids. Also, I will send you a copy of the Research and Development Plan for the stabilization effort. Please give me your name and address.

I wanted to take a moment here and thank Randy Erickson and Jeff Kass. These are scientists at national laboratories that we asked to help us plan the workshop. They did a very good job, initially, and they continued to influence the evolution of the workshop. They took their jobs very responsibly and did an excellent job. I commend them for the effort.

The organization is to divide the session into two categories. First are some of the programmatic aspects of the stabilization program, i.e., the standards that we are working towards, the facilities and materials that we are dealing with in the program, and the results of the Research and Development Committee.

The second category covered in this session is the technology of stabilization. Plutonium residues can be stabilized by conversion to borosilicate glass using the Glass Material Oxidation and Dissolution System (GMODS) discussed here. Technology demonstrated by the Russian participants in this session is the adsorption of plutonium into silica gel and calcination to bind the plutonium to a dried silica matrix. Microwave calcination, as indicated by results from Rocky Flats, Colorado, will stabilize residues with substantial organic content, and is planned for this use. Finally, this session exhibits ceramification (by staff at the Rocky Flats site), and vitrification and encapsulation into glass with high level waste (by researchers at four sites) as a means of dispositioning plutonium ash residues. This session should give you knowledge of the Department's programs for stabilization, and a sense of the many technologies that can contribute safely to the stabilization of plutonium-bearing materials that we will treat. We can select treatments for the economic and timely stabilization of these plutonium-bearing materials.

DISCLAIMER

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Plutonium Storage Criteria

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ABSTRACT

The Department of Energy has issued a technical standard for long-term (>50 years) storage and will soon issue a criteria document for interim (<20 years) storage of plutonium materials. The long-term technical standard, "Criteria for Safe Storage of Plutonium Metals and Oxides," addresses the requirements for storing metals and oxides with greater than 50 wt % plutonium. It calls for a standardized package that meets both off-site transportation requirements, as well as remote handling requirements from future storage facilities. The interim criteria document, "Criteria for Interim Safe Storage of Plutonium-Bearing Solid Materials", addresses requirements for storing materials with less than 50 wt % plutonium. The interim criteria document assumes the materials will be stored on existing sites, and existing facilities and equipment will be used for repackaging to improve the margin of safety.

INTRODUCTION

In the past, plutonium was generally either "in-process" or "in-use". Storage of plutonium was mostly short-term, and storage packages were designed to last no more than a few years. The end of the Cold War has left the Department of Energy with a surplus of plutonium that must be stored until their final disposition. Plutonium materials containing more than 50 wt % assay are required to be conditioned and packaged for retrievable long-term storage. Plutonium placed in long-term storage must be in either metal or oxide form.

The lack of demand for plutonium also led to the stoppage of processing of plutonium-bearing residues and oxides, which generally contain less than 50 wt % plutonium. These left over materials were not intended to persist in existing manufacturing facilities without remediation. To improve the margin of safety in facilities, "DOE Implementation Plan for DNFSB Recommendation 94-1" has identified plutonium-bearing materials that must be stabilized and packaged for safe interim storage.

GENERAL REQUIREMENTS - DOE-STD-3013-94

The DOE Standard, "Criteria for Safe Storage of Plutonium Metals and Oxides," addresses requirements for stabilizing and packaging metals and oxides containing more than 50 wt % plutonium for safe long-term storage.

The package is required to be suitable for off-site transportation and 50-year storage with minimum maintenance. The criteria in the Standard eliminates the need for re-conditioning or repackaging of the stored plutonium before shipping. Organics such as oils, plastics, organic coatings and elastomeric gaskets are excluded from the package.

Material Quantity

The maximum quantity of plutonium permitted per storage package is based on criticality safety and heat generation rates. Depending on the isotopic compositions, the heat generation can vary (See Table 1). The maximum quantity allowed may be lower depending on limits for existing storage facility. The Standard limits the quantity of plutonium to 4.5 kg; and heat generation per package to less than 30 watts, which complies with the maximum rate allowed for currently available transportation overpacks[1].

TABLE 1. Properties of plutonium isotopes and significant daughter of decay.

Property	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am
Half-life (years)	89.6	24,000	6,600	13.2	380,000	432.7
Principal means of decay	Alpha	Alpha	Spontaneous fission	Beta	Spontaneous fission	Alpha, Gamma
Significant daughters of decay	None	None	None	^{241}Am	None	None
Energy per decay[2], MeV	5.592	5.243	5.255	0.007	4.98	5.64
Curies per gram	17.0	0.061	0.22	112	0.004	3.46
Decay heat (Watts/gram)	0.56	0.002	0.007	0.003	0.0001	0.12

Conditioning for Storage

The Standard requires that metals and oxides be conditioned prior to storage to assure material stability and minimize gas generation during storage.

Metal pieces must be stored free of loose oxides. Bulk metals have high ignition temperature (>450 °C) (see Figure 1) and are not easily dispersible in accidents. Plutonium foils and small pieces of plutonium metal having large surface area-to-volume ratio can be potentially pyrophoric when exposed to air. To minimize this risk, stored metals are required to have thicknesses greater than 1.0 mm or a specific surface area less than 1 cm^2/g. Metals that do not meet these requirements must be converted to an oxide and conditioned according to the requirements for plutonium oxide.

Plutonium oxide is hygroscopic. It has active surfaces that strongly absorb atmosphere constituents like H_2O and CO_2., and can adsorb up to 8 percent of their weight as water on the surface. Adsorbed water molecules can decompose by radiolysis into explosive mixtures of hydrogen and oxygen and pressurize sealed storage containers.

To minimize the risk from pressure buildup in containers, the Standard requires that oxides be thermally stabilized at sufficiently high temperature to remove adsorbed organics and water. A Loss On Ignition test (LOI) is required to validate that volatile materials, primarily moisture, are removed to less than 0.5 percent.

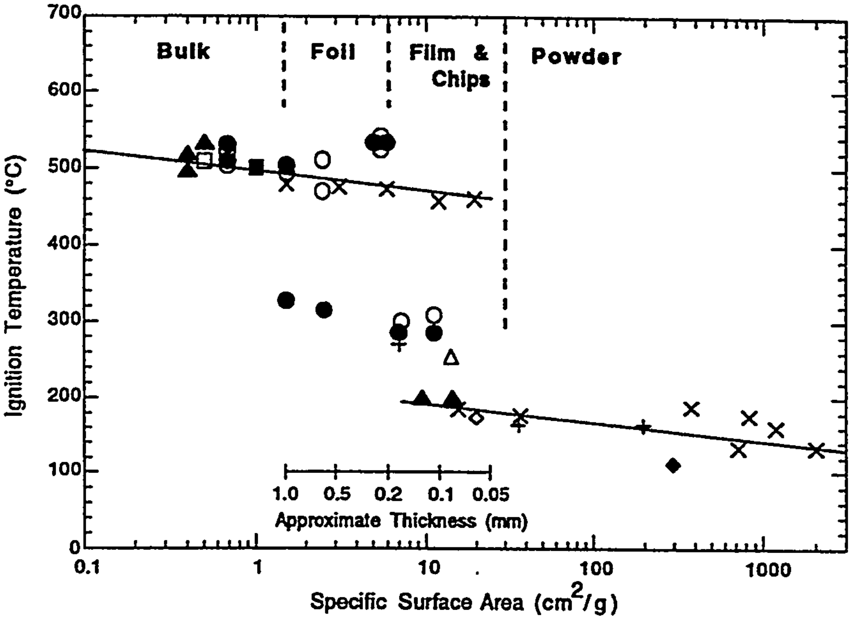

Figure 1. Measured ignition temperatures of plutonium as a function of specific surface area and metal dimension.[3]

Thermal stabilization at higher temperature also has the benefit of increasing particle size, and decreasing the fraction of particles in the respirable range (<3mm geometric dimension). Increasing particle size also reduces surface area and thus slows the re-adsorption rate for moisture[4]. This makes it easier to retain the stabilized characteristic through the packaging process. When the thermal stabilization temperature is increased from 650° to 700°, and to 1,000 °C, the percent of particles in the respirable range decreases from 40 to 25 and to 10 percent[5], respectively.

Packaging for Safe Long-term Storage

The Standard requires that the plutonium metals and oxides be protected by a minimum of two sealed barriers. The storage package must also be qualified for shipping offsite when nested into a qualified shipping container and overpack. The barriers must protect bulk metals from oxidation and stabilized oxides from re-adsorbing moisture. The package should be essentially maintenance free.

Pressure Build-up

Over 50 years, the maximum pressure that can accumulate in a seal container of plutonium oxide may be estimated using the following equation:

$$P = P_i + [(LOI)(m)(T)] / [V - (0.0873\ m)] + [1.3x10^{-4}\ (m)(t)(T)] / [V - (0.0873\ m)]$$

- P_i is the initial packaging pressure in psia,
- LOI is the maximum allowable loss on ignition value in %,
- m is the mass of packaged oxide in kg,
- T is the maximum anticipated storage temperature in K,
- V is the internal volume of the container in liters, and
- t is the elapsed storage time in years.

The last term, which defines the build-up of helium pressure over time, is formulated for ^{239}Pu and is applicable to oxides containing the isotopic distribution of weapon-grade plutonium. For oxide, the helium generation rate is 1.055 x 10^{-4} mole He/kg PuO_2•yr[6]., and pressure increase over 50 years from helium build-up is only 4 psi. If the oxide to be stored contains a high concentration of ^{238}Pu, this term should be evaluated accordingly. For plutonium metals, little if any pressure rise is anticipated because helium is retained in the metal and does not reach the gas phase.

For a three-liter container containing 5 kg of plutonium oxide that has been thermally stabilized to 0.5% LOI, the theoretical maximum internal pressure would be 309 psia. This pressure would be dominated by the pressure rise from decomposition and desorption of moisture. Based on years of successful storage experience with stabilized oxide, the likelihood of a pressurization of this magnitude is considered extremely small.[7]

In-Line and Out-of-Line Storage

The Standard accepts in-line storage enclosure (e.g., glove box, or the Stacker/Retriever Storage Vault and the X-Y Retriever Vault at Rocky Flats), as an acceptable outer package barrier. Therefore, within these storage enclosures, plutonium has to be packaged in at least one sealed barrier. Storage areas and walk-in vaults are not considered package barriers and the plutonium has to be, at a minimum, doubly contained.

Boundary Container

The boundary container is a required container barrier. The standard sets the maximum dimensional limits for a boundary container so that it will fit into a primary containment vessel, which is a part of the packaging scheme for transportation.

A boundary container has to be corrosion resistant. The suggested container material is 304 L stainless steel, based on ductility, and resistance to stress corrosion. It also has to comply with ANSI N14.5 leak-tight requirements after the following one-time abnormal occurrences:

- 4-foot drop onto a flat, essentially unyielding, horizontal surface,
- 2-foot crush in which identical containers collide, and
- compression by the weight of five boundary containers.

Boundary containers must be capable of maintaining an internal pressure that is greater than 1.5 times the theoretical maximum pressure for 50-year storage.

Primary Containment Vessel

The double container requirement can also be satisfied by nesting the boundary container in a primary containment vessel. The primary containment vessel is to be designed for dual use as the "primary containment vessel" for shipping, and a barrier for long-term storage in a centralized storage facility that employs capabilities for nondestructive examination and remote handling[8]. The vessel is also capable of surviving design basis accidents such as a major facility fire. A few primary containment vessels have been fabricated by Westinghouse Savannah River Corporation for evaluation.

Packing material that goes into the primary containment vessel has to be noncombustible and inorganic (no plastics). The free volume in the vessel, including the free space in the inner container(s), has to be at least 2.5 liters. This volume criterion is based on a maximum theoretical pressure at 204°C (400°F) that might result from a major facility fire. Additionally, the criterion requires the space between boundary container and outer vessel to be free of removable contamination.

Material Container

The material container is an optional materials handling container that has to fit inside a boundary container. Until the primary container is available, the double containment requirement may be met by using a sealed material container nested in a boundary container. For a material container to be accepted as a sealed barrier, it has to be leak-tight in accordance with ANSI N14.5.

INSPECTION AND SURVEILLANCE FOR SAFETY

Inspection and surveillance provides the required administrative barrier to prevent release. A package of bulk metal that leaks will have measurable weight gain as the metal converts to oxide. Oxide buildup on bulk plutonium metal is also visible by radiography. Formation of oxide is accompanied by a large (at least 40%) volume expansion. If the bulk metal is wedged in the container, this expansion can breach the package and cause release. For stored plutonium bulk metal, oxidation is a slow process. Documented container breaches resulting from oxide expansion have occurred with packages over 10 years old. Sealed packages of plutonium oxide that contain excess moisture or organics could pressurize over a short time (within days) and cause container failure[9].

Double contained packages stored out-of-line can be inspected using radiography (see Figure 2). For a package doubly contained in a primary containment vessel, sampling of the atmosphere between the inner and outer container can also be used to check for inner container failure. The free space between the boundary container and outer primary containment vessel is free of removable contamination. Any radiological contamination detected would be an indication of possible inner container failure.

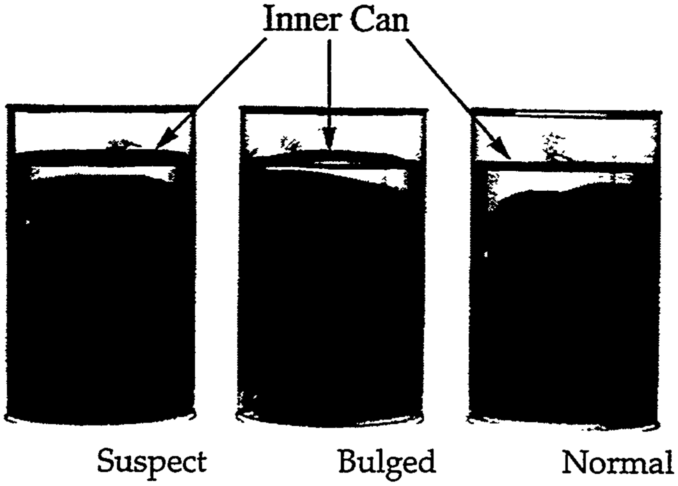

Figure 2. Radiograph of packages showing condition of inner cans.

GENERAL REQUIREMENTS - CRITERIA FOR THE INTERIM STORAGE OF PLUTONIUM BEARING SOLID MATERIALS

The document, Criteria for the Interim Safe Storage of Plutonium-Bearing Solid Materials, is currently being finalized. It is scheduled to be issued in 1995.

The interim Safe Storage Criteria cover materials identified in the DOE plan for implementing DNFSB Recommendation 94-1, and assume that these plutonium-bearing materials could be stored on-site for up to 20 years before final disposal. One goal of this interim criteria document is to provide a complex wide consistent approach to assure safe interim storage. Sites are required to evaluate material compatibility, gas generation, decay heat generation rate, and design life of storage packages to provide specific technical safety bases for their storage packages. However, due to the broad range of materials covered and diversity among storage sites, considerable flexibility is permitted. The typical materials covered by the interim storage criteria include: residues, compounds, scraps, alloys, oxides and salts. The interim criteria do not cover plutonium 238 and 242, spent nuclear fuel, plutonium-bearing liquids, waste items whose surfaces are contaminated with low levels of plutonium and sealed (fabricated) components.

Material Quantity

The storage package technical safety bases will be relied on to provide the material quantity limit.

Conditioning for Storage

The interim storage criteria document does not specify how to condition plutonium-bearing materials intended for interim storage. The criteria exclude materials that are pyrophoric, explosive, flammable, or contain or accumulate free liquid. Each site is responsible for selecting the processes for conditioning materials into acceptable storage forms.

Packaging for Storage

The interim storage criteria require storage packages to have at least two barriers to prevent material release. Containers are required to be leak proof[10] and have sufficient impact resistance to be able to withstand handling accidents. The criteria allow either sealed or vented (with filter) containers to be used. Examples of containers that could be counted as a barrier include food pack cans and welded cans.

The interim storage criteria does not allow plastic bags to be in direct contact with the stored plutonium-bearing materials. Plastic bags and slip-lid cans can be included in a storage packaging but they would not be accredited as one of the two required barriers. The interim storage criteria do not place any restriction on container dimensions.

INSPECTION & SURVAILLANCE

Surveillance of storage packages are required throughout the storage period. The requirements are very similar to what is required in DOE-STD-3013-94.

CONCLUSION

Both DOE-STD-3013-94 and the Interim Storage Criteria call for a minimum of two protective barriers to prevent material releases and to safely store plutonium until final disposition. The DOE-STD-3013-94 applies to plutonium metals and oxide containing at least 50 wt % plutonium. The interim storage document covers primarily materials with less than 50 % assay, which are mostly residues.

DOE-STD-3013-94, Criteria for Safe Storage of Plutonium Metals and Oxides

Plutonium metals and oxides are to be stored either in a sealed container protected by an in-line storage enclosure, or in a minimum of two nested, sealed containers. The outer container (either boundary container or primary containment vessel) is designed structurally to remain leak-tight under both normal and postulated storage accident conditions. The plutonium package must be free of any organic or volatile material that can undergo radiolysis. Surveillance and inspection are required to validate that the condition of the package has not degraded while in storage. The storage package is also designed to nest into a transportation overpack without needing repackaging prior to shipping. Plutonium packaged to these storage criteria should not need subsequent repackaging to ensure maintenance-free safe storage for at least 50 years or until final disposition.

Interim Criteria for Storage of Plutonium-Bearing Solid Materials

Plutonium-bearing materials other than metals and oxides are generally not suitable for long-term storage. They may be stored on-site for an interim period while waiting further disposition. For interim storage, the store packages may either be sealed or vented, and must be designed to survive normal handling incidents. Organic materials are permitted in the storage package. Plastic bags are not permitted to be in direct contact with stored plutonium-bearing materials. Plastic bags and slip-lid cans are not acceptable as one of the two required barriers. The barriers can be containers currently in used in the DOE Complex, such as crimped food pack cans and welded cans. There are no dimensional limitations on the storage package for the purpose of transportation. Materials packaged to the Interim Criteria will require surveillance and inspection.

TABLE 2. Comparison of DOE-STD-3013-94 Standard with the "Interim Storage Criteria for Plutonium-Bearing Solid Materials."

DOE-STD-3013-94	Interim Storage Criteria
Safe storage for at least 50 years	Safe storage for up to 20 years
Container must meet ANSI 14.5 Standard for leakage.	Containers can be vented with secured filter vent. Sealed container need to meet 49 CFR 178.604 for leakproofness.
Metals and oxides with a minimum of 50 weight percent plutonium.	Plutonium-bearing solids, most will be less than 50 % assay.
Does not apply to liquids, process residues, waste, sealed weapon components, or material containing more than three weight percent ^{238}Pu	Does not applied to spent nuclear fuel, liquids, sealed (fabricated) components, ^{238}Pu and ^{238}Pu.
Package shall have at least 2 barriers.	Package shall have at least 2 barriers.
For out-of-line storage, the primary containment vessel is the second barrier. It is specially design both for safe long-term storage and as the primary containment vessel for shipping. It is a uniform design for the complex. Alternatively, until a primary containment vessel is available, a sealed material container nested in a boundary container may be used.	The two barriers can be food pack can, welded can, etc.
Package designed to meet all transportation requirements without repackaging.	Package is designed to be stored on-site only.
Package dimension is limited for the purpose of uniformity, ease of shipping and receiving. It will nest into existing overpack for shipping. It is designed to facilitate remote handling and surveillance in future storage facilities.	Package dimension is left to each site.
No organic materials allowed in packages.	Organic materials may be included in the storage packages. No plastic bags in direct contact with plutonium metal, oxide or compounds. Plastic bags are not accredited as required barriers.
The storage package (when including the primary containment vessel) is designed to survive major facility fire and 30 foot drop and 30 foot crush with loaded package.	The storage package is design to survive handling incidents such as a storage height drop (4-foot minimum), and 2-foot crush test with drop of loaded package , and compression weight of 5 storage package.
Package designed to require no routine maintenance.	Package may require some routine maintenance (e.g. testing vent filter).

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Facilities for Stabilization and Stabilization End States

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ABSTRACT

The Department of Energy (DOE) has embarked upon an aggressive program to stabilize and package nuclear materials for safe, interim storage. The scope and approach to accomplish this objective is documented in the DOE Implementation Plan prepared in response to Defense Nuclear Facilities Safety Board (DNFSB, or the Board) Recommendation 94-1.[1] In support of this plan, DOE-Headquarters formed a Nuclear Material Stabilization Task Group (NMSTG) and each major site prepared a Site Integrated Stabilization Management Plan (SISMP) providing resource-loaded schedules to achieve the objectives. To assure intersite integration of the plans, DOE assembled an Integration Working Group (IWG), comprising contractor representatives from each site, with the primary initial purpose of preparing an Integrated Facilities Plan (IFP).[2] This paper provides a brief summary of the IFP, with particular emphasis on the plutonium materials and facilities.

INTRODUCTION

In its Recommendation 94-1, the Board recommended that an integrated program plan be formulated, on a high priority basis, to integrate use of facilities and capabilities to deal with concerns about liquids and solids containing radioactive substances, located in spent fuel storage pools; reactor basins; reprocessing canyons; and various other facilities that were used for processing and weapons manufacture. Further, the DNFSB recommended that facilities that might be needed for future handling and treatment of these materials be maintained in a usable state.

The Department of Energy (DOE) acknowledged and concurred with the Board's concerns and developed an Implementation Plan (IP)[3] to address the urgent safety problems identified by the Board. The IP established the programmatic requirements and stabilization plan for all at-risk material categories: plutonium materials, including solutions, metals and oxides, and the various residue types; spent nuclear fuel (SNF); uranium; and special isotopes. In addition to its IP commitment to stabilize materials, DOE committed to develop a research plan and a long-range facilities plan based upon a detailed evaluation of the range and quantities of materials to be stabilized and stored.

The NMSTG was formed to coordinate this effort. Supporting the NMSTG are a Research Committee (responsible for the Research Plan) and an Integration Working Group (IWG), which was responsible for the preparation of the IFP. The IP, IFP, and Research Plan together form the Integrated Program Plan (IPP) for DOE's continuing program to deal with the issues identified in Recommendation 94-1 and with issues involving the interim and long-term management of nuclear materials and facilities.

INTEGRATION WORKING GROUP

Shortly after issuing the IP in February 1995, the NMSTG Director established the IWG to prepare the IFP and to serve as a forum for identifying common concerns, evaluating intersite integration options, and recommending tasks necessary for the completion of the stabilization program. The group consists of a chairman and representatives from key field and program organizations. Its facilities core team, detailed below, prepared the Integrated Facilities Plan. Analytical and technical support for IWG tasks is provided by the Nuclear Materials Planning Support Group of Westinghouse Savannah River Company and other organizations.

Chairman: Frank Holmes, Nuclear Materials Stabilization Task Group

Facilities Core Team:
Gilbert Arriola, Nuclear Materials Stabilization Task Group
Don Bridges, DOE Savannah River Operations Office
Shirley Cox, Lockheed Martin Energy Systems, Oak Ridge Y-12 Plant
Don Dustin, Safe Sites of Colorado, Rocky Flats Environmental Technology Site
Scott Gibbs/Ken Chidester, Los Alamos National Laboratory
Roger Henry, Lockheed Martin Idaho Technologies, Idaho National Laboratory
Brent Ives, Lawrence Livermore National Laboratory
Roger McCormack, Westinghouse Hanford Company, Hanford Site
Mike Sujka, Westinghouse Savannah River Company, Savannah River Site
George Werkema, DOE Albuquerque Operations Office

INTEGRATED FACILITIES PLAN APPROACH

The IFP documented assessments of the readiness, capability, and capacity of the existing and new facilities proposed for use in the stabilization and storage missions. This plan was developed using a disciplined systems engineering approach to identify opportunities for facility integration that would further mitigate safety risks, enhance cost effectiveness, and improve stabilization schedules. Figure 1 shows the framework and key elements of the systems analysis as it was applied in development of the IFP.

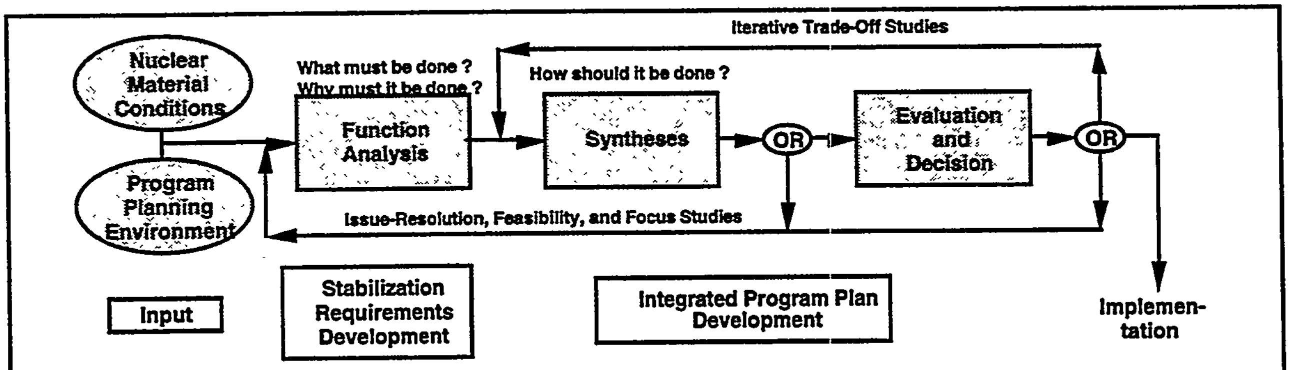

Figure 1: Systematic Approach to Facility Evaluation

Where systems review indicated the potential for improvement or for elimination of potential barriers, special "trade studies" and focus studies were initiated.

The foundations for the IP were the SISMPs, describing each site's baseline plan, resources, schedules, and facilities proposed for execution of the 94-1 mission. A major task for the IWG was to evaluate the site plans against capabilities that exist, or may be provided, at other sites—to identify potential further benefits that could be gained through integrating the program across the DOE complex. Figure 2 shows the generic functional framework for the flow of materials and activities within the 94-1 program and beyond (shaded area).

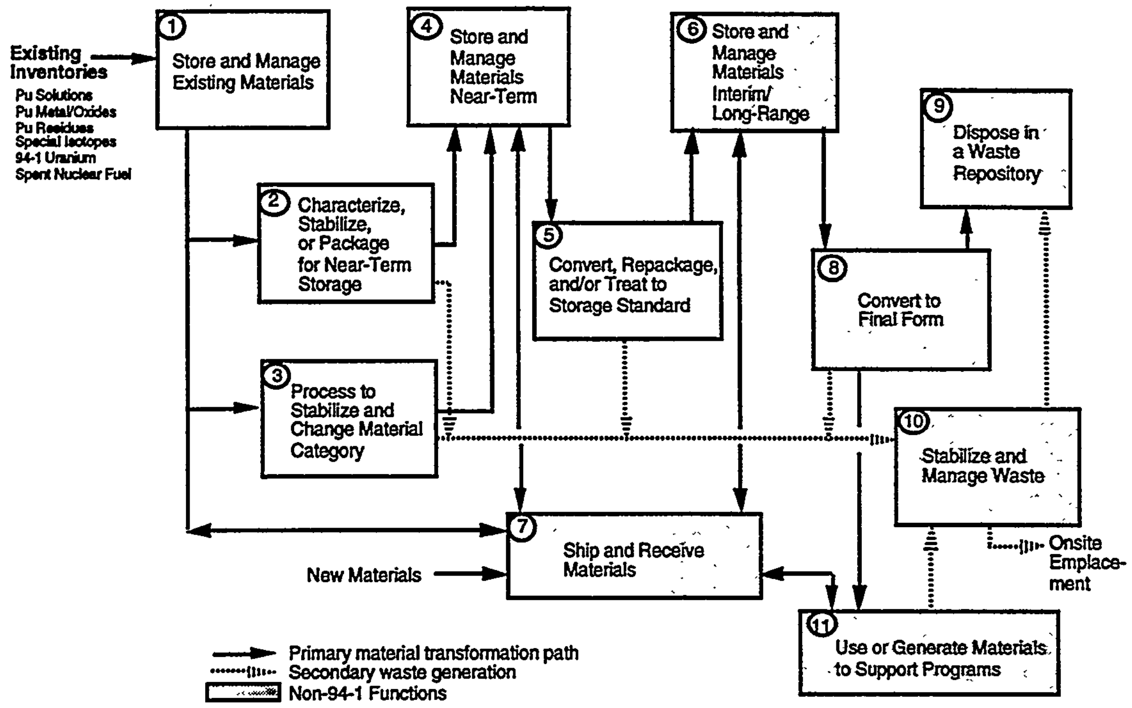

Figure 2: Integrated Functional Flow Diagram

Baseline programs were evaluated for their ability to meet program requirements safely, cost-effectively, and in a timely manner. Specifically, the following types of questions were asked:

- Does the baseline plan meet program objectives?
- What barriers could potentially limit program success?
- Do the capabilities of the facilities meet the stabilization and operating requirements?
- Do alternative approaches exist?
- What policy or program objectives must integrated with the 94-1 activities?
- Are facilities and capabilities that are needed for safe, interim storage and management, pending disposition decisions identified and provided for?

Figure 3 shows the formal systems approach followed by the IWG in assessing plans and alternatives. Employing this process, the site plans were screened to identify potential barriers and excess capabilities. Where integration opportunities with the potential to improve program performance were identified, trade and other studies (some of which are still active) were commissioned to develop quantitative cost/benefit analyses and to flag issues that require further resolution.

Basic tenets of the evaluation process included: (1) The specific stabilization goals and timetables outlined in the IP are to be adhered to, and (2) any changes to the objectives would be accompanied by formal change control. Existing policy planning assumptions and Records of Decision were used to bound the scope of possible integrative strategies.

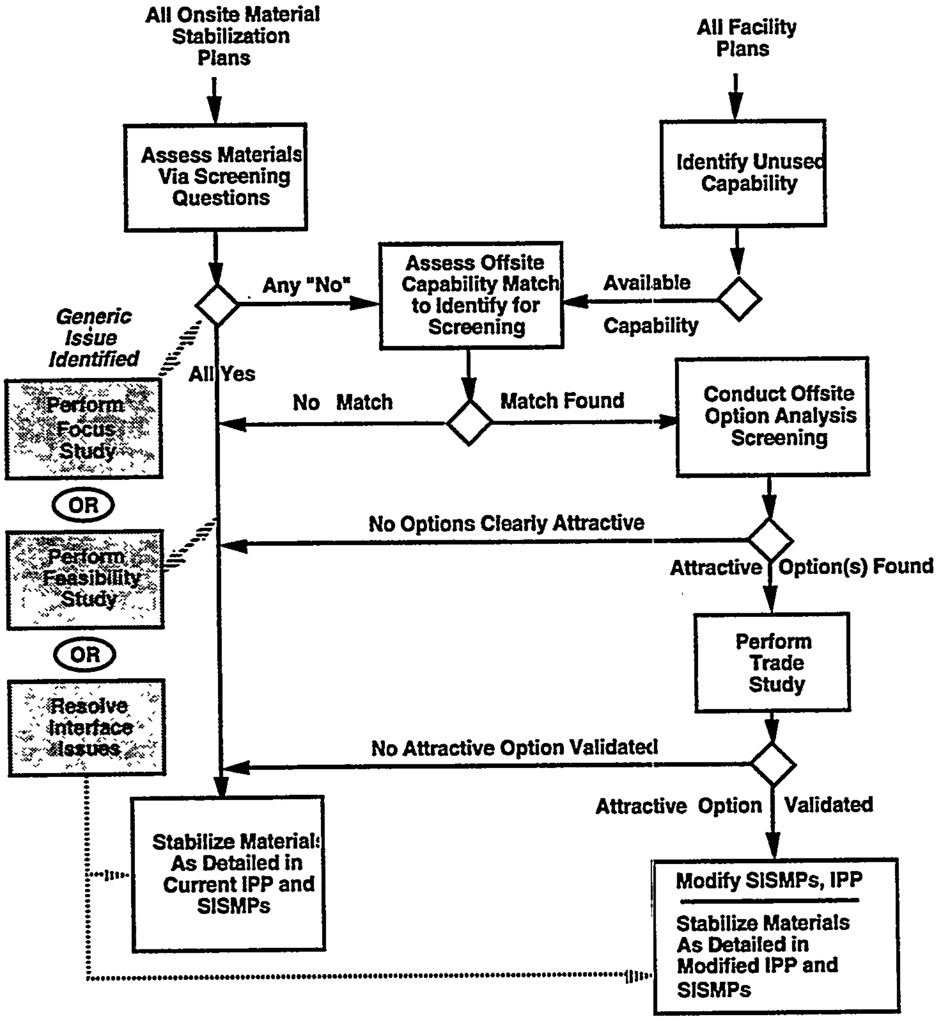

Figure 3: Process for Option Evaluation and Analysis

Consequently, activities under the National Environmental Policy Act (NEPA) and internal studies within DOE may impact the plans' implementation.

Finally, the long-range facility needs were evaluated against the facility capabilities—existing, modified, and new—that DOE will have available after the conclusion of the stabilization program. This evaluation served two purposes: to show the facilities that will (or may be) available to perform interim or long-range missions after stabilization is completed, and to ensure that continuing stabilization and storage capability will be retained.

The results of the materials-oriented, systems analysis and a listing of the resultant required facilities are summarized briefly (for plutonium materials only) later in this paper.

PLUTONIUM END STATES (94-1) AND PROGRAMMATIC INTERFACES

One major task of the systems analysis was the development of "stabilization requirements." Immediate goals for plutonium materials focus on safety issues, especially those related to solutions storage and materials in contact with plastic packaging. Longer-term goals include the conversion of all materials to forms that are safe and stable for low-maintenance interim storage and the packaging of these forms in containers that meet defined standards for safe future handling and maintenance. Whenever there is more than one option available to meet the safety and storage goals, the compatibility of the "end state" produced by the program (the material's chemical and physical form and packaging) can be assessed against the proposed options for disposition or continued management.

Excluding fuel forms, acceptable end states for plutonium materials involved with the 94-1 remediation program include:

- plutonium metals, and oxides that contain more than 50% plutonium by weight, that meet the *Criteria for Safe Storage of Plutonium Metals and Oxides*[4]

- plutonium residues that meet DOE criteria for interim safe storage of plutonium-bearing solid materials ("Interim Storage Standard"), currently under development [5]

- transuranic waste that meets appropriate standards for transportation (Nuclear Regulatory Commission TRUPACT-II criteria) and disposal (DOE Waste Isolation Pilot Plant [WIPP] Waste Acceptance Criteria)

- solid low-level and high-level waste forms and packaging that meet appropriate DOE, site, state, and federal requirements for onsite, offsite, or repository disposal.

Often the criteria and constraints associated with these end states are evolving and activities are in progress to resolve uncertainties. The areas of greatest potential impact, as identified in the IFP, include:

- <u>WIPP Disposal</u>: Assumptions for the final WIPP disposal criteria and timing significantly impact the long-range plans for plutonium storage and management, particularly at the Rocky Flats Environmental Technology Site (RFETS).

- <u>Residue Storage Standards</u>: Interim storage criteria are under development for stabilized residues and other materials that contain less than 50% plutonium by weight. The resultant criteria could significantly impact program cost and timing.

- Disposition: Development of a national policy for ultimate disposition of plutonium continues. Ideally, the 94-1 end states and the ultimate disposition starting point should be the same, to minimize the costs, hazards, and difficulty of future material handling to prepare materials for ultimate disposition.

Some of the key interfaces that will affect the planning environment for plutonium management include: international safeguards; weapons dismantlement; the Fissile Materials Disposition program; the Stockpile Stewardship program; NEPA activities; small-site, research program, and decommissioning support; and other nuclear materials "user" programs.

PLUTONIUM MATERIALS AS THEY EXIST TODAY

Existing plutonium inventories covered by the stabilization program fall into three major categories: solutions, metals and oxides with plutonium-239 contents above 50 percent by weight (wt.%), and residues. Additional separated plutonium materials could be generated in the near term by the aqueous stabilization of aluminum-clad targets at the Savannah River Site (SRS). Further reductions in weapons stockpiles and the decontamination and decommissioning of process facilities will produce additional quantities in the long term. Most of the plutonium-239 materials defined in the Implementation Plan are considered excess to National Security needs. Thus, the treatments can focus on the remediation of risks and the preparation for interim storage awaiting final disposition.

Figure 4 shows the distribution of plutonium materials in the DOE complex. (This chart includes not only materials that are primarily plutonium-239, but also materials that are enriched in other isotopes such as plutonium-238 and plutonium-242.

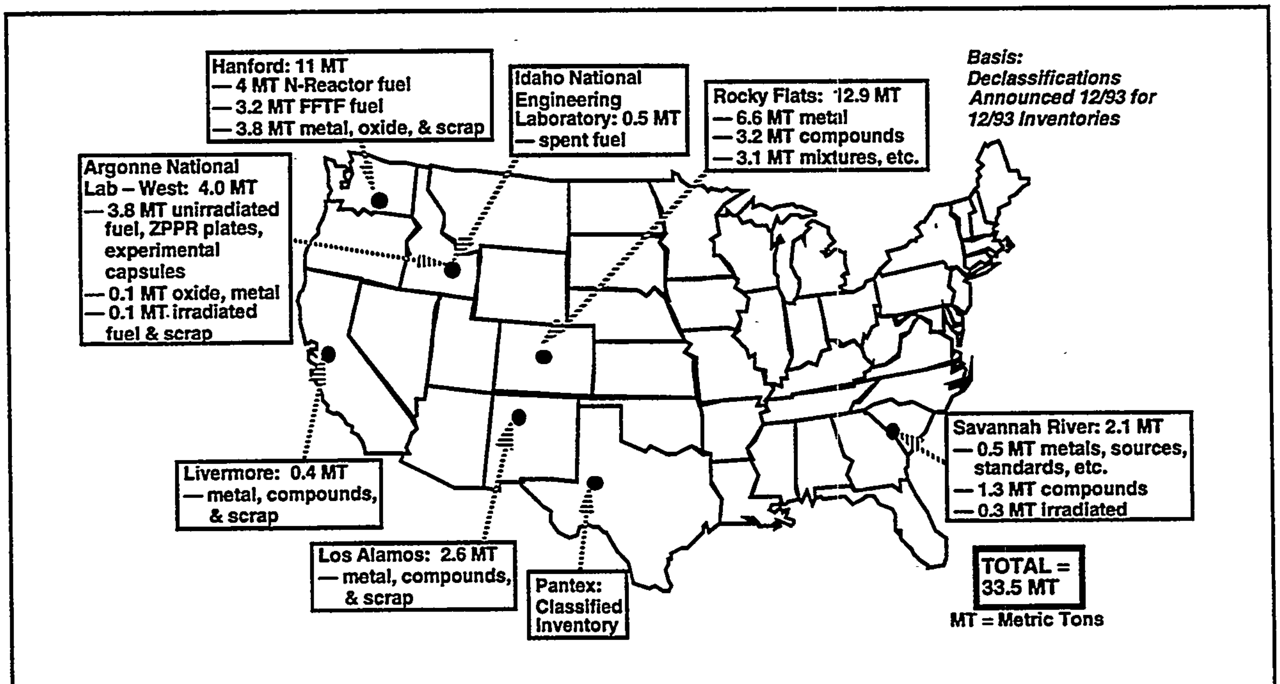

Figure 4: DOE's Plutonium Inventories (December 1993)

The major defense and former-defense plutonium sites that are the focus of the program include Hanford, Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), RFETS, and SRS. Savannah River has a substantially larger quantity of solutions (354,000 liters) than other sites, and Rocky Flats has a substantially larger quantity of residues (20,000 units) than other sites. Rocky Flats and Los Alamos hold the greatest quantity of metals and oxides (6700 and 4000 units, respectively).

The separated plutonium materials at these sites total nearly 21 metric tons (MT) and are currently stored in approximately 35,000 storage containers. Plutonium contained in irradiated fuels and targets is not included in these totals.

PLUTONIUM MATERIALS AFTER STABILIZATION

Of particular importance to the disposition program are the characteristics of the interim storage forms that will be produced by the stabilization program. Some of the forms will be suitable "starting points" for some of the proposed immobilization and disposition options, while other forms may require extensive chemical or physical processing if they are to be accommodated by an immobilization process.

Three major categories will be produced by the baseline 94-1 stabilization program: metals and oxides, greater than 50% plutonium, that meet the 50-year storage criteria; a smaller group of materials that contain mixtures of plutonium with other actinide isotopes; and residues that are stabilized to meet the criteria for safe interim storage or disposal as transuranic waste, but that do not meet the purity or concentration criteria of the 50-year standard. Some of the stabilized residues may contain chemical impurities that would be undesirable for several immobilization options.

Figure 5 shows the current and projected composition of the affected plutonium inventory, broken down by the total plutonium content and by the total number of storage containers. Most of the plutonium mass exists today as metal or oxide that can be treated and packaged to meet the DOE standard. Smaller, but significant, quantities of plutonium will be stabilized in lower-assay forms before they are transferred to disposition programs.

These residues and the stabilized lower-assay forms are grouped into two categories, depending on how much plutonium is contained in a storage container: containers with less than 200 grams per can could more readily be prepared for direct disposal as transuranic waste, should that disposition option be chosen.

After stabilization and storage consolidation, the number of storage units will decline by fewer than about 3000 if all stabilized residues with less than 50 wt.% plutonium are packaged to contain less than 200 grams per can, as assumed for Figure 5. If the stabilized residues are judged suitable for an immobilization process and are packaged more densely after stabilization, a further reduction in storage containers (to about 28,000 units) is possible. However, if WIPP assumptions change, the number of containers could increase by several factors. Since the SRS and LANL residues will be largely eliminated, the remaining residues will predominately be at RFETS and Hanford (only a few thousand cans).

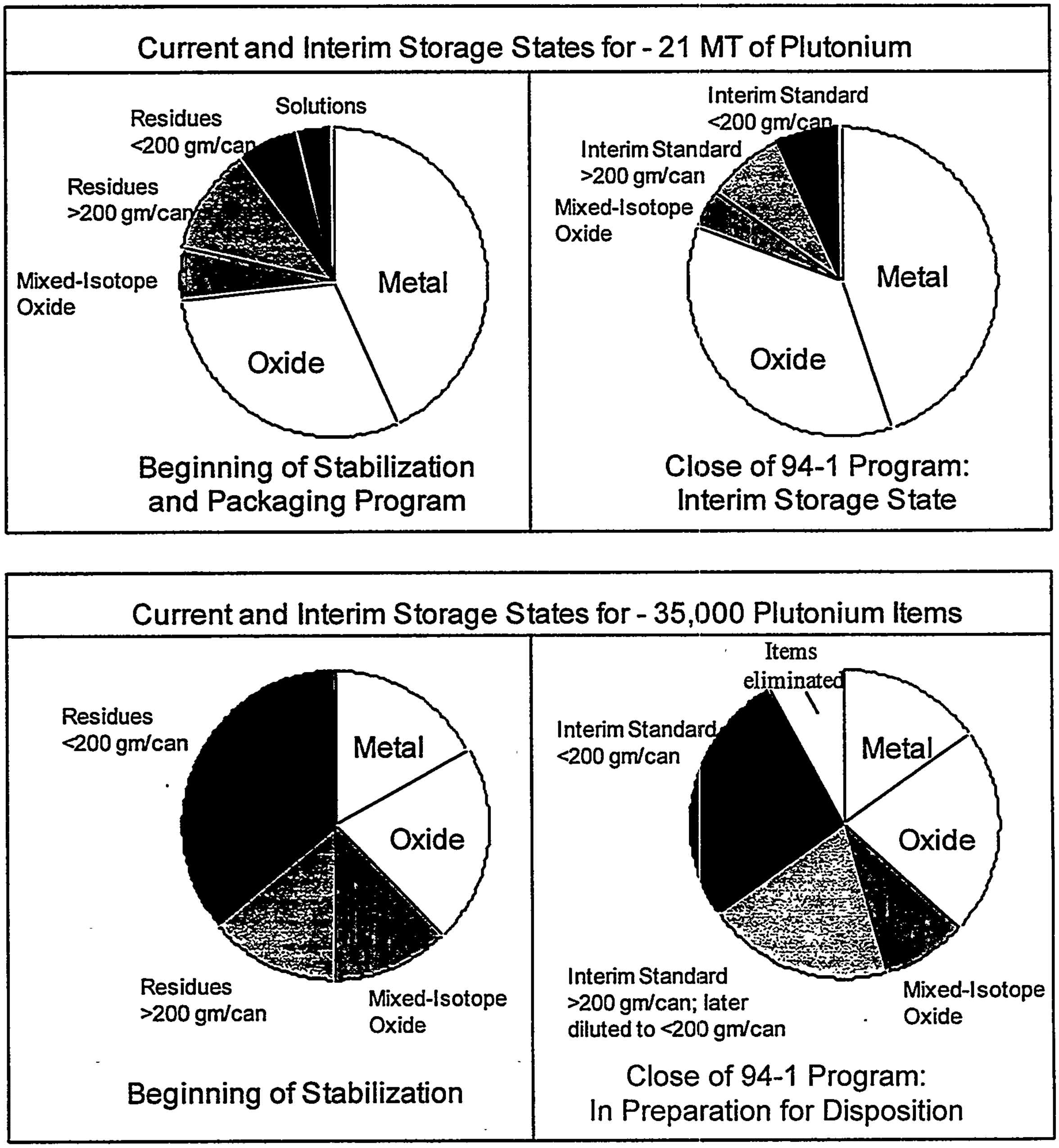

Figure 5: Plutonium Inventory Composition Before and After Stabilization

PLUTONIUM STABILIZATION PLANS AND FACILITIES

To achieve the stabilization and interim storage-form objectives of the 94-1 program, a significant effort must take place across the DOE complex. The relative magnitude of the stabilization task at each site is shown in Figure 6. For each site and plutonium category, the plot depicts the "footprint" of associated facilities, the number of items requiring stabilization or repackaging, and the number of potentially limiting concerns (identified through the IWG screening process) that may impact implementation of the site plans.

Figure 7 depicts the facilities planned for use, by function, in meeting 94-1 Implementation Plan objectives. The shaded areas in each figure reflect the assumed interfaces with out-year programs.

Stabilization processes include aqueous processing for solutions, often followed by precipitation and thermal stabilization; mechanical treatment (brushing), thermal stabilization, and repackaging for metals and oxides; and numerous processes including characterization, mechanical treatment, thermal stabilization, pyrochemical or aqueous processing, and repackaging for the residue forms.

To perform these processes and provide long-range capabilities, sites must install new equipment or modify existing equipment and facilities. In some cases, alternative facility-use strategies are being explored. Major facility implications include:

- Rocky Flats: Besides the restart of existing equipment and facilities, major new or modified processes will be installed in existing buildings. Key new capabilities include: (1) precipitation and calcining equipment in Building 371 for solutions; (2) pyrochemical oxidation equipment for salt residues; (3) treatment equipment for combustible residues; (4) a thermal stabilization process for ash residues in Building 707; and (5) a calcination and packaging line in Building 371 to convert and package metals and oxides to the storage standard.

- Savannah River: Required activities include restart of F and H Canyons and their associated ancillary facilities (e.g., FB Line and HB Line) and completion of a project to construct a new Actinide Packaging and Storage Facility.

- Hanford: Activities include installation of new thermal stabilization equipment and a new packaging system at the Plutonium Finishing Plant, modification of an existing vault, and upgrades to several plutonium and support facilities.

Figure 8 provides a plot of the footprint of facilities actively involved in plutonium storage at the major sites. The cumulative square footage of the footprint is plotted for the current configuration, the anticipated configuration after stabilizing the materials, and at the end of the 94-1 program; it does not reflect total operating area associated with multi-level facilities or with other operations The facility footprint provides an approximation of the magnitude of effort and cost required to actively manage the inventories within the facility.

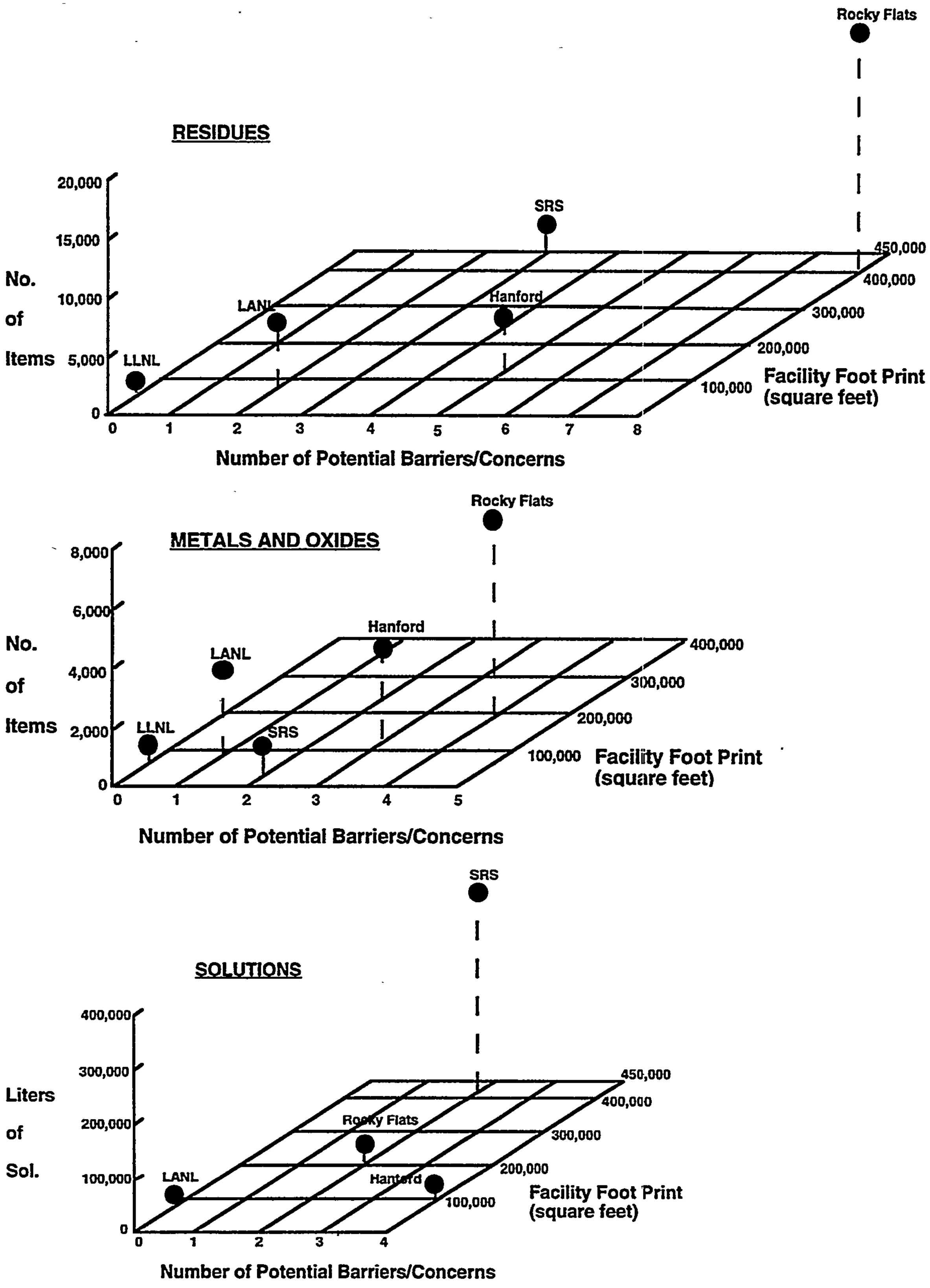

FIGURE 6: Magnitude of Plutonium Stabilization Effort by Site

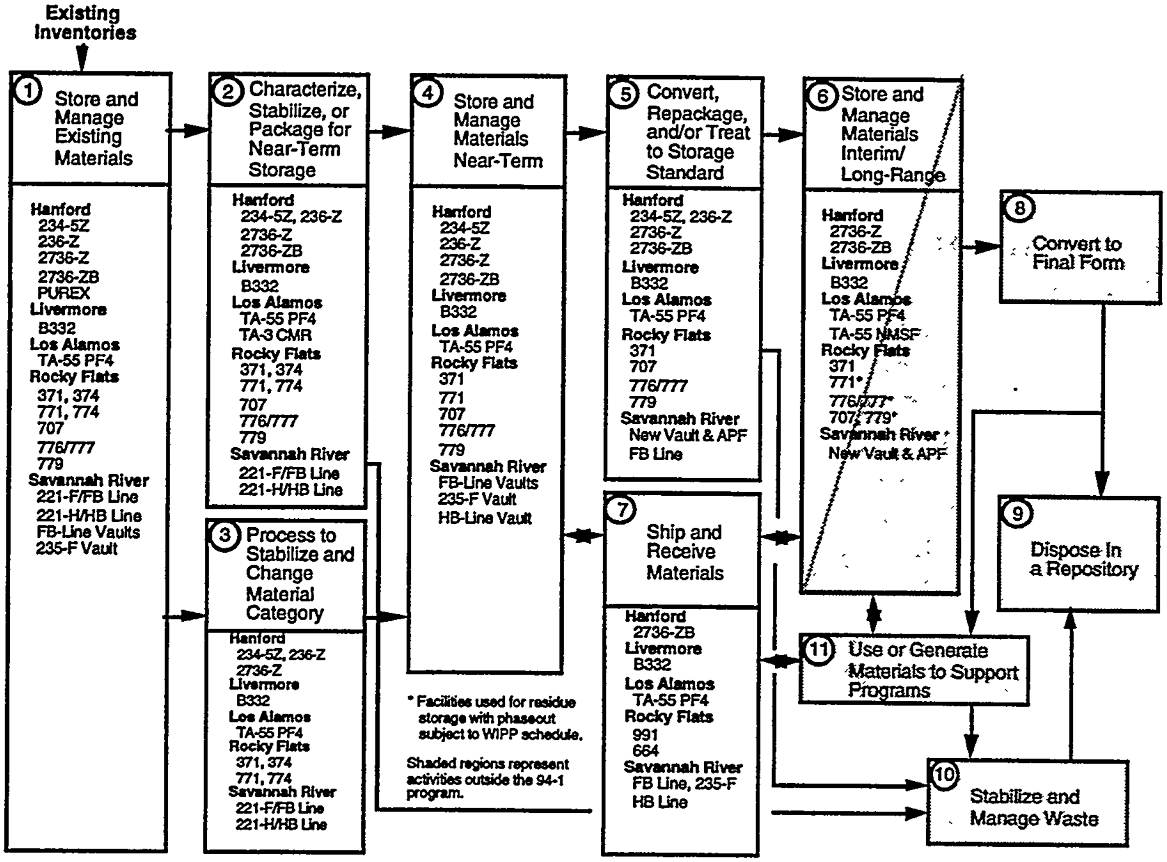

Figure 7: Plutonium Facilities at Major Sites Involved in 94-1

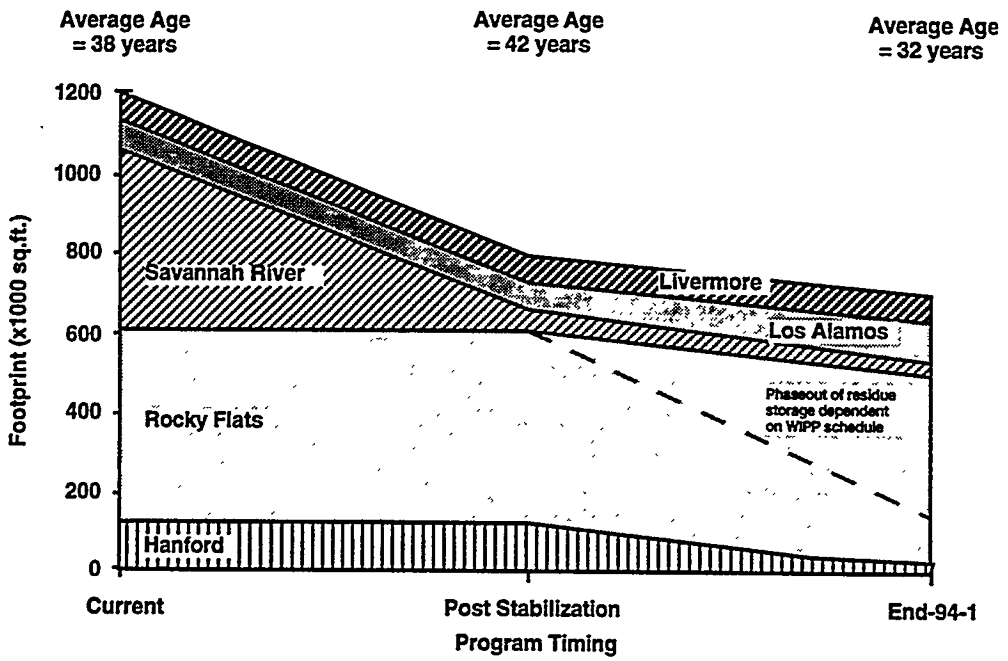

Figure 8: Plutonium Storage Facility Footprint

Also shown is the average age of the facilities. In general, older facilities are more difficult and costly to maintain and are more vulnerable to design-basis accidents. Although significant reductions in footprint and average age are accomplished during 94-1, additional reductions are possible and may provide substantial cost benefits.

Figure 9 provides a high-level overview of the facilities, their ages and conditions, utilization during the 94-1 program, and potential uses after the close of the 94-1 task. Further detail regarding processing and storage of plutonium materials and the interactions among facilities is provided in the IFP.

Part of the 94-1 effort includes ensuring that sufficient facilities remain operational to store and process material and provide other needed functions for the long term. Facilities are identified that provide these capabilities in the interim until final storage and disposition decisions are made by other active programs (e.g., Fissile Materials Disposition and Stockpile Stewardship and Management). In some cases, use of these facilities will require structural and system modifications, or replacement may prove to be cost effective. The NMSTG maintains continuing liaison with these out-year programs both to provide a starting point for their facility-planning deliberations and to ensure that any impact, emanating from their evolving plans, is formally factored into the timely execution of the 94-1 program commitments.

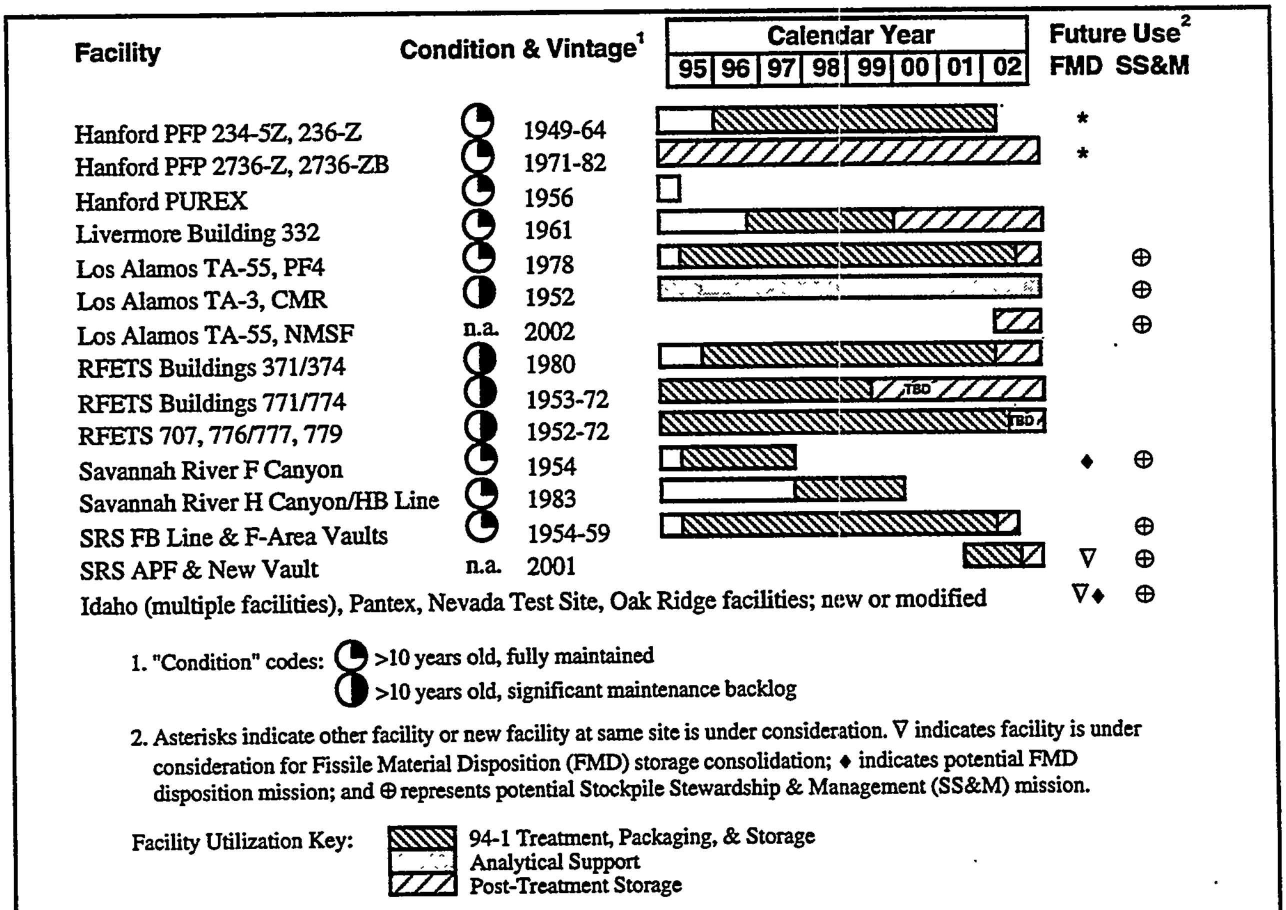

Figure 9: Plutonium Facility and Program Summary

CONCLUSIONS AND PATH FORWARD

The identified facilities can provide the capability and capacity to fulfill 94-1 objectives as now documented. However, defining and implementing the stabilization and storage activities is not a static process. The Department identified a need for follow-on studies to determine the best options and approaches to overcome uncertainties and barriers to implementation:

- Plutonium metals and oxides stabilization timing analysis
- Alternatives for scrub alloy at Rocky Flats
- Alternatives for pyrochemical salts at Rocky Flats
- Alternatives for the disposition of other non-salt residues
- Other studies: small sites; residues at Mound
- Transportation feasibility

Three current initiatives, in particular, may influence the plans:

- The evaluation of seismic resistance of facilities at Rocky Flats, as identified in DNFSB Recommendation 94-3. The results of this evaluation may result in restructuring site plans for material stabilization and storage.

- The development of criteria for the safe interim storage of plutonium-bearing solids. These criteria may alter the scope of the Rocky Flats stabilization requirements.

- The Environmental Impact Statement (EIS) on Interim Management of Nuclear Materials at the Savannah River Site. The Record of Decision for this EIS may require changes in the current strategies for all site facilities, particularly those used for the management of spent nuclear fuel.

The 94-1 program feeds several out-year programs for which planning is not yet complete. These programs will influence choices of existing, modified, and new facilities to perform long-range remediation tasks similar to those required for the 94-1 program as well as to perform other nuclear material storage, management, and disposition tasks. There are, however, a sufficient number of attractive options to assure the needed functional capabilities to safely store the materials, monitor and inspect the inventories, and respond to any adverse storage conditions that may develop can be provided. Key decision points for National programs related to plutonium include:

- Record of Decision for the Programmatic EIS on Fissile Material Disposition
- Record of Decision for the Programmatic EIS on Stockpile Stewardship and Management

A number of significant NEPA decisions concerning the disposition of other materials (e.g. spent nuclear fuels, enriched uranium) can significantly impact the future use of plutonium facilities. In addition, the need to consolide materials at Sites and within the complex will become more important as DOE continues to reduce the overall facility cost and risk.

The Integration Working Group will continue to monitor, recommend, and coordinate activities aimed at resolving intersite treatment and storage opportunities and interfaces between the 94-1 program and other DOE programs involved with materials management and disposition.

DISCLAIMER

REFERENCES

1. Defense Nuclear Facilities Safety Board Recommendation 94-1 to the Secretary of Energy,
May 26, 1994.

2. Department of Energy, Nuclear Material Stabilization Task Group, *Integrated Facilities Plan*, September 30, 1995.

3. Department of Energy, *Defense Nuclear Facilities Safety Board Recommendation 94-1—Implementation Plan*, February 28, 1995.

4. Department of Energy Standard DOE-STD-3013-94, *Criteria for Safe Storage of Plutonium Metals and Oxides*, December 1994.

5. Department of Energy, *Criteria for Interim Safe Storage of Plutonium-Bearing Solid Materials*, September 29, 1995 Draft.

Summary of Findings of the R&D Committee

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ABSTRACT

In March 1995, the Department of Energy's (DOE) Nuclear Materials Stabilization Task Group (NMSTG) chartered a committee to formulate a research and development (R&D) plan in response to Sub-recommendation (2) of Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1. The NMSTG was established as an organizational unit operating under the auspices of the DOE Office of Environmental Management. As a result of its efforts, the Research Committee concluded that, in general, the technology needs for stabilizing 94-1 nuclear materials are being adequately met by existing or planned DOE programs. At the same time, the committee, in the form of recommendations, noted specific R&D program areas that should be addressed by the NMSTG. These recommendations are documented in the R&D plan and formulated based on: (1) existing "gaps" in DOE's R&D stabilization program, (2) the relative maturity of various technologies, and (3) other important R&D program issues that, in the judgement of the committee, should be addressed by the NMSTG. A systems engineering approach, derived from the aerospace industry, was applied to the various stabilization technologies to assess their relative maturity and availability for use in treating 94-1 nuclear materials.

INTRODUCTION

On May 26, 1994, the DNFSB issued Recommendation 94-1, which expressed the Board's concern about nuclear materials left in the manufacturing "pipeline" after the United States halted its nuclear weapons production activities. The DNFSB emphasized the need for remediation of these materials. DOE accepted DNFSB Recommendation 94-1 on August 31, 1994. After establishing the Nuclear Materials Stabilization Task Group, DOE issued an implementation plan to address these concerns ("Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," February 28, 1995).

As part of Recommendation 94-1, Sub-recommendation (2) stated "that a research program [should] be established to fill any gaps in the information base needed for choosing among the alternate processes to be used in safe interim conversion of various types of fissile materials to optimal forms for safe interim storage and the longer term disposition. Development of this research program should be addressed in the program plan called for by [the Board]."

Consequently, in March 1995 the NMSTG chartered a committee to accomplish the following: (1) assess the nuclear materials stabilization program outlined in the implementation plan, (2) formulate an R&D

plan to address the technology and core program needs of the stabilization program, and (3) prepare task statements defining R&D activities required to accomplish program objectives.

The methodology used by the committee to formulate the plan included a review of the Implementation Plan and Site Integrated Stabilization Management Plans; visits to the Savannah River Site (SRS), the Hanford Site (Hanford), Lawrence Livermore National Laboratory (LLNL), and Los Alamos National Laboratory (LANL); and regular meetings of the Research Committee, including ex-officio members and technical advisors.

In developing the plan, the committee addressed five of the six material categories discussed in the 94-1 Implementation Plan, which consisted of plutonium solutions, plutonium residues and oxides (< 50% Pu), plutonium metals and oxides (> 50%), uranium metals, and special isotopes. R&D efforts related to spent nuclear fuel stabilization, the sixth category, were specifically excluded from consideration in the plan. These efforts are being coordinated through the Technology Integration Technical Working Group established by the Office of Spent Fuel Management in June 1993. In addition, issues related to funding, schedules, logistics planning, and facilities were not within the scope of the plan and are being addressed by the Integration Working Group and by other groups as designated by the Director of the Nuclear Materials Stabilization Task Group.

The committee selected to develop this R&D plan consists of 10 members: 2 independent consultants serving as co-chairmen and 8 technologists representing five DOE national laboratories and three production sites. In addition, ex-officio members from the DOE Office of Fissile Materials Disposition; the Office of Environment, Safety and Health; and other national laboratories were invited to attend the Research Committee's meetings. Organizationally, the Research Committee reported directly to the NMSTG Director.

In responding to DNFSB Recommendation 94-1, DOE committed to complete specific nuclear materials stabilization tasks assigned to 3- or 8-year timeframes. The Research Committee focused its review on existing technologies and on technologies currently under development to determine their adequacy relative to the 3-year commitments shown in Table 1. The committee also outlined R&D requirements to address technologies needed to support the Department's 8-year commitments.

Table 1. Three-Year Stabilization Commitments

Commitment	Date
Transfer PUREX solutions to tank farms (Hanford)	August 1995
Stabilize plutonium residue sludge (Hanford)	September 1995
Stabilize 220 kgs of residues (LANL)	October 1995
Vent 2,045 drums of residue (RFETS)	October 1995
Process F-Canyon plutonium solutions (SRS)	January 1996
Stabilize 46 packages of ash (Hanford)	March 1996
Repackage all metal in contact with plastics (All)	September 1996
Vent inorganic and wet/miscellaneous residues (RFETS)	October 1996
Remove and ship high enriched uranium solutions (RFETS)	December 1996
Stabilize high-hazard pyrochemical salts (RFETS)	May 1997
Stabilize high-hazard sand, slag, and crucible residues and graphite fines (RFETS)	May 1997
Process H-Canyon Pu-242 solutions (SRS)	November 1997
Convert HEU solutions to stable oxide (SRS)	December 1997
Stabilize remainder of high-hazard pyrochemical salts (RFETS)	December 1997
Stabilize sand, slag, and crucible residues (SRS)	December 1997

The Research Committee's first objective was to identify technology baseline requirements for all categories of nuclear materials and for related issues that must be addressed by the plan. These requirements are presented in the R&D plan and provide the formal basis for all technologies needed to address nuclear materials stabilization, regardless of the status of the required technologies. Programs that are either in place or are currently being developed are discussed in the plan, but are too voluminous for presentation in this paper. The format used for plutonium residues was based on the outline of categories established in DOE-STD-Draft-SAFT-0045, "Criteria for Safe Storage of Plutonium-Bearing Materials." By comparing baseline requirements with existing programs, the committee identified technology "gaps" that must be addressed if DOE is to implement a thorough and effective nuclear materials stabilization program.

The technology "gaps" identified by the Research Committee will be translated into task statements that will be issued separately, as needed. In addition, a systems engineering approach was used to evaluate the relative maturity of technologies now under development at various DOE facilities. The results of the analysis are also presented in the plan. These systems engineering data were used to determine (1) whether certain technologies designated as part of the baseline for stabilizing various categories of nuclear materials are sufficiently mature to require minimal attention from NMSTG and (2) whether certain competitive alternative or backup technologies should be pursued to ensure that methods for stabilizing nuclear materials will be available in a timely manner. The resulting maturity scores were based on information available at the time the plan was prepared and should be updated, as appropriate, before being used to support important programmatic decisions.

To ensure the timely development and implementation of the technologies outlined in the plan, the NMSTG will continuously track the progress of the R&D program. If a baseline technology seems unlikely to achieve the desired results or if a single competitive alternative technology must be selected, the NMSTG may, at its discretion, charter a trade study as part of the decision basis for that technology.

The plan was based solely on those nuclear materials stabilization requirements available to the committee at the time the plan was developed. In part because these requirements are still evolving, the nature of the R&D required to support this effort will change over time. Thus, the plan represents a snapshot in time and will need to be updated on a regular basis. The Research Committee was disbanded as of the issuance of the R&D Plan. Responsibility for tracking the information contained in the plan and for preparing updates to the plan will fall to the Plutonium Focus Area, an organizational unit charged with fulfilling the functions formerly assigned to the Research Committee. At present, the NMSTG plans to issue the first major update of this document in November 1996.

CONCLUSIONS

As a result of its efforts, the Research Committee concluded that, in general, the technology needs for stabilizing 94-1 nuclear materials are being adequately met by existing or planned DOE programs. At the same time, the committee has noted specific R&D program areas that should be addressed by the NMSTG. The recommendations summarized in Tables 2, 3, and 4 address these issues. To accomplish its objectives, the committee developed a comprehensive set of technology baseline requirements against which existing stabilization technologies should be measured. This comparison resulted in the identification of technology "gaps" in DOE's R&D stabilization program. These gaps are identified as recommendations in Table 2. Using a systems engineering approach, the committee also developed recommendations based on the maturity score of each technology considered. The recommendations listed in Table 3 relate to those technologies that, because of high maturity scores (low relative maturity), should be closely tracked by NMSTG to ensure their availability to meet 94-1 commitments. The recommendations provided in Table 4 identify important R&D program issues that, in the collective judgment of the committee, should be addressed by the NMSTG. These recommendations are offered to provide direction in key areas related to R&D and to identify potential programmatic weaknesses that may require attention from NMSTG management.

The recommendations offered in Tables 2, 3, and 4 are constrained by the following caveats:

- If significant changes are made in DOE-STD-3013-94, “Criteria for Safe Storage of Plutonium Metals and Oxides,” or in DOE-STD-Draft-SAFT-0045, “Criteria for Safe Storage of Plutonium-Bearing Materials,” significant changes in R&D needs may result.
- The ranking of technologies is based on meeting near-term goals (3 or 8 years) for stabilization. Since facility readiness and operational safety readiness for new or modified facilities may not be completed within a 3-year (and perhaps within an 8-year) schedule, new technologies are identified but are not ranked.
- Economic evaluation of alternative process options was not conducted.

Table 2. Recommendations to Address Technology "Gaps" in the Stabilization Program

RECOMMENDATIONS	COMMENTS
Develop standards for the stabilization and storage of each of the special isotopes (Pu-238, Pu-242, and isotopes of Np and Am/Cm).	Site-specific rather than DOE-wide standards should be acceptable for each of these materials. Am/Cm isotopes will be stored in a highly shielded facility. Neptunium will require additional shielding because of its decay product. Pu-238 will require heat removal, venting to prevent helium buildup, and shielding.
Develop analytical methods for determining moisture content, gas composition from radiolysis, and reactive metals present in pyrochemical salts.	A process will be required to characterize moisture and reactive metals in salts treated for stabilization and to analyze the effects of radiolysis on stored salts.
Develop a flowsheet for stabilizing neptunium solutions at SRS.	Neptunium flowsheet development will require some R&D; however, the development of major new technologies should not be required.
Develop large-volume storage containers for low-assay (<10%) plutonium residues.	Existing storage configurations include containers that are larger than those prescribed by DOE-STD-3013-94. Larger containers (which will minimize the number of storage positions required) must be compatible with vaults planned for storage.
Evaluate the need for corrosion-resistant containers for halide salts and other corrosive residues.	Pyrochemical salts may either be processed for actinide separation or stored. If stored, corrosion-resistant containers must be used to ensure the long-term safe storage of salts.
Develop a surveillance system for monitoring Am/Cm and Pu-238 in storage.	Because of the high radiation levels for Am/Cm and the high heat generation rate for Pu-238, additional surveillance measures will be needed for storing these materials.

Table 3. Recommendations for Tracking Technologies to Meet Stabilization Commitments

RECOMMENDATIONS	COMMENTS
Complete the timely development and startup of the vertical calciner at Hanford.	Although backup technologies are more mature, the vertical calciner will eliminate generation of a byproduct waste stream. This technology has been accepted by Hanford stakeholders.
Continue the concurrent development of multiple processes for stabilizing all categories of hazardous combustibles containing plutonium.	Multiple technologies are required if all hazardous combustible materials are to be treated (e.g., pyrolysis for other combustibles, catalyzed chemical oxidation, polycube pyrolysis, ion exchange denitration, chemical oxidation). Incineration is the most mature of these technologies; however, institutional issues currently preclude its use. Consequently, less mature technologies should be closely tracked by NMSTG management.
Continue the development of the modular concept at LANL as a means to eliminate startup of processing facilities at various sites.	Successful implementation of this innovative technology could produce substantial savings, allowing facilities that would otherwise be needed for accomplishing 94-1 goals to shut down.
Continue the development of technologies to address U-233 criticality safety issues at the MSRE facility.	Multiple technologies are being evaluated to determine the best option for addressing U-233 criticality safety issues associated with the MSRE Remediation Project.
Continue development of the bagless transfer system as a baseline technology and of electrolytic decontamination as a close-coupled backup technology for plutonium packaging.	The bagless transfer system is costly and needs to be demonstrated. Electrolytic decontamination coupled with manual loading and packaging could be a less costly alternative that is more readily implemented.
Complete development of digital radiography and/or digital radiography/tomography for monitoring plutonium packages in storage.	Noninvasive surveillance systems will minimize the need to sample and analyze materials in storage.

Table 4. Other R&D Program Recommendations

RECOMMENDATIONS	COMMENTS
Evaluate the institutional issues—particularly, negative public perceptions—that prevent deployment of incineration technology, which the RC believes to be the most viable method for treating combustible residues.	Incineration is the preferred technology for treating combustibles. Institutional issues preventing its use require further investigation. A favorable resolution of these issues can reduce R&D related to the stabilization of combustibles.
Maintain an ongoing core technology program to support stabilization technologies, to address unforeseen problems associated with long-term storage, and to provide technology for predicting the long-term behavior of nuclear materials.	As long as nuclear materials require stabilization and storage, R&D support will be needed to provide a better understanding of their behavior in order to address anomalies that may occur.
Provide R&D to identify and support the development and implementation of an interim storage standard for residues.	The interim storage standard is in a state of change. R&D support will be required to establish a technical basis for the standard.
Continue basic R&D studies of plutonium oxide behavior in support of DOE-STD-3013-94 (>50 and <80 wt % plutonium.)	Pure plutonium oxides (>80 wt % plutonium) can be stabilized at lower calcination temperatures and can contain higher levels of moisture for long-term storage. Less pure oxides should be evaluated to determine whether they can also be stabilized at lower temperatures.
Approve a DOE-wide storage standard for uranium metals and oxides and for other corrosive residues.	A site-specific standard is being used at the Oak Ridge Y-12 Plant, where most of DOE's high enriched uranium is stored. A DOE-wide standard, now under consideration, needs to be approved.
Develop an integrated approach for the storage and surveillance of plutonium packages, using nonintrusive technologies that minimize personnel exposures and maximize safeguards and security.	Although surveillance procedures are being developed for specific items, no systematic overall approach has been developed to monitor plutonium materials in storage. Noninvasive surveillance should be emphasized, minimizing the need for labor-intensive activities.

The approach used by the Research Committee to develop the plan involved a review of those technologies applicable to 94-1 Implementation Plan issues. Thus, this document does not reflect an R&D plan in the traditional sense, but rather it illustrates the breadth of technologies available to the NMSTG for addressing 94-1 requirements. The plan also identifies gaps in technological information that should be considered in order to ensure the successful and timely stabilization of DOE's nuclear materials.

This process used in developing the R&D Plan is consistent with the problem-solving approach endorsed by the Secretary for examining a wide range of issues faced by the Department in the post-Cold War era. By emphasizing cooperation and information sharing within the Complex and by adopting proven techniques from a variety of external sources, DOE has been able to allocate its limited resources more efficiently. This R&D plan is also an integral part of the Department's commitment to ensure the health and safety of workers and the public through the responsible management of its inventory of nuclear materials.

Based on the results of its efforts, the Research Committee concluded that, in general, the technologies necessary to address 94-1 issues are currently available, are under development, or have been identified as gaps that should be addressed by NMSTG management. Thus, the committee concludes that new initiatives involving costly R&D programs for extensive technology development are not necessary. However, the NMSTG must establish the funding and tracking mechanisms to ensure that baseline and competitive alternative technologies are implemented to meet 94-1 commitments. The systems engineering approach used in formulating the plan offers an effective model for tracking and decision making and should prove valuable to the NMSTG in ensuring the timely implementation of these technologies.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

Ceramification: A Plutonium Immobilization Process

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ABSTRACT

This paper describes a low temperature technique for stabilizing and immobilizing actinide compounds using a combination process/storage vessel of stainless steel, in which measured amounts of actinide nitrate solutions and actinide oxides (and/or residues) are systematically treated to yield a solid article. The chemical ceramic process is based on a coating technology that produces rare earth oxide coatings for defense applications involving plutonium. The final product of this application is a solid, coherent actinide oxide with process-generated encapsulation that has long-term environmental stability.

Actinide compounds can be stabilized as pure materials for ease of re-use or as intimate mixtures with additives such as rare earth oxides to increase their degree of proliferation resistance. Starting materials for the process can include nitrate solutions, powders, aggregates, sludges, incinerator ashes, and others. Agents such as cerium oxide or zirconium oxide may be added as powders or precursors to enhance the properties of the resulting solid product. Additives may be included to produce a final product suitable for use in nuclear fuel pellet production.

The process is simple and reduces the time and expense for stabilizing plutonium compounds. It requires a very low equipment expenditure and can be readily implemented into existing gloveboxes. The process is easily conducted with less associated risk than proposed alternative technologies.

INTRODUCTION

Ceramification is a term “coined” to describe a specific chemical ceramic process that can be used to immobilize actinide oxides, actinide nitrate solutions, and actinide residues. The process converts actinide nitrates and dispersible actinide oxides and residues into solid coherent oxide articles. Actinide compounds can be stabilized as pure materials for ease of re-use or as intimate mixtures with additives to effect criticality safety, radiation exposure reduction, and/or enhanced proliferation resistance.

A similar chemical ceramic process has been used in industry for 25 years to prepare metal oxide coatings. Additionally, a version of the process was developed for molten metal containment in weapons applications and was in production at the Rocky Flats Site for over 15 years. Ceramification applies this well proven technology in a novel way to effect the stabilization of actinide compounds.

The process is simple and reduces the time and expense for stabilizing actinide compounds. The process requires a very low equipment expenditure and can be readily implemented into existing gloveboxes.

Stabilization and Immobilization Issues

The long-term stabilization and immobilization of the Department's actinide inventories require a multi-attribute analysis. Each approach must systematically consider the material form, material packaging, and the storage facility including the safety system criteria. Each alternative requires in-depth analysis of material processing capabilities, packaging capabilities, storage spacing requirements, safety and security surveillances, actinide disposition determinations, licensing and permitting requirements, and program life-cycle costs and schedules. In addition, consideration must be given for increased proliferation resistance, including international (IAEA) inspections.

The near-term initiatives require the Department to stabilize its actinide material forms, reducing the material, packaging, facility, and institutional vulnerabilities. Desired initiatives are those that expeditiously stabilize the material forms to reduce or eliminate the current respective health and safety risks and to minimize future liabilities and costs.

Additional issues regarding the stabilization and immobilization initiatives include the adaptation of approaches that minimize by-product waste generation, incorporate improved principles of ALARA, and allow disposition options (e.g., re-use, long-term storage, proliferation resistance) to proceed unencumbered. Also, appropriate considerations should be given to options that benefit life-cycle costs, reduce safety surveillance requirements and corresponding exposures, minimize the reliance on safety systems, reduce a site's release fraction risks, and reduce the future mortgage.

In general, the greater the stabilization of the material form, the less is the packaging and facility requirements. More robust packaging also reduces the facility requirements. The future mortgage required by safety systems, surveillances, and transportation will decrease as material stabilization/
immobilization and packaging increase.

Ceramification -- The Concepts

Ceramification is a chemical ceramic process resulting in a product that is a polycrystalline ceramic with a long-term environmental stability. Precursors are mixed with actinide material forms and heated at a low temperature to produce this solid metal oxide article. The materials combine in an orderly fashion, allowing excellent process control and reproducibility. The process can incorporate and accommodate actinide nitrate solutions.

The ceramification process bonds thermally stable materials together, for example, plutonium oxide. The process also bonds unstable mixtures that thermally convert to a stable mass, for example, plutonium bearing ash (residue).

Ceramification offers the duo-option capability of a high concentration actinide for reuse and subsequent encapsulation of a homogeneous mixture for proliferation resistance.

Ceramification -- The Process

This immobilization process is based on a chemical ceramic coating process that produced rare earth oxide coatings for defense applications involving the containment of molten plutonium. It is a low temperature process for immobilizing actinide compounds using a combination process/storage vessel of stainless steel, where measured amounts of actinide nitrate solutions, actinide oxides, and/or actinide residues are systematically treated in the vessel to yield a solid article. By-product waste streams are not produced with this process.

The process is a single operation with a rapid process time of about one hour. Ceramification employs relatively low temperatures, between 300°C and 600°C, as compared to traditional ceramic processing at 1500°C and above, "oxide calcination" at 1000°C, and vitrification at 1050°C to 1450°C. The process requires a very low equipment expenditure and can be readily implemented into existing gloveboxes. Furnaces are typically less than $1,000, requiring 110 volts. The process is therefore more easily conducted with less associated risk than other proposed technologies.

Since the final actinide product is a solid article, requirements for material movements, storage, surveillances, and transportation are all drastically simplified. Accountability becomes an issue of article identification, greatly reducing exposure and expense. Since Ceramification is a flexible process, it can accommodate numerous additives to effect criticality safety (i.e., neutron absorbers), radiation exposure reduction, and provide enhanced degrees of proliferation resistance.

Ceramification is capable of preparing porous articles that have an exceptional density to strength ratio. Ceramification is ideal for applications such as waste stabilization that takes advantage of this simple property. The process forms ceramic bonds that bind these porous articles together into a cohesive structure that resists thermal and mechanical shock and absorbs expansive and contractual stresses from the formation of daughter products. Therefore, Ceramification forms tough resilient articles which when crushed under sufficient stress will yield large chunks with few fines. Reinforced ceramification articles strongly resist any significant deterioration from external forces. As a result, porous articles produced by Ceramification compare quite favorably to other materials such as glasses, enamels, traditional ceramics, and glass ceramics.

Ceramification can be employed to stabilize and immobilize wastes containing significant amounts of ash. During the thermal curing process of Ceramification, ash is converted to carbon monoxide and carbon dioxide while nonvolatile contaminants are immobilized into a solid article. Even though the ash bearing waste contains constituents such as metals, metal oxides, carbides, nitrides, and potentially metal chloride salts, solid coherent articles can still be formed with minimal process impact using Ceramification. The waste can also contain materials that thermally decompose to stable compounds during the processing.

The basic solid product of Ceramification has not been subjected to leach testing so its leach resistant is unknown. However because of the flexibility of the process, several techniques can be employed to increase leach resistance, if required.

Ceramification -- Benefits

Ceramification has several advantages over traditional stabilization techniques. First, the capital costs of implementing Ceramification for stabilization of actinide nitrates, oxides and ashes are low compared to calcination or other proposed alternatives. Unlike the alternatives, Ceramification employs relatively low temperatures between 300^0C and 600^0C and can be performed in low cost furnaces. Other equipment and supply costs are nominal. The main capital expense for all stabilization alternatives is the procurement and installation of gloveboxes to perform the work. Since, Ceramification is a simple process requiring little equipment and limited space, it could be incorporated into an existing glovebox line.

Since Ceramification produces a solid product that is non-dispersible, several advantages are gained as compared to simply storing oxide or residues in dispersible forms. A solid end-product reduces potential contamination of facilities, equipment, and personnel during handling of material. Also, Ceramification reduces the long-term risks of storing actinide oxides and residues in a dispersible form in the event of an accident involving the storage facility. Implementation of Ceramification could impact (reduce) the requirements of a storage facility and its safety systems for plutonium oxides and dispersible residues. Transportation issues are also simplified.

Rocky Flats' plutonium oxides (containing 3,200 kgs of plutonium) could be processed within one to two years, because of the rapid processing time, for example. It is believed that this is less time than required for calcination that does not significantly reduce the dispersibility risk associated with storing oxides as powders; and, much less time than alternatives that, like Ceramification, immobilize plutonium oxide. Ceramification produces an environmentally stable product that can be later readily combined with other technologies to produce a long-term storage material form.

Ceramification should bond plutonium oxide together for a non-dispersible product that yields a pure plutonium resource. The bonded articles can be ground to a powder for use in nuclear fuel production. Also, the bonded article can be treated with direct oxide reduction or chemical dissolution to take the oxide to the metal. Since Ceramification is a flexible process, it can accommodate numerous additives to effect a tailored product need, for example, criticality safety, radiation exposure reduction, enhanced degrees of proliferation resistance. Composite ceramic articles of plutonium oxide as intimate mixtures with additives can be created to meet the needs of long-term storage incorporating the most stable forms of ceramic minerals.

Ceramification provides a single stabilization/immobilization process for actinide nitrates, actinide oxides, and actinide bearing residues without by-product waste streams. The process is simple and reduces the time, exposure, and expense for stabilizing the actinide compounds. The product can be tailored to the need, allowing an open slate for disposition options, while at a minimum, eliminating near-term storage risk issues. Future liabilities and the mortgage reductions can be realized since the product form is a solid.

Ceramification -- Companion Industrial Technologies

The technology of using precursors to prepare metal oxide articles has been utilized in industry for over 25 years. The technology has been used for wear and corrosion resistant components, for example, the coated molds for $\text{CORELLE}_{\text{TM}}$ dinnerware. Sharpening steels, the "Sportsman" model by Buck Knives, utilize this technology. In addition, the technology was utilized in pure and composite erbium oxide coatings for the containment of molten plutonium in foundry operations and other defense applications.

Ceramification -- Implementation Steps

The technology has been demonstrated using precursors to prepare the metal oxide articles or rare earth and lanthanide metals. Products composed of both non-radioactive materials and actinide surrogates have been completed.

Testing utilizing actinides remains to be completed. Compounds to be tested include uranyl nitrate - $UO_2(NO_3)_2$, plutonium oxide - PuO_2, plutonium oxide plus plutonium nitrate - $PuO_2 + Pu(NO_3)_4$, plutonium nitrate - $Pu(NO_3)_4$, and plutonium bearing ash. Tests are to include data regarding: 1) product compliance with DOE's LOI storage standard; 2) product crushing with respect to dispersion resistant product; and 3) homogeneity and repeatability of product formation.

Ceramification -- Summary and Conclusions

Ceramification is an effective treatment process for quickly and economically immobilizing actinide nitrate solutions, actinide oxides, and actinide residues as solid articles.

Proprietary Information

This paper is a brief introduction to the Ceramification process. The subject matter embodies intellectual property rights. Detailed discussion will require a binding confidentiality and disclosure agreements.

Disclaimer

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Investigation of the Possibility of Using Hydrogranulation in Reprocessing Radioactive Wastes of Radiochemical Production Facilities

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INTRODUCTION

Radio-chemical production facilities are constantly accumulating liquid radioactive wastes (still residues as the result of evaporation of extraction and adsorption solutions etc.) which are a complex multicomponent mixtures. The wastes are frequently stored for extended periods of time while awaiting disposition and in some cases, and this is much worse, they are released into the environment.

In this report, I would like to draw your attention to some results we have obtained from investigations aimed at simplifying handing of such wastes by the precipitation of hard to dissolve metal hydroxides, the flocculation of the above into granules with the help of surface-active agents (in this case a polyacrylamide - PAA), quickly precipitated and easily filtered. The precipitate may be quickly dried and calcinated, if necessary, and transformed into a dense oxide sinter. In other words it may be transformed into a material convenient for storage or burial.

Description of the process

Optimum conditions for precipitation and granulation were determined by using a system that simulates the still solution of the sorption processes. High aluminum and fluoride ion concentrations are typical for many of the wastes. Many of the investigations we conducted, the results of which are presented in this report, were for this reason conducted on systems containing these elements. In all cases the water polyacrylamide solution (10 g/l commercial solution) is introduced into the system after the precipitation of metal hydroxides.

The data in Table 1 indicate that conditions exist for significant co-precipitation of aluminum and fluoride and the granulation of precipitants. A pH = 6.5 - 7.0 for ammonia precipitation and a pH= 5.5 - 6.5 for sodium alkali precipitation. It is felt that the results indicate the formation of polymerized mixed aqueous hydrooxofluoride complexes like $[Al_x(H_2O)_y(OH)_zF_u]^{n+}$, which combine into micelles and by adsorbing some hydroxy complexes on their surface acquire a positive charge which determines interaction with such anionogenic surfactants, as the polyacrylamides.

Table 1. The effect of pH values on precipitation and granulation efficiency.
(Initial solution: Al -10 g/l; HF - 0.12 mole/l; HNO_3 - 0.2 mole/l).

pH PRECIPITATION	**pH GRANULATION**	**CONTENT OF MOTHER LIQUOR**		**GRANULE SIZE (mm)**	****m_{PAA}**
NH_4OH		Al, mg/l	F^-, mole/l		
9.0	9.0	-	-	gel	310
9.0	7.5	1.0	0.00034	<0.5	74
9.0	7.0-6.5	1.0	~0.00020	2.0-4.0	77-78
9.0	6.0	5.4	0.00024	2.0-4.0	85
7.5	6.0-7.0	~1.0	~0.00010	0.5-1.0	115-130
7.5	5.5	10	0.00025	0.5-1.0	155
NaOH					
8.5-7.8	7.0-6.0	~0.5	0.00015- 0.00020	3.0-5.0	68
7.5	7.5	1.8	0.00065	<0.5	88
6.0-6.5	6.0-6.5	~0.5	~0.00010	1.0-2.0	80-72
5.5	5.5	1.5	0.00013	1.0-2.0	112

* the pH is adjusted by the addition of the necessary amount of acetic acid; ** m_{PAA} - minimal amount of polyacrylamide (mg) per I g of precipitated cation, needed for the granulation of precipitant.

The results indicate that by applying the method of alkali concentration in the presence of PAA, aluminum and fluoride can be separated from liquid waste. However, such systems always contain equipment corrosion products and other technological admixtures. Table 2 shows the results of alkali concentration and granulation of aluminum-fluorides mixtures in the presence of such admixtures. It follows that with pH= 6.0 - 7.5, aluminum nitrate solutions containing fluoride will quite satisfactorily co-precipitate corrosion products (iron, chrome, nickel) and copper. Magnesium and calcium are only partially precipitated (up to 40 - 50%). In all cases the granulation is good.

Table 2. Cation behavior in a Al - F system during precipitation and granulation. (Precipitating agent - NaOH - 15 mole/l).

K^{m+}	COMPOSITION OF INITIAL SOLUTION				pH GRANULATION	m_{PAA}	MOTHER LIQUOR		GRANULE SIZE
	HNO_3, mole/l	Al, g/l	F, mole/l	K^{m+}, g/l			Al, mg/l	K^{m+}, mg/l	mm
Fe3+	1.0	10.0	0.12	3.4	6.0	90	1.0	0.1	0.5-1.0
					6.6	78	<0.5	0.2	1.0-2.5
					7.0	69	<0.5	0.2	1.0-2.5
					7.5	60	2.8	0.6	1.0-2.5
Cr^{3+}	1.0	10.0	0.12	0.60	6.0	91	1.0	0.1	1.0-1.5
					6.5	75	<0.5	0.05	1.0-2.0
					7.5	70	2.2	0.1	1.0-4.0
Ni^{2+}	1.0	10.0	0.12	0.63	6.0	90	1.0	40	0.5-1.0
					6.5	75	<0.5	20	1.0-2.0
					7.0	75	1.2	4.5	1.0-3.0
					7.5	76	1.7	0.05	1.0-3.0
Mg^{2+}	1.0	10.0	0.12	7.6	6.0	120	<0.5	5000	0.5-1.0
					6.5	112	0.5	4300	1.0-2.0
					7.0	104	0.6	4200	1.0-3.0
					7.1	100	0.6	3200	1.0-4.0
Ca^{2+}	1.0	10.0	0.12	2.5	6.0	88	0.6	1500	0.5-1.0
					6.5	80	0.8	1400	1.5-2.5
					7.0	72	1.3	1300	1.5-2.5
					7.5	60	6.1	1300	3.0-4.0
Cu2+	1.0	10.0	0.12	0.50	6.0	99	1.0	1.3	0.5-1.0
					6.5	88	0.5	0.2	1.5-1.0
					7.0	80	0.5	0.05	1.0-2.0
					7.5	76	1.7	0.05	1.0-3.0

Note: 1. K^{m+} - the added cation; 2. Granulation temperature was 20 - 24^0 C.

Aluminum fluoride solutions were used to study the effect of some other technological parameters (Table 3 - 4).

The results shown in Table 3 indicate that the largest, easily filterable granules are formed when the amount of PAA is in the range of 65 - 98 mg per gram of aluminum. This value is not constant for a system that contains not only aluminum, but other precipitating cations as well. One should note that the excess PAA remains in the mother liquor and the granules themselves lose mobility and bind into conglomerates.

Table 3. The effect of m_{PAA} on the filtration rate of granulated residues.
(The initial solution: Al - 1.5 mole-l; NaF - 0.5 mole/l; NHO_3 - 3.0 mole/l; precipitant - NaOH - 15 mole/l; pH= 6.5)

m_{PAA}	MOTHER LIQUOR, %						GRANULE SIZE (mm)
	5"	30"	60"	2'	5'	10'	
0	13.2	28.9	47.4	76.3	97.4	1000	gel
10.9	13.9	36.1	55.5	83.3	98.5	100	<0.5
21.7	13.0	27.7	47.2	75.0	97.2	100	<0.5
43.5	27.8	80.5	94.4	97.4	100	-	<0.5
65.2	61.0	97.2	100	-	-	-	1.0-3.0
97.8	61.0	100	-	-	-	-	1.0-3.0

Note: A Nutsche filter overlaid with a paper "blue ribbon" filter at a vacuum of 0.14 kg/cm^2 was used.

Table 4. The effect of the presence of nitric acid in the initial solution prior to precipitation. (Initial solution: Al - 10 g/l; HF - .12 mole/l; precipitant - NH4OH).

HNO_3	m_{PAA}	pH		t ^{0}C		GRANULE SIZE
mole/l		PRECIPITATION	GRANULATION	PRECIPITATION	GRANULATION	mm
0.1	74	8.5	7.0	24	24	2.0-4.0
0.5	74	8.5	7.0	25	24	2.0-4.0
1.0	78	8.5	7.0	30	28	2.0-4.0
2.0	97	8.5	7.0	32	30	1.0-3.0
3.0	388	8.5	7.0	38	35	0.5-1.0
3.0*	124	8.5	7.0	37	24	1.0-3.0
4.0	290	8.5	7.0	45	38	gel
4.0*	74	8.5	7.0	46	24	1.0-3.0
5.0	388	8.5	7.0	55	48	gel
5.0*	74	8.5	7.0	55	24	1.0-3.0

* the system was cooled prior to regulating the pH level.

Table 4 shows that granulation proceeds quite successfully in the initial systems with a wide range of nitric acid concentrations. However, when NHO_3 exceeds 2 mole/l, the hydroxide residue requires preliminary cooling.

To sum up the results, it may be stated that still residues from the evaporation of sorption and extraction solutions (with a wide range of compositions) are suitable for hydrogranulation in the presence of PAA.

Since the solutions always contain some quantity of plutonium and americium, it was necessary to investigate their behavior during this process in order to determine the fate of the mother liquor. The following simulated still solution was used for this purpose: K^{m+}=11.3 g/l; (Al = 8.1 g/l;), NaF = 0.10 mole/l; NHO_3 = 4 mole/l; Pu = 5 mg/l; Am = 5 mg/l. Precipitation was induced by sodium alkali (15 mole/l) and the amount of PAA was 52 mg per kg of metal (see Table 5).

Table 5. The correlation between the pH environment and the plutonium and americium content of the mother liquor.

pH GRANULATION	MOTHER LIQUOR CONTENT mg/l	
	Pu	Am
7.1	10 - 19	0.06
7.5	6	0.03
8.0	6	-
8.5	6	0.006
9.0	5	0.008

The results of the investigations show that in certain conditions significant amounts of plutonium and americium pass into the residue with insignificant amounts remaining in the mother liquor. Similar results were obtained with actual still solutions.

Along with the standard wastes of a more or less known composition, the radio-chemical production facilities often accumulate and store for extended periods of time wastes-concentrates of quite complex composition (one example is shown in Table 6).

Table 6. Composition of mixed waste from extraction processes.

ELEMENT	CONTENT g/l	ELEMENT	CONTENT g/l	ELEMENT	CONTENT g/l
U	0 - 15	Pr	0 - 0.5	Cs	0.5
Pu	0.05	Nd	0 - 0.2	HNO_3	240-360
Fe	2 - 25	Eu	0.2	SO_4^{2-}	4 - 6
Cr	0.5 - 2.0	Y	0.2		
Ni	2 - 10	Sm	0.2 - 0.6		
Ca	1.5 - 2.0	Gd	0.2 - 0.6		
Na	25 - 40	La	0.2 - 0.6		
Al	5 - 20	Ce	1.0		
Mo	0 - 0.5	Pd	0.05		

This concentrate was subjected to hydrogranulation with PAA. It was determined that effective granulation of residues occurs with a pH = 5 - 7. In order to ensure full precipitation of hydroxides, the working pH level was set at 6.5 - 7.0. The effect of PAA concentration on granulating characteristics was studied at this pH level (see Table 7).

Table 7. The effect of PAA concentration on granulating characteristics.

NN	pH	mg PAA/1g ΣMe	CHARACTERISTICS OF GRANULES
1	6.6	44.5	Weak granulation. Loose, large granules.
2	6.65	66.6	Good granulation. Granules are mobile and do not stick together when filtered.
3	.6.6	133	Slight sticking of granules to filter.
4	6.7	178	Very sticky during filtration.

When this process is carried out in set conditions (pH = 6.5 - 7.0; PAA 100 mg/1 g of metal), granulation is determined by the intensity of mixing, with almost immediate separation of phases. The precipitate is easily filterable and easily separated from the filter surface.

Calcination of the granulate at temperatures reaching 850^0C showed that in several instances, the oxides sintered to form large conglomerates, which formed rather strong bonds with the stainless steel cuvette. The explanation for this lies in the unwashed sodium hydroxide residues, which melted when temperatures reached 300^0C and the results were as described.

This phenomenon may be totally eliminated if the granulate is flushed twice with water. The oxides, produced after calcination at a temperature of 850^0C, are weak, easily separated agglomerates. In order to measure the characteristics of the oxides they were passed through a sieve with a 1 mm mesh. For the 1mm polyfraction, the measured bulk density was 1.02 - 1.23 g/cm^3, and the flow rate - 1.0 - 2.15 g/sec (through a 6mm diameter funnel). It was noted that the so called "dust" fraction accounted for less than 6 - 10% of the mass. The fluidity of the material indicates that there will be no problem with is transfer by pneumatic devices. We feel that this material can also be used to fill special containers for eventual storage (or burial). It is also possible to form it into briquettes.

This technology provides for the oxidation of 93 - 96% of the mass of cations, precipitated in the form of hydroxides.

The remaining liquid phase is for the most part a solution of sodium nitrate and calcium nitrates, cesium, strontium. The filtrate contains approximately 10 mg/l of precipitated cations.

We feel that the described method for the treatment of liquid radioactive waste could become a part of the technological processes that are currently in use, or are being developed, for radio-chemical production facilities within programs for waste utilization.

DISCLAIMER

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ABSTRACT

Both the Mixed Waste and Landfill Stabilization Focus Areas as part of the Office of Technology Development efforts within the Department of Energy's (DOE) Environmental Management (EM) Division have been developing various vitrification technologies as a treatment approach for the large quantities of transuranic (TRU), TRU mixed and Mixed Low Level Wastes that are stored in either landfills or above ground storage facilities. The technologies being developed include joule heated, plasma torch, plasma arc, induction, microwave, combustion, molten metal, and in situ methods. There are related efforts going into development of pretreatment and off gas treatment facilities that are a necessary part of any integrated thermal treatment approach. In addition, compositional studies are being conducted to develop glass, ceramic, and slag waste form windows of opportunity for the diverse quantities of heterogeneous wastes needing treatment. These studies look at both processing parameters, and long term performance parameters as a function of composition to assure that developed technologies have the right chemistry for success.

INTRODUCTION

A joint technical peer review was held from November 13 through 15 in Dallas, TX covering all the vitrification technologies either currently or previously funded by Environmental Management (EM). The purpose of this peer review was to look at the development activities primarily within the Mixed Waste (MWFA) and Landfill Stabilization Focus Areas (LSFA) to determine the current status, strengths/weaknesses, future needs, and any duplication of efforts. These programs were reviewed by both a "blue ribbon" independent technical panel made up of industry, university, and international experts in the fields of glass and ceramic processing, off gas systems, geochemistry, and nuclear physics, and a users group panel consisting of site representatives, stakeholders groups, and EM division representatives. It is expected that the recommendations from these panels will be heavily factored into the direction and funding decisions of future developments in this area.

A broad spectrum of vitrification technologies are currently under study and are in various stages of technical maturity. This paper provides an overview of these various technologies highlighting the strengths and weaknesses of each and the target problems they are best suited to address.

MELTER SYSTEMS

There are a number of melter systems currently being developed. The major distinction between any of these systems is the method employed to heat the batch. Some systems such as joule heated melters are well suited for operation at lower temperatures with a cold cap of unmelted material providing a blanket to minimize volatilization. Other systems such as the plasma torch and plasma arc systems and cold crucible systems are better suited for higher temperature operation which can provide a more omnivorous approach to heterogeneous and mixed waste problems. The basic unit operation in either case is to heat the waste plus glass making additives to the point where they become a fluid molten pool. This melt process destroys associated organics and then upon discharge solidifies into a reduced volume, leach resistant solid glass, ceramic, or slag waste form.

Recently a down selection of melter technologies was conducted for treatment of Hanford low-level tank waste. This is one of the only studies where a number of melter systems have been compared under a nearly identical set of criteria for a specific waste problem. A two phased melter vendor testing program was initially planned, however only the first phase was completed in which seven vendors went through a preliminary technology evaluation, and down selection. The primary technical objective was to evaluate the melter feed preparation, melter performance, and off gas treatment system as a whole to get at melter material balances, and evaluate process control, process limits, and product quality. In general the cold top joule heated melter technologies rated best based on mass balance, reduced volatilization, and maturity of the technology. Also slurry feeding was preferred over dry feed for off gas considerations. More studies such as this are needed under a variety of operating conditions and waste types.

Following is a brief discussion of each technology receiving funding over the past several years that was reviewed during the Dallas technical peer review. A summary of each technology with pertinent characteristics is tabulated in Table 1. Some of these characteristics are somewhat subjective and may not be all inclusive of every possible variation but can provide a common starting basis for comparison.

Plasma Arc - Plasma arc systems have been around for some time as they were initially developed for the metal refining (primarily steel) industry. There are basically two types of plasma arc melter systems, which are either AC and DC powered. Both are capable of reaching relatively high melt temperatures in excess of 1800^0C. At these temperatures most wastes will melt without regard to composition. Generally these melters operate in a transferred arc mode, meaning that the electricity flow is from the electrodes directly to and through the melt. The electrodes are generally made out of graphite, and therefore the melter is operated in a reducing atmosphere to prolong the life of the electrodes which would be rapidly consumed in an oxidizing atmosphere. Operation in a reducing mode will generate a metallic layer on the bottom of the melter from the various metals components found in the wastes. The bulk of the radioactive components will partition into the slag or glassy top phase, therefore a relatively clean metal phase can be separated from such melters when equipped with separate tap holes..

Such systems can be operated with either a long arc, a short arc, or a submerged arc. As the arc length (distance between electrode and melt decreases) the joule heating component increases and the radiation component decreases. Therefore, there is a large joule heating component to such systems. This normally implies an increase in electric efficiency, therefore it is advantageous to operate with a short or submerged arc. Also the ability to use a submerged arc allows operation with a cold cap which minimizes volatilization of radioactive components and RCRA metals that one would like to retain in the melt.

Such melters generate a minimum of off gas since no torch gas is employed. Only organics, water, and other volatiles constitute the off gas. Both types of melters have been developed for potential waste treatment but the current emphasis seems to favor the DC rather than AC powered systems due to their simpler operation and greater efficiency. The AC arc melter work has been carried out by the US Bureau of Mines while the DC arc melter work is being performed at Idaho National Engineering Lab (INEL),

Pacific Northwest National Lab (PNNL), Savannah River Site (SRS), and Massachusetts Institute of Technology (MIT) under the LSFA.

The big advantage to arc melters is the ability to be relatively omnivorous in their approach to waste treatment. Much drummed waste and soils could be directly fed to large scale systems without need for detailed characterization and sorting which would be cost prohibitive on a large scale. The primary disadvantage is that most of the testing to this point has been done on surrogate wastes, therefore there remain major concerns about both radioactive partitioning and potential off gas problems.

Plasma Torch - The other plasma units under development are based on torch technology. In these systems a gas is used to stabilize and focus the arc and ionized gases onto the melt surface. At the same time the gas stream helps to transfer the heat energy and mix the melt as it impinges on the surface. Plasma torch systems can generate gas temperatures up to 10,000°C while the melt may be 1600 to 2200°C or more. Either a transferred or non-transferred arc torch may be used. The transferred arc torch is similar to the DC arc melters in that a large joule heating component is present while the non-transferred torch strikes the arc directly within the torch housing and uses solely the gas stream to push the plasma out of the torch and transfer the heat. As such the non-transferred arc torch is less efficient than the transferred arc torch, however the torch life of such systems may be as much as ten times greater which can be a major consideration in high activity alpha or other remote handled types of wastes.

The plasma torch systems generally do no use graphite electrodes. Therefore, they can operate in an oxidizing mode, which can potentially drive all of the metals into a single glassy or slag phase depending on the relative benefits offered by such waste forms. Although a gas is used to stabilize and focus the torch the quantity is not large, therefore the required off gas treatment system should be only marginally more involved than the plasma arc systems. However, a secondary combustion system is generally employed to insure complete destruction of all organic components.

Two basic systems are currently under development. The first is the Plasma Hearth Process. This consists of a stationary hearth and gimbled plasma torch which can be rotated around the hearth at will. This system is being developed by Science Applications International Corp (SAIC) STAR Center and Argonne National Lab (ANL)-West at INEL for the MWFA. Studies to date suggest that the system is well suited to handling drummed waste generating a slag type of waste form which meets all Toxicity Characteristic Leach Procedure (TCLP) requirements and surpasses Product Consistency Test (PCT) High Level Waste(HLW) standards. To date only surrogate wastes have been studies, but a bench scale radioactive unit is being developed which should be ready for testing in early 1996.

The second system is the Plasma Centrifugal Furnace which is being developed by MSE at the Western Environmental Technology Office (WETO) facility also for the MWFA. This plasma torch system operates inside a large rotating tub that uses the centrifugal force to retain the waste and melt inside the tub while it is being melted, then upon slowing the rotation, the melt can be discharged through a central bottom port. Similarly the off gases exit through the bottom port and are directed to the secondary combustion chamber. This system has been demonstrated on only surrogate wastes, but has demonstrated an ability to handle very high metal contents up to nearly 70 % as Fe_2O_3 and an ability to handle small amounts of energetic ordnance without upset to the off gas system or other fugitive emissions.

The advantages of such systems are the relative ease with which they can handle drummed waste and the ability to operate in either oxidizing or reducing modes. The disadvantages are the higher degree of mechanical complexity and relatively short lifetimes of the torch components which lead to reduced on line percentage and higher maintenance requirements.

Joule Heated - Joule heated melter technology is probably the most advanced technology since it has been used extensively by the glass industry for more than 50 years. Also, it is relatively well developed specifically for treatment of HLW by both Savannah River and West Valley. A similar facility is planned for treatment of Hanford high level tank wastes. Joule heated melter technology uses submerged electrodes to conduct an electric current through the melt with heat generated by the resistive nature of the melt. As such the melt must exhibit certain conductivity and viscosity properties to be a good candidate. This puts more restrictions on the composition of the melt to remain within this operating window. In general joule heated melters are lower temperature systems operating below 1300°C, however some special systems have been developed to go up to 1500°C with narrowly defined operating conditions and well defined melt compositions. Obviously as temperatures increase the erosion and corrosion of electrode and refractory materials increases which can severely limit the useful life of such systems.

Such systems are generally limited in their ability to handle high iron, high organic, or high halide/sulfate content wastes. Also, such melters are not generally suited to handling large sized feeds such as drums due to the lower operating temperatures and limited ability to rapidly incorporate large bulk components into the melt. The advantages of such systems is the broad range of experience which already exists, and the generally stable operating conditions which can be expected.

In addition to the HLW development work, several other joule heated systems are and have been under development. One LSFA system that has already been tested on radioactive wastes is the Minimum Additive Waste Stabilization (MAWS) GTS Duratek melter demonstration that took place at Fernald, Ohio on a mixture of sludges and soils containing uranium and thorium. This demonstration processed several thousand gallons of waste to produce over 4500 kg of glass gems. This successful demonstration was then leveraged to a privatization bid to treat about 670,000 gallons of radioactive low level waste sludge at Savannah River's M-area which should begin processing in early 1996, and to provide a higher temperature version for vitrification of Fernald K-65 silo wastes which are high in radium bearing ores and radon gas. Also, this technology is being commercialized in a joint venture between GTS Duratek and Chem Nuclear for the treatment of radioactive ion exchange resins from commercial nuclear power plants. A MWFA effort is developing a Transportable Vitrification System using an Envitco joule heated melter which will be first tested on various wastes at Oak Ridge. Also, several joule heated melter systems have been developed at Battelle PNNL for a variety of purposes, and with emphasis on higher temperature operation innovations. This technology is relatively mature with a number of capable vendors offering a range of system sizes and capabilities.

Induction Heating - This type of melter heating mode has been promoted most heavily by the international community with major developments by the French and Russians. Only recently are such melters being evaluated in the US through cooperative research efforts with the Russians. Two systems are being considered. The first is a high frequency cold wall induction melter design which has application to high metal content wastes and uses a cold crucible approach to minimize corrosion/erosion of the containment vessel. Such systems can operate at relatively high temperatures up to 1650°C. However, such systems are generally limited in size to smaller waste volume applications due to an inability to adequately scale up the induction heated coupling in larger geometries. It is planned to test this unit at the Clemson Technical Center on Hanford and INEL simulants.

The other development is the hybrid plasma induction cold crucible melter which combines a plasma torch and induction heated melter in a single package for treatment of high metal content wastes. This overcomes some of the throughput rate limitations associated with the simpler induction version melter due to the use of the plasma torch capability as discussed previously. Also, the unit has the ability to continuously cast the metal phase from the bottom of the melter. Such units have a long test and operation history in Russia.

This approach is being investigated particularly for drummed Pu-238 and Pu-Mixed TRU wastes at the Savannah River Site. It is expected that the system will be installed and tested at Georgia Tech. At a rate of 15 drums per day, one of these melters could potentially treat the 15,000 drums of existing TRU waste at Savannah River which represents roughly 60% of the complex activity in about 5 years. In both instances the Russians are building these melter systems which are planned for evaluation on specific waste streams both in Russia and here in the US.

In Situ - In situ vitrification is an off shoot of the graphite arc melters in which the electrodes are inserted directly into the ground and a molten pool generated in a top down treatment of the affected area. Generally treatment depths are limited to about 20 feet with such an approach, however recent developments with plasma torch and shielded plasma arc systems in bore holes would allow deeper and bottom up approaches to in situ treatment of wastes. Melt temperatures are in the 1600 to 2000°C range sufficient to melt most soils. Limitations to the technology application are highly refractory soils and high water tables. In situ vitrification technology is fairly mature and being commercialized by private interests. Its application to the treatment of plutonium bearing wastes is fairly limited.

Microwave - A microwave melter system had been studied at Rocky Flats under the MWFA. Microwaves are good for calcination, stabilization, and vitrification processing. This system is essentially an in can melter in that a small amount of dry feed is initially introduced into a drum and the microwaves directed onto the top of the waste via wave guides. Typical melt temperatures up to 1300°C are developed in the process. As the melt develops additional feed is introduced into the drum and melted until the drum is nearly full. The microwaves do not penetrate very far into the melt, therefore the melt zone moves up with additional feed. This tends to lead to a rather heterogeneous final waste form, however tests have shown it to be largely non-leachable. The advantages to this system is that in-drum melting eliminates the corrosion/erosion problems associated with electrodes and refractories, and there is really no optimum processing window of viscosity and conductivity. Also, the equipment is relatively low maintenance with no moving parts and readily adaptable to small volume wastes. Such a system has a limited application to mostly dry and finely divided feeds, and probably would not be very applicable for TRU or Pu bearing wastes.

Combustion - A Vortec cyclone combustion melter is being considered for treatment of several Low Level Waste (LLW) soils, concrete, and drilling mud wastes at the Paducah, KY gaseous diffusion plant that are contaminated with chromium, trichloroethane (TCE), uranium, and polychlorinated biphenyls (PCB). The melter can be fueled with various hydrocarbons including pulverized coal, oil, and natural gas. The waste feed is optimally less than 1 mm if non-combustible and up to 10 mm if combustible. The fuel and waste are simultaneously injected and ignited into the cyclone combustion chamber where they rapidly melt in seconds at temperatures up to 1650°C which also destroys the organic contaminants. The disadvantages of such a system are that a relatively large off gas stream is generated due to the combustion of hydrocarbons which needs appropriate off gas treatment, and also the feed must be relatively fine to promote rapid melting in the short residence time combustion chamber cyclone. It would be expected that erosion of the cyclone might be a problem over time. Again such a system would probably not be appropriate for treatment of Pu bearing wastes.

A SYSTEMS APPROACH

In trying to select any one melter technology, it must be considered in the context of a complete system which includes both required pretreatment and off gas or secondary waste generation. Some systems such as the joule heated melters or microwave and combustion systems can only process relatively small sized feed in either dry or slurry feed form. Such systems would require some type of sorting or size reduction classification prior to feeding to the melter. Other systems such as the various plasma units can process relatively large units of wastes such as drums. Some systems such as joule heated melters or microwave may not be able to handle large quantities of organics, therefore some sort of incineration or other destruction technology may be required first for such wastes with only the residual ashes fed to the melter. There are a number of non-thermal and incineration technologies being developed to deal with organic wastes prior to feeding to melters.

No melter technology is very acceptable for dealing with mercury or other high percentage sulfate or halide containing wastes. One could try to remove these prior to introduction to the melter or deal with them in the off gas system which is usually the approach taken. Off gas systems need to be an integral part of the various melter technologies. Two approaches are being considered. The more conventional is the wet scrubber which would capture the various acid gases and particulates in a basic solution as a neutral salt followed by various High Efficiency Particulate (HEPA) filters to remove any residual particulates. Also some sort of NOX catalyst system may be incorporated to convert it to nitrogen or some other form.

The other approach is a dry filter system followed by a wet system. Recently various ceramic and sintered metal filter systems of HEPA quality have been proposed which can filter out a large proportion of the radionuclide particulates prior to getting into the wet scrubber system which then removes the acid gases. If these systems can be proven not to blind off over time then it may help to insure that less radionuclides find their way into the other downstream systems, and thereby alleviate the public concerns over potential release of these constituents.

COMPOSITIONAL AND WASTE FORM STUDIES

A number of composition studies have been on going to better define potential waste forms for the various radioactive and hazardous constituents. The most obvious is glass waste forms similar in effect to the high level waste program. The Minimum Additive Waste Stabilization (MAWS) program in an effort to increase waste loading, however has been trying to broaden the window of acceptable glasses. A number of non-borosilicate based glasses have been developed which are as good or better than the standard high level waste glasses. These studies have concentrated on real waste streams where obtainable from Hanford, Oak Ridge, and INEL.

Also, studies have focused on vitreous ceramic or glass crystalline composite waste forms where the composition contains a high quantity of intermediates that promote crystallization upon cooling from the vitreous melt. These glass crystalline composite waste forms have been evaluated for containment of plutonium in a series of crucible melts. Through minor adjustments of the composition, crystalline phases have been promoted to form similar in structure to Synroc which has been developed by the Australians for containment of plutonium. These crystalline phases form naturally upon slow cooling of the melt and do not require the high pressures required to form Synroc. The crystalline phases appear to readily incorporate the radioactive and hazardous constituents, thereby leaving the good glass forming materials behind in a leach resistant glass phase.

Other compositional and testing studies have been carried out on the various slag waste forms which are the product of the plasma processes which incorporate high amounts of ferrous materials. Similarly in these studies, cerium surrogates have been observed to partition into the slag in crystal phases rather than volatilize into the off gas at the very high temperatures developed. This suggests that plasma or other high temperature processes could be used to vitrify various plutonium wastes, however much more study really needs to be done in this area as there are a large number of potentially influential variables which have not yet been well studied such as compositional effects, halide concentrations, redox conditions, etc. The amount of hard data on actual plutonium wastes is extremely limited.

The Reactive Additive Stabilization Program (RASP) has also developed a series of glass compositions with small particle size rapid melting additives designed for high throughput type joule heated melters such as the Transportable Vitrification System (TVS). Enhanced processing and leach resistance are claimed for these non-equilibrium glass waste forms.

Testing of waste forms for long term performance is very important to assure that the contained radionuclides can not cause problems for future generations. The primary tests that are performed on waste forms are the Toxicity Characteristics Leach Procedure (TCLP), the Product Consistency Test (PCT) or variations thereof which are referenced to standards for HLW glasses, and other accelerated tests such as the vapor hydration test. The TCLP is an Environmental Protection Agency (EPA) mandated test, however none of the others have any relevance to regulatory standards or other Waste Acceptance Criteria. In fact there is considerable debate as to exactly what data is required since all are relatively short term in nature, and only through models can one hope to predict performance over the geologic time frames required for long lived radionuclides such as Pu-238. Therefore comparison to geologic analogues and modeling is important, but has not received sufficient attention to develop any degree of confidence in their abilities beyond about a 1000 years. Particularly with high alpha containing waste the integrity of the waste form is in question.

CONCLUSIONS

1. Environmental Management has a number of vitrification technologies in various stages of development that are applicable for treating a variety of wastes including LLW, MLLW, TRU, TRU Mixed, and HLW. Some of these technologies could potentially be used to treat plutonium bearing wastes.

2. Although a great deal of compositional studies have been performed to develop many variations of glass, ceramic, and slag waste forms, there is still a paucity of data using actual plutonium. Therefore, there are major questions yet to be answered as to the factors affecting partitioning of the plutonium between glass, crystal, metal and off gas in actual melter systems.

3. Melter off gas treatment is an area that needs further development due to the apparent similarity to incineration technologies which have a poor reputation in the public view. Many waste constituents such as mercury, sulfates, halides, cesium, other metals may volatilize and dioxans can form as the off gases cool. The factors controlling these processes need to be better understood particularly for heterogeneous or poorly characterized wastes.

4. Maintenance of melter systems which includes replacement of refractories, electrodes, torches, and other components is a major consideration for remotely handled wastes, therefore systems are sought and being developed which are robust yet flexible in meeting waste challenges.

5. In the years ahead it is likely that there will be a down selection of these technologies for continued development. The joule heated melters and in situ vitrification technologies are viewed as commercially mature technologies which need little further development.

6. Additional waste form testing and modeling studies are needed to better determine the fate of the various waste forms over geologic time frames.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Table 1. Technology Property Matrix

Technology	Feed Sizing	Melt Temp. (C)	Melt Redox	Off Gas Volume	Volatilization/Cold Cap	Waste Form Type	Mechanical Complexity	Stage of Development	Testing To Date
DC Graphite Plasma Arc	<1 Meter	1200-2000	Reductive	Low	High/Possible	Slag/Metal	Low	Bench Pilot	Radioactive/Pu Surrogate
AC Plasma Arc Melter	<1 Meter	1200-1800	Reductive	Low	High/No	Slag/Metal	Low	Pilot	Surrogate
Plasma Hearth Process	~1-2 Meter	1200-1800	Either	Moderate	High/No	Slag/Metal	Moderate	Pilot Bench	Surrogates Radioactive 96
Plasma Centrifugal	<0.5 Meter	1200-1800	Oxidative/ Either	Moderate	High/No	Slag	High	Pilot	Surrogates & Energetics
Joule Heated Ceramic	<0.25 Meter	1000-1250	Either	Low	Low/Yes	Glass/ Ceramic	Low	Commercial	Radioactive MLLW
Hi-Temp Joule Heated	<0.25 Meter	1200-1500	Either	Low	Moderate/Yes	Glass/ Ceramic	Low	Bench	Surrogate & Rad MLLW
Transportable Vit. System	<0.1 Meter	1100-1400	Either	Low	Low/No	Glass/ Ceramic	Low	Pilot	Surrogate 95 Rad MLLW 96
Russian Hi Freq Induction	<0.1 Meter	800-2000	Either	Low	Low/Yes	Glass/ Ceramic	Low	Full Scale in Russia	Radioactive
Russian Hybrid Plasma	<0.25 Meter	1200-1800	Reductive	Moderate	High/No	Slag/Metal	Moderate	Bench Scale at GA Tech 96	Surrogate Russian Rad 96
Microwave Melter	<0.01 Meter	1100-1300	Reductive	Low	Moderate/No	Slag	Low	Bench & Full Scale	Rad Sludges Surrogates
Vortec Cyclone Combustion	<0.001 Meter	1100-1650	Oxidative	High	High/No	Glass/ Ceramic	Moderate	Pilot	Surrogate
In Situ Electrode	NA	1600-2000	Reductive	Low	High/No	Glass/Slag	Low	Commercial	Surrogate & Radioactive
In Situ Plasma	NA	1600-2000	Either	Moderate	Moderate/Yes	Glass/Slag	Moderate	Bench Pilot	Surrogate
Molten Metal	<1 Meter	1200-1500	Reductive	Low	Moderate/Yes	Slag/Metal	Low	Bench Pilot	DU Testing Surrogates

Conversion Of Plutonium Scrap And Residue To Borosilicate Glass Using The GMODS Process

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ABSTRACT

Plutonium scrap and residue represent major national and international concerns because (1) significant environmental, safety, and health (ES&H) problems have been identified with their storage; (2) all plutonium recovered from the black market in Europe has been from this category; (3) storage costs are high; and (4) safeguards are difficult.

It is proposed to address these problems by conversion of plutonium scrap and residue to a CRACHIP (CRiticality, Aerosol, and CHemically Inert Plutonium) glass using the Glass Material Oxidation and Dissolution System (GMODS). CRACHIP refers to a set of requirements for plutonium storage forms that minimize ES&H concerns. The concept is several decades old. Conversion of plutonium from complex chemical mixtures and variable geometries into a certified, qualified, homogeneous CRACHIP glass creates a stable chemical form that minimizes ES&H risks, simplifies safeguards and security, provides an easy-to-store form, decreases storage costs, and allows for future disposition options.

GMODS is a new process to directly convert metals, ceramics, and amorphous solids to glass; oxidize organics with the residue converted to glass; and convert chlorides to borosilicate glass and a secondary sodium chloride stream. Laboratory work has demonstrated the conversion of cerium (a plutonium surrogate), uranium (a plutonium surrogate), Zircaloy, stainless steel, and other materials to glass. GMODS is an enabling technology that creates new options. Conventional glassmaking processes require conversion of feeds to oxide-like forms before final conversion to glass. Such chemical conversion and separation processes are often complex and expensive.

INTRODUCTION

In the United States, significant ES&H concerns[1] have been identified with the storage of plutonium scrap and residue. A similar situation is thought to exist in Russia. All of the plutonium recovered from the black market in Europe has been from this category. Storage costs are high and safeguards are difficult. These difficulties are a direct result of the characteristics of these materials. Plutonium scrap and residue normally consist of only a few weight percent plutonium, but the total volume and mass exceed that of clean plutonium. The materials have highly variable chemical and nuclear characteristics. Some of the chemical forms are hazardous and corrode their containers.

It is proposed to address these problems by conversion of plutonium scrap and residue to a CRACHIP (CRiticality, Aerosol, and CHemically Inert Plutonium) glass using the Glass Material Oxidation and Dissolution System (GMODS). CRACHIP refers to a set of requirements[2] for plutonium storage forms that minimize ES&H storage and transport risks. Conversion of plutonium from complex chemical mixtures and variable geometries into a certified, qualified, homogeneous CRACHIP glass with fixed

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dimensions in standard containers (1) creates a stable chemical form that minimizes ES&H risks, (2) simplifies safeguards and security (number count safeguards), (3) provides an easy-to-store form, (4) decreases storage costs, and (5) allows for future disposition options.[3]

GMODS is a new process[4,5] for directly converting scrap and residue into glass. Earlier glassmaking processes required that plutonium feed material first be a relatively pure oxide-like material before being converted to glass. This requirement implied a complex processing step to yield an oxide form acceptable for conventional glass melters. The technical and economic difficulties in conversion of plutonium scrap and residue to CRACHIP glass have been major barriers for this treatment option. The objective of GMODS development is to provide a low cost, technically feasible process to make CRACHIP glass.

A NEW APPROACH TO PLUTONIUM STORAGE AND DISPOSITION

Before any option to treat plutonium scrap and residue can be undertaken, the requirements for the anticipated product must be defined. A CRACHIP glass must (1) be mechanically stable and must not form aerosols under storage or accident conditions, (2) be chemically inert, and (3) contain sufficient neutron poisons to prevent nuclear criticality with any quantity of material and/or any geometry. This addresses the near-term ES&H issues. This glass must also allow multiple disposition options: long-term storage, recovery of plutonium (with some difficulty), and disposal of plutonium as a waste. In the intermediate term, a CRACHIP form minimizes storage costs and ES&H storage risks, and simplifies safeguards.

The requirements and criteria for CRACHIP glass are similar to those required for high-level-waste (HLW) glasses. Radioactive wastes become less hazardous with time; hence, the fundamental concept in waste management is to isolate (store) these wastes until they are nonhazardous. Glass has been chosen worldwide as the preferred HLW storage and transport form because of several of its properties: (1) acceptance of impure feeds, (2) low solubility in water, (3) chemical inertness, (4) acceptable mechanical integrity, (5) ability to handle high heat loads from decay heat, and (6) avoidance of nuclear criticality by use of neutron poisons. The similar requirements of waste management and plutonium scrap and residue management provide the basis for defining performance requirements for CRACHIP glass: storage with performance equivalent to that of HLW glass.

Several groups are developing optimum compositions[6,7] for high-plutonium-loaded glass. For plutonium scrap and residue, traditional HLW glass compositions may also be modified for the plutonium and other components in the feed. In this case, plutonium is a minor component in the glass. Glass compositions must be optimized to accept both the plutonium and the other components in the feed.

Regardless of the long-term disposition of plutonium scrap and residue, storage is the only viable near-term option. This implies that the near-term incentive for conversion of plutonium scrap and residue to any storage form is to minimize storage costs. CRACHIP glass reduces the *storage requirements* and, in turn storage costs for plutonium scrap and residue by the following mechanisms:

- *Nuclear Criticality.* Plutonium is currently stored in vaults in small containers (traditionally <5 kg of plutonium per container) that are widely spaced to avoid nuclear criticality. CRACHIP glass with neutron poisons eliminates criticality control as a vault requirement and thus reduces the vault size. In large vaults, most of the space is empty for geometric criticality control and can be eliminated if the material is stored as CRACHIP glass.

- *Volume Reduction.* Conversion of heterogeneous materials to a high-density, monolithic glass further minimizes storage costs.

- *Safeguards.* Conversion of highly heterogeneous materials to homogeneous glass in a standardized package allows for (1) more precise and reliable safeguards, (2) automated systems, and (3) number-count safeguards. This minimizes the costs of safeguards.

THE PROCESS: GMODS

Conversion Of Metals, Ceramics, Amorphous Solids, And Organics To Glass

GMODS converts plutonium and the other elements within the scrap and residue directly to borosilicate glass. GMODS is a batch process (Fig. 1) during which sequential process steps convert feeds to glass. The initial condition for the process is a melter filled with a molten oxidation–dissolution (lead borate) glass, which has a composition of 2 or more moles of lead oxide (PbO) per mole of boron oxide (B_2O_3). The PbO is a component of the glass and a sacrificial oxide. The process consists of the following steps:

- *Addition of feed material to the molten dissolution glass (Fig. 1.b).* The ceramic (plutonium oxide (PuO_2), etc.) and amorphous components in the feed dissolve into the glass. While metals and organics do not dissolve into conventional molten glasses, the GMODS dissolution glass has special properties to process these materials *in situ*. The inclusion of the sacrificial oxide—PbO—in the molten glass provides a method to oxidize *in situ* (a) metals to metal oxides and (b) organics to carbon dioxide (CO_2) gas and steam. When plutonium or another metal is fed to the melter, it is converted to a metal oxide. These metal oxides dissolve into the glass; carbon oxides (in gaseous form) and steam exit the melter. The reaction product, molten lead, separates from the glass and sinks to the bottom of the melter to form a separate layer,

$$Pu + 2PbO \rightarrow PuO_2 + 2Pb \downarrow$$

$$C + 2PbO \rightarrow CO_2 \uparrow + 2Pb \downarrow$$

- *Addition of glass additives [silicon oxide (SiO_2) etc.] to improve the product quality (Fig. 1.c).* The optimum compositions of glasses for rapid oxidation-dissolution of materials in molten glass are different in composition from those for long-term durability; thus, additives that create a more durable glass are introduced after feed oxidation-dissolution takes place.

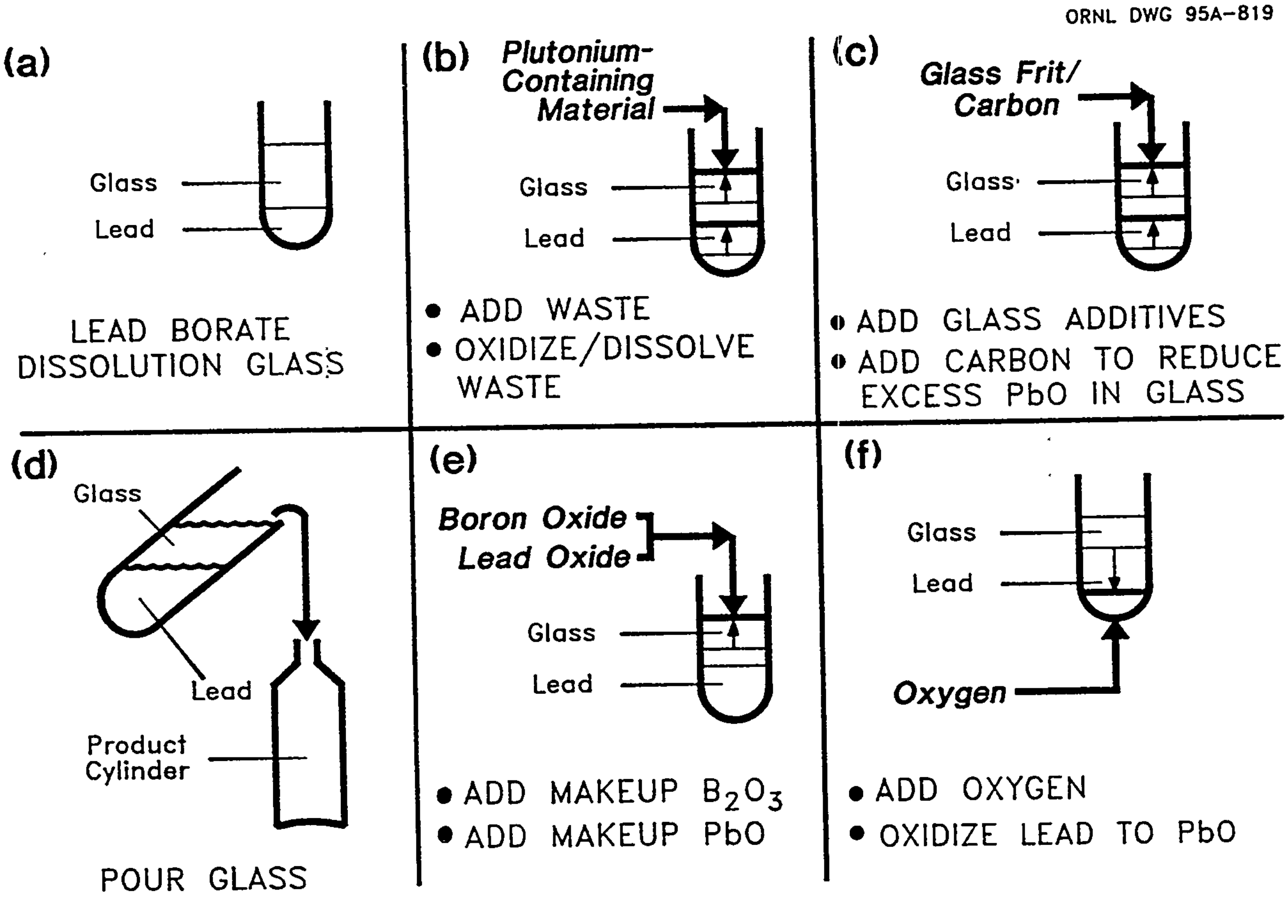


Fig. 1. GMODS batch processing of plutonium-containing material to borosilicate glass.

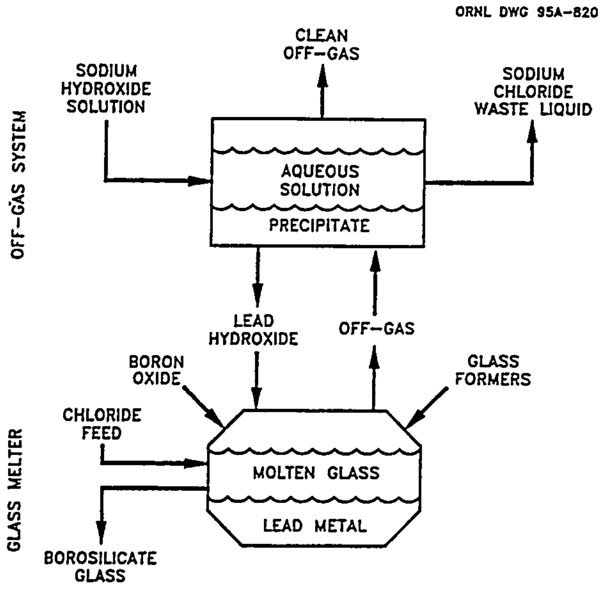
- *Addition of carbon to remove excess PbO (Fig. 1.c).* Carbon reduces the PbO to lead metal while producing gaseous CO_2. Excess PbO is removed from the dissolution glass for multiple reasons: (1) more durable glass, (2) reduction of the volume of glass, and (3) avoidance of the costs to provide added sacrificial PbO. The final glass may contain some or no lead, depending on the final desired glass composition.

- *Pouring glass from the furnace followed by solidification (Fig. 1.d).*

- *Addition of B_2O_3 and PbO, as needed, to the melter for processing the next batch of materials (Fig. 1.e).*

- *Reoxidation of the lead at the bottom of the melter to PbO by addition of oxygen (Fig. 1.f).* This oxidation creates the new dissolution glass for the next batch of feed to be processed. Lead is an oxygen carrier that does not leave the system. The oxidation reaction is

$$2Pb + O_2 \rightarrow 2PbO$$



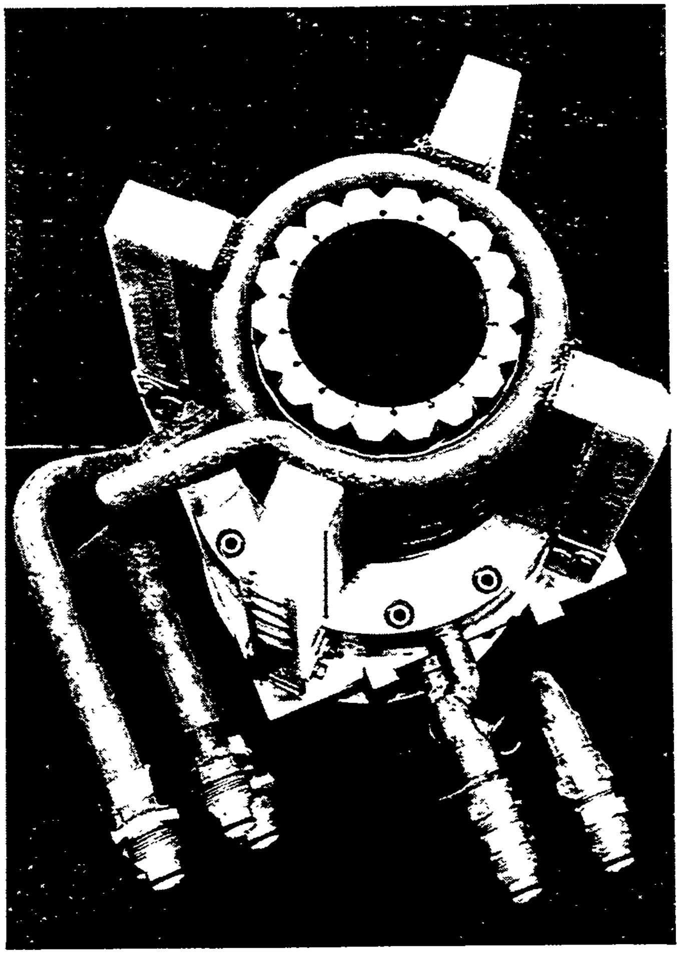


Fig. 2. GMODS processing of chloride-containing feed materials.

Fig. 3. Small commercial, cold-wall induction-heated melter (Courtesy of Consarc)

Conversion Of Chlorides to Low-Chloride Borosilicate Glass And A Secondary Sodium Chloride Stream

GMODS is designed to convert chloride-containing plutonium residues to glass and create a separate nonradioactive sodium chloride (NaCl) waste stream. Halogens, such as chloride, make poor-quality storage forms; hence, they must be separated from other components in plutonium residues. The analogy used in waste management is that good storage forms (silica, titanates, etc.) for radioactive materials can be found at any ocean beach. Materials that dissolve in seawater (chlorides, etc.) make poor storage forms.

The separation process for chlorides is shown in Fig. 2. In the dissolution glass, chlorides in the feed form lead chloride ($PbCl_2$), which is volatile at glass melter temperatures and exits to the aqueous sodium hydroxide (NaOH) scrubber. In the scrubber, the $PbCl_2$ reacts with the NaOH to yield insoluble lead hydroxide [$Pb(OH)_2$] and soluble NaCl salt. The insoluble $Pb(OH)_2$ is recycled back to the melter where it decomposes to PbO and steam, while the aqueous salt stream (NaCl) is cleaned and discharged as a chemical waste.

Conversion Of Heterogeneous, Poorly Characterized Feed Materials To High-Quality Homogeneous Glass

A certified, qualified, high-quality, homogeneous glass product is required. Thus, an approach similar to that used to produce speciality metals and glass is used, where scrap and residue are fed to the melter and a homogeneous molten glass solution is produced. With a homogeneous glass solution, composition can be determined by limited sampling using mass spectrometric analysis. From the chemical analysis, the required compositions of additives can be determined to produce an appropriate product glass. This strategy, which depends on the ability to create a homogeneous glass from poorly characterized feed materials, is achieved by two mechanisms:

- GMODS can accept wide variations in the chemical composition of the feed and convert the materials to a homogeneous glass. This capability is a prerequisite because it avoids the need for detailed sampling of feed materials to ensure processability.

- The GMODS melter uses process tomography instrumentation[8,9] to determine in real-time when a homogeneous glass solution has been created. Homogeneous solutions imply homogeneous radiation fields that instrumentation can detect. With variable feeds, dissolution times will vary widely. Instrumentation ensures homogeneous feeds without requiring that tests be conducted on every feed to determine required dissolution times.

EQUIPMENT

The primary GMODS equipment is an induction-heated, cold-wall melter (Fig. 3 shows a small commercial type), which is required because of the corrosive characteristics of the initial dissolution glass. Cold-wall melters have cooling jackets in the wall to produce a "skull" of solidified material that protects the wall from the melter contents. They are used to melt high-temperature materials (e.g., titanium and superalloys) and to produce ultrapure materials (e.g., glass for fiber optics). Russia, France, and the United States are modifying such equipment for processing various radioactive wastes. Batch size may be as large as several hundred kilograms for plutonium scrap and residue with low plutonium concentrations. In Europe, cold-wall melters are currently being developed for throughputs of up to 800 kg/h - far in excess of the size required for this mission.

STATUS OF DEVELOPMENT

Investigations of Process Steps

Some steps of the GMODS process are new, while others are parts of standard industrial processes. Experiments were performed to understand and prove the unique features of GMODS. Literature searches have been conducted to understand those parts of the process that are used in other industrial processes. Each step has also been accomplished in our laboratory.

Laboratory experiments were conducted in platinum and high-fired aluminum oxide crucibles within vertical tube furnaces. Platinum was used for experiments that did not involve lead (lead dissolves into platinum at high temperatures). Various ceramic crucible materials were investigated for use in oxidation process experiments. While the dissolution glass dissolves oxides, the rate of dissolution with Coors™ high-fired aluminum oxide crucible is sufficiently low for short-time experiments.

A typical experiment involved several hundred grams of material, with uranium and cerium being used as plutonium surrogates. Plutonium tests have been proposed. The plutonium content of scrap and residue is, at most, a few weight percent; hence, in terms of chemical processing, plutonium is a minor component.

Addition of feed material to the molten dissolution glass (Fig. 1.b). The addition of feed materials involves oxidation, dissolution, and mixing of feeds with the molten dissolution glass. Each of these steps has been investigated.

Tests demonstrated the dissolution of UO_2, ZrO_2, Al_2O_3, Ce_2O_3, MgO, and other oxides. The glasses were examined by a variety of methods to ensure complete dissolution. As expected, the high-boron oxide glass melt had good dissolution capabilities for oxides. In analytical chemistry, B_2O_3 is the standard chemical reagent for fusion dissolution of unknown oxides because of its capability to dissolve such materials. Boron oxide is also the key component in many welding fluxes, which are used to dissolve iron oxides into a glassy slag during the welding process so that they are not incorporated into the weld.

Oxidation-dissolution tests demonstrated the oxidation of the following metals and alloys followed by the dissolution of their oxides into the melt: U, Ce, Zircaloy-2, Al, stainless steel, and other metals. Figure 4 shows 'cerium glass and lead by-product from a test of oxidation of cerium metal (plutonium surrogate).

Oxidation-dissolution tests also demonstrated the oxidation of carbon and graphite, with production of CO_2. For centuries, lead oxide has been used to oxidize organics[10]. It is the basis for the fire assay method for recovering noble metals (primarily gold) from silicate rock. Lead oxide, various organics, and silicate rocks are mixed together and heated. As the mixture melts, the lead oxide is reduced to metal by the organic. The noble metals in the molten mass then dissolve into the lead, which forms a separate layer that sinks to the bottom. This layer is then processed to separate the noble metal from the lead.

Limited chloride dissolution tests with NaCl demonstrated that lead exits the dissolution glass as $PbCl_2$ thus providing a separation of the chloride from other materials. This is a major mechanism for lead to escape from processes where lead and chlorides coexist at high temperatures.[11] The basic chemistry is well understood.

Experimental measurements were made of the viscosity of the dissolution glass with various added materials. Experience in the glass industry indicates that molten glass viscosities should be below 100 centipoise (about the viscosity of olive oil) for good mixing and creation of homogeneous glasses. Based on our experimental data, the GMODS dissolution glass temperature will need to be between 800 and 1000° C. The final processing temperature after addition of the silica will be above 1000° C because this addition increases glass viscosity.

Addition of glass additives [silicon oxide (SiO_2) etc.] to improve the product quality (Fig. 1.c). This process step is essentially identical to that used for producing many specialty glasses.[12]

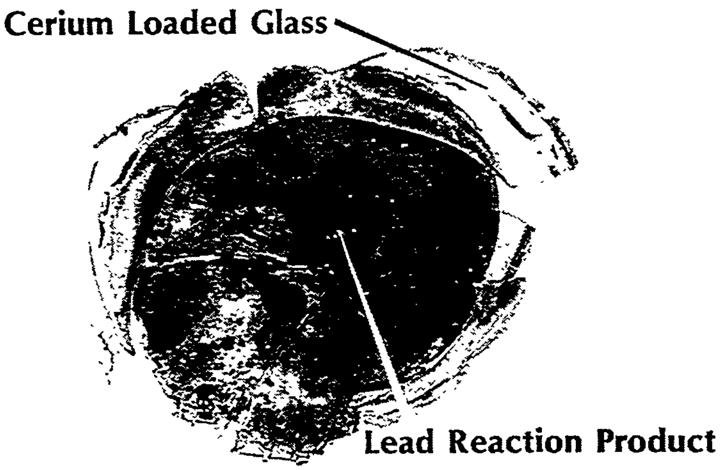


Fig. 4. Cerium glass and lead metal from completed oxidation-dissolution test with cerium metal.

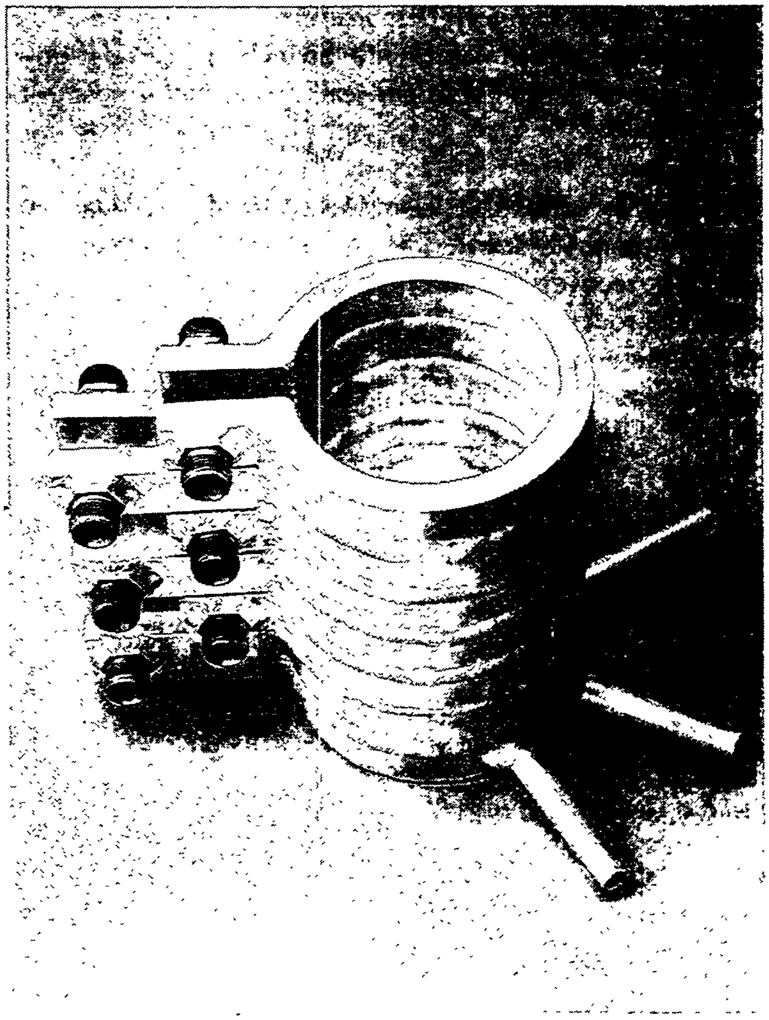


Fig. 5. ORNL single-turn, cold-wall, induction-heated glass melter.

Addition of carbon to remove excess PbO (Fig. 1.c). This process step is used in several lead-smelting processes, such as the QSL process, to recover lead metal from lead oxide in molten slag.[13] This step has also been demonstrated with HLW glass in hot cells for recovery of fission product noble metals at Pacific Northwest Laboratory,[14] using a modification of the fire-assay method described above. Because some proposed plutonium glasses are variants of HLW glasses, this experience is particularly relevant.

Pouring glass from the furnace followed by solidification (Fig. 1.d). This is a standard operation used by the glass industry.

Addition of B_2O_3 and PbO, as needed, to the melter for processing the next batch of materials (Fig. 1.e). This is a standard operation used by the glass industry for producing lead borosilicate glass (fine crystal).

Reoxidation of the lead at the bottom of the melter to PbO by addition of oxygen (Fig. 1.f). This is one of several processes used for producing lead oxide for batteries and other uses.[15]

Flowsheet Analysis

An analysis of GMODS was performed using the process simulator FLOW.[16] The simulator includes a set of rules to choose glass compositions that meet process (viscosity, etc.) and performance requirements, using Savannah River HLW glass as a basis. The analysis identified critical process parameters when processing plutonium scrap and residue to a borosilicate glass, which is designed to be equivalent in performance to HLW glass. The two key observations were as follows:

- Incentives exist to maximize the GMODS operating temperature. For example, processing 1 kg of plutonium-containing chloride salt residues at 1103° C yields 6.5 kg of glass under standard conditions. Allowing the processing temperature to increase to 1167° C reduces the final glass quantities to about 3 kg. In this case, the waste loading in the glass is limited by the need to minimize molten glass viscosity during process operations to ensure good glass mixing. Increasing the processing temperature decreases the glass viscosity, minimizes the need to add sodium oxide to lower glass viscosity by changing the chemical composition, and allows a higher waste loading in the product glass. With the use of cold-wall, induction-heated melters that are not temperature-limited, the limitation on the maximum process temperature is volatilization of selected glass components.

- Incentives also exist to blend different feeds to minimize glass volumes. For example, blending plutonium salt and ash residue streams and converting them to glass reduces the final volume of glass by about 50% as compared with separate conversion of the two materials to glass. Final glass volumes are minimized because the ash stream provides necessary silica and aluminum to the final product glass, while the chloride stream provides necessary sodium to the final product glass.

The flowsheet simulator also afforded a bounding estimate of glass quantities if scrap and residue at Rocky Flats were converted to glass by GMODS. For "lean" scrap, 232 m^3 of glass would be produced with an average plutonium content of 0.06%. For "rich" scrap, 34 m^3 of glass would be produced with an average plutonium content of 2.4%. The actual quantities of glass may be significantly less when higher process temperatures are used.

The quantities of glass produced from processing plutonium scrap and residue are not determined by the plutonium (due to its low concentration) but, rather, by other components in the scrap or residue. The set of constraints includes: glass processing temperatures, solubility limits of specific elements in the product glass, and glass durability under repository conditions. If the goal is to minimize glass volumes in order to minimize storage or disposal volumes, selected pre-processing of some residues can be undertaken to minimize specific elements that most impact glass volumes. This choice involves a series of trade-offs between multiple processes. (Note that organics and chlorides in feeds have little impact on final glass volumes because GMODS is a separations, as well as a glassmaking process.)

Equipment

In making a survey of cold-wall, induction-heated melters, the range of operating conditions was found to substantially exceed the potential range of GMODS operations. Industrial melters are designed to operate at up to 2500° C; some of them operate with molten metal and slag. Recently, a small experimental melter has been built in our laboratory (Fig. 5) to provide a better understanding of this technology. Tests of this melter are under way.

Development Perspective

The analytical testing and laboratory development work have demonstrated each step required for GMODS and identified equipment, instrumentation, and other components required for GMODS. A significant effort, however, will be required to convert GMODS into an industrial technology. This effort will include a better understanding of the process, integration of process steps into a system, and development of equipment.

SUMMARY

GMODS is a new process for the direct conversion of plutonium scrap and residue to CRACHIP glass. It is designed to (1) convert metals, ceramics, and amorphous solids to glass; (2) oxidize organics with conversion of residues to glass; and (3) convert chlorides into a chloride-free borosilicate glass and a secondary clean NaCl stream. GMODS is an enabling technology, since it creates new plutonium scrap and residue management options. Because these options address common national security, non proliferation, and ES&H concerns, they may be acceptable to both the United States and Russia. As a new technology, however, GMODS has significant technical uncertainties that must be resolved in additional studies.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Immobilization of Plutonium from Solutions on Porous Matrices by the Method of High Temperature Sorption

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INTRODUCTION

Currently plutonium is viewed as an element suitable for further utilization:

- plutonium 239 - as fissile material;
- mixtures of plutonium isotopes - as material for the manufacture of mixed uranium-plutonium fuels.

However, the amount of accumulated plutonium significantly surpasses current demand for the material. Tens of tons of plutonium are already in storage facilities. The utilization of such vast amounts of plutonium, when you take into account the fact that new shipments continue to arrive from power plants, and as a result of the dismantling of nuclear weapons, makes it necessary to develop simple and reliable methods for its storage and for the burial of waste containing plutonium (1, 2).

Plutonium is primarily stored in the form of plutonium dioxide, but for the purposes of the burial of plutonium, the following options are being considered:

- immobilization of plutonium in inorganic matrices (glass, ceramic) with the purpose of eventual burial in geological formations;
- launch into space in a compact form;
- transmutation.

All of these options have advantages and disadvantages.

This report presents the results of investigations of plutonium immobilization from solutions on inorganic matrices with the purpose of producing a solid waste form. The solidified material is convenient both for temporary storage and for long-term storage and/or final burial of the plutonium.

In our search for an answer we used high-temperature sorption, which entails the adsorption of radionuclides from solutions on porous, inorganic matrices, for example silica gel. The solution is brought to a boil (100 - 130^{0}C) with additional thermal processing (calcination) of the saturated granules (3). The process was developed jointly by the All Russian Institute of Chemical Technology and the Mayak Production Facility, initially for the processing of high level radioactive waste (3). However, the results achieved recently indicate that this method could be used for the immobilization of plutonium on inorganic matrices (4).

EXPERIMENTS

Methodology and Results

Plutonium distribution during the high temperature sorption process was studied at the laboratory facility equipped with a heated reactor, cooler and a hotwell.

The silica gel was saturated with plutonium - up to 200 or 300 mg of plutonium per g of sorbent (with the exception of those experiments that were performed to determine maximum saturation levels). In most of the experiments that were conducted after the silica gel was saturated, the material was subjected to "steaming," which was as follows: at that moment when the solution had completely evaporated, but while the sorbent was still moist, 3 - 5 ml of hot nitric acid with a concentration of 3 mole/l was added to the vessel and then the silica gel was dried until granulation occurred. The drying and calcination procedures were carried out at temperatures of 220 - 900^{0}C. Calcination time at this temperature was one hour. A standard KSKG silica gel with a 0.5 - 4.0 mm granule size was used in the experiments.

Nitric acid solutions of plutonium with different isotopic composition (IV) were used in the investigations. Plutonium concentrations were 0.1 - 0.2 mole/l and the nitric acid concentration was 3 mole/l. In order to simulate the solutions used in the Purex process, sulfuric and acetic acid, carbamide, hydroxylamine and DTPA were added. The desorbed materials, washoff from the laboratory equipment and the condensate were all analyzed.

Experiments on the saturation of silica gel allowed us to determine the maximum plutonium saturation levels of silica gel as - 800 mg Pu per 1 g SiO_2.

Investigations of plutonium distribution during the high temperature sorption process were carried out, beginning with the determination of the removal of plutonium into the vapor-gas phase and the determination of the purification coefficient at the saturation point of the silica gel granules. As shown in Table 1, the removal of plutonium at different saturations was no greater than 0.1% of the initial amount of plutonium at the start of the evaporation stage. The rest of the plutonium was distributed between the silica gel granules and the walls of the reactor vessel.

Table 1. Plutonium distribution during the silica gel saturation process.

ELEMENT	INITIAL SOLUTION CONCENTRATE, g/l	SATURATION OF SiO_2, mg/g	DISTRIBUTION, %		
			REMOVAL WITH CONDENSATE	REMAINED ON VESSEL WALLS	ADSORBED ON SiO_2
Pu	24.0	200	0.005	7.6*	92.4
	24.0	200	0.05	2.1	97.9
	40.0	800	0.005	2.5	97.5

* the experiment was conducted without steaming

Moreover, the completeness of the sorption of plutonium even when saturation was near the maximum reaches 92 - 96% and depends to a significant degree on the conditions under which the test was carried out: the intensity of the evaporation process and the relationship between the amount of sorbent and the shape of the reactor vessel. In order to decrease the non-inclusion of the residue an additional step, that of steaming, was added. This allowed us to increase the completeness of the sorption process to 99%. The removal of plutonium into the vapor-gas phase depends to a great degree on the evaporation conditions and when the boiling intensity is moderate, the removal of plutonium can be lowered to 0.005% without any additional measures, while the maximum purification coefficient becomes greater than 2×10^4 (Table 2).

Table 2. Removal of plutonium into the vapor-gas phase.

ELEMENT	ACTIVITY OF SOLUTION, Bq/l		SATURATION OF SiO_2, mg/g	PURIFICATION COEFFICIENT	EVAPORATION CONDITIONS (boiling intensity)
	INITIAL	CONDENSATE			
Pu*	$3.0*10^{11}$	$1.6*10^{6}$	300	1900	moderate
Pu	$1.3*10^{11}$	$1.6*10^{6}$	200	20000	very moderate
Pu	$2.0*10^{11}$	$9.7*10^{6}$	800	20500	very moderate

* plutonium of a different isotopic composition was used for these tests

Calcination of the samples that were to be used in the preparation of the solidified material with the possibility of plutonium extraction at a later date, was carried out at a temperature of 220 - 650°C and for those samples that were designated for burial at 800 - 900°C. The addition of complexing agents and reducers to the solution simulated the re-extracts of plutonium, which are produced when the Purex process is used.

The strength of the adsorption of plutonium onto the granules of silica gel was determined by the amount of plutonium in the desorbing solution. Desorption of plutonium was conducted under stationary conditions in four operations with nitric acid at a temperature of 25°C. Nitric acid concentration was 3 mole/l. The first batch of desorbing solution was poured off after an hour and a new batch of acid was added. The duration of the second and third desorption processes was 24 hours and the fourth - 72 hours. In tests conducted to determine the effect of temperature and acidity, the desorption time was 20 minutes long in the first three instances and 180 minutes in the fourth. There was a periodic mixing of the solution.

The results of low-temperature tests (Table 3) call attention to the low levels of plutonium in the desorption solutions (43.9%) for samples saturated with nitric acid solutions and calcinated at a temperature of 220°C. The results of tests conducted with the admixture of sulfate during the saturation operation were completely different. The results of these tests showed that more than 80% of the plutonium was desorbed during the first of the desorption operations. Raising the temperatures of calcination for samples saturated with nitric-sulfuric acid solutions up to 650°C, to the point at which the sulfate complex degrades, increases the residues on the silica gel to 78.7%. Experiments with the other admixtures showed good plutonium desorption results for systems with carbamide and somewhat worse results for systems with DTPA.

The effect of temperature and acid concentration on plutonium extraction was determined by plutonium desorption from silica gel with a nitric-sulfuric acid saturation of 100 mg/g (Test 2 in Table 3) and calcinated at 220°C. Plutonium extraction during one desorption operation carried out under different conditions shows result variations of 5 to 20%. However, during four operations this difference was never greater than 2% and the residue on the silica gel constitutes from 0.2 to 0.3% during desorption with nitric acid concentrations of 3 - 8 mole/l at 60 - 100°C.

The possibility of recycling plutonium desorbed from silica gel for reuse in the technological cycle was investigated in tests of plutonium extraction with a 30% solution of TBF with a hydrocarbon diluent. Plutonium extraction from all the desorbed materials, with different temperatures and different acid concentrations, was performed, and the distribution coefficients were typical for standard systems. The rate of the aqueous-organic phase separation was in the range of 0.5 - 2.5 mm/sec. No interphase formations and phenomena, indicating deterioration of the extraction process and possible effect of silicon, were found.

The possibility of limitless storage was assessed on the basis of the chemical stability of the solidified materials. Stability was assessed on the basis of the plutonium leaching rate. Leaching tests were conducted under stationary conditions in nitric acid concentrations of 10^{-4} mole/l at 25°C. The volume of the solution during the leaching tests was equal to the volume of the initial solution used for saturating the sorbent. The leaching data is presented in Table 4. With the increase in the calcination temperatures of the silica gel saturated with plutonium from 800° to 900°C, the removal of plutonium into solution during leaching decreases 3 - 5 times and is equal to 1 - 2 mg of plutonium per gram of saturated silica gel. No significant differences were noted between the leaching rates from silica gel saturated with systems with admixtures of complex-forming agents and systems without such agents.

Table 3. The effect of calcination temperatures and admixtures on the strength of Pu adsorption onto silica gel.

ELEMENT		ADMIXTURE	ADMIXTURE CONCENTRATION mole/l	CALCINATION TEMP, ^{0}C	DESORPTION, %				RESIDUE ON SiO_2	HYPOTHETICAL FORM OF ELEMENT	GRANULE COLOR
					1	2	3	4			
Pu	1	--	--- 0	220	36.0	6.8	0.6	0.5	56.1	PuO_2	green
	2	H_2SO_4	0.2	220	80.6	15.6	2.8	0.9	0.1	$Pu(SO_4)_2*4H_2O$	orange
	3	H_2SO_4	0.2	400	54.5	30.3	10.7	3.5	1.0	$Pu(SO_4)_2$	orange
	4	H_2SO_4	0.2	650	19.8	1.2	0.3	---	78.7	PuO_2	light green
	5	CH_3COOH	2.0	220	23.3	8.7	2.0	1.6	64.4	PuO_2	green
	6	NH_2OH	0.2	220	22.7	4.7	0.7	0.8	71.1	PuO_2	green
	7	DTPA	0.1	220	51.0	25.5	8.6	2.7	12.2	complex with Pu	blue
	8	$(NH_2)_2CO$	0.2	220	68.9	21.7	6.7	1.6	1.1	complex with Pu	yellow

Table 4. The correlation between the calcination temperature of the silica gel and the plutonium leaching rate.

ELEMENT		SATURATION mg/g	CALCINATION TEMP, °C	WASH-OUT WITH SiO_2 AFTER CALCINATION mg/g	LEACHING (mg/g) TIME IN WEEKS		
					1	4	16
Pu	1*	300	800	0.05	0.050	0.014	0.005
	2*	300	900	0.02	0.025	0.004	--
	3**	200	900	0.19	0.011	0.004	0.001
	4	700	900	0.09	0.007	0.002	0.004

*saturated with nitric-sulfuric acid
**without steaming

Discussion of the results
Investigations of plutonium behavior during high temperature sorption processes were carried out with the following goals:

- optimization of the plutonium adsorption mode of silica gel;
- preparation of solid forms for temporary storage of plutonium with its possible future extraction and re-utilization in the fuel cycle or for its eventual burial.

Silica gel stability to radiation is quite good. Therefore limitations on plutonium saturation could only be based on nuclear safety considerations, or on the possibility of large heat releases during storage of the saturated granules with an increased specific concentration of short-lived isotopes, for example, the plutonium 238 isotopes.

With average silica gel plutonium saturations (100 - 300 mg/g), the composition of the initial solution does not affect the adsorption and distribution of plutonium. As shown in Tables 1 and 2, plutonium distribution correlates closely with the conditions under which the process is carried out. The removal of plutonium into the vapor-gas phase is strictly mechanical in nature and can be reduced by lowering the boiling intensity or by the proper correlation between the volume of sorbent and the volume of the solution so that the level of the liquid always remains below the upper layer of the silica gel. One of the main goals is the achievement of purification coefficients that would allow the transfer of the condensate into a low level waste category. The solution to this problems lies with the choice of equipment that will be used in this process.

The introduction of an additional step in this process, i.e., "steaming," made it possible to decrease the residue on the reactor vessel walls to 1 - 2%, although this is not such an important aspect in an industrial scale application, since in that case the subsequent batches will dissolve the residues from the previous batch. We feel that a more valuable aspect of "steaming" is that it forces the adsorbed element into a deeper layer of the silica gel granules leading to relative depletion of the surface layer which consequently reduces the leaching rate after calcination (tests 7 and 8 in Table 4).

Solidification of plutonium for storage with possible later extraction

The extraction of plutonium from inorganic matrices is made possible by the low calcination temperatures to which the saturated silica gel is subjected and is accomplished by desorption with acid.

Proposed compounds of plutonium for storage after adsorption on silica gel must meet two requirements: have high stability to radiation and provide for relatively simple extraction of plutonium into solution. Plutonium oxides have such properties and they were at the center of the studies we conducted. It is known that plutonium dioxide produced with calcination at 275^{0}C retains its reactivity and dissolves in mineral acids (5). If plutonium nitrate is calcinated at a temperature greater than 150^{0}C, unstable plutonyl nitrate is formed, which completely degrades into plutonium dioxide when it is heated to 220 - 250^{0}C (6). The silica gel releases the adsorbed water when heated to a temperature of 120 - 200^{0}C and the process of plutonium desorption is easily initiated after the temperature reaches 400 - 425^{0}C (7). Our results show that less than 50% of the plutonium dioxide that is adsorbed onto the silica gel as a result of calcination at 220^{0}C after saturation with various solutions (tests 1, 5, and 6 in Table 3) is dissolved.

Plutonium yield does not increase as a result of desorption by boiling nitric acid with concentrations of 3 mole/l. Plutonium yield approaches 95% only after the addition of 0.025 mole/l of fluoride. However, the use of fluoride is to be avoided because it not only dissolves the plutonium, but the silica gel as well. Based on the observed plutonium behavior we can draw the conclusion that it replaces the silicon in the lattice, is adsorbed like plutonium (IV) and is incorporated into the structure of the silica gel. That is why solutions that form plutonium dioxide during the saturation process are of little value as solidification methods for the preparation of materials for storage and possible eventual conversion back to usable form. We investigated the following solutions: nitric acid, nitric-acetic acid, and nitric acid with admixtures of hydroxylamine.

We studied other compounds of plutonium and found that plutonium sulfates have the most desirable properties for our purposes. Plutonium is adsorbed from nitric-sulfuric acid solution as a sulfate, which has good solubility and extraordinary stability to radiolysis. According to the available scientific data (6), samples stored in standard glass vessels with relative humidity up to 75% showed little evidence of changes in plutonium content and water adsorption after being stored for 28 months or evidence of radiolysis of the crystallized water. The loss of water from plutonium sulfate tetrahydrate ceases at a temperature of 270 - 280^{0}C, and degradation into dioxides begins at approximately 500^0 and ends at approximately 700^{0}C (5). The results of the tests (test 2 - 4 in Table 3) correspond quite well with this data. The removal of 99.9% of plutonium during desorption allows us to draw the conclusion that this form of plutonium is suitable for storage with possible eventual extraction.

We investigated the desorption process itself by studying the effect of variations in temperature and solution concentrations. The results of our tests indicate that the optimum conditions for desorption are similar to the optimum conditions for adsorption: boiling point temperatures for the solutions and high acidity. The desorption process itself confirmed the hypothesis of the uniform saturation of the silica gel - the decoloration of the granules of the sorbent proceeds uniformly.

Tests with DTPA and carbamide were also positive. The removal of carbamide during desorption was 99%. However, it is premature to consider storage of plutonium in this form until we have data on the radiolysis of the compounds.

The preparation of solid forms for the burial of plutonium

The strong adsorption of plutonium onto silica gel after calcination with high temperatures is the result of the formation of non-soluble forms of the element and the closing of the pores of the silica gel during fusion. Plutonium dioxide is such a compound with low reactivity capabilities after calcination at 800 - 1000^{0}C (2, 5). For silica gel the complete removal of internal water and hydroxyls is achieved at 1000^{0}C and its melting temperature (1000 - 1450^{0}C) is determined by the adsorbed cations and their number (7).

The optimum temperature for calcinating silica gel with plutonium is 900^{0}C. Flushing operations reduce the already insignificant levels of silica gel dust generation (low in comparison with the dust generating levels for plutonium dioxide in powder form). To provide for an even more reliable immobilization of long-lived radionuclides, it is possible to enclose the saturated silica gel granules in phosphate or borosilicate glass by applying melting or hot pressing technologies.

The technology for the immobilization of plutonium on solid matrices that is being developed can be applied to liquid wastes containing plutonium regardless of composition. Along with plutonium, other fission products will be adsorbed onto the silica gel, as well as admixtures of stable metals and other transuranic elements.

The solid waste forms for plutonium storage are characterized by low dust generation rates on the one hand and a good flowability coefficient on the other. Also, transformation of the material from a form suitable for interim storage into one that is suitable for final burial can be done easily by calcination at a high temperature.

At the present time, we do not have data from long-term storage experience with silica gel granules, saturated with plutonium. However, the results from experiments indicate that high temperature adsorption can be successfully applied to the immobilization of plutonium on inorganic matrices for its storage for several years (with possible later extraction) as well as for purposes of transfer of the materials to other sites.

Conclusive recommendations on the final burial of plutonium in the form of saturated and calcinated silica gel granules will be made after additional data is obtained on the effects of radiolysis.

The authors would like to express their deep gratitude to the Department of Energy of the United States for sponsoring the above mentioned studies.

DISCLAIMER

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Microwave Calcination for Plutonium Immobilization and Residue Stabilization

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ABSTRACT

In the late 1980's development was begun on a process using microwave energy to vitrify low level mixed waste sludge and transuranic mixed waste sludge generated in Building 374 at Rocky Flats. This process was shown to produce a dense, highly durable waste form. With the cessation of weapons production at Rocky Flats, the emphasis has changed from treatment of low level and TRU wastes to stabilizaiton of plutonium oxide and residues. This equipment is versatile and can be used as a heat source to calcine, react or vitrify many types of residues and oxides. It has natural economies in that it heats only the material to be treated, significantly reducing cycle times over conventional furnaces. It is inexpensive to operate in that most of the working components remain outside of any necessary contamination enclosure and therefore can easily be maintained. Limited testing has been successfully performed on cerium oxide (as a surrogate for plutonium oxide), surrogate electrorefining salts, surrogate residue sludge and residue ash. Future plans also include tests on ion exchange resins. In an attempt to further the usefullness of this technology, a mobile, self-contained microwave melting system is currently under development and expected to be operational at Rocky Flats Enviromental Technology Site by the 4th quarter of FY96.

INTRODUCTION

Microwave vitrification was originally developed, at Rocky Flats in the late 1980's as a process to stabilize by-pass sludge generated in Building 374. By-pass sludge is generally a low level mixed waste (LLMW). Microwave was selected because it could economically reduce waste volume, treat to meet land disposal restrictions and immobilize the material for shipment. While the microwave's vitreous waste form was decidedly superior to the cemented grout process, with which it competed, life-cycle costs drove the selection of the process for treatment of this waste.

Initial work was performed on one and two liter containers of material that were heated by a variable, zero to six kilowatt (kW) power supply. These bench-scale experiments were very successful in treating a wide range of surrogate wastes as well as plutonium contaminated waste. The unit was also demonstrated on rasching rings, soils, ash, salts and other miscellaneous wastes. At this relatively small scale, the unit was very versatile.

The microwave process uses a metal or ceramic container as part of the microwave chamber. After a heating/solidification cycle is completed, the inexpensive, single use containers are removed from the chamber to cool and become part of the waste form. Concurrent with cooling, the next run may proceed.

Subsequent work was performed with the aim of scaling the process up to thirty gallon drum size. This larger size in its current configuration uses a 60 kW generator for studies on surrogate by-pass sludge. Again this work was very successful. The system was designed to operate in a continuous or semi-batch mode filling the 30 gallon drum to 750 pounds. Figure 1 is a schematic of the microwave unit which includes the generator, wave guide, container as part of the cavity, and continuous feed. Figure 2 is a photograph of the large system. This large scale work is currently the subject of privatization negotiations.

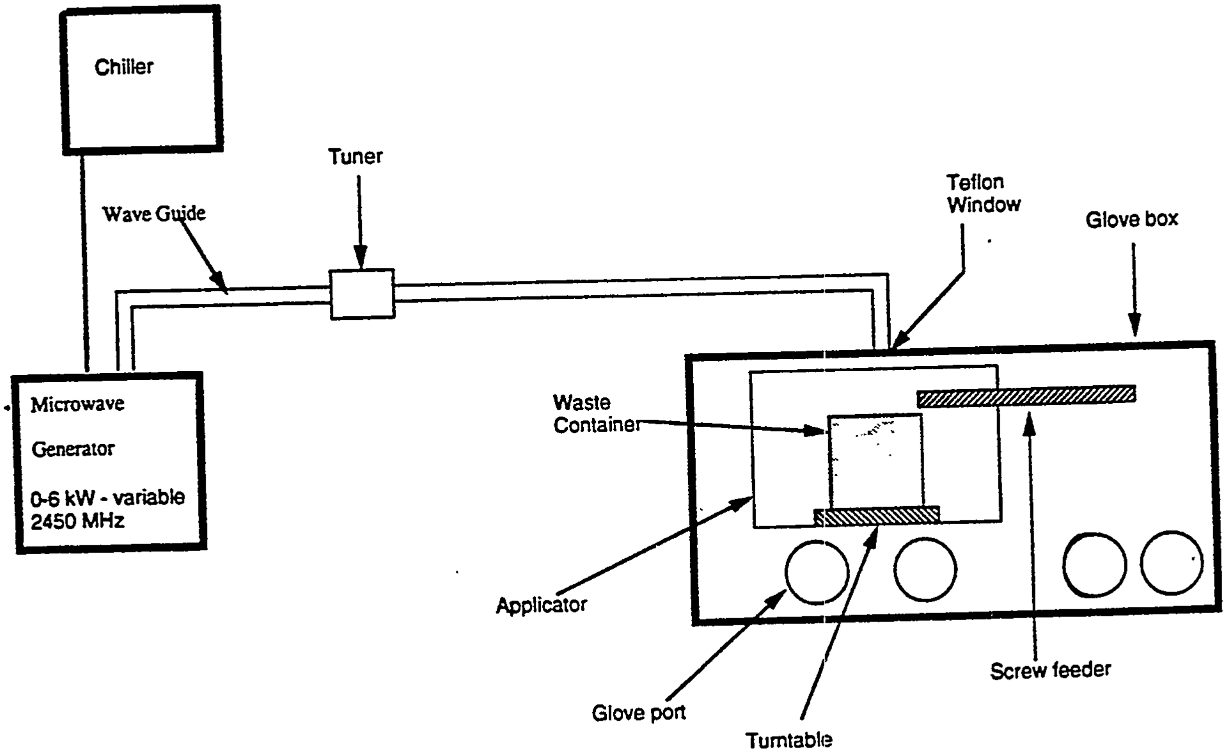

Figure 1: Schematic Diagram of Microwave Treatment System

RESIDUE AND OXIDE STABILIZATION

After the Rocky Flats weapons production mission was suspended in 1992, the site was confronted with the need to stabilize residues and plutonium oxide. Prior to that time, residues and plutonium oxide were accumulated for reprocessing. Conventional residue recovery technologies could conceivably have been employed to stabilize all of the residues. However, many of the facilities at Rocky Flats have been shut down and are no longer available for residue and plutonium oxide processing. As a result new processes are necessary to treat residues and plutonium oxide.

FIGURE 2
Large Scale Microwave Vitrification System With Chamber Open

Microwave heating is an attractive candidate for residue and plutonium oxide stabilization. It is a relatively mature technology with a 6 kW system currently operating in a plutonium contaminated glove box (see figure 3). It can be used as a generic heat source to vitrify, calcine, and react. It can produce waste forms that can readily be transported, stored, disposed of at the Waste Isolation Pilot Project (WIPP) or incorporated in the Defense Waste Pilot Facility (DWPF) via the can-in canister concept. Therefore, program emphasis has been shifted from LLMW and TRU sludges to residues and plutonium oxide. For these applications, criticality concerns make the smaller units (1 to 4 liters) more desirable than larger units (30 gallons). This fact is somewhat serendipitous, since the smaller units are much easier to control and will require very little additional development.

EXPERIMENTAL WORK

Sludges

Both surrogate and actual contaminated sludges have been processed in the bench-scale units.1,2,3,4,5 With the addition of a suitable source of silica, such as glass frit or crushed rasching rings, the resultant product is vitreous or crystalline with a specific gravity that can range above 3.0. Toxic Characteristic Leach Procedure, (TCLP) tests show that the resultant product is very resistant to leaching and would be a nearly ideal waste form. The plutonium also appears to remain bound up in the matrix material. TCLP studies were performed on surrogate sludges spiked with RCRA hazardous metals to levels representative of actual by-pass sludge at Rocky Flats. The metals of concern were chromium, nickel, lead, cadmium and silver. Several tests were performed with varying percentages of surrogate sludge to glass formers, simulating varying waste loadings. TCLP results demonstrated that for all spiked metals, the leachability could be reduced below the universal treatment standards for non-waste water as set forth in 40 CFR 268. In general leachability results were two to three orders of magnitude below the spiked sludge concentrations.3 Figure 4 is a photograph of the sludge waste form before and after vitrification.

Salts

Salts are not generally amenable to vitrification. However, the need for salt stabilization stems from reactivity concerns. Water that is tied up in the salts is available for hydrogen generation and the presence of reactive free metals such as calcium, sodium, and plutonium decrease the stability of the residue form. Heating in an oxidizing environment is an obvious method for stabilizing salts. Conventional stationary furnaces, without major modification, can perform this function in an eight hour shift. However, if a microwave 'melter' is employed, dramatically reduced cycle times can result. Because microwave energy directly heats the material and not the equipment or refractory, heating and cooling are rapid. Potentially, three or more batches per shift are possible. Microwave processing could be done in approximately one third the space for approximately one third the cost. Experimental work has been performed on electro-refining salt surrogates6 (Figure 5). Results of tests show that pure salt does not exhibit sufficient coupling with microwave energy to obtain temperatures necessary to oxidize the reactive metals. However, the addition of sodium carbonate, commonly used in salt stabilization as an oxidizing agent does result in sufficient coupling to oxidize the reactive metals and solidify the mixture.

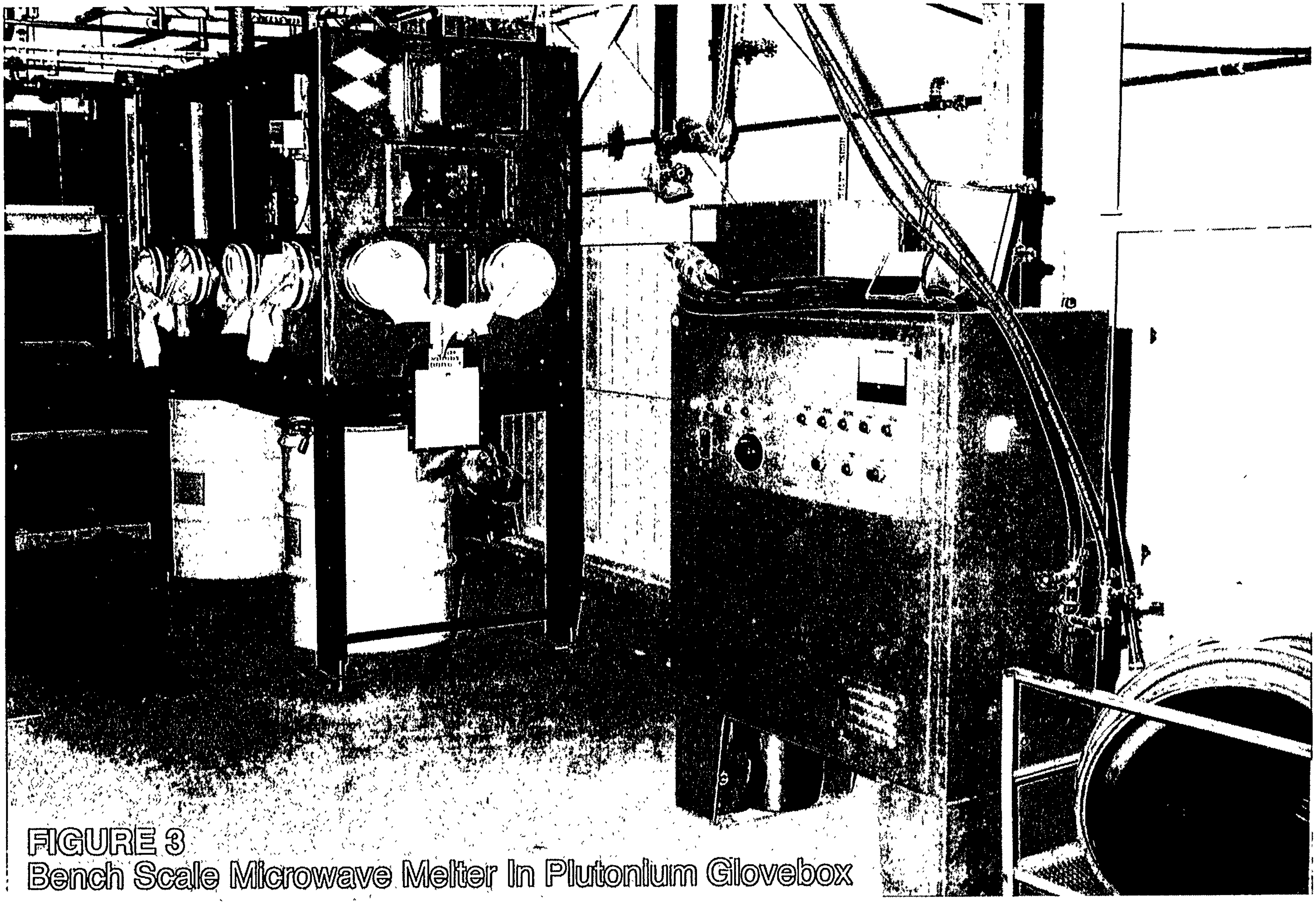

FIGURE 3
Bench Scale Microwave Melter In Plutonium Glovebox

Oxides

The Defense Nuclear Facility Safety Board (DNFSB) 94-3 requires stabilization of plutonium oxides at Rocky Flats. Microwave heating has been proposed to achieve this by calcining and/or vitrifying oxides for the same reasons that it was proposed for stabilization salts. The microwave process can heat the oxides faster and cheaper. Current microwave treatment systems were intentionally designed to be standard, uncomplicated equipment and therefore are unable to control temperature to the close tolerances that can readily be achieved in conventional furnaces. However, to achieve adequate stabilization, it has been determined that the oxide must be heated to a minimum of 1000°C. Since no upper temperature limit is necessary, the close temperature control available with standard furnaces is not required as long as the minimum temperature can be assured. Experimental results show that pure cerium oxide (surrogate for Pu02) does not couple with the microwave field well enough to achieve this required temperature. Cerium oxide heated in non-glazed ceramic crucibles did not couple with the microwave energy, while samples heated in glazed crucibles produced a mixture of sintered oxide held together with remelted glaze. Impurites in the actual plutonium oxide may help to increase the coupling or crucibles made from silicon carbide or graphite (which do couple with the microwave field) could be used for this operation.

Additional tests were conducted in which borosilicate glass was added to the cerium oxide to improve the coupling with the microwave field. These mixtures produced a vitreous product upon heating (see Figure 6). The vitrified material completely eliminated all cerium oxide fines. Mixtures of up to 60 percent cerium oxide have been vitrified. These surrogate experiments demonstrate that microwave treatment has the potential for stabilizing plutonium oxide in crucibles which are compatible for storage in 3013 containers. Since the same piece of equipment is versatile and can be used for several other stabilization operations, microwave technology is an economical and practical method of processing oxides.

Ash

Both surrogate and contaminated ash have been vitrified5. Ash makes an ideal feed for microwave vitrification. Its high silicon content allows it to be processed with little or no frit additive. Tests have demonstrated that up to 20% elemental carbon can be mechanically incorporated into the glass matrix. Microwave vitrification is a very attractive method for stabilizing ash.

Ion Exchange Resins

If a microwave 'melter' is available, it may be possible to use it to stabilize DNFSB 94-1 resins. Experiments in oxidation and pyrolysis are planned to determine the potential for this application. Some of the major technical questions that need to be resolved are:

1. What will happen when the resins are heated in air?
2. Will they spontaneously react due to their nitration?
3. Will the combustion products interfere with microwaving by causing arcing?
4. Are the pyrolyzed graphite resin beads a satisfactory storage/shipment form?

FIGURE 4
Surrogate Dried Sludge, Glass Frit and Vitrified Final Product

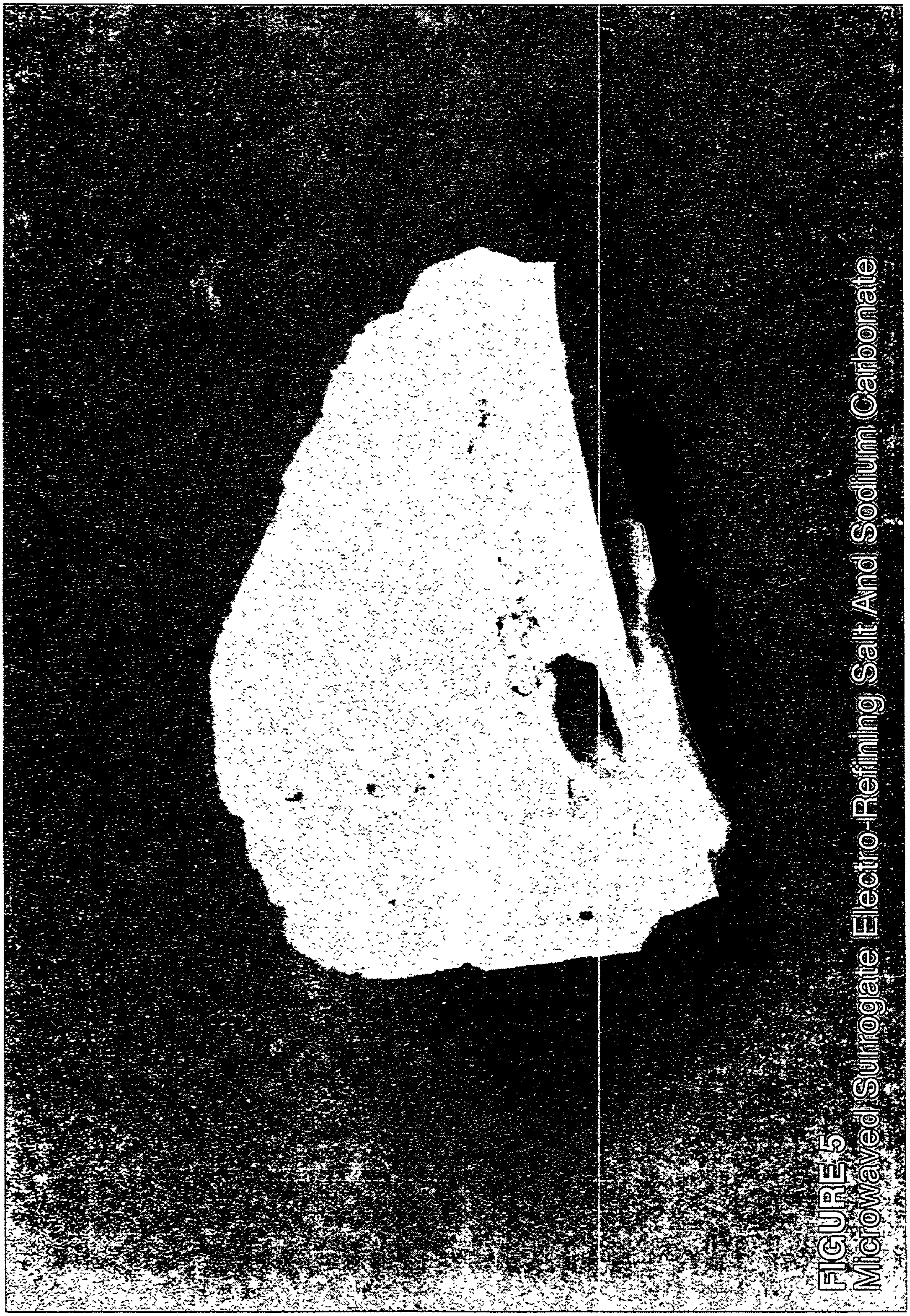

FIGURE 5
Microwaved Surrogate Electro-Refining Salt And Sodium Carbonate

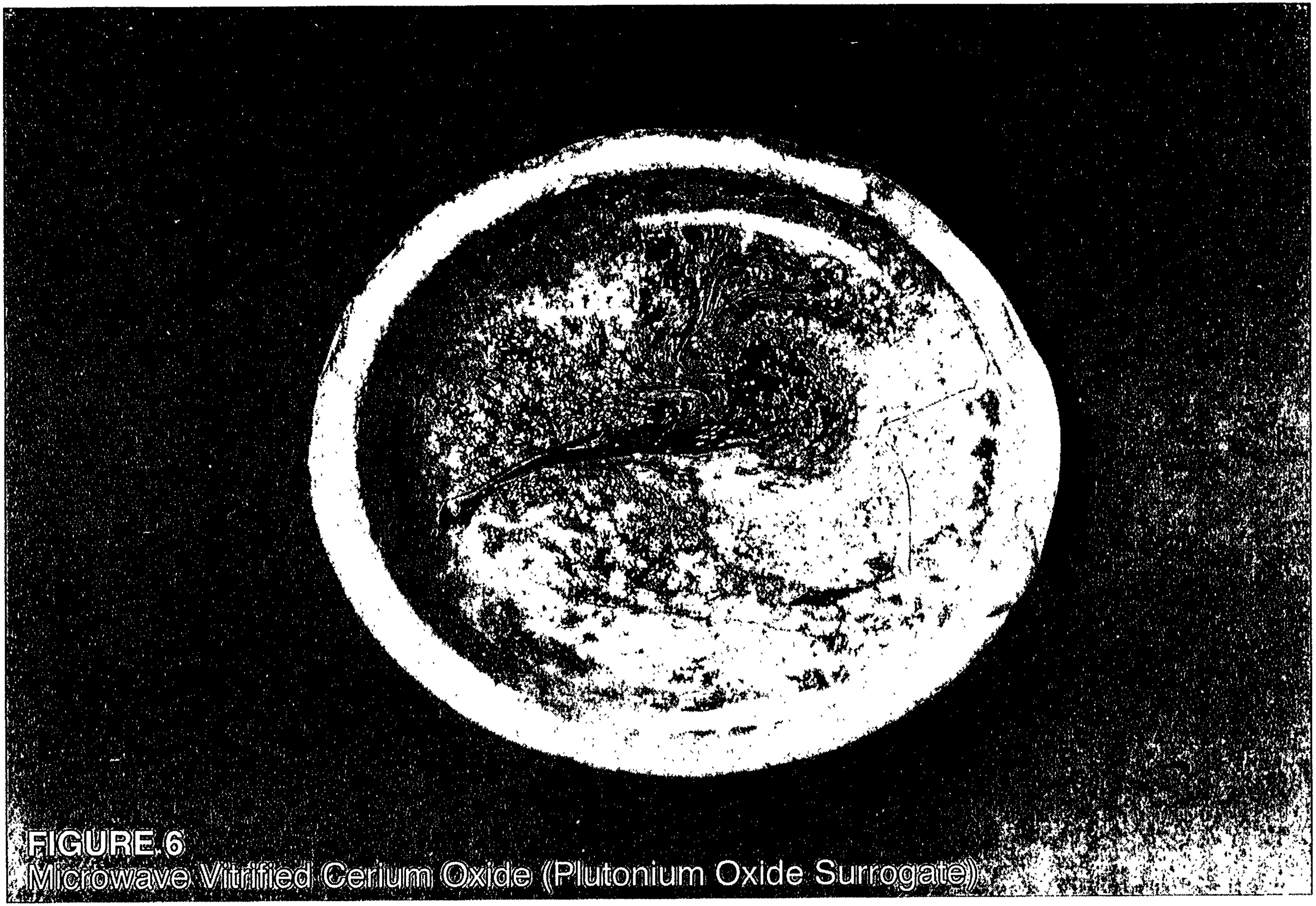

FIGURE 6
Microwave Vitrified Cerium Oxide (Plutonium Oxide Surrogate)

CONCLUSION

Microwave processing appears to be applicable to all of the residue forms studied and perhaps some others as well: (Sand, Slag and Crucibles, Raschig Rings, Graphite, Heels, Fire Brick etc.). The process was developed to treat LLMW and TRU sludges and consequently performs quite well on residue sludges. Initial results indicate that another good application is calcining and/or vitrifying oxides. Also salts could potentially be stabilized in the microwave melter. Testing with actual plutonium contaminated salts need to be performed to verify this. With little or no modification, a simple low-to-medium technology unit or duplicate units will be able to stabilize many different residue types.

However, there is one problem that has not been addressed. At Rocky Flats residues are stored in many locations and transporting them to one, or more, central microwave unit is an expensive process. One possible solution to this problem is to make a portable, modular unit(s).

A conceptual design for a prototype portable microwave system was prepared as part of the microwave technology transfer initiative. Additionally, a new small, portable microwave system has been designed for Safe Sites of Colorado (SSOC) (see Figure 7). The first physical unit should be available by the end of 3rd quarter FY96. This unit is being developed for processing residues in or near their storage location. This approach will save tremendous cost by eliminating or minimizing transfer operations.

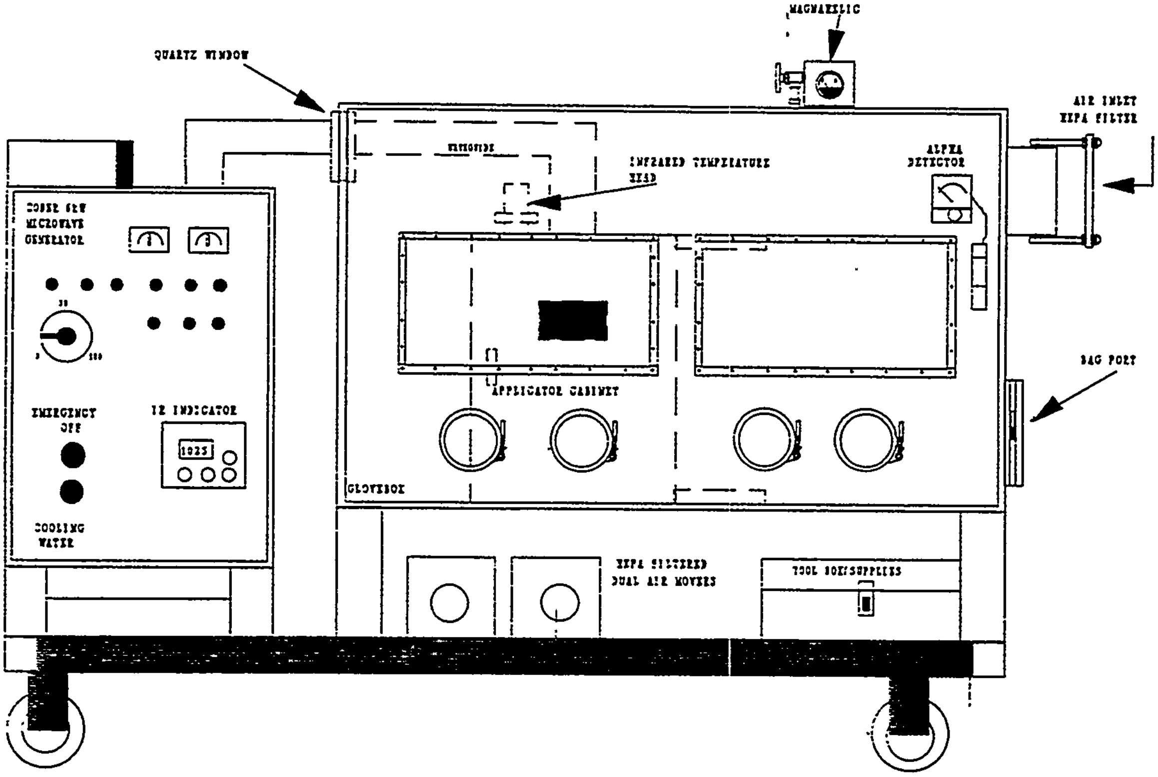

Figure 7. 6 kW Portable Microwave System

DISCLAIMER

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Vitrification of Rocky Flats Ash Followed by Encapsulation in the Defense Waste Processing Facility

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ABSTRACT

Approximately 10 to 20 metric tons of plutonium in the U.S. is in the form of scrap, residues, oxides, ash, metal, sludge, compounds, etc. Not all of this material is chemically stable or in packaging acceptable for storage. Thus, it constitutes a significant potential hazard to employees and to the public.

This paper describes a relatively simple concept for stabilizing most of this type of plutonium by converting it into encapsulated glass. A full-scale hot demonstration of the concept is proposed, in which Rocky Flats ash would be vitrified and sealed in small cans, followed by encapsulation of the cans in Defense Waste Processing Facility (DWPF) canisters with high-level waste glass. A team of experts from Savannah River Site (SRS), Los Alamos (LANL), Rocky Flats (RF), Argonne National Laboratory (ANL), and Pacific Northwest Laboratory (PNL) would provide oversight of the planning and execution of the demonstration.

In the overall concept, the vitrification processing (following the demonstration) would take place in shielded glove boxes at the four sites where most of the material is now stored. The small cans of glass would allow safe, secure, and monitorable interim onsite storage, or transportation to a centralized site. To permanently dispose of this material an additional step would be taken. The small cans of plutonium-glass would be mounted in a frame and placed in an empty DWPF canister which would be

filled with molten high-level waste (HLW) glass. The canister would subsequently be sent to the national HLW geologic repository.

The proposal described in this paper offers an integrated national approach for early stabilization and disposition of the nation's plutonium-bearing residues.

INTRODUCTION

During the decades of the Cold War, plutonium was produced in the U.S. to support nuclear weapons production. When the production of weapons was terminated, the production facilities, and to a lesser degree research facilities, were left with substantial quantities of plutonium-bearing residues, most of which had been destined for recycle and recovery. However, the production facilities that could be used to purify and/or stabilize these residues are shut down, leaving the current dilemma of how to stabilize, secure, safeguard, and dispose of them.

Two different reviews have been conducted to assess the risks associated with present storage methods for these materials, one by the Department of Energy[1] (DOE) and another by Congress's Defense Nuclear Facilities Safety Board[2] (DNFSB). The DOE assessed the "environmental, safety and health vulnerabilities of the entire DOE inventory of fissile materials". The principal conclusion was "Overall, the Department's inventory of plutonium presents significant hazards to workers, the public and the environment, and little progress has been made to aggressively address the problem."

The DNFSB Recommendation 94-1 to DOE concluded that "...imminent hazards could arise within two or three years unless certain problems are corrected.", and offered recommendations for correcting the problems that had been identified. In a subsequent report to the Congress[3], DNFSB concluded "the risks posed by those materials are more serious than appear to be recognized by DOE, and ...schedules for stabilizing ... need to be accelerated...".

BODY

The Material

A detailed accounting of plutonium inventories by type and location cannot be given in this report because of security classifications of some of the material. However, enough information has been released to conclude that the total amount of plutonium in various scrap and residue categories is between 10 and 20 metric tons, excluding classified material, fuels, and targets. This is the material addressed in this paper. The approximate distribution of these types of materials among DOE sites is shown in Table 1.

Table 1. Distribution of Residues Among DOE Sites

DOE Site	Wt. % Pu
Rocky Flats	64
Hanford	14
Los Alamos	12
Savannah River	8
7 National Labs	2

Lawrence Livermore National Laboratory prepared an unclassified report[4] that identified types of plutonium-bearing materials that need to be stabilized and disposed of. That report used data from DOE's Nuclear Materials Management and Safeguards System (NMMSS), and characterizes materials as follows, (excluding pits and fuel):

- Clean Metal Essentially pure plutonium, regardless of grade.
- Impure Metal/Alloys Impurities < 50% by weight.
- Clean Oxide PuO_2, with < 3% impurities.
- Impure Oxide PuO_2, with 3 to 50% impurities
- Compounds (other than oxide) Plutonium fluorides, carbides, chlorides, etc., with $\leq$ 50% impurities.
- Rich Scrap Metals, alloys, oxides, compounds, etc., 2% to 50% plutonium.
- Lean Scrap Metals, alloys, oxides, compounds, etc., generally < 2% plutonium
- Reactor Fuel, Unirradiated
- Reactor Fuel, Irradiated
- Miscellaneous

A recent DOE report[5], produced for accountability purposes, gives some unclassified inventory data for DOE sites, and in December, 1993 DOE Declassification Office declassified and released some relevant plutonium inventory data[6].

Several DOE sites group their plutonium-bearing materials in ways that are different from the NMMSS categories, above. They do this for specific purposes. For example, one of the ways Rocky Flats groups theirs is into five "buckets" based on possible methods to treat them for disposal. The "Ash Bucket", for example, contains not only ash, but all "ash-like" materials such as impure oxides, "sand, slag, & crucibles", firebrick, etc.

Rocky Flats ash is proposed for demonstrating the concept of onsite vitrification in existing glove boxes and final disposal at DWPF via the Can-in-Canister method, which is described in another paper in this conference. The scrap material in the Rocky Flats "Ash Bucket" contains about 1,200 kg of plutonium in a bulk weight of about 28,000 kg, giving an average plutonium content of about 4%; the maximum plutonium content in any lot is 43%. Most of the plutonium in this "bucket" is PuO_2, but the various lots contain a wide variety of other chemical compositions. Therefore, vitrification of a range of ash types would have value as a demonstration for other types of scraps and residues at Rocky Flats and elsewhere by establishing concentration limits of certain elements in the glass.

The approximate distribution of DOE residue materials by material type is shown in Table 2.

Table 2. Approximate Distribution of Residues by Type

Residue Type	Wt. % Pu in Type
Ash and Oxides	46
Metal and Alloys	20
Compounds with Cl, F	16
Combustibles	1
Miscellaneous & Sol'ns	17

Demonstration Proposal

The initial step is to prepare a proposal for a demonstration that includes the following distinct tasks:

- Document material types, quantities, compositions, locations, and packaging
- Document best judgment on what constitutes acceptable glass quality for disposition in either a geologic (HLW) repository or the Waste Isolation Pilot Plant (WIPP).
- Conduct small lab vitrification tests with samples of Rocky Flats ash to establish glass-making parameters, compositions, limits, etc. for candidate materials.
- Determine batching and blending strategies to eliminate or minimize pretreatment.
- Identify materials that would require more complicated pretreatments or other immobilization methods
- Select melter based on lab tests and disposal (Can-in-Canister) requirements.
- Procure and install equipment for demonstration in Rocky Flats glove boxes.
- Vitrify a selection of ash materials, destructively examining glass to validate quality.
- Vitrify a larger selection of ash materials, storing cans onsite for subsequent transfer to SRS.
- Transport cans to SRS and demonstrate Can-in-Canister encapsulation with hot HLW-glass.
- Provide best judgment cost and schedule for above.

Most, if not all, of the data on material types, etc. is available, and needs only to be consolidated in one report that presents the data in ways that are focused on this particular mission.

The section on "acceptable glass" has been drafted, and takes the position that the glass must meet the criteria for HLW glass disposal in Yucca Mountain.

Some lab vitrification tests on Rocky Flats ash have been, and are being, performed. Sufficient tests need to done to cover the full range of chemical compositions of materials in the "Ash Bucket". The tests will reveal melting characteristics, viscosity vs. temperature, characteristics of the glass product such as degree of cracking, strength, durability, dissolution rates, etc. The tests will establish chemical composition bounds for acceptable glass and melter conditions.

The full-scale demonstration runs at Rocky Flats will be conducted as Research and Development tests, with direct oversight by the inter-site team. A full complement of safety analyses, criticality assessment, training, and procedure preparation will be necessary to assure safe conduct of the demonstration. Routine melter feed preparations will include pulverizing, blending, roasting, analyzing and batching, with treatments tailored to specific feed batches to assure good material accountability and good quality glass. The first cans produced will be destructively examined to validate the glass quality. Subsequently, additional cans would be made for shipment to SRS for the second phase of this "hot" demonstration – final encapsulation of the cans in DWPF canisters with HLW-glass, called Can-in-Canister disposal option. The details of the Can-in-Canister option are presented in another paper in this conference.

Conceptual Process

An overview of the entire integrated national program of stabilizing residues, as currently envisioned, is given in Figure 1. The demonstration that is proposed in this paper is the initial phase of that program.

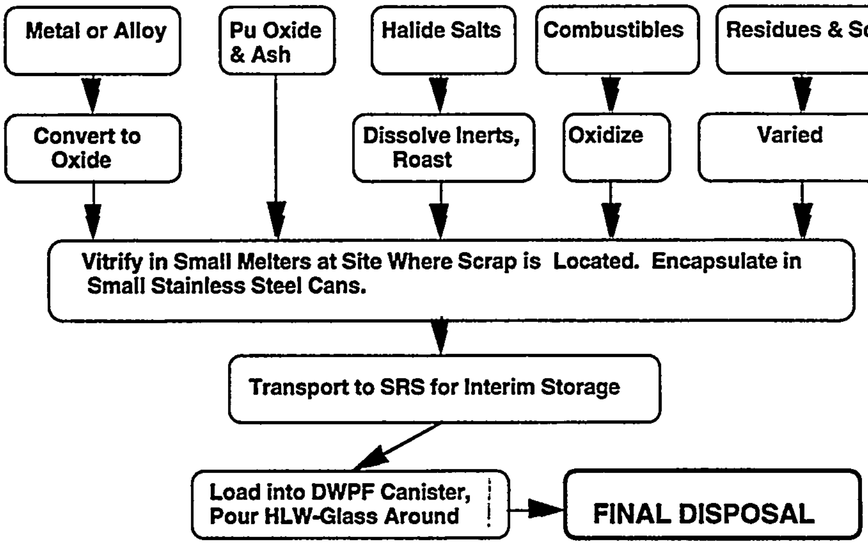

Figure 1. Overall Concept - Residue Stabilization and Disposal

The vitrification process, as currently conceived, is shown in a block diagram in Figure 2. Drums of residue would be unloaded into the processing glove box train. This may consist of a single lot of material, or more than one lot if blending is required. The residue will be unpackaged and a weighed batch will be pulverized and then mixed thoroughly with a weighed quantity of clean glass frit (coarse powder).

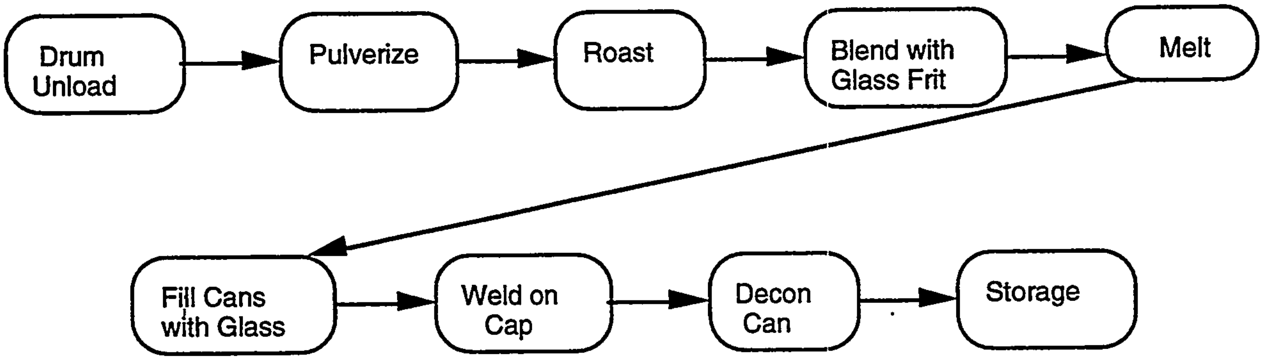

Figure 2. Vitrification Block Flow Diagram

Pulverizing the residue will achieve a particle size (to be determined in lab tests) to assure an acceptable dissolving rate in the molten glass. The residue will be roasted to remove moisture or any other volatile materials. A weighed quantity will then be thoroughly mixed with a weighed quantity of clean, dry, glass frit to produce the final melter feed batch.

The feed batch will be added to the melter and kept in a molten state for sufficient time to assure complete dissolution and homogenization of the components. The molten glass will be poured into stainless steel cans, nominally 3.5" x 15". After the glass has cooled, a top will be welded on each can and the exterior of the can will be decontaminated, probably by blasting with solid CO_2 to minimize secondary waste generation. The decontaminated cans will be removed from the glove box train for storage.

Benefits of Concept

Because this stabilization/disposal method would use existing facilities and spread the work out among the affected sites, it is likely to be the cheapest and fastest way of stabilizing DOE plutonium-bearing residues.

The plutonium-glass in the small cans would make a relatively durable package and be critically safe, relatively non-dispersible, and chemically stable. Material Control and Accountability of the plutonium in these forms during storage would be relatively simple, essentially a piece count. Since the cans of plutonium-glass would be virtually identical, regardless of their source, the same shipping cask and permit can be used for all material.

The concept is also flexible; the cans could accommodate other disposal options — WIPP for example — or, if national policy changed, the plutonium could be recovered for use by pulverizing the glass and dissolving the plutonium in nitric acid.

This concept offers a realistic and cost-effective merger of the goals of both affected DOE offices — Environmental Management and Material Disposition.

Issues

- Clear direction, including a statement of goals and expectations is needed.

- For this program to proceed expeditiously, a clear line of DOE authority and oversight is needed to provide for prompt decisions and flexible compliance with DOE Orders. Early involvement by DOE-EH, -RW, and the Nuclear Regulatory Commission is recommended.

- Authorization and funding is needed now to develop the proposal and initiate studies.

- Before the hot demonstration of DWPF encapsulation of the cans can begin, several things must occur:
  - Unambiguous approval of this waste form for geologic disposal. It would not be advisable to make HLW-glass canisters with no assured way of getting rid of them.
  - Upgrade security and safeguards at DWPF. The DWPF is currently a "Property Protection" area, handling no Special Nuclear Material.
  - Obtain favorable assessment on acceptability of DWPF's Glass Waste Storage Building for storage of this new waste form.
  - Reassess, and perhaps revise or create addenda for DWPF's National Environmental Policy Act (NEPA) documents.
  - Complete modifications and authorizations in F-Area to receive and store plutonium-glass cans, mount them in frames, place the frames in DWPF canisters, and weld on the canister top head and nozzle.

SUMMARY

This paper describes and proposes an integrated national approach for early stabilization and disposition of the nation's plutonium-bearing residues. The proposal is to vitrify residues at the major sites where they are now stored into a common plutonium glass form in existing facilities and with available technology. The primary container for the plutonium-glass would be a robust, seal-welded stainless steel can. This package would be safe, stable, secure, monitorable, and easily transportable. This program appears capable of satisfying the recommendations of DNFSB 94-1. Also, final disposition of this material could be achieved in a way that meets the criteria and objectives of the fissile material disposition (MD) program.

DISCLAIMER

REFERENCES

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2. Defense Nuclear Facilities Safety Board Recommendation 94-1 to the Secretary of Energy, May 26, 1994.

3. Defense Nuclear Facilities Safety Board Report to the Congress, February 16, 1995.

4. "Plutonium-Bearing Materials Feed Report for the DOE Fissile Materials Disposition Program Alternatives", W. G. Brough and S. T. Boerigter, UCRL-ID-120749, April 6, 1995

5. "Plutonium and Nuclear Materials Management and Safeguards System Materials – Materials in Inventory Report", Martin Seitz, USDOE, Office of Environmental Management.

6. DOE Office of Declassification Communiqué, Volume VI, Number 2, December, 1993.

Session Chair for Stabilization Standards, Technologies and Applications: Martin Seitz, DOE Office of Environmental Management
Tuesday December 12, 1995; 3:00 pm

Question / Comment 1:
John Bates, Argonne National Laboratory
These aren't anymore than comments, but under the disadvantages that you listed, Paul. With regard to the disadvantages, I just wanted to say that in the United States, we tend to look at our own problems. While we have recognized that the Russians certainly have experience in melter technology, I think we have to look at some of the other countries that certainly have experience in high level melter technology. Consider that to our advantage when we are evaluating the technology and its usefulness. Also, with regard to testing and evaluation of materials: currently, almost all the testing with high level waste is being done on fully radioactive or actinide-doped waste. For the High Level Waste repository, it makes no sense to do testing on surrogates. As a matter of fact, for the Plutonium Immobilization Program, it also makes little sense to do testing on surrogates. So, for both of those programs, the majority of the testing is being, and will be, done on actual HLW or plutonium containing materials. I think I have made two of the three points, but the one that I really want to get across is, and I think you would agree, is that in order to evaluate the behavior of the actinides and the materials, you really need to work with those materials. And I think that in the MD program, we are going to be doing that.

Question / Comment 2:
Larry Penberthy, Penberthy Vitrification
I made a comment about borosilicate glass being inadequate for the control of radioactive materials. I wrote a paper on that at the request of the Defense Nuclear Facility Safety Board. It is “The Rise and Demise of Borosilicate Glass for Rad Waste.” Now, that is a very pointed title there are copies of it out there on the desk, and I'm getting some more in case those are gone. Now, the question was raised immediately. "Well, if you don't like borosilicate glass, what do you advocate?" And the answer is the standard glass of 4000 years that has been made commercially and that is aluminosilicate glass. No boron in it at all. Aluminosilicate glass was the standard glass bottles, plate, everything exposed to the elements, and has been tested all that long. Some aluminosilicate glass was lost in vessels, that is, containers, domestic containers in ships sunk in the Aegean Sea 2000 years ago. And the alteration there in salt water was only about a half millimeter in 2000 years. That’s an alteration layer; it doesn't mean it's dissolved. Now, we know a lot about the aluminosilicate glass because it's been standard for so long in glass containers. The Atomic Energy of Canada, Ltd., however, went one better. They raised the alumina content by 2 or 3% and made some excellent glass. They called it nepheline cyanate glass that starting in 1956 and 1958, they made 30 blocks of this, 4 kilogram blocks. They buried these blocks in the wet soil where there was moving ground water. They have exhumed some of those blocks every 5 years. They've got something close to 35 years of testing. And there is actual waste being tested and the only effect they have found on the glass is a slight iridescence of the surface, which is an optical dimension of loss of material from the glass.

Question / Comment 3:
Leonard Gray, Lawrence Livermore National Laboratory
Mr. Chung, I think I heard you say that the material going into the 50 year can, would have to be totally free of organics. Is it possible to achieve that?

Answer:
Donald Chung, Scientech, Inc.
When we say organic, we mean moisture and plastics. Right now we're also excluding plastic coatings, things that are practical. I know if you are talking in the absolute sense of it, the concern has to do with gas generation from radialysis. Now, if you have a very minute amount on the inside of the can and it is radialyzed to gas, it is not going to be significant enough to pressurize the container to create a problem. Then you won't have to worry about it. But basically, the concern is not having any plastic bags, plastic components; moisture content has to be less than 0.5% by weight.

Gray:
Moisture less than, not totally free of it?

Chung:
Totally, in a practical sense.

Gray:
I'm pushing you a little bit on this, as you can tell.

Chung:
Yes, you are right. It is not totally.

Gray:
That raises another question about the can itself. I gather that it is not a simple matter to create this double layer 50 year can. As an outside observer, I would have thought it to be relatively simple, but it's evidently very difficult. What is the effect of the heat from welding the container shut on the contents, and how can you determine what the effect of the heat is on the contents, if you are actually sealing a container? Have you tested it with plutonium itself?

Chung:
Yes, several packages. Los Alamos has created two packages, thus far, that meet 3013 requirements. This being a twenty minute presentation, I did not go into a lot of detail. One of the requirements has to do with how much material that you can put in the container. Based on criticality and transportation limitations, you are limited to less than 4.5 kg. Also, the volume of the container, a primary container vessel, you are looking at little over 3 liters. So, if you could visualize something a little bit taller than this container right here of, I guess, 4.5 Kg of plutonium, there would be about 2 golf balls. Most of the container volumes are actually void. The welding of the container does not effect the materials itself. It is tig welded. I regret I do not have a picture with me to show it to you right now.

Gray:
I raise this question on behalf of someone that is not here who raises it every time he gets a chance. Bill will know that you have heard this question. I would like to have you go there and answer him. Thank you.

Chung:
Sure, I will be glad to talk to Bill afterwards. Thank you for the question.

Question 4:
Viktor Kushnikov, Institute of Inorganic Materials
I represent the Institute of Non-organic Materials. If I may, I would like to ask two questions of the two presenters and would also like to make a brief comment. The first question is for Mr. Rask. You have described the advantages of your technologies very well and have quite convincingly illustrated its end product in the form of a plate, a knife. Would you please be so kind as to satisfy the curiosity of Russian specialists and perhaps say a few words about the technology itself. The first question is to you; the second directed to Mr. Paul Krumrine.

When you were assessing, excuse me, when you speak of the advantages of the vitrification process, everything sounds marvelous! Yet, when you spoke of the negative aspects of this technology, you mentioned, for one, it's high cost. I would like to ask you, were you calculating only the cost of conducting the process itself or were you studying the whole system, from the beginning of the process to disposal? What about those cases when you are disposing of waste in a much smaller volume? This pertains in particular to liquid waste and especially to that waste which has a low weight volume. Thank you. And, if possible, I would like to make a comment later.

Answer:
William Rask, DOE Rocky Flats
We have shown the knife sharpening stone. Examples are to demonstrate that the technology is not new. It's in our industry; it's basically available technology that has been used. To get into all the various details of that, we have some issues in regard to patents. So, to get into very specific details, then we have to go through lawyers with our contractor at the site.

Question 5:
Martin Seitz, US DOE, Office of Environmental Management
Bill, let me ask a question of you: I think it refers to a comment that we had. You talked about the ceramification of that aluminum oxide. You didn't describe what the aluminum oxide looked like before the ceramification. I think that would help at least in describing the process. It was a powder. I don't know if you know if it was very small granular sizes, or whatever. But, maybe you can describe it. That would help me a little bit.

Answer:
William Rask, US DOE Rocky Flats
This particular sample was aluminum oxide, to represent the plutonium oxide. The gradient of powder was much like what we find in our oxide inventory at the site. We have roughly 3 tons of plutonium tied up in our oxides. So, it's represented from that site, the small fine particle.

Seitz:
So, it was poured into that stainless steel crucible and ceramified and then it comes out as that block?

Rask:
Yes, that is correct.

Question / Comment 6:
Martin Seitz, US DOE, Office of Environmental Management
This specific question is for Mr. Paul Krumrine on some issues of vitrification.

Answer:
Paul Krumrine, Waste Policy Institute
You ask about the cost associated with vitrification. Obviously, the costs can be on a broad spectrum. When you look at HLW, for instance, it is remotely handled with the labor that goes into some of those casks, I have numbers of up to a million dollars per cask. That is very expensive glass. The glass industry makes glass for about 7 cents a pound. So, there is a broad spectrum there. Certainly vitrification is more expensive compared to cementation, or grouting or some other type of technology. But there are ways of bringing that cost down. If you look to increase the waste loadings, what have you, if you look to mixing waste together like in the MAWS type process. There are many ways of bringing that cost down to a reasonable number. It can make vitrification a very attractive technology to employ.

Question / Comment 7:
Viktor Kushnikov, Institute of Inorganic Materials
Among the negative aspects, of high temperature processes are products such as Cesium, which can lead to undesirable volatility of Cesium. Those specialists, who work on the solidification of high active waste, know that this is one of the leading problems in the course of technical process implementation. Therefore, with the existing operational experience and the use of the industrial furnace at MAYAK. They include studies we are conducting with cold crucible technologies. We are paying a great deal of attention to this problem and already have experimental results and technical solutions, which provide for minimal Cesium volatility, even with temperatures exceeding 1,500 degrees C.

When you are speaking about the endless ways for the management of radioactive waste, specifically from the standpoint of vitrification and all the many options for technical solutions. As I understood it, based on your presentation, the induction melters possess maximum advantages and a minimum of shortcomings. At least that was my impression and you said here, that the U.S. is studying this melter in order to somehow evaluate it's applicability for the nuclear fuel cycle sites in the United States. My question and comment consist of the following. For quite some time now, I have heard about, and had frequent opportunities to discuss, this industrial melter with American specialists and I would like to ask this. When will the Americans finally show some genuine (financial) interest in this melter, instead of making promises, saying that the matter needs to be studied further or that additional consultations are needed on this matter, etc.? Thank You.

(Note: Session Chair, Martin Seitz suggested that we may want to have a follow-on discussion of this topic and deferred the question to Paul Krumrine.)

Answer:
Paul Krumrine, Waste Policy Institute
I'm not sure I'm the best person to respond to the total question that you have asked. But in my involvement down at Savannah River, I have been involved to some extent with, exposed to some the technologies that they plan to use for the TRU Waste. Down at Savannah River, they have about 15,000 drums of TRU Waste that they are looking to dispose of. Now, this hybrid Russian cobalt melter is one of the technologies that is being proposed at this point to use on that waste. It seems to be a good marriage, from what I have heard, from the technologists that are looking at it. Because it can operate at high temperatures, it's ideal for melting the drums without possibly having to open them and characterize every one. And the waste forms that you get from it are volume reduced, so there are a lot of benefits for doing that. As I understand it, the melter is being built in Russia and should be delivered to U.S. in early '96. It'll be first tested at Georgia Tech. and pending the results of those tests, and on further review by some other independent technical people, I would expect it'll be given a fair assessment. I can't say exactly when that would happen.

Answer:
Leonard Gray, Lawrence Livermore National Laboratory
Someone from Savannah River would be much better to answer this than me. We had Viktor at Savannah River yesterday, and we discussed the melter that is to be received at Georgia Tech. It is not the melter that Viktor is talking about. It is a different concept that the one that Viktor is talking about all together. It is a melter being built in Russia, so all the things you said was correct. It is just not the melter that Viktor is talking about.

Question / Comment 8:
Leonard Gray, Lawrence Livermore National Laboratory
[Dr. Gray expressed some concerns about the Research and Development Plan. It was weak in describing activities, schedules, milestones, budget, and is devoid of accountability for the projects. A more detailed implementation plan to augment this needs statement would be required.]

The next one is to Bill Rask. Bill, it's very easy to stand up and propose something when you are not looking at all the problems. I saw what you have presented. I find it very difficult to believe that glass is going to flow in there. Right now, we are concerned about whether or not the glass will flow around the cans, can-in-canister concept, much less try to get down in the very small pores that you will have in that material. I'm also concerned about the fact that the ground rules that we are trying to operate under, between EM and MD, is that EM will not do things to the plutonium that MD has to turn around and spend more money on undoing what you have done, such that we can disposition the material. I am very much concerned about the product you are showing being very difficult to handle in a downstream process . I really think that we need the two organizations really talking to one another and developing processes that can be handled downstream. Not handling materials, in such a way as to make it more difficult to process in a down stream process. I would like to talk to you about it. But, I think you are headed in the wrong direction.

Answer:
Robert Kenley, US DOE, Office of Environmental Management
Yes, we received your letter, Leonard, regarding your comment. There is a letter coming out of Hank Dalton's office to respond to you. We are meeting commitments that have to stabilize materials in three or eight years and we feel that we have evaluated technologies that fit within that time frame.

Martin Seitz, Session Chairman. Purpose of the Research Plan.
I am the Program Manager at the Department of Energy for the stabilization of plutonium solutions. As exemplified by the Research Plan, I believe the Department has successfully met the commitment made in the Implementation Plan for Recommendation 94-1. The commitment is that, by November 1995, the Research Committee will have assessed current research and development efforts against complex-wide nuclear materials stabilization needs, and identified areas where initial research and technology efforts are to be strengthened. Others can judge. As announced at this workshop, I have sent the Research Plan to everyone who has requested it. The Research Plan is not a contract from the Department to a laboratory for specific deliverables.

[The Office of Nuclear Materials Stabilization is developing a technology implementation plan to be completed by June 1996. The plan contains specific technical activities, milestones, and budget.]

I understand that you at Livermore have been developing a research plan for the Fissile Materials Program. I look forward to reviewing the plan when it becomes available.

Question / Comment 9:
William Rask, US DOE Rocky Flats
In regard to the form, one of the unique things about that particular product is we eliminate our risk today. No longer how long it's stored, we now have a solid article. If you want to proceed on further, in any form, whether it's an MOX fuel or whether we go into a vitrified product, it's amenable to either one of those. The worst, from the standpoint of an MOX fuel, would be the

grinding of it. You would have to particle size it and put binders with it, and do your compression at high temperature or take it as is, if it is purified enough right now, and you could make mox fuel simply in the future. So, it does not stop you from going forward; it's a matter of grinding, which we would have to do anyway with all of our oxides, or the density is about 60 to 65%. And when we do multiple impregnations of it presently, we have basically good flow of material through the product.

Question / Comment 10:
Martin Seitz, US DOE Office of Environmental Management
I would like to ask one question to Xavier Ascanio. We had heard one recommendation that we propose to develop standards for packaging curium and other actinide materials. I would ask Xavier if, in fact, his office is taking that on as the next challenge after the less than 50% criteria.

Answer:
Xavier Ascanio, US DOE, Office of Defense Programs
The answer is, Martin, I haven't really thought about that yet. But it certainly would fall within the range of things that we do, and we will consider that.

Question / Comment 11:
Pete Macedo, Catholic University of America
We do vitrification and opening packages is always a problem. So, if you decide to put the uranium oxide into a package, figure out how one ever gets vitrified sometime in the future. How does one open? How does one not contaminate the outside can so that you do not end up with a lot of extra other waste, so that you only have the inside can contaminated? Think of not just putting it in, but taking it out, because taking it out always causes a lot more waste.

Answer:
Donald Chung, Scientech, Inc.
That is a recognized problem. Thank you.

Question / Comment 12:
Larry Penberthy, Penberthy Vitrification
I have been working with glass for a very long time, four decades or more, now. We have a lot of fun with it. So when we have some glass, which we said was very good, we would give you a written guarantee for stability for 4000 years, based on what the Mesopotamians did, and the Greeks did 2000 years ago, the Venetians 1400 years ago. We'll give you a written guarantee on it. But to supplement that guarantee, let's make absolutely sure it's okay. So, we poured some of our glass, a stream of glass about a pencil size in dimension, molten glass, and we put it in there as a container some 8 oz. pickle jars. The pickle jars are encased in a little container that was heated, and so, up to the lower end needle temperature so the pickle jar would not fracture when the hot glass hit it. So we moved under the glass and then fill up the pickle jar, sprinkle a lot of the same kind of glass, pickle jar glass, crushed this time, and then fuse it down. And, now we have glass in glass. We have a glass that was guaranteed for 4000 years before it ever gets to the inner material. We thought it was a pretty good idea.

Closing Remarks:
I think this is a good working discussion. I think that at the moment we are not ceramifying materials at Rocky Flats, but it is an extremely interesting technology. This clearly is a dialogue, certainly, with the entire community in the US of stakeholders, including environmental management and disposition folks. I think it is quite within the bounds of the workshop here. Let me take a break here to make two announcements.

DISCLAIMER

The views expressed in this report are those of the author(s) or the individuals identified as making the remarks, and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

IMMOBILIZATION WASTE FORMS

SESSION CHAIR: LEONARD GRAY, LAWRENCE LIVERMORE NATIONAL LABORATORY

SURVEY OF GLASS PLUTONIUM CONTENTS AND POISON SELECTION

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ABSTRACT

If plutonium and other actinides are to be immobilized in glass, then achieving high concentrations in the glass is desirable. This will lead to reduced costs and more rapid immobilization. However, glasses with high actinide conconentrations also bring with them undesirable characteristics, especially a greater concern about nuclear criticality, particularly in a geologic repository.

The key to achieving a high concentration of actinide elements in a glass is to formulate the glass so that the solubility of actinides is high. At the same time, the glass must be formulated so that the glass also contains neutron poisons, which will prevent criticality during processing and in a geologic repository.

In this paper, the solubility of actinides, particularly plutonium, in three types of glasses are discussed. Plutonium solubilities are in the 2 - 4 wt% range for borosilicate high-level waste (HLW) glasses of the type which will be produced in the U.S. This type of glass is generally melted at relatively low temperatures, ca. 1150°C. For this melting temperature, the glass can be reformulated to achieve plutonium solubilities of at least 7 wt%. This low melting temperature is desirable if one must retain volatile cesium-137 in the glass. If one is not concerned about cesium volatility, then glasses can be formulated which can contain much larger amounts of plutonium and other actinides. Plutonium concentrations of at least 15 wt% have been achieved. Thus, there is confidence that high (≥ 5 wt%) concentrations of actinides can be achieved under a variety of conditions.

INTRODUCTION

The easing of tensions between the former Soviet Union and the United States has led to consideration of immobilization of the nuclear materials produced for national defense purposes. This work is focused on the actinides, primarily plutonium, which have been used in nuclear devices. An important driver for this is the concern that the material might be diverted, for example by a terrorist group, who could reconstitute the material into a crude weapon. This could constitute an even greater threat than the material does now. Thus, in the United States, the immobilization task within the Materials Disposition program is funding programs to look at glass and crystalline ceramics as hosts for these materials.

The vitrification working group (which includes representatives from Argonne National Laboratory, Battelle-Pacific Northwest Laboratory, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, and Savannah River Technology Center) is currently performing research and development to support the U.S. NEPA process, and to assist in selection of a reference process and glass composition, for detailed development and design.

Several process and facility options are being considered and are discussed in other papers in this workshop. For all of the options being considered, a high loading of actinide (≥ 5 wt%) in the glass is desirable. High plutonium loadings can mean a more rapid completion of immobilization. As a result, the period of heightened vulnerability for these materials would be shortened. A more rapid completion of immobilization also would lead to a lower total cost of the program. High plutonium loading can also lead to smaller, less expensive, facilities, particularly for storage of the material.

It must also be recognized that glasses containing large amounts of actinides, particularly Pu-239, also have undesirable facets.

- A glass with a high loading of plutonium is a more attractive target for diversion than a less-concentrated form.

- Processing may be complicated by the need to preclude the possiblity of a nuclear criticality in process vessels, and in the offgas system.

- Assuring that the form does not present a significant potential for criticality in a repository may be made more difficult.

For this paper, the options being considered can be consolidated as follows:

- Addition of high-level waste to make the immobilized actinides a less attractive target for diversion. The nuclear material would be immobilized in a heavily shielded facility, such as the Defense Waste Processing Facility at the Savannah River Site. This option has the least technical risk, because the technology is in hand to vitrify HLW.

- Immobilization of the actinides in a glass containing large amounts of radioactive cesium (or other high dose rate material), to achieve the same purpose. This option entails somewhat greater risk than the first option, because it requires development of new glasses, and potentially new types of melters.

- Production of a highly stable interim glass form. If it were decided to dispose of this material, the waste forms could then be interspersed with either HLW glass or another source of radiation, at a later date. This option potentially could be initiated more rapidly than the others (for example using existing remote facilities), and would make retrieval of the actinides unattractive from a processing standpoint. This option also has a larger technical risk than the first.

Thus, the vitrification working group is concentrating much of its efforts on determining how much plutonium can be dissolved by molten glass to support each of these options. As an important part of these efforts, the group is also working with the repository program to identify the potential for nuclear criticality in a repository due to glasses containing large amounts of actinides. In the sections below, the current state of our progress is summarized.

CRITICALITY PREVENTION STRATEGY

Assuring that a glass containing large concentrations of actinides does not have a significant criticality potential in geologic storage is a daunting challenge. Little or no credit can be taken for man-made structures or components during the long period of time during which such a glass might pose a significant criticality hazard. Thus, chemical means - nuclear poisons (neutron absorbers which can prevent nuclear criticality) - must be included in the glass formulation to prevent nuclear criticality.

Another important part of the challenge comes from the solubility of the actinides in repository groundwater. It is well-known that plutonium is only sparingly soluble in aqueous solutions representative of those in a repository. However, depending on the time frame of interest, the daughter of Pu-239 - U-235 - may pose a more significant risk of a nuclear criticality. Uranium is likely to be more soluble in oxidizing aqueous environments, where U(VI) predominates. However, under reducing conditions, UO_2 forms, which is insoluble in groundwater. Thus, the working group is including both water soluble and insoluble nuclear poisons in the glass formulation. Boric oxide is included in all of the glasses which might be used to immobilize actinides. For each of the options below, different species are used as insoluble poisons.

HIGH-LEVEL WASTE GLASS

Vitrification of a high-level waste is best thought of as a dissolution process. Glass-forming chemicals, either as unreacted chemicals, or as premelted glass frit, are mixed with the waste, and heated to 1150°C. At this temperature, the glassforming chemicals form a melt which dissolves the high-level waste (HLW). The melt is then poured into a canister, which is sealed for storage, and, ultimately, disposal. Ideally, the resulting glass is homogeneous - it contains no separate second phases, either crystalline or amorphous. Thus, the glassformer can be thought of as a solvent, which is formulated to maximize waste solubility and other important properties (such as chemical durability).[1]

Glassformer compositions for HLW have been developed to dissolve large amounts of HLW. In general, actinide solubility has not been a consideration. The concentrations of actinides in U.S. HLW glasses are very small. In the case of Savannah River Site's HLW, concentrations of plutonium are on the order of 10^{-2} to 10^{-3} wt% of the waste.[2] Thus, for HLW, the focus has been on developing glassformer compositions which can tolerate the variations in major non-radioactive components in HLW, such as sodium, iron, and aluminum.

As a result, little systematic work has been done on plutonium solubility in HLW glass. In Russia, at least one production facility has produced HLW glasses containing 1 wt% plutonium.[3] In France,[4] Germany, and the United States, glass doping studies, performed to examine radiation effects, have been the primary source of information about actinide solubility. In these studies, plutonium or other actinides have been added to glass batches to achieve concentrations in excess of 1 wt%.[5] Unfortunately, because of the focus of these studies, little effort was made to ensure that the plutonium was completely dissolved. Often, characterization of the amount and distribution of plutonium actually dissolved in the glass was incomplete. However, these studies all lead to the same general conclusions. For HLW glasses,

- The solubility of plutonium is limited to about 2 - 4 wt%.
- The solubility of thorium is approximately the same, or somewhat higher.
- The solubility of uranium is considerably higher, and depends on the redox state of the glass. The solubility of "UO2" is approximately 10 - 12 wt%; the solubility of higher oxides is higher.
- The actual solubility depends on the glass composition.

In perhaps the only study which specifically examined plutonium solubility in HLW glasses, Plodinec was able to dissolve up to 7 wt% PuO_2 in a HLW glassformer composition.[6] Although he could not determine an exact solubility for plutonium in HLW glass, he was able to provide an upper bound through visual examination of glasses produced from batches containing various concentrations of plutonium. At 4 wt% PuO_2, he concluded that the solubility of plutonium had definitely been exceeded. He also explored the effects of glass composition on plutonium solubility. He came to the following conclusions:

- Higher alkali contents in the base glass increased the solubility of plutonium. Higher boron contents also appeared to have the same effect, but he could not rule out a kinetic effect for boron.
- Waste content, and waste type, played a major role in plutonium solubility. It appeared that +3 cations in the waste were competing with plutonium for the same sites.
- Based on the emerald green color of the glasses which contained only glassformer and plutonium, it appeared that the plutonium was incorporated into the glass in the +3 state. If this is, in fact, true, it means that plutonium solubility will be affected by glass redox.

Plodinec also performed similar studies with uranium oxides.[7] In these studies, the solubility of "UO_2" was 10 - 12 wt%, and depended on the glassformer composition in the same way as indicated for plutonium. The solubility of more oxidized uranium oxides was at least 25 wt%. Again, the redox state of the actinide appears to play an important role in the solubility.

A typical American borosilicate HLW glass composition is shown in Table 1. This glass represents a blend of all of the HLW at the Savannah River Site (SRS). Soluble nuclear poisons include both lithium and boron. However, the criticality safety basis for the glass is based on the water-insoluble neutron poisons, iron and manganese.[8] If a HLW glass needed more than these species to prevent criticality, rare earth oxides could be included. The solubility of rare earth oxides, for example Gd_2O_3, in SRS HLW glass is approximately 10 wt%.

Table 1. Projected composition of initial DWPF glass. Minor components not included.

Component	Amount (wt%)
Al_2O_3	4.85
B_2O_3	7.66
$BaSO_4$	0.22
CaO	1.16
$CaSO_4$	0.12
Cr_2O_3	0.10
Cs_2O	0.08
CuO	0.40
Fe_2O_3	12.47
K_2O	3.47
Li_2O	4.40
MgO	1.36
MnO	2.05
Na_2O	8.58
Na_2SO_4	0.10
NaCl	0.31
NiO	0.74
SiO_2	49.61
ThO_2	0.36
TiO_2	0.65
U_3O_8	0.53

An important unresolved issue is whether insoluble poisons actually could be separated from Pu-239 (or U-235) through differential migration or colloidal transport. While there are no definitive data, the work of Bates, et al., is very encouraging.[9] A glass similar to that in Table 1 was doped with 2 wt% Pu, and an equimolar amount of of gadolinium. Longer-term, high surface area, static leach tests are being performed to provide source terms for glass performance under various conditions. Although the data is only preliminary, it appears that the release of plutonium and gadolinium to solution is occurring congruently. The plutonium and gadolinium are apparently both held in the leached layer on the glass surface, and are not involved in formation of any clay layer, which could form colloidal material.[10] If these observations are borne out by subsequent results, it would provide important evidence that an insoluble neutron poison in the glass can be relied upon to stay with the plutonium, and, hence, prevent a nuclear incident in the repository. Clearly, additional work is needed to determine whether differential migration of plutonium and neutron absorbers is likely, or even possible.

LOW TEMPERATURE CESIUM — ACTINIDE GLASS

As noted above, another option for immobilization of actinides from nuclear weapons is to include them in a glass which contains a high concentration of a gamma emitter. The high dose rate from Cs-137, for example, would make it more difficult to process glass forms containing high concentrations of actinides, and thus discourage diversion.

However, it is well-known that cesium readily volatilizes from glass melts. In order to retain it in the glass, the melting temperature should be kept as low as possible. The melting temperature for HLW glasses - 1150°C - represents a practical maximum for cesium retention. However, since the current generation of HLW glasses have not been formulated to contain either actinides or cesium at high concentrations, reformulation to contain both is being pursued. Since current HLW glasses are formulated to tolerate the non-radioactive components (Fe, Al, and Na) which dominate HLW, a new glass, which did not have to tolerate HLW, can be "tailored" to provide improved properties (for example, enhanced durability).

Ellison has formulated an alkali-tin-silicate glass which appears to achieve both goals.[9] It contains nearly 1 wt% Cs_2O, and has been shown to be capable of dissolving up to 7 wt% PuO_2. He used the following strategy to design the glass in Table 2. In order to achieve low melt temperatures, the glass must contain a significant alkali metal oxide concentration (including Cs_2O). As noted above, alkali also enhances the solubility of actinides in the melt.

Table 2. Typical alkali-tin-silicate glass composition for plutonium immobilization.

Component	Amount (wt%)
Al_2O_3	2.6
B_2O_3	13.7
Cs_2O	0.8
Gd_2O_3	3.5
K_2O	5.9
Li_2O	4.6
Na_2O	10.4
SiO_2	47.3
TiO_2	2.3
ZrO_2	6.0

Several studies have established that the corrosion of glass in a repository is highly dependent on the concentration of silicate in the groundwater. The difference between the saturation concentration and the actual concentration acts as a driving force for the dissolution process. The saturation concentration of silicon in solution increases rapidly with increasing pH, for pH values above 9. Glasses with large amounts of alkali tend to push the pH of aqueous solutions in contact with them to high values. Thus, high alkali glasses tend to be non-durable.

In order to suppress the potential high pH due to the alkali metal content, boron is included in the glass. Quadrivalent cations - Ti, Sn, and Zr - are also included in the formulation, to tie up the alkali in the glass. These +4 oxides also have positive free energies of hydration, and thus should render the glass inherently more durable.[11] Based on this reasoning, it is likely that plutonium itself also would enhance the durability of the glass. The concentrations of elements such as aluminum and calcium are minimized, because of the potential for secondary reactions which may precipitate silicon, and thus reduce its concentration in solution. This would result in a large difference between the solution concentration and the silicon saturation concentration, which would drive the reaction betwen glass and water to proceed more rapidly.

The glass in Table 2 has been shown to have a solubility of about 7 wt% for Pu, higher than that of HLW glasses. With further development, this is expected to go higher. Tests similar to those for the plutonium-doped SRS HLW glass have also been performed for this glass. The results indicate that this glass avoids formation of clay minerals usually found as corrosion products of HLW glasses. Again, plutonium and the neutron absorber, gadolinium, are found to behave similarly.

Thus, while short-term releases from the glass are slightly higher than those for the SRS HLW glass, the evidence indicates that this glass may be more durable in the longer-term. Further work is needed, however, before any definitive statement can be made.

The major unknown with this glass formulation is its processing behavior. While it appears to readily form a glass at 1150°C, the viscosity and volatility of cesium are not known. These must be determined before a process can be designed which employs this formulation.

INTERIM GLASS

As noted above, there may be significant cost advantages to begin immobilization of actinides as soon as possible. SRS expects to begin immobilization of unneeded process solutions containing americium and curium in about one year. A small high temperature "bushing" melter will be used to produce the glass. This glass will then be sent to Oak Ridge National Laboratory to be stored until needed as a raw material for production of more exotic isotopes, e.g., Cf-252. This can serve as a model of what might be done with unneeded plutonium.

According to this scenario, the plutonium is mixed with a glass-forming frit, either as a solution or as an oxide. This material is then melted, and poured into small (approximately 10 cm diameter x 40 cm high) canisters, for interim storage. At a later date, the plutonium could either be recovered (for example, to be made into a mixed oxide fuel), or included in a canister of HLW glass. A test is underway to demonstrate the feasibility of the latter process.

The glass type which is being used for development of this concept is based on the commercial "Löffler" glasses.[12] These optical glasses typically contain up to 55 wt% rare earth oxides. Their solubilities for plutonium should also be high, because the chemistry of the actinides and the rare earth oxides often are similar. The boron and the barium provide the "flux" which allows these glasses to be melted. PbO is known to form adherent surface layers during glass leaching, and thus should enhance glass durability.

A typical glassformer (frit) composition is shown in Table 3. Notice that these glasses have almost no alkali content. Thus, reaction of the glass with water generally produces near-neutral pH values. As a result, the saturation concentration of silicon in solution is lower than for typical HLW glasses (e.g., that in Table 1). This implies that these Löffler glasses should be more durable than typical HLW glasses. This is, in fact, observed. A Löffler glass containing 13 wt% Pu was 25 times more durable than the glass in Table 1 using the Product Consistency Test. In these tests, it was also observed that the Sm and Pu were released congruently to solution.[13] This further supports the earlier observations about the likelihood of insoluble neutron poisons remaining with plutonium.

Table 3. Typical Löffler glass composition for plutonium immobilization.

Component	Amount (wt%)
Al_2O_3	11.1
B_2O_3	6.1
BaO	3.6
La_2O_3	9.4
PbO	15.1
SiO_2	35.0
Sm_2O_3	19.7

Solubilities of actinides in this type of glass are currently being determined. Up to 20 wt% ThO_2 or UO_2 can be dissolved in this glass. Melts have been formed containing up to 2 wt% of a mixture of americium and curium, with no evidence that a solubility limit was reached. Up to 15 wt% plutonium has been dissolved into a composition similar to that in Table 3.

For both plutonium and thorium, the apparent solubility when the actinide nitrate is used as the starting material is greater than when the oxide is used. At this time, it is not clear whether this effect is due to the oxidation state of the glass melt, or to the slow kinetics of dissolution of the oxide. Tests are underway to determine the cause.

This family of glasses shows great promise for immobilization of actinides. However, long-term glass / water interaction testing is needed, to develop a better understanding of how these glasses will behave during geologic disposal.

SUMMARY AND PATH FORWARD

From the preceding, it is clear that the solubility of actinide elements in glass varies widely, and depends on both the actinide and the type of glass. Plutonium solubilities are in the 2 - 4 wt% range for borosilicate high-level waste glasses of the type which will be produced in the U.S. This type of glass is generally melted at relatively low temperatures, ca. 1150°C. For this melting temperature, the glass can be reformulated to achieve plutonium solubilities of at least 7 wt%. This low melting temperature is desirable if one must retain volatile cesium-137 in the glass. Plutonium concentrations of at least 15 wt% have been achieved in Löffler glasses, which are melted at high temperatures. Thus, there is confidence that high (≥ 5 wt%) concentrations of actinides can be achieved under a variety of conditions.

For each of the types of glasses discussed here, further work is needed. If actinide contents in excess of 5 wt% are needed, and a decision is made to use an existing HLW vitrification facility, then reformulation of the glass will be necessary. While it appears that there is a family of glasses (the alkali-tin-silicates) which is compatible with existing HLW processing equipment, important processing characteristics of this family of glasses must be determined. The high temperature Löffler glasses have high solubilities for the actinides, but their production is as yet undemonstrated. Use of a "bushing" melter with its long commercial history for production of this glass reduces the degree of technical risk. The campaign to immobilize americium and curium at SRS should eliminate any questions about the viability of this approach.

For all of the glasses, work currently underway is providing important evidence that inclusion of rare earth oxides (e.g., gadolinium or samarium) in the glass formulation may provide the means to eliminate concerns about nuclear criticality in the repository setting. These species, which are insoluble in water, apparently behave similarly to plutonium, and appear to stay with plutonium during interaction of the glass with water. While further testing is needed, these preliminary results are very encouraging.

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The Role of Troublesome Components in Plutonium Vitrification

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ABSTRACT

One option for immobilizing surplus plutonium is vitrification in a borosilicate glass. Two advantages of the glass form are 1) high tolerance to feed variability and, 2) high solubility of some impurity components. The types of plutonium-containing materials in the United States inventory include: pits, metals, oxides, residues, scrap, compounds, and fuel. Many of them also contain high concentrations of carbon, chloride, fluoride, phosphate, sulfate, and chromium oxide. To vitrify plutonium-containing scrap and residues, it is critical to understand the impact of each component on glass processing and chemical durability of the final product. This paper addresses glass processing issues associated with these troublesome components. It covers solubility limits of chlorine, fluorine, phosphate, sulfate, and chromium oxide in several borosilicate based glasses, and the effect of each component on vitrification (volatility, phase segregation, crystallization, and melt viscosity). Techniques (formulation, pretreatment, removal, and/or dilution) to mitigate the effects of these troublesome components are suggested.

INTRODUCTION

Vitrification is a means by which plutonium-containing materials are converted to a durable, homogeneous, easily accountable glass form. This allows the incorporation of both neutron absorbers and/or proliferation deterrents in the same homogeneous form as plutonium. Vitrification is considered as an option for both safe storage and disposal of plutonium-containing feeds[1].

The plutonium immobilization program under the fissile materials disposition (MD) office currently considers three vitrification options[2]: can-in-canister (C-C), greenfield (GF), and adjunct (ADJ). For each option, a candidate glass composition has been selected: Pu10A for C-C, Pu10B for GF, and Pu10C for ADJ (see Table I). These compositions were designed for incorporation of high plutonium concentrations, except for the adjunct melter feed which was designed to vitrify high-level waste (HLW) at the Savannah River Site (SRS).

Some plutonium-containing materials in the United States inventory also contain significant quantities of carbon, chlorine, fluorine, phosphate, sulfate, and chromium oxide. These troublesome components may limit the loading of plutonium-containing materials in glass and/or hinder glass processing. These troublesome components are likely to cause problems to a different extent in different melters. Therefore, the presence of troublesome components in the feed will affect melter selection. Furthermore, the volume of a feed to be vitrified is also an important factor, particularly for species with a high tendency towards phase segregation and high volatility, such as chlorides and sulfates. In order to mitigate the effects of these troublesome components, one or more of the following strategies may be considered.

- The material can be blended with other feeds to dilute the troublesome components.
- The material can be pretreated to remove troublesome components.
- Glass compositions can be designed specifically for the incorporation of the material.
- The material can be added to glass in low enough loading to not exceed the solubility limit of the troublesome component(s).

Whether the above techniques or other procedures are used for the incorporation of the troublesome components in glass, it is useful to know their solubility limits in the glass. This paper addresses the following aspects: 1) solubility limits of troublesome components in borosilicate glasses, including Pu10A plutonium candidate glass, 2) glass compositional effects on the component solubility limit and interaction between phosphate and sulfate, 3) the effects of the troublesome components on glass processing, and 4) mitigation techniques in dealing with these troublesome components.

PLUTONIUM RESIDUES

Information regarding compositions of those plutonium residues is limited. Table II shows the compositions of one type of plutonium-containing materials: Rocky Flats incinerator ash and ash heel[3,4], IDC419 and IDC428 (IDC-item description code). The components of interest shown in boldface in Table II are:

- **Carbon**[3] is mainly from graphite crucibles, molds, scarfings, fines, filters, and heels. Ash/ash and soot heels also contain carbon (i.e., 5 to 40 wt% C) in addition to SiO_2, Al_2O_3, CaO, Fe_2O_3, and Na_2O.
- **Chloride**[4] is from pyrochemical operation which uses molten chlorides (such as NaCl, MgCl, CaCl, or KCl) to purify plutonium metal, reduce plutonium oxide, and remove plutonium from residue salts.
- **Fluoride**[4] is from contaminated plutonium fluorides (mostly PuF_4), such as grease fluoride at Rocky Flats Environmental Technology Site (RFETS), which was generated by plutonium fluoride in contact with grease from the fluorination equipment. Fluoride also comes from slag which consists of chunks of calcium fluoride containing calcium metal and unreacted PuF_4.
- **Phosphate**[5] and **Sulfate**[5] may be originated from bismuth phosphate cycle for the recovery of plutonium, in which $BiPO_4$ is used as a specific plutonium carrier and sulfuric acid (H_2SO_4) is added during the cycle to prevent the precipitation of uranyl phosphate.
- **Chromium Oxide**[3] is originated from fire brick used to provide a heat and corrosion resistant liner for the firebox and after burner. The spent fire brick was subject to a mechanical scarfing process to remove plutonium bearing surface layer.

As shown in Table II, the concentrations of these troublesome components in the plutonium-containing materials vary significantly. Therefore, it is fundamental to determine their solubility limits in the glass and their roles in plutonium glass processing.

SOLUBILITY LIMITS

A method of one-at-a-time, single component addition was used to determine the solubility limit of a component of interest in several borosilicate glasses which are formulated for plutonium immobilization (PI), low-level waste (LLW), and HLW (see Appendix A). The solubility limit of each component was defined by its concentration in the glass, at which level both quenched and annealed samples are transparent, amorphous to x-ray, and no detectable second phase(s) under the optical microscope. The samples, 100 g of each, were fused for 2 hrs in a Pt-10%Rh crucible covered with a Pt-lid at the vicinity of the glass melting temperature (defined by the melt viscosity of 5 Pa·s for low-melting glasses [1150°C] or by 10 Pa·s for high-melting glasses [≥ 1300°C]). Since no controlled atmosphere was imposed on the melt during glass fusion, each melt is considered to be in a steady-state with the component of interest, rather than in an equilibrium state.

Table III summarizes the solubility limits of chlorine, fluorine, phosphate, sulfate, and chromium oxide in the borosilicate glasses investigated (the solubility limits of carbon in plutonium candidate glasses are currently under investigation). It can be seen that glass composition generally affects the component solubility limit. According to data obtained for L6-5412 glass, the melting temperature minimally affects the solubility of each component in the glass.

In terms of the compositional effect, the solubility limit of fluorine increased with the removal of CaO as seen when comparing fluorine results between L6-5412 with 5 wt% CaO and L4-9012 without CaO. Phosphate solubility is also significantly higher in L4-9012 glass without CaO. The change in concentrations of Na_2O and Al_2O_3 has an additional effect on phosphate solubility[6]. It can also be found in this study when comparing the phosphate solubility of Pu10A with that of L4-9012. (Note: The source of Na_2O in Pu10A glass came from sodium phosphate employed).

The phosphate solubility is also related to Na_2O/P_2O_5 ratio. Recent nuclear magnetic resonance (NMR) spectroscopic studies[7] demonstrated that in sodium-silicate glasses, PO_4^{3-} exists as an isolated entity in the spatial of the silica network, bonded with three Na^+ ions. Accordingly, it seems that the stability of phosphorous depends on the availability of sodium in the glass. On the other hand, these $(Na^+)_3$-(PO_4^{3-}) groups tend to form clusters once concentration reaches the saturation level, resulting in the precipitation of Na_3PO_4 as previously reported in LLW glasses[8].

The solubility limit of sulfate was shown to be dependent on glass composition as characterized in terms of nonbridging oxygen (NBO) and bridging oxygen (BO) in the glass network[9] provided that other glass melting conditions are the same, such as oxygen partial pressure and melting temperature. The data in Table III show that the difference in the sulfate solubility among those glasses can be as high as 100%. Based on the concept of NBO-BO, the results of our preliminary study(a) showed that a trend of sulfate solubility limit versus $[NBO]^2/[BO]$ (the bracket refers the concentration by mol%) exists in the glasses as depicted in Figure 1. Glass basicity was shown to affect the sulfate solubility as well[10]. However, the sulfate solubility data significantly deviated from the theoretical expectation[10]. Furthermore, the sulfate data (see Table III) for complexant concentrate waste (CCW) glasses investigated here exhibit various trends with respect to the glass basicity number[11].

Sulfate and phosphate were found to interact with each other resulting in glass amorphous phase separation; the interaction depends on the extent of saturation of both species[12]. As a result, it reduces the solubility limits of both phosphate and sulfate in the glass. However, phosphate-sulfate interaction seems to prevent the formation of crystalline Na_2SO_4 in the melt even though the sulfate concentration level was in excess of the solubility limit[12]. Higher values of apparent sulfate solubility determined in

CCW4-2 and CCW4-3 glasses (containing 3.5 and 8.0 wt% P_2O_5, respectively) are suspected to be associated with phosphate-sulfate induced phase separation[12].

(a) 1995, unpublished work by H. Li, M.H. Langowski, and P. Hrma.
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For chromium oxide, solubility data in borosilicate glasses are limited. The results shown in Table III suggest that boron is beneficial for chromium solubility. The presence of borate compounds was also shown to markedly increase the chromium solubility in the glass[13].

Although carbon solubility limits in the borosilicate glasses employed in this study are not available, numerous literature data on carbon dioxide in silicate and borate melts exist, which provides the current knowledge of how carbon dissolves in the glass and the solubility dependency on glass composition, melt temperature, and oxygen partial pressure. For both silicate and borate system, the solubility of carbon was shown to increase with glass basicity or alkali content at a given temperature and partial pressure of CO_2[14-16]. The mechanism can be described in terms of[14,16]:

$$CO_2\ (\text{gas}) + 2O^-\ (\text{NBO}) \Longleftrightarrow CO_3^{2-}\ (\text{melt}) + O^0\ (\text{BO}). \qquad \textbf{(1)}$$

The majority of carbon dissolved in the glass network is in a form of CO_3^{2-} according to the previously published Raman spectroscopic data[17]. Assuming the reaction **(1)** is valid for borosilicate glasses, carbon solubility limit is expected to be influenced by the concentrations of NBO and BO as well. However, the CO_2 solubility data reported are for those molten glasses in an equilibrium with carbon dioxide/oxygen atmosphere. For processing plutonium glasses, carbon, rather than carbon dioxide, is to be introduced into the melt; the extent of carbon oxidation depends on the batch reaction rate. Additionally, the melt may not reach an equilibrium state for a practical time period in the vitrification process. In either case, higher concentration of total carbon in the glass is expected.

ISSUES CONCERNING WASTE VITRIFICATION

Volatility

Figure 2 displays the measured concentrations of chlorine, fluorine, phosphate, sulfate, and chromium oxide in the glass versus their nominal concentrations at 1300°C, 1350°C, and 1400°C. All melts were mechanically stirred after the first hour of melting to achieve compositional homogeneity. Within experimental error, phosphate and chromium oxide can be completely retained in the glass. On the other hand, volatility of chlorine, fluorine, and sulfate was found to be significantly high, depending on the extent of their saturation levels. The volatility of chlorine, sulfate, and fluorine increases with increased concentrations in the batch, among which chlorine volatility seems to be the greatest. It can be seen that there exists a concentration threshold for chlorine and sulfate, above which these two species tend to completely evaporate from the melt. Although fluorine loss increases with increased fluorine concentration in the batch, its retention in the melt is also higher. The mechanism of fluorine loss at these temperatures may be convection currents driven by surface tension and density gradients[18]. As will be discussed in the next subsection, volatilization of chlorine or sulfate involves several sequential steps: molten salt segregation, accumulation of the segregated phase on the melt surface, and subsequent evaporation.

Volatility of carbon in borosilicate glass is expected to be analogous to that of sulfate, depending on batch reaction rate, temperature, and oxygen partial pressure. In addition, carbon is a strong reductant. With the presence of carbon and sulfate in the batch, melt foaming may be a problem when sulfate (S^{6+}) reduces to sulfide (S^{2+}) and SO_2 gas releases from the melt. A study of carbon influence on vitrification of plutonium candidate glasses is currently in progress.

Phase Segregation, Crystallization, and Amorphous Phase Separation

Once the troublesome components in the glass are in excess of their solubility limits, glass inhomogeneity falls into two categories: phase segregation occurred at the melt temperature and amorphous phase separation or crystallization occurred during the melt cooling. Table IV summarizes crystalline phases identified by x-ray diffraction (XRD) analysis in the glasses studied.

For Pu10A composition, chlorine, fluorine, and sulfate were found to cause glass amorphous phase separation once they were over-saturated in the glass, which occurred during the melt cooling. However, for L6-5412 and L4-9012 compositions, molten salt segregation of NaCl or Na_2SO_4 was found at the melt temperature[8], and the bulk of glass appeared to be clear without exhibiting amorphous phase separation. Molten salt segregation initiates in an early stage of glass melting[8,18]. It has several consequences: de-stabilizing glass melting rate, increasing melt volatility for chlorine and sulfate (as discussed earlier), and extracting other species from the coming feed materials (assuming a continuous melter is used). Formation of phosphate-rich phase was found on the melt surface when molten sulfate segregated from the melt of L6-5412 glass with sulfate in excess[8]. Sulfate induced phosphate segregation was also reported in other HLW glasses[19]. Fluorine in L6-5412 and L4-9012 glasses induces either crystallization of NaF and/or CaF_2, or amorphous phase separation, which depends on the extent of fluorine saturation and glass composition. In either case, the second phase was formed during the melt cooling.

For phosphate, agglomerates of $CePO_4$ were found in Pu10A glass, which formed at the melt temperature. The segregated $CePO_4$ phase remains undissolved after 2 hrs at 1450°C, which was either on the melt surface or at the bottom of the melt. On the other hand, crystalline Na_3PO_4 uniformly precipitated in the bulk of L6-5412 and L4-9012 glasses with phosphate in excess of its solubility limit; however, no phase segregation was observed[8].

Precipitation of Cr_2O_3 usually occurred once concentration in the glass exceeded the solubility limit[8]. The precipitation appears to take place during the melt cooling. No settlement of Cr_2O_3 crystals was evident in Pu10A glass nor in L6-5412 and L4-9012 glasses[8]. However, in glasses with Fe_2O_3 or MnO, or NiO at a elevated concentration level, spinel crystals tend to form in the glass with relatively high concentration of Cr_2O_3 at melt temperature; agglomeration and settlement of spinel crystals may occur.

Glass Melt Viscosity

Glass melt viscosities were determined in L6-5412 and L4-9012 glasses with separate additions of chlorine, fluorine, phosphate, sulfate, and chromium oxide at or below their solubility limits (the concentrations at the solubility levels are in bold face). Table V summarizes the glass melting temperature (T_{10}) for L6-5412 and L4-9012 glasses, which is defined by melt viscosity of 10 Pa·s. In both glass systems, T_{10} is significantly decreased with addition of fluorine, but increased with addition of chlorine or phosphate. Interestingly, the presence of sulfate or chromium oxide in the glass increased T_{10} in L6-5412 glass, but slightly decreased T_{10} in L4-9012 glass. Overall, the effect of fluorine on glass viscosity or melting temperature was the most significant.

The role of fluorine in silicate glasses is still in debate regarding whether it replaces BO or NBO, or stays as free ions in the network[20-22]. A significant reduction in glass viscosity by fluorine provides strong support that fluorine should not act as free ions in the network. Instead, its substitution for BO, forming Si-F bonds, is favorable, resulting in the de-polymerization of the network and, therefore, the reduction in glass viscosity.

MITIGATION TECHNIQUES

Depending on compositions of plutonium-containing scrap and residues, mitigation methods should be considered to deal with some feeds containing excessive amounts of troublesome components.

Glass Formulation

Formulating a glass composition with a higher solubility limit for the troublesome component(s) is one choice. Incorporating a higher concentration of the troublesome component will decrease the overall volume of the final vitrified product and, therefore, decrease the cost for plutonium immobilization and disposal.

If a designated glass frit cannot tolerate a feed with high concentrations of troublesome components, several mitigation techniques can be considered. The mitigation strategy will result from the evaluation of processing constraints and cost of both feed processing and product storage. Several mitigation techniques are listed below.

Feed Blending

The level of troublesome minor components can be adjusted by blending feeds with excessive levels of troublesome components with those containing these components at low concentration to obtain a blend with an acceptable composition. Therefore, the blended feed can be vitrified without reducing feed loading. Although feed blending can reduce concentrations of troublesome components, it may create a feed that contains all of troublesome components at elevated concentrations. However, the effect of mutual interaction between different troublesome components on vitrification process has not been well studied. Problems are likely to arise as a result of interactions between these components. For example, increasing amount of sulfate in the batch containing phosphate was reported to induce phosphate segregation during vitrification of HLW[19].

Feed Pretreatment

The removal of troublesome components is another option. For example, graphite can be removed from a dry feed by oxidation to CO and CO_2. Other species, such as chloride, fluoride, and sulfate, can be decomposed or evaporated at a high temperature. Water washing may be an alternative to remove chloride, fluoride, and sulfate. Phosphate and chromium oxide, however, cannot be removed from the feed in a gaseous form nor by water washing. For these species, wet chemical process may be feasible. However, removal of troublesome components using either water or chemical solution(s) generates secondary waste streams in which radioactivity is also an important issue.

Reducing Feed Loading

Reducing feed loading is the easiest method of controlling the concentration of any troublesome component to meet processing requirements, to minimize potential vitrification problems, and probably to reduce the cost for off-gas treatment. However, the volume of the final product increases as well as the overall cost for vitrification and storage.

SUMMARY

Efforts to determine and understand solubility limits of the troublesome components (chlorine, fluorine, phosphate, sulfate, and chromium oxide) have begun for borosilicate glass candidates for the immobilization of plutonium-containing scrap and residues. The results obtained from this study demonstrate that the component solubility limit varies with the change of glass composition. Specific glass vitrification problems associated with the troublesome components in excess of their solubility limits were identified, such as volatility, phase segregation, and crystallization. Several mitigation techniques are considered to be viable to deal with feeds with high enough concentrations of the troublesome components which cannot be successfully vitrified by proper formulated glass alone. However, a solution to each specific problem needs thorough evaluation to balance the overall vitrification process in terms of efficiency and costs as well as the costs for plutonium immobilization and storage.

DISCLAIMER

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Table I. Nominal Compositions of Pu Glass Candidates (wt%)

Glass ID	Pu10A	Pu10B	Pu10C
SiO2	31.40	43.96	49.80
B2O3	5.50	11.49	7.95
Na2O		8.69	8.86
Li2O		3.80	4.36
CaO			1.03
MgO			1.34
Fe2O3			10.33
Al2O3	9.90	2.20	3.95
ZrO2	0.20	4.90	
BaO	3.20		0.18
Cl			0.12
Cr2O3			0.12
Cs2O		0.90	0.12
CuO			0.44
F			0.03
Gd2O3		3.20	
K2O		5.00	3.83
MnO2			2.47
NiO			0.88
La2O3	8.50		
P2O5			0.03
PbO	13.60		0.06
PuO2	10.00	11.29	0.62
SO3			0.22
Sm2O3	17.70		
SnO2		2.60	
ThO2			0.19
TiO2		2.00	0.89
U3O8			2.12
ZnO			0.08

Table II. Composition Assessment of Incinerator Ash and Ash Heel

Constituent [a]	IDC 419	IDC 421
	Range (wt%)	
Al2O3	60.95 - 5.70	1.10 - 7.20
AmO2	0.02	0.02
B2O3	0.32 - 3.20	0.02 - 3.20
BaO	0.58 - 1.20	0.06 - 0.58
C	7.50 - 36.0	10.4 - 44.8
CaO	1.10 - 7.00	1.10 - 5.60
Cl [b]	0.80 - 6.40	0.02 - 0.05
Cr2O3	0.44 - 0.88	0.58 - 2.90
CuO	0.63 - 1.30	0.50 - 0.60
F [b]	0.04 - 1.80	2.80 - 8.00
Fe2O3	1.11 - 10.3	0.72 - 11.7
K2O	0.24 - 1.20	0.02 - 0.60
MgO	0.83 - 8.30	0.83 - 1.70
MnO2	0.03 - 0.08	0.03 - 0.16
Na2O	0.00 - 2.40	0.00 - 1.20
NiO	0.25 - 0.64	0.25 - 0.64
P2O5	0.23	0.00 - 2.30
PbO	0.58 - 0.92	0.09 - 0.58
PuO2	1.80 - 3.80	1.60 - 16.4
SO3 [c]	---	---
SiO2	14.2 - 74.1	0.00 - 81.5
SnO2	0.00 - 0.25	0.00 - 0.38
Ta2O5	0.00 - 0.73	0.61 - 1.20
TiO2	1.00 - 1.70	1.00 - 5.00

[a] See Reference 2
[b] See Reference 3
[c] Many IDCs were found containing several wt% sulfate (private communication with A. Ellison, Argonne National Laboratory Argonne, IL, September, 1995)

Table III. Solubility Limits (wt%) of Troublesome Components in Borosilicate Glasses

Glass ID	Tm (C)	Cl	F	P2O5	SO3	Cr2O3
				PI Glass		
Pu10A	1450	(0.81) [a]		0.52	(2.28) [a]	0.59
	1400		0.72			
				LLW Glass		
L6-5412	1300	0.56	0.77	1.94	0.75	0.46
	1350	0.57	0.92	2.1	0.75	0.48
	1400	0.52	0.91	2.28	0.75	0.48
L4-9012	1350	0.49	1.67	5.57	0.47	1.04
				HLW Glass		
CCW1-1	1150				0.66	
CCW1-2	1150				0.94	
CCW1-3	1150				1.17	
CCW1-4	1150				1.09	
CCW1-5	1150				1.06	
CCW2-1	1150				0.64	
CCW2-2	1150				0.85	
CCW2-3	1150				1.13	
CCW2-4	1150				1.34	
CCW3-1	1150				1.13	
CCW3-2	1150				1.02	
CCW3-3	1150				1.01	
CCW3-4	1150				0.89	
CCW4-1	1150				1.04	
CCW4-2	1150				1.15	
CCW4-3	1150				1.36	

[a] Values are based on the nominal concentrations (see Appendix A).
Note: The experimental errors in the solubility data are within 10 percent of the reported values.

Table IV. Crystalline Phases Identified by XRD in the Samples with Saturated Troublesome Components

Glass ID	Component	Crystalline Phase
Pu10A	Cl	(a.p.s.) [b,d]
	F	(a.p.s.) [b,d]
	P	CePO4 [a]
	S	(a.p.s.) [b,d]
	Cr	Cr2O3 [c]
L6-5412	Cl	NaCl [a]
	F	NaF, CaF [b]
	P	Na3PO4, Na2Ca4(PO4)2*SiO4 [b]
	S	Na2SO4 [a]
	Cr	Cr2O3 [c]
L4-9012	Cl	NaCl [a]
	F	NaF [b]
	P	Na3PO4 [b]
	S	Na2SO4 [a]
	Cr	Cr2O3 [c]
CCW	P	Li3PO4, Ca5(PO4)2*SiO4, Ca2P2O7 [b]
	S	Na2SO4 [a]

[a] Formed at glass melt temperature
[b] Formed during glass melt cooling
[c] Likely formed during glass melt cooling
[d] Amorphous phase separation (a.p.s.)

Table V. Glass Melting Temperatures at Viscosity of 10 Pa.s for LLW Glasses with Additions of Troublesome Components

Glass ID	Component	(wt%)	T10 (C)
L6-5412	baseline		1351
	Cl	0.44	1363
	Cl	0.56	1374
	F	0.77	1284
	P2O5	1.94	1361
	SO3	0.50	1357
	SO3	0.75	1361
	Cr2O3	0.48	1354
	Cr2O3	0.80	1361
L4-9012	baseline		1345
	Cl	0.49	1352
	F	1.67	1216
	P2O5	5.57	1366
	SO3	0.47	1342
	Cr2O3	1.04	1320

Note: Values in bold face represent solubility limits.

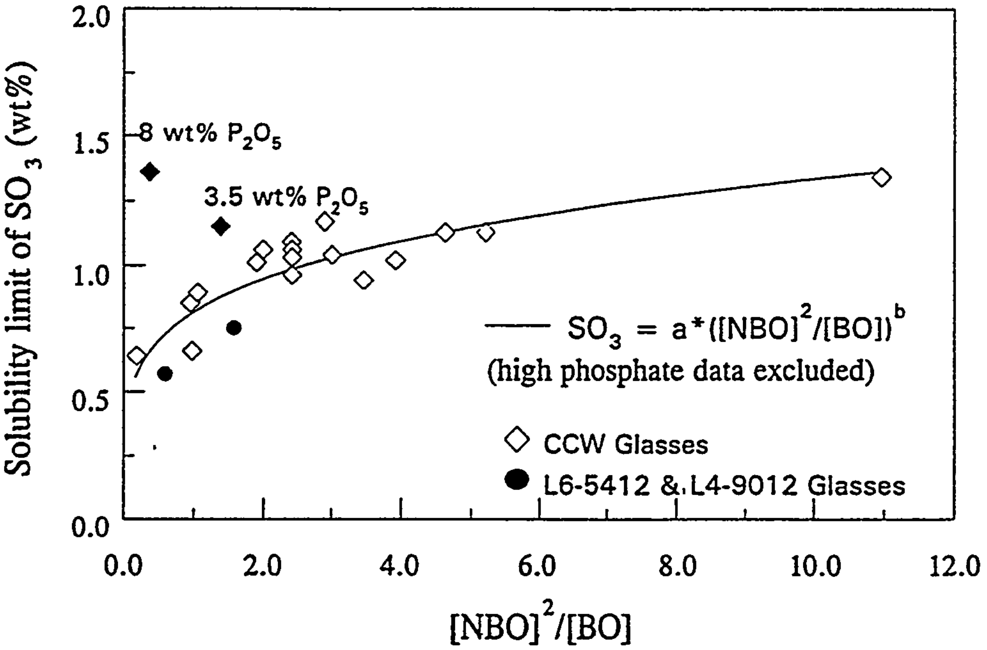

Figure 1. Solubility of Sulfate in the Glass as a Function of Glass Composition as Characterized in Terms of Concentrations of Nonbridging Oxygen and Bridging Oxygen, $[NBO]^2/[BO]$

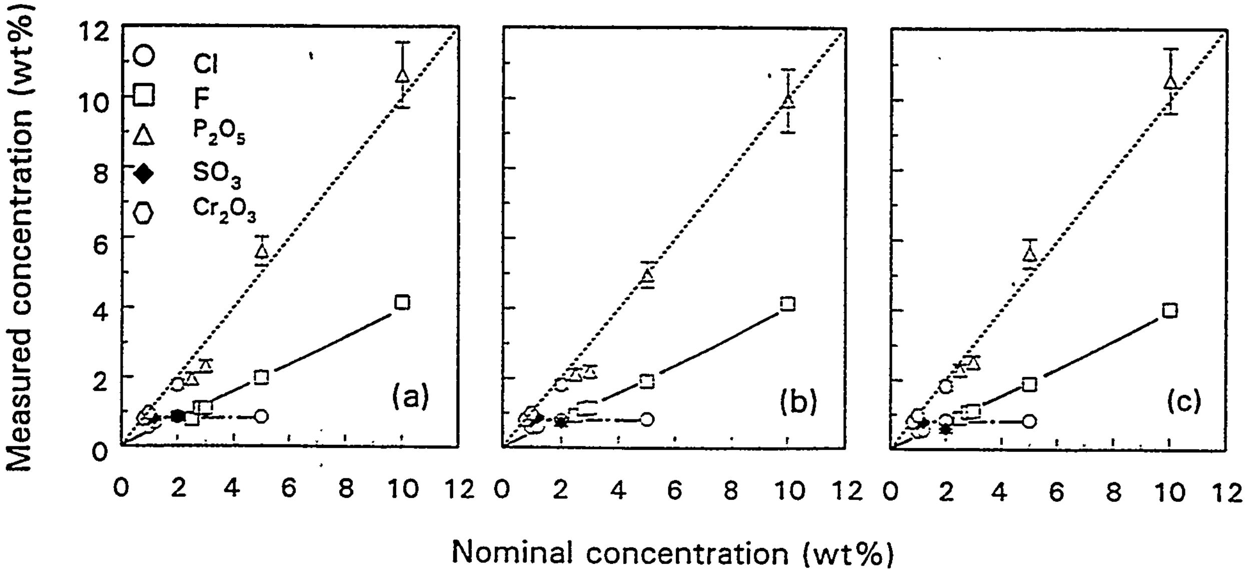

Figure 2. Component Volatility Assessment in L6-5412 Glass at (a) 1300°C, (b) 1350°C, and (c) 1400°C (Glasses Were Fused for 2 hrs at Each Given Temperature). Error bars represent one standard deviations based on the instrumental calibrations for the elements of interest.

Appendix A

Nominal Compositions (wt%) of Glasses for Plutonium Immobilization (PI), Low-Level Waste (LLW), and High-Level Waste (HLW)

Category	PI	LLW		HLW (Complexant Concentrate Waste, CCW)															
Glass ID	Pu10A	L65412	L4-9012	1-1	1-2	1-3	1-4	1-5	2-1	2-2	2-3	2-4	3-1	3-2	3-3	3-4	4-1	4-2	4-3
SiO2	32.64	56.78	56.78	63.51	61.23	59.16	57.09	55.02	48.24	51.82	60.02	60.53	66.10	62.73	52.26	46.57	57.92	54.92	50.42
B2O3	5.72	5.00	9.00	12.59	11.96	11.40	10.82	10.25	27.00	19.43	5.11	1.02	9.44	9.80	13.35	13.97	10.83	10.83	10.83
Na2O	0.00	20.00	20.00	11.17	11.17	11.17	11.17	11.17	6.62	9.09	12.89	15.11	11.17	11.17	11.17	11.17	11.17	11.17	11.17
Li2O	0.00	0.00	0.00	6.84	6.84	6.84	6.84	6.84	4.05	5.57	7.89	9.25	6.84	6.84	6.84	6.84	6.84	6.84	6.84
CaO	0.00	4.00	0.00	0.08	0.12	0.15	0.19	0.22	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
MgO	0.00	0.00	0.00	0.05	0.08	0.10	0.12	0.14	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Fe2O3	0.00	0.01	0.01	0.32	0.47	0.61	0.76	0.90	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Al2O3	10.26	12.00	12.00	3.19	4.77	6.20	7.63	9.06	7.64	7.64	7.64	7.64	0.00	3.00	9.93	15.00	7.64	7.64	7.64
ZrO2	0.21	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
OTHERS																			
BaO	3.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi2O3	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.09	0.09	0.37	0.55	0.71	0.88	1.04	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88
CeO2	6.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr2O3	0.00	0.04	0.04	0.12	0.18	0.23	0.29	0.34	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
F	0.00	0.21	0.21	0.20	0.31	0.40	0.49	0.58	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
K2O	0.00	0.33	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La2O3	8.83	0.00	0.00	0.04	0.06	0.08	0.10	0.12	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
MnO	0.00	0.01	0.01	0.15	0.22	0.28	0.35	0.41	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
MoO3	0.00	0.00	0.00	0.06	0.10	0.13	0.15	0.18	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Nd2O3	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.00	0.00	0.00	0.05	0.08	0.10	0.13	0.15	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
P2O5	0.00	1.19	1.19	0.56	0.84	1.09	1.35	1.60	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35	0.50	3.50	8.00
PbO	14.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO3	0.00	0.32	0.32	0.67	1.00	1.30	1.60	1.90	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
Sm2O3	18.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Status of Plutonium Ceramic Immobilization Processes and Immobilization Forms

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ABSTRACT

Immobilization in a ceramic followed by permanent emplacement in a repository or borehole is one of the alternatives currently being considered by the Fissile Materials Disposition Program for the ultimate disposal of excess weapons-grade plutonium. To make Pu recovery more difficult, radioactive cesium may also be incorporated into the immobilization form. Valuable data are already available for ceramics from R&D efforts to immobilize high-level and mixed wastes. Ceramics have a high capacity for actinides, cesium, and some neutron absorbers. A unique characteristic of ceramics is the existence of mineral analogues found in nature that have demonstrated actinide immobilization over geologic time periods. The ceramic form currently being considered for plutonium disposition is a synthetic rock (SYNROC) material composed primarily of zirconolite ($CaZrTi_2O_7$), the desired actinide host phase, with lesser amounts of hollandite ($BaAl_2Ti_6O_{16}$) and rutile (TiO_2). Alternative actinide host phases are also being considered. These include pyrochlore ($Gd_2Ti_2O_7$), zircon ($ZrSiO_4$), and monazite ($CePO_4$), to name a few of the most promising. R&D activities to address important technical issues are discussed. Primarily these include moderate scale hot press fabrications with plutonium, direct loading of PuO_2 powder, cold press and sinter fabrication methods, and immobilization form formulation issues.

INTRODUCTION

To an average person, plutonium is a mysterious element: toxic, dangerous, and unnatural. These perceptions lead many to have a great fear of plutonium even when present in barely detectable quantities. With the ultimate disposition of plutonium now at stake, what better way to combat the fear of the unnatural than with the tried and true demonstrated method of immobilization found in nature? Although plutonium does not exist in nature in significant quantities, its neighboring elements, uranium and thorium, are present at relatively high concentrations in many minerals such as zirconolite ($CaZrTi_2O_7$), pyrochlore ($Gd_2Ti_2O_7$), monazite ($CePO_4$), and zircon ($ZrSiO_4$). These minerals have all shown demonstrated immobilization of actinides and decay products over periods exceeding 100 million years. This data base of demonstrated actinide immobilization is unique to certain ceramic immobilization forms, but does not in any way imply that other ceramic, glass, metal, and cement forms are any worse in performance. Without natural actinide-bearing mineral analogues, however, an assessment of long term performance will always be less certain.

The existence of natural actinide bearing mineral analogues is an important criteria in defining an ideal immobilization form for Pu disposition, but other criteria are equally as important:

- relative ease of fabrication;
- high capacity for actinides, cesium, and other material impurities;
- high capacity for neutron absorbers (Gd, Hf, etc.);
- high durability;
- insignificant radiation damage effects; and,
- difficult to recover the Pu

Fabrication methods are generally well known for ceramic immobilization forms: hot pressing in bellows; cold pressing and sintering; and melting and crystallizing. Data are available that clearly demonstrate a high capacity of ceramics for actinides, cesium, and some neutron absorbers in ceramic forms. For example, Pu loadings in ceramic minerals can easily range from 10 to 70 wt%. A significant fraction of the excess plutonium in the U.S. is in the form of residues. This makes immobilization in ceramic slightly more complicated, but with the possible exception of pyrochemical salts, immobilization in ceramic should be easily achieved. This will require a tailored composition, however, for maximum waste loading and durability. Durability, radiation damage effects, and Pu recoverability are extremely important, but will not be specifically discussed in this paper except for the following general comments: Durability is very high for ceramics, radiation damage effects can be significant, and Pu recoverability is thought to be relatively difficult.

As part of the Fissile Materials Disposition Program (FMDP), immobilization of Pu in ceramic is being considered as an alternative for final disposition of weapons Pu. Since the amount of excess weapons grade Pu to be dispositioned (50 metric tons) is small compared to the amount of reactor grade Pu present in commercial spent fuel (several hundred metric tons) there is no point in making the weapons grade Pu more difficult to recover than the reactor grade Pu existing in commercial spent fuel. Therefore, the primary goal of the FMDP is to reduce security risks associated with the excess weapons grade Pu by converting it to a form at least as proliferation resistant as spent commercial LWR fuel. For most immobilization options this requires the addition of radionuclides such as ^{137}Cs.

To reduce security risks associated with the storage of weapons grade Pu, three ceramic immobilization disposition alternatives are being considered, each with a different end state. In two alternatives, the material would ultimately be disposed of in a repository for high-level wastes (HLW). One end state is a ceramic with an internal radiation barrier ("Ceramic Greenfield Alternative"), and the other end state is a ceramic with an external radiation barrier ("Ceramic Can-in-Canister Alternative"). In the third alternative, the ceramic would be disposed of in a deep borehole, where no radiation barrier is required. Most scrap and residues are currently being considered in the disposition program, but only to bound the most extreme case. If these low grade materials are dropped from the FMDP, they would likely be disposed of directly in a repository for TRU wastes. However, immobilization may still be desirable. For purposes of this paper, therefore, a fourth hypothetical end state is considered (i.e. not excluded as a possibility), that is immobilization in ceramic followed by disposal in a repository for TRU wastes.

Historical Perspective

Immobilization of radioactive wastes in a crystalline ceramic was first conceived of by Hatch in 1953[1]. He proposed immobilization of actinides and fission products in a clay mineral, montmorillonite. From that time until about the mid 1970s, little if any additional work was conducted. The first titanate-based immobilization form for HLW, a dried and hot-pressed inorganic ion-exchange resin, was developed by Sandia Laboratory in 1975[2], and the first glass-crystal composite forms for HLW were studied at the Hahn-Meitner Institute in 1976[3]. In 1978, Ringwood proposed the Synthetic Rock (SYNROC) concept[4], which relied heavily upon mineralogical compatabilities exhibited in nature. Although the initial formulation was not very successful, a later formulation (SYNROC-C) composed primarily of zirconolite ($CaZrTi_2O_7$), perovskite ($CaTiO_3$), hollandite ($BaAl_2Ti_6O_{16}$), and rutile (TiO_2) was very successful. From about 1980 to 1983 an intense research program was dedicated to the study of immobilization forms for defense HLW. These HLW solutions had been neutralized with sodium hydroxide and contained a considerable amount of silica, alumina, and iron oxide, which made them incompatible with the SYNROC-C formulation. Therefore, a new ceramic capable of incorporating these additional materials (SYNROC-D) was proposed and studied extensively at Lawrence Livermore National Laboratory (LLNL). With the selection of borosilicate glass in the early 1980s as the preferred HLW form, research on ceramic immobilization forms diminished significantly in the U.S. At the Australian Nuclear Science and Technology Organization (ANSTO), however, development continued with the completion of the SYNROC demonstration plant in 1987, which was operated in the following years on various short campaigns to demonstrate full scale SYNROC processing using surrogate HLW solutions[5]. Development of ceramic immobilization forms was revived in 1993 at LLNL when they were selected as the preferred immobilization form for the Mixed Waste Management Facility (MWMF).

Overview of Processing Technologies

In the past, ceramic immobilization forms have been fabricated primarily by hot pressing or hot isostatic pressing. Development for SYNROC has favored the method of hot pressing in stainless steel bellows[6]. If a fine-grained precursor material is used, and if the waste materials are loaded as nitrates, a homogenous and fully reacted product is obtained by hot pressing at about 15MPa and 1150°C. For hot pressing to be cost effective, it must be done on a large scale. Full scale is envisioned to be 30 cm diameter ceramic disks weighing approximately 30 kg. A more cost-effective process is cold pressing and sintering, but fully reacted and dense products are difficult to obtain[7]. Whereas densities greater than 98% are routinely achieved with hot pressing, densities between 90 to 95% are about the maximum obtainable for cold pressing and sintering. Another class of ceramic-like immobilization forms are the glass-crystal composites made by melting and crystallizing. This process offers the durability of ceramic with a vitrification-like process. Cesium volatilization is not significant when hot pressing in bellows, and it is therefore the best technical choice for the ceramic product with an internal radiation barrier. For the ceramic with an external radiation barrier, however, the cold pressing and sintering or the melting and crystallizing processes are probably more attractive for process simplicity reasons. The three primary fabrication processes for ceramic immobilization forms are summarized in Table 1.

Table 1. Summary of ceramic immobilization form fabrication processes.

	Hot Pressing in Bellows	Cold Press & Sintering	Melting and Crystallizing
fabrication process	sintering	sintering	vitrification
product description	ceramic disk (~30 kg, ~30 cm dia)	ceramic pellets (6 to 60 mm dia)	glass-crystalline monolith
density	>98%	90-95%	~100%
Cs retention	>99%	low	very low
processing temperature	1150°C	1200-1450°C	<1350°C melt <1200°C crystallize
applied pressure	~ 15 MPa (hot)	~150 MPa (cold)	ambient
container	stainless steel bellows	none	cold wall crucible
feed preparation	slurry blend and calcine at 750°C	slurry blend and calcine at 600°C	dry blend with glass frit

Immobilization Form Formulation

In order for a ceramic immobilization form to be of any use to the FMDP, it must be possible to accommodate a significant amount of Pu into the mineral structure, assumed to be at least 12 wt% for repository disposition and 1 wt% for borehole disposition. The immobilization form must also be able to incorporate neutron absorbers. The amount required has not yet been determined, but for planning purposes a one-to-one correspondence on an atom basis with Pu is assumed. For Gd this corresponds to about 8 wt% and for Hf about 9 wt%. For the ceramic with an internal radiation barrier, radioactive cesium (^{137}Cs) must also be incorporated into the ceramic at about 0.15wt%. Fortunately, data are available for many of the ceramic immobilization forms that clearly show that all of these materials can be easily accommodated. For the zirconolite phase, some Pu must be present in the +3 state to exceed the 12% capacity required for the repository options. However, the capacity of pyrochlore is much greater than needed. Both monazite and zircon have Pu analogues which set the strict upper limits to loading[8,9]. It is not known if these materials form continuous solid solutions between their end members, $CePO_4$ and $PuPO_4$ for monazite and $ZrSiO_4$ and $PuSiO_4$ for zircon. It is known that at least 10 wt% Pu can be incorporated as a continuous solid solution into $ZrSiO_4$[10]. In titanate based ceramics, Cs is commonly incorporated into hollandite. The limit in hollandite is around 22 wt%, but in an actual mineral assemblage Cs content may be limed by the process or by equilibria with other phases[11]. Pollucite ($CsAlSi_2O_6$) is also an attractive host phase for Cs, and very high loadings are theoretically possible. However, complete saturation of Cs in pollucite is difficult to obtain due to volatilization during processing. The maximum loadings of Pu, Cs and two neutron absorbers (Gd and Hf) in some mineral host phases are summarized in Table 2.

Table 2. Solid solubility limits in ceramic phases.

mineral type	composition	loading	Pu valence
zirconolite	$CaZr_{0.85}Pu_{0.15}Ti_2O_7$	10 wt% Pu	+4
zirconolite	$Gd_{0.7}Ca_{0.3}ZrTi_{1.3}Al_{0.7}O_7$	27 wt% Gd	
zirconolite	$Ca_{0.6}Pu_{0.4}ZrTi_{1.6}Al_{0.4}O_7$	23 wt% Pu	+3
zirconolite	$CaHfTi_2O_7$	42 wt% Hf	
pyrochlore	$CaPuTi_2O_7$	49 wt% Pu	+4
pyrochlore	$GdPuTi_2O_7$	40 wt% Pu, 26 wt% Gd	+3
monazite	$PuPO_4$	72 wt% Pu	+3
zircon	$PuSiO_4$	72 wt% Pu	+4
hollandite	$Cs_{1.3}Al_{1.3}Ti_{6.7}O_{16}$	22 wt% Cs	
pollucite	$CsAlSi_2O_6$	42 wt% Cs	

When immobilizing Pu or Pu residues, the immobilization form will probably not contain only a single phase. At the present time, the baseline assumed for Pu disposition is a variation of SYNROC-C: a mixture of zirconolite (~80%), hollandite (~15%), and rutile (~5%), if cesium is present, and just zirconolite (~90%) and rutile (~10%), if cesium is not present. Zirconolite is the actinide host phase and is chosen as the preferred phase since it has received considerable study as a constituent of SYNROC, it is compatible with a Cs host phase (hollandite), and is the most durable actinide host phase in SYNROC. For the purposes of defending and demonstrating reasonable confidence in the ceramic immobilization process, a zirconolite formulation has the highest probability of success with a minimal amount of experimental work.

Although most of the excess weapons grade Pu falls into the category of high-grade (pure or nearly pure) materials, most of the bulk falls into the category of scrap and residue. Many of these are listed in Table3 along with nominal Pu contents. Other categories, such as combustibles, graphite, and leaded gloves are not shown, because they would have to be treated before immobilization in ceramic. Of the categories listed in Table 3, ash is the largest by volume, but ZPPR is the largest by total Pu content. Because residue materials contain a variety of non-Pu elements, some additional phases are required in the formulation. Suggested mineral formulations to accommodate each residue category also appear in Table 3. For ash, it may be easier to make a glass or glass-crystalline composite, but immobilization in a high-silica content mineral such as zircon is also possible. For other residues, except possibly pyrochemical salts, immobilization in ceramic will be significantly easier than in a glass. This is due primarily to the refractory nature of the consituents which favors the formation of high-melting immobilization forms, i.e. ceramics. In the case of pyrochemical salts, there are no really good phases in which to immobilize the materials directly. Two possibilities are given, but neither is highly recommended. In most cases where zirconolite appears as a suggested mineral, pyrochlore, zircon, or monazite could just as well be used.

Table 3. Summary of Pu-bearing residue types and possible mineral formulations.

category & composition	nominal Pu content	possible mineral formulations
ash (lean & rich)	~ 0.2 & 5%	
-SiO_2, Al_2O_3, Na_2O, TiO_2, etc.		zircon($ZrSiO_4$)/feldspar($NaAlSi_3O_8$) or zirconolite($CaZrTi_2O_7$)/glass
ceramic crucibles	~ 1%	
-MgO or Al_2O_3		zirconolite/spinel ($MgAl_2O_4$)
-ZrO_2		zirconolite
sand, slag, & crucible	~ 2%	
-MgO/MgF_2		zirconolite/spinel/sellaite (MgF_2)
		or apatite ($Ca_5(PO_4)_3F$)
pyrochemical salts	~ 6%	
-NaCl/KCl based		sodalite ($Na_4Al_3Si_3O_{12}Cl$)
-$CaCl_2$ based		apatite ($Ca_5(PO_4)_3Cl$)
ZPPR fuel	~ 25%	
-U/Pu/Mo		zirconolite/titanium alloy (Mo-Ti)
-U/Pu/Al		zirconolite
mixed oxides	~ 20%	
-UO_2/PuO_2		zirconolite
other alloys & oxides	varies	
-Zr/Pu, U/Pu, ZrO_2/PuO_2		zirconolite
-Be/Pu, BeO/PuO_2		zirconolite/chrysoberyl ($BeAl_2O_4$)
-Al/Mg/Pu, Ga/Pu		zirconolite/spinel

Feed Preparation of Radioactive Cesium

Cesium can easily be formulated in ceramic immobilization forms. However, radioactive cesium is not available in a conveniently pure form such as $CsNO_3$. Primary sources are the CsCl capsules stored at Hanford, HLW solutions in tanks stored at SRS, Hanford, INEL, and West Valley, and HLW calcine in bins stored at INEL. The purest available source is the CsCl capsules which are contaminated with a significant quantity of decay product, Ba and $BaCl_2$. To meet the ~1000 R/h at 1 m assumed radiation-field requirement, it is estimated that only about 0.15 wt% of ^{137}Cs is required in the ceramic matrix. This is a low enough content that incorporation of CsCl directly into the ceramic may be feasible.

However, chlorine is expected to reduce the product durability of ceramics. In addition, CsCl is extremely volatile and will be harder to contain during processing.

An attractive option for incorporating radioactive cesium into a ceramic immobilization form is to use crystalline silico-titanate ion-exchangers. These materials were developed to selectively extract Cs and Sr from HLW solutions[12,13]. They are molecular sieve materials, similar to Zeolite, and are composed primarily of SiO_2 and TiO_2, which are easily accommodated in ceramics. Silico-titanates can be used to extract the Cs from the CsCl capsules while leaving behind the chloride, or they can be used to extract Cs from HLW solution tanks, leaving behind materials undesirable for the ceramic immobilization form such as sodium nitrate. Ion-exchanger loadings up to about 1 wt% are obtained from ppm-level Cs solutions and can be made as high as 50 wt% from concentrated solutions. Solid-liquid distribution coefficients for Cs are extremely high, ranging from about 2,000 in basic solutions to about 20,000 in acidic and natural solutions. Performance is not affected by radiation exposure (less than 5% variance in performance after 10^9 rads exposure) and the Cs is difficult to remove once loaded into the crystalline silico titanate (less than 1% elution after 24 hours in 0.1M formic acid).

Important R&D Issues

The best demonstrated process for ceramic fabrication, particularly the ceramic with internal radiation barrier, is hot-pressing in bellows. This process has been demonstrated on large scale (~30 kg) with HLW surrogates, but only on small scale with plutonium (10 to 20g total mass). Consequently, an important R&D effort is to increase the scale of the hot-pressing-in-bellows process for plutonium. At LLNL, a hot press capable of producing ~ 0.5 kg ceramics in 7.5 cm diameter bellows is being built. The apparatus has been tested once, but heat transfer was too great for the cooling water system, so the press is being rebuilt with added insulation. The press is expected to be fully operational sometime in January, 1996.

Other important tasks that are planned are the demonstration of the cold-press-and-sinter process with Pu materials both at LLNL and ANSTO. The process has had only limited demonstration with U- and Pu-bearing materials. However, it has had extensive demonstration and has been shown to be very promising for immobilizing RCRA-regulated ash materials for the MWMF program. The primary issue in cold-pressing and sintering is to formulate the precursor feed and establish processing conditions so the product is fully reacted and greater than 90% dense. The properties of ceramics produced in these studies will be compared to those of ceramics obtained by hot pressing in bellows. The size and morphology requirements to incorporate PuO_2 directly into ceramics and the feed impurity tolerances will also be studied. Direct incorporation of PuO_2 into the ceramic is expected to be more difficult than the standard method using nitrates. If shown to be feasible, however, it will have a major impact on the overall ceramic fabrication process for Pu bearing materials. Studies on feed impurity tolerances will include chloride from sources such as CsCl, neutron absorbers where additional data are needed, and common impurities in the Pu-bearing residues.

There are some other important issues that have not been studied to any significant extent. The crystalline silico-titanates are fairly well developed for the extraction of Cs and Sr from HLW solutions. The process is expected to work easily for CsCl but needs demonstration so that appropriate processing conditions can be defined. Likewise, the crystalline silico-titanate material has never been formulated in a ceramic form with Pu-bearing residues. Although this is expected to be relatively easy, it has not yet been demonstrated. Cs volatilization during the calcination process will also need to be evaluated.

For glass-crystal composites, the process is fairly well developed. However, only limited demonstrations have been performed with Pu-bearing materials and, even then, only at low concentrations. Demonstration with higher Pu contents (>10 wt%) and development of a lower temperature process to limit Cs volatilization is needed for this alternative. The crystallization process also needs to be better understood to be certain that there are no criticality concers due to accumulation of Pu-rich minerals.

An important aspect to the immobilization form is its proliferation resistance. Is it as difficult to recover plutonium from the final form as it is from commercial spent fuel? Assessments are planned to evaluate proliferation resistance, but this does not include any experimental testing. Plutonium cannot be recovered from titanate-based ceramics using standard PUREX type processes. The primary reason is that these ceramics are not soluble in nitric and hydrofluoric acids, and acids that can be used to dissolve the ceramic will interfere with the PUREX processing steps. Although some possible schemes have been identified, Pu recoverability has never been demonstrated for ceramic immobilized forms. Therefore, the true proliferation resistance is difficult to evaluate. Another aspect to consider is the possibility of including "spoiler" atoms into the ceramic formulation to thwart any key process steps that may be identified in the possible recovery schemes. Two such possibilities are Th and Ce since they have chemical behavior similar to that of Pu.

SUMMARY AND CONCLUSIONS

In summary, a variety of viable process options are available for the fabrication of ceramic immobilization forms: hot pressing in bellows, cold pressing and sintering, and melting and crystallizing. The processes are fairly well developed for immobilization of HLW and sufficient work has been completed to demonstrate that ceramics have a high capacity for actinides, neutron absorbers, cesium, and many common residue impurities. Although radioactive cesium is available in somewhat undesirable forms for immobilization in ceramic, the material should be easily extractable from available sources, namely CsCl capsules and HLW solutions, and incorporated into ceramics using crystalline silico-titanate ion exchangers. Research and development efforts are currently focused on demonstrating the immobilization process with Pu-bearing materials.

DISCLAIMER

The views expressed in this paper are those of the author(s) and no not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Immobilization of Actinides in Stable Mineral Type and Ceramic Materials (High Temperature Synthesis)

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Alternative vitrification technologies are being developed in the world for the immobilization of highly radioactive waste in materials with improved thermodynamic stability, as well as improved chemical and thermal stability and stability to radiation. Oxides, synthesized in the form of analogs to rock-forming minerals and ceramics, are among those materials that have highly stable properties and are compatible with the environment.

In choosing the appropriate material, we need to be guided by its geometric stability, the minimal number of cations in the structure of the material and the presence of structural elements in the mineral that are isomorphs of uranium and thorium, actinoids found in nature. Rare earth elements, yttrium, zirconium and calcium are therefore suitable.

The minerals listed in the table (with the exception of the zircon) are pegatites by origin, i.e. they are formed towards the end of the magma crystallization of silicates from the residual melt, enriched with Ta, Nb, Ti, Zr, Ce, Y, U and Th. Uranium and thorium in the form of isomorphic admixtures form part of the lattice of the mineral. These minerals, which are rather simple in composition and structure and are formed under high temperatures, may be viewed as natural physio-chemical systems that are stable and long-lived in natural environments.

The similarity of the properties of actinoids and lanthanoids plays an important role in the geochemistry of uranium and thorium; however, uranium (IV) is closer to the "heavy" group of lanthanoids (the yttrium group) while thorium (IV) is closer to the "light" group (the cerium group). That is why rare earth minerals contain uranium and thorium in the form of isomorphic admixtures.

Table 1. Stable minerals, including U and Th.

Mineral group	Name	Stoichiometric formula
Zircon	Zircon	$ZrSiO_4$
	Thorite	$ThSiO_4$
	Uranothorite	$(Th,U)SiO_4$
Tortveinite	Talenite	$Y_2Si_2O_7$
	Yttrialite	$(Y,Th)_2Si_2O_7$
Perovskite	Perovskite	$CaTiO_3$
	Zircolite	$(Ca,Fe,Th)_2(Zr,Ti)_2O_5$
	Zirconolite	$CaZrTi_2O_7$
Euxinite	Euxinite	$(Y,U)(Nb,Ti)_2O_6$
	Aeschynite	$(Ce,Th)(Nb,Ti)_2O_6$
	Samarskite	$(Y,U)(Nb,Ta)_2O_6$
	Brannerite	UTi_2O_6
Fergusonite	Fergusonite	$Y(Nb,Ta)O_4$
	Foramanite	$YTaO_4$
	Yttrotalite	$Y(Nb,Ta)O_4$
	Polymagnite	$Y(Zr,Ti,Nb,Ta)O_4$

Transuranic elements are almost never found in nature. It is known, however, that plutonium dioxide is an isomorph of uranium dioxide and thorium dioxide. Therefore, we may conclude that the behavior of uranium, plutonium and other actinoids will be identical in solid phase high-temperature processes.

Many countries are currently conducting research on the immobilization of actinoids with high-temperature synthesis in minerals listed on table 1 (the pervoskite and zircon groups). It is possible to synthesize materials that are not found in nature and which have the physio-chemical properties and stability of natural materials. The proposals to bind actinoids with dioxides of cubic zirconium and yttrium-aluminum granite (YAl_5O_{12}) are well known.

There are proposals to create highly stable oxides containing actinides by using stable (isotopes) fission products (yttrium, zirconium, rare earth elements). Out of the total number of fission fragments, 50% of the stable isotopes may be use to create stable oxide matrices. Calculations of the accumulation of actinides and stable isotopes (irradiated for 480 days) for a ton of MOX-fuel indicate that with 1 - 5 years of curing after irradiation the total number of stable isotopes of Y, Zr and rare earth elements is more than three times greater than the number of nuclides of Am and Cm. It follows that if we separate and trap actinides (Am, Cm) and rare earth elements with yttrium during radio-chemical reprocessing of spent fuel, we get the necessary initial mixture of stable minerals with actinides replaced by isomorphs (Table 2).

Table 2. Actinide and stable isotope accumulation (kg) in fuel elements of BN-600 reactors.

Isotopes	Amounts (kg)	Isotopes	Amounts (kg)
Am-241, 242, 243	7.0	Ag-109	0.55
Cm-243, 244, 245,246	0.28	Ce-140, 142	4.8
		Pr-141	2.4
Total Am, Cm	7.28	Nd-142+146, 148, 150	7.58
Y-89	0.53	Sm-150, 152, 154	0.52
Zr-90, 91, 92, 94, 96	4.65	Cd-152, 154, 158	0.25
		Eu-153	0.20
Total Y, Zr	5.18	Tb-159	0.02
Mo-95+98, 100	10.03	Total RE	18.4
Ru-101, 102, 104	6.12		
Rh-103	2.12		
Pd-104, 105, 106, 108	4.37		
Total	12.61		

The synthesis of oxide materials requires complex high-temperature melter technologies. It also requires maintenance of the interaction between the products for long periods of time in a high temperature environment. These flaws in this technology can be eliminated if the process is carried out in a self-propagating synthesis mode (SPS) - a new technology for manufacturing refractory compounds and materials.

SPS is a highly exothermic solid-phase interaction between chemical reagents that proceeds spontaneously after initiation. The chemical transformation occurs in the wave front, which moves through the powder-like mixture at the rate of 0.5-15 cm/sec. The mixture contains energy producing components in the form of metallic powders with a great affinity for oxygen, as well as solid oxidizers and admixtures, including solid highly radioactive waste. In order to produce a high density product the material is sintered (SPS-compacting).

The possibility of applying SPS-compacting to immobilize high level waste has been demonstrated experimentally with calcinates, simulating actual waste. These investigations were carried out by specialists of the Institute of Macrokinetics of the Russian Academy of Sciences with the participation of the authors of this report.

The mixture used in the studies was composed of 10% calcinite. The reducer was titanium powder and the oxidizer was calcium nitrate with admixtures, which played the role of the diluent and included structure forming components - CaO, TiO_2, and ZrO_2.

We have plans to carry out the following exothermic reactions with the purpose of creating analogs of minerals of the perovskite group:

$$2Ca(NO_3)_2+9Ti+4CaO+TiO_2=6CaTiO_3+4TiN+\Delta H \qquad (1)$$

$$2Ca(NO_3)_2+9Ti+CaO+TiO_2+3ZrO_2=3CaZrTi_2O_7+4TiN+\Delta H \qquad (2)$$

Prior to the initiation of the process by an electric primer, the mixture was pre-pressed and upon completion of the process the hot mass was again compacted.

X-ray-phase analyses of the samples from the mixture, which stoichiometrically was an analog of perovskite, showed that a phase of the mineral was synthesized. However, in preparing a mixture, which stoichiometrically corresponded to a more complex mineral, that of zirconolite, we did not find it in any of the analyzed samples. A simpler material, resembling $CaTiO_3$ and $CaZrO_3$, was synthesized instead. In the SPS mode with time limitations, conditions are not conducive to the crystallization of materials composed of three structure-forming oxides.

In the samples the leach rate for rare earth elements (La and Ce), modeling the behavior of actinoids, into water at a temperature of 20^0 and 95^0 was below their detection levels in water and was equal to $<3 \times 10^{-6}$ g/cm^2 per day, which indicates high stability to water of the materials created.

We are currently conducting investigations on the synthesis in the SPS mode of ceramic matrices for immobilizing highly radioactive graphite waste. This waste is produced as a result of the decommissioning of uranium-graphite channel reactors. This waste is in the form of partial graphite stacks which had come in contact with defective fuel elements and consequently contain actinides and fission products.

In our search for reprocessing technologies for such waste, we investigated the chemical reactions in the SPS mode using metallic powders as reducers and carbon in the form of graphite and oxides as oxidizers.

$$xC + yMe^1 + Me^{11}{}_xO_y = yMe^1O + Me^{11}C + \Delta H$$

This process includes two exothermic reactions: the reduction of oxide ($Me^{11}{}_x O_y$), containing a carbide forming element, with metallic powder (Me^1) and the concomitant oxidation of the carbide forming element which transforms it into a stable form of carbide. The addition of oxides, simulating materials from nuclear fuels and fission products (20% of the mass) makes the process milder than it would be without this admixture.

The end products of the reaction that formed the matrix were quite hard and chemically stable carbon oxides in the form of composite ceramics.

CONCLUSION

It has been demonstrated that stable fission isotopes Y, Zr and rare earth elements may be used to create mineral oxides and that selfpropagating high temperature synthesis (SPS) may be used to immobilize dry radioactive waste on stable mineral type and ceramic matrices.

Some unique aspects of the technology and end product:

- the creation of geochemically stable mineral oxides
- the presence in the element structure of actinide isomorphs
- utilization of the stable fission isotopes in the materials
- the SPS process does not require an external power source
- high stability in water with the proper pH level.

DISCLAIMER

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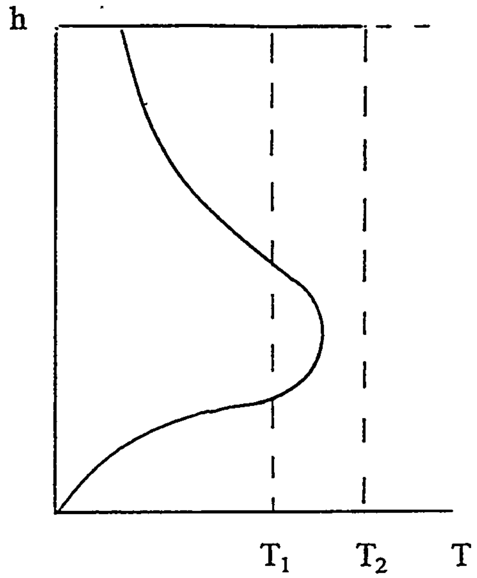
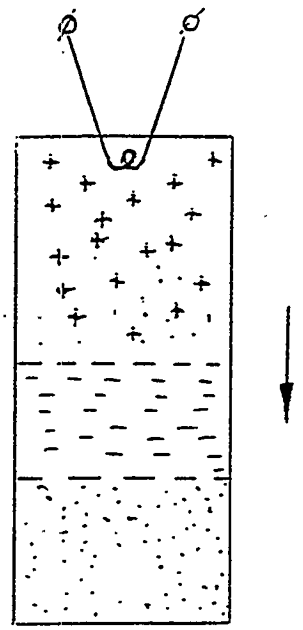
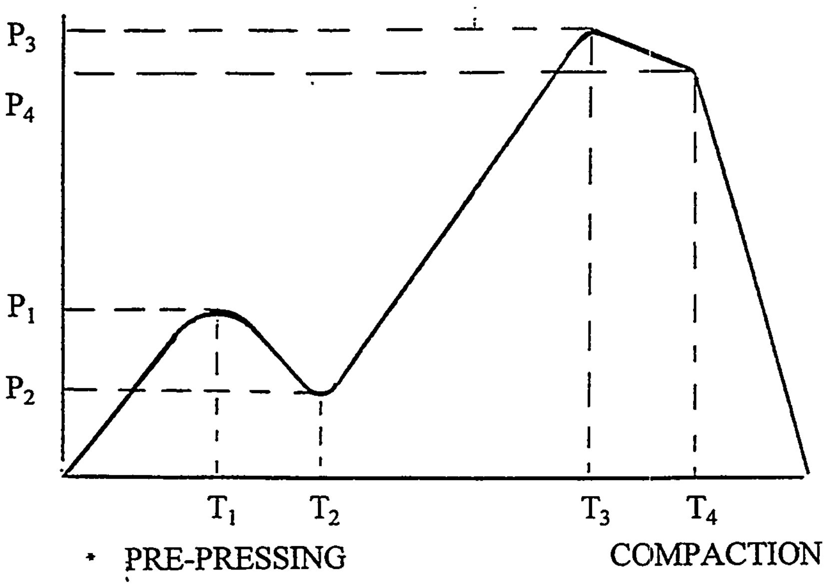
SPS - typical parameters







** Incomplete formula. Unclear on original.*

Crystalline Matrices for the Immobilization of Plutonium and Actinides

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ABSTRACT

The management of weapon plutonium, disengaged as a result of conversion, is considered together with the problem of the actinide fraction of long-lived high level radioactive wastes. It is proposed to use polymineral ceramics based on crystalline host-phases: zircon $ZrSiO_4$ and zirconium dioxide ZrO_2, for various variants of the management of plutonium and actinides (including the purposes of long-term safe storage or final disposal from the human activity sphere). It is shown that plutonium and actinides are able to form with these phases on $ZrSiO_4$ and ZrO_2 was done on laboratory level by the hot pressing method, using the plasmochemical calcination technology. To incorporate simulators of plutonium into the structure of $ZrSiO_4$ and ZrO_2 in the course of synthesis, an original method developed by the authors as a result of studying the high-uranium zircon $(Zr,U) SiO_4$ from Chernobyl "lavas" was used.

INTRODUCTION

Weapon plutonium, as well as transplutonium elements (actinides) of high-level wastes: Am, Np, and Cm, are exceptionally toxic long-lived radionuclides. The disposal of these materials from the sphere of human activity is considered at present within the scope of the two main concepts:

> Plutonium and radioactive actinides of nuclear wastes should be transferred into thermodynamically stable crystalline compounds (glass or ceramic compounds similar to the most durable natural minerals). The final isolation must be into deep geological formations.
>
> Plutonium as an element having a high energy value should be "burned" as a component of nuclear fuel. It is assumed that the use of the mixed uranium-plutonium fuel is economically more expedient that its isolation as radioactive wastes.

As is well known, the Russian concept of plutonium management (both the power and the weapon one) is based, in the long run, just on this postulate: the reclaiming of plutonium into the nuclear fuel cycle. The basis of the short-term programme of plutonium management in Russia is its reliable and safe storage until it can be used in reactors.

In either event, but irrespective of what final solution will be taken in the end, it seemed evident to us that technologies should be developed for plutonium (as well as actinides) immobilization in strong enough matrices meeting the requirements of long-term safe storage. Such technologies must be also acceptable for variants of final disposal in deep geological formations.

As to the idea of plutonium vitrification, it has been expressed and is being actively discussed recently in many works. Not dwelling on this option of plutonium immobilization, note only that undoubtedly, in spite of all the existing difficulties and problems, it is a promising variant deserving attention for realization in the nearest future.

In this presentation, I will touch upon an alternative idea of plutonium immobilization, namely, in crystalline mineral-like matrices. This idea is also well known and seems attractive, because it proposes to imitate from nature stable for millions of years crystalline-compounds minerals containing radioactive elements. It was first put forward by the Australian professor Ringwood. It is realized in creating a technology that was named SYNROC and was based on using mainly titanate minerals (hollandite-$BaAl_2Ti_6O_{16}$, perovskite - $CaTiO_3$, zirconolite (zirkelite) - $CaZrTi_2O_7$ and rutile - TiO_2).

Different combinations of SYNROC's main components, being a polycrystalline matrix, allow to fix the whole sum of unseparated HLW, including REE, TPE, U, Pu, as well as Sr and Cs (for which it was intended). Advantages of the SYNROC in comparison with glass are well known: a high resistance to mechanical, thermal, and radiational impacts; by 6 orders lower leaching-out of radionuclides; a high heat conductivity, etc.

In the recent years at the V.G. Khlopin Radium Institute, scientific-research and experimental works have been under way, aimed at creation of high-strength crystalline mineral-like matrices. These works concern, mainly, the development of technology of HLW management for the new radiochemical plant RT-2 under construction in Russia in Krasnoyarsk for SNF reprocessing. One of the basic key moments in the designed scheme of HLW management it's partitioning (fractionation) - separation into independent fractions of TPE and REE, Cs-Sr, U and Pu, and a subsequent independent management of each fraction. The Cs-Sr fraction is proposed to be vitrified, while TPE and REE are subject to immobilization in mineral-like matrices. Here the investigation of the investigations of the Radium Institute's specialists have progressed quite considerably and their results may be considered from the viewpoint of the subject-matter of the present seminar: "the technology of stabilization and immobilization of plutonium and Pu-containing wastes".

The Choice of Mineral Phases

The possibility to apply these or those minerals as crystalline matrices for the immobilization of plutonium and actinides is determined first of all by their physico-chemical stability and the isomorphous capacity of their crystal lattice. If it is proposed to dispose crystalline matrices with plutonium and actinides into deep geological formations, then one more requirement is imposed on the matrices. That is the existence of natural analogues, proving an exceptional resistance of these minerals to the influence of a real geochemical medium during a long time ($>10^4...10^5$ years). Of course, there are also requirements of economical expediency of applying these or those crystalline materials as matrices. A synthesis and investigation of quite a number of matrices has been carried out at the Radium Institute.

Having considered all the principal characteristics of these minerals and limitations to the choice of mineral phases for the immobilization of plutonium and actinides, we came to the conclusion that the most promising materials are zircon $ZrSiO_4$ and cubic zirconium dioxide $ZrSiO_4$ and ZrO_2.

It should be noted, that to similar conclusions concerning zircon came also our American colleagues from the University of New Mexico in Albuquerque - Rodney C. Ewing and research fellows. We had been working on these problems simultaneously and independently of each other for several recent years, but met and got acquainted only last spring at the workshop of the NATO and Russian scientists in St. Petersburg, devoted to problems of plutonium localization. It seems that further on, it would be expedient to unite our efforts in working out these problems.

Let is note principal characteristics of these minerals:

> zirconium dioxide ZrO_2 forms broad areas of solid solutions in the system PuO_2-ZrO_2 [1], as well as with oxides of rare-earth elements - simulators of radioactive actinides [2];
>
> zircon $ZrSiO_4$ is able to incorporate into its lattice considerable quantities of uranium - up to 10...12% [3,4,5], plutonium [6] and rare-earth elements [7];
>
> zircon and cubic zirconium dioxide ZrO_2 are exceptionally strong minerals, have natural analogues demonstrating their stability to the impact of a geological medium for millions of years.

Crystalline ceramics based on zirconium minerals are attractive for economic reasons, too. For its synthesis as a source of Zr may be used the material of zircalloy cans of reactor fuel rods, that in the course of nuclear fuel reprocessing gets to the high-level waste fraction after a joint dissolution with fuel and a chemical separation (in the Russian NFC). The irradiated nuclear fuel reprocessing in Russia is connected with disengagement of a large amount of zirconium - the main component of fuel cans. The existing in Russia technology of plasmo-chemical calcination allows the use of the source of zirconium for the production of ZrO_2 directly from nitrate solutions [8].

By the way, in this connection a promising product for the synthesis of zirconium ceramics can be zirconium-enriched HLW of the chemical plant in Idaho, USA.

An experimental synthesis of ceramics based on zircon $ZrSiO_4$ and zirconium dioxide ZrO_2 by the hot pressing method

In developing an industrial technology for the synthesis of zirconium ceramics for the immobilization of plutonium and actinides, it is proposed to use the methods of sintering or of hot pressing. Results of successful synthesis of zirconium powders by means of hot pressing at 1200...1300 C are known [9]. In this way, however, there are essential difficulties connected with a search of optimal synthesis conditions in the systems "temperature-pressure-time", as well as with development of acceptable ways of preparation of the starting blend.

In particular, the first difficulty is connected with the fact that in the course of synthesis, the whole volume of plutonium and actinides should be isomorphously incorporated into the lattice of the host phase, which causes the problem of observing a strict stoichiometry in forming the starting oxide mixture.

The other difficulty is that crystalline zirconium dioxide ZrO_2 is a chemically inert and thermally stable material. To release an interaction between crystalline oxides of zirconium, silicon, plutonium, and actinides in the course of hot pressing, a considerable temperature, or pressure, or time, is needed. This can put to doubt the economical expediency of the given technology.

The technology for the synthesis of crystalline zirconium matrices, under development at the Radium Institute, allows one to avoid these difficulties. The main peculiarities of this technology are:

> the final product of synthesis is preset to be polymineral ceramics on the basis of two host-phases simultaneously: zircon $ZrSiO_4$ and cubic zirconium dioxide ZrO_2
>
> the starting materials of synthesis are ultra-fine powders of oxides of plutonium, silicon, zirconium, and actinides, obtained by the plasmo-chemical method. Plasmo-chemical powders are distinguished by partial or full amorphousness (in the sense of crystallinity), i.e,. they are more reactionable chemically. In individual cases, a simultaneously plasmo-chemical denitration of a mixture of radioactive and non-radioactive solutions allows one to obtain phases of solid solutions, for example, $(Zr,U)O_2$ [8]
>
> a powder of zirconium metal is added into the starting mixture of oxides. This admixture assures an electric conductivity of the blend in the course of inductional heating. It also promotes the incorporation of plutonium and actinides into the lattice of the host-phases by the scheme deciphered as a result of investigation of high-uranium zircon from Chernobyl "lavas" [5]:

$Zr + MeO_x$ Zr-Me-O, where *Me*-U, Pu, Am, Np, Cm,...;
Zr-Me-O + SiO_2 $(Zr,Me)SiO_2$ - zircon;
Zr-Me-O + O_2 $(Zr,Me)O_2$ - zirconium dioxide.

An excess of zirconium metal oxidizes to ZrO_2 in the course of synthesis. This enables not to observe a strict stoichiometry of the starting blend's chemical composition. Real experiments on the synthesis of polymineral ceramics based on zircon $ZrSiO_4$ and cubic zirconium dioxide ZrO_2 by the hot pressing method were conducted at the Radium Institute in a broad range of conditions. The maximum temperature of synthesis did not exceed 1500 C, the maximum pressure was $4.5\ 10^9$ Pa, the synthesis time was from 1 minute to 30 minutes. A plasmo-chemical powder of cerium oxide CeO_2 was used as a simulator of plutonium and actinides.

All the experiments were successful. The maximum yield of zircon $(Zr,Ce)SiO_4$ was 38% *mass*, but the main phases in all the samples were mixtures of cubic, tetragonal and monoclinic zirconium oxides $(Ze,Ce)O_2$. The developed method for synthesis of zircon $ZrSiO_4$, doped with isomorphous admixtures, was patented, [10] and experimental work is going on at present.

CONCLUSION

1. The idea of plutonium and actinides immobilization has been realized on the laboratory-experimental level with a use of radionuclides' simulators.

2. A new original method is proposed for the synthesis of crystalline zirconium matrices, using zirconium metal and technologies of plasmochemical calcination and hot pressing.

3. In perspective, the investigation results can be used in other fields of technology: in creation of new types of especially strong ceramics, ionizing radiation sources for work under conditions of high temperatures, aggressive medium, etc.

4. The conducted experiments are not exhaustive. The work on the synthesis of zirconium ceramics for plutonium and actinides immobilization is continued at present.

DISCLAIMER

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An Approach to Meeting the Spent Fuel Standard

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There are underlying policy ideas to every technical approach to dealing with the plutonium question. The basic tension has been, (and continues to be unresolved as demonstrated by the previous two speakers), whether plutonium is an asset or a liability. If you do any calculations based on current values, uranium is clearly cheaper. This is generally acknowledged. It is also known that plutonium has a substantial energy content in physical terms and potentially could be a large energy resource in the far future, if the economics work out. No one can say what will happen five decades, or ten decades or two hundred years from now or what the energy situation shall be.

Those, who say that plutonium is an asset, may say that five decades from now we will need plutonium. Those who say that it's a liability (and I belong to the latter school just to put my cards on the table) may say that you can't spend a lot of money for five decades or a century from now, when clearly in the foreseeable future, you can't see when uranium might become un-economical. This is partly because we can't even predict the future of nuclear power beyond two decades.

I don't think that the debate can be resolved in policy or technical terms alone, but we do need to resolve the debate because of urgent environmental and non-proliferation concerns. The approach that we believe should be considered, although we're not yet advocates of it, is one that resolves, or tries to resolve, at least for now and the coming decades, this apparently unresolvable tension between plutonium being an asset and a liability.

We believe that there can be a technical and financial approach to resolving that tension with appropriate technology. It's not a term that's usually used in connection with plutonium, but having dealt with it in the village technology side, I will now introduce it to the plutonium technology side. The underlying idea of the spent fuel standard is that there should be a high surface gamma radiation to prevent theft. For purposes of preventing theft, containers should be massive, and finally, the plutonium should be difficult to re-extract. Those are the criteria. Also, there is the timeliness criterion. The DOE has now adopted a ten year goal to meet this criterion. So, we need technologies that can be implemented relatively rapidly.

I believe that the nonproliferation goals underlying the technical ideas of the spent fuel standard are two distinct ones. One goal is to prevent re-use by the state itself that has surplus plutonium, like the United States and Russia, which are already weapons states. The second is to prevent theft, sale and use by third parties, whether governmental or non-governmental. Now, in the United States, Russia, France, Britain and so on, the weapons states, there is a substantial sentiment in favor of using plutonium as an energy resource, whatever the national policy may be at any time. There's nothing, really, that prevents the re-extraction of plutonium from glass or spent fuel, whether it is civilian or military, at any particular time. The greater issues of immediate proliferation concern are the potential for sale, theft, diversion and not knowing where it might wind up. So the resistance to theft is, in my opinion, a primary technical criterion for the spent fuel standard. Difficulty of re-extraction is a very important criterion, but it has some minuses. If you make re-extraction very difficult, then those who believe that plutonium is an asset may argue that an asset is deliberately being made un-economical. The idea of an alternative approach to a spent fuel standard other than mixing plutonium with fission products such as cesium in the bulk of the glass has been proposed in the use of the Defense Waste Processing Facility (DWPF). I think that the people at Savannah River and I came up with this idea independently. I proposed it in our national symposium last year. After that, I called up John Plodinec at Savannah River who helped me with some of the calculations. I'll present to you with the basics of the idea. And also, I must acknowledge my debt to some researchers, Marvin Miller and his colleagues, and students at the Massachusetts Institute of Technology, for their technical data. We have a book, Fissile Materials in a Glass Darkly where this is described in some detail. I have a few copies of it for those who are interested that I can distribute at no charge. If I run out, you can certainly call my office for a copy.

The basic idea is that you can make it moderately difficult to re-extract plutonium by mixing it with some analog, some element that's a close analog of plutonium (e.g., thorium). Thorium also has decay products that make it more radioactive over time. Now, you have a glass from which it is moderately difficult to separate plutonium, but certainly not as difficult as it would be if you had poisoned it thoroughly with fission products, and added only a small amount of plutonium, as might be done, for instance, by simply mixing plutonium in the glass melt at the Defense Waste Processing Facility at Savannah River or some other place.

The main problem, as I see it, with this approach of mixing plutonium with thorium or uranium and melting it in the glass, is that it really has an inadequate resistance to theft. The only resistance to theft is that the glass is likely to be bulky. If you cast a very large DWPF-like log, several tons in weight, it would be very hard to steal, but certainly not impossible as Frank Hippel stated, "One only has to take the log and throw it in the back of a pick-up truck and drive away." This is the principal objection to doing this.

One of the great advantages of not mixing plutonium with fission products is that it can be done relatively rapidly so that the timeliness criterion can be met much more easily. Another feature, which is at once an advantage and a disadvantage, is that those who believe it's an asset will see in it that it is easier to re-extract. It would be a disadvantage to those who put primary emphasis on the nonproliferation criterion and don't care about any potential economic value in the future. They would say that it is not as difficult to re-extract as it should be.

The middle position here (although I must say there's no happy middle, all of the options being relatively unhappy for dealing with this material in my view) is to create a skin that is radioactive. For instance, a metal steel canister that is poisoned with a small amount of cesium would create the same external field as glass that has been mixed with cesium-137. One of the great advantages of doing this is that the amount of cesium that you need is reduced by an order of magnitude or more because none of the radiation is absorbed in the bulk of the glass. Essentially, using the skin or the can to create the external radiation field would require a relatively small amount of fission products resulting in a reduction in the processing cost, thus changing the kind of facility needed to do this. You can also separate the manufacturer of the radioactive can from the manufacturer of the liquefied glass so that the verification, itself, can proceed relatively rapidly. You could do this in other ways, also, as being proposed in Savannah River. The same external gamma radiation may also be produced, by inserting plutonium inside the glass or inserting cesium capsules inside the glass, and so on. This is the concept that I'm after. I think engineering evaluation of the various concepts is only now beginning. Therefore, I think it is too early to say which particular concept might be most suitable. The basic idea is that vitrification of plutonium can proceed without mixing the fission products in the bulk of the glass. This allows a relatively rapid vitrification of plutonium.

Subsequently, one can put the glass log in containers where the external gamma field would be very high (e.g., 1,000 rad at one meter). This kind of radiation field reduces the basic resistance to theft because you've got a log with 1,000 rad at one meter; this simply cannot be picked up and thrown into the back of a pick-up truck, because by the time you are ready to drive off you are likely to be gravely injured or dead. Now especially if you say 1,000 rad at one meter 30 years from now, it means that in the near future the radiation field would be much higher and any handling during theft may not be always just at one meter. I believe that this particular approach should be thoroughly investigated in view of the basic difference between the United States statements about surplus plutonium being a liability and the views prevalent in Russia that it is a national treasure. A basic compromise around the concept of immobilization of plutonium that I have discussed, or the concept that has been presented by the speaker before me (Dr. Anderson), would immobilize plutonium and put it in a relatively inaccessible form resistant to theft. This leaves the question of potential reuse to be decided in the future without precluding either the option of burying it in a repository or perhaps re-extracting it, should it ever become economical.

I think that the urgent problems that we face with regards to potential illegal sales, diversions, black markets, and so on, are so grave that we do not have the time to settle these questions. There has not been a decent conversation on these kinds of issues. The differences are so fundamental that it is with great reluctance that I myself propose this kind of idea, but I do recognize that it is very important to put forward a technical concept that might bridge what seems to be a un-bridgeable gap between those who believe plutonium is an asset and those who believe plutonium is a liability. I think that we have to recognize that plutonium is not an asset today because it is not an economical fuel today and proceed on that basis without precluding options, perhaps, for either school of thought.

DISCLAIMER

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ABSTRACT

The Materials Research Society Nineteenth Annual Symposium on the Scientific Basis for Nuclear Waste Management was held in Boston on November 27 to December 1, 1995. Over 150 papers were presented at the Symposium dealing with all aspects of nuclear waste management and disposal. Fourteen oral sessions and one poster session included a Plenary session on surplus plutonium dispositioning and waste forms. The proceedings, to be published in April, 1996, will provide a highly respected, refereed compilation of the state of scientific development in the field of nuclear waste management. This paper provides a brief overview of the selected Symposium papers that are applicable to plutonium immobilization and plutonium waste form performance. Waste forms that were described at the Symposium cover most of the candidate Pu immobilization options under consideration, including borosilicate glass with a melting temperature of 1150 ^{0}C, a higher temperature (1450 ^{0}C) lanthanide glass, single phase ceramics, multi-phase ceramics, and multi-phase crystal-glass composites (glass-ceramics or slags). These Symposium papers selected for this overview provide the current status of the technology in these areas and give references to the relevant literature.

INTRODUCTION

The Materials Research Society Nineteenth Annual Symposium on the Scientific Basis for Nuclear Waste Management was held in Boston on November 27 to December 1, 1995. The Fall MRS Meeting includes over 30 technical symposia on interdisciplinary research with topics ranging from thin films to manufacturing and over 100 exhibitors. The Nuclear Waste Symposium at the Fall MRS meeting has become one of the major technical meetings on applications of materials research to nuclear waste management and spent fuel dispositioning. This Symposium is recognized as having more of a technical focus than other waste-related meetings such as Waste Management '95 or Spectrum '94.

Over 150 papers were presented at the Symposium dealing with all aspects of nuclear waste management and disposal. Fourteen oral sessions and one poster session included a Plenary session on surplus plutonium dispositioning and waste forms. Other session topics included disposal geology and transport; glass, cement and ceramic waste forms; waste processing; natural analogs; performance assessment; corrosion; and spent fuel durability. Symposium sponsors include DOE-EM, NRC, PNC, Southwest Research Institute, and BNFL. The proceedings, to be published in April, 1996, will provide a highly respected, refereed compilation of the state of scientific development in the field of nuclear waste management.

This paper provides a brief overview of the selected Symposium papers that are applicable to plutonium immobilization and plutonium waste form performance. Waste forms that were described at the Symposium cover most of the candidate Pu immobilization options under consideration, including borosilicate glass with a melting temperature of 1150 ^{0}C, a higher temperature (1450 ^{0}C) lanthanide glass, single phase ceramics, multi-phase ceramics, and multi-phase crystal-glass composites (glass-ceramics or slags). These Symposium papers selected for this overview provide the current status of the technology in these areas and give references to the relevant literature.

SESSION SUMMARY

V1 Plenary Session. The opening plenary session, "Surplus Plutonium Dispositioning and Criticality Assessment," was chaired by M. J. Apted, R. Van Konynenburg, and W. Lutze. The session included an invited paper by Richard Garwin, IBM Fellow Emeritus, describing his assessment of the options and choices for plutonium dispositioning. Other papers in the Plenary included Pu immobilization in zirconolite-rich SYNROC (ANSTO, Australia), Pu immobilization in SYNROC containing Nepheline (ANSTO), synthesis of zircon for immobilizing actinides (U of NM, Khlopin Institute, Russia, and PNL), radioactive glasses containing actinides and reprocessing wastes (SRS), a glass waste form for immobilizing Pu (ANL), performance assessment of zircon as a Pu waste form under deep borehole conditions (U of NM and PNL), Pu burning in a non-uranium-containing ceramic fuel (Scherrer Institute, Switzerland), and nuclear criticality in geologic disposal (LLNL and U of CA, Berkeley).

Glass Waste Form Sessions (V6 Oral, V14 Posters). The glass waste form sessions included 12 oral and 9 poster papers. While most of the papers had some applicability in determining glass characteristics which would apply to the long-term durability of plutonium glass waste forms, the following papers are included in this overview: Long-term results from unsaturated water vapor hydration testing of actinide-doped DWPF and WVDP glasses to determine accelerated corrosion (ANL), zirconia solubility in boroaluminosilicate glass and potential for partitioning and immobilizing actinides in the secondary phases (INEL), 7-year leaching tests of nuclear power plant vitrified radioactive waste under shallow burial conditions (Radon), and secondary phase formation during accelerated water vapor phase corrosion of the French nuclear waste glass (U of NM, CEA, and ANL).

Ceramic Waste Form Sessions (V25 Oral, V15 and V17 Posters). The ceramic waste form sessions included 12 oral and 2 poster papers. Papers applicable to Pu dispositioning included solubilities of potential added neutron poisons Gd and Hf in zirconolite to minimize criticality during storage and disposal (LLNL), partitioning, leach data, and secondary phase development of Np-doped SYNROC to assess durability of Np immobilization (ANSTO), radiation damage and annealing of neutron-irradiated zirconolite for predicting long-term radiation damage effects (ANSTO), immobilization of separated Tc and Cs/Sr in SYNROC to support a potential DOE HLW mangement scenario (ANSTO), a melting route to SYNROC for Hanford HLW immobilization as an alternative to hot pressing (ANSTO), investigation of aeschynite and euxenite structures-types as host phases for rare earths and actinides (U of NM and Chinese Academy of Sciences), investigation of urtite as a natural analog for a slag waste form formed in a high temperature melter (Radon), effects of added rare earth elements on zirconia phase stability for immobilizing actinides (BNFL, Britain), and application of glass-crystal composites for a new highly durable alternative to glass (ANL).

PLUTONIUM IMMOBILIZATION IN GLASS

The focus of most of the papers was to assess the maximum loading of plutonium in a glass and the resulting durability of the waste form. Two papers reported new glass formulations prepared with plutonium: a high-temperature 1450 ^{0}C lanthanide glass (Bibler, V1.4) and a lower temperature 1150 ^{0}C alkali-tin-silica glass (Bates, V1.5). One paper reported long-term leach tests with actinide-doped glasses (Fortner, V6.3). These and additional glass papers which are applicable to Pu vitrification will be described briefly in the following.

The high-temperature lanthanide glass (Bibler, V1.4) prepared at the Savannah River Technology Center has the potential to incorporate a high Pu loading and is based on a 1932 literature composition. Glasses were prepared with Pu oxide loading of up to 15 wt% and, separately, with < 1 wt% americium-curium loading. The 15 wt% Pu loading was found to contain some PuO_2 crystals, while a loading of 13 wt% was reported to be homogenous. These high temperature glasses were found to be 25-50-fold more durable, as measured by PCT leach rates, when compared with DWPF radioactive waste glass samples.

An alkali-tin-silicate glass (Bates, V1.5) which has a melting point of 1150 ^{0}C in a similar range to other HLW glasses was prepared at ANL with 10 wt% Pu oxide loading, including small amounts of the neutron poison gadolinium. The glass composition was engineered based on ANL experience and the literature to accommodate a high Pu loading and to be durable under conditions likely to accelerate glass reaction. The glass dissolved 7 wt% Pu and appears to be resistant to accelerated corrosion under batch tests with small quantities of water such as would be expected in a Yucca Mt. type of repository and under exposure of glasses to water vapor at elevated temperature conditions to accelerated corrosive attack. Based on these tests, rates of diffusion of water into the glass surface were estimated to be similar to those for a durable obsidian mineral.

ANL has performed long-term drip tests on reference DWPF and WVDP glasses for over 8 years which are designed to simulate the unsaturated conditions such as those found at the Yucca Mt. site (Fortner, V6.3). The reference DWPF and WVDP glasses were doped with neptunium, plutonium, and americium in contact with sensitized stainless steel, under periodic dripping of equilibrated groundwater. The importance of such integrated testing has been demonstrated through the observation of complex interactions of all test components. Actinides, except Np, were found to concentrate into alteration phases or sorb onto the stainless steel. The subsequent transport of the actinides would then be expected to be controlled by the respective alteration phases. Spalling of the alteration phases could result in the possibility of colloid formation and subsequent transport and release.

Other related Pu glass papers include the following: The results of 7-year leaching tests of radioactive glass blocks buried in shallow soil or stored in an open area under weathering conditions were reported by Radon Institute (Barinov, V14.8). The leach tests were run on glass prepared from intermediate-level nuclear power plant wastes using 25-30 kg glass blocks stored both in loamy soil and in the open. From bimonthly sampling of the groundwater over seven years, only cesium-137 was detected in the leachate, and the leach rates exhibited periodic fluctuations attributable to new glass surface exposure such as might be expected from crack formation. In a paper on secondary phase and microstructural evolution of surface layers of the French inactive waste glass composition under accelerated vapor phase testing (Gong, V14.8), the French HLW glass prepared with non-radioactive simulants was tested from 91 to 1021 days under accelerated water vapor hydration conditions at 200 ^{0}C. Experimenters at U of NM, CEA, and ANL identified six zones containing crystalline and amorphous precipitates with evidence of redistribution of waste elements in the zones. The rate of layer growth was found to be approximately one-fourth as much as that of DWPF glass under similar conditions. In an INEL study (Raman, V6.8), the solubility of Zr was measured in boro-aluminate glasses with added magnesia and soda. A ternary composition surface was constructed, and the potential for partitioning of transuranics and transition elements in some of the phases was discussed.

PLUTONIUM IMMOBILIZATION IN CERAMICS

Many of the ceramic waste form papers presented at the Symposium applied to plutonium immobilization with the goal of determining the loading limits in the waste form for Pu, fission products and neutron poison materials for criticality control and to asses the durability. The approaches included the options for using a single crystalline phase, multiple crystalline phases, and crystalline-amorphous materials. Most of the ceramic waste form papers reported on tests using SYNROC originally developed at ANSTO in Australia, especially the zirconolite phase as an actinide host. Zircon, which is also considered a very durable host for plutonium, was prepared and tested in several papers. Additional host phases for Pu were proposed and tested.

SYNROC-related papers included the following. A zirconolite-rich SYNROC was prepared and tested at ANSTO for 10-20 wt% Pu-239 loading in a range of zirconolite compositions (Vance, V1.2). Previous tests have also been run with 11 wt% Pu-238 to simulate long-term high radiation tests. In the present tests, Gd and Hf were also added as neutron poisons. Low levels of CsCl were added to the hollandite phase to chemically simulate the us of Cs-137 for producing high radiation fields to protect against potential diversion. No product degradation was found for the required CsCl content of up to 1000 ppm Cl. The use of SYNROC containing Pu in deep boreholes was discussed as resulting in a storage temperature of 200 ^{0}C which would lead to self annealing of the expected radiation damage. The aluminosilicate phase nepheline was also prepared with the SYNROC components as an alternative material to immobilize 10 wt% Pu (Vance, V1.3). The leach rates for Pu were low, on the order of 10^{-5} grams per square meter per day and comparable to SYNROC without nepheline. The solubilities of Hf and Gd in zirconolite at 1200 ^{0}C were measured at LLNL by establishing the phase equilibria using X-ray diffraction and electron microprobe analyses (Swenson, V25.8). The partitioning, leach data and secondary phase development of neptunium-doped SYNROC was measured at ANSTO (Smith, V25.6). None of the secondary phases contained observable amounts of Np indicating a potential for high durability. A TEM study of the radiation damage and annealing of neutron irradiated zirconolite was reported from ANSTO (Lumpkin, V25.7). The neutron irradiation was used to simulate alpha decay and resulted in the transformation to an amorphous structure. With increased dose, the damaged microstructures resembled those caused by other doped experimental and natural mineral alpha-decay damage. Separated Tc and Cs/Sr were immobilized in SYNROC and tested at ANSTO as a potential application to DOE wastes in which radionuclides may be separated and concentrated prior to immobilization (Hart, V25.1). Tc was present as a metal, alloyed with other metallic fission products. Cs and Sr could be suitably immobilized in the hollandite phase. A melting process to form SYNROC was developed at ANSTO for Hanford HLW immobilization (Vance, V25.2). The SYNROC process usually uses a hot press to achieve the desired phases. The waste form consisted mainly of crystalline SYNROC phases in an aluminosilicate matrix after melting at 1350-1450 °C in a neutral atmosphere with waste loadings up to 70 wt%. Seven-day PCT leach tests resulted in leachability of all measured elements of <0.1 gram per square meter per day at 90 °C.

A new method for zircon synthesis for immobilizing actinides was reported from the Khlopin Institute, U of NM, and PNL (Burakov, V1.6) based on the observation that zircons had been crystallized from the melt of the reactor core during the accident at Chernobyl Nuclear Power Plant. The results demonstrated the efficacy of using metallic zirconium in synthesizing high-actinide zircons, and an adaptation and modification of the mixed-oxide (MOX) reactor fuel production process was proposed as a possible method for preparing such a zircon waste form for excess plutonium. Model predictions were made by PNL and U of NM to assess the performance of zircon in borehole disposal (Weber, V1.7). Zircon is an extremely durable ceramic and is often found as an accessory mineral in Precambrian terranes with ages up to 4 billion years. Model predictions indicate that under the worst case scenario, only a few grams of Pu were predicted to be released from 50 metric tons of Pu in 420 tons of zircon over 500,000 years.

Aeschynite and euxenite structure types were proposed by the U of NM and Chinese Academy of Sciences as host phases for rare earth elements and actinides (Gong, V17.2). The anticipated waste loadings of rare earths and actinides are estimated to be at least 40 wt% based on chemical compositions of naturally occurring materials. The sol-gel preparation of each structure is described, including the proposed mechanism. Based on investigation of naturally occurring minerals, the radiation damage and chemical alteration were assessed and found to be similar to other natural phases such as zircon, zirconolite, and pyrochlore. A natural analog material, urtite, was investigated by Radon Institute (Dmitriyev, V15.1) to determine potential long-term waste form behavior for similar structures formed as slag at high temperatures. The main phases in urtite which hosted geochemical analogs of radioactive waste components were found to be nepheline (Rb and possibly Cs), feldspar (Ba), sphene (Zr, Nb, rare earths, and actinides), and apatite (Sr, rare earths, and actinides). The ability of the cubic phase of zirconia to accommodate the oxides of rare earth elements was measured by BNFL (Maddrell, V25.12). The presence of the smaller rare earth ions was found to help stabilize the presence of larger ions such as found in actinides. Glass-crystal composite waste forms were produced at ANL from waste streams containing high proportions of phosphorus, transition metals, and /or halides (Wronkiewicz, V25.10). The crystalline phases include apatite, monazite, spinels, and a Zr-Si-Fe-Ti phase, which readily incorporate radionuclides and toxic metals into their crystal structures with up to 300-fold higher durability than glass.

ARCHIVAL SAMPLES CONTAINING PLUTONIUM

During the discussion at the Symposium, a preliminary list of archival samples which contain plutonium and other radioactive elements was compiled. Some of these samples may be useful for further testing and are described in the following:

PNL. At the Pacific Northwest Laboratories, Dr. Weber reported that his archival samples include zircon with 10 wt% Pu-238 which is incorporated on the zirconium site of the material. This sample was prepared in 8/81 and is estimated to have undergone 2.5×10^{19} alpha disintegrations per gram (d/g). Borosilicate glass with the same chemical composition and containing different amounts of plutonium include 1 wt% Pu-239 with an estimated dose of $<10^{15}$ alpha d/g; 0.9 wt% Pu-239 and 0.1 wt% Pu-238 with an estimated dose of 1.6×10^{17} alpha d/g, and 1 wt% Pu-238 with an estimated dose of 1.6×10^{18} alpha d/g. These glasses were prepared in 7/82. Dr. Weber estimated that over a disposal period of 10^5 to 10^7 years an immobilized Pu-239 waste form would experience 5×10^{20} alpha d/g for a 20 wt% loading and about 1×10^{20} alpha d/g for a 5 wt% Pu loading.

ANSTO. Archival ANSTO SYNROC samples containing Pu-239 include five 75 g samples containing 0.03 wt% Pu prepared in 1985, ten 1-g samples containing 10-30 wt% Pu prepared in 1993-5, and ten 10-g samples containing 10 wt% Pu prepared in 1994-5.

SRS. At the SRTC, a Cm-doped glass was prepared in 11/7/83, originally at a 0.90 % loading of Cm-244/Pu-240 in a DWPF-type glass containing frit and waste simulants, called "black frit." Dr. Bibler estimates that at the time of preparation, the Cm-244 content of the glass was 0.73 % and using the half-life of 18.1 yr, he calculates that the current dose experienced by the glass is 3.4×10^{18} alpha d/g. SEM measurements and PCT tests are planned and will be compared to similar glass which does not contain the Cm-244 to assess the radiation effects. Other older glasses containing Pu-238 have been prepared in the past but may have been discarded.

Other Sites. LANL prepared Pu-containing zirconolite in the early 1980s which may still be available. In addition, other countries with nuclear waste glasses or ceramics materials such as Britain, France, Russia, Belgium, Germany, and Japan may have radioactive archival samples.

CONCLUSIONS

The Symposium on the Scientific Basis for Nuclear Waste Management provided a forum for reporting and evaluating the state of the research in the immobilization of plutonium and other radioactive and hazardous waste components. The proceedings, which will be available in the Spring of 1996, will have been critically reviewed by experts in the field and will provide a timely volume of applicable research information for future research and development of plutonium immobilization processes and materials.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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V25.7 G. R. Lumpkin, K. L. Smith, and R. G. Blake, "TEM Study of Radiation Damage and Annealing of Neutron-Irradiated Zirconolite," ibid.

V25.8 D. Swenson, T. G. Nieh, and J. H. Fournelle, "The CaO-TiO_2-ZrO_2 System at 1200 ^{0}C and the Solubilities of Hf and Gd in Zirconolite," ibid.

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V25.12 E. R. Maddrell, "Effect of Conjoint Additions of Rare Earth Element Oxides on the Phase Stability of Zirconia," ibid.

Session Chair for Immobilization Waste Forms:
Leonard W. Gray, Lawrence Livermore National Laboratory, Livermore, CA
Wednesday, December 13, 1995; 10:00 am

NOTE: The tape recorder was accidentally turned off for this session. These notes are reconstructed as the best recollection of the session chairman, the panel members and some of the questioners.

Larry Penberthy, Penberthy Vitrification, Inc., Seattle, WA: I have six comments for the audience.

1. There have been repeated references to borosilicate glass as a host for plutonium for long term storage/disposition but no references to the soda-lime-alumino-silicate glass of commerce and antiquity. The Atomic Energy of Canada Ltd. researchers published in 1956-58 on an advanced variation for radionuclide sequestering by increasing the alumina. The American Nuclear Society published that the AECL glass is 1,000 to 10,000 times better for leaching resistance than is borosilicate glass. Plutonium has a long half-;life. Why is that superior waste form being ignored? There is an urgency to this question. Once borax is added to the glass composition, the glass is ruined forever. It is impossible financially to get the borax out and start over to make the good AECL alumino-silicate glass. The problem with borax in the melt composition is that the alkali-borate phase is soluble and is phase separated from the alumino-silicate phase. By keeping the alumino-silicate lacy, the alkali-borate solubilizes the glass.

2. To a glassmaker, it is misleading to express the percentages of plutonium oxide in a glass by weight. Ten wt% plutonium oxide is the equivalent of only 2 wt% of other glass forming oxides. Cesium is also "heavy" with respect to sodium. For instance, 40 wt% Cs_2O is chemically equivalent to 10 wt% Na_2O.

3. Plutonium is more likely to be in the glass as Pu_2O_3, as evident by the fact that the plutonium increases the melt viscosity of the glass, in parallel with Al_2O_3 and Fe_2O_3. Reversal of this increase is done by increasing the CaO content. This is well known in the glass industry.

4. Fused silica glass attacked by pure water is not suitable as a leaching resistance comparison. To the glass chemist, silica is an acid, and water is an alkali. There is direct chemical reaction between the two. The picture changes completely when the glass is multicomponent and the water is groundwater containing FeO, CaO, MgO and SiO_2. Adding Ca and Al oxides makes the glass more basic and increases chemical resistance in water. CaO, an alkaline earth, is used in all common glass to repel water.

5. Cs volatility is caused by the presence of borate in the melt. Cs borate is present as a separated phase having high vapor pressure. This has been proven be weight loss measurements at respective temperatures (1150°C for borosilicate glass Vs 1320°C for alumino-silicate) the borosilicate glass loses 5X as much weight (one hour test).

6. The fundamental error being made in all the radwaste glass studies is that each of borate and silicate makes a rational glass system, but not the two together.

Response from **Hong Li, PNL, Richland, WA:** Whether boron separates from the silicate glass depends on glass composition, i.e., the availability of alkalis in the glass. Several components¾Si, B, Fe, Zr, Al, tend to consume alkalis in the glass. Sufficient amounts of alkalis available for boron leads boron tetrahedrally bonded with oxygens and so boron will be in the glass network instead of separating from the glass in a separate phase. Otherwise, boron phase separation will take place in the glass. Therefore, it is very important to formulate glass such that the composition is outside of the glass immiscible boundary and so boron will not separate from the glass network.

Werner Lutze, University of New Mexico, Albuquerque, NM: I have a two-part comment.

1. In response to the previous comment concerning phase separation¾it should be noted the regions of glass-in-glass phase separation are well known in the open literature. Much work has been done to prove that high Level Waste Glasses are not phase separated.

2. Would the Panel please describe the analytical techniques used to determine solubility of Pu and the glass homogeneity?

Panel Response:

W. G. Ramsey, WSRC, Aiken, SC: We used X-ray Diffraction and Scanning Electron Microscopy to determine if a glass contains undissolved Pu. Transmission Electron Microscopy was done to determine if glass-in-glass phase separation is present. Small angle neutron scattering has not been performed to date.

Hong Li, PNL, Richland, WA: We used the over-saturation method, that is, spike a given component in the glass. If a second phase was observed, the concentration of the component of interest would be reduced. This was done until the component concentration reached a level at which no second phase in the glass was found by means of optical microscopy (from low magnification to high magnification), Scanning Electron Microscopy, and sometimes Transmission Electron Microscopy.

Carl Cooley, U.S. DOE/EM, Washington, DC: What guidelines do you work against with respect to Pu glass durability? I have heard durability values for different glasses and durability tests. What are your limits and how good does the glass have to be?

Panel Response:
W. G. Ramsey, WSRC, Aiken, SC: This is a loaded question but I will take a stab at it. There are no fixed glass or ceramic Pu waste form durability specifications. The baseline we use at Savannah River is the specification for high level waste glass. I think there is general agreement that there are several forms that are much more durable, (by that I mean orders of magnitude more durable) than the glass used as a specification for high level waste. One of the reasons we are investigating the interim, high temperature glass is the very high chemical durability. Obviously, no one will argue that zircon is not extremely durable. We, at Savannah River, have been using standard ASTM, the American Society for Testing and Materials, Tests developed for high-level waste. We also baseline our tests versus fused silica and quartz since they are well known and common materials.

Edwin S. Lyman, NCI, Washington, DC: I have been told and have heard presentations that indicate it would be possible to stack a metal plutonium alloy independent of geometry. Why are we not using or investigating these forms more?

Panel Response:
W. G. Ramsey, WSRC, Aiken, SC: If you remember, I showed the Sm to Pu ratio for one glass. This amount of neutron absorber would allow stacking independent of geometry. The problem is not stacking¾it is in production. You must handle and process the materials prior to stacking.

Dieter Knecht, LITCO, Idaho Falls, ID: I believe that the main problem is the ability to produce the plutonium boride. Boride may be less stable than oxide in a repository also.

Edwin S. Lyman, NCI, Washington, DC: What can you say about leach rates of neutron absorber versus Pu?

Panel Response:
L. W. Gray, LLNL, Livermore, CA: Ed, if I may, could we postpone that question until tomorrow? John Bates will be presenting a paper on just this topic, and it would be much better to defer this question to John.

John Bates, ANL, Argonne, IL: If I may, I would prefer to answer the question with the full paper tomorrow.

DISCLAIMER

The views expressed in this report are those of the author(s) or the individuals identified as making the remarks, and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

IMMOBILIZATION FACILITIES

SESSION CHAIR: THOMAS GOULD, WESTINGHOUSE SAVANNAH RIVER COMPANY

Immobilization Facilities Session Summary

Tom Gould, Westinghouse Savannah River Company

The objective of the Immobilization Facilities session was to discuss the engineering aspects and facility concepts for the various immobilization technologies proposed for plutonium. Regardless of the immobilization technology that might be chosen for implementation, there remains a major challenge to transform the science-based technology into a well engineered production plant that can immobilize the approximate 50 metric tons of surplus weapons plutonium in a manner that is: (1) safe, secure, and environmentally benign; (2) efficient to operate and maintain; (3) timely in its implementation; (4) cost effective; and (5) capable of producing durable immobilization forms acceptable for geologic disposal. This session provided an opportunity to learn about how several immobilization technology concepts will address these important factors.

The session's papers presented facility related information for tow immobilization forms, glass and ceramics. They described a number of immobilization processing options and facility concepts that are being developed or implemented for high level wastes in France, Russia, Australia, and the United States. Applications of these technologies to the immobilization of plutonium with high level waste were described and included information on pre-treatment, immobilization equipment concepts, waste and off-gas considerations, integrated process flowsheets and use of existing facilities.

Because of time constraints, only two questions were addressed at the end of the formal presentations. The first, asked of Adam Jostons by Jeffrey Kass, dealt with the apparent difference in Synroc leach rates for plutonium and gadolinium, a neutron absorber important to preventing criticality in a repository. Dr. Jostons pointed out that the tests were performed in distilled water and that the leach rates for both species were extremely low. Also, under the repository's geochemical conditions, he indicated that the leaching of the two elements should be congruent and exhibit similar characteristics to the natural mineral forms that have existed for hundreds of millions of years.

The second questions, from the session chair, Tom Gould, to both Victor Kushnikov and Antoine Jouan, addressed the similarities and differences of the cold crucible, induction melter techniques being applied in Russia and France to immobilize high level wastes. In general, their are many similarities between the two approaches. The major difference is the frequency of the high voltage source; the Russian application uses a high frequency source while a much low frequency source is used in the French program. The lower frequency was adopted in the French program to facilitate transmission through thick shield walls and the use of larger capacity melters. Both countries have successfully demonstrated the cold crucible, induction melting technology with high level waste at production scales.

In conclusion, the papers presented in the Immobilization Facilities session indicate that both glass and ceramic forming technologies are available that could be effectively applied to the immobilization of surplus plutonium with high level waste. A significant effort will be required to develop and engineer one or more of these technologies into an efficient immobilization plant capable of producing repository-acceptable waste forms.

DISCLAIMER

Glass and Ceramic Immobilization Alternatives and the Use of New Facilities

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INTRODUCTION

The Department of Energy (DOE) is examining options for placing weapons-usable surplus nuclear materials (principally plutonium [Pu] and highly enriched uranium [U]) in a form or condition that is substantially and inherently more difficult to use in weapons either by the Host Country or by a sub-national group.

The goals of the program as recommended by the National Academy of Sciences study "Management and Disposition of Excess Weapons Plutonium"[1] are:

(a) Minimize the time during which the plutonium is stored in forms readily usable for nuclear weapons.

(b) Preserve material safeguards and security during the disposition process, seeking to maintain the same high standards of security and accounting applied to stored nuclear weapons;

(c) Result in a form from which the plutonium would be as difficult to recover for weapons use as the larger and growing quantity of plutonium in commercial spent fuel; and

(d) Meet high standards of protection for public and worker health and for the environment.

The two most promising alternatives for achieving these aims, according to the study are:

- Fabrication and use as fuel, without reprocessing, in existing or modified nuclear reactors; or
- Vitrification in combination with high-level radioactive waste.

A third option, burial of the excess plutonium in deep boreholes is also being investigated.

IMMOBILIZATION

Immobilization is the fixation of surplus fissile materials, in this case plutonium, in an acceptable matrix to create an environmentally benign form for disposal in a repository. In addition to the traditional characteristics required of an immobilization form to achieve isolation of the plutonium from the biosphere over geologic time periods, the immobilization for the Fissile Materials Disposition (FMD) Program must also possess the property that it is inherently as difficult to recover the fissile material from the immobilized form as from spent fuel. This latter requirement is part of the so called "spent fuel standard" invoked in the National Academy of Sciences (NAS) study on plutonium disposition. From this perspective, high level waste (HLW) or other radioactive species, such as cesium (^{137}Cs), can be added with the fissile material into the waste form to create a radiation field which can serve as a proliferation deterrent.

The mission of the immobilization technologies considered in this paper and the paper, "Use of Savannah River Site (SRS) Facilities for Glass and Ceramics," is to produce a waste form by incorporating plutonium in either an amorphous glass or a crystalline ceramic matrix for final disposal in a geologic repository. This paper summarizes all the glass and ceramic alternatives under consideration in the immobilization program and presents, specifically, those options which use new facilities. The subsequent paper presents the immobilization options which use existing facilities at the Savannah River Site.

Assumptions and Design Basis

The major assumptions used in the development of the various immobilization alternatives are shown in Table (1).

Table 1. Immobilization planning assumptions.

Feed material to immobilization	**Pits and the various stabilized plutonium forms stored as a result of the DNFSB recommendation 94-1 remediation program and declared excess for national needs.**
Processing duration	**10 years for 50 metric tons of Plutonium***
Number of waste canisters	**600–1200**
Size (maximum) of canister	**3 m long by 0.6 m diameter**
Radiation dose rate	**1000 R/hr at 1 m 30 yr after fabrication**
Weight % Pu per canister	**0.4 –12**
RCRA listed materials	**Minimized or eliminated**
All waste generated	**Must have disposition path available**
TRU waste	**Must meet WIPP-WAC**
Inadvertent criticality	**Possibility very low; requires several independent and unlikely events to occur**

*Includes all separated weapons-usable plutonium declared surplus to defense and other (National) programmatic missions other than inventories with >5% ^{233}Pu.

Five immobilization alternatives, three glass and two ceramic, were analyzed in detail from an end-to-end perspective as illustrated in Figure (1). Each alternative receives feed in the form of pits and materials resulting from the 94-1 remediation program which is processed at a Pu conversion and immobilization facility, stored on site for an interim period, and then transported for final disposal at a geologic repository. The source of the radiation spike for the new facility alternatives will be ^{137}Cs in the form of CsCl contained in capsules from Hanford. The radiation source for the existing facility alternatives will most likely be HLW in existing waste tanks at SRS.

Glass and Ceramic Immobilization Alternatives

Pre-conceptual designs for the three glass and two ceramic alternatives have been analyzed. Table (2) summarizes the characteristics of these five alternatives and Figure (2) illustrates the physical configuration of the waste canisters which are the output products of the immobilization facilities.

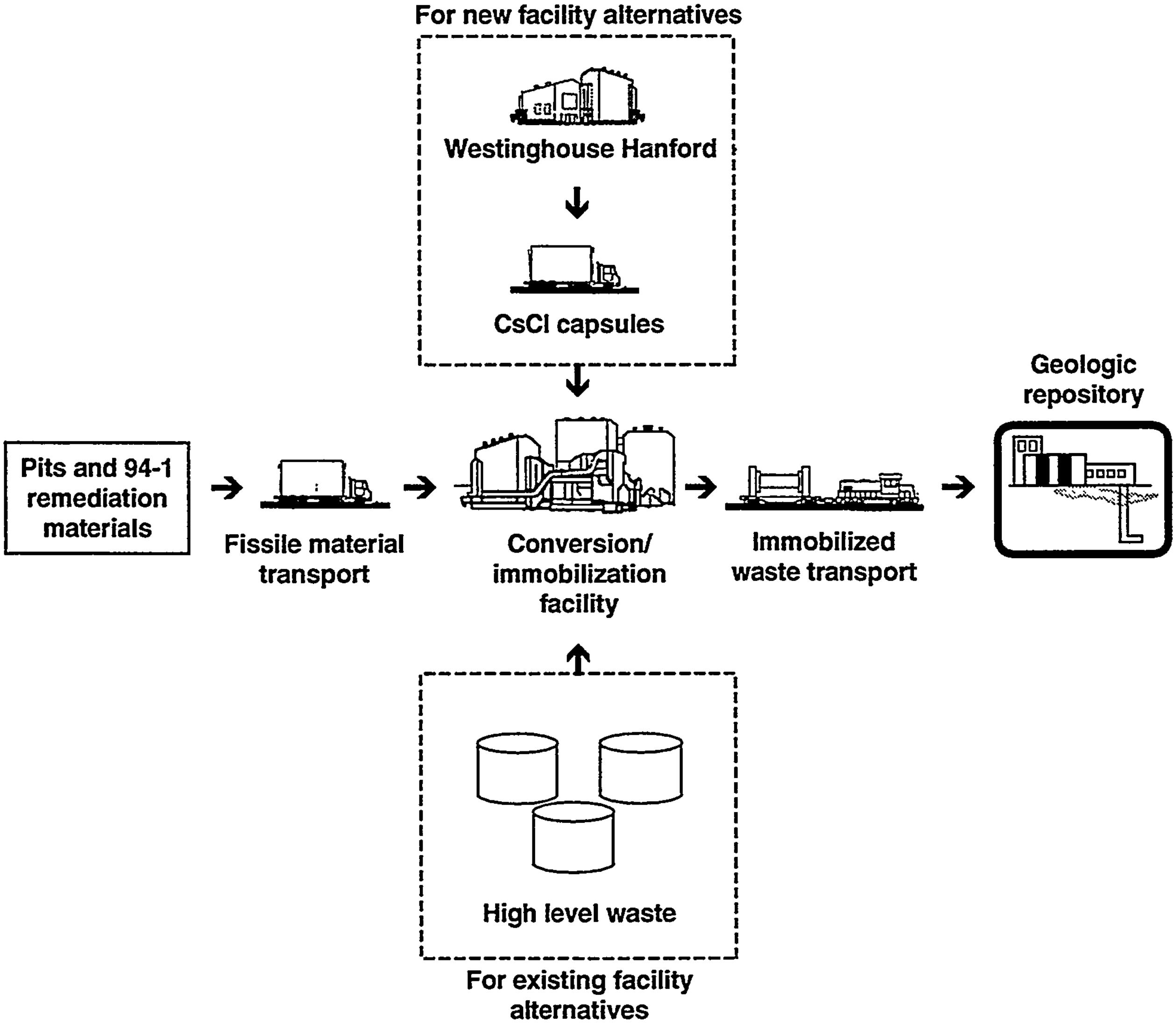


Figure 1. Immobilization end-to-end alternatives.

Table 2. Characteristics of glass and ceramic alternatives.

Alternatives	Waste form containing Pu	Nominal Pu loading wt %	Source of radiation spike	Number of waste canisters
Glass				
New Facility	Low-temp. borosilicate glass	5	^{137}Cs within matrix	600
Adjunct melter	Low-temp. borosilicate glass	5	HLW within matrix	600
Can-in-canister	High-temp. borosilicate glass	10*	HLW surrounding matrix	1000 (200 incremental)
Ceramic				
New Facility	Titanate based ceramic	12	^{137}Cs within matrix	640
Can-in-canister	Titanate based ceramic	12**	HLW surrounding matrix	640

*Pu loading in the cans containing Pu only glass. The loading average over the canister is ~3%.
**Pu loading in the cans containing Pu only ceramic. The loading averaged over the canister is ~3%.

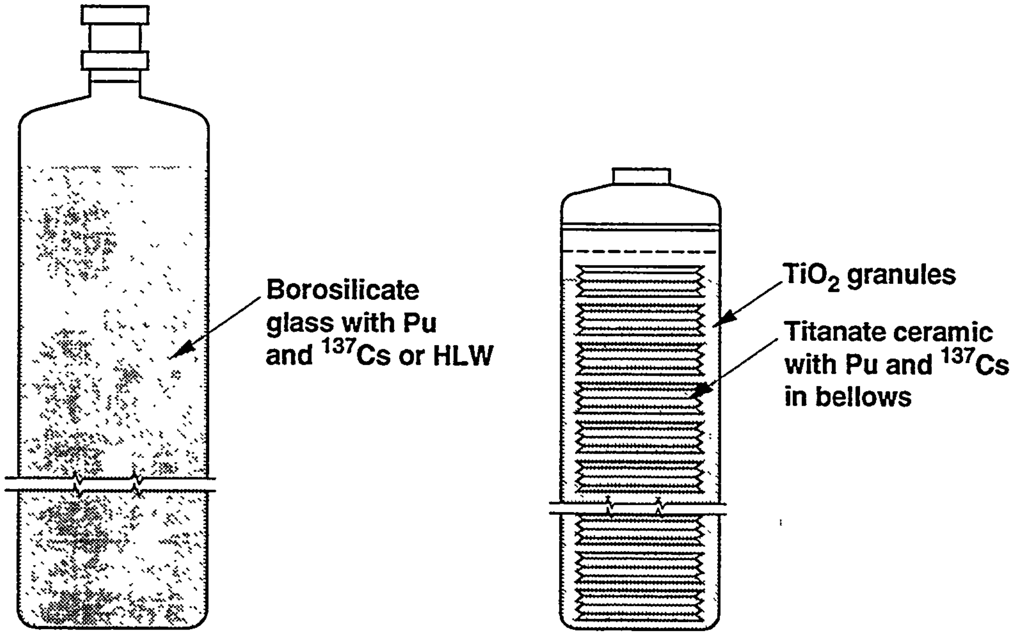
NEW FACILITY ALTERNATIVES

First Level Flow Diagram

The first level flow diagram, for the glass and ceramic new facility alternatives, are shown in Figure (3). The input feed materials are first processed into Pu oxide by equipment located in the glove box operation part of the facility. In a glass facility, the oxide is fed to a first stage melter which produces Pu glass frit. This frit is then processed in the second melter to produce the waste form within a canister. In a ceramic facility, the oxide in solution is first calcined, then hot pressed within a container (bellows) to produce the waste form which is then loaded into the canister. ^{137}Cs, the radiation spike material, is introduced into the process at the points indicated. The ^{137}Cs is derived from CsCl contained in capsules located at the Hanford Site. The portions of the equipment which involve processing with ^{137}Cs are located in the remote operation (hot cell) part of the facility. Neutron absorbers, such as gadolinium, samarium or hafnium, are also added to the waste form for criticality control. After interim storage, the canisters are transported for disposal in the geologic repository.

Conceptual New Facility

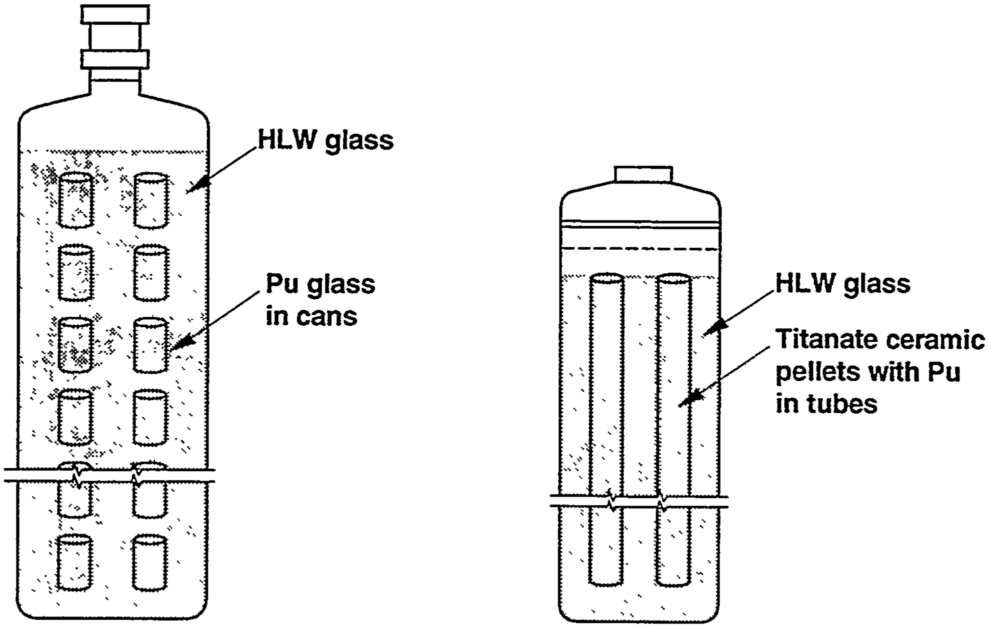
Figure (4) illustrates a conceptual design for a new glass or ceramic immobilization facility. The Pu conversion and immobilization building will contain all plutonium processing and immobilization operations, including front-end processing to convert the pits and 94-1 materials into plutonium oxide, cesium preparation, final immobilization of feed materials into a homogeneous plutonium glass or ceramic waste form containing a ^{137}Cs spike, and interim canister storage. The process areas will be a safety class Category I reinforced concrete structure. Support facilities include an administration building, maintenance shops, substation, cooling tower, guardhouses, fan house and stack, radwaste building, and chemical and water storage tanks.



New Facility and Adjunct melter glass

New Facility ceramic

Internal radiation barrier



Can-in-canister glass

Can-in-canister ceramic

External radiation barrier

Figure 2. Physical configuration of waste canisters.

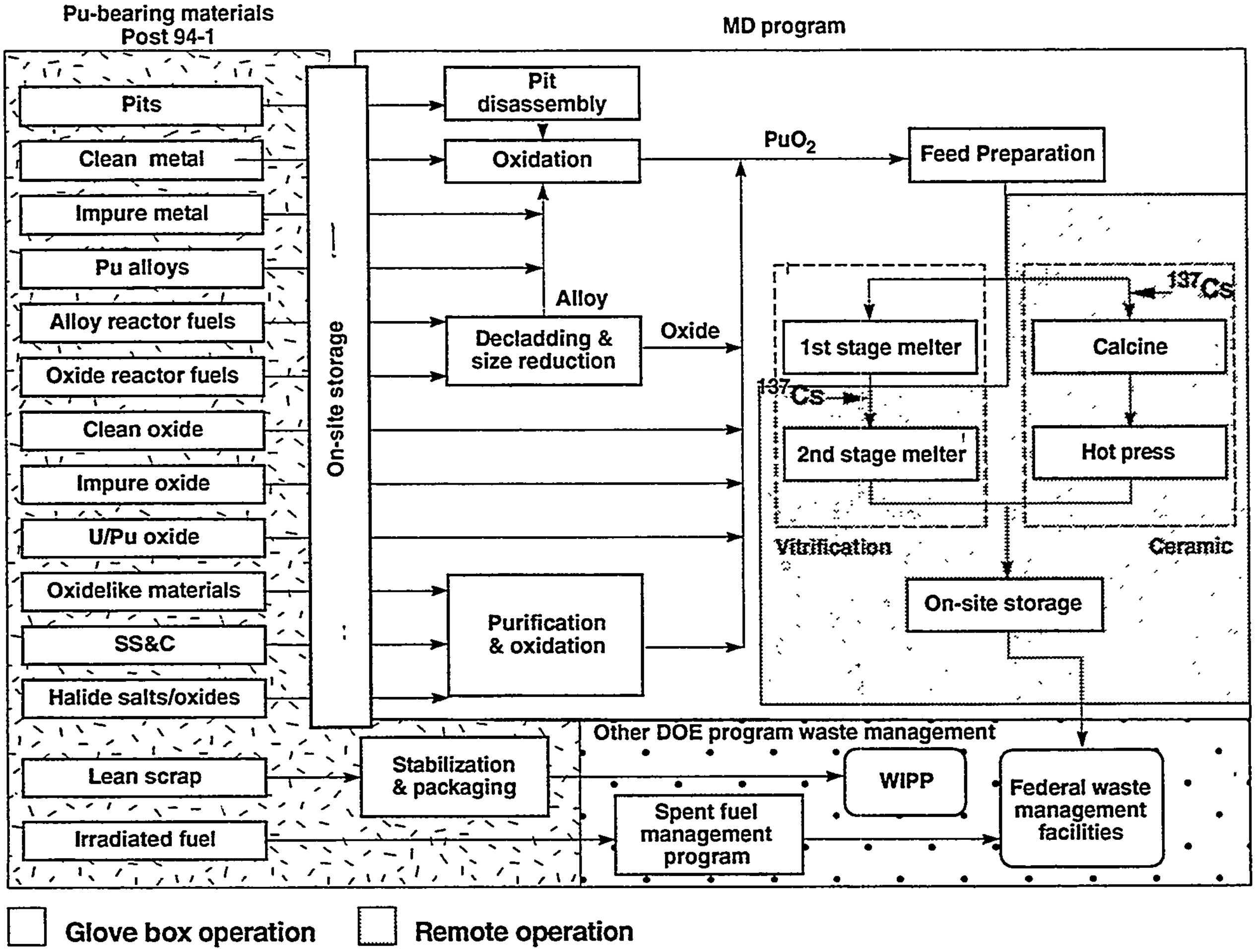


Figure 3. First-Level Flow Diagram, End-to-End New Glass and Ceramic Alternatives. A facility will contain either the glass or ceramic back-end portion of the flow sheet, but not both.

Second Level Flow Diagrams

Figure (5) shows the second level flow diagram for the front-end Pu conversion unit operations which produces Pu oxide from the feed materials. These unit operations are essentially identical for all of the five glass and ceramic alternatives. The hydride/dehydride oxidation unit is used to convert pits, unirradiated fuel elements, and alloy components to the oxide. Halide-containing materials undergo a halide wash followed by pyrolysis and calcination. Oxides and oxidelike materials are fed directly to immobilization pre-treatment via interim storage.

The second level flow diagrams for the back-end immobilization processing are different for the five alternatives. Figures (6) and (7) are the second level flow diagrams corresponding to the new glass and ceramic facility alternatives respectively. In the new glass facility alternative, Pu oxide is combined with glass frit containing neutron absorbers in the first stage melter to produce a Pu glass frit. This frit is blended with ^{137}Cs and additional glass frit in the second stage melter to produce a Pu glass containing a radiation spike which is poured into a canister. The CsCl is dissolved and then converted using an ion exchange process, prior to blending in the second stage melter.

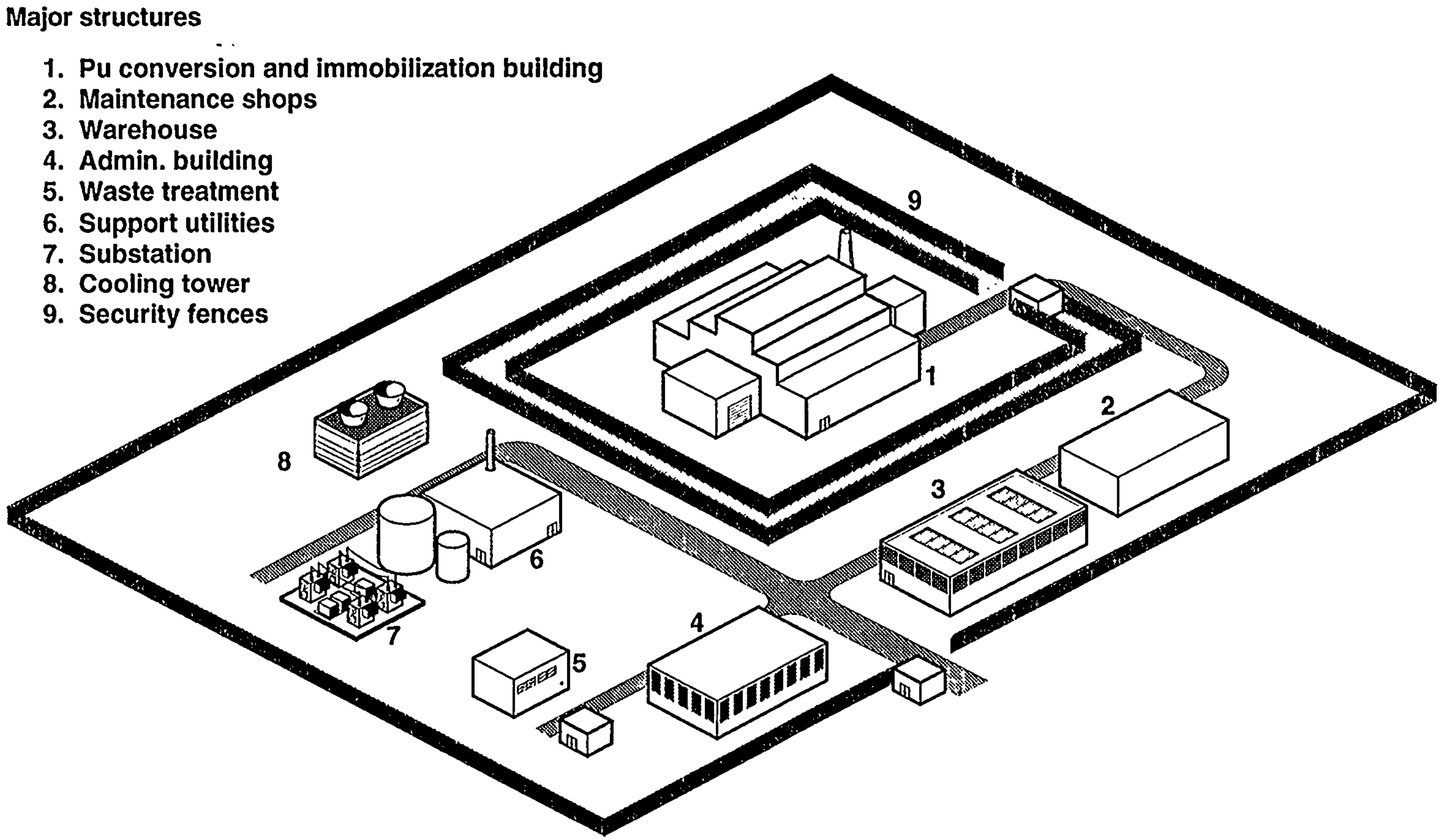


Figure 4. Conceptual new immobilization facility.

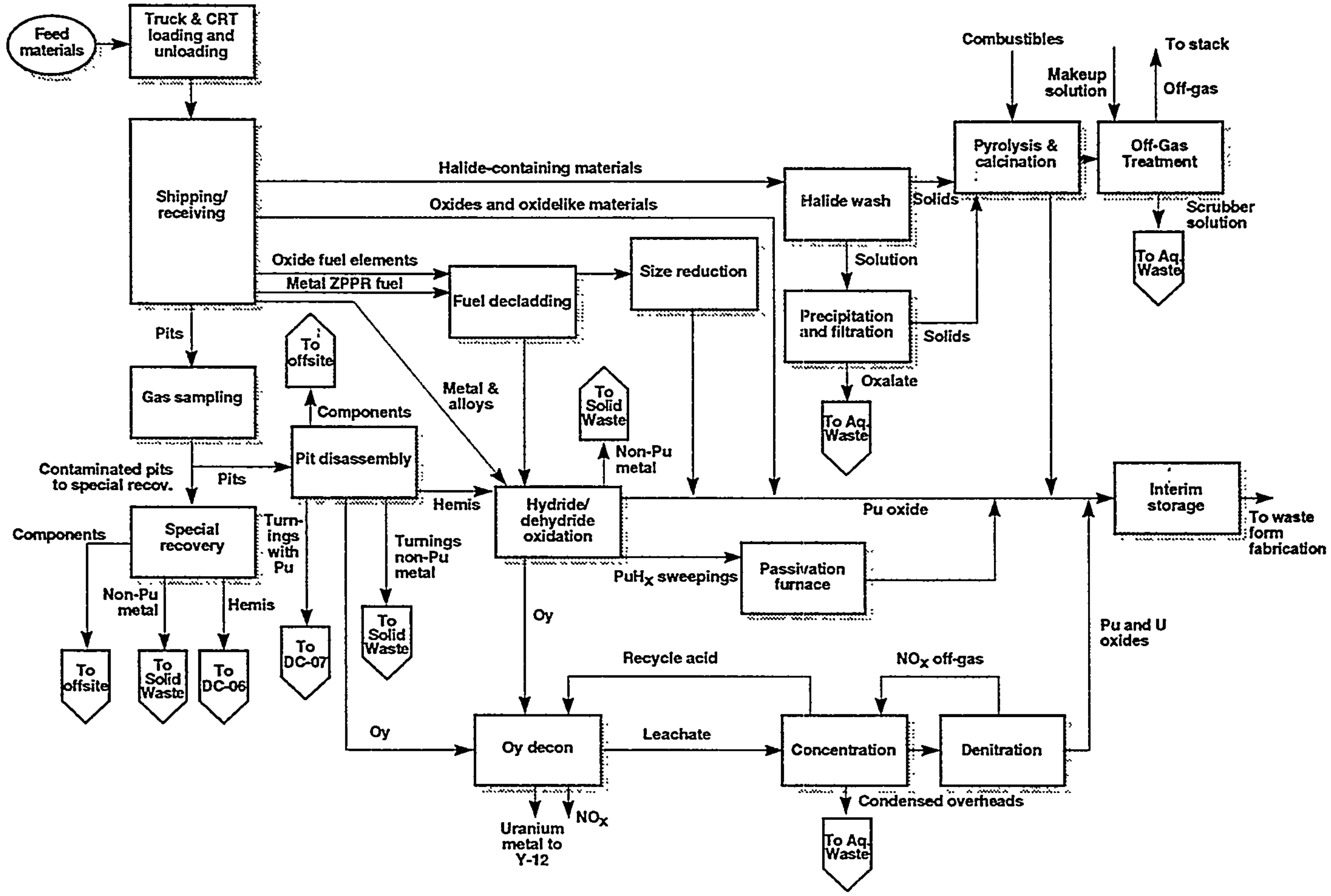


Figure 5. Second-level flow diagram, front-end Pu feed material processing.

In the new ceramic facility alternative, Pu oxide is combined with ceramic precursors and neutron absorbers and fed to a calciner. The resultant powder material is loaded into bellows, sealed, and then hot pressed to produce the waste form. The individual product bellows are then loaded into a canister.

New Facility Schedule

Figure (8) shows the schedule for design, licensing, construction, operation and decontamination and decommissioning (D&D) of the new facility when its mission is completed. A number of the activities can be accomplished in parallel so the total time required for all activities is approximately 25 years. Congressional funding and initial activities are expected to take five years. Research and Development, prototyping and process engineering are expected to take ten years to fully develop the glass or ceramic process for production scale operations. Development of conceptual designs, NEPA support for license application, and permitting are expected to take six years. Project authorization, Title I design, and preparation for the NRC license application with a Safety Analysis Report (SAR) are expected to take four years. The NRC license process is expected to take five years and construction of the new facility, startup, and the Operational Readiness Review (ORR) are also expected to take five years. Facility operations should be for about ten years and D&D of the facility will require about three years.

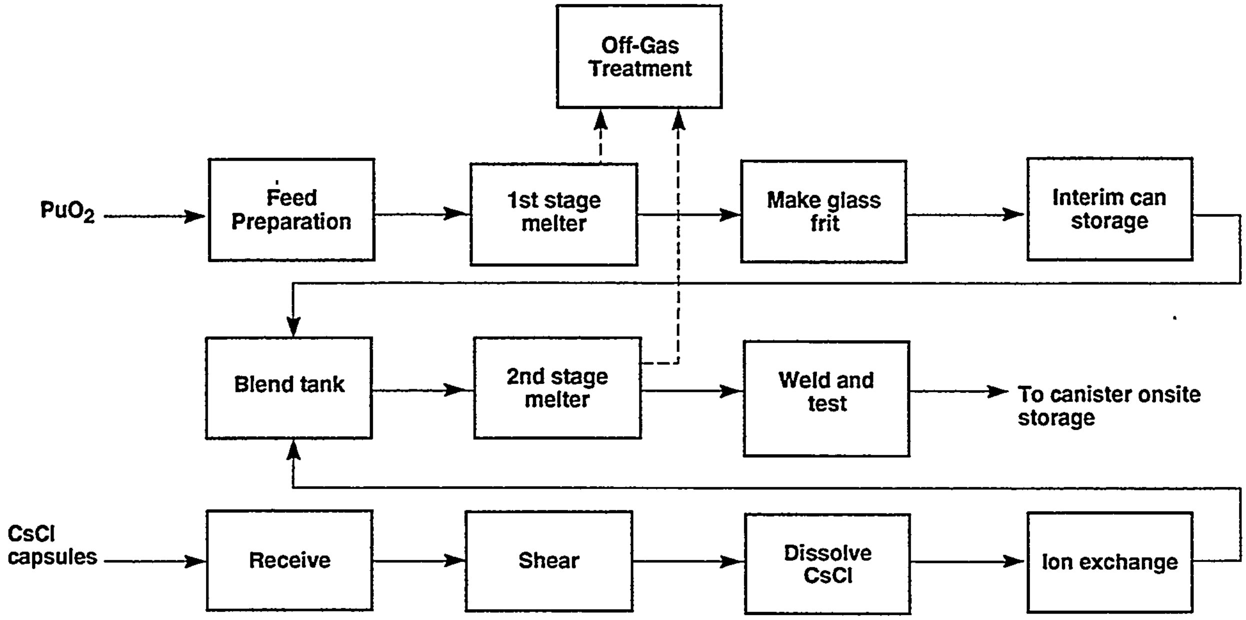


Figure 6. Second level flow diagram, glass back-end immobilization processing.

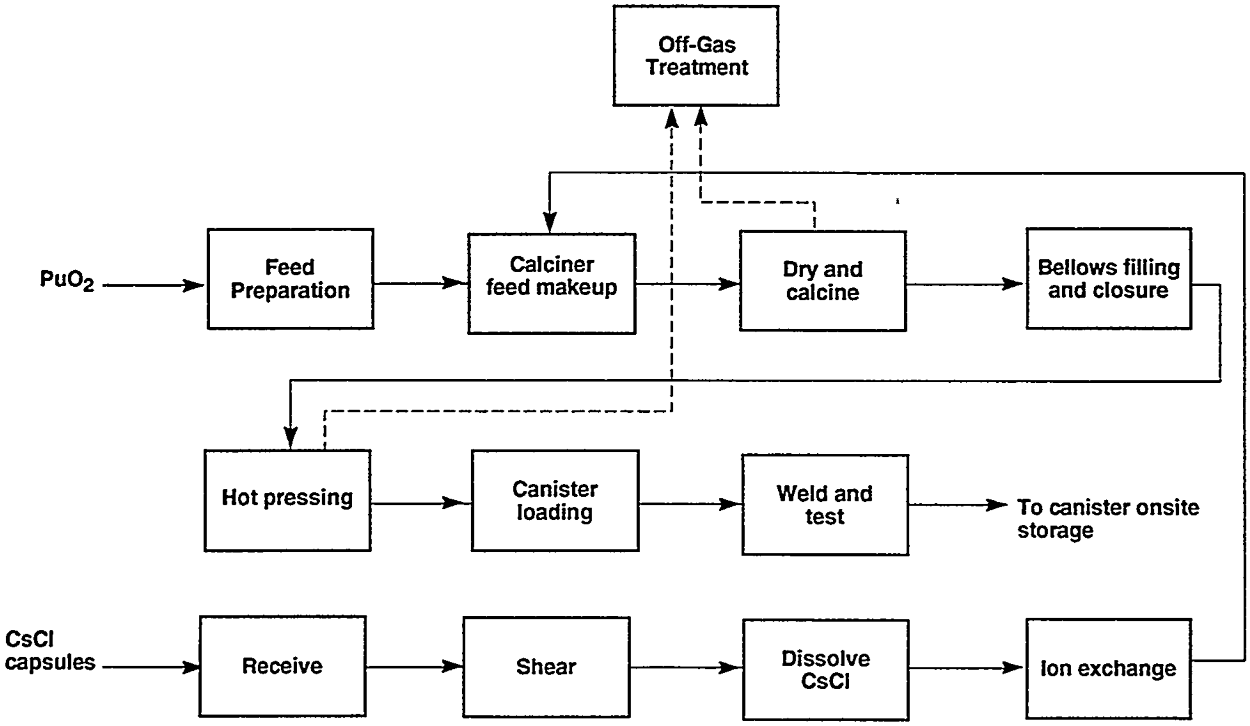


Figure 7. Second level flow diagram, ceramic back-end immobilization processing.

R&D Needs

Extensive worldwide experience with vitrification has been accumulated from the processing of glass containing low level and high level waste. Much less experience has been obtained with ceramics. Despite this background, the database for incorporation of significant amounts of plutonium in glass and ceramic is very limited. Therefore a certain amount of research and development (R&D) must be performed before the design of Pu conversion and immobilization facilities can begin with acceptable risks. Technical areas where research and development are needed include:

- Pu solubility and kinetics
- Processibility issues
- Waste form dissolution characteristics
- Criticality during processing and in the repository

Summary

The planning basis for the immobilization program assumes that 50 metric tons of plutonium is dispositioned within 10 years of operation of an immobilization facility.

Immobilization of surplus plutonium in a glass or ceramic waste form is technically viable. However, immobilization of the quantities of surplus plutonium to be dispositioned requires additional research and development. The end-to-end immobilization alternatives were analyzed from an end-to-end perspective which encompasses receipt of surplus feed materials as pits and other materials resulting from the 94-1 remediation program, processing to oxide and the immobilized waste form, interim storage and final disposition in a repository.

Three glass and two ceramic immobilization alternatives were developed and analyzed at the pre-conceptual level. Glass and ceramic alternatives producing waste forms incorporating Pu and ^{137}Cs uniformly distributed in the waste matrix and which use new stand-alone facilities were reviewed in detail.

Disclaimer

The views expressed in this paper are those of the author(s) and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

Reference

1. *Management and Disposition of Excess Weapons Plutonium,* National Academy Press, Washington, D.C., 1994.

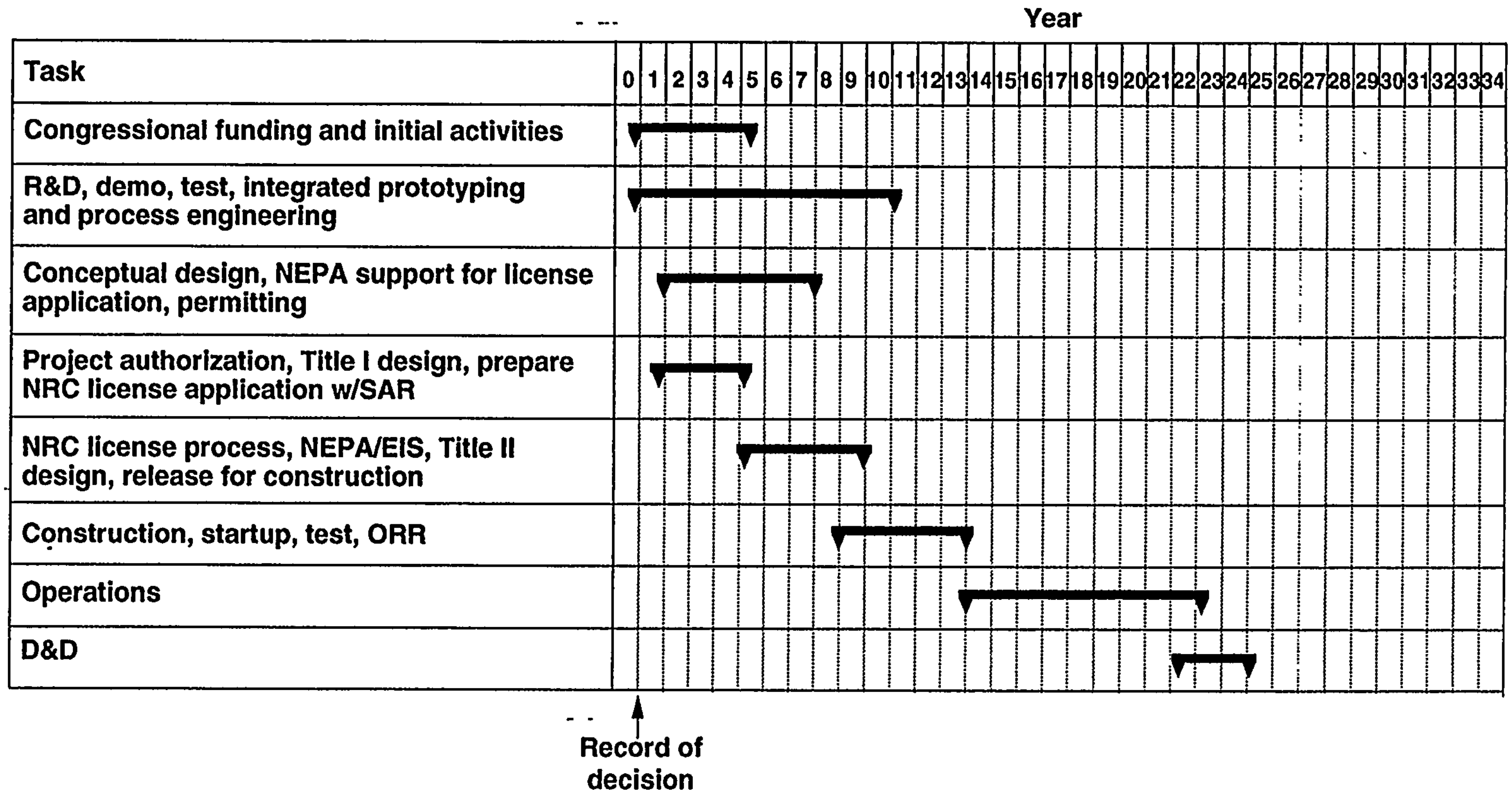


Figure 8. New Facility Immobilization Alternative Schedule.

Use of Savannah River Site Facilities for Glass and Ceramics

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ABSTRACT

Existing structures and processing facilities at the Savannah River Site are being considered for immobilization of plutonium. The Defense Waste Processing Facility (DWPF) which has completed cold testing and is scheduled to begin radioactive operation later this year to vitrify High Level Waste (HLW) has been considered for vitrification of plutonium and a means to provide a radiation barrier for plutonium glass. Introduction of plutonium into the DWPF processing stream and incorporating the plutonium in the (HLW) glass matrix would require significant modifications and upgrades to the facility. These would impact the schedule for its primary mission which is to vitrify HLW stored in tanks at the Savannah River Site. This paper discusses three options that utilize the DWPF with significantly less impact on its primary mission. Two of the options place small cans of plutonium glass or ceramic matrices containing plutonium into a DWPF canister and then pour HLW glass around the cans to provide proliferation resistance. The processing of HLW glass is not affected by the cans. The third option uses a portion of the DWPF feed process and a new facility in S Area where DWPF is located. All of these options use the existing 221F Separations Canyon building for processing the plutonium feed material and preparing the plutonium glass or ceramic containing plutonium.

INTRODUCTION/SUMMARY

In the process of evaluating immobilization of surplus plutonium the Department of Energy is considering using existing facilities. Vitrification is one of the options for immobilization, so utilizing the Defense Waste Processing Facility (DWPF) at the Savannah River Site was investigated. The initial focus was on adding the plutonium to the melter feed. As this was studied, it became apparent that this would have a significant impact on the schedule for the primary mission of DWPF which is to immobilize High Level Waste (HLW) stored in tanks at the Savannah River Site. Three options are now being considered which would utilize the DWPF, facilities in Building 221-F in F Area and the infrastructure of the Savannah River Site. The existing and near-future infrastructure includes analytical and development laboratories, liquid and solid waste treatment facilities, a new actinide Packaging and Storage Facility, a large, well trained work force, fire and medical facilities, site security systems and training facilities.

One option is to make a plutonium glass, encapsulate this plutonium glass in small cans and then place these small cans in a DWPF canister in Building 221-F. These canisters would then be transported to DWPF and filled with HLW glass. The HLW glass provides proliferation resistance. With this option there is no change in the feed preparation or glass production process in DWPF and minimal impact on the primary mission of DWPF. Another option employing this general approach is to immobilize the plutonium in a ceramic, encapsulate the ceramic in small cans or rods and then place these small cans or rods in a DWPF canister.

A third option is to utilize a portion of the DWPF feed preparation process and then to construct a new facility adjacent to DWPF for adding plutonium to the melter feed stream and incorporating the plutonium in the HLW glass. A plutonium glass frit produced in Building 221-F is one of the input streams in the new facility.

These options entitled Vitrification Can-in-Canister, Ceramic Can-in-Canister and Vitrification Adjunct Melter to DWPF are discussed in this paper.

DISCUSSION

Utilizing the DWPF for immobilization of surplus plutonium is being evaluated by the Department of Energy as part of the Fissile Material Control and Disposition Program. This use of the DWPF would be an extension to its primary mission which is to immobilize HLW stored in tanks at the Savannah River Site. This waste will be immobilized in a borosilicate glass matrix and encapsulated in large (approximately 10 foot by 2 foot diameter) stainless steel canisters. This process is shown schematically in Figure 1.

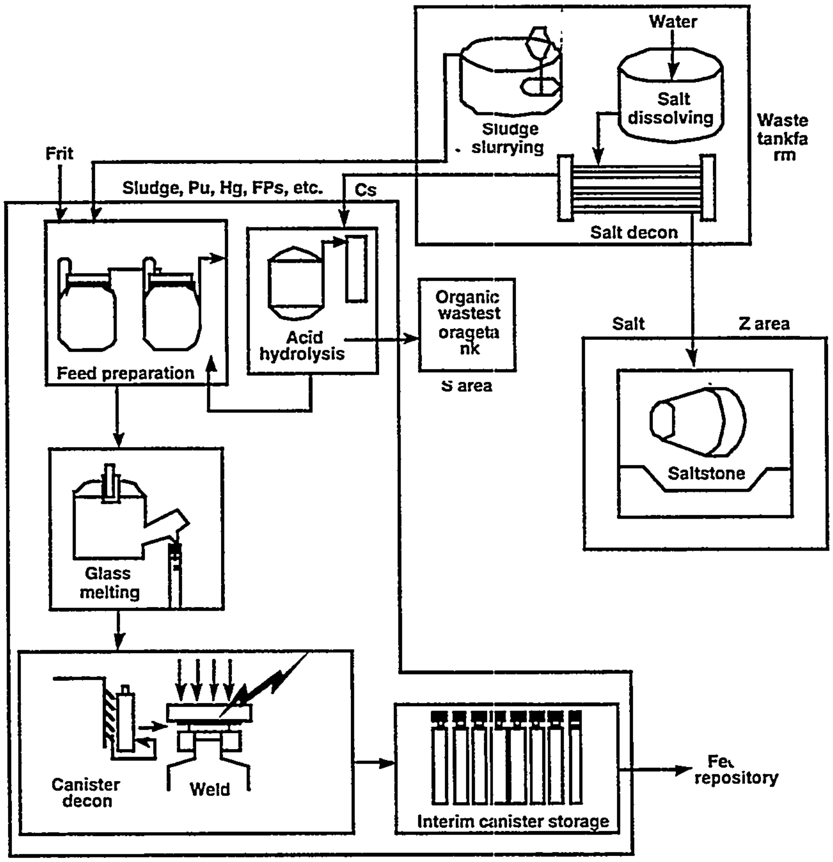

Figure 1. DWPF Schematic

One option considered earlier for utilizing DWPF was to add plutonium to the glass used to make the frit for the Feed Preparation process. In DWPF this would require extensive modifications/upgrades in the facility to address criticality safety with large quantities of plutonium in the large, cylindrical process vessels, criticality safety in the melter, recovery of plutonium from the off gas system, the addition of plutonium to the source term for postulated accidents and material accountability as metric tons of plutonium are processed in conjunction with HLW. The expected impact to the DWPF process schedule is significant. Therefore alternative options were developed.

The Vitrification Can-in-Canister option would place small cans of plutonium glass in the DWPF canister shown schematically in the block labeled "Glass Melting" in Figure 1. The Ceramic Can-in-Canister option would place small cans or rods of ceramic containing plutonium in the DWPF canister. With both of these options there is no change in the feed preparation or glass production process in DWPF and minimal impact on the primary mission of DWPF. The Vitrification Adjunct Melter to DWPF would utilize the DWPF for Acid Hydrolysis and the first step in the Feed Preparation where the product from Acid Hydrolysis is mixed with the sludge slurry and the mixture treated with nitric acid in the Sludge Receipt and Adjustment Tank. The product from this process would be transferred to a new facility where frit containing plutonium would be added to prepare the melter feed. The Glass Melting, the Canister Decon and Weld would be done in the new facility, which would be designed to address the issues discussed above.

For each of these options there is a feed stream that is the product of a first stage process to immobilize plutonium - a plutonium glass log, ceramic pellets containing plutonium and a plutonium glass frit. These processes would be carried out in existing facilities at the Savannah River Site in one of the chemical separation areas - F-Area Building 221-F. The Plutonium Storage Facility (PSF) sits atop Building 221-F and provides the following capabilities:

- a fully safeguarded vault for manual transport, automated stacking
- and storing of shipping containers containing plutonium in primary
- containers
- facilities and instruments for non-destructive assay and computer
- accountability of special nuclear material, and
- gloveboxes for opening shipping containers and removing and inspecting their
- contents.

PSF was essentially complete in 1991 when Department of Energy directed that it be placed in a standby condition due to changed mission objectives. New Special Recovery also sits atop Building 221-F. The facility was built to dissolve plutonium scrap, oxide or metal from various sources throughout the DOE Complex to produce purified plutonium metal or oxide powder. It was designed in the early 1980's under DOE Draft Order 6430.1 and includes state-of-the-art features such as near real time accountability, remote operation using a distributed control system, shielded gloveboxes, waste handling and seismic design. Installed equipment and capabilities include:

- a glovebox for feed preparation
- a glovebox for waste handling
- two gloveboxes for dissolving and anion exchange purification
- of dissolver solutions
- a spare room for additional facilities, and
- a remote control room with a distributed control system

NSR was essentially complete in 1991 when the Department of Energy directed that it be placed in a standby condition due to changed mission objectives. Building 221-F is a remotely operated and maintained facility consisting of a warm canyon, a hot canyon and a utilities and services center section. The center section area and the 3rd level would be used for processing of stabilized plutonium. Over 35,000 square feet of clean, usable space is available in these areas. A project for a new vault - the Actinide Packaging and Storage Facility - designed to store packages of stabilized plutonium for up to 50 years has been initiated. The design is modular and its capacity could be expanded to accommodate the plutonium feed for any of these immobilization options. The new vault is expected to be complete by the year 2002.

The feed for first stage process is plutonium bearing materials that have been stabilized for intermediate storage as specified in the Defense Nuclear Facilities Safety Board Recommendation 94-1. The processing of these stabilized materials would also take place in Building 221-F. This overall process for the Vitrification Can-in-Canister is shown schematically in Figure 2.

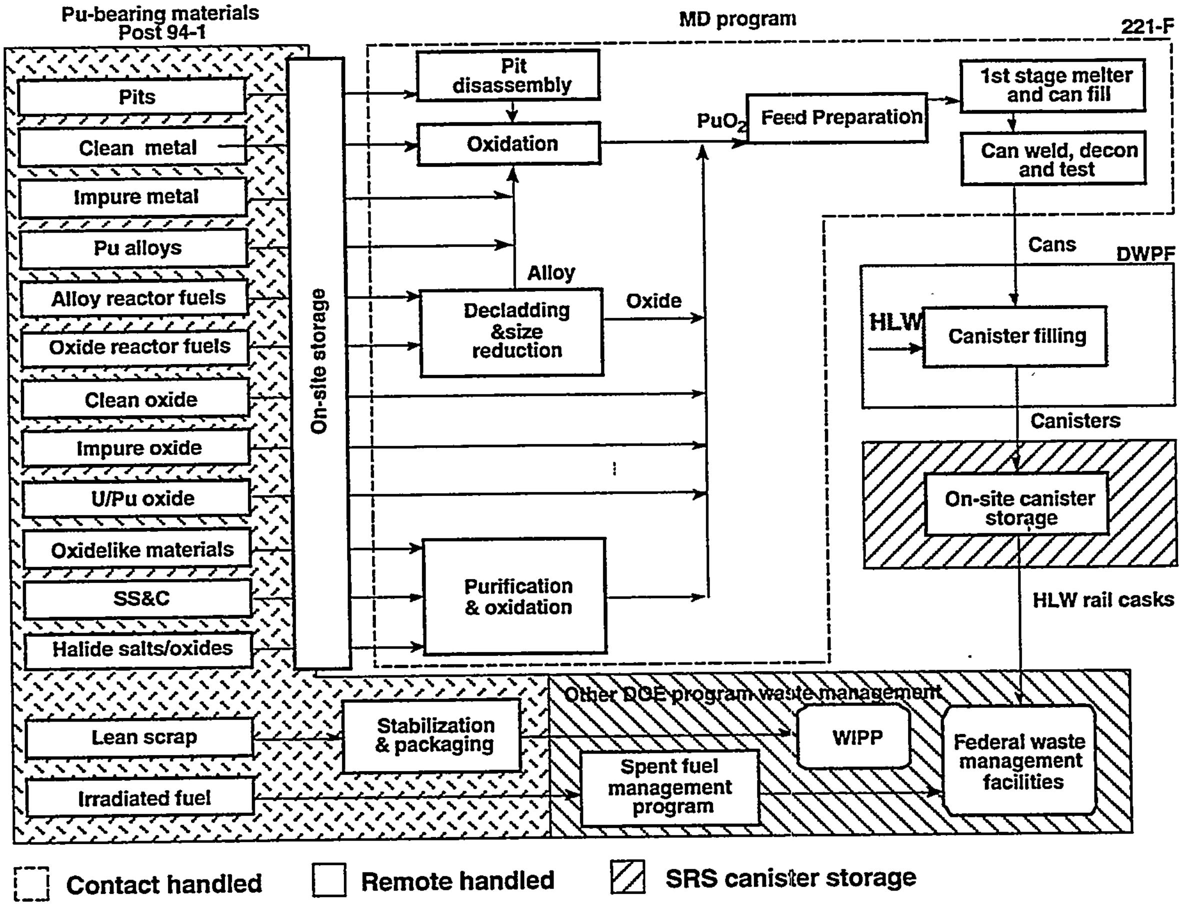

Figure 2. Top Level Flowsheet Vitrification Can In Canister

Except for feed preparation and processes specifically related to filling cans with Pu glass, the processes for Ceramic Can-in-Canister at SRS and the Vitrification Adjunct Melter to DWPF are the same.

Front End Processes

The processes for converting stabilized plutonium materials to oxide feed are the same for all three options. The material would be received and unloaded in the existing Plutonium Storage Facility. The rest of the processes will be carried out in New Special Recovery and areas within Building 221-F.

There are five basic streams:

- The pits are gas sampled to check for contamination. Uncontaminated pits are sent to disassembly. Contaminated pits go to Special Recovery where they are decontaminated and disassembled. The plutonium forms go to Hydride/Dehydride/Oxidation.
- Metals and alloys go to Hydride/Dehydride/Oxidation.
- The metal Zero Power Physics Reactor (ZPPR) fuel is declad and then goes to Hydride/Dehydride/Oxidation.
- Oxide fuel elements are declad and then ground to form an oxide powder.
- Halide containing materials are washed. Solids will be filtered and sent to pyrolysis and calcination. Plutonium in the wash solution will be precipitated, filtered and then sent to pyrolysis and calcination.

Vitrification Can-in-Canister

The back end flow diagram for the reference process in which PuO_2 feed goes into a plutonium glass log in a small can and small cans are encapsulated in HLW glass in a DWPF canister is shown in Figure 3.

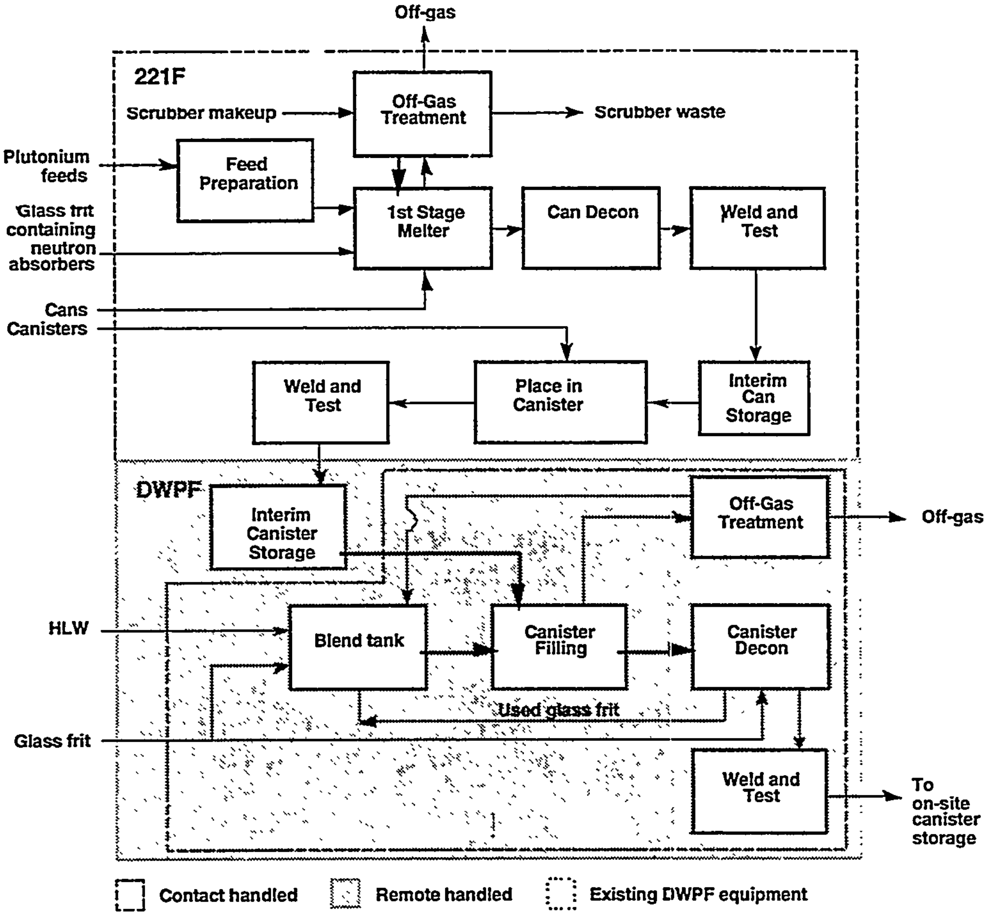

Figure 3 Vitrification Can In Canister

The SRS facilities to be utilized for this option are in Building 221-F and DWPF. In 221-F the plutonium glass will be made and poured into small cans and the cans placed in interim storage. Equipment will be installed in the Warm Canyon Truck Well to place the small cans on a rack, place the rack into a DWPF canister and welded the top onto the DWPF canister. In DWPF an interim canister storage vault will be constructed in the Service Building adjacent to Building 221-S. The rest of the process steps will be carried out in existing facilities in Building 221-S.

In this flow sheet, the Feed Preparation would be grinding the oxide to obtain adequately sized oxide for feed to the First Stage Melter. If testing planned for next year indicates that a wet plutonium feed (Pu dissolved in nitric acid) is needed to obtain desired processing rates through the first stage melter, then this processing block would be dissolution of oxide. The decision to go to a wet feed for the first stage melter could lead to a reevaluation of the front end flow sheet. In terms of the vitrification flow sheet, it would be desirable to avoid high fired oxide, which is difficult to dissolve.

Nuclear criticality is a primary consideration. The first stage melter would be designed to be critically safe. A potential choice for the melter is a small bushing melter, which is in the shape of a slab. A melter of this design is being tested at the Savannah River Site for another program to vitrify curium and americium. The Off Gas Treatment will be designed to cool the gases and trap plutonium that is entrained as particles in the melter off gas. This plutonium would be returned to the first stage melter feed. Plutonium dissolved in the scrubber solution would be sent to the Savannah River Site waste tanks. By vitrifying the plutonium without HLW the offgas system will not have the very high radiation associated with Cs-137.

To process 50 metric tons of plutonium in 10 years will require multiple first stage melter process lines. The frit for the first stage melter will contain neutron absorbers that, together with the plutonium, will be a part of the glass matrix. The composition of the glass will be measured and the poison will be credited in establishing that configurations for the subsequent process steps and for on-site storage are subcritical. Work is in progress to establish the effectiveness of these poisons in a repository environment, where the leach rates of the poison may be greater than that of the fissile material. The glass will be poured into small cans (approximately 4 to 6 L). A plug cap will be installed, the can will be decontaminated and then the cap will be welded onto the can. The cans will be weighed, bar coded and assayed non destructively.

Because the first stage vitrification will proceed the processing in DWPF and there may be a time lag before processing in DWPF, interim storage of the cans will be provided in Building 221-F. When the canisters are removed from interim storage they will again be decontaminated. They will be placed on support racks designed to keep the cans out of the DWPF pour stream during filling of the canister. The racks and cans will be placed into a DWPF canister without a head. After the rack and cans have been placed in the canister, the head will be welded onto the canister. These canisters will be required to meet the same specifications (in terms of weld quality, dimensions and cleanliness) as canisters now purchased from a vendor. This process will be automated to reduce personnel exposure from the ^{241}Am in the plutonium.

The canisters will be transported from F Area to DWPF using a shipping container designed to minimize the vibration or acceleration loads on the rack. A security force will accompany the canister during transport. At DWPF the canisters will be placed in a storage vault that will be constructed in the loading area of the Service Building. The vault will be shielded for ^{241}Am and be provided with safeguards and security equipment commensurate with the material being handled. The canisters with the cans of plutonium glass will be transported to the DWPF melt cell along an existing corridor, which will be upgraded to provide shielding from the ^{241}Am and safeguards and security equipment.

Once the canister is in the DWPF melt cell, the operations will be identical to those for a standard DWPF canister. The canister will be placed on the melter pour table, moved under the melter, filled with HLW glass, rotated away from the melter and plugged and leak tested. The canister will then be decontaminated and sent to the weld station to have a permanent plug installed. An appropriate security force will accompany the canister as it is transported to the second Glass Waste Storage Building, which will be designed to receive canisters with cans of plutonium glass. The eventual transfer of these canisters to a Federal Waste Management Facility will require adapting the Waste Qualification Program already developed for DWPF HLW glass to the plutonium glass.

The primary areas to be addressed in the R&D program for this option are:

- The composition and plutonium loading of the glass in the cans.
- The effect of the cans on filling of the DWPF canisters

The glass selected for the first stage of this option will have to have a relatively high loading of plutonium (~ 10 weight percent). A neutron absorber will be incorporated in the glass matrix. The absorber will be selected based on preventing nuclear criticality during processing, interim storage and long term behavior in the repository. The effect of reheating to about 900°C during the pouring of HLW glass into the DWPF canister on crystallization and durability will be evaluated. The effect of the cans on the filling of the DWPF canister will be studied. The selection of a glass composition and the number of cans per DWPF canister will take into consideration:

- the number of DWPF canisters that will contain plutonium glass
- the total plutonium loading in each DWPF canister
- the voids, if any, in the DWPF canisters due to the presence of the small cans

Ceramic Can-in-Canister

In this option PuO_2 is immobilized in ceramic pellets which are encapsulated in small cans or rods and the small cans or rods are encapsulated in HLW glass in a DWPF canister. The back end flow diagram for the reference process is shown in Figure 4.

The SRS facilities to be utilized for this option are in Building 221-F where the ceramic pellets will be prepared, pressed and sintered and loaded into cans or tubes. Equipment will be installed in the Warm Canyon Truck Well to place the small cans or tubes on a rack, place the rack into a DWPF canister and welded the top onto the DWPF canister. As in the Vitrification Can in Canister, an interim canister storage vault will be constructed in the Service Building adjacent to Building 221-S in DWPF. The rest of the process steps will be carried out in existing facilities in Building 221-S.

The processes in Building 221-F will take place in gloveboxes. One glovebox would be used for Feed Preparation. For the reference process this is dissolution of oxide. If a dry process were used this would be vibratory milling. Calciner Feed Makeup, Dry and Calcine and Milling and Granulation would be in another glovebox. Pellet Pressing and Sintering would take place in individual gloveboxes. The rest of the operations would be essentially the same as those for Vitrification Can in Canister.

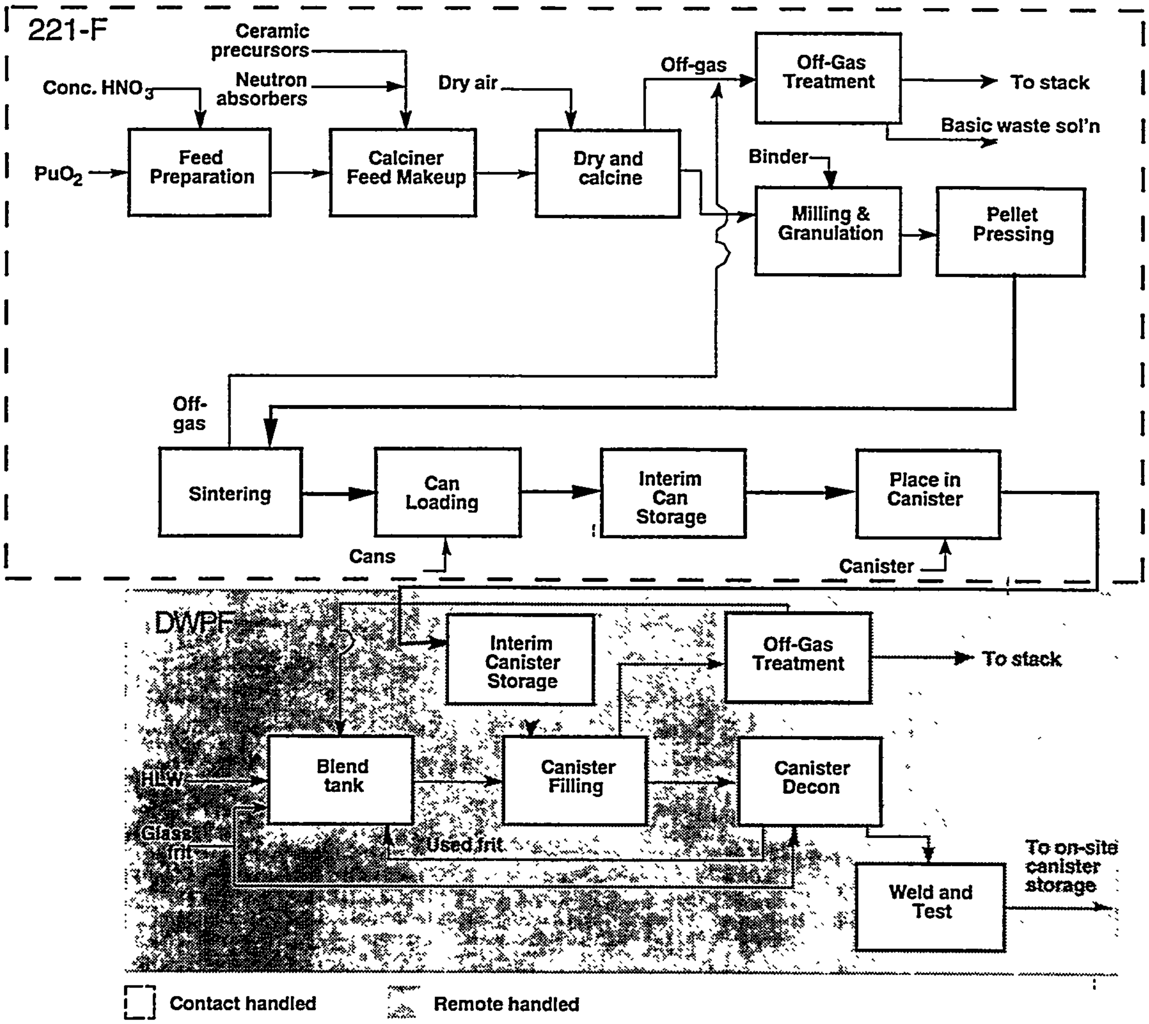

Figure 4 Ceramic Can In Canister

The eventual transfer of these canisters to a Federal Waste Management Facility will require modifying the Waste Qualification Program already developed for DWPF HLW glass to account for the cans in the canister and developing a Waste Qualification Program for the ceramic containing plutonium.

As was the case for Vitrification Can in Canister, the primary areas to be addressed in the R&D program for this option are:

- The precursor feed composition/morphology and processing conditions
- Simultaneous loading of plutonium and a neutron absorber
- The effect of the cans or tubes on filling of the DWPF canisters

The ceramic selected for this option will have to have a relatively high loading of plutonium (~ 12 weight percent). A neutron absorber will be incorporated in the ceramic matrix. The absorber will be selected based on preventing nuclear criticality during processing, interim storage and long term behavior in the repository. The effect of reheating to about 900°C during the pouring of HLW glass into the DWPF canister will be evaluated. The effect of the cans or tubes on the filling of the DWPF canister will be studied. The selection of a ceramic composition and the number of cans or tubes per DWPF canister will take into consideration:

- the number of DWPF canisters that will contain plutonium in a ceramic matrix
- the total plutonium loading in each DWPF canister
- the voids, if any, in the DWPF canisters due to the presence of the
- cans or tubes of a ceramic containing plutonium.

Vitrification Adjunct Melter to DWPF

This option in contrast to the two options discussed earlier would require construction of a new canyon facility in S-Area at the Savannah River Site. The new facility could be constructed while the DWPF is operating. DWPF would have to be shutdown for the tie in between the facilities. The back end flow diagram for the reference process in which PuO_2 feed goes into a plutonium glass frit which is then blended with HLW to make the feed for a second stage melter is shown in Figure 5. The plutonium-HLW glass from the second stage melter is encapsulated in a DWPF canister.

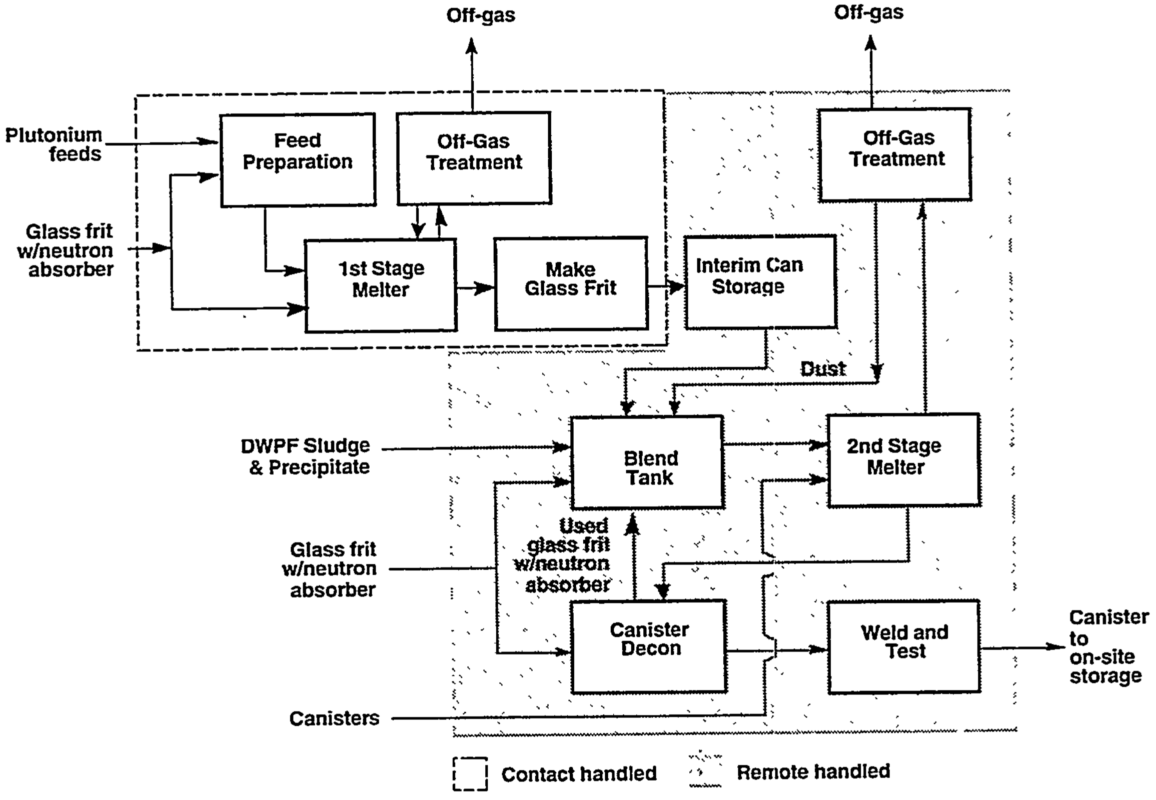

Figure 5 Vitrification Adjunct to DWPF

The SRS facilities to be utilized for this option are in Building 221-F where the plutonium glass frit will be made and put into storage cans and the cans placed in interim storage. The Adjunct to DWPF will tie into the existing DWPF building at the outlet to the Sludge Receipt and Adjustment Tank (SRAT). This stream will be one of the feeds into the blend tank in the new facility. This new facility will also utilize the lines setup to recycle waste streams from DWPF back to the tank farm.

In this flow sheet, as in the Vitrification Can in Canister, the Feed Preparation in the reference process is grinding the oxide to obtain adequately sized oxide for feed to the First Stage Melter. The melter and offgas systems would be essentially the same as those for Vitrification Can in Canister. To make the glass frit the stream exiting the melter enters a thermal crusher where nitrogen-cooled rollers cause the stream to solidify and flake. These flakes are collected in cans which are decontaminated and sealed for interim storage in Building 221-F.

The cans of plutonium glass frit will be transported from F Area to the Adjunct to DWPF in a shipping container. A security force will accompany the canister during transport. At the Adjunct to DWPF the canisters will be placed in a storage vault until they are ready to be opened and their contents added to the process stream. The vault will be shielded for ^{241}Am and be provided with safeguards and security equipment commensurate with the material being handled.

In the Adjunct to DWPF the plutonium glass frit, glass frit containing a neutron poison and the process stream from the SRAT are combined in a vessel that will duplicate the process in the Slurry Mix Evaporator in the DWPF. The product stream will go to a melter feed tank and then be fed to the second stage melter. The designs of these vessels and the melter will have to address nuclear criticality safety. Accountability for the plutonium in the HLW stream will also be a design and operational constraint. The output stream from the second stage melter will go into a standard DWPF canister. The rest of the process steps will be the same as those in the DWPF process discussed above for the Vitrification Can in Canister option. The eventual transfer of these canisters to a Federal Waste Management Facility will require adapting the Waste Qualification Program already developed for DWPF HLW glass to the HLW-plutonium glass.

The primary areas to be addressed in the R&D program for this option are:

- The composition and plutonium loading of the glass frit
- The composition and plutonium loading of the HLW-plutonium glass.
- Plutonium accountability in the feed stream, melter and off gas of the HLW-plutonium glass process

The plutonium glass selected for the frit for this option will have to have a relatively high loading of plutonium (~ 10 weight percent). Data to be developed for the HLW-plutonium glass include the plutonium loading, the neutron absorber loading and durability. A neutron absorber will be selected based on preventing a nuclear criticality during processing, interim storage and long term behavior in the repository.

CONCLUSION

For the three options discussed, Building 221-F and the DWPF at the Savannah River Site can be used to immobilize surplus plutonium without having a significant impact on DWPF's primary mission to immobilize high level waste. Vitrification Can in Canister and Ceramic Can in Canister require no new heavily shielded facilities. For these options plutonium is immobilized without fission products and then the DWPF HLW glass provides a source of radiation. The Vitrification Adjunct Melter to DWPF requires a new heavily shielded facility to incorporate plutonium into a HLW glass. The new heavily shielded facility incorporates downstream processes similar to those in the existing DWPF operation.

DISCLAIMER

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ACKNOWLEDGEMENTS

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Using an Induction Melter With a Cold Crucible for the Immobilization of Plutonium

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Significant reductions in defense programs and the dismantling of large numbers of nuclear weapons have placed on today's agenda questions of safe handling, utilization and burial of weapons-grade plutonium. The optimum approaches to the management of surplus plutonium stocks in the United States and Russia may differ because of the differences in policies of the two countries on the plutonium fuel cycle, the infrastructure of reactors and the reprocessing of radioactive waste.

There are two approaches to this issue that are closest to satisfying safety criteria for handling of surplus plutonium:

- utilization of the plutonium as fuel in existing or modified reactors
- vitrification of plutonium along with high level waste.

This report looks at the possibilities for immobilizing weapons-grade plutonium in glass-type materials that satisfy requirements for eventual burial in deep geological formations and correspond to the standards set for spent fuel.

The proposed plan for the reprocessing of weapons-grade plutonium (Figure 1) and its immobilization in glass-type materials may be regarded as a vitrification operation for separated high level waste, produced during the regeneration of spent fuel.

High level waste separation calls for the extraction of the cesium and strontium fraction (total concentration 12 g/l), the transplutonium elements and rare earth fraction (maximum concentrations for transplutonium elements - 2.5 g/l; for rare earth elements - 26 g/l) and the residual solution that contains the rest of the radionuclides and the equipment corrosion products.

The process of vitrifying plutonium with the necessary admixtures so that it satisfies the standards set for spent fuel and provides for a decrease in criticality, will be, to a great extent, quite similar to the vitrification process for the transplutonium and rare earth fractions.

After warheads are dismantled the fissile material must be ground up and oxidized producing a chemically highly active plutonium dioxide with the necessary physio-chemical properties that will simplify its further reprocessing. We all know that the dissolution of metallic plutonium in mineral acids poses significant problems and as a rule the plutonium is never completely dissolved. If hydrochloric or hydrofluoric acid is used to achieve greater dissolution of plutonium, problems are created further down the line in the reprocessing because of the presence of Cl and F ions in the solution. However, we can significantly reduce the volume of secondary waste products containing plutonium (hard to dissolve residues formed when metallic plutonium is dissolved) from plutonium reprocessing if we use the chemically active plutonium dioxide (dissolution in nitric acids, direct solidification of the dioxide as it fuses with fluxing admixtures).

At the next stage we can consider two options as further steps in the handling of the plutonium dioxide.

The first option calls for "wet processing" and requires at the initial stage the preparation of a solution of plutonium dioxide in nitric acid. This is necessary if technology used for the vitrification of high level liquid waste is applied to plutonium. The choice of this option means that the vitrification process will produce glass containing plutonium together with fission products (prior to vitrification the solution with plutonium is mixed with high level liquid waste from the reprocessing of spent fuel). Fluxing admixtures are added at the high temperature synthesis stage to satisfy specifications for the final product and to produce materials with the desired properties.

The second option is the "dry processing" of plutonium, which makes it possible to avoid the dissolution step and, on the one hand, simplifies the technological process, while, on the other hand, makes possible the production of either an intermediate material with both plutonium and high concentrations of fissile materials (for later synthesis with the proper admixtures into a glass-type composite material) or the direct production of a vitrified product.

The molten glass products are poured into containers of the proper shape and after decontamination are transferred to interim storage facilities or to burial sites.

The proposed approach for the reprocessing of weapons-grade plutonium makes it possible to use the vitrification technology to produce vitrified materials with a plutonium concentration up to 20%.

The proposed technology for the vitrification of weapons-grade plutonium could be based on the two-stage solidification process used in the reprocessing of high level waste that uses an induction melter with a cold crucible (IMCC). The melting process in the IMCC is based on the ability of high frequency electromagnetic fields to penetrate the whole thickness of the material and to release their energy as they subside. The special feature of IMCC is that it allows synthesis of different types of material with a broad range of compositions. It becomes possible to apply the IMCC melting technology for the purpose of solidifying waste from various technologies used in the reprocessing of spent fuel, including waste produced as a result of the separation of high level waste, as well as toxic waste, containing heavy metals.

Most of the work in the development of the IMCC technology was connected to the solidification of high level liquid waste at Mayak. Most of our experience was with the vitrification of simulated high level waste that was immobilized in phosphate and borosilicate glass.

Composition 1

Na_2 o - 5.0
Cs_2O - 5.3
K_2O - 3.7
NiO - 0.2
CaO - 0.3
Fe_2O_3 - 1.3
Cr_2O_3 - 0.3
MnO_2 - 0.5
SrO - 2.1
BaO - 2.2
ZrO_2 - 6.8
MoO_3 - 4.5
RuO_2 - 4.0
Rh_2O_3 - 1.7
PdO - 1.7
oxides
REE - 16.7

Composition 2

Al_2O_3 - 41.9
Na_2O - 3.1
NiO - 0.1
Fe_2O_3 - 1.2
Cr_2O_3 - 0.3
oxides
REE - 0.2

Composition 3

Al_2O_3 - 18.9
Na_2O - 54.0
CsO - 0.5
NiO - 7.6
CaO - 5.6
Fe O - 14.3
Cr O - 3.0
MnO - 3.2
SrO - 0.4

Composition 4

Al O - 19.0
Na O - 67.4
NiO - 6.3
Fe O - 7.0
Cr o - 3.0

Composition 5

Cs_2O - 9.2
SrO - 4.5
BaO - 4.8
PbO - 1.1

Composition 6

Oxides
Fe, Cr, Ni 64.3

Composition 7

Oxides
REE - 30.3
ZrO - 8.5

We also applied the IMCC technology and studied some of the physio-chemical properties of pyroxene type mineral matrices (aegirine, jadeite, aegirin-augite, orthite and others) and of orthosilicates (andradite, sphene, lovchorrite and others). The total concentrations of oxides and other waste components that were incorporated onto these materials were equal to 15% of the mass: Cs_2O - 5.0; SrO - 3.0; CeO_2 - 5.0; Fe_2O_3 - 2.0.

Based on the results of a series of studies of solidification technologies for various simulated high level wastes, a pilot facility was created at the Mayak vitrification site with a two-stage process for the immobilization of high level waste on phosphate and borosilicate glass as well mineral type materials.

The solidification process for liquid high level waste at the pilot facility includes the following steps:

- selection of the composition of liquid high level waste and their fluxing with orthophosphoric acid for the production of phosphate glass of a given composition;
- processing of the initial simulated high level waste in a concurrent flow evaporator in order to produce a highly concentrated solution;
- vitrification of the concentrated salty melt;
- drainage of the melted glass into cans;
- placement of cans in cases;
- decontamination from gas releases.

The fluxed solution of high level waste (Figure 2 and 3) continuously enters the concurrent flow evaporator at a rate of 100 dm^3/hr. The evaporator, heated by steam at 0.5 MPa, is co-located with the separator. Monitoring of the concentration process is done through the measurement of pressure at the point the solution enters into the evaporator (EV), and the pressure of the steam used for heating, by flow-meters, and through the measurement of the salt concentrations in the initial solution.

The concurrent flow evaporator is a vertical assembly with the main working section in the form of a spiral enclosed in a steam jacket. The solution enters in countercurrent to the steam. The stationary zone for the separation of the vapor-gas phase and the salt melt is the interior shell of the steam jacket - the separator.

The processes in the concurrent flow evaporator develop in the following order as the material progresses though the system: heating, evaporation and the removal of nitric acid, partial interaction of the nitrates with the orthophosphoric acid, and drying. After the separation of the vapor-gas phase and the melt in the separator unit, the melt flows by gravity into the IMCC at the rate of 30 - 40 kg/hr. The vapor-gas phase enters the first purification stage - the sparger-cooler.

Dehydration and denitration occur in the IMCC at 1100 - 1200^{0}C with the production of phosphate glass at the rate of 15 - 18 kg/hr.

The IMCC is a rigid construction composed of cooling pipes mounted around a water collector. The crucible is surrounded by the water-cooled inductor that is connected to a high frequency generator (Figure 4).

The molten product is discharged from the crucible into 200 dm^3 containers placed on a circular conveyer belt.

Scales will be used to monitor the filling operation.

During the normal mode of operation of the IMCC, the crucible will continuously discharge the melt into containers. A special device will interrupt the drainage operation until a new container is in place.

Start up of the IMCC requires initial heating, which is achieved through the interaction between the high frequency field and the conductive material brought into the crucible. The start-up operation can be accomplished by a mixture of materials or broken glass (initial), or with glass that has hardened in the crucible (secondary).

The filled containers are cooled and placed in cases, which are sealed by welding and, after the seals are tested, are transferred to storage.

The first step of the gas purification process during the vapor-gas phase separation stage is the sparger-cooler, where the vapors are condensed, the condensate is cooled, and the first phase of aerosol capture takes place.

When tests are conducted at the EV-IMCC facility with simulated solutions, the second gas purification step is an adsorption column for the capture of nitric oxide, after which the decontaminated gas is released into the atmosphere.

During the vitrification of actual high level liquid waste in the EV-IMCC, the gas purification system of the direct heating electrical furnace will be used. The radionuclide removal coefficient for the gas purification system is 10^8 - 10^9.

A closed cooling system with demineralized water or condensate with a specific resistance below 20,000 Om*cm is used for cooling both the IMCC and the high frequency generator in order to provide for accident-free operations.

The two-stage pilot facility is located in a hot chamber and is being used for the following tasks:

- perfecting solidification technology for high level waste on the basis of simulated and actual waste products;
- perfecting the functioning of connectors and mechanical assemblies for operation in a remote mode;
- perfecting transfer technology for the removal of containers with solidified waste and other equipment.

The dimensions of the chamber are given in mm:

Length	8750
Height	4100
Width	2000

The chamber where the EV-IMCC is located has a space for a conveyer for containers with the following dimension:

Length	2000
Height	1200
Width	2000

The technical parameters of the simulated HLW solidification facility are:

• throughput volume of initial solution, l/hr	100
• temperature of the glass melt entering the containers, ^{0}C	1200

Concurrent flow evaporator:

• throughput volume of initial solution of simulated HLW	100
• steam consumption, kg/hr	120
• steam temperature at evaporator inlet, ^{0}C	150
• operating pressure at evaporator inlet, MPa	0.4-0.5
• dimensions, m	
diameter	0.55
height	1.2

Cold crucible (a two-zone crucible):

• nominal capacity of the tank	22.6
• melting mirror area, dm^2	
boiling zone	6.7
processing zone	1.8
• maximum operating temperature, ^{0}C	1500
• glass throughput by mass, kg/hr	up to 18
• oscillating power of the high frequency generator, kW	160
• power consumption, kW	240
• operating frequency, Mhz	1.76
• inductor cooling water consumption, m^3/hr	2
• crucible water consumption, m^3/hr	4
• cooling water temperature, ^{0}C	
inlet	
outlet	25±5
• cooling water pressure, MPa	45±5
	0.4

Sparger-cooler:	210
• vapor-gas mixture consumption, m^3/hr	
• vapor-gas mixture temperature, ^{0}C	
inlet	300-600
outlet	55
• cooling water flow rate, m^3/hr	25
• cooling water temperature, ^{0}C	
inlet	25
outlet	30
• cooling water pressure, Mpa	0.4

Circular conveyer:	
• load-carrying capacity, N	$1.2*10^3$
• number of slots for containers, pc	2
• angle of swing, degrees	180

Weighing equipment:	
• weight of container filled with glass, kg	600
• the weighing device is an electronic tensometer	

The phosphate glass product is placed in containers with the following parameters:	
• diameter, mm	575
• height	1000
• material	steel #3

Weight of empty container, kg	95±10

Volume of container, dm^3	
• total	220
• useable capacity	200

Volume of glass mixture poured into container, dm^3	190±10

The pilot two-stage vitrification facility for high level waste will be the prototype for the industrial scale technologies of that type to be installed at the second production line at Mayak (Figure 5 and 6).

The unique features of the melting process in the IMCC make it possible to use this technology for the reprocessing of liquid radioactive waste and toxic waste.

Induction melting in a cold crucible offers the following unique possibilities not available with melters of other types:

- the possibility to vary melting temperatures within a wide range of both temperatures and solidification mixtures from glass to mineral-type;

- high intensity of convective mixing of the melt making it possible to significantly increase the throughput capacity without preliminary mixing of the waste components with the fluxing admixtures;
- the possibility to provide for remote installation and dismantling of the equipment, as well as its removal for storage and reprocessing in accordance with provisions for the transportation of vitrified waste;
- a layer of slag is formed on the water-cooled walls of the crucible during the melting process, thereby protecting the crucible from the corrosive action of the melt products;
- the fact that the parameters of the generator are dependent on the condition in the tank with the melt makes it possible to automate the process using indicators from standard measurements from the generator instruments;
- the capability to stop and start the melter if any problems should rise in any part of the process.

The limitations and deficiencies of the IMCC process also need to be addressed. They are as follows:

- the complexity of the manufacture of the power equipment, which decreases the reliability of melters as a whole;
- the complexity of the equipment itself mandated by the requirements of the induction heating process;
- because of the small dimension of the crucible, although the specific melting capacity is high, the output of glass is measured in kilograms per hour;
- low positive thermal coefficient (0.2 - 0.35) and its dependence on the thermal and physical properties of the processed mixture;
- the need for specially formulated water for the cooling of the generator and crucible.

However, the obvious advantages of the IMCC technology in comparison to its disadvantages made this process quite attractive for the vitrification of weapons-grade plutonium.

DISCLAIMER

Equipment list (Figures 2 and 3):

1. Concurrent flow evaporator
2. Flux tube
3. Cold crucible
4. Container with glass melt
5. Circular conveyer
6. Weighing equipment
7. Mechanism for closing the tops of the cases
8. Crane
8. Case with containers
9. Welding equipment for sealing the top of the case
10. Bin for fluxing admixtures
11. Sparger-cooled

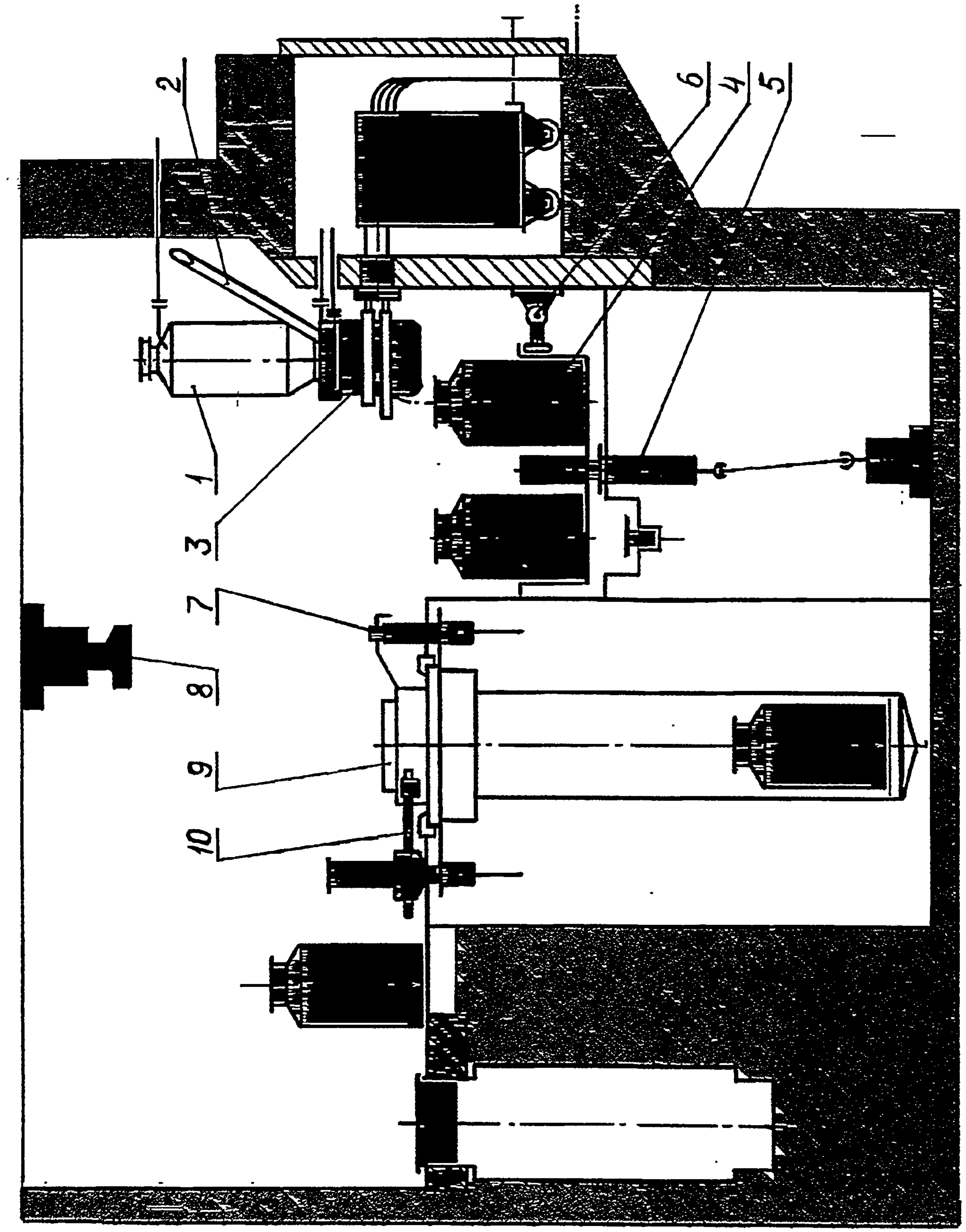


Рис. 2

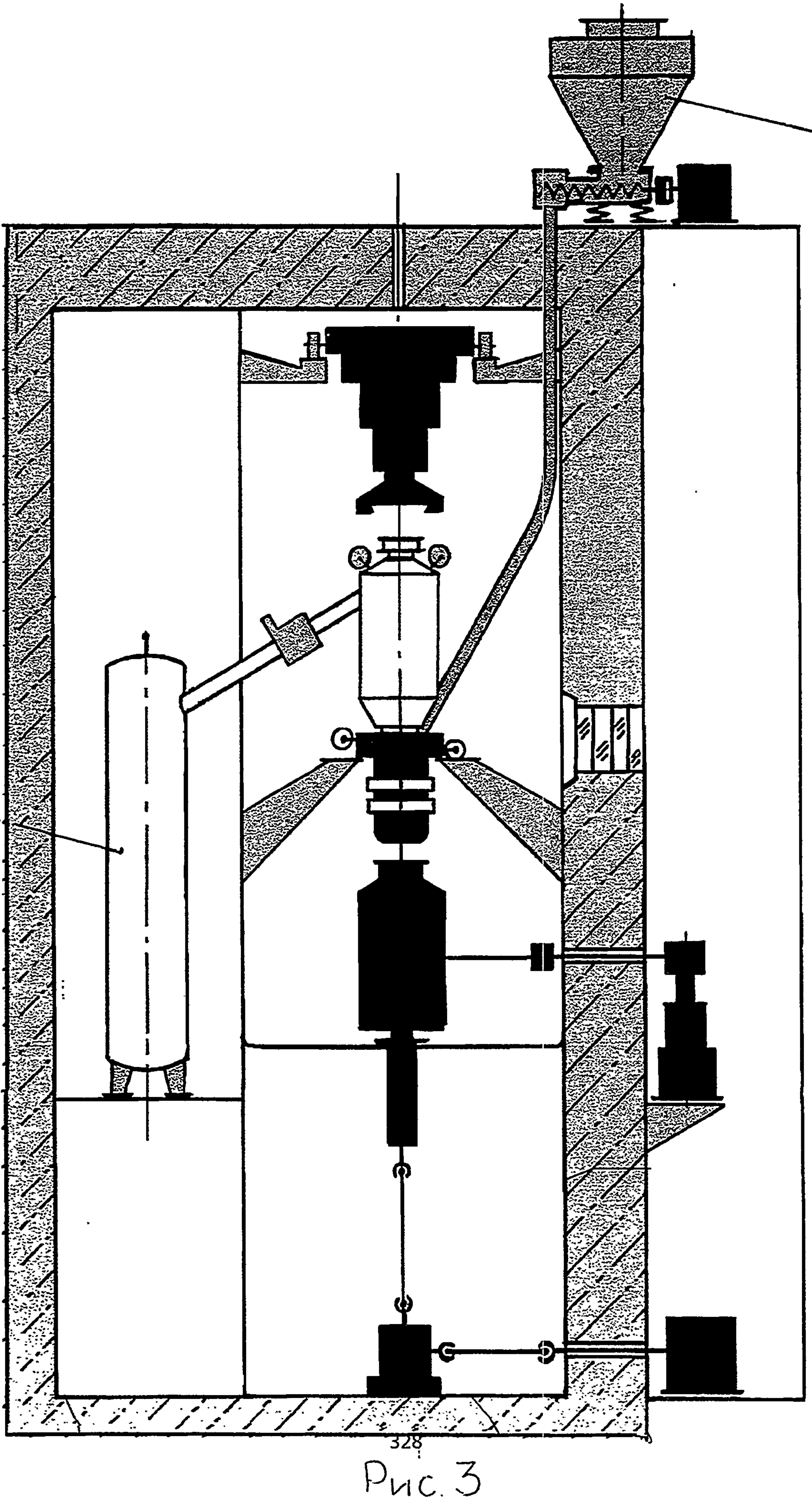


Рис. 3

INDUCTION MELTER WITH A COLD CRUCIBLE (IMCC)

1. Fusible connector
2. Pipe section cooling water
3. Inductor
4. Melter inlet for material
5. Pipe section of crucible
6. Melt
7. Partition
8. Outlet for melt

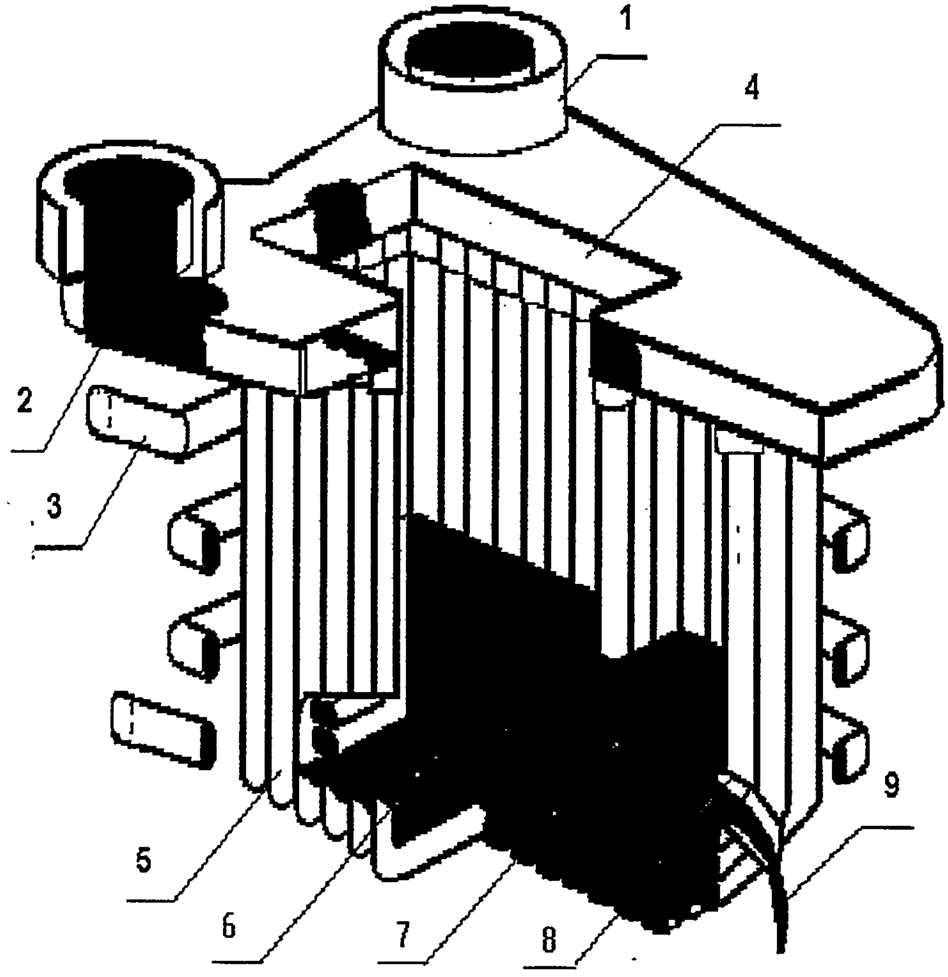
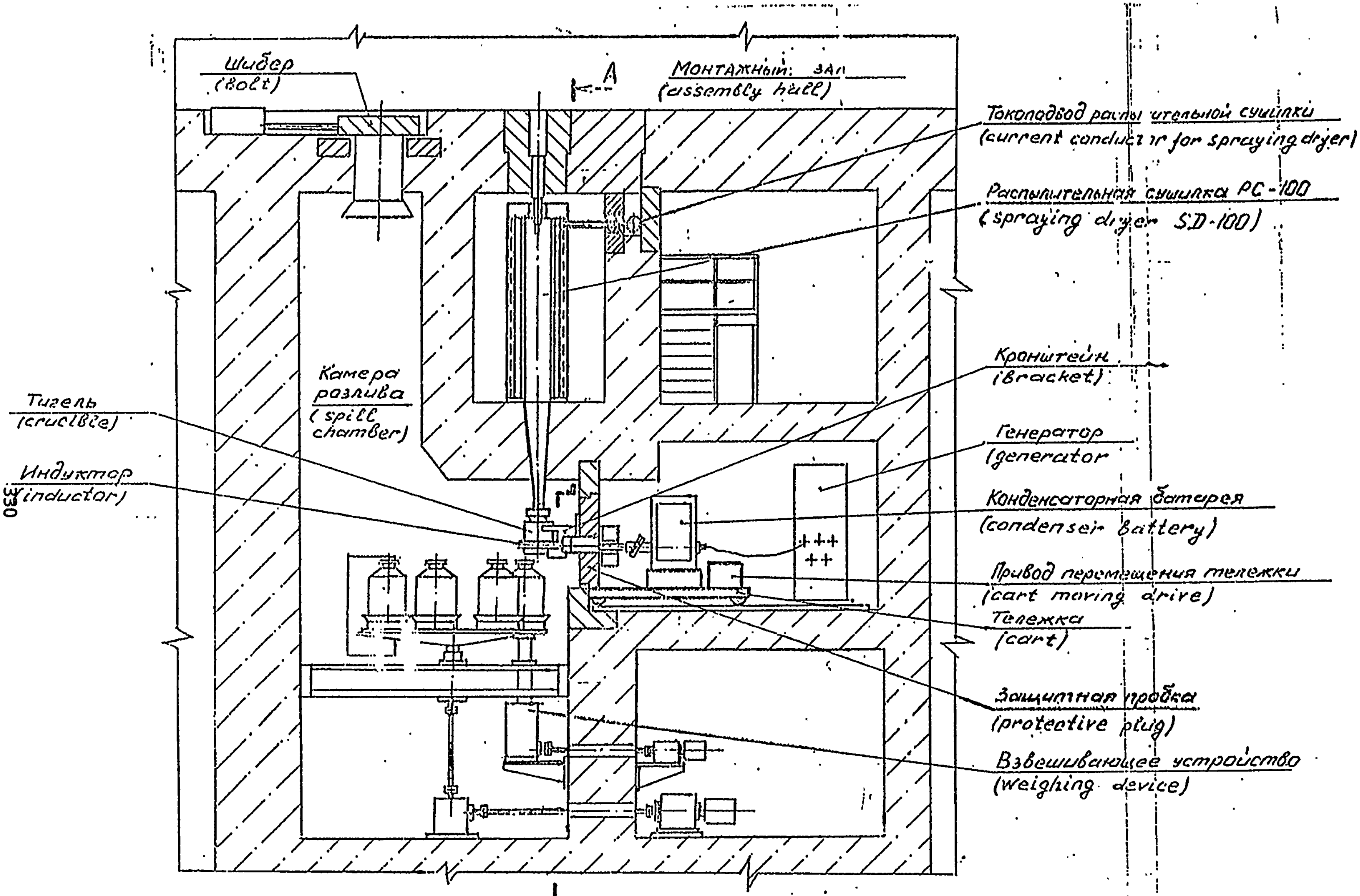


Рис. 4



Двухстадийная установка РС-ИПХТ
(Double-stage SD-IMCC installation)

Рис.5

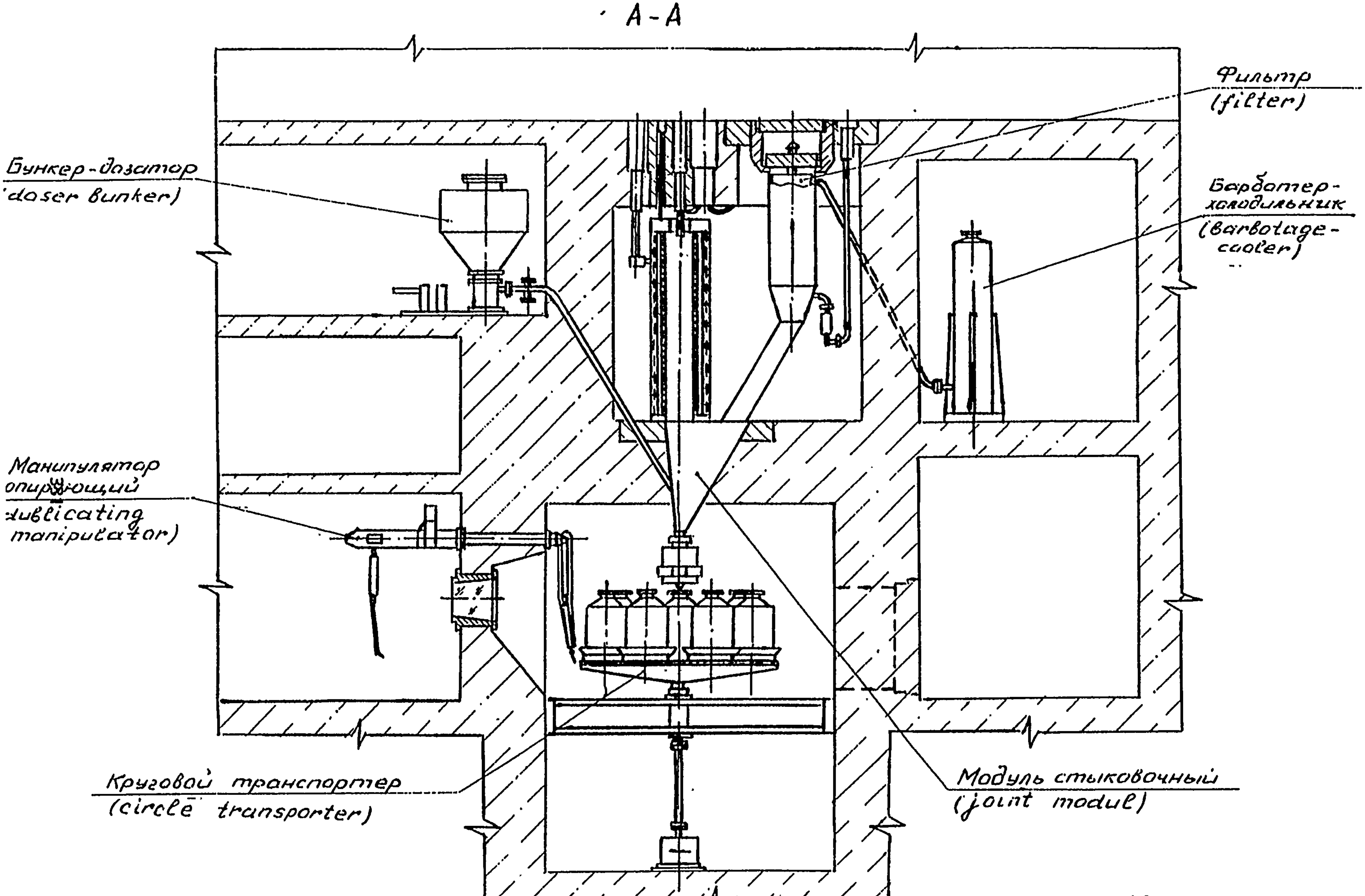


Рис.6

Двухстадийная установка РС-ИПХТ
(Double-stage SD-IMCC installation)

Melter Technologies Assessment

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ABSTRACT

The problem of controlling and disposing of surplus fissile material, in particular plutonium, is being addressed by the U.S. Department of Energy (DOE). Immobilization of plutonium by vitrification has been identified as a promising solution. The Melter Evaluation Activity of DOE's Plutonium Immobilization Task is responsible for evaluating and selecting the preferred melter technologies for vitrification for each of three immobilization options: Greenfield Facility, Adjunct Melter Facility, and Can-In-Canister. A significant number of melter technologies are available for evaluation as a result of vitrification research and development throughout the international communities for over 20 years. This paper describes an evaluation process which will establish the specific requirements of performance against which candidate melter technologies can be carefully evaluated. Melter technologies that have been identified are also described.

INTRODUCTION

The U.S. Department of Energy (DOE) has been directed to complete a comprehensive review of long-term options for surplus fissile material control and disposition, taking into account technical, nonproliferation, environmental, safety, budgetary, and economic considerations. Immobilization of surplus fissile material has been identified as a promising alternative. Following an extensive review, vitrification was selected as one of the preferred immobilization options for the surplus fissile material, plutonium.

The DOE Plutonium Immobilization Task is evaluating three vitrification options: 1) designing and constructing a new facility, termed Greenfield that produces a borosilicate glass incorporating plutonium, neutron absorber, and cesium-137 and then encapsulates it in a storage canister; 2) an adjunct melter facility added to the existing Defense Waste Processing Facility at the Savannah River Site, near Aiken, South Carolina that produces a glass incorporating plutonium, neutron absorber, and high-level waste and then encapsulates it in a storage canister; and 3) a can-in-canister option in which an array of cans incorporating glass, plutonium and neutron absorbers is encapsulated in a high-level waste-containing glass all within an outer storage canister.

One of the activities of the Plutonium Immobilization Task is the Melter Evaluation Activity. It is the responsibility of the Melter Evaluation Activity to identify the melter design and operating requirements, develop criteria by which to evaluate available melter technologies, and identify and prioritize glass melters suitable for use. Based on these results, preliminary flowsheets of the equipment and processes as well as cost estimates will be prepared for the recommended candidates. This paper describes vitrification technologies that should be considered for use and the approach that is proposed to evaluate and prioritize the candidate systems.

MELTER TECHNOLOGIES ASSESSMENT

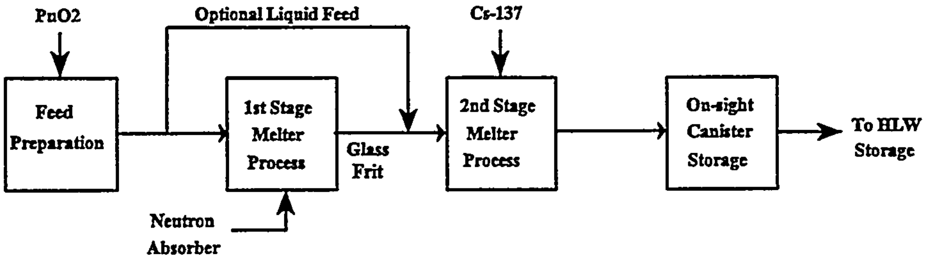
Melter technologies for the vitrification of radioactive materials have been under development and evaluation for more than 20 years by DOE.[1,2] Systems have been or are being developed, tested and demonstrated, including remote operations, for a variety of specially designed and commercially available melters. As a direct result of these efforts, a strong foundation exists from which to perform an evaluation of melter technologies applied to plutonium immobilization. However, plutonium immobilization has unique requirements for which scientific and engineering solutions must be found. Most important are the issues of plutonium oxide or metal accumulation in a melter, a significant graphite content (for the scrap and residue fraction), and a heterogeneous waste stream. The present understanding of melter requirements is discussed in this section, followed by a summary of melter technologies identified to date as potential candidates. Finally, the process by which the melter technologies will be evaluated is described.

Melter Performance Requirements

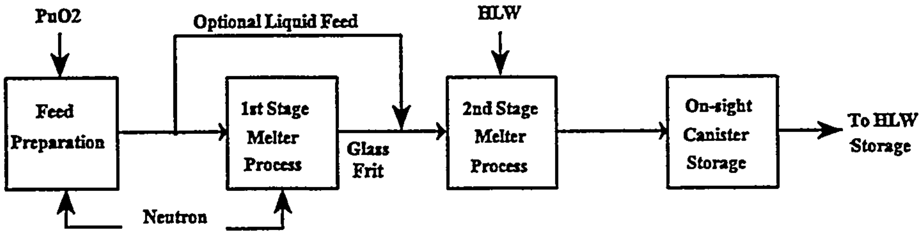
Several basic requirements must be met by each of the three vitrification process options described above. These requirements are the capability to:

- process a maximum of 50 MT of plutonium over a 10-year period
- process 10 to 20 MT of the total inventory in the form of scrap, residues, oxides, ash, metals, sludge, compounds, etc.
- incorporate a maximum of 10 % plutonium by weight into the glass
- ensure the plutonium is inherently as difficult to recover from the glass and convert to weapons grade material as it is to recover it from commercial spent fuel

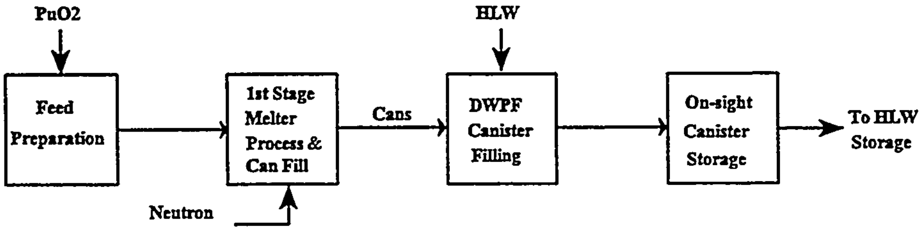
Figure 1 depicts simplified flow diagrams of the three vitrification process options the Plutonium Immobilization Task is evaluating. The Greenfield Facility Option and the Adjunct Melter Facility Option require evaluation of both stages of a possible two-stage melter system. The Can-In-Canister Option only requires evaluation of the first stage of its melter system. The function of the first melter is to produce either a glass frit or, in the case of the Can-In-Canister Option, small cans of plutonium-bearing glass. This activity would need to be conducted within a glovebox. The first-stage of the melter system could be located at a single DOE site or placed at the sites possessing a majority of the plutonium materials. At present it is not known whether it is preferable to feed a dry or a liquid plutonium stream to the first melter. Therefore, this melter must be capable of processing both a dry plutonium oxide feed



Greenfield Facility Option



Adjunct Melter Facility Option



Can-In-Canister Option

Figure 1. Simplified Flow Diagrams of Immobilization Options

stream or a nitric acid solution containing plutonium. The function of the second stage of the melter process varies depending on the option.

Greenfield Facility Option - The second melter for this option must be able to process either a liquid or a solids feed stream. The optional liquid stream could be a nitric acid solution containing dissolved plutonium or a neutral or alkaline solution containing a crushed glass frit into which the plutonium has already been melted. The glass forming additives, cesium-137, and neutron absorber could be blended into the liquid feed stream, or added as separate solids or liquid streams. The glass forming additives and neutron absorbers could also be pre-made into a frit. The source of the cesium-137 is the isotopic source capsules stored at the Hanford Site near Richland, Washington. Presently there are over 1,300 capsules accounting for almost 2,900 kg of cesium. The vitrification processes associated with the cesium-137, including the melter, must be operated and maintained remotely. The final glass product would be produced at a temperature less than 1,200°C and discharged into cylindrical storage canisters identical to those planned for use in high-level waste (HLW) processing in the U. S.; i.e., 3 m tall by 0.6 m in diameter.

This approach has the benefit of plutonium materials being effectively immobilized and stored using the first-stage melter while the new facility is being designed and constructed for the second-stage melter. Therefore, early stabilization of the plutonium inventory in a vitreous form can occur. It may also prove to be a much more effective approach because implementing safeguards, criticality engineering, and accountability control can be more effectively performed in glovebox lines rather than remotely operated hot cells. The optional liquid feed scenario assumes the surplus plutonium will be delivered to the facility for direct melting with neutron absorber and cesium-137 in the second stage. This sub-option of the Greenfield option eliminates the need for the first-stage melter.

Adjunct Melter Facility Option - The second melter for the Adjunct Melter Facility Option would be installed in a vitrification facility in close proximity to the existing Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS). A glass incorporating plutonium, neutron absorber, and SRS HLW would be produced and stored in HLW canisters. The optional liquid stream could be a nitric acid solution containing dissolved plutonium or a neutral or alkaline solution containing a crushed glass frit into which the plutonium has already been melted. The glass forming additives, SRS HLW and additional neutron absorber, could be blended into the liquid feed stream or added as separate solids or liquid streams. The vitrification processes associated with the SRS HLW, including the melter, must be operated and maintained remotely. The final glass product would be produced at a temperature less than 1,200°C and discharged into cylindrical storage canisters identical to those planned for use in HLW processing in the U. S.; i.e., 3 m tall by 0.6 m in diameter.

This approach also has the benefit of the plutonium materials being effectively immobilized and stored using the first-stage melter while the new facility is being designed and constructed for the second-stage melter. The optional liquid feed scenario assumes the surplus plutonium will be delivered to the facility for direct melting with neutron absorber and SRS HLW. This sub-option again eliminates the need for the first melter.

Can-In-Canister Option - The Can-In-Canister Option obviates the need for a new facility and reduces the lead time required to begin operations. The first melter will combine the surplus plutonium material with neutron absorbers into a glass produced at a temperature between 1,300°C and 1,600°C. The glass product will be poured into small cans (e.g., 46 cm tall by 9 cm outside diameter) and allowed to solidify. The small cans will ultimately be transported to the Savannah River Site and placed in a circular array inside the DWPF canisters. The canisters will then be filled with DWPF HLW glass to nominally 80-90% of the volume. The HLW glass will be at a temperature of between 1,050 and 1,150°C when it enters the canister. If the plutonium glass is reheated to above its glass transition temperature, devitrification may occur upon final cooling. This could call into question the quality of the final glass product. Therefore, the plutonium glass must be processed at the higher temperatures (1,300°C-1,600°C) described above.

Candidate Melter Technologies

To be considered for surplus plutonium immobilization, the melter technologies must have been developed and demonstrated to the point that there is a high degree of confidence they can perform the required functions. Therefore, heavy reliance will be placed by this activity on melter systems that have been developed under previous or ongoing programs. Programs with significant experience in developing melters that are being evaluated include:

- DWPF technology development projects
- Hanford Tank Waste Remediation Systems (TWRS) project and its predecessor, Hanford Waste Vitrification Plant project
- HLW vitrification development projects in France, Germany, and Russia
- DOE Environmental Management Technology Development program (EM-50)
- Savannah River Technology Center's Americium/Curium Vitrification project
- Rocky Flats' microwave solidification projects

Candidate melter technologies that have been identified to date and which will be closely evaluated are summarized in Table 1 and briefly described below.

Table 1. Candidate Melter Technologies

System	Potential Supplier	Maximum Process Temperature (°C)	Suitable for Glovebox
DWPF-type JHCM	DOE	1,200°C	Possibly
KfK-type[1] JHCM	Germany	1,200°C	Possibly
High-Temperature JHCM	Envitco	1,700°C	Yes
Stirred JHCM	Stir Melter, Inc.	1,100°C	Yes
Resistance Melting	GAF Bushing	1,700°C	Yes
Microwave Melting	DOE	>1,700°C	Yes
Induction Melting	Russia/France	>1,700°C	Yes

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1. KfK - Kernforschungszentrum Karlsruhe, Karlsruhe, Germany

Joule-Heated Ceramic Melters - Joule-heated, ceramic-lined melter (JHCM) technology development for radioactive materials vitrification has been underway since the late 1970s. JHCMs are characterized by refractory-lined cavities with electrodes submerged in the glass pool. Thermal energy is generated within the glass pool by resistively heating the glass melt by passing an alternating current between electrodes extending through wall or roof penetrations. The heat is transferred to the feed material by convection and conduction. Because the glass is heated electrically the composition must be tailored to ensure glass conductivity and viscosity properties fall within specified parameters. The glass product is discharged either through a side wall discharge trough or through a bottom drain. In the U. S., the best example of a low-temperature JHCM is the DWPF melter shown in Figure 2. German and Japanese designs employ steeply sloped walls and bottom drains to remove sludge or metal accumulations at the bottom of the melt pool. These are particularly attractive features for plutonium immobilization where greater assurance is required that no accumulations of fissile material can occur. Figure 3 is an illustration of an advanced German HLW melter design.

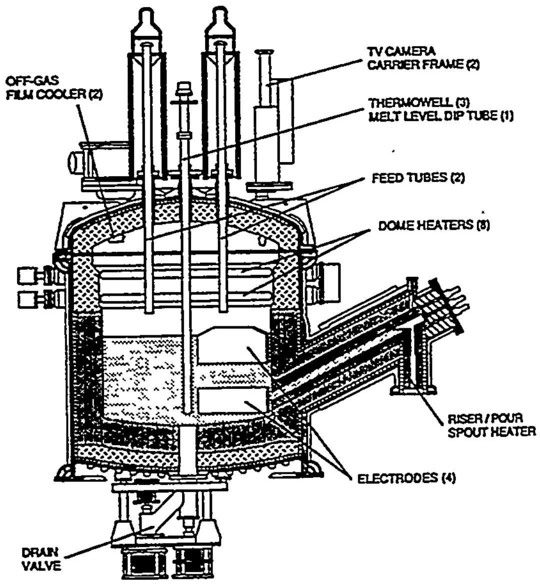

Figure 2. DWPF Melter System

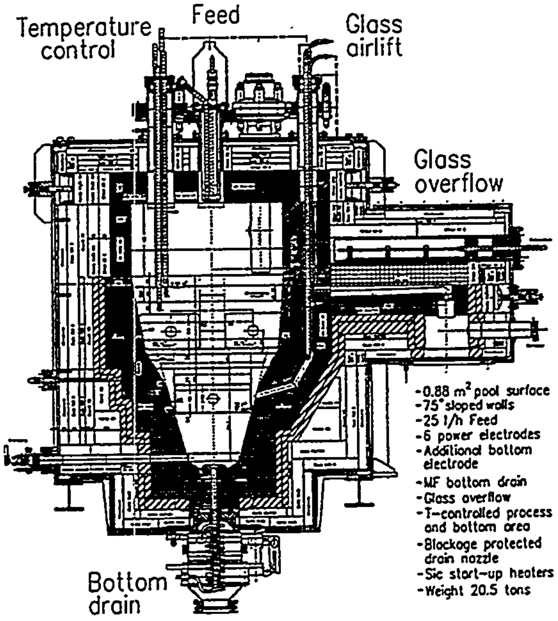

Figure 3. German KfK Melter System

Principal development of the JHCM technology in the U.S. for the treatment of DOE HLW wastes has occurred at the Pacific Northwest National Laboratory and Savannah River Technology Center. Significant development work has also been performed in Germany, Japan, and Russia. Processing of acidic and alkaline HLW has been demonstrated using either dry calcine or slurries containing approximately 50% solids by weight. JHCM systems have already been operated remotely in production facilities in Russia and Mol, Belgium. Remote demonstration projects have also been conducted at the Hanford Site in the U. S. and in Japan at scales larger than required for the Greenfield and Adjunct Melter Facility options.

High-temperature JHCM systems have also been demonstrated at a scale sufficient to support the Can-In-Canister Option. Significant testing has occurred under DOE EM-50 and TWRS sponsorship. The basic design of these systems is similar to the low-temperature systems. However, use of different electrode materials allows higher processing temperatures. Unique design features of some systems allow for significantly higher process rates per unit area of glass pool; e.g., the Envitco, Inc.® cold top vitrification system. This can reduce the size of melter unit required by a factor of 50% or more. However, the higher process temperatures do impose greater restrictions on electrode and refractory material options. Therefore, glass chemistry and composition options are not as flexible as with the low-temperature JHCM, and materials interaction and reliability will need to be more thoroughly understood than for the low-temperature JHCM.

Active mixing or agitation within JHCMs has several advantages. The combined action of the joule heating and stirring action result in the melt area being only 10 to 15% of that of a conventional cold top electric melter of equivalent output. This compact size is very important for use in glovebox lines. Because natural convection is not relied on to mix the glass and transfer heat to the batch, working temperatures are 50 to 100°C below conventional glass melting furnaces. Figure 4 is a schematic of the Stir Melter, Inc.'s low-temperature melter system. To date no production units are reported to be in service. However, several demonstration units have been in use for several years, testing simulated radioactive high-level, mixed, low-level, and hazardous wastes. The majority of this testing has been supported by the DOE EM-50 Office of Technology Development. Testing units have been designed to process liquid or solid waste streams at glass rates ranging from a few pounds per hour up to 2 tons per hour. The smallest unit has a 230 cm^2 (0.25 ft^2) glass melting surface area, and the largest unit delivered to date has a 0.8m^2 (9 ft^2) glass melting surface area. Therefore, the basic technology has been demonstrated at a scale larger than is anticipated to be required for surplus plutonium immobilization.

The joule-heated melter developed by Stir Melter, Inc. is constructed from nickel alloy or refractory ceramics depending on the temperature range required for the waste stream. At a processing temperature of 1050°C the stirrer and tank walls are constructed from Inconel® alloy 690. The stirrer and walls act as the electrodes through which the AC current is passed. At higher process temperatures, a refractory lining is employed and molybdenum bottom-entering electrodes are positioned in the four corners of the tank. The stirrer also is constructed of molybdenum. To minimize the forced entrainment of unreacted feed material into the glass discharge entrance, the stirrer is positioned in the upper half of the glass tank. Glass can be discharged continuously or in batches using an overflow discharge channel or a bottom drain.

Electric Resistance Melters - A bushing resistance-heated melter is being evaluated at Savannah River Technology Center as part of the Americium and Curium vitrification project.[3] The melter is a platinum/rhodium alloy bushing melter commonly used in the glass fiber industry. As depicted in Figure 5, the melter is an alloy box with tabs on each end for an electrical connection. Current is passed through the bushing and heats it similar to a resistance heater. At voltages of 2 to 5 volts, 6,000 to 15,000 amps will be required for a 30 kW system. Significant production rates can be achieved in compact units. Also, because current is not passed through the glass, glass composition requirements are relaxed somewhat since glass resisitivity is not a variable. The existing geometric design of the bushing

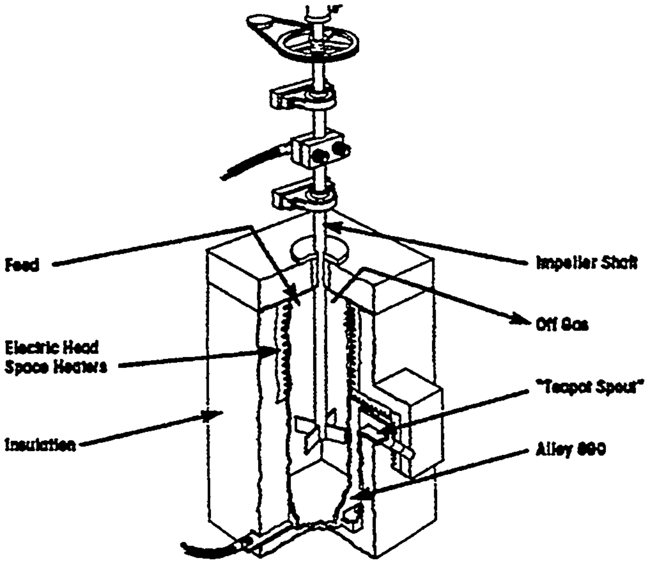

Figure 4. Stir Melter, Inc.® Low-Temperature Melter System

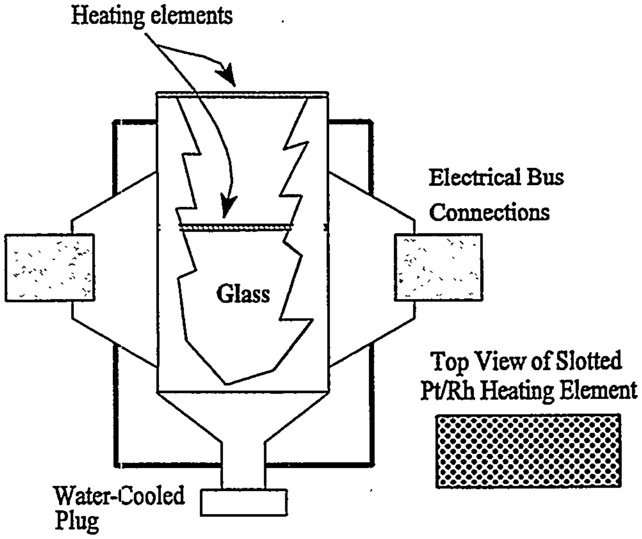

Figure 5. Schematic of Bushing Melter System

melter precludes criticality should a significant amount of plutonium accumulate. Because the existing geometric design of the bushing melter precludes criticality should a significant amount of plutonium accumulate. Because the bushing melter has just recently been applied to radioactive waste treatment, a significant amount of processing experience does not yet exist. However, because of its size and design this technology should receive serious consideration. Similar to the other melter technologies under consideration one or more units could be operated in glovebox lines or remotely, if necessary.

Microwave Melters - Microwave vitrification technology has been under development for several years. Principal development of the technology for the treatment of DOE wastes has occurred at the Rocky Flats Plant and Oak Ridge National Laboratory. A significant amount of laboratory and bench-scale testing has been performed to evaluate the drying, sintering, or melting of a large variety of inorganic waste streams, such as fly ash, nitrate salts, soils, metal hydroxides sludges. The process has successfully treated precipitation sludges contaminated with heavy and radioactive metals and reduced the volume by up to 80%. A large-scale microwave melter has been operated for several years at Rocky Flats attaining process rates on the order of 50 kg/hour. Therefore, the basic technology has been demonstrated at a scale larger than is anticipated to be required for surplus plutonium immobilization. Microwave vitrification operation in a glove box application has also been demonstrated at the Rocky Flats Plant. Therefore, no significant or unanticipated engineering or process issues should exist.

The melting process is achieved through three primary mechanisms: frictional heat caused by the vigorous vibration of dipolar molecules due to oscillation of the electromagnetic field, frictional heat caused by the vigorous vibration of magnetic materials due to oscillation of the magnetic component of the field, and generation of heat by electrically conductive materials due to the current generated by the electrical component of the field. Processing is performed in batch or semi-continuous modes depending on the application and scale. Standard systems employ 915 or 2,450 megahertz microwave energy.

Development efforts at Rocky Flats have been focused primarily on producing waste forms that meet Waste Isolation Pilot Plant and/or U.S. Environmental Protection Agency disposal requirements. Although limited small-scale testing has been conducted to demonstrate production of a predominantly amorphous product, the characteristics of the final waste form for HLW repository disposal need to be evaluated.

Induction Melters - Vitrification of HLW in induction-heated vessels has been underway in France since 1978. As a result there is a strong technical base for this technology. In induction melting, a magnetic field potential is applied across the glass. According to Lenz's Law, the variation in the magnetic field causes a variation in magnetic flux passing through the glass. The majority of HLW experience is based on French technology which inductively heats the melter vessel and processes glasses at temperatures less than 1,100°C. As is true for electric melters, heat transfer is primarily through convection and conduction from the molten pool to the waste material unless active mixing of some means is employed.

Significant work is underway in France and Russia to develop high-temperature induction melting for HLW treatment. Processing at temperatures in excess of 1,600°C is possible in these units. The higher temperature is achieved by inductively heating the glass directly. Specially designed water-cooled vessels called "cold-wall melters" freeze a very thin (i.e., 1 to 3 mm) layer of glass which protects the metal vessel. An example of an induction melter designed by Cogema to process HLW is shown in Figure 6. Test units as small as 27 to 35 cm (glass pool diameter) have been built and tested in France and Russia. Units of this size have achieved glass rates of approximately 10 kg/hour when processing dry feeds. Radioactive testing and demonstration has also been done to a significant extent. Liquid feeding is not known to have been done to a sufficient extent to know how effectively it can be done.

Evaluation Process

To successfully evaluate melter technologies, it will be crucial to identify and properly weight concise and measurable criteria. Close interaction with the other Plutonium Immobilization Task elements will be required, particularly with those responsible for glass formulation development, facility and process systems, and criticality assessment. The following activities are proposed to evaluate melters:

- compile preliminary list of melter criteria and functional requirements
- in parallel, compile technical data packages on melter technologies, citing relevent design, testing, cost, and performance data
- based on consensus of experts, establish relative weighting factors for criteria and requirements
- identify those technologies that meet minimum requirements
- update criteria and functional requirements based on evaluation by the Plutonium Immobilization Task

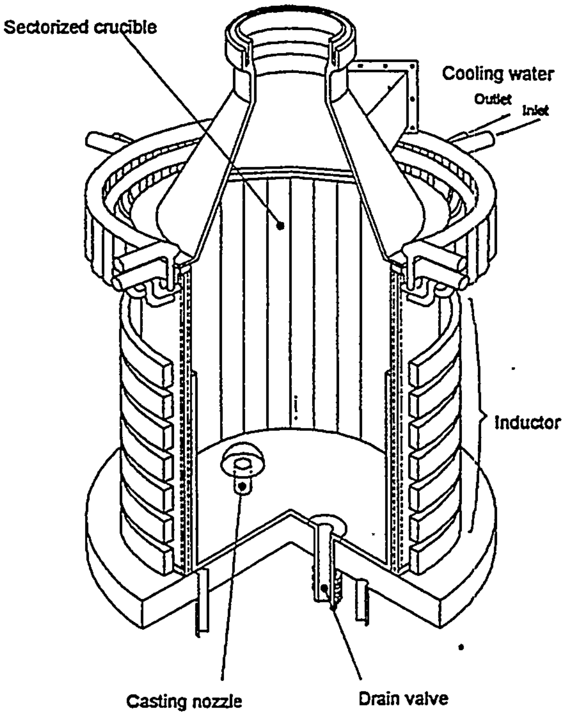

Figure 6. Cogema HLW Induction Melter System

- assemble expert panel and perform rigorous evaluation of remaining technologies
- finally, rank technologies and identify one preferred melter technology and one optional melter technology for each immobilization option: Greenfield Facility, Adjunct Melter Facility, Can-In-Canister.

Preferred technologies will be those which provide a high degree of confidence that they will meet the requirements. An optional technology may also be identified if it offers a significant potential for improvement in performance, costs, safeguards, criticality, etc. over the mature technology. The optional technology may not be identified as the preferred technology because of a lack of data.

Preliminary evaluation criteria for the melter systems are provided in Figure 7. Refinement of the criteria and inclusion of additional criteria will be ongoing as the performance requirements are better understood. The potential attributes of the criteria, which can be directly measured, are discussed in the following subsections. The order of presentation does not imply priorities or weighting of the criteria.

System Requirements - The system requirements are the minimum standards for which there must be a high degree of certainty that the technology under consideration would meet the requirement. "Can the technology do the job?" is the question to ask for each of the following system requirements:

- Plutonium processing rate of 5 metric tons/year
- Glass product that meets performance assessment criteria
- Maximum operating temperature

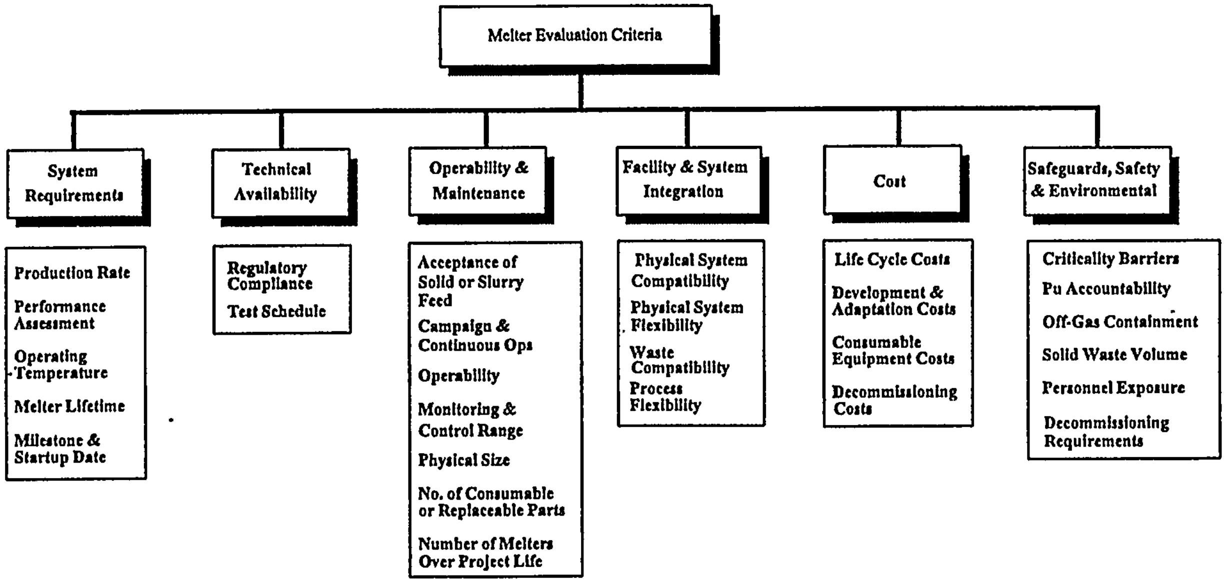

Figure7. Preliminary Evaluation Criteria

- Minimum melter lifetime (e.g., 3 years based on 60% plant efficiency)
- Deployment that meets programmatic milestones and startup date

Technology Availability and Schedule - The technology needs to be available and able to meet all standards and requirements. "Will the technology be available to do the job when needed?" is the question to ask when considering the following:

- Regulatory compliance
- Process equipment that is readily available for testing and evaluation

Operability and Maintenance - The criteria of operability and maintenance should show how the technology will perform under operating conditions. "How well is the technology likely to work within the plant?" is the question to ask when considering the following:

- Melter will accept solid and/or slurry feed
- Melter can be operated intermittently as well as for extended campaign periods
- Melter will have a high degree of operability (tolerate off-normal operation, handle restarts, be easy to operate, tolerate abuse, operate outside the nominal range), measurable by impact, consequence, and response actions of off-normal conditions
- Melter will have a wide control range, measurable by required monitoring and control equipment
- Melter size will be as small as possible, including footprint, height, weight, and weight of heaviest component, measurable by dimensions, weight of heaviest component, and total weight, measure by providing dimensions and weight for total and heaviest component(s)
- Melter system will minimize the number of replaceable or consumable parts; any replaceable or consumable part can be changed with a minimum amount of time and labor, measurable by the number/volume, size, frequency, and impact on operations (production capacity, number of people, amount of time) of replaceable and consumable parts
- Melter can be drained at the end of its life, if necessary, for disassembly, transport, and final disposal, measurable by providing size (dimensions) and weight (full and empty), length of time to remove/replace, and number of people to perform

Facility and System Integration - Facility and system integration should show how the technology will fit with the balance of plant equipment as well as potential site operating schemes. The fit will encompass physical equipment and operational planning during the mission. Scales must be constructed in order to assess the following:

- Physical system compatibility--how the melter system under evaluation fits with the range of vitrification support system alternatives, which include offgas system and waste form alternatives
- Physical system flexibility--whether the system is flexible enough to receive recycle streams (eg. glass, filters, in-plant secondary waste)
- Waste compatibility-- how the product produced will fit with the remaining processing alternatives: pre-processing needs and post-processing needs of ensuing processes, including the volume and type of secondary waste create.
- Process flexibility--whether the technology can incorporate and treat various waste types, taking into consideration both constituent range of waste feed and range of waste types. Constituent range of waste feed applies to the ability to treat a waste type with constituent concentrations that are widely varying. Range of waste types applies to the ability to treat a varying range of waste types.

Cost - The relevant costs required to support deployment of the technology in the required time frame should be based on the following:

- Life-cycle cost, measurable by providing cost estimates, which include equipment/initial costs, operations, and maintenance costs
- Development and adaptation costs, measurable by providing estimated development/adaptation costs
- Consumable equipment cost, measurable by the number of melters during lifetime
- Decommissioning cost

Safeguards, Safety, and Environment - The criteria of safeguards, safety, and environment include radiological and hazardous components and are defined by the following:

- Melter will have at least two barriers to criticality with engineered controls as the preferred control options, measurable either as affirmative or negative
- Processed plutonium can be monitored, measurable by technical feasibility, potential for redundancy, reliability, etc.
- Melter will be completely enclosed to control spread of contamination and hazardous or corrosive gases or fumes, measurable either as affirmative or negative
- Total volume of solid waste will be minimized, measurable by providing estimated volume of solid waste produced, including secondary waste streams
- Melter will be decommissioned with minimum human exposure (i.e., ALARA principles applied here), measure by providing an estimate of the number of people and length of time required to perform decommissioning

SUMMARY

The Melter Evaluation Activity of the Plutonium Immobilization Task will evaluate and recommend preferred melter technologies for each immobilization option. A significant number of melter technologies are available for evaluation as a result of vitrification research and development throughout the international communities for over 20 years. Many technologies are very mature and have a significant database of experience. Other technologies offer the possibility for significant improvements in design and operation for this specific application but have not been demonstrated to the same extent as the mature technologies. An evaluation process has been described which will establish the specific requirements of performance against which each of the melter technologies can be carefully evaluated. All major requirements and a majority of the other requirements must be defined and included in the evaluation. Following the evaluation, preliminary equipment and process flowsheets and cost estimates will be prepared for the recommended candidates.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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Experience Gained with the Synroc Demonstration Plant at ANSTO and its Relevance to Plutonium Immobilization

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ABSTRACT

The Synroc Demonstration Plant (SDP) was designed and constructed at Lucas Heights to demonstrate the feasibility of Synroc production on a commercial scale (10 kg/hr) with simulated Purex liquid HLW. Since commissioning of the SDP in 1987, over 6000 kg of Synroc has been fabricated with a range of feeds and waste loadings. The SDP utilises uniaxial hot-pressing to consolidate Synroc. Pressureless sintering and hot-isostatic pressing have also been studied at smaller scales. The results of this extensive process development have been incorporated in a conceptual design for a radioactive plant to condition HLW from a reprocessing plant with a capacity to treat 800 tpa of spent LWR fuel. Synroc containing TRU, including Pu, and fission products has been fabricated and characterised in a glove-box facility and hot cells, respectively. The extensive experience in processing of Synroc over the past 15 years is summarised and its relevance to immobilization of surplus plutonium is discussed.

INTRODUCTION

Immobilization of surplus fissile materials in a stable wasteform followed by disposal in a geological repository or deep borehole, is one of the disposition options currently under investigation by the US Department of Energy (DOE). Prime immobilization options (1) are to vitrify plutonium in borosilicate glass or to incorporate it in a tailored ceramic such as Synroc. The disposition process requires that the Pu for disposal must be rendered inherently more proliferation-resistant than the original form. The US National Academy of Sciences (2) proposed the concept of a "spent fuel standard" that could be met (3) by including an adequate amount of radioactive ^{137}Cs in the Pu containing wasteform. Alternatively, deep borehole disposal of the wasteform would reduce significantly the unauthorised recovery of the Pu-containing material.

The avoidance of nuclear criticality is essential during processing of Pu-rich mixtures into the wasteform, during its storage, and over the very long term in the repository environment after disposal. ^{239}Pu has a half-life of 24,000 years and its daughter, ^{235}U, has a 700 million year half-life. The criticality requirement implies that all unit operations in the immobilization plant must employ equipment that is critically safe either by geometry, mass, inclusion of neutron poisons, or a combination of these three methods. Gadolinium added as a neutron poison at the head end of the Synroc process meets most of the requirements (4). Further criticality safety can be achieved by substituting Hf for some of the Zr in the zirconolite phase of Synroc (5).

Synroc is an advanced titanate ceramic comprising a thermodynamically stable assemblage of phases chosen for their geochemical stability and collective ability to immobilize radioactive elements present in

HLW. These phases are similar to titanate minerals that have successfully immobilized naturally occurring radioactivity (eg. U, Th) in a wide range of geochemical/geological settings. Natural samples of zirconolite exist (6) which have immobilized U, Th and their decay products for periods approaching one billion years. An extensive data base exists (7) on the chemical durability of Synroc, and the status of Synroc development has been reviewed recently (8). The present paper describes the salient features of Synroc as a wasteform for Pu immobilization and the process development based on the operation of the Synroc Demonstration Plant (SDP) since 1987. The discussion also draws on a conceptual design study of a radioactive Synroc Plant and investigations of alternative process steps at ANSTO in the context of the plutonium immobilization program being pursued in USA.

SYNROC WASTEFORMS

Most of the process development at ANSTO has focused on Synroc-C, a formulation developed for the immobilization of HLW from the reprocessing of commercial LWR spent fuel. It consists mainly of zirconolite $CaZrTi_2O_7$, barium hollandite $Ba(Al,Ti)_2Ti_6O_{16}$, perovskite $CaTiO_3$ and excess titanium oxides. A combination of the first three phases has the capacity to accept, in solid solution, most of the elements present in HLW. Under the redox conditions chosen for Synroc fabrication, a number of waste elements, such as Ru, Rh, Pd and Tc, are reduced to the metallic state and form alloys that are microencapsulated within the titanate phases. The alloys also contain Mo, Ni, Te and some Fe. The composition and mineralogy of Synroc-C are given in Table 1.

Table 1. Composition and Mineralogy of Synroc-C

Composition (wt.%)		Mineralogy (approx wt.%)	
TiO_2	57.1	hollandite	30
ZrO_2	5.3	zirconolite	30
Al_2O_3	4.3	perovskite	20
BaO	4.5	TiO_2 + minor phases	15
CaO	8.8	alloys	5
HLW	20.0		

Hollandite is the host for Cs, Ba, and Rb; perovskite is the major host for Sr; and zirconolite and perovskite are the hosts for rare earths and actinides. The partitioning of radwaste species between the various phases in Synroc has been described (7,9,10,11) extensively. Trace amounts of other phases such as calcium aluminium titanate are usually found in Synroc (7) but they do not contain significant amounts of HLW species. The minor phase content may be influenced by the presence of high concentrations of process contaminants such as Na_2O and Fe_2O_3(10). Significant amounts of sodium rich phases such as freudenbergite and loveringite are produced by sodium-bearing HLW in Synroc (12) containing more than about 1 wt% Na_2O. Experiments (13) on Synroc-C made with nominal levels of anionic impurities (Cl, F, SO_4) at 0.5 wt% loadings did not reveal significant loss of chemical durability. The phase location of these impurities was not determined.

Titanium metal powder is added to calcined Synroc at the 2 wt% level for redox control during consolidation by hot-pressing. This is an important aspect of Synroc chemistry. An excess of reduced rutile provides Synroc with the capability to maintain the desired phase assemblage (by changes in the relative abundance of the phases) even if unexpected fluctuations occur in the HLW stream composition.

This process flexibility is evidenced by the ability to use the same Synroc precursor composition for waste loadings in the range 0-30 wt.% without deleterious effects on the chemical durability.

The Synroc microstructure, as produced in the SDP, Fig.1, is fine grained ($\leq 1 \mu m$), with the metallic particles of about 10-50 nm in size encapsulated by the titanate phases. The sub-micron grain size accounts for the resistance of Synroc to micro-cracking as the result of alpha-decay damage. The effects of α-decay damage have been studied extensively (4,8) in accelerated tests on Synroc-C, zirconolite and perovskite using ^{238}Pu (up to 11.8 wt% PuO_2) and ^{244}Cm (up to 4 wt%). Ewing et al. (14) have critically reviewed radiation effects on nuclear wasteforms for HLW and their significance for plutonium immobilization will be discussed by Ewing at this Workshop.

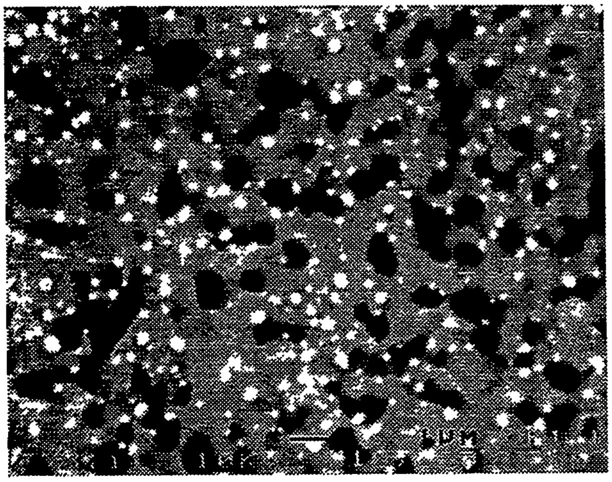

Figure 1

Microstructure of Synroc-C showing a multiphase ceramic with grain size less than 1μm. The small bright areas show the reduced metallic components microencapsulated within the titanate matrix.

The solubility limit of PuO_2 has not yet been determined because it is dependent on the content of zirconolite and perovskite phases and competing radwaste ions such as Gd. The mechanisms for actinide incorporation in Synroc have been reviewed recently by Vance (15) who also has discussed some early results on zirconolite-rich Synroc formulations.

The extensive (7) data base on the chemical durability of Synroc has been mainly established by MCC-1 static leach tests, with frequent replacement of the leachant, using specimens containing up to 24 non-radioactive elements simulating HLW. These have been supplemented by tests with radioactive fission products and actinides. Figure 2 summarises the results of leach tests on Synroc-C containing plutonium, relevant neutron poisons and Cs at 70°C in deionised water. The leach rates for Zr are very low. Further work on a plutonium-rich Synroc with the full suite of neutron poisons (Gd and Hf) would be useful.

The key physical properties of Synroc are listed in Table 2. The higher density and thermal conductivity compared with borosilicate glass wasteforms permits higher waste loadings per unit volume, particularly in cases where the solidified waste is intended to be stored for extended periods in engineered facilities prior to geological disposal. This is further enhanced by the high melting point of Synroc.

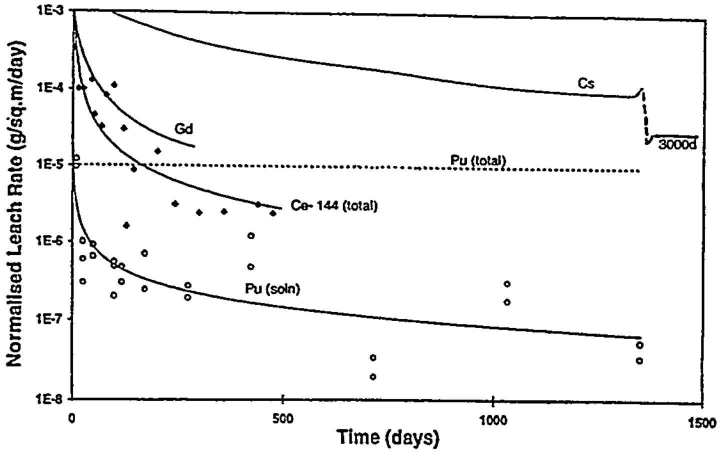

Figure 2 - Synroc Leach Results

Normalised leach rates of Pu-239, Ce, Gd, and Cs from Synroc-C in deionised water at 70°C with frequent replacement of water.

Table 2	**Physical Properties of Synroc**
Density	4.48 g/cm^3
Young's Modulus (25°C)	200 GPa
Thermal Conductivity (0-500°C)	2.5 W/m.K
Thermal Expansion (75-1000°C)	10x10^{-6}K^{-1}
Melting Point (incongruent)	1620K
Fracture Toughness	2MPa.m$^{-1/2}$
Poisson's Ratio	0.3
Compressive Strength	700-800 MPa

THE SYNROC DEMONSTRATION PLANT

The primary purpose of the Synroc Demonstration Plant was to demonstrate that Synroc, of a quality equal to that produced in the laboratory, could be fabricated on a commercial scale of 10 kg/hr with a simulated waste loading of 10-20 wt.%. The SDP will never handle radioactive wastes. It was decided, however, that critical equipment and process steps, that hitherto had not been demonstrated in a radiochemical environment, should be operated remotely. This included powder filling, bellows handling and hot-pressing operations. The SDP has been described in some detail by Levins et al.(16) and an overall process flow diagram is shown in Fig.3.

The SDP was designed for flexibility to enable a variety of feedstocks and a range of operating conditions to be accommodated so that the process could be optimised prior to the design of a conceptual radioactive plant. For economic reasons, hot-cell operations that were well established were not made to be remotely operable. Nevertheless, the SDP was highly automated with critical operations controlled by programmable logic controllers. The overall supervision of the plant and monitoring of process parameters was under computer control.

The process steps in Synroc fabrication are as follows:

a) mixing of acid HLW solutions with Synroc precursor powders containing the oxides shown in Table 1 to produce a slurry feed to the calciner;

b) calcination to decompose nitrates, at about 700°C for 1-2 hours in a rotary (AVM type) calciner under counter current flow of 3.5%H_2/N_2 reducing gas;

c) off-gas treatment;

d) blending of the calcined powder with 2 wt% titanium powder to control the redox potential during subsequent calcine consolidation;

e) loading of the blended product into stainless steel bellows containers;

f) cold-pressing of the bellows container;

g) hot-pressing at 1150-1200°C under moderate pressure (14-21 MPa) for 2 hours to yield a dense Synroc with about 99% of theoretical density;

h) loading of the bellows containers into standard canisters for storage and disposal. The space between the bellows and canister is filled with an appropriate heat transfer medium.

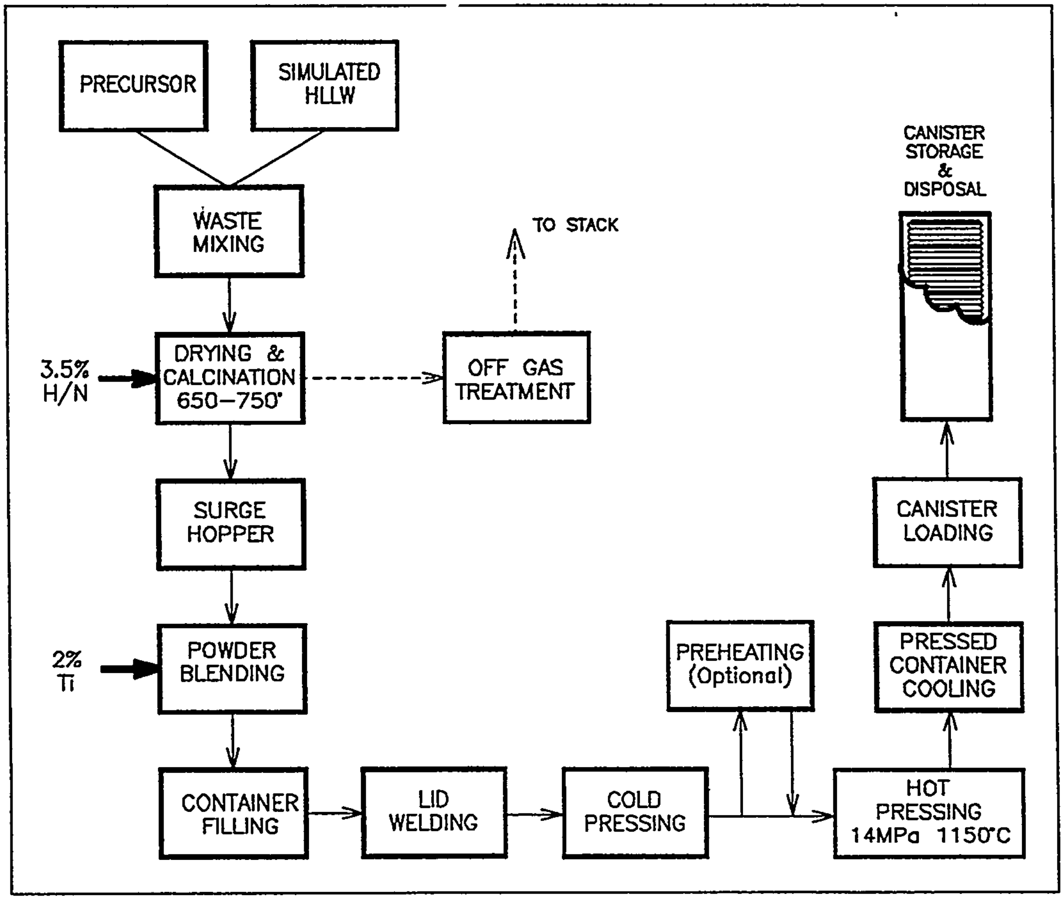

Figure 3 - SDP Process Flow Diagram

Furnaces for heating and cooling of the bellows were provided in the SDP. Pre-heating prior to hot-pressing increases the utilisation of the hot-press. Cooling furnaces were included to study and control the effects of thermal stress on cracking of Synroc inside the bellows.

The starting point for Synroc fabrication is a precursor containing the Synroc-forming elements in the proportions shown in Table 1. Ideally, the precursor should:

- have a high specific surface area to permit hot-pressing at the minimum temperature and pressure;
- be a chemically homogeneous blend of all its components to avoid segregation of some elements or formation of unwanted non-equilibrium phases;
- be of acceptable purity (eg. concentrations of silica above 0.1% are undesirable);
- have good rheological properties when slurried (low viscosity and low shear stress at relatively high pulp density);
- be stable when mixed with HLW;
- produce a free-flowing, non-dusty feedstock after calcination and have a high bulk density to facilitate bellows filling and compaction.

A variety of materials, including oxides, hydrous oxides, hydroxides, nitrates and carbonates (which are decomposed by the acidic waste) have been investigated for use as precursors. The results of early experience have been described by Levins et al. (17). The current precursor is made by a modified alkoxide hydrolysis route that yields powder with a surface area of 200 m^2/g before calcination and about 20 m^2/g after calcination. The tap density of the calcine has been improved from 700 kg/m^3 to about 1500 kg/m^3.

The precursor and waste slurry is fed to a rotary calciner that is very similar to the rotary calciners developed and proven in hot cells at the Marcoule plant in France and subsequently employed at the large reprocessing facilities at La Hague, France and Sellafield, UK. The calciner is designed for a maximum operating temperature of 900°C and a production rate of 10 kg solids/h. The calciner tube is constructed of 310 stainless steel, 300 mm in diameter and 7000 mm long. Heating is provided by an 80 kW resistance-heated refractory furnace comprised of eight independent heating zones which enable the temperature profile to be closely controlled.

Slurry is fed to the calciner at a rate of about 30 l/h. A reducing atmosphere is required during calcination to prevent the formation of leachable non-Synroc phases (particularly caesium molybdate). This is achieved by passing 4 m^3/h of 3.5 vol.% hydrogen in nitrogen (below the explosive limit in air) countercurrent to the slurry. The calciner is designed for a solids residence time of two hours but this can be varied by adjusting the tilt and/or rotational speed. Rabble-bars are used to prevent accumulation of cake on the calciner tube walls. Water is driven off in the calciner and nitrates are decomposed. The usual maximum temperature in the calciner is 750°C. The hot powder leaving the calciner is collected in a discharge hopper ready for removal to the powder blending stage.

The off-gas from the calciner consists mainly of nitrogen and steam with NO_x, NH_3, and traces of O_2 and H_2. The off-gas module was designed to treat 100 m^3/h of gas at a dust loading of 5g/m^3. Powder entrainment in the off-gas from the calciner has varied from 1.5 to 12.0% depending on the precursor, waste loading (ie nitrate content) and the number of rabble-bars. The entrained powder is removed in a filter vessel containing thirteen sintered stainless steel filter elements that are cleaned automatically by a reverse pulse of nitrogen. The collected dust is recycled to the feed tanks. The off-gas then enters a condenser to remove steam. The NO_x is removed using a catalytic converter (Pt/Rh) or O_2 injection prior to scrubbing in caustic and nitric acid columns. After scrubbing, the off-gas is heated and discharged via

HEPA filters. The off-gas system has worked under stable conditions even with 20 wt% waste loading in Synroc and no evidence has been found of the transfer of volatiles such as Cs, Tc, beyond the dust filter.

The calcined powder is stored in hoppers, sampled, and transferred to a blending/bellows filling station. Approximately 2 wt% titanium metal powder (<300 mesh) is added to the calcined powder for redox control during subsequent hot-pressing. Stainless steel bellows (18) containers have been developed to enable uniaxial hot-pressing of Synroc. The filled bellows container is sealed and transferred to decontamination, if required. The original SDP had provision for cold-pressing of the bellows prior to transfer either to a preheating furnace or directly to a hot-press. Generally, 5-6 hours are required to heat up the bellows container to 1150°C. The bellows container is hot pressed at 14MPa for 2 hours at 1150-1170°C. After hot-pressing the bellows container can be transferred to a cooling furnace or insulated box for controlled cooldown. After cooling the compacted bellows are loaded into a large stainless steel canister and the interspace filled with appropriate material. The bellows hot-pressing has been demonstrated up to a diameter of 43.6cm (60 kg Synroc). Fig. 4 shows an example of the bellows containers before and after hot-pressing. Bellows made from 310 and 321 stainless steel, 253 MA and inconel 600 have been evaluated. Experiments have shown that the Synroc powder near the bellows walls develops significant strength as the result of sintering during heat-up to hot-pressing temperatures. No loss of powder occurred from a bellows which partially melted, as the result of chemical interaction between impurities in the calcine and the bellows material, prior to hot-pressing. The use of the bellows containers facilitates powder transport and minimises the creation of process wastes such as failed melters.

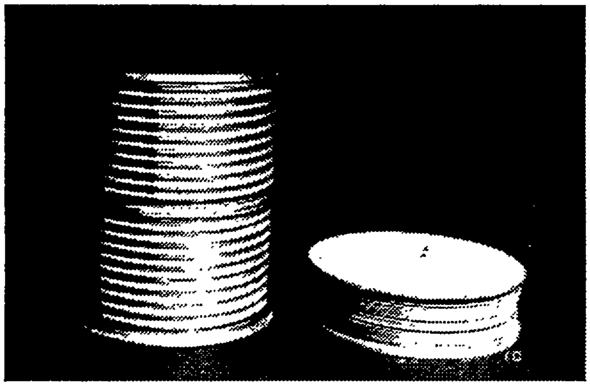

Figure 4

30 cm diameter bellows containing Synroc, before and after hot-pressing

The original hot press employed MA956 pressure pads that limit operation to 1150°C - 1170°C and 14MPa. Silicon nitride pressure pads, currently under evaluation, can tolerate higher temperatures and loads. The robotic tools employed to transfer the bellows, weighing up to 120kg, demonstrated the ability to maintain high positional accuracy (± 1.5 mm) and the materials employed on the grips have operated successfully at 1200°C.

The SDP has produced more than 6000 kg of calcine with 10-20 wt% simulated HLW over more than 850 hours of operation in 35 campaigns. More than 100 uniaxially hot-pressed bellows have been processed. Extensive tests have confirmed that the quality of Synroc produced at commercial scale in the SDP is equivalent to that produced in the laboratory. Precursors that yield higher tap density calcine than that for which the SDP was designed have been developed. This permits the elimination of the bellows cold-pressing step prior to hot-pressing. The redox control exercised during calcination with counter current flow of 3.5% H_2 in nitrogen, and the use of titanium metal powder during hot-pressing, have been shown to limit volatilisation of simulated waste elements to less than 0.15%, which is the level of detection in a non-radioactive facility.

ALTERNATIVE SYNROC PROCESS TECHNOLOGIES

The choice of slurried precursor oxides in the SDP resulted in the need for a larger rotary calciner than employed in the AVM plant at Marcoule in order to evaporate the excess water. To reduce the size of the Synroc calciner a program was implemented to develop a free flowing dry Synroc precursor that could be readily impregnated with HLW to levels required for 20 wt% waste loadings. These aims have been largely achieved (19) and a dry precursor feed has been selected in the design of a conceptual radioactive Synroc plant. The use of a dry precursor simplifies the off-gas system. Process development is continuing at ANSTO using simulated waste as part of a continuing refinement of the design. Densification of Synroc has also been investigated (20, 21) using hot isostatic pressing (HIP). The HIP case designs have been optimised for Synroc calcine and full densification has been achieved (22) at 1100°C and 100MPa.

Pressureless sintering is an alternative route for Synroc consolidation. Solomah et al. (23) have described the results of incorporation of HLW in Synroc pellets sintered at 1240°C in Ar-4% H_2 reducing atmosphere. Stewart (24) was able to achieve Synroc densities greater than 98% theoretical by sintering at 1300°C but observed significant grain growth. Whilst excessive loss of volatile fission products such as Cs, Ru during sintering has not been observed, a number of intermediate powder milling steps may be required for the production of homogeneous Synroc. Pressureless sintering is an established technology in glove-box facilities and in MOX fuel production but its use in HLW immobilization requires further development.

CONCEPTUAL DESIGN OF A RADIOACTIVE PLANT

A conceptual engineering design for a radioactive Synroc plant for an 800 tpa LWR reprocessing plant was completed in 1991 by ANSTO. This study was based on experience with the SDP and ongoing process developments. Dry precursor feed was chosen to reduce the size of the calciner and equipment redundancy was included to ensure plant availability 210 days/year. A low flow ventilation canyon was selected to house the process plant in an atmosphere of recirculating argon. This builds on the considerable experience accumulated at HFEF (ANL-West). The approach emphasises the capture and treatment of effluents from the process in concentrated form rather than dilution and release to the atmosphere. The use of an argon atmosphere is seen as prolonging lifetimes of high temperature process plant, and enhancing fire protection and powder handling.

The conceptual design incorporates two remotely repairable advanced servo-manipulators developed at ORNL (25), capable of 25kg capacity at end effector with an integral 450kg winch. The canyon includes an overhead crane to ensure all items in the process cell can be demounted and removed for maintenance and replaced by spare modules. Advanced robots are included for a number of operational and maintenance duties. Extensive use is envisaged of hardened stereo vision CCTV units. The overall placement of equipment within the cell is more flexible than in conventional radioactive plants since length and strength constraints of through the wall master/slave manipulators do not apply. The design has addressed unique issues associated with powder handling.

PLUTONIUM IMMOBILIZATION

The extensive experience at ANSTO with the SDP, subsequent process development and the conceptual design for a radioactive Synroc plant are highly relevant to the Pu immobilization option requiring the wasteform to include ^{137}Cs for proliferation resistance. This would require a nitric acid feed of Pu.

Mature technologies on industrial scale have been developed (26) at La Hague for the Ag^{2+} catalysed electrochemical dissolution of PuO^2. The Ag^{2+} mediated dissolution has the added advantage that it would be applicable to a wide range of plutonium residues and thus ensure a common feed to the immobilization process. Avoidence of criticality could be ensured by early blending with Gd and by appropriate design of dissolution and storage vessels. The complementary neutron poison, Hf, is envisaged to be in the Synroc precursor. The immobilization of Pu and ^{137}Cs requires a heavily shielded facility and we would envisage a dry feed of precursor to minimise the amount of water involved in the process.

Synroc is capable of immobilising most of the constituents present in plutonium compounds, alloys or residues slated for disposition. Ga and Ba, present in ^{137}Cs sources would reside in hollandite. Zr would be hosted by zirconolite and U, Th and the actinide decay products would partition between perovskite and zirconolite. At realistic plutonium loadings, halides are not expected to degrade the quality of Synroc. Indeed, CsC1 can be introduced directly to the feed to meet the desired (3) radioactive level of 1000R/hour at 1m after 30 years in a canister since the C1 content would be about 700 ppm. For some Pu ashes high in Na and SiO_2 the Synroc formulation can be modified (27) to include nepheline instead of hollandite, as envisaged in the original (28) Synroc-D formulation for defence waste immobilization.

The acid nitrate feed of plutonium to the Synroc process yields a homogeneous product with optimised chemical durability. Oxide feeds have been investigated at ANSTO in the context of both pressureless sintering and hot-pressing but more studies are required to determine trade-offs between operational parameters and product quality. Oxide feed is likely to require intermediate powder grinding steps.

Criticality control during processing, and in the long-term in a geological repository, is essential. Apart from the use of neutron poisons such as Gd and Hf, in both the upstream liquid processing and calcination/hot-pressing the use of the bellows containers provides another avenue of control. At about 12 wt% PuO_2 loading, each bellows of 30 cm diameter can be made to contain about 33 kg of Synroc, ie. 4kg of PuO_2 and about 50gm of Cs. Additional neutron poisons can be incorporated in the space between the bellows and the disposal canister. One process line, with durability of 200 days per year, in a plant of similar capacity to the SDP, could immobilize 50 MT of plutonium in 20 years. The chemical durability of Synroc, the similarity of leach rates between Pu and the neutron poisons shown in Fig.2, and the evidence of stability of natural mineral analogues of Synroc provide confidence that criticality is not important in repository environments despite the long half-lives of the important fissile elements.

The requirement to meet the "spent fuel standard" through incorporation of ^{137}Cs in the plutonium wasteform has significant economic penalties. Without the need to incorporate ^{137}Cs, the plutonium conditioning plant could be in a glove box facility rather than in a heavily shielded plant. An alternative approach (4) is to fabricate Synroc without ^{137}Cs and to use a shielded annex to incorporate ^{137}Cs in an appropriate form, eg. a titano-silicate ion exchanger, between the bellows and the disposal canister. Deep borehole disposal would represent an effective means of preventing unauthorised recovery of Pu. Synroc maintains its chemical durability (7) at the higher temperatures (~ 200°C) expected in deep boreholes. These temperatures will also limit the extent of possible damage from alpha-decay processes in Synroc.

The economics of immobilization of plutonium in Synroc are likely to be competitive with other options if a green field site is considered. The conceptual design study at ANSTO indicated that a shielded Synroc plant would cost less to construct than vitrification plants at the large reprocessing facilities in Europe. Earlier studies (29, 30) in the USA also indicated that Synroc was competitive with glass. Clearly, an economic comparison of plutonium immobilization and disposition requires further definition of requirements such as the need for spiking with ^{137}Cs, maximum permissible Pu loadings and other criticality demands. Nevertheless, in a systems analysis, the higher density of Synroc wasteforms compared with glass and the opportunity provided for waste immunisation by the use of bellows containers will be important advantages for Synroc.

CONCLUSIONS

Synroc is the most developed crystalline wasteform for immobilization of excess Pu. Process feasibility has been demonstrated by ANSTO, at the scale required by the Pu disposition program, with non-radioactive simulants. A conceptual design has been completed of a radioactive plant that would be required if ^{137}Cs is to be included in the wasteform. Alternative technologies such as pressureless sintering for production of ceramic wasteforms have been investigated but further development is required before plant designs can be initiated. Economic evaluations show that Synroc process technologies are competitive with glass.

The data base on Synroc containing Pu, neutron poisons and ^{137}Cs for diversion resistance is extensive. Further optimisation of waste loadings, neutron poisons and tolerance to impurities is warranted when better understanding exists of the nature of the plutonium and its residues destined for immobilization. The use of neutron poisons that are in solid solution in phases which contain Pu together with evidence of long-term durability of the relevant Synroc phases from mineral analogues, give confidence that nuclear criticality will not be an important issue in repository environments. Synroc is a wasteform that can be envisaged for disposal in deep boreholes and this permits consideration, with significant economic advantages, of glove box processing because ^{137}Cs may not be needed for diversion resistance.

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DISCLAIMER

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Selecting a Plutonium Vitrification Process

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ABSTRACT

Vitrification of plutonium is one means of mitigating its potential danger. This option is technically feasible, even if it is not the solution advocated in France.

Two situations are possible, depending on whether or not the glass matrix also contains fission products; concentrations of up to 15% should be achievable for plutonium alone, whereas the upper limit is 3% in the presence of fission products. The French continuous vitrification process appears to be particularly suitable for plutonium vitrification: its capacity is compatible with the required throughout, and the compact dimensions of the process equipment prevent a criticality hazard.

Preprocessing of plutonium metal, to convert it to PuO_2 or to a nitric acid solution, may prove advantageous or even necessary depending on whether a dry or wet process is adopted. The process may involve a single step (vitrification of Pu or PuO_2 mixed with glass frit) or may include a prior calcination step - notably if the plutonium is to be incorporated into a fission product glass.

It is important to weigh the advantages and drawbacks of all the possible options in terms of feasibility, safety and cost-effectiveness.

INTRODUCTION

What can be done with the surplus military plutonium still held by the two power blocs to avoid its proliferation? This is clearly a strategic problem to be solved by the politicians, but there are also considerable technical problems.

Apart from its explosive capacity, plutonium is also extremely radiotoxic over a very long timescale; more so, for example, than the uranium fission products which are associated with it when it is produced in reactors (cf. figure 1).

Several options are available; some involve its destruction by fission in reactors, for example, while others advocate isolating it after confinement in suitable matrixes. Both of these categories have been recommended for research by the US National Academy of Sciences.

THE CHOICE BETWEEN BURNING AND VITRIFICATION

Which strategy should be applied?

- Controlled fission means consuming the plutonium in power reactors as their fuel. This is the MOx process, in which France and other countries, notably Britain, Germany, Belgium and Japan are currently engaged.

It seems only reasonable to benefit from the energy released by plutonium fission : one gram of plutonium, after all, is equivalent to a ton of oil - with no impact on global warming. Proven technology already exists in which Pu is used to fabricate mixed oxide (MOx)) fuel for use in power reactors.

MOx fuel was first used in 1963 in Belgium, with the BR3 demonstration PWR at Mol and in Germany at Obrigheim in 1970. In France, MOx fuel experience has developed progressively since the first irradiation in the Chooz plant in 1974, followed by the MOx program in light water reactors operated by the French electrical utility EDF at Saint Laurent des Eaux in 1987. Seven French nuclear power stations are currently operating with MOx fuel, and EDF intends to extend its use into 20 to 28 units by the end of the century.

In the longer term controlled fission will also involve using plutonium in fast reactors. Russia, in particular, is advocating this direction, even if it appears not to have the resources to do anything about it at the moment.

- Vitrification is the incorporation of plutonium into a relatively insoluble glass network from which recovery would be difficult. This is a technical possibility, even if many years of development would be necessary before it could become an industrial solution.

FRENCH EXPERIENCE IN VITRIFICATION

France has undeniably acquired considerable experience in the field of vitrification. Radioactive glass blocks weighing a few hundred grams were produced as early as 1957. In subsequent years laboratory facilities were established at Saclay and Marcoule producing increasingly large glass blocks until the process finally assumed industrial proportions. It is now nearly 30 years since 1968 when the CEA began operating a vitrification unit called PIVER using a batch or pot vitrification process in which a radioactive fission product solution was converted into glass in a single induction-heated metal melter, used for the evaporation, calcining and vitrification steps (figure 2). About 200 glass blocks weighing about 100 kg each were fabricated. Twenty years after it was commissioned, PIVER was named a Nuclear Historic Landmark by the American Nuclear Society on November 15, 1989 : "high-level waste vitrification prototype and its storage facility both began operating in 1969. PIVER successfully demonstrated one of the essential safety conditions of the nuclear power option : the safe disposal and storage of long-lived radioactive waste".

The transformation into an industrial process came in 1978 when COGEMA brought into operation its Marcoule Vitrification Facility, adjoining the UP1 reprocessing plant. This was followed by two other facilities of larger capacity at La Hague - R7 and T7, attached to the two reprocessing plants UP2 and UP3. COGEMA uses the "continuous vitrification" process in all these facilities, as does the British operator BNFL. This two-stage continuous process (figure 3) is designed to convert high level liquid waste from Purex reprocessing plants into borosilicate glass. The High Level Waste solution in nitrate form is fed at a metered rate into an electrically heated rotating calciner where the salts are evaporated and the nitrates are partially calcined to oxides ; the calcine is then supplied together with glass additives into an induction-heated metal crucible. The process thus converts the nitrate solution into a dry oxide form suitable for glass production. The current R7/T7 melter design has a total volume of 200 liters and weighs less than 500 kg : glass is poured about 70 liters at a time every 6 to 8 hours. The results logged by the French vitrification units are summarized in Table 1. Over 5000 canisters have been produced representing nearly 2000 tons of glass containing more than 1500 million curies of fission products.

Table 1 - Operating statistics for French vitrification facilities (as of December 31, 1994)

Operating Statistics	Reprocessing Plant		
	UP1 (Marcoule)	UP2 (La Hague)	UP3 (La Hague)
Vitrification facility	AVM	R7	T7
Startup date	1978	1989	1992
Evaporation capacity ($l.h^{-1}$)	40	60	60
Glass fabrication rate ($kg.h^{-1}$)	10-15	20-30	20-30
Vitrified solution volume (m^3)	1800	1750	587
Glass production (metric tons)	806	806	344
Number of canisters produced	2275	2048	869
Volume reduction factor	5.7	5.6	4.5
Vitrified $\beta\gamma$ activity(MCi)	384.3	745.7	380.4

The process continues to evolve. The CEA has been developing a new glass melting technique in recent years, using an induction-heated cold crucible melter (figure 4). This highly efficient heating technique could no doubt be used to vitrify plutonium ; compared with existing processes, it can produce more refractory glass or vitrocrystalline formulas with even better containment properties than the current fission product glasses if required. This process has two major advantages : temperatures of 1500°C can easily be reached and the melter is corrosion-free.

PLUTONIUM VITRIFICATION METHODS

Plutonium vitrification has not been a subject of major research in France to date ; only a few fission product containment glass blocks were fabricated in the 1970s with a few percent of PuO_2 to dope them with alpha emitters in order to investigate alpha irradiation damage in the glass. The incorporation of PuO_2 in sufficient quantities proved difficult because of segregation problems and PuO_2 was replaced by alpha emitters with shorter half-lives such as AmO_2 or CmO_2. Vitrification is as previously said routinely used in the COGEMA reprocessing plants at Marcoule and La Hague to produce containment glass for concentrated fission product solutions, but the glass contains only negligible amounts of Pu. Glass containing PuO_2 has been fabricated by KfK in Germany, but Pu vitrification has only been seriously investigated in the USA at Savannah River.

Broadly speaking, there seem to be two main ways to vitrify plutonium :

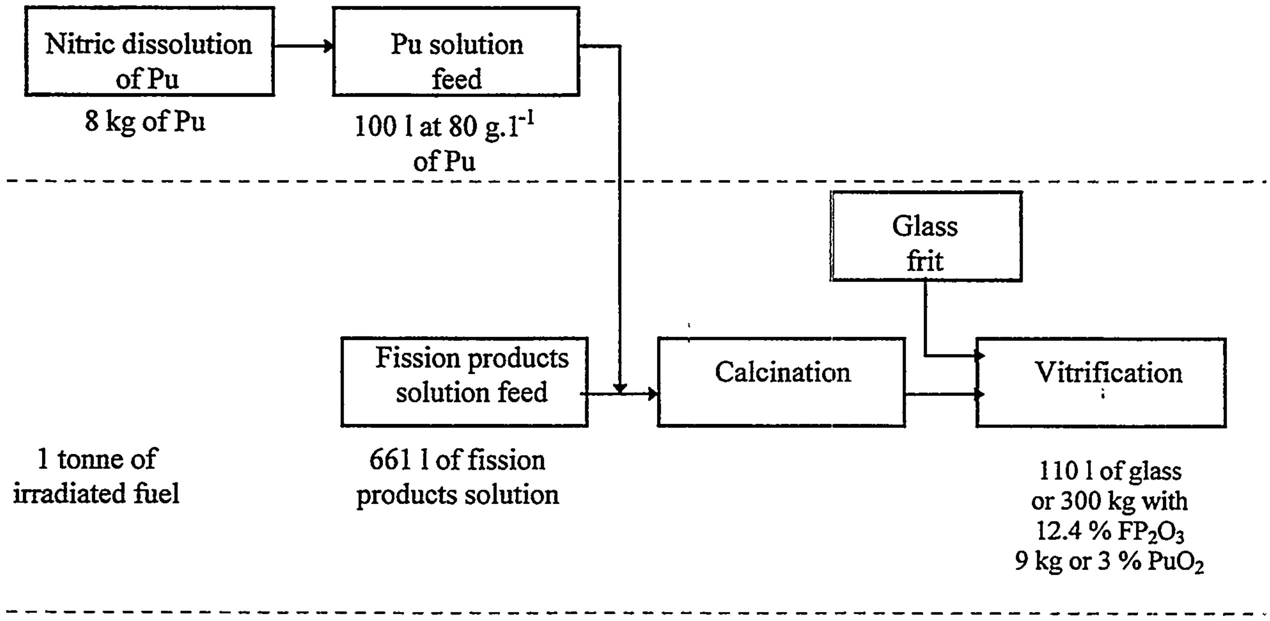
- The first is by incorporating it into borosilicate glass together with fission products, as recommended by the NAS. The intention here is to make recuperation as difficult as possible.

- The second involves determining the optimum formulation for incorporating PuO_2 alone into a glass matrix ; it should be noted that the maximum PuO_2 concentration in the glass would not only depend on its solubility in the glass, but could be limited by the risks of criticality and/or heat release in interim storage or after final disposal. The behavior of alpha emitting glass (helium production, leaching resistance) and its long-term behavior in repository conditions must also be investigated.

Let us now go into more detail on these two possible options :

- While the safer way may be to mix the plutonium with fission products in borosilicate glass, it is also the more difficult and subject to more constraints.

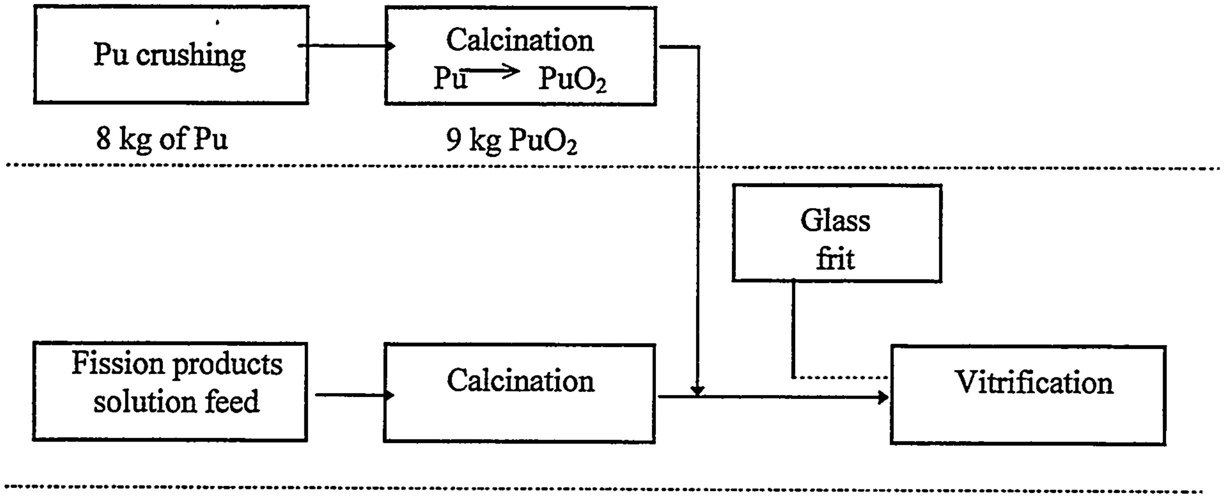
We are assuming that PuO_2 could be incorporated into fission products glass at a rate of 3% and, to use an example, let us consider the known process of the R7/T7 glass currently produced industrially at La Hague. The following simplified diagram shows what would probably be the most feasible method :



To ensure a homogeneous mixture and to avoid any plutonium segregation, the plutonium could be put into nitric solution and then fed into the calciner either parallel to or mixed with the fission products solution. Calcination would then change it into PuO_2. Closely mixed with the fission products calcinate, the PuO_2 would then be vitrified at the same time as the fission products oxides.

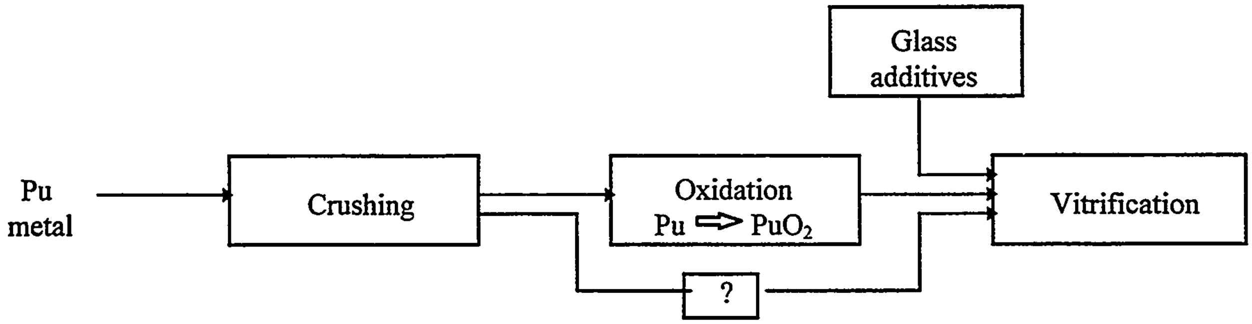
- Another possible technique could be the separate oxidation of the plutonium into PuO_2 followed by direct metered feeding at the vitrification stage. This would have the disadvantage of having to meter the feed in powdered form, certainly more difficult than a liquid feed, but would, on the other hand, be simpler and reduce the risks of criticality.

In any case, we would make 300 kg of glass for 8 kg of plutonium and using equipment like that at La Hague which produces about 800 canisters of 400 kg per year we could, theoretically, vitrify 8,5 metric tons of Pu in a year. Obviously, in reality the calculation is not as simple as that since the facilities at La Hague have not been designed to take account of criticality, particularly not for such an operation as this!



- Vitrification of plutonium on its own, without fission products would clearly result in the confinement of the PuO_2, but the plutonium could be more easily re-extracted.

Studies at Savannah River show the possibility of including 14% of PuO_2 in the lead-silicate formulae called "Löffler glass". In that case we could envisage the following scheme :



1 kg Pu $\longrightarrow$ 1.13 kg PuO_2 $\longrightarrow$ 8 kg of glass (14% PuO_2)

The metallic plutonium would first be crushed and the granulate or pulverized pieces would then be oxidized by heating in air at 500°C. Given the considerable reducing capacity of plutonium, we can even imagine the possibility of feeding Pu powder directly onto the surface of the glass melt where it would oxidize immediately in air or oxygen.

Disregarding the problems of criticality, it is easy to imagine a melter producing 50 $kg.h^{-1}$ of glass per hour which would thus vitrify 6.25 kg of Pu. Working at a rate of 4000 hours a year, 2 years would see the vitrification of 50 t of Pu in 400 t of glass. These are, of course, only hypotheses and there is still much work to do on glass formulations and their properties, as there is on safety aspects, above all criticality.

CHOICE OF EQUIPMENT

The main stages in the plutonium vitrification process, whichever option is chosen, PuO_2 alone or mixed with fission products, are the following :

- Pu crushing
- oxidizing Pu into PuO_2
- vitrification as such

Since the first two stages are already well known and in industrial operation, we now need only concern ourselves with the vitrification itself. A direct induction cold crucible melter (figure 5) would seem to have all the advantages needed for the delicate operation we are considering :

- it is completely static and its volume has been reduced to the minimum (about 60 cm diameter and 40 cm high) for an output of 50 $kg.h^{-1}$ of glass,

- all glass formulations are possible, including the most refractory, since there is no limit to the melt temperature,

- there is no risk of either corrosion or wear even at the highest temperatures,

- since the surface of the melt consists of a layer of ingredients for the vitrification, thus cold, any potential volatility is limited. This greatly simplifies the gas treatment equipment,

- the melt can be mechanically agitated, if necessary, which could prove useful to ensure that the glass is homogeneous,

- it enables the glass to be poured at any rate desired and started and stopped at will,

- the only contaminated wastes which could be produced in any possible incident would be easily dealt with owing to the absence of refractory and the nonadherence of the glass to the cold walls.

In passing, we might mention that a panel of international experts assembled by the Washington Hanford Company has recently selected this type of melter to vitrify the waste from Hanford.

Cold crucible technology is well understood by the CEA which, of course, developed it. It is already accepted in French non-nuclear industry and is being seriously considered for use in the nuclear field.

COMMENTS AND CONCLUSION

Apart from its attendant financial burdens, the vitrification of plutonium mixed with fission products will always remain a delicate operation compounding the problems of fission products and the criticality of plutonium, not to mention the political ramifications. It would, for example, be preferable for the both the plutonium and the fission products to come from the same country and that adequate controls be maintained on the vitrified product since it would contain weapons grade material ; otherwise, serious complications are no doubt inevitable.

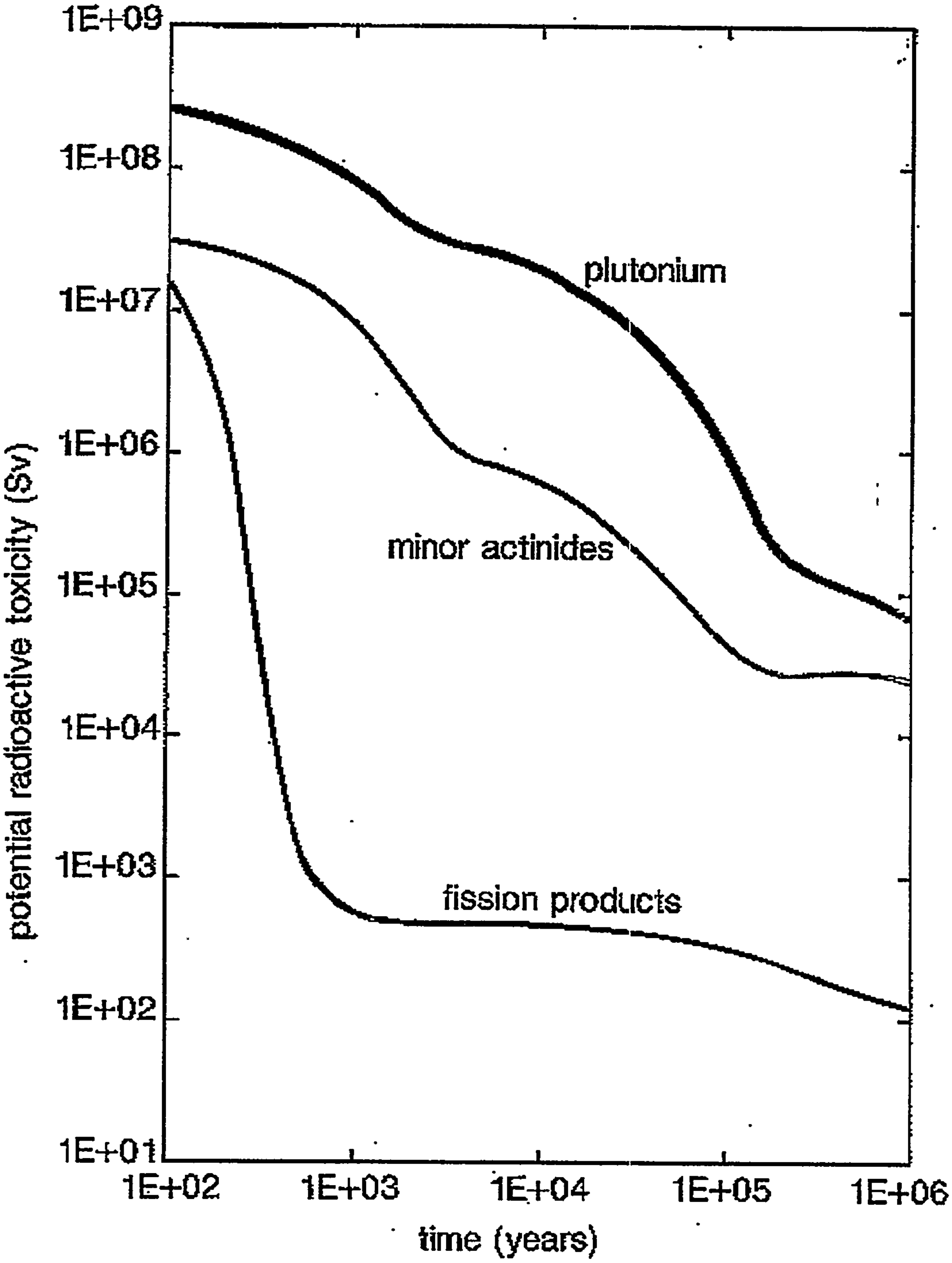
The vitrification of plutonium alone, without fission products would obviously give a less secure product and would not entirely satisfy the criteria of the NAS. Although this process will also require the perfection of numerous techniques, it appears, nevertheless, to be simpler and certainly less costly. The chief reasons for this are that hot cells would not be necessary (the operation could, we think, be done in glove boxes) and that the quantity of glass needed would be much smaller. We estimate that it would probably be about ten times cheaper!

In any case, the vitrification of plutonium, the most energetic of all elements, seems anachronistic in a world where energy needs will continue to escalate.

Man has been in effect extracting energy sources from the earth since the beginning of time, but this must surely be the first time he has ever considered getting rid of fuel by rendering them useless and burying them!

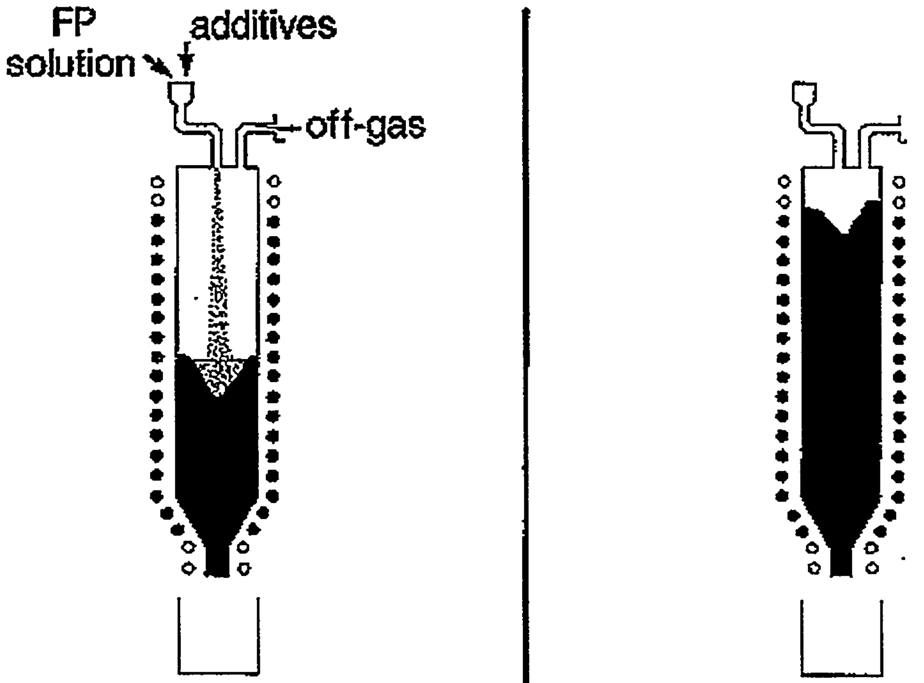
Would we not be better inspired to put this fabulous metal to good use?

DISCLAIMER



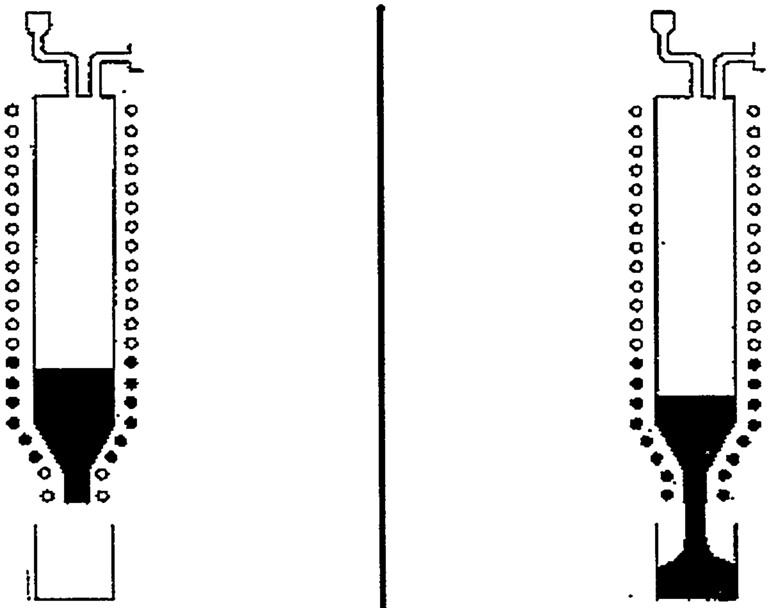
POTENTIAL RADIOACTIVE TOXICITY of ONE TON of UOX1 FUEL

FIGURE 1



1-FEEDING/EVAPORATION

2-CALCINATION

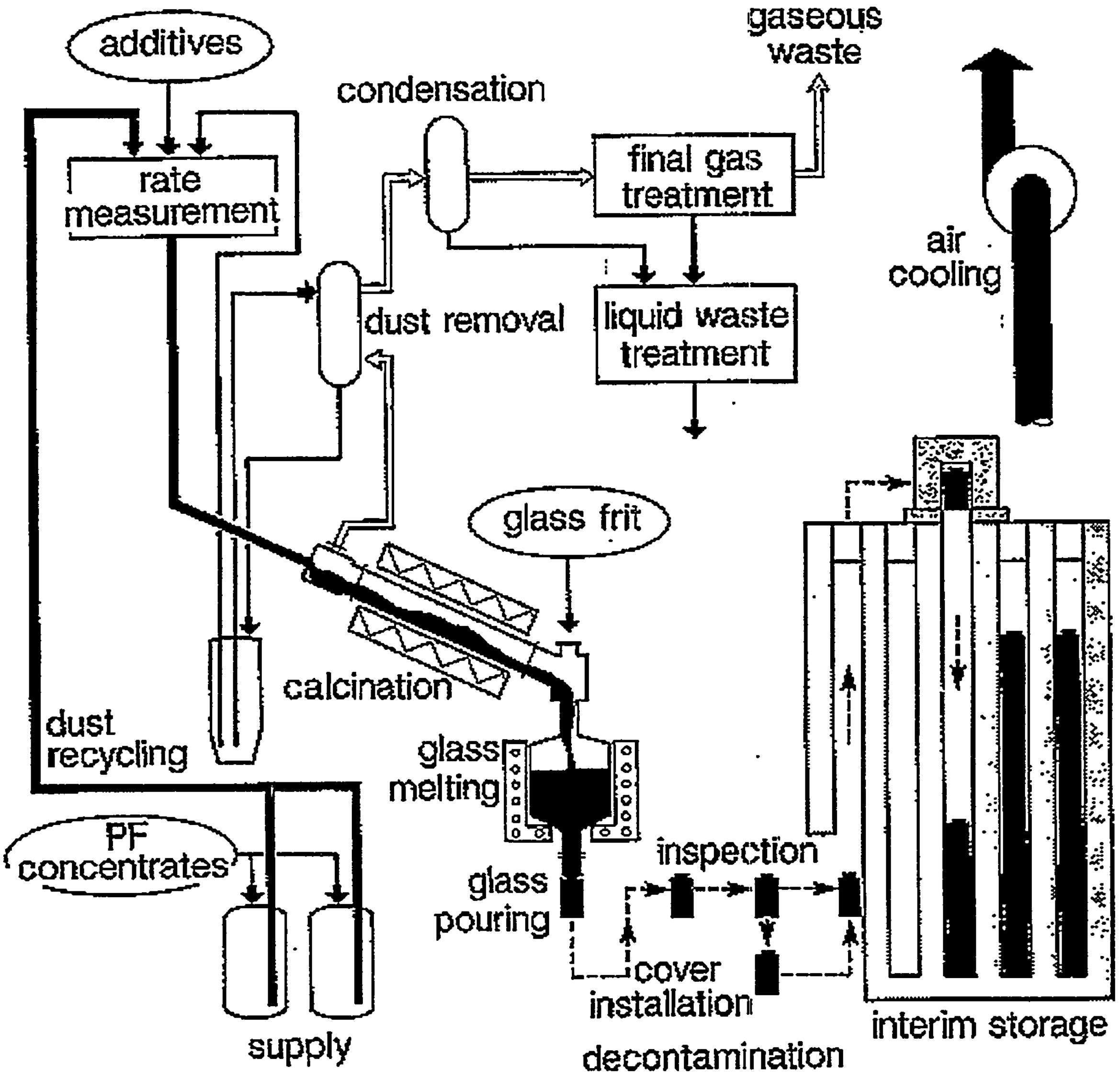


3-MELDING/REFINING

4-POURING

POT VITRIFICATION PROCESS

FIGURE 2

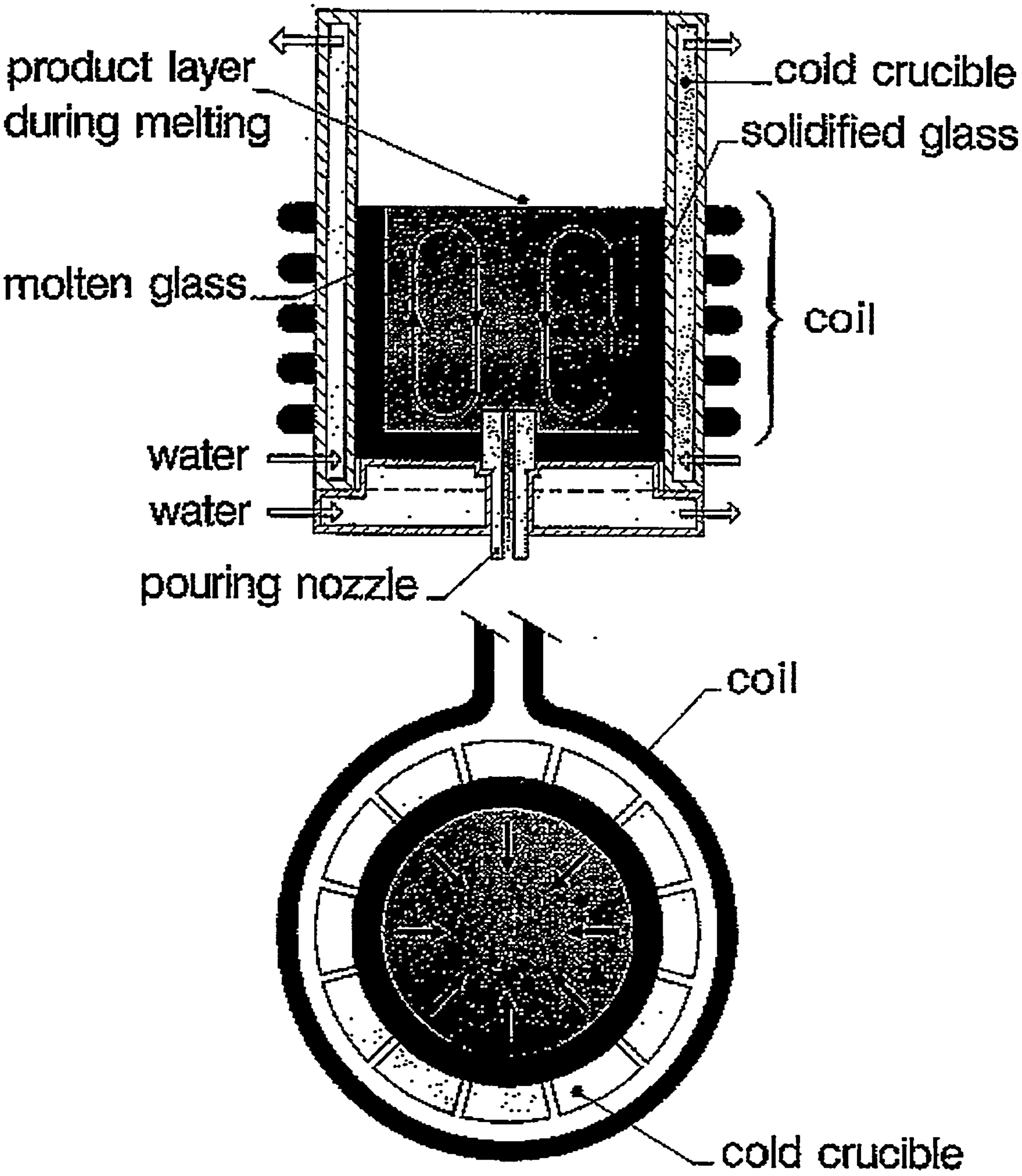


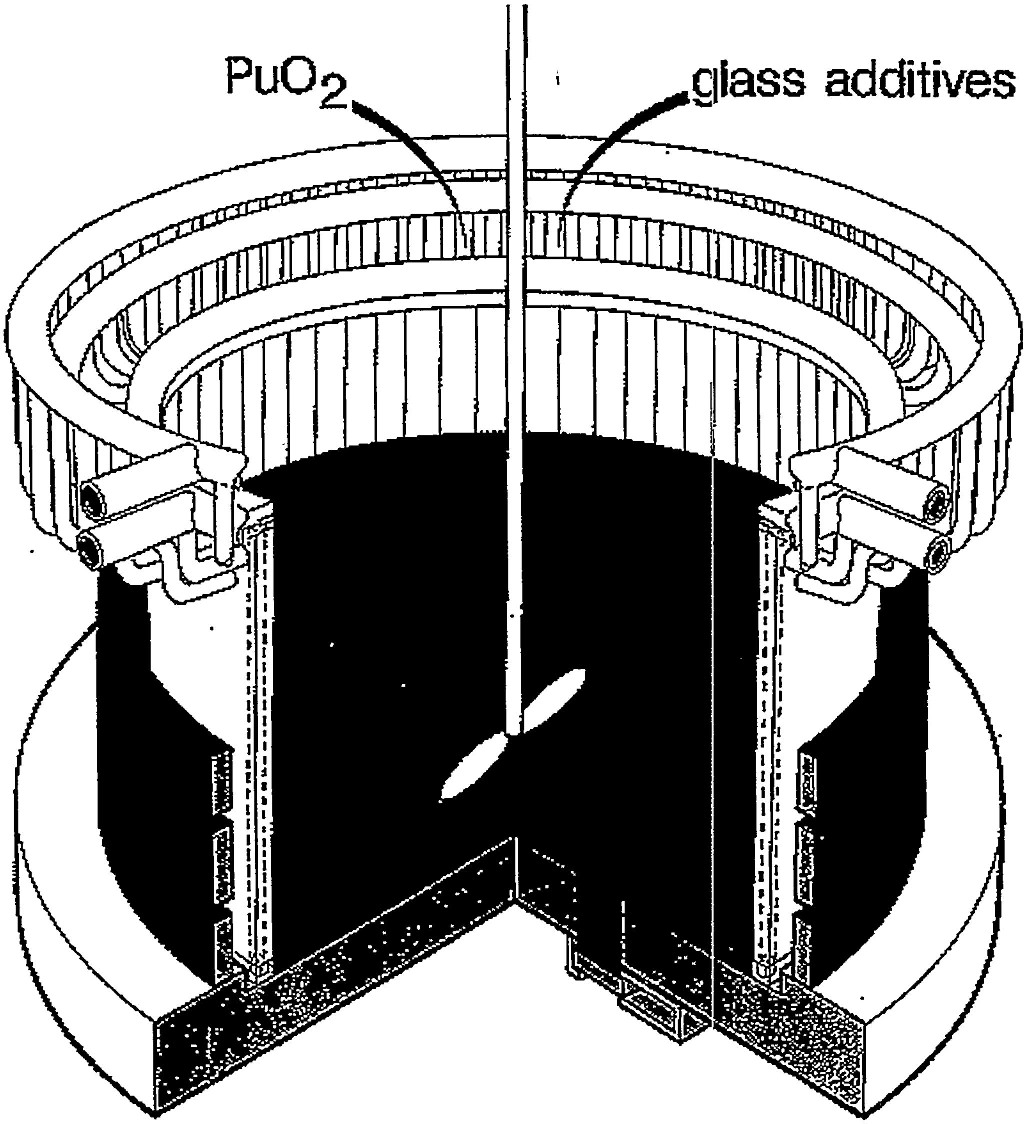
FRENCH TWO-STAGE CONTINUOUS VITRIFICATION PROCESS

FIGURE 3

FIGURE 4

COLD CRUCIBLE MELTING PRINCIPLE





SCHEMATIC VIEW of a COLD-CRUCIBLE PLUTONIUM VITRIFICATION MELTING

FIGURE 5

Session Chair for Immobilization Facilities:
Tom Gould, Westinghouse Savannah River Company, Aiken, SC
Wednesday, December 13, 1995; 2:15 pm

Question / Comment 1:
Jeff Kass, Lawrence Livermore Nat'l Laboratory
My questions is for the folks from Australia. My questions is for a little bit of clarification on the relative leach rates between the plutonium and the gadolinium. From what I saw, it looked like the gadolinium leach rates were higher than plutonium leach rates by a fairly substantial factor. I thought I heard you say that it turned over and later on it became quiet similar, but I didn't see that from the data, could you please explain that?

Answer:
Adam Jostons, Australian Nuclear Science & Technology Organization
I think what you saw on my data was plutonium leach rates split into two curves. One is what you call total plutonium, that is colloids, what sticks on the leach vessel wall, and then I also showed you how plutonium in solution changes and at that particular time, you're right, it crossed one of the curves and I think by implication, a couple of things I say. First of all, they are very low leach rates, so differential amount material separating is very small, in realistic terms. I think I would also say that they were done in distilled water. If you leach the same material in silicate water or even in carbonated water, the leach rate would almost be a order of magnitude lower, and if you do it in different pH's, the amount of separation between in solution changes. But the real point, I think, is by the time you lose one or two surface grains, eventually the leach rates will drop to that. It will be congruent and that what happens in the mineral world in the real geochemistry, I mean that why you can have interesting mineral deposits over hundreds of millions of years.

Question / Comment 2:
Thomas Gould, Westinghouse Savannah River Company
While you all are thinking of questions, I'd like to ask a question and direct it to both Dr. Kushnikov as well Antoine Jouan. The question is would they care to comment on the similarities and differences in the induction, melting cold walled technique as used in Russia verses the technique that is used in France? Viktor, do you want to start it off?

Answer:
Viktor Kushnikov, Institute of Inorganic Materials
At this time the experimental work we don't have samples to show you. Maybe next time, I will be able to bring a shot glass made from a zirconium ceramic form. In any case, in our opinion it is preferable to convert plutonium to a more stable form, into a form of crystallized ceramics.

Answer:
Antoine Jouan, Commissariat a l'Energie Atomique
What I could add seems to be very difficult, because there is a difference of the frequency that we use. We use a low frequency, that means 100,000 kilohertz, that is about 10 less than the Russian one. We use this low frequency because we intend to use this system in odd cell and it is very difficult for us today to cross the shield of cell of one meter of concrete if we are very high frequency and very high current. So for this reason we prefer to use low frequency. The low frequency also opens a way of a large diameter, large capacity melter. We have today in operation now in Markwool, 200 Kg per hour capacity melter, which is 1 meter diameter. We are able, we are designed, we have <inaudible> of melter which is able to melt one ton per hour, so it means that the diameter is 2.5 meter, and for that we need to approve low frequency, the physical <inaudible>.

DISCLAIMER

LONG TERM PERFORMANCE

SESSION CHAIR: STEPHEN HANAUER, US DEPARTMENT OF ENERGY,
OFFICE OF CIVILIAN RADIOACTIVEWASTE MANAGEMENT, RW-2

GLASS CORROSION AND IRRADIATION DAMAGE BEHAVIOR

by

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INTRODUCTION

Several options are under consideration for the disposition of surplus Pu resulting from weapons dismantling and site remediation. One option is immobilization of the Pu and scrap metal in glass, followed by repository disposal. However, the final composition of glass has not been selected, and the information regarding the long-term behavior of high Pu-loaded glasses under potential unsaturated repository conditions is limited. Additionally, several issues exist that are relevant to the feasibility of using glass as a waste form. In this paper, we discuss (1) the general behavior of Pu-loaded glasses when corroded by water; (2) the distribution of Pu, ^{235}U, together with neutron absorbers during corrosion; (3) the effect of irradiation damage on glass corrosion behavior; and (4) the role of glass modeling in the calculation of long-term performance.

The high-level waste glass compositions that are currently under consideration in the United States are based on wastes that result from the reprocessing of used reactor fuel [1]. In general, the feed streams contain a range of components that are either glass formers or modifiers, but very little Pu. The resulting glass contains about 0.01 wt% Pu and considerable Al, Fe, Na, Ca, and Mg. These glasses, therefore, have been optimized to accommodate high loadings of compositionally complex wastes. Adaptation of the existing glasses to incorporate high concentrations of Pu has not been required and thus only a limited data base is available for evaluating precisely how much Pu can be dissolved in glass. However, the work that has been done on Pu solubility in glasses [2-5] suggests that fairly high Pu loadings (2-13 wt%) should be achievable. This work also suggests compositional adaptations based on glass chemistry that can be used to ensure high Pu loadings. Additional work regarding the development of high Pu-loaded glasses is reported elsewhere in these proceedings [6].

While past compositional studies have not focused on Pu, considerable emphasis has been placed on the behavior of Pu and other actinides during exposure of glass to water [7]. This focus exists because the actinide elements are of concern from a regulatory standpoint. This previous work has resulted in the derivation of Figure 1 which provides a schematic of the reaction pathway by which glass reacts. In a thermodynamic sense, the reaction of glass with water proceeds in a manner that minimizes the free energy of the system and also minimizes the chemical potential gradients between the solution and the glass. When the gradients are steep, particularly for major glass-forming components such as SiO_2, the rate of reaction will be relatively high, whereas when the gradients are comparatively shallow, the rate of reaction will be relatively low. The slope of the chemical potential gradients and the energy required to extract the rate-limiting component from the surface of the glass are controlling factors in determining the rate of glass corrosion. For silicate-based glasses, the rate controlling step is the hydrolysis of the last Si-O-Si bond and the formation of H_4SiO_4 (silicic acid). The chemical potential gradients between the glass and water are initially large (Stage I) because the leachant is dilute, and the reaction proceeds at the forward rate. As the silicic acid concentration in solution increases, the chemical potential gradient decreases (Stage II). Glass reaction during Stages I and II usually results in the formation of a reacted layer, which may or may not be crystalline, but this change does not increase the glass reaction rate. However, certain alteration phases that nucleate during glass corrosion can serve as a sink for silicic acid. When this occurs, the rate of glass corrosion is controlled not by the chemical potential gradient between the glass and solution, but by the gradient between the glass and alteration phases. This, in turn, may accelerate the rate of glass corrosion (Stage III). This increased rate may be controlled by the precipitation of the silicic acid consuming phases, or by the forward rate of the glass at the conditions of temperature and pH of Stage III.

The reaction pathway is useful in conceptualizing glass behavior, but to calculate glass behavior over a range of conditions, modeling must be performed. This activity requires that the reaction mechanism be elucidated through the results from well-designed experiments and expressed as a mathematical kinetic rate equation. This rate equation can then be used in concert with a number of computer codes to calculate the long-term behavior of glass under disposal conditions. Typically, the kinetic expression contains all the chemical and physical parameters that are important to the rate-limiting step in the kinetic mechanism. For glass, the important parameters appear to be the silicic acid concentration $[H_4SiO_4]$, the temperature, and the pH of the surrounding solution. A glass dissolution model, therefore, is a well-defined mathematical expression of the kinetics by which glass interacts with water and for which the kinetic parameters are known. While testing provides valuable information about the distribution of actinides and neutron absorbers and about glass reaction during each stage of the reaction pathway, no single test can provide all the information that is required to calculate glass behavior. Thus, the development of a predictive model, as opposed to an empirical extrapolation, is necessary to complete a performance assessment of Pu glass in a repository setting.

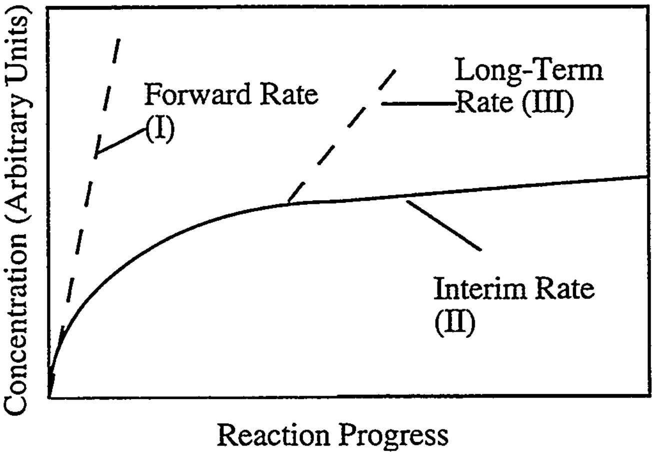

Figure 1. Schematic of the reaction progress pathway for glass. The reaction stages are defined in the text. The curves represent the behavior of the most soluble element in the glass, usually boron.

Testing is required to provide data with which to develop and validate such predictive models. Long-term testing of actinide doped and fully radioactive glasses that are within the compositional envelope of potential glasses to be produced at the Defense Waste Processing Facility (DWPF), indicates that the behavior of Pu is dependent on the test conditions. Static tests with a large ratio of the surface area of the glass to the volume of solution (S/V) result in the initial release of Pu being dominated by a colloidal fraction in which the Pu is associated with clay phases [8,9]. Ultimately, however, the majority of the Pu released from the glass is sorbed to the metal test vessel. Uranium in these tests initially is released more rapidly than Pu. As the reaction proceeds into Stage III, the U forms alteration phases that precipitate from solution and are found on the glass surface. Of potential neutron absorbers, B is released rapidly to solution and is not incorporated into alteration phases. Transition metals and rare earth elements have a release pattern similar to that of Pu, although most studies have not evaluated the release characteristics of these elements in detail. Thus, tests to evaluate the behavior of high Pu-loaded glasses must be designed specifically to evaluate the distribution of the neutron absorbers and of Pu and U in solution, in the alteration products, and in the reacted glass.

Other tests with DWPF-type glasses have evaluated the reaction of glass with water vapor under conditions that accelerate the reaction into Stage III. The goals of these tests are to determine which alteration phases form and which of these phases contain actinide elements. In general, U forms alteration phases, such as weeksite $[K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O]$, while Pu remains associated with the clay layer that forms as the glass reacts.

Considerable testing has also been done to determine whether the corrosion behavior of glass would be affected by irradiation damage that may accumulate during disposal. Studies have considered all aspects of irradiation damage, including alpha decay that would result from the decay of Pu. In these studies irradiation damage has been accelerated by using a variety of techniques. For standard borosilicate waste glasses, the indication is that any increase in the reactivity of the glass will be within errors associated with performance calculations [10-12].

Each of the above points must be reconsidered when evaluating the behavior of a high Pu-loaded glass for repository disposal. In this paper, available information on information related to the behavior of high Pu loaded glasses is reviewed.

COMPOSITION AND BEHAVIOR OF HIGH PU-LOADED GLASSES

High Pu DWPF Glass

The reference composition to be produced in the DWPF is termed the blend glass. This composition will **not** be used as the high Pu-loaded glass; however, there is a large data base on its reactivity under potential disposal conditions [7], and these data are being used in initial performance assessments to determine whether a high Pu-loaded glass raises issues different from those identified for the blend glass. To assist the Yucca Mountain Project (YMP) in evaluating issues unique to high Pu-loaded glass, a set of preliminary experiments is in progress with the blend glasses that contains 2 and 7 wt% Pu (P2 and P7 glass) and 2 wt% Pu plus an equal mole percent Gd (G2 glass). The Gd is added as a neutron absorber and its behavior during reaction is largely unknown. The blend glass was chosen because of the ongoing YMP preliminary performance assessment efforts and because the results can be analyzed within the context of the reaction pathway.

To establish the corrosion behavior of the glass, samples were reacted using the product consistency test, version B (PCT-B) and the Argonne vapor hydration test (VHT). The PCT-B test conditions include a temperature of 90°C, an S/V of 20,000 m^{-1}, and concentrated ground water as the leachant [13]. The VHT tests were conducted at 200°C under saturated vapor conditions. It has been found that there is a correlation between the formation of alteration phases in the VHT and the reactivity of glass under PCT-B conditions [9]. Additionally, the distribution of radioelements in the alteration phases can provide information regarding the eventual release of these elements to solution. It is not anticipated that waste glasses will be exposed to a temperature of 200°C under repository conditions, but previous results [14] have indicated that this temperature can be used to accelerated glass reaction without altering the mechanism, thereby providing insight into potential reactions that may occur under long-term storage conditions.

The results of PCT-B tests on the P2, P7, and G2 glasses have been reported through 215 days [4]. The test solutions were analyzed extensively [e.g., 13], but for comparison with other glasses, only the results for B, Pu and Gd are given (Table I). Boron provides an upper bound of the glass reaction, and information on Pu and Gd are required for criticality calculations. The values in Table I include a contribution from the leachate and the acid strip of the test vessel. These data indicate that the reaction of the P2 and P7 glasses remains in Stage II of the reaction pathway. Glass G2 shows a seven-fold increase in normalized release of B, $(NL)_B$, at the 215-day period, while the releases of Pu and Gd are within a limited range for the entire test period. The normalized releases of Pu and Gd are equivalent. However, there is evidence from the P7 test results that as the glass reacts it forms clay colloids that entrain PuO_2 crystals from the glass (Fig. 3a) These results suggest that glass compositions should be designed to dissolve completely the Pu and to react with water without the formation of clays.

Table I. Selected results from testing of high Pu loaded glasses.

Waste Form	Test Conditions	Duration (days)	Normalized Release, (g/m^2) B	Pu	NA[a]
P2 [13]	PCT-B	215	0.5	0.002	—
G2 [13]	PCT-B	215	6.0	0.004	0.006
P7 [13]	PCT-B	215	0.5	0.004	—
ATS[c] [4]	PCT-B	98	0.7	0.0008	0.0009
Lanthanide 15 wt% [3]	PCT-A	7	0.003	0.0001	0.0001
SRL 165 Frit [20]	MCC-1	28	0.5	<0.01[b]	<0.01

[a] Neutron absorber.
[b] Th replaces Pu.
[c] ATS = alkali-tin-silicate glass.

In the VHT, the glasses reacted to reach Stage III (Fig. 2a), and the distribution of Pu, Gd, and U between the reacted glass, and alteration phases was determined. Plutonium and Gd remain associated with the reacted glass as smectite clay. To the extent measurable with energy dispersive spectroscopy (~0.2 wt%), Pu was not observed in any of the alteration products that formed on the surface of the reacted glass. However, U is readily incorporated into weeksite, which is seen as the bright regions in Fig. 2a. Gadolinium remains with the Pu, in the clay layer.

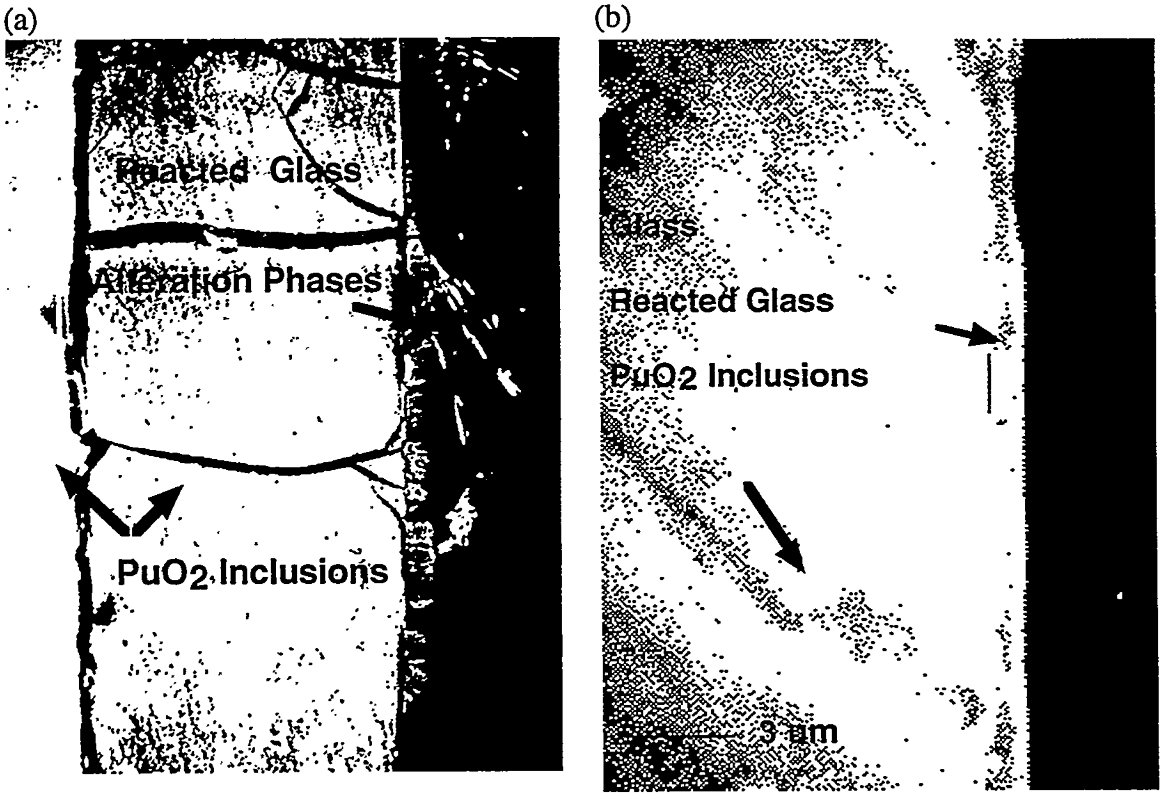

Figure 2. Glasses reacted for 56 days using the VHT (a) P7 glass and (b) ATS glass

From the results of the VHT, Pu and Gd remain closely associated with the reacted glass, and these elements have little tendency to concentrate to a significant degree in alteration phases. However, U is readily immobilized as an alteration phase that is dispersed among other phases on the surface of the reacted glass. Information from these tests is being used in the YMP criticality studies.

Lanthanide Glass

Based on the general chemistry of commercial optical borosilicate glasses with high lanthanide oxide contents, two Pu-loaded glasses were produced [15]. This general composition was chosen because actinides and lanthanides often have similar chemistries in glasses, thus a high Pu loading was likely. Additionally, this glass contains no Na so the durability should be greater, and Pb is known to form a layer on the glass surface during corrosion tests in solution and vapor that appears to cause a decrease in the corrosion rate. Both glasses were processed at 1450° C, with the first having batched concentrations of PuO_2 and Sm_2O_3 of 15 and 6.1 wt% respectively and the second with 13 and 17.1 wt%, respectively. For the first glass, the Pu was added as the oxide that did not all dissolve in the glass. For the second glass PuO_2 dissolved in HNO_3 was the feed, and the Pu was completely dissolved in the glass. In both cases Sm_2O_3 was added as a neutron absorber.

Both glasses were tested by using the standard PCT version A (PCT-A) (ASTM C-12850) [15]. The glasses were reacted in triplicate at 90°C in DIW for a period of 7 days. While the PCT-A does not specify an S/V ratio, a value of ~1100 m^{-1} was calculated by approximating the density of the glass to be 5 g/m^2. At this time, only leachate analyses are available, because an acid strip of the test vessel is not required in the procedure. However, acid strips are now being performed to make the data comparable with the other results given in Table I. The main points noted from the 7-day tests for the 15wt% glass are the minimal pH rise from 6.3 to 7.8, the low release of Pu compared to B, and the equivalency of the releases of Pu and Sm. In comparing the results of Pu and Sm from these tests, it should be noted that some of the Pu is in the undissolved PuO_2 crystals in the original glass and unlikely to dissolve in aqueous solution. Thus, the normalization procedure yields $(NL)_i$ values that are slightly lower than if the Pu were completely dissolved in the glass. For the 13 wt% Pu glass, in which the Pu is totally dissolved, the $(NL)_{Pu}$ values are the same as for the 15 wt% Pu glass. No Sm release data are available for the 13 wt% Pu glass. It was suggested that the small rise in pH (compared to that observed for DWPF glasses) favors increased durability and is due to the absence of Na in the glass [3,15]. The short-term reactivity of these glasses is better that the standard DWPF glass by about a factor of 25. The long-term corrosion behavior of these lanthanide glasses has not been determined.

Alkali-Tin-Silicate Glass

An alkali-tin-silicate glass (ATS) was specifically formulated to take advantage of glass chemistry and information contained in the reaction pathway to increase Pu loading and glass durability. In a borosilicate glass structure, Pu competes with Al, Fe, and Ca to stabilize alkali non-bridging oxygen atoms. The Pu solubility can be increased by reducing the concentration of these elements that compete more effectively than Pu and replacing them with Sn, Zr, and Ti [4,13]. Tin, Zr, and Ti also have the advantage of not forming major silicate alteration phases in natural hydrothermal systems. The resulting glass should be less likely to reach Stage III in the reaction pathway.

This ATS glass was produced and is being tested [13]. It was thought initially that 10 wt% Pu could be dissolved into this glass. However, the initial formulation dissolved 7.2 ± 0.3 wt% Pu, with the undissolved fraction remaining as $PuO_{(2-x)}$. This level of Pu meets the 5 wt% requirement for the Greenfield and adjunct melter processing options [1] and the composition is being refined to achieve a higher Pu loading.

This glass was reacted using the same matrix as the high Pu-loaded blend glasses described previously, but deionized water (DIW) was used instead of ground water. While the pH values for the P2, P7, and G2 glasses exceed 11 by 98 days and increase to 11.7 by 215 days, the pH for the ATS glass increased only slightly from its initial value of 10.3 at three days. The initial B release from the ATS glass is slightly greater than for the other glasses. For short time periods, the release in DIW is usually greater by a factor of 2-5 than in ground water [7]. The release of Pu from the ATS glass is slightly less than that of Gd, and the values for both elements are less than those measured for the Pu-loaded DWPF glasses. The manner by which the glass reacts was examined with transmission electron microscopy (TEM). Figure 3b shows a section of the reacted surface of the glass after 98 days. There is no evidence of a clay layer forming on the glass, and it appears that the early stages of the reaction are controlled by dissolution of the glass matrix. These results, though preliminary, suggest that the short-term reactivity of the ATS glass is similar to that of the blend glass, the long-term behavior may result in slower reaction with minimal release of Pu.

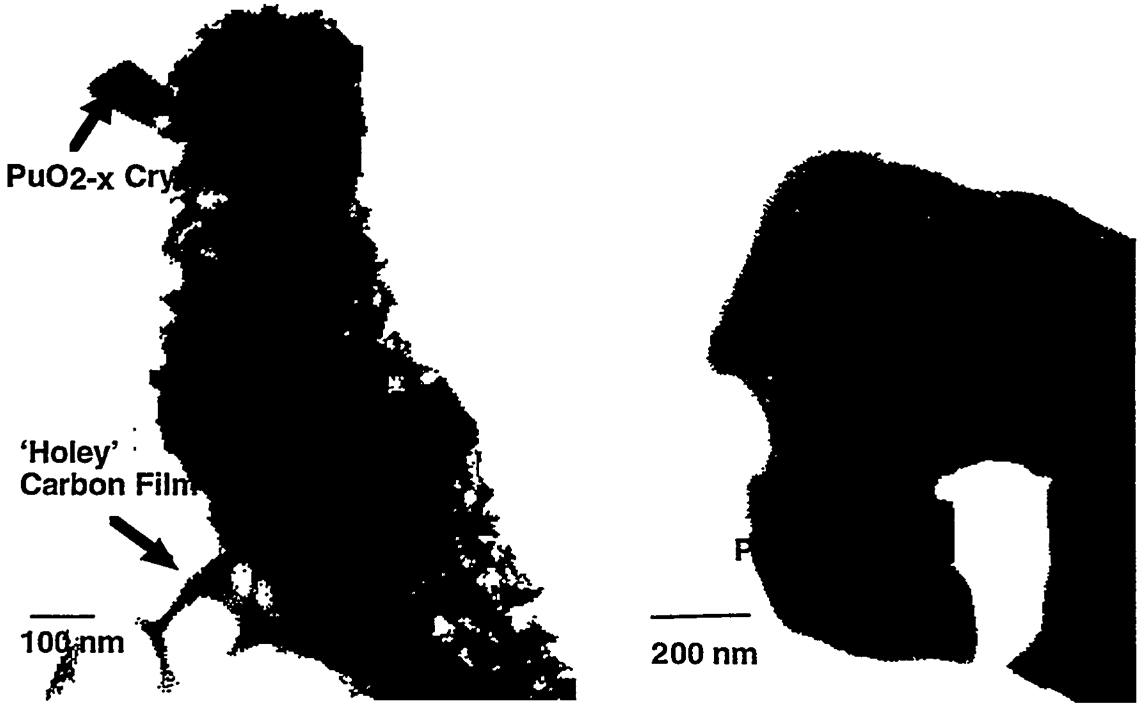

Figure 3. TEM micrographs of (a) a clay colloid containing a PuO_{2-x} crystal extracted from the leachate of a test with P7 glass (the holey carbon film is a support material) and (b) a cross section of corroded ATS glass showing little reaction of the glass surface (98 days).

In the VHT, the tendency of a glass to undergo reaction to form alteration phases is accelerated, and the distribution of actinide elements between the reacted glass and the phases can be determined. The reacted glass samples were analyzed with optical microscopy, scanning electron microscopy (SEM), and TEM. A thin reacted layer forms on the ATS glass and is detectable after 56 days. The layer is about 1.5 µm thick, compared to ~250 µm for the P7 glass reacted under the same conditions (Fig. 2). No alteration phases are found on the surface of the layer, indicating the glass has not reached Stage III in the reaction pathway. The Gd and Pu remain in the reacted layer, which itself appears to be hydrated, without any of the restructuring that is often seen in vapor-reacted glasses [4]. The rate of reaction of the glass, as measured by the thickness of the hydrated layer, is similar to that observed for the natural glass obsidian reacted under the same conditions [16]. These results suggest that the glass will not undergo reaction to form rate-accelerating alteration phases, and that only a very minimal clay layer will form. Additionally, the Pu and Gd remain in the reacted glass without apparent segregation.

Other Waste Glasses

Other compositions that have been evaluated for high Pu loadings include two phosphate glasses [3,17] and two early European Community borosilicate glasses [5,18]. Phosphate glasses in general have the advantages of low processing temperature and high durability [19], but they are limited in their Pu loading to about 3 wt% for a homogeneous glass. The durability of the high Pu-loaded glasses has not been quantitatively reported. The early borosilicate glasses also dissolved about 3 wt% Pu and 5 wt% U. The glasses were reacted at 200°C in DIW and NaCl solution at an S/V of about 10 m^{-1}. Analysis of the reacted glasses indicated that the actinide elements were retained within the altered layer. No results for potential neutron absorbers were given.

Simple Glass Analogs

The issue of the behavior of Pu and neutron absorbers during reaction and in the reacted glass is important for the entire immobilization concept. The plutonium group at the Massachusetts Institute of Technology [20] has examined the corrosion behavior of simple DWPF glass analogs using the MCC-1P test method. The glasses tested were a SRL 165 frit and the reference glass ARM-1. Both glasses were doped with 2 wt% each of Th, Eu, Gd, and Sm. Thorium was used as a stand-in for Pu, and the rare earth elements were used as neutron absorbers. The ARM-1 glass is similar to SRL waste-containing 165 glass, except that it does not contain Fe. For each glass, each of the dopants was completely dissolved in the glass. The MCC-1P tests were run in DIW at 90°C for up to 28 days with an S/V ratio of 10 m^{-1}. The $(NL)_i$ values are given in Table I. Boron is released more rapidly than Th and Eu, which were below detectable limits in solution. The analyses focused on Eu because criticality calculations using the neutron transport code Monte Carlo Neutron Photon (MCNP) indicate that for corroded SRL 165 glass, Eu is the most effective neutron absorber, of the elements studied. While the results are not definitive because of the low levels of Th and Eu in solution, the general trend observed for the glasses described above is followed: that is, B is released most rapidly, while the actinide and rare earth elements are released at a much lower rate.

IRRADIATION BEHAVIOR

There have been many studies on the effect of ionizing radiation on glasses. These studies have ranged from basic research investigating trapped defects induced in the glass by radiation to more practical studies to determine if radiation affects the ability of a glass to immobilize nuclear waste. Results of both types of research have been reviewed several times [11,12]. Nearly all of the practical studies have been directed toward investigating glasses for immobilization of defense high-level wastes. These wastes contain radioactive fission products and actinides. The glass is thus exposed to gamma, beta, alpha, and alpha recoil radiation. Properties studied include radiation-induced volume changes, stored energy, changes in microstructure and mechanical properties, and the effect of radiation on radionuclide release and radiolytic decomposition. Also, helium accumulation has been investigated. Most of these results were from studies performed between 1970 and 1990. Several effects were observed. For example, it was observed that alpha radiation and its associated alpha recoil radiation could increase radionuclide release from glass by up a to factor of three. It was also observed that ionizing gamma and beta radiation could increase radionuclide releases by up to a factor of four, but a later study using the leach PCT-A showed no effects from the radiation. Examination of the irradiated glass by TEM also indicated no radiolytic decomposition of the glass. New data for the blend glass frit also indicated no effect of gamma radiation on radionuclide release through a total dose of 4×10^9 rads, and while possible increases in glass corrosion were observed in short-term tests, no data are available on the effect of radiation on Pu release under long-term conditions. It has been concluded that all of the effects that were observed in the various studies were not great enough to cause glass to be unsatisfactory as a matrix to immobilize nuclear waste. Thus the United States, Great Britain, Russia, France, and other countries are using or will use glass to immobilize their nuclear waste.

The Savannah River Site (SRS) has initiated a study of the effects of radiation on the lanthanide glasses for immobilization of Pu. A glass doped with Cm-244 to accelerated alpha decay events in the glass has already been fabricated. Initial TEM studies of nonradioactive lanthanide glasses in which Ce is substituted for Pu have shown that the glass does not decompose in the intense electron beam of the microscope. This suggests that these glasses may have good radiation stability. (Glasses with DWPF type compositions are very sensitive to beam damage, primarily because of the presence of Na in the glass [21].) Gamma irradiation studies to investigate possible bubble formation have been initiated. The durability of these glasses will also be measured by the ASTM test. In addition, SRS has Cm-244 and Pu-238 doped DWPF-type glasses that have accumulated very large doses of alpha radiation. In the near future, these will be examined by SEM for damage and leached according to the standard PCT method to determine if the alpha/alpha recoil radiation has affected the durability of the glass.

MODELING

There are basically two models for glass dissolution. In the first model, developed at the SRS [22,23], the glass is treated as an ideal mechanical mixture of mineral phases. The interaction of these phases with water is expressed as a "free energy of hydration." This is a thermodynamic construct, not a kinetic mechanism. The outcome of the calculation is a thermodynamic driving force that can be translated into a kinetic rate. The second model was first developed by Grambow [24] and is based on the work of Aagaard and Helgeson [25]. In this model, the kinetic driving force is based on nonequilibrium thermodynamics, and the minimum reaction rate is provided by the "residual affinity" or the inability of the dissolving phase to equilibrate with solution. The original mathematical kinetic expression by Grambow was modified by McGrail and Olson [26], but only to refine its mathematical underpinnings. Typically, this model (kinetic rate law) is used in conjunction with a geochemical computer code to account for all the other reactions that take place in solution as the glass dissolves, i.e., as the glass dissolves. For example, the model can account for the fact that as the glass dissolves, Al^{3+} increases in solution until the solubility of a mineral phase, such as gibbsite $[Al(OH)_3]$ is reached, at which time the phase precipitates. Grambow's model is the basis for the models used by Bourcier [27], and Delage and Dussossoy [28]. For a more complete review of the state of modeling see Bourcier [29] and Strachan, Bourcier, and McGrail [30] and the references therein.

The available data from various glass/water experiments suggest that the rate-limiting species is H_4SiO_4. Glass, when first placed in water, dissolves at an initial fast rate known as the forward rate. As H_4SiO_4 builds in solution, the dissolution rate of the glass begins to slow, until, at some long time, depending on experimental conditions, the rate reaches a minimum value. Any event along the reaction pathway that causes a decrease in the $[H_4SiO_4]$ causes an increase in the dissolution rate of the glass. For example, Van Iseghem and Grambow [31] noted that the dissolution rate increased for a glass for which the mineral analcime was calculated to precipitate. Ebert [8] and Bates and coworkers [9] noted similar results but were able to identify analcime and other mineral phases on the surface of glasses. The increase in dissolution rate, however, was found to be coincident with the formation of the analcime phase.

As noted above, however, the solubilities of various mineral phases are exceeded during the course of glass dissolution. As these solubilities are exceeded, the mineral phases precipitate. This is reflected in the apparent incongruent nature of the dissolution process as monitored in the solution composition. This behavior is shown in Fig. 4, where congruent dissolution is shown as a straight line of unit slope, typical of the behavior of boron. Other elements are shown to depart from congruent behavior as the minerals that control their solution concentrations precipitate. The release of plutonium and any neutron absorbers is expected to be controlled by solid phases to which the glass alters during its reaction with water.

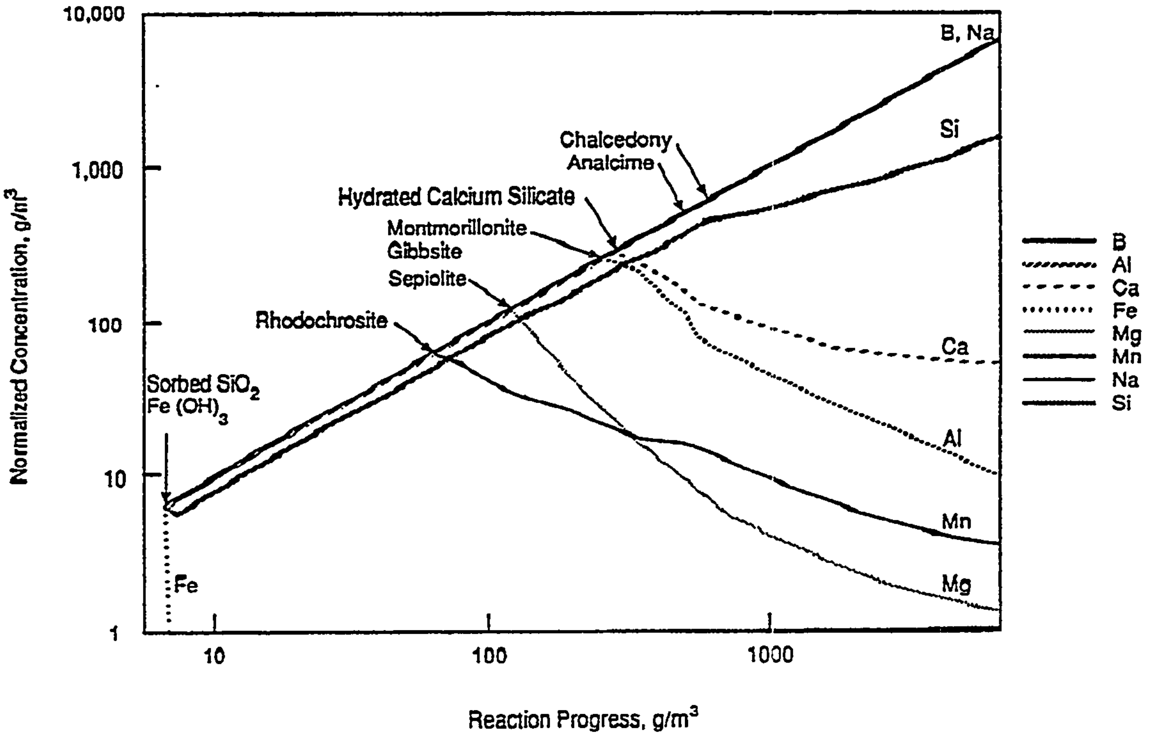

Figure 4. Calculated behavior of 200 frit-based glass

Plutonium, as such, in the glass is not expected to change the dissolution rate significantly, nor are the neutron absorbers. However, the research community's experience with glasses containing large quantities of these elements is very limited. Still, it is expected that any deleterious effects on the glass dissolution rate may be ameliorated by a change in the composition of the glass. The important aspect of the problem is the behavior of the Pu and neutron absorbers. It is likely that plutonium will be controlled by the precipitation of an oxide phase (such as PuO_2) or a hydrated form, or a hydroxide phase (such as $PuO_2(OH)_2$), or by adsorption on a clay material that forms during glass dissolution. The type of Pu-bearing or neutron absorber-bearing phase that forms is strongly dependent on the solution composition and redox properties. Similarly, the neutron absorbers will precipitate as oxides, phosphates, or hydroxides, depending on the solution chemistry from which they precipitate. Thus, the behavior of the Pu and neutron absorbers is dependent on the solution chemistry, which is dominated by the glass/water interaction close to the glass, by the engineered barrier system components a short distance from the glass, and by the host rock at some distance from the engineered barrier system.

Transport of the dissolved Pu and neutron absorbers is controlled by the solubility of the precipitated mineral phase, the ground water, and the rate at which that ground water flows through the host rock. However, these elements may also be transported if colloids form. Sorption of Pu on colloids has been the subject of many papers [e.g., 32]. Colloids can form as a result of the corrosion of the glass [6] or the engineered barrier components. The phenomenon of colloid formation is not part of the current waste form modeling.

The remaining issue with respect to high loadings of Pu in glass is the effects of radiation damage and transmutation of the Pu to U. Currently, these effects are evaluated experimentally and to date have not been incorporated into models. However, the result of nitric acid formation and its effect on glass reaction can be added to models by adding acid to solution based on the acid formation rate. The need to incorporate radiation damage and transmutation effects on glass corrosion behavior into current models will have to be evaluated.

CONCLUSIONS

Much of the data on which the behavior of a high Pu loaded glass will be evaluated with respect to disposal in a high-level waste repository are preliminary, short term, and incomplete. Other data are based on glass compositions that will not be used for high Pu loading. However, the results from testing indicate that it is important to dissolve the Pu fully in the glass and to formulate the glass to limit the formation of alteration phases. If these two goals are met, it is unlikely (1) that the glass will reach Stage III in the reaction pathway, thereby limiting the long-term reaction rate and (2) that Pu will be released at the same rate as the glass dissolves. Under these circumstances, the Pu release will be solubility-limited and therefore quite low. The results also indicate that B is released more rapidly than Pu and thus will act as a neutron moderator for the solution, while Pu and rare earth elements are released at nearly equivalent rates, suggesting that Pu remaining in the glass will also remain in the presence of a moderator.

Preliminary testing of glasses specifically formulated to accommodate high loading of Pu show an improvement in corrosion behavior compared to the standard DWPF glass. Accelerated vapor tests done with the alkali-tin-silicate glass show no tendency to reach Stage III in the reaction pathway, while short-term batch tests with both the high lanthanide and alkali-tin-silicate glasses show performance better than or equal to the standard DWPF glass. While these results are encouraging, longer-term tests must be completed with both glasses to fully describe their behavior and provide input for modeling.

Limited modeling has been done for Pu loaded glasses. However, the reaction of the P2, P7, and G2 glasses suggests that Pu loaded glasses will follow the general outlines of current glass corrosion models. This means that the models currently have the correct basis for describing glass reaction but need additional development to account for compositional differences, the manner by which Pu and neutron absorbers are released from the glass, and radiation damage effects.

Finally, while no radiation damage studies have been completed on the high Pu compositions under development, work on other nuclear waste glasses indicates that the production of acids will have little effect on the rate of glass reaction or Pu release. This work also indicates radiation damage may be of some concern, the increase in reaction rate may not translate into an increase in the release of Pu, and that any effect probably is within the ability to do a reliable performance assessment of the near-field repository environment.

DISCLAIMER

ACKNOWLEDGMENTS

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Ceramics: Durability and Radiation Effects

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ABSTRACT

At present, there are three seriously considered options for the disposition of excess weapons plutonium: *i)* incorporation, partial burn-up and direct disposal of MOX-fuel; *ii.)* vitrification with defense waste and disposal as glass "logs"; *iii)* deep borehole disposal [1]. The first two options provide a safeguard due to the high activity of fission products in the irradiated fuel and the defense waste. The latter option has only been examined in a preliminary manner, and the exact form of the plutonium has not been identified. In this paper, we review the potential for the immobilization of plutonium in highly durable crystalline ceramics apatite, pyrochlore, zirconolite, monazite and zircon. Based on available data, we propose zircon as the preferred crystalline ceramic for the permanent disposition of excess weapons plutonium.

INTRODUCTION

During the period from 1977 to 1982, there was a tremendous diversity in the types of nuclear waste forms under development. In the United States, much of this work ended with the decision to use borosilicate glass as the waste form for defense waste at Savannah River. Synroc, a ceramic waste form, was selected as the alternative waste form, but further development in the United States ended in the absence of funded programs. Major research and development programs for the development of Synroc continued in Australia culminating in the construction of a "cold" Synroc pilot-scale processing plant. Basic research on the properties of Synroc has been continued at the Australian National University and at the Australian Nuclear Science and Technology Organization with collaborative work at the Japan Atomic Energy Research Institute and AERE Harwell in the United Kingdom. Synroc remains perhaps the most thoroughly studied ceramic alternative to borosilicate glass. Lutze and Ewing [2] have provided a summary of work on waste forms through early 1987, as well as one of the first efforts to compare the performance of borosilicate glass with that of a crystalline ceramic waste form, Synroc [3]. Investigations into the properties and performance of other ceramic waste forms have revived during the past five years for application to special waste stream compositions. At Lawrence

Livermore National Laboratory, a Mixed Waste Management Facility is being developed in order to demonstrate an alternative to incineration. The waste form is a derivative of a Synroc composition originally developed for the immobilization of reprocessed residues at Savannah River, and typical phases include zirconolite, perovskite, spinel, nepheline and rutile. Although the radioactivity is low, this does illustrate the ubiquity of a rather limited set of crystalline phases. Additionally, the zirconolite phase in Synroc has received increased attention as a host phase for actinides, particularly excess weapons plutonium [4]. At the Idaho National Engineering Laboratory, an iron-enriched basalt waste form has been under development, and the addition of ZrO2 and TiO2 has produced zirconolite crystals as an actinide host in a silicate ceramic. A "glassy" slag and a "vitreous" ceramic are being developed at Pacific Northwest Laboratory, both of which are composed of crystals which include zirconolite, perovskite and zircon (up to 80 volume percent) in a silicate glass matrix. At the Khlopin Radium Institute in St. Petersburg, Russia, a program has been initiated for the development of crystalline hosts for actinide wastes, with an emphasis on zircon, yttrium-aluminum garnet and cubic zirconia [5]. Most recently, spent fuel - a metal clad, ceramic oxide - has received important consideration as a waste form because its use eliminates the need for reprocessing, and it is highly stable under reducing conditions [6], and the MOX-fuel option for weapons Pu is a simple extension of the concept of direct disposal of spent nuclear fuel. Thus, there are considerable data and experience in the design, evaluation and selection of waste forms [7-9]. We draw on this experience in evaluating crystalline ceramics as waste forms for the immobilization and disposition of weapons plutonium [10].

IMPORTANCE OF THE WASTE FORM

Despite the great challenge of handling chemically complex wastes, which are highly radioactive and of great volume, the greatest challenge still lies in the development and evaluation of the *long-term durability* of waste forms. Materials scientists will have to design materials to performance standards that are not measured in decades, but rather are measured in 10^4 to 10^6 years, particularly in the case of long-lived radionuclides such as ^{239}Pu. The issue of long-term durability is unusual in materials science and requires interdisciplinary research programs with rather unusual combinations of subdisciplines -- processing/synthesis technologies, materials properties, mineralogy and geochemistry. Thus, even after issues of technological feasibility and cost are considered and settled, the most difficult scientific question remains: *What is the long-term durability of the waste form?* and *What is the effect of improved durability on repository performance assessments and the calculated dose to humans?*

Thus, the development of durable waste forms can play a critical role in reducing the uncertainty in performance assessments. The reduced uncertainty should lead to greater public acceptance of proposed disposition and disposal concepts. The specific value of the waste form has been previously discussed [7], but it is useful to recall the requirements for waste form development and acceptance:

i.) careful consideration of synthesis and processing technologies;
ii.) a detailed characterization of the wastes and the waste form after immobilization;

iii.) an extensive data base of corrosion/alteration experiments over a wide range of conditions, and in some cases, for extended periods (both repository-relevant and special experiments designed to elucidate the corrosion mechanism);
iv.) kinetic models of the corrosion/alteration process and thermodynamic models that predict the formation and stability of phases which will control solution compositions;
v.) knowledge of the effects of other materials, e.g., canisters and bentonite overpack, on waste form stability;
vi.) studies of relevant natural phases or systems to confirm experimental and extrapolated results.

The last requirement is particularly important in the selection of waste forms for the disposition of weapons plutonium, as a twenty half-life durability criterion leads to disposal periods of a 500,000 years. This would reduce the Pu inventory of 100 metric tons to well below a critical mass for Pu; however, the 100 metric tons of Pu is transmuted to fissile ^{235}U. Using the same twenty half-life criteria, the disposal period of concern for the ^{235}U daughter product is 14 billion years. Thus, the discussion in this paper of crystalline phases is limited to those phases which occur naturally and for which some assessment of long-term durability is possible. Additionally, for ^{235}U, the decay product of ^{239}Pu, the waste form must provide a means of reducing the probability of criticality events.

PRINCIPLES OF NUCLIDE ISOLATION IN CERAMICS

In contrast to glass waste forms in which the radionuclides are in principle homogeneously distributed throughout the waste solid, ceramic waste forms incorporate radionuclides in two ways:

(1) Radionuclides may occupy specific atomic positions in the periodic structures of constituent crystalline phases, that is as dilute solid solutions. The coordination polyhedra in each phase impose specific size, charge, and bonding constraints on the nuclides that can be incorporated into the structure. This means that ideal waste form phases usually have relatively complex structure types with a number of different coordination polyhedra of various sizes and shapes and with multiple substitutional schemes to allow for charge balance with radionuclide substitutions. Extensive nuclide substitution can result in cation and anion vacancies, interstitial defects, and finally changes in structure type. One expects, and finds, the formation of polytypes and twinning on a fine scale. The point defects can themselves become sites for the radionuclides. Except in unusual situations (e.g., monazite, CeP04), the complexity of the waste composition results in the formation of a polyphase assemblage (e.g., Synroc consists of phases such as zirconolite, CaZrTi207; perovskite, CaTi03; and "hollandite", BaAl2Ti6016), with unequal partitioning of radionuclides between the phases, and some elements which are not accommodated at all (e.g., Mo and Tc) and may exist in the reduced metallic state.. In Synroc, actinides partition preferentially into the zirconolite phase [11]. The polyphase assemblages are sensitive to waste stream compositions, and minor phases form, including glass, segregated along grain boundaries. Ideally, all waste stream elements, radioactive and non-radioactive, are important components in the phases formed. In some rare cases, a single phase (e.g., monazite or sodium zirconium phosphate, NZP) can incorporate nearly all of the radionuclides into a single structure.

(2) Radioactive phases, perhaps resulting from simply drying the waste sludges, can be encapsulated in non-radioactive phases. The most common approach has been to encapsulate individual grains of radioactive phases in Ti02, Al203, or ZrO2, mainly because of their extremely low solubilities. This usually requires major modifications to the waste stream composition and special processing considerations to maintain temperatures that are low enough to avoid volatilization of radionuclides. A similar approach may be taken with low temperature assemblages (e.g., mixing with concrete), but in this case there is the possibility of reaction between the encapsulating phase and the radioactive phases. Some phases, such as zircon, can both incorporate a radionuclide at the atomic scale (e.g., Pu substituting for Zr in the structure of zircon) and encapsulate unreacted materials from the synthesis (e.g., PuO2 as inclusions in zircon crystals). The combined incorporation and encapsulation can lead to a very durable waste form. Finally, the complexity of ceramic waste forms is mostly the result of the compositionally complex waste streams that must be solidified. In the case of weapons plutonium, the disposal of a pure nuclide is an ideal situation for the use of highly durable ceramics which have specific atomic sites for the incorporation of Pu and its decay product, U.

ADVANTAGES AND DISADVANTAGES OF CERAMICS

The main advantage of ceramic waste forms lies in the fact that they hold the potential for engineering a phase assemblage which provides unique structural hosts for specific radionuclides. Ideally these hosts should be thermodynamically stable, but for most repository environments this is unlikely (a notable exception is titanite, CaTiSiO5, in the ground waters of the Canadian shield); but one can already demonstrate greater stability for some of the ceramic phases than for the metastable borosilicate glass. The development of ceramic waste forms which are stable at high temperatures has even more important implications: 1) higher thermal stability provides the possibility of higher waste loadings, and thus a reduction in the amount of material to be handled and space required for disposal; 2) higher thermal stability means that disposal can occur in rock units at greater depth or in canister arrays with closer spacings. The decreasing stability of borosilicate glass with increasing temperature is well known, and in fact, disposal concepts for borosilicate glass are shaped by the limitations imposed by its thermal instability. Even without the higher thermal stability, higher waste amounts are incorporated into ceramics because of their higher density (a factor of two over borosilicate glass).

A final consideration is that many of these ceramic phases occur in nature (e.g., zirconolite, pyrochlore, perovskite, zircon, monazite, uraninite, and coffinite). This provides the possibility of evaluating the long-term durability of these phases in the presence of aqueous solutions and at a-decay doses that reach values comparable to those which the waste form will experience in the first 1,000 to 10,000 years after disposal. The ability to validate projected long-term behavior is a critical part of the performance assessment of the nuclear waste containment strategies.

The disadvantages of ceramic waste forms are an inherent part of their complex microstructures. First, for polyphase ceramics, the corrosion process may be inherently more complicated than the corrosion process of an essentially single phase glass (although most glasses contain a proportion of crystalline phases). Despite a considerable amount of experimental data, there is no confirmed model for the long-term corrosion of Synroc. Second, the atomic periodicity of crystalline materials is disrupted by a-decay damage. Thus, there is the possibility of a radiation-induced transformation from the periodic-to-aperiodic state (amorphization or metamictization). This is a well known process in minerals which contain uranium and thorium and is observed in actinide-doped phases (e.g. Pu-doped zirconolite and zircon). The process is mitigated by natural annealing (which increases with higher temperatures), and some phases anneal at low enough temperatures that they are only found in the crystalline state (e.g., uraninite and monazite). Still, this transformation can result in decreased chemical durability, and the volume expansion associated with the transformation can cause microfracturing with an increase in the surface area exposed to corroding fluids. For any selected ceramic phase, there must be a through understanding of its behavior at high radiation doses.

CERAMICS FOR PLUTONIUM DISPOSITION

There has been no concerted research program to develop ceramic waste forms specifically for the disposal of excess weapons plutonium; however, there is extensive enough experience with crystalline phases to review at least five possible phases: apatite, pyrochlore, zirconolite, monazite and zircon. We restrict ourselves to these five phases, as they all occur in nature and may often contain uranium and thorium; thus, all five of these phases may be evaluated in terms of their long term durability in their natural geologic occurrences.

Additionally, one must note the special features of excess weapons plutonium which distinguish it from typical radioactive wastes:

i.) The plutonium is almost isotopically pure ^{239}Pu; therefore, it is ideal for the synthesis of specific phases of high durability.

ii.) ^{239}Pu has a long half-life (24,500 years), as compared to most fission products; therefore, extended, confirmable durability is a highly desired attribute.

iii.) ^{239}Pu is fissile; hence, one must always be concerned about criticality events; furthermore, ^{239}Pu decays to ^{235}U which has a half-life of 700 million years and is also fissile. Thus, the durability of the waste form is not only essential to the retention of Pu and U, but is also required in order to maintain the presence of any added neutron absorbers (e.g., B, Li, Gd, or Hf).

iv.) The multiple oxidation states of Pu and U make the processes of dissolution, oxidation, transport and reconcentration (= supergene enrichment) over geologic periods a possible event in the development of scenarios for performance assessments, particularly in oxidizing environments (e.g., the dissolution of volcanic glass, where U is in ppm concentrations, with the subsequent release and concentration of uranium to form high concentrations of uranium in roll-front ore deposits).

Apatite

Rare-earth silicates with the apatite structure have been observed or proposed as actinide host phases in a borosilicate nuclear waste glass [12], a multiphase ceramic waste form [13], a glass ceramic waste form [14], and a cement waste form [15]. These apatites generally have the compositions: Ca4-xREE6+x(SiO4)6-y(PO4)y(F,OH,O)2 (where REE = La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd) and are isostructural with the natural mineral apatite, Ca10(PO4)6(F,OH)2. Plutonium and other actinides readily substitute for the rare earths in this hexagonal crystal structure. At least 6 wt. % actinides (^{244}Cm and ^{240}Pu) have been incorporated into an apatite phase in a devitrified waste glass [12], and a phase-pure apatite containing 1.8 wt % actinides (^{244}Cm and ^{240}Pu) has been prepared [19]. Much higher weapons Pu-loadings are feasible in the rare-earth apatites by substitution for the rare earths. In addition, rare earths, such as Gd, can be included as neutron poisons.

Natural apatites with appreciable Th- and U-contents provide analogues for the performance and properties of actinide-containing apatites over geologic periods. For example, natural apatites with significant amounts of rare earths and Th are reported to be partially metamict as a result of self-irradiation damage from the a-decay of Th [16]. Fission track analysis in U-containing natural apatites is used for geologic age dating, and annealing studies provide data on fission track recovery kinetics [17,18]. Of more relevance is the recent discovery of natural apatites formed near the Oklo natural reactors that indicate significant amounts of ^{239}Pu and U were incorporated into the apatites, leading to ^{235}U enrichment that has been retained for 2 billion years [17].

Natural apatites [16] and rare-earth silicate apatites containing actinides [12,13,19] do undergo an a-decay-induced crystalline-to-amorphous transformation. The mechanism [20] and temperature dependence [21] of this transformation is well understood and modeled. The macroscopic swelling associated with the amorphization process is 9.5 percent and has also been modeled [20]. Other property changes associated with this a-decay-induced transformation have been summarized in a recent review by Ewing et al. [22]. Fission track annealing studies of natural apatites [17] and ion-beam irradiation studies of natural and synthetic apatites [21,23] suggest that simultaneous thermal recovery processes will minimize or even prevent amorphization in Pu-containing apatites under deep borehole conditions (temperature > 150-200°C). The chemical durability of natural apatites is well demonstrated by the 2 billion year old, ^{235}U-enriched Oklo apatites [17]. In a study of a rare-earth silicate apatite containing ^{244}Cm and ^{240}Pu [24], the dissolution in deionized water at 90°C occurred congruently, and the measured Pu dissolution rate for the undamaged crystalline phase was 0.035 g/m^{2}d (this dissolution rate does not account for the 22 percent porosity of this material). Alpha-decay-induced amorphization increased the average Pu dissolution rate in this apatite by a factor of 12.

Pyrochlore and Zirconolite

Pyrochlore (*Fd3m,* Z = 8), $^{VIII}A_2{}^{VI}B_2{}^{IV}X_6{}^{IV}Y$ is a derivative of the fluorite structure type in which the A-site contains large cations (Na, Ca, U, Th, Y and lanthanides) and the B-site consists of smaller, higher valence cations (Nb,Ta, Ti, Zr, Fe^{3+}). The essential feature of the structure is sheets of corner-sharing, BX_6 octahedra parallel to the (111) plane which are arranged into three- and six-membered rings (the hexagonal tungsten bronze structure). Monoclinic zirconolite (the principal actinide bearing phase in Synroc) is a derivative of the cubic pyrochlore structure. Actinides may be accommodated in the A-site, and charge balance is maintained by cation deficiencies in the A-site and substitutions on the B-site. Rare-earth titanates with the pyrochlore structure have been observed as actinide-host phases in nuclear waste glasses, in titanate ceramic waste forms, and in a glass ceramic waste form. A full summary of work on pyrochlore and zirconolite can be found in references [2,4,22].

The effect of a-decay on the pyrochlore phase Gd2Ti2O7 containing ^{244}Cm and ^{240}Pu has been extensively investigated by x-ray diffraction analysis and transmission electron microscopy [25,26]. At a dose of 3.1 x 10^{18} a-decay events/g, the material became fully amorphous with no evidence of any residual crystallinity. Wald and Weber [24] studied the radiation-induced changes in dissolution kinetics of Cm-doped Gd2Ti2O7 by testing fully-damaged (amorphized specimens and a second set of specimens that had been fully recrystallized to the original structure by a 12 hour anneal at 1,100°C). Specimens were immersed in distilled, deionized water at 90°C for 14 days. The measured ^{240}Pu release rate was 0.009 g/m^{2}d in the crystalline material and increased by a factor of 50 due to amorphization. The concentration of Ti in solution was below the detection limit, suggesting some dissolution resistance of the titania network. Analysis for non-network Gd was not performed. These results suggest that the dissolution may occur incongruently, selectively leaching the non-network ions. Similar behavior is observed for zirconolite [24]. The increase in dissolution rate due to amorphization is probably due to the increase in the size of the network tunnels as the structure disorders and expands.

Systematic studies [27-30] have been completed of a-decay event damage of natural, isometric pyrochlore structure types. Actinides may be accommodated in the A-site, and in natural pyrochlores the substitution of uranium can be extensive (up to 30 wt. %). Charge balance is maintained by cation deficiencies in the A-site and substitutions on the B-site (typically, Nb, Ta and Ti). Depending on the age of the sample, the total calculated displacements per atom, dpa, may be as high as 80. Careful analysis of samples from the same deposit, e.g., the Harding Pegmatite in New Mexico which is 1300 million years old, have allowed detailed studies of radiation damage over a range of dpa (0.2 to 49) as function of the uranium concentration (0.05 to 8.6 wt. % UO2). Members of the pyrochlore group are quite susceptible to hydrothermal and lower-temperature surface alteration [32-34]. In general the alteration involves the loss (or ion exchange) of large cations (Na and Ca) and the loss of Pb due to long-term diffusion. The alteration effects are enhanced by amorphization and fracturing due to the a-decay damage.

Zirconolite (monoclinic CaZrTi2O7) is one of the three principal phases of Synroc, and zirconolite is one of the most extensively studied waste form phases, as it is the primary actinide host. Monoclinic zirconolite is a fluorite-derivative structure closely related to pyrochlore. The (001) layers of the corner-sharing arrangement of TiO6 octahedra are similar to the (111) layers in pyrochlore and the (001) layers in the hexagonal tungsten bronzes. The A-site cations (Ca, Zr and actinides) are "sandwiched" between the (001) sheets of B-site cations (corner-sharing Ti06 octahedra). There can be several polytypes depending on the stacking arrangements of the sheets. In this section, we discuss the damage response as investigated by study of synthetic compositions doped with the short half-life actinides, ^{238}Pu (87.7 y, a-decay to ^{234}U) and ^{244}Cm (18.1 y, a-decay to ^{240}Pu), and natural zirconolites damaged by a-decay of uranium and thorium.

^{238}Pu-substituted zirconolite can be synthesized with the substitution of PuO2 for ZrO2. X-ray absorption spectroscopy demonstrated that the ^{238}Pu was incorporated into the A-site [35]. The effect of this chemical substitution is to convert the zirconolite composition to an

isometric, pyrochlore derivative structure [36,37]. A major change in $CaPuTi2O7$ with increasing dose is the large decrease in density. Storage at ambient temperature (approximately 350 K, due to self-heating) resulted in macroscopic swelling, up to a saturation value of approximately 5.5 vol. % in material that had reached an a-decay dose of 2-3 x 10^{25} a-decay events/m^3.. Storage at 575 K resulted in less swelling, which required a longer time (300 days) to reach saturation. When this material was held at 875 K, swelling was minimal. Transmission electron microscopy conducted after various storage times and temperatures [36,37] showed that with sufficient a-decay damage, Pu-zirconolite at 350 and 575 K converts from the crystalline to the aperiodic, metamict state. EXAFS/XANES studies completed on ^{238}Pu-substituted zirconolite held at 350 K for at least 500 days helped to identify details of the damage state [35]. For comparison, measurements were made on essentially undamaged material (that is, substituted with ^{239}Pu with a half-life of 24,500 years, as compared to that of ^{238}Pu of 87.7 years). In the heavily-damaged material, the Pu/O nearest-neighbor bond length contracted by 0.003 nm, while expansion was observed for the more distant coordinating atoms, corresponding to a 6 to 7% overall volume expansion. This observation is close to the measured volume swelling of 5.5 %.

^{244}Cm-doped zirconolite has been synthesized and self-damage studies of zirconolite have also been carried out by substituting ^{244}Cm, an a-active isotope with a half-life of 18.1 y, and ^{240}Pu for Zr [26]. Changes in swelling, microstructure, hardness, fracture toughness, leachability, and recrystallization behavior were assessed. The Cm-doped zirconolite retained the monoclinic structure; whereas, the ^{238}Pu-doped zirconolite was isometric (although up to concentrations of 5 mole % $PuO2$, the monoclinic, zirconolite structure was retained [36]). More importantly, the composition of the Cm-doped zirconolite was not greatly changed by the substitution; whereas, the Pu-substituted structure was significantly changed by replacement of $ZrO2$ by $PuO2$. Density measurements at 350 K indicate a saturation swelling value of 6.0 vol.% at a dose of 2 x 10^{25} a-decays events/m^3. These results are in good agreement with those for the Pu-substituted material, which exhibited saturation swelling of 5.5 vol.% at nearly the same damage level [36,37]. TEM images and diffraction patterns confirmed that Cm-doped zirconolite amorphized by the accumulation of damage tracks produced by the ^{240}Pu recoil ions that are emitted during a-decay of ^{244}Cm. The dissolution (leaching) characteristics of the Cm-doped zirconolite were determined [26] by testing fully-damaged (amorphized) specimens and a second set of specimens that had been fully recrystallized to the original structure by a 12 h anneal at 1,100°C. Testing was performed in distilled, deionized water at 90°C for 14 d. The measured ^{240}Pu release rate was 0.002 g/m^2d and increased by a factor of 15 due to amorphization. The high final pH is believed to limit the solubility of the Cm. The low concentrations of Ti, as compared to that of Ca, suggests that the dissolution is incongruent, with the Ti ions (which are part of the $TiO6$ octahedra comprising the network structure) being more resistant to leaching than the interlayer cations (e.g., Pu and Ca). The mechanism for the enhanced leaching of the radiation-induced amorphous state may be associated with the broken bonds and the increased free volume (a more open framework) of the amorphous state.

Natural zirconolite occurrences are rare, but selected specimens have been the subject of extensive studies [38-43]. Samples from Sri Lanka (550 million years old) typically can have concentrations of UO2 of 2 weight percent and of ThO2 of 20 weight percent, thus reaching doses of 10^{16} a-decay events/mg (=10^{26} a-decay events/m^3). This is a dose equivalent to nearly two displacements per atom. X-ray diffraction analysis of fully-metamict zirconolite shows no diffraction maxima, confirming that zirconolite is X-ray diffraction amorphous. Because of the paucity of samples which span a range of a-decay event doses, it is not possible to follow the change of diffraction maxima intensity and position with increasing a-decay event dose. A zirconolite annealed at 1130°C did give a diffraction pattern with sharp peaks which could be refined on the basis of a monoclinic unit cell [44]. High resolution transmission electron microscopy showed no evidence of crystallinity [44], and in approximately ten percent of the grains examined, there were subspherical microvoids ranging in diameter from 100 to 400 nm [39]. The microvoids are attributed to He-gas accumulation which is a result of the radioactive decay. Annealed samples (1,100°C) recrystallized producing crystals up to 2,000 nm in length. The crystallites were often twinned at the unit cell scale as a result of different stacking sequences of the TiO6 sheets, thus resulting in laminar intergrowths of the various zirconolite polytypes. The same texture of fine-scale twinning has been observed in synthetic zirconolite in Synroc C [45] and synthetic zirconolite of Ca0.6Sm0.4ZrNb0.4Mg0.4Ti1.2O7 composition [46]. The defects along the twin boundaries may become sites at which actinide elements are incorporated. In some instances [44], there was evidence for the formation of crystals (5-100 nm) with *d* -spacings similar to those of the fluorite structure type. Lumpkin et al. [44] suggested that metamict zirconolite may recrystallize initially with a disordered, fluorite-type structure. Continued heating to higher temperatures (1,000° to 1,200°C) appears to favor the highly twinned, monoclinic zirconolite structure. Differential thermal analysis (30° to 1,200°C) showed exothermic recrystallization at 780°C with a heat of recrystallization of 50 J/g for a zirconolite with a total dose of > 10^{26} a-decay events/m^3. This is similar to the value obtained by Foltyn et al. [47] for synthetic CaPuTi2O7 at nearly the same a-decay event dose of 10^{26} a-decay events/m^3 after 1,200 days. Although the measured energy release for the natural zirconolites and Pu-doped zirconolites of equivalent dose are nearly identical, both of these values are distinctly lower than the value (84 J/g) measured for Pu-doped zirconolite that had experienced a smaller dose (approximately 10^{25} a-decay events/m^3) [47] or for Cm-doped zirconolite (126 J/g) and (Gd,Cm)2Ti2O7 at doses of 2.0 X 10^{25} a-decay events/m^3 [26,48]. Foltyn et al. [47] have suggested that the decrease in released energy with increasing dose is due to a continuing damage process than results in a reordering of atoms in the metamict state. Leaching studies of natural zirconolites (which have accumulated significant a-decay event damage) have leach rates in the range of 1 to .001 g/m^2d at temperatures in the range of 95 to 200°C (based on Ca release) at times between 10 to 100 days [49]. The chemical durability of natural zirconolite has been confirmed by microprobe analyses which reveal only minor alteration (comparison of core to rim areas in the natural samples) [44]. The low release of actinides has been confirmed in laboratory experiments with Synroc-C formulations. Measured leach rates are in the range of 10^{-4} to 10^{-8} at 70°C in experiments that have run up to 1200 days [50].

Monazite

Monazite has been proposed as a single-phase ceramic to incorportate a wide variety of nuclear wastes, particularly those rich in actinides [51,52]. The mineral monazite is a mixed lanthanide orthophosphate, LnPO4 (Ln = La, Ce, Nd, Gd, etc.), that often contains significant amounts of

Th and U (up to 27 wt. % combined). As a result, many natural monazites have been subjected to significant a-decay event damage over geologic time (some samples are over two billion years of age). In spite of the large radiation doses received by natural monazites, Ewing [53,54] has noted that monazite is always found in the crystalline state. The apparent resistance of natural monazites to radiation-induced amorphization was an important factor in the initial proposal of monazite ceramics as potential candidates for the immobilization of nuclear wastes. Further, the durability of monazite has led to its increasing use in U/Pb dating of minerals in both igneous and metamorphic rocks [55]. One should note that the closure temperature for Pb-loss for monazite (approximately 725°C) is lower than that of zircon. Karioris et al. [56] have established that natural monazite (Ce,La,Y)PO4 can be readily transformed to an amorphous state by irradiation with 3 MeV Ar^+ ions to moderate doses. In natural monazite that was irradiated to a partially amorphous state (diffraction intensities were reduced by one-third), complete recovery of the fully crystalline state occurred after annealing at 300°C for 20 hours. The apparent stability of natural monazite is attributed to this relatively low temperature of recovery of the radiation damage. Differential scanning calorimetry (DSC) measurements of natural [57] and synthetic [57,58] monazites irradiated with 3 MeV Ar^+ ions have been performed. In natural monazite, the stored energy released during recrystallization was 33 J/g, the peak in the release rate occurred at 450°C, and the activation energy associated with the recovery process was estimated to be 2.77 eV. For synthetic monazite, CePO4, the stored energy release was 30.5 ± 1.3 J/g, the temperature for maximum release was slightly lower at 370°C, and the activation energy was estimated to be 2.7 ± 0.3 eV. Leaching studies on synthetic monazite containing 20 wt. % simulated Savannah River waste (MCC-1 leach test, 28 days at 90°C) show release rates of uranium to be on the order of .001 gm/m^2d [59]. The leach rate of the host matrix of a synthetic monazite, LaPO4, containing simulated waste remains low even after the material has been transformed to an amorphous state by irradiation with 250 keV Bi^+ ions. However, work by Eyal and Kaufman [60] on natural monazite indicate that there is a preferential dissolution of the radionuclide daughter-products, ^{234}U, ^{230}Th, and ^{228}Th, by factors of between 1.1 and 10 relative to the structurally incorporated parent isotopes ^{238}U and ^{232}Th. This isotopic fractionation is attributed to radiation damage in the tracks of the recoil nuclei emitted during a-decay of the parent isotopes. While there have been some concerns regarding these results [52], the increases in dissolution rates are similar to those observed in other actinide-host phases. The same phenomenon has been identified in Th-doped borosilicate glass [61].

Zircon

Recently, zircon, ZrSiO4, (*I4$_1$/amd*; Z = 4) has been proposed as the preferred crystalline ceramic for the disposal of excess weapons plutonium [5 and 62, note extensive references therein]. Zircon occurs in nature with uranium and thorium concentrations up to 5,000 ppm. Zircon is an extremely durable mineral, often found as a heavy mineral in stream sediments that after transport over great distances shows limited chemical alteration or physical abrasion. Indeed, zircon has been extensively studied, because it is a phase commonly used in the U/Pb dating of samples that may be as old as four billion years . Numerous studies have analyzed the conditions under which the U/Pb systematics are disturbed as a result of radiation damage, thermal events, or alteration. Additionally, zircon has been identified as an actinide-bearing phase in polyphase ceramic waste forms.

The zircon structure is well known, consisting of triangular dodecahedral ZrO8 groups which form edge-sharing chains parallel to the *a*-axis, and SiO4 tetrahedral monomers which form edge-sharing chains with alternating ZrO8 groups parallel to the *c*-axis. In natural zircons, U and Th replace the Zr in low concentrations; however, compositions of ASiO4, in which A^{4+} = Zr, Hf, Th, Pa, U, Np, Pu and Am, have been synthesized. The regular increase in the unit cell volume with the increasing ionic radius of the A-site cation confirms the homologous topologies of these structures [63]. Four of these compositions, hafnon (HfSiO4), zircon, coffinite (USiO4) and thorite (ThSiO4), occur naturally. Present structure refinements and structural analyses suggest complete miscibility between ZrSiO4 - HfSiO4, but there are miscibility gaps on the ZrSiO4 - USiO4 - ThSiO4 joins [64]. Zircon with 9.2 atom percent plutonium (8.1% Pu^{238}; 1.1% Pu^{239}) substituting for Zr has been synthesized. This is equal to a waste loading of 10 wt.% Pu [65], but the maximum extent of the solubility of Pu in zircon has not been determined. The fact that a pure, endmember composition, PuSiO4, has been synthesized suggests extensive substitution of Pu for Zr is possible.

Radiation damage studies of zircon have a long history. Zircon undergoes the radiation-induced transformation from the periodic-to-aperiodic state (metamict state) at doses over the range of 10^{18} to 10^{19} a-decay events/g (= 0.2 to 0.6 dpa) with a density decrease and a corresponding volume expansion of 18% [66-71]. These studies include analysis of natural zircons which have accumulated a-decay event damage up to doses of 0.7 dpa over 550 million years, ^{238}Pu-doped zircons (^{238}Pu has a half-life of 87.7 years), up to doses of 0.7 dpa in 6.5 years and heavy ion beam irraidiations using 2 Mev He^+, 0.8 MeV Ne^+, 1.5 MeV Ar^+, 1.5 MeV Kr^+, 0.7 MeV Kr^+ and 1.5 MeV Xe^+ to doses of 0.2 to 2.3 dpa in times of less than an hour. All three types of damage experiments include detailed studies of annealing kinetics [72]. These experiments cover a dose rate range of $>10^8$ and provide a firm basis for predicting the microstructure of the radiation-damaged zircon as a function of dose, temperature, and type of radiation. There are few crystalline ceramics for which such a wide variety of data are available. Based on these data, for a waste loading of 10 wt.% of ^{239}Pu, the zircon will reach the saturation value of damage (1.2 x 10^{19} a-decay events/g or 0.8 dpa) in approximately 1,700 years; thus, the properties of zircon must be considered in light of its radiation-damaged, aperiodic state. By comparison a borosilicate waste glass with a similar waste loading will attain an apparent saturation damage at a dose of 3 x 10^{18} a-decay events/g in approximately 400 years and will have a partially decomposed network containing a significant concentration of helium/oxygen bubbles. Studies of borosilicate glasses to higher doses have never been performed; consequently, the effects at high doses are not predictable. Finally, transmutation effects (^{239}Pu decays to ^{235}U) are important in crystalline materials, as they may lead to phase instability. In the case of zircon, the solubility of U in zircon is only known approximately (4 ± 2 mole percent); thus, for higher concentrations of U one may expect the formation of USiO4 which also has the zircon structure.

Stored energy values have been carefully determined by transposed temperature drop calorimetry over the range of the periodic-to-aperiodic transition on a suite of zicons from Sri Lanka (550 million years old) [73]. The energy released during annealing varies sigmoidally as a function of a-decay event dose reaching a saturation value of 322 ± 16 J/g at doses greater than 5 X 10^{18} a-decay events/g. This is greater than values typical of nuclear waste glasses, which are generally less than 150 J/g and saturate at dose on the order of 10^{18} a-decay events/g; however, sudden release of this energy is not anticipated to cause a signficant rise in temperature for either the glass or zircon. The magnitude of the enthalpy of annealing suggests that the damage is pervasive on the scale of fractions of nanometers, perhaps leading to the formation of micro-domains of amorphous SiO2-rich and ZrO2-rich regions in the metamict state. This suggestion is consistent with observations made by secondary ion mass spectrometry (SIMS) and high resolution transmission electron microscopy (HRTEM) and extended x-ray absorption fine structure spectroscopy (EXAFS) of annealed zircons [69,70,74].

Alteration of natural zircons has important implications to the use of U/Th/Pb techniques in geochronology; thus, there is an extensive literature that describes the alteration [75-79]. Physical degradation can occur due to microfracturing that is the result of the volume expansion caused by the defect accumulation with increasing a-decay dose and results in an increase of surface area [68]. Chemical alteration can involve disturbed U/Pb systematics due to diffusion of Pb and an increase of leach rate. Under extreme geologic conditions, e.g., zircons subjected to deformation in shear zones and altered by hydrothermal solutions, disturbed U/Pb systematics are clearly documented. Differential etching experiments (using 48% HF) have shown by scanning electron microscopy the removal of radiation damaged zones with improved concordance of U/Pb systematics in the remaining, unaltered material. Despite this evidence of alteration in samples that may be hundreds of millions to several billions of years old, one must state that the alteration is minor and the disturbed U/Pb systematics are of elements that are present in concentrations of hundreds to thousands of ppm. The minor alteration of zircon over long periods of time and under rather extreme conditions (e.g., meteorite impact [75]) stands in contrast to the observations of natural glasses which are readily altered and rarely have ages in excess of tens of millions of years. Natural glasses have been studied extensively as natural analogues for the long-term behavior of nuclear waste borosilicate glasses and are certainly less stable than zircon [84].

Leaching studies of natural zircons under extreme laboratory conditions have confirmed the loss of U, Th and Pb under hydrothermal conditions (e.g., 2 molal NaCl solution at 500°C and 1,000 bars pressure) . The lead loss can be the result of grain boundary or volume diffusion (in which there is no dissolution of the zircon), or with time the dissolution of zircon [77]. However, at lower temperatures (< 80°C) and near neutral pH values, i.e., conditions more pertinent to nuclear waste disposal, zircon is extremely insoluble [78]. There are much less data in the literature than necessary for a full evaluation of zircon as a waste form. Crystalline zircon is stable to such an extent that the equilibrium concentrations of Zr and Si are in the order of 10^{-9} moles/L (0.1 ppb) at 25°C. Dissolution of amorphous zircon (cyrtolite) followed a first order reaction, based on Si concentrations. Zr concentrations remained below 0.05 ppm, the instrument detection limit, due to precipitation of ZrO2 and ZrSiO4. The dissolution of natural zircons at 87°C as a function of a-decay event damage causes an increase in weight loss (10^{-3} to 10^{-1} weight percent for the transition from the crystalline ($\leq 10^{16}$ a/g) to the amorphous state ($\geq 10^{19}$ a/g)). To detect zirconium in solution, these experiments had to be performed in KHCO3 solution. Comparing the dissolution rate for cyrtolite , R $= 10^{-7}$ moles/m^2/d at 80°C, pH = 5, with the long-term rate of a nuclear waste borosilicate glass, R = 10^{-5} moles/m^2/d (= 10^{-3}g/m^2/d) in water at 98°C shows that the dissolution rate of amorphous zircon is still considerably lower than that of glass in stagnant, silica-saturated solutions. In an open system (e.g., moving ground water), the leach rate for zircon used in this comparison does not increase; however, the leach rate of borosilicate glass may increase by three orders of magnitude until reaching the forward rate of reaction. Thus, one of the main advantages of zircon may be its high durability where large volumes of water have access to the waste form, as this allows considerably greater flexibility in repository design.

Physical properties of zircon have been determined as a function of increasing a-decay event dose, 0.15 to 0.65 dpa [68]. The radiation-induced softening leads to a decrease in hardness of 40 percent and of the bulk elastic modulus of up to 70 percent, but there is an increase in fracture toughness probably caused by crack-tip blunting by the aperiodic domains.

Criticality must be a concern for any Pu-waste form, both during processing as well as in the final waste form configuration. This concern can be mitigated by adjusting the waste loading in the zircon, and also by including neutron "poisons" in the formulation. Natural zircons can contain up to several thousand parts per million rare earths, including up to 500 ppm of Gd (or up to 5,000 ppm at Oklo [17]). Thus, neutron absorbing nuclides may be incorporated into the zircon structure as dilute solid solutions or, at higher concentrations, used as a binding material intimately mixed with the zircon. There is no evidence of selective loss of gadolinium from zircons, but laboratory experiments with natural and synthetic material should confirm this observation.

Production technologies are always an important consideration in the adoption of a waste form, as one should not underestimate the difficulties of processing large volumes of radioactive material. In the case of zircon, phase relations in the system ZrO2 - SiO2 were investigated as early as 1967 and the system ZrO2 - SiO2 - ThO2 - UO2 has been investigated by Mumpton and Roy [64] in which they report the solubility limits of Th (< 4 mole %) and U (4 ± 2 mole %) in zircon. As already discussed, Pu-doped zircons have been synthesized with 9.1 mole percent Pu. The apparent increase of solubility of Pu over U and Th in zircon is expected as the ionic radius of the A^{4+}-site cation approaches that of Zr^{4+}. Komarneni and Roy [80] have reviewed the well established hydrothermal and solid-state synthesis of zircon as either single crystals or powders, as well as sol-gel synthesis. Most recently, Mori and others [81] have synthesized zircon by sintering (1,200 to 1,300°C) and have obtained yields of nearly 90 percent in less than one day. Although larger-scale pilot demonstrations are required, as well as detailed studies of the effect of Pu (and any potential impurity) on zircon synthesis conditions, much is already known about the requirements for synthesis. In the case of weapons plutonium, one can take advantage of the essentially reagent grade of the waste in engineering the process and the waste form. The final processing technology can draw on the experience of producing mixed-oxide fuels from powders. Some modifications of the industrial MOX process are necessary to make zircon. Safeguard and criticality aspects of the MOX process have been reviewed by the IAEA and need not be reestablished if zircon is produced by this process. Theft and recovery of

Pu from zircon may be a concern prior to disposal in deep borehole; however, this will be difficult, as zircon is a highly refractory substance (melting point > 1,500°C).

In summary, zircon is an extremely durable phase which may be used as a Pu-host for the disposal of weapons plutonium. The long-term durability is confirmed from natural occurrences in diverse and extreme geologic environments over geologic time. Leaching experiments confirm the extremely low solubility. The very low solubility, as compared to borosilicate glass, will insure that Pu is not concentrated by later cycles of geochemical alteration to values that might lead to criticality. Several processing options, sol-gel or sintering, have been demonstrated on a laboratory scale. Zircon does experience a radiation-induced crystalline-to-amorphous transition, but even the aperiodic (metamict) material is extremely durable. Finally, the lower volume (due to higher waste loading and the higher density of zircon as compared to glass) and greater durability, particularly at elevated temperatures, expand the range of geologic disposal possibilities, e.g, deep boreholes [82], a third, less studied option suggested by the U.S. National Academy of Sciences. In fact, retention of the most mobile element, Pb, in zircons to depths of over 4,000 meters (>300°C) has already been demonstrated [83,84].

CONCLUSIONS

There is every reason to expect that waste form performance can be much improved over what is now accepted for borosilicate glass. Ceramic phases, such as zircon or zirconolite, have already demonstrated this improved performance under certain conditions (e.g., hydrothermal, up to 300°C). Prudence requires that further research and development of these ceramic waste forms be conducted for the following reasons:

i.) Any strategy of isolation should emphasize the near-field containment of the radionuclides. This is primarily a function of waste form or "waste package" performance. Strategies that rely solely on long travel times, dispersal or dilution, implicitly presume release and movement of radionuclides. In the case of the disposal of weapons plutonium, this leads inevitably to concerns over criticality.

ii.) The long-term performance assessment of the success of radionuclide containment requires the development of deterministic models of the future physical and chemical behavior of each part of the barrier system. Although difficult, it is certainly easier to model the chemistry and physics of corrosion and alteration of waste forms, with the subsequent release or retention of radionuclides over some range of conditions, than it is to develop coupled hydrologic, geochemical and geophysical models of the movement of radionuclides through the far-field of a geologic repository or a deep borehole. The extrapolation of corrosion behavior over long periods rests on a firmer scientific foundation for a waste form as chemically simple as zircon than the extrapolated behavior of, as an example, hydrologic systems that are site specific and highly dependent on idealized boundary conditions (e.g., climate and hydrologic recharge). This is a particularly important consideration in proposals for deep borehole disposal where the geophysical, geochemical and hydrologic regimes are more uncertain and less amenable to engineered barriers.

iii.) Natural phases, minerals, provide a means of "confirming" the hypothesized long-term behavior of waste form phases in specific geochemical environments to very high a-decay event doses. Indeed, the study of natural phases provides an essential confirmation of performance assessments in which the corrosion or alteration behavior of waste form phases over long periods is an essential component.

iv.) Finally, the availability of a well established process (e.g., the modified MOX-process for the production of zircon) for the handling of large quantities of fissile material is certainly an important criterion in the selection of a waste form for plutonium.

Considering each of the above criteria and based on the present state-of-knowledge, we propose that zircon is the preferred crystalline, ceramic waste form for the disposal of excess weapons plutonium [82].

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DISCLAIMER

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Non-Proliferation, Safeguards, and Security for the Fissile Materials Disposition Program Immobilization Alternatives

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ABSTRACT

The Department of Energy is analyzing long-term storage and disposition alternatives for surplus weapons-usable fissile materials. A number of different disposition alternatives are being considered. These include facilities for storage, conversion and stabilization of fissile materials, immobilization in glass or ceramic material, fabrication of fissile material into mixed oxide (MOX) fuel for reactors, use of reactor based technologies to convert material into spent fuel, and disposal of fissile material using geologic alternatives.

This paper will focus on how the objectives of reducing security and proliferation risks are being considered, and the possible facility impacts. Some of the areas discussed in this paper include:

1) domestic and international safeguards requirements, 2) non-proliferation criteria and measures, 3) the threats, and 4) potential proliferation, safeguards, and security issues and impacts on the facilities. Issues applicable to all of the possible disposition alternatives will be discussed in this paper. However, particular attention is given to the plutonium immobilization alternatives.

INTRODUCTION

The US Department of Energy (DOE) established the Fissile Materials Disposition Program (FMDP) to address the disposition alternatives applicable to the long-term storage and disposition of surplus fissile material. The primary program goal is to render weapons-usable fissile material inaccessible and unattractive for weapons use while protecting human health and the environment. The National Academy of Sciences (NAS) recommended the plutonium (Pu) disposition efforts attain a "spent fuel standard". This standard asserts that the final disposition form be "...roughly as inaccessible (unattractive)..." as the residual Pu existing in the much larger and increasing world-wide supply of spent commercial nuclear fuel. When such a standard is achieved, the proliferation risk is generally considered the same as that associated with commercial spent fuel. Technologies that go beyond the spent fuel standard are not currently being considered in this program.

A "cross-cutting" team of subject matter experts was formed to focus on the issues of non-proliferation, safeguards, and security (NP/S&S). The NP/S&S Team is composed of representatives from Sandia, Los Alamos, and Lawrence Livermore National Laboratories.

After an initial screening process, several Pu disposition alternatives were selected for further evaluation during the next decision phase. Those remaining alternatives included emplacement in deep boreholes, reactor related, and immobilization. This paper will generically discuss the immobilization alternatives, which include:

- Vitrification Can-in-Canister
- Vitrification Greenfield
- Vitrification Adjunct Melter to DWPF
- Vitrification Electrometalurgical Treatment
- Ceramic Can-in-Canister
- Ceramic Greenfield

Generically, the immobilization alternatives consist of a Pu processing facility, immobilization facility, and a high-level waste repository. The Pu processing facility receives a variety of Pu feed material and converts this material into Pu oxide. The immobilization facility involves processing to mix and dilute the Pu oxide within a glass or ceramic matrix, and the addition of a highly radioactive "spike" material (as a barrier to theft). The repository is a subsurface facility for the permanent isolation and protection of the material. Potentially, future variants to these alternatives may also be evaluated.

APPLICABLE SAFEGUARDS REQUIREMENTS

Domestic Safeguards and Security (S&S)

DOE and/or Nuclear Regulatory Commission (NRC) safeguards and security guidelines may apply depending on the facility characteristics. Current NRC licensed operations (e.g., commercial reactors) are expected to remain under NRC jurisdiction. However, much of the initial feed material (Pu) will be classified. The presence of classified data, may require that the initial Pu processing facility be strictly a DOE facility (not necessarily subjected to NRC regulation). The remaining facilities will be governed by NRC guidelines, as appropriate.

Domestic S&S for special nuclear material (SNM) and nuclear weapons is composed of two subsystems: nuclear materials control and accounting (MC&A), and physical protection against threats of diversion and theft. Domestic safeguards are primarily concerned with unauthorized actions by individuals or sub-national groups.

An essential element of ensuring the resistance of fissile material to theft, diversion, and proliferation is the safeguards and security applied to the material, based on its form. The form of the material reflects the intrinsic properties of the material, which dictates the attractiveness for use in nuclear weapons. However, the form of the material alone does not provide proliferation resistance. Safeguards and security systems should be applied in a graded approach based on the form of the material (attractiveness).

The DOE defines the attractiveness of plutonium, and other SNM, through a categorization of types and compositions that reflects the relative ease of processing and handling required to convert that material to a nuclear explosive device. Table 1 is derived from the DOE Order 5632.3B *"Control and Accountability of Materials"* (9-7-94).

The level, or degree, of protection accorded to material is dependent on the quantity and attractiveness of the Pu. Each category of protection has its own requirements ranging from the highest level of protection, Category I-A for assembled weapons, to Category IV-E for somewhat "self-protecting" forms. Protection of the material is accomplished through a graded system of deterrence, detection, delay, and response as well as material control and accountability. Layers of protection may then be applied to protect material of greatest attractiveness within the innermost layer, and with the highest controls. Material of lesser attractiveness does not require as many layers of protection, and fewer controls.

International Safeguards

The International Atomic Energy Agency (IAEA) is the primary agency for the promulgation and independent verification (inspection) of material use, according to international safeguards (ISG). ISG is also composed of two subsystems: nuclear materials accountancy, and materials containment and surveillance (C/S). Both are required to satisfy international inspection agreements. Containment and surveillance are used to provide continuity of knowledge during inspector absences, and provides supplemental information to ensure inventory integrity when measurement uncertainties might otherwise lead to a conclusion of an inventory "discrepancy". IAEA inspections are conducted to verify the facility's declared nuclear inventory values. The proliferation safeguards requirements for alternatives will be based on IAEA Information Circulars, and negotiated facility agreements. Nuclear material forms will fall under the IAEA categories of unirradiated direct use (e.g., Pu metal and compounds) and irradiated direct use (after addition of a high level radiation spike).

Additionally, to maintain consistency among all storage and disposition alternatives being considered in this program, the following specific *assumptions* are made:

- Material under IAEA safeguards will remain so
- Material not declared surplus to stockpile and the strategic reserve will be exempt from IAEA safeguards
- Surplus unclassified material may be offered by DOE to the IAEA for IAEA safeguards and will remain under those safeguards
- Surplus materials will not be offered for IAEA safeguards until classified information has been properly protected.

FMDP CRITERIA AND MEASURES FOR S&S AND NON-PROLIFERATION

Several criteria, and dozens of sub-criteria (measures), have been identified for evaluating the various alternatives. Two of the criteria are:

- Criteria I - Safeguards and Security (S&S) --Resistance to theft, diversion, and use by unauthorized parties; and,
- Criteria II - Nonproliferation (NP) -- Resistance to diversion, retrieval, extraction and reuse by the "host" nation.

The evaluation of alternatives is being done from both the domestic S&S and international NP perspectives, and are based on two important factors, the "threats," and the protection "regimes" that exist to address threats. Threat "consequences" are not a part of our current evaluations, as they are felt to be the same as many existing assessments. The areas of responsibility are separated into domestic (internal to the host nation) and international (external to the host nation). The "domestic" responsibility (protection regime) of the host nation government is, traditionally, to prevent unauthorized access to its material either by individuals or groups within its own organizations (e.g., disgruntled workers) or by other sub-national threats (terrorist groups, criminal organizations, etc.). The responsibility of the international regime is to detect the unauthorized diverting, retrieving, or converting of material by the host government. This establishes a clear demarcation of threats associated with each criterion.

The first criterion involves domestic S&S, while the second involves ISG. Measures have been developed for each of these criteria to evaluate the various alternatives. The evaluation will address requirements and measures, as discriminators, and identify the S&S and proliferation risks at each of the various steps in each disposition alternative. The risks have been defined in terms of material form, operational environment, and level of S&S applied to the material.

The first criterion addresses the domestic risk of weapon-usable nuclear material primarily during transportation, storage, and processing, as well as the risk of theft after disposition is completed. The measures identified for this criterion are the operational environment, material characteristics, and S&S.

The environment measures include processing steps, bulk throughput, inventory, and transportation. Throughput for bulk operations is particularly important because of the possible measurement uncertainties in large scale operations. The material form (attractiveness) is based on physical, chemical, or nuclear (isotopic and radiological) makeup of the nuclear material, and the presence of other fissile materials. The S&S measures are based upon the form of the material, need to protect classified information, nuclear material accountability systems, uncertainty of nuclear measurements, and physical accessibility of the material.

For the second criterion, the ability to divert or retrieve, extract, and reuse a significant quantity (SQ) of material depends on the environment, material characteristics, and ISG. The environmental measures include bulk throughput, inventory, and processing steps. IAEA material characteristics are used to assess the material characteristics. The type of nuclear accounting system, the measurement uncertainty, classified information, and accessibility are all factors of ISG. In addition, the irreversibility of the material form is important for assessing its reuse in nuclear devices. Irreversibility primarily depends upon the material form and location (permanent intrinsic barriers).

THREATS

Based upon the previous paragraphs, the primary threats to the disposition program can be simply defined as:

- theft (intentional, unauthorized removal of nuclear material to a location not authorized to contain nuclear material) by an individual or sub-national group;
- diversion (unauthorized removal of nuclear material from its approved use or authorized location) by a member of the host nations own nuclear organization infrastructure, in violation of the international regime before final disposition has taken place);
- retrieval (unauthorized access by the host nation or others in violation of the international regime after final disposition); and,
- conversion (the converting of dispositioned material back into weapons usable form either by the host nation or others).

POTENTIAL FACILITY RISKS, IMPACTS, AND ISSUES

It is assumed that all facilities will meet the existing appropriate S&S requirements, and that these measures will help mitigate any risks. Still, the threats defined above will differ depending on the form of the material, the facility activities, and the barriers to theft and diversion (both intrinsic to the material and the facility). Each facility is also assumed to represent some potential risk of theft, diversion, and proliferation. The remainder of this section will briefly discuss generically the facilities/activities for the immobilization alternatives. Table 2 summarizes some of the information discussed in this section.

Plutonium Processing Facility

For this facility, most of the material is in a very attractive form, possessing minimal intrinsic barriers. In the case of pit conversion, the attractiveness decreases from I-B to I-C (see Table 1). For oxides and other high-grade material, the attractiveness level remains at I-C. In some cases, the feed material may be low-grade and the mixing activities would actually increase attractiveness from II-D to I-C. The material is very transportable. Item accountancy will initially be used for material received into this facility (such as pits and containers protected by tamper indicating devices). Once material has been removed from containers, bulk accountancy becomes necessary. Except for the initial handling of pits and containers with tamper indicating devices (TIDs), many of the operations will involve "hands-on" activities and the material is very accessible. The items being handled are not necessarily large and, as such, do not require special handling equipment (SHE). Most of the operations will be performed within the confines of gloveboxes.

Typically, the material is in a very pure form, such as a metal or oxide, and its isotopic composition makes it readily usable for a nuclear device. Considering the quantity and attractiveness of the material, the facility will be a Category I facility. There are a large number of complex processing steps with a relatively high bulk throughput. This combination provides increased opportunities for covert theft and diversion. Waste streams containing fissile material will be generated and thus require monitoring to detect possible diversion. There will be no intrasite transport movements of the Pu. Safe Secure Transport vehicles (SSTs) will be necessary for delivery, and movement to another site. Since many of the processes involve bulk material, accountability measurements may utilize destructive and non-destructive assay (NDA) techniques.

Material balance areas (MBAs) and nuclear measurement points need to be strategically placed in bulk processing areas to minimize the uncertainty of material accountability, and localize anomalies. However, since this facility involves large throughputs of bulk material it may be very difficult to prevent or detect the diversion of a significant quantity of material using material accountability alone. Thus, it will be necessary to have additional S&S measures to ensure that material is not being diverted. All movement of fissile material across security or MBA boundaries must be monitored (e.g., bulk and item movements and waste streams). Operations that minimize access to nuclear material are needed. This could include the use of automated or robotic devices, remote handling and other barriers to minimize material access. Bulk material, when not actively in process operations, should be stored in containers protected by tamper indicating devices (TIDs) to minimize the opportunities for diversion.

Pits, and some other weapons materials, being processed are classified as Restricted Data. The presence of classified material complicates safeguards, particularly with respect to international inspection. Material within this facility may not be under international safeguards (ISG) unless classified information can be protected. This may also apply to waste streams. Classified information protection may need to be implemented differently and more stringently than is currently necessary in US facilities. Under current laws Restricted Data cannot be divulged to IAEA inspectors (unauthorized disclosure of weapons design information violates the Atomic Energy Act and the 1978 Nuclear Nonproliferation Act). Therefore, part or all of this facility may not be under ISG, and verification by the IAEA is not currently possible. A number of different options are being considered to address this problem. These include making material available to the IAEA only after the material has been converted into an unclassified form, or the use of modified IAEA safeguards until the material is rendered unclassified.

Immobilization

In the initial stages of handling and processing the Immobilization Facility will be a Category I facility. Within this facility material will again be changing form and concentration, decreasing the protection category and attractiveness. With the addition of a self-protecting property (radiation barrier) the material meets the definition for Category IV-E.

The facility operations involve a medium number of processing steps and relatively accessible bulk materials. As the plutonium oxide is blended with matrix materials the concentration of the plutonium decreases. Since these forms are still accessible and transportable (prior to radiation spike) they are still somewhat attractive targets for both covert and overt theft. After fabrication into a glass or ceramic matrix the Pu is less transportable (more resistant to overt theft).

The final product is encased in stainless steel canisters, and has a low concentration of Pu. The material is now subject to item accountancy, again representing reduced opportunities for covert theft. The material has been given a self-protecting barrier by the introduction of a high level radioactive "spike" material (cesium chloride or other high level waste). This spike significantly reduces certain S&S requirements. The DOE Category and Attractiveness level is now IV-E (highly radioactive material: a radiation dose rate in excess of 100 rems per hour at a distance of 1 meter). If after a period of time the self protecting barrier no longer meets the above radiation dose criteria, it may be considered as Category III-D, depending upon the quantity of SNM present and the additional barriers that may exist at that time (as is true with commercial spent fuel).

There is some concern with the capability to perform accurate accountancy measurements after the addition of the radiation spike, and criticality control “poisons”. However, it is reasonable to assume that containment and surveillance, coupled with accurate measurements prior to spiking, and item accounting thereafter, will be as acceptable in this facility as it is in others (e.g., spent reactor fuel). Research and development should be conducted, however, to assure that the best technically viable methods can be used to satisfy the public and the international community that this concern, for weapons program materials, has been adequately addressed.

Repository

The immobilized material is received in shipping casks and placed into disposal casks. The material has low attractiveness for covert and overt theft, being highly radioactive and with each cask weighing approximately 22 tons. Although a large amount of material will be entering the repository, the operations are relatively simple and few in number. The operations only involve very large discrete items that are placed and remain in secured underground tunnels (drifts). Item accountability is used for the casks. No access is available to the material itself, although access to the casks is possible. All movements of the casks require special handling equipment.

The radiological barrier will decrease over a relatively long period of time such that the material will no longer be radiologically self-protecting. This makes necessary the utilization of other measures to help minimize the threat of diversion. Placement of the material in an underground repository makes retrieval more difficult, but not improbable. Therefore, it is necessary for long-term disposition to make the material as inaccessible as possible independent of a radiological barrier (the same is true of spent reactor fuel). Additional safeguards and C/S measures should be utilized to help protect this material. It is also important that accurate accountability of the material be maintained so there is a high degree of confidence that the material was not diverted before, or after placement in the repository. Methods and procedures for long-term international monitoring are still under development.

Transport

For all Category I material, Safe Secure Transport vehicles (SSTs) will be used to move the material between sites. After the concentration of Pu is substantially reduced and a radiation barrier (spike) has been added, the requirement for SST protection is removed, making commercial transportation possible. SNM transport activities have inherent risks for overt theft scenarios and a lowered risk for covert theft attempts. Minimizing the number and/or duration of the transport steps is desirable. Much of the risk for transportation is related not so much with the actual SST movements, but rather with the shipping and receiving activities at the various facilities. There are no known major impacts on commercial transportation that will result from IAEA safeguards being applied.

However, SST shipment activities are classified. Some sort of "casual" inspection, e.g., a cursory inspection that does not permit measurements or disclosure of sensitive SST design information, might be permitted. Classification rules prevent IAEA tracking or monitoring of SST shipments. In order to meet IAEA safeguards requirements negotiated agreements will be needed. It may be possible to place IAEA seals on the individual containers and on the doors of SSTs, without the disclosure of classified operational security procedures.

International Atomic Energy Agency (IAEA)

The impact of the International Atomic Energy Agency (IAEA) upon the FMDP is not yet fully understood. The philosophies, goals, and implementation of International Safeguards (ISG), commonly referred to as IAEA safeguards, are substantially different from domestic S&S. IAEA inspections involve different techniques than domestic S&S inspections. Nuclear measurements play a very important role in verifying material accountability and use, since the goal is to ensure that the host nation does not misuse the material. Currently the IAEA does not recognize "compensatory" safeguards measures (e.g., defense-in-depth, item monitoring) that have allowed DOE facilities to extend domestic inventory frequencies.

It is assumed that all facilities, except the Pu processing facility, will be subject to full IAEA safeguards. It is likely that ISG compliance requirements will require additional accountability verification (e.g. identification, weighing, sampling and analysis and NDA), increased inventory item checks, C/S measures installed throughout the facilities (e.g. IAEA controlled surveillance, seals, monitors, tags), space for inspectors, and equipment for independent measurements by international inspectors.

SUMMARY

It is assumed that all facilities will meet necessary S&S requirements and that appropriate protective measures will be taken. Integration of domestic S&S and ISG to reduce cost and operational impacts would be beneficial. The final disposition form of the immobilization alternatives will meet the spent fuel standard. Facilities that handle large quantities of bulk material, have high throughputs, and involve complex operations, such as Pu processing and immobilization facilities (and reactor fuel fabrication) have a greater risk that material can be diverted. A relatively accessible material form, coupled with measurement uncertainty, may create a situation where diversion of a SQ of material may be difficult to detect. As the material is made into items (e.g., glass or ceramic "logs"), the likelihood of theft or diversion decreases. The radiation barrier, along with the location and mass of the canisters, makes theft, diversion and/or retrieval more difficult. The relatively low number of transport moves, miles, and handling steps for immobilization alternatives contributes to an acceptable level of risk for theft and diversion. This risk can be further reduced by minimizing the handling and processing of the material and by strict application of appropriate S&S measures.

In this paper, we have presented a discussion of factors to be considered in evaluating an FMDP facility for proliferation and S&S risk. This approach is intended to complement the traditional S&S vulnerability assessments (VAs) done by sites and facilities, and to provide insight into the inherent proliferation risks for the individual processes. This information can then be used to aid in the evaluation and mitigation of risks. All nuclear facilities have inherent proliferation, safeguards, and security risks, contingent upon their environment, processes, material forms, available S&S measures, and independent inspection activities. The DOE/MD establishment of safeguards and non-proliferation as two primary decision criteria, along with a technical evaluation process, clearly indicates the importance of proliferation resistance to the program. The evaluation of the disposition criteria, measures, and methodology is ongoing. Results of the decision processes will be available in the future.

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DISCLAIMER

Table 1 -- DOE Nuclear Material Attractiveness and Safeguards Categories for Plutonium

Nuclear Material Attractiveness and Safeguards Categories for Plutonium	Attractiveness Level	PU/U-233 Category (Quantities in Kgs)			
		I	II	III	IV[a]
WEAPONS Assembled weapons and test devices	A	All Quantities	N/A	N/A	N/A
PURE PRODUCTS Pits, major components, buttons, ingots, recastable metal, directly convertible materials	B	≥ 2	≥ 0.4 < 2	≥ 0.2 < 0.4	< 0.2
HIGH-GRADE MATERIAL Carbides, oxides, solutions (≥ 25 g/l) nitrates, etc., fuel, elements and assemblies, alloys and mixtures, UF_4 or UF_6 (≥ 50% U-235)	C	≥ 6	≥ 2 < 6	≥ 0.4 < 2	< 0.4
LOW-GRADE MATERIAL Solutions (1 - 25 g/l), process residues requiring extensive reprocessing, moderately irradiated material, Pu-238 (except waste), UF_4 or UF_6 (≥ 20% < 50% U-235)	D	N/A	≥ 16	≥ 3 < 16	< 3
ALL OTHER MATERIALS Highly irradiated forms, solutions (≥ 1 g/l), uranium containing < 20 % U-235 (any form or quantity)	E	N/A	N/A	N/A	Reportable Quantities

a/ The lower limit for category IV is equal to reportable limits in the Order

Table 2 -- Facility Attributes for Proliferation Resistance Measures

Criterion 1 **Domestic S&S**	**Plutonium Conversion Facility**	**Immobilization Facility**	**Repository Facility**
Environment			
# of processing steps	• high # of processing steps	• medium to low # processing steps	• no processing steps
Max Pu inventory	• large Pu inventory	• large Pu inventory	• large inventory as final repository
Bulk Pu throughput	• high bulk throughput	• high bulk throughput	• no bulk throughput
# SST trips/miles	• SSTs required for receiving & shipping	• SSTs for receiving only	• no FM wastes
Fissile material(FM) wastes	• FM waste streams exist	• no FM waste streams	• no SSTs
Material Form			
DOE category-attractiveness	• I-B/II-D converted to I-C	• I-C converted to IV-E	• IV-E, @ 100 yrs radiation barrier is less
Other separated FM present	• other separated FM is present	• no separated FM	• no separated FM
Safeguards & Security			
Accessibility	• accessible & transportable	• accessible, better when immobilized	• access to casks but not to material
Type of nuc acct system	• primarily bulk accountancy	• initially bulk, then item (immobilized)	• item accountancy
Measurement uncertainty (MU)	• relatively low measurement uncertainty	• initially low MU, difficult to measure after radiation barrier added	• MU difficult to measure with radiation barriers
Classification	• classified material/data present	• no classified data present	• no classified data present
Criterion 2 **Non-proliferation**			
Detectability			
IAEA Safeguards	• high bulk throughput may cause difficulty in meeting IAEA measurement uncertainty requirements • classified material/data prevents normal IAEA inspection activities	• high bulk throughput may cause difficulty in meeting IAEA measurement uncertainty requirements • adequate containment & surveillance • normal IAEA inspections	• item accountability • Pu is not accessible • very good containment & surveillance • normal IAEA inspections
Irreversibility			
Material form (IAEA)	• direct use, unirradiated material	• direct use, unirradiated to irradiated material	• direct use, irradiated material
Material location	• processing location	• processing location	• underground repository location

Safeguardability of the Vitrification Option for Disposal of Plutonium

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ABSTRACT

Safeguardability of the vitrification option for plutonium disposition is rather complex and there is no experience base in either domestic or international safeguards for this approach. In the present treaty regime between the U.S. and the states of the former Soviet Union, bilateral verifications are considered more likely with potential for a third-party verification of safeguards. There are serious technological limitations to applying conventional bulk handling facility safeguards techniques to achieve independent verification of plutonium in borosilicate glass. If vitrification is the final disposition option chosen, maintaining continuity of knowledge of plutonium in glass matrices, especially those containing boron and those spiked with high-level wastes or ^{137}Cs, is beyond the capability of present-day safeguards technologies and nondestructive assay techniques. The alternative to quantitative measurement of fissile content is to maintain continuity of knowledge through a combination of containment and surveillance, which is not the international norm for bulk handling facilities.

INTRODUCTION

The end of the cold war and anticipation of the potential outcome of bilateral and multilateral arms control negotiations have contributed to numerous intellectual discourses supporting the cause of reducing/eliminating nuclear weapons. The management of excess fissile materials resulting from proposed arms reduction has been the subject of intensive examination by several committees of the National Academy of Sciences (NAS) and a special panel of experts appointed by the American Nuclear Society (ANS).[1-4] A screening process conducted by the Department of Energy (DOE) Office of Fissile Material Disposition evaluated a total of 37 options to determine reasonable alternatives for future evaluation both in the Programmatic Environmental Impact Statement (PEIS) and in a detailed technical, economic, and nonproliferation evaluation process.[5] The on-going PEIS process recognizes the contexts of policy initiatives for fissile material disposition vary substantially in the U.S. and FSU.

Two major issues important to both near- and long-term management and disposition of plutonium are (1) environmental safety and health of all plutonium processing, storage, and management, and (2) safeguardability of weapons dismantlement and plutonium disposition options. In the U. S., the current environmental, safety, and health vulnerabilities have been identified as major concerns.[6, 7] The corrective actions initiated are planned to result in a safe, secure, and inspectable interim-storage condition within a decade.[8] This plan represents the baseline for evaluation of options for long-term storage and disposition of weapons useable materials in the U.S. However, major concerns over fissile materials inventories in Russia center on safeguards and security and the reliability of institutional controls.

In1994, the National Academy of Sciences (NAS) examined in great detail the issues of management and disposition of plutonium from arms-reduction agreements.[1] The three "preferred approaches" recommended by NAS are (1) the spent fuel option, (2) the vitrification option, and (3) the deep borehole option. The first two are considered "promising alternatives" by the NAS, which recommended detailed investigations of these two alternatives.[2] In this discussion of safeguards issues, we will primarily consider the vitrification option and, as appropriate, compare it with the safeguardability of the spent fuel option.

In August 1995, a special panel appointed by the ANS reported their findings on the protection and management of plutonium.[4] The panel had reviewed all previous reports by both the DOE and the NAS and went further to examine the future of all plutonium and the role of plutonium in future energy production world-wide. Although the ANS panel report endorses the findings of the NAS 1994 report, they argue that the "plutonium problem" is not limited to excess plutonium from proposed weapons dismantlement. The ANS panel went on to recommend several national and international actions calculated to protect and manage plutonium from all sources for the future. While noting the progress in advanced reactor concepts in Japan, Russia, and Europe, the panel strongly recommended a reversal of U. S. decisions to stop all development of reprocessing and breeder reactor technologies.

Before we discuss the safeguards issues of disposition options here, it should be mentioned that considerable experience and expertise in present domestic and international safeguards regimes can be brought to bear on the safeguards issues inherent in most of these disposition scenarios. Systems and technologies developed and used at present for domestic and international safeguards can be readily applied or adapted to meet the needs of bilateral or third-party verification of weapons dismantlement and special nuclear materials (SNM) disposition.[1, 9]

NUCLEAR MATERIAL MANAGEMENT AND GENERAL SAFEGUARDS ISSUES

Key functions of nuclear materials management regime are safety, stability of materials, secure transportation and storage, physical protection, materials control, accounting, and verification. Several of these functions are also collectively known as nuclear material safeguards. Safeguards are those measures designed to guard special nuclear materials and source materials against the diversion from uses permitted by law and to give timely indication of possible diversion or credible assurance that diversion has occurred. In general, domestic safeguards measures include materials accountancy and control measures, the latter involving a judicious combination of containment and surveillance.

International safeguards is a verification system within the framework of international nuclear nonproliferation policy applied to peaceful uses of nuclear energy. In the international safeguards arena, sovereign nations are considered potential diverters of nuclear materials. According to present guidelines for international safeguards, systems designed for safeguarding SNM should account for such materials, and the accounting must be independently verifiable by an agent of the IAEA. Effectively applied IAEA safeguards should ensure that no State diverts nuclear materials from peaceful applications to weapons. This goal is different from that of domestic safeguards, which rely on the State's own physical protection and materials accounting measures. Because the independent IAEA verification provides assurance that States are complying with their commitments to peaceful uses of nuclear energy, it contributes to increased confidence among States.

The U.S. has been at the forefront in the development and implementation of international safeguards since 1945 when the term "safeguards" was first introduced in the Baruch Plan. The formation of the IAEA in 1957 and the nuclear nonproliferation treaty of 1970 are among major initiatives by the U.S. to prevent nuclear proliferation. In 1980, the U.S. concluded a Safeguards Agreement with the IAEA, that makes eligible for safeguards all source and special fissionable materials at all nuclear facilities in the U.S. except those associated with activities of direct significance to national security.[10] Under this agreement, approximately 230 nuclear facilities, including all commercial nuclear power plants in the U.S., are eligible for IAEA inspections. In March 1995, President Clinton's voluntary offer to withdraw 200 Mt of fissile materials from the US stockpile and place it under IAEA safeguards is another expression of U.S. confidence in the international safeguards regime and its importance to nuclear nonproliferation.[11] This U.S. proposal to place excess fissile materials from weapons dismantlement under IAEA safeguards is a desirable alternative in the near-term. For the long-term, either consumption by means of energy production or isolation in geologic formations is a likely means to prevent nuclear proliferation.

SAFEGUARDABILITY OF VITRIFICATION OPTION

In the proposed arms-reduction treaty regime between the U.S. and the states of the former Soviet Union, bilateral verifications are considered likely with potential for IAEA (third-party) participation. The goal of mutually assured weapons plutonium reduction can be achieved through bilateral or third-party verification of both disposition of excess SNM inventories and the absence of clandestine plutonium production.

Because storage of intact warheads has the potential for a "breakout," it would be highly desirable to dismantle the warheads and properly dispose of the SNM under appropriate safeguards to prevent their reentry into the weapons fuel cycle. The SNM recovered from dismantled warheads can be disposed of in several ways, and the final choices are determined by the country that owns the SNM. Recognizing that the underlying objective of arms-reduction treaties is to prevent fissile materials from reentering the weapons fuel cycle, it is necessary to establish a verifiable disposal scheme that includes stringent safeguards requirements. In realistic scenarios for the disposal of SNM from the weapons fuel cycle, safeguardability of the SNM should be a major factor.

There are a variety of safeguards challenges inherent in dismantling weapons, interim storage, processing, alternative uses, transportation, and final disposal. Systems and technologies developed for domestic and international safeguards of various parts of nuclear fuel cycles can be generally adapted to meet the needs of bilateral or third-party verification of weapons dismantlement and SNM disposition.[12, 13] Well-known safeguards issues of civilian fuel cycles are common to one disposition option - the use of plutonium in reactor fuels. However, the knowledge base for safeguarding fissile materials in heterogeneous vitrified matrices is probably the more challenging.

Various stages are common to all three plutonium disposition options being considered: dismantling of weapons, altering the physical and/or chemical configuration of fissile components, packaging, transportation, and interim safe storage, consumption or processing for disposal, and long-term internment.

Vitrification Operation

One disposition alternative recommended by the NAS would combine plutonium with radioactive high-level wastes as they are vitrified into glass through existing technologies. Another variant to this option proposes to replace high level wastes with separated fission products such as ^{137}Cs. Safeguards issues for both these approaches are rather complex. All vitrification experience world-wide has been in the stabilization of high-level wastes, which are measured discards from nuclear fuel cycles; therefore, vitrification is outside both domestic and international safeguards regimes. To safeguard vitrification, it is necessary to establish credible safeguards systems as well as the technologies to verify such a regime. In the U.S., the proposed use of defense facilities for vitrifying excess plutonium would require additional initiatives to bring the facilities into a safeguards regime and to allow bilateral or international verification.

Borosilicate glass, the glass form being considered for high-level waste vitrification in the U.S., poses some unique problems for maintaining continuity of knowledge of fissile content and independent verification. Nondestructive assays for safeguards measurements, especially those based on neutron detection, are not suitable for nonhomogeneous vitrified matrices that contain neutron absorbers. Other nondestructive assay techniques, such as gamma-ray spectrometry and calorimetry, are also not applicable to this matrix. Furthermore, the potential for a plutonium-enriched phase to separate or segregate in molten glass is considered a serious criticality safety concern.[5] Therefore, existing plant designs in the U.S. may not be appropriate for plutonium vitrification in glass matrix. Although the same technology can be engineered into a smaller plant, maintaining continuity of knowledge of plutonium in the glass matrix and verifications are beyond the capabilities of present-day safeguards technologies and nondestructive assay techniques.[14-17] Unfortunately, the vitrification option has been highly promoted by those who favor plutonium elimination but do not recognize the safeguards issues of this option.[18, 19]

If vitrification of plutonium is the option chosen, the only pragmatic approach to safeguards is through containment and surveillance, which is normally reserved for item accounting facilities. To perform containment and surveillance for a bulk handling facility such as the vitrification facility that contain high-specific activity radionuclides, it is essential to have a detailed facility design verification followed by maintenance of continuous presence of inspectors to follow every movement of materials through the facility. The final product - glass logs - is not suitable for independent verification of fissile content; therefore, sealed containers of vitrified glass must be the unit for verification. Tamper-resistant seals and remote verification of such seals are essential requirements for maintaining safeguards. Because the geologic disposal schedule is uncertain, maintaining continuity of knowledge until geologic internment and repository closure is a tedious and expensive undertaking. Many of these system requirements are not part of current safeguards technology, and a considerable initial investment is necessary to develop, demonstrate, and implement new technologies.

Long-Term Storage

Plutonium contained in a vitrified matrix may be stored in critically safe configurations in sealed containers after independent verification of declared quantities. For indefinite long-term storage, it may be preferable to use engineered geologic repositories rather than surface facilities. It is possible to design these geologic repositories so that access is almost impossible without detection. At present, the international safeguards community is already discussing the development of systems and technologies to maintain safeguards for geologic repositories of spent fuels.[20, 21] Each of these repositories would contain several hundred thousand tons of spent fuel and other strategically important materials. Some features of the integrated safeguards systems being considered for such repositories would also be appropriate to safeguarding the proposed repository for vitrified plutonium removed from nuclear warheads.

Measured containers of plutonium could be placed in a geologic repository and all access to the repository could be sealed under supervision. During construction and operational phases of the geologic repository, unannounced design verification of the repository and engineered facilities could provide additional deterrence to facility alterations or design changes. Because periodic verification is not a viable option after closure of the repository, systems can be designed to provide adequate assurance through containment and surveillance alone. To prevent access to the SNM containers in the repository through minimally intrusive methods such as borehole drilling, it is possible to design and build engineered features into the containers that will be placed in geologic repositories.

During the sealing of such repositories, remote monitoring systems similar to those now used to detect seismic activities could be installed to detect intrusions (large earth movements, mining operations, etc.) into the repository. Special devices could be designed to continuously monitor possible intrusions at these storage facilities and to instantaneously alert interested parties anywhere in the world through satellite-based communication system.[22] This scenario assumes that large-scale mining operations for mineral extraction or geologic exploration will not take place in the vicinity of these repositories.

SUMMARY

The weapons dismantlement and permanent withdrawal of fissile materials from U.S. and Russian stockpiles are activities that require stringent and independent verification regimes. Application of principles of international safeguards for nuclear materials is highly desirable to establish confidence among the parties involved and to establish credibility among the international community. Although nuclear material safeguards technologies are continuously improving, there are still major gaps in our ability to adequately verify some of the disposition options being considered for excess fissile materials from proposed weapons dismantlements. The vitrification option is one such option with no knowledge base to draw on, while conversion to spent fuel standard is the one option that can readily adapt existing safeguards technologies.

Vitrification was developed as part of nuclear fuel cycles to stabilize high-level wastes that result from spent fuel reprocessing. In safeguards parlance, the high-level waste is a "measured discard from a safeguards envelope" and vitrification has never been subjected to a safeguards regime. However, in the case of vitrifying plutonium for geologic disposal, a safeguards system is essential and must allow for independent and periodic verification. There are serious technological limitations in applying nondestructive assay techniques to achieve independent verification of plutonium in borosilicate glass. The alternative to quantitative measurement of fissile content is to maintain continuity of knowledge through a combination of containment and surveillance. Containment and surveillance ideally require facility design verifications and use of tamper-resistant and tamper-indicating seals, and in this case, ability to remotely verify the integrity of seals. Although a safeguards system for vitrification is conceivable, it will require considerable investment of resources, technology development, and demonstration before it can be applied to the vitrification process and associated facilities.

DISCLAIMER

The views expressed in this paper are solely those of the author and does not necessarily reflect the views of the Los Alamos National Laboratory or any of the agencies of the United States Government.

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Long-Term Retrievability and Safeguards for Immobilized Weapons Plutonium In Geologic Storage

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ABSTRACT

If plutonium is not ultimately used as an energy source, the quantity of excess weapons plutonium (w-Pu) that would go into a U.S. repository will be small compared to the quantity of plutonium contained in the commercial spent fuel in the repository, and the U.S. repository(ies) will likely be only one (or two) locations out of many around the world where commercial spent fuel will be stored. Therefore excess weapons plutonium creates a small perturbation to the long-term (over 200,000 yr) global safeguard requirements for spent fuel. There are details in the differences between spent fuel and immobilized w-Pu waste forms (i.e. chemical separation methods, utility for weapons, nuclear testing requirements), but these are sufficiently small to be unlikely to play a significant role in any U.S. political decision to rebuild weapons inventories, or to change the long-term risks of theft by subnational groups.

INTRODUCTION

Typical commercial reactors produce a few hundred kilograms of plutonium per year. Therefore the smallest spent-fuel repository (one reactor lifetime), and most reactor sites, prior to spent-fuel removal, contain plutonium inventories of at least a few metric tons. Upon reaching a threshold of a few metric tons, the proliferation risk from adding additional spent fuel at a storage location does not increase in proportion to the total plutonium inventory, because the inventory is already sufficient for the fabrication of several hundred nuclear explosives. This nonlinear relationship between the plutonium inventory and proliferation risk provides motivation for the "spent-fuel standard," where the proliferation risk from separated excess weapons plutonium is reduced by transforming it into a form protected by a radiation levels of similar magnitude to spent fuel, and ultimately utilizing or disposing of it in the same manner and location as a much larger quantity of commercial spent fuel.

Spent fuel repositories present long-term proliferation risks due to their fissile material inventories. The Internation Atomic Energy Agency has determined that geologic repositories containing fissile material will require safeguards until the material has been consumed or diluted sufficiently that it has become practically irrecoverable.[1] For spent fuel, this implies safeguards for time periods of several plutonium half lives, or over 200,000 years.[†]

[†] Linsley and Fattah 1 pp. 22 state further, "For spent fuel in repositories, the IAEA safeguards department's policy is to continue safeguarding after repository closure...The acceptance of a requirement for open-ended surveillance of spent fuel in repositories raises two issues: 1) a contradiction with one of the objectives of radioactive waste management, that is not to impose a burden on future generations; and 2) the troubling aspect of making economic provisions for an activity of unknown duration and, therefore, with a cost that cannot be estimated reliably."

Immobilized weapons plutonium, co-located in a repository with a much larger inventory of plutonium in commercial spent fuel, generates only an incremental increase in the proliferation risk from the repository. This paper reviews briefly the potential long-term risks associated with repositories for commercial spent fuel. Commercial spent fuel repositories are also discussed in greater detail elsewhere.[2] This paper then discusses the incremental risk associated with adding smaller quantities of immobilized weapons plutonium to the repository. The paper concludes that the incremental differences between immobilized weapons plutonium and commercial spent fuel are likely too small to influence significantly a U.S. political decision to break out and rebuild its nuclear weapon stockpile.

The appropriate technical questions in assessing the long-term security risks from geologic repositories are these:

- how easily (cost and manpower) could fissile materials be obtained by mining a repository, compared to alternative production methods;
- how easily might access to a repository be gained, and how difficult is detection;
- what would the duration of overt mining activities be before recovery and chemical separation of plutonium could begin;
- once spent-fuel retrieval starts, how rapidly could fissile material be produced;
- and what is the probability that functional nuclear explosives could be produced from the fissile material?

These questions must be compared with the corresponding questions for alternative methods of procuring fissile material, the most important alternatives being:

- diversion of material from an existing civilian nuclear power program;
- production using dedicated reactors and reprocessing facilities;
- and production using isotopic enrichment of uranium.

These questions must be addressed both for diversion by a national group and for theft by a subnational group.

Previous investigations of the performance of geologic repositories have focused primarily on the potential for releases of radioactive materials by natural mechanisms or accidental human intrusion.[§] Methods for monitoring geologic repositories for unauthorized diversion of plutonium have also been proposed and are likely to be relatively inexpensive and simple. Proposed safeguard methods include the analysis of periodically obtained satellite images and periodic inspection of the above-ground site by international inspectors,[1] and the use of remotely operated seismic stations to detect drilling or tunneling operations in the vicinity of the repository.[3] Booby traps or other devices to prevent access or make access difficult may be considered, although such devices will most likely be rejected, because they also prevent legitimate access to the repository. Yet to be decided are the types of mining, industrial, and other activities that must be restricted at repository sites, how far from the sites the activities must be

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[§] An extensive body of literature treats natural release mechanisms. For future human activities, an OECD NEA Working Group[4] states "Disruptive human actions can be divided into those in which the barrier system is intentionally disrupted and those in which it is inadvertently disrupted. Human actions leading to the release of radioactivity and committed intentionally, rather than inadvertently, can be considered the responsibility of the society that takes these actions. These intentional actions have not been considered quantitatively in past safety assessments, whereas actions in which the disposal system is inadvertently disrupted have received consideration in most programmes."

restricted, and what institutional and economic systems can be put in place to maintain adequate safeguards at multiple repository sites over time periods exceeding a hundred millennia.

LONG-TERM SAFEGUARDS FOR COMMERCIAL SPENT FUEL IN REPOSITORIES

Due to the threshold effect*, the long-term proliferation risks from commercial spent fuel will depend primarily on the number and location of repositories (and above-ground sites) where spent fuel is stored, rather than on the quantity of spent fuel in a given repository. If current plans are followed, there potentially may be as many as 25 repositories containing concentrated fissile materials.[2] For diversion by national groups, after radioactive barriers decay (i.e. after 300 years) the safeguard challenges increase, due to the relatively short duration of the overt activity required to divert a large quantity of plutonium. For subnational groups diversion can be prevented with relatively simple policing (assuming that the spent fuel has been placed in repositories rather than remaining in above-ground storage, and that continuous policing can be maintained indefinitely for all repositories).

Time Scales for Tunneling

The two parameters of primary interest for setting safeguard and security requirements for repositories are the maximum anticipated tunneling advance rate and the maximum distance around a repository at which surface facilities for tunneling might be located. Noise levels generated by tunneling activities are also important if acoustic monitoring for safeguards is contemplated.

Currently the fastest tunneling advance rates are achieved with full-face tunnel boring machines (TBM), which drive numerous disk-shaped cutting tools mounted on a rotating cutterhead against the tunnel face to excavate the tunnel. Buckets on the rotating cutterhead collect the debris, or muck, and carry it to the top of the machine, where the muck drops on a conveyor belt to be carried to the back of the machine. Either a long conveyor belt or rail cars then remove muck to the tunnel entrance.

Table I presents data for a selection of recent tunneling projects. Based on the current state of the art, a tunneling advance rate of 100 m/day is a credible upper bound in both granite and tuff using a tunnel boring machine (TBM). Initial TBM set up activities at the surface, which would include blasting of a starter tunnel of a few tens of meters depth, can be accomplished in 2 weeks. Conventional drill and blast methods could also be employed for the entire tunnel with significantly lower equipment costs, though advance rates would be reduced to under 5 m/day.

Table I Selected tunneling projects.[2]

Project	Date	Diameter (m)	Rock	Length (km)	Daily Shift Length (hr/day)	Average Daily Advance (m)	Maximum Daily Advance (m)
Oahe Dam	1955	7.8	shale	-	-	15.2	42.8
IVAR (Norway)	1989	3.5	phyllites	8.1	18	24.1	96.6
Kelano Power Tun.	1991	5.7	granite	6.1	14	28.9	80.5
SYAR (Utah)	1990	3.6	shale/sandstone	9.2	24	47.1	127.0

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* The threshold effect, as defined here, states that the incremental proliferation risk in increasing the spent-fuel inventory at a site from several reactor years (i.e. many hundreds of nuclear explosives), to hundreds of reactor years, is much smaller than the proliferation risk from storing the initial several reactor years inventory at the site.

Tunnel lengths of 10 km are now routinely constructed from a single point of surface access. TBMs are currently the most economical technology for excavating tunnels over 1 km in length; however, this is due primarily to reduced labor requirements and reduced interest charges from shorter construction time requirements. A low technology group may select drill and blast methods to reduce capital costs for equipment. Drill-and-blast methods typically would achieve advance rates of 2.5 m/day to 5.0 m/day. A new TBM of a size about 4 m diameter would cost 4 to 5 million dollars (1983 dollars). Two recent tunneling projects about 9 km long cost between 15 million dollars (1983) and 43 million dollars (1990), including extensive civil and other additional work. A state-of-the-art drilling jumbo for drill-and-blast excavation costs about 11 to 13 percent of that of a new TBM.[2]

In general, rapid tunneling is most feasible in "competent," unbroken rock. In particular, conditions such as excessive faulting can slow tunnel advance rates due to the looseness of the material and the difficulty in supporting and removing material from the tunnel face. Unforeseen adverse geologic conditions are the principal impediment to tunneling. Because potential repositories will likely be well characterized and information on the geological conditions will likely be available publicly (and more likely will be available to the national group which originally constructed the repository), groups mining a repository will be better prepared than many tunneling projects to minimize and mitigate delays from adverse rock conditions.

The U.S. Department of Energy is currently characterizing Yucca Mountain in southern Nevada to serve as a potential repository for U.S. spent fuel and high level waste. If constructed, the repository will be 200 m beneath Yucca Mountain, with access via a gently sloping tunnel entering from the side of the mountain. The shortest distance for mining of the repository would be to tunnel from the side of the mountain, requiring a tunnel length of 1 kilometer. The minimum time required to access spent fuel in a repository in Yucca Mountain, at the current state-of-the-art advance rate, would then be 24 days including 14 days surface set up time, assuming that difficulties with incompetent rock could be mitigated sufficiently. Current tunneling operations at Yucca Mountain have progressed more slowly than this estimate. The first 800 m of tunnel required 6 months. Advance rates increased substantially after that, reaching weekly averages of 30 m/day (24-hr shifts, 5 day/week) after the rock became less fractured and several modifications were made to the TBM. Using lessons learned from the current tunneling operations, a reasonable best estimate for the time required to access a repository at Yucca Mountain, with current TBM technology, is 6 months.

Because rock conditions would likely be more favorable, access into a granite repository would likely be faster than into the highly fractured tuff found at Yucca Mountain. A generic high-level waste repository would be located 500 to 1000 m below the surface in relatively flat terrain. For a tunnel with a 1:2 downward slope (27°) the required tunnel length would be 1120 m to 2240 m. At 100 m/day the time required to access spent fuel would be 25 to 37 days.

When the access tunnel reaches the repository horizon, the rate at which spent fuel can be removed will depend on the physical condition and layout of the spent-fuel canisters, the nature of the back-fill material in the repository tunnels, and the repository temperature. Many engineered aspects of repositories that would affect plutonium recovery rates remain to be decided. For a canister spacing of 5 meters, back-fill material can likely be removed to expose two to three canisters per day. A single 125-ton multi-purpose canister contains approximately 100 kg of plutonium, setting a plutonium recovery rate of a few hundred kilograms per day.

Potential advanced technologies include the subterrenne, a tunnel boring machine that melts and displaces rock using an electrically heated, refractory metal head. This type of tunneling machine has been demonstrated at small scale, using a 5 cm diameter device in laboratory and field trials, and using analytic and numerical models to study basic parameters of melting penetration.[5] The device performs well in variable ground conditions, stabilizing the tunnel walls with a glass lining. Debris can be removed in glass rod, glass pellet, and glass wool forms. Alternatively, in porous rock like tuff, small-scale experiments demonstrated that the higher density of the melt material allowed the melt to be entirely consolidated in the glass tunnel wall lining, eliminating the need to remove debris. By eliminating mechanical chipping and abrading, noise levels associated with rock melting can be reduced below those of conventional TBMs.

Reprocessing Old Spent Fuel

Reprocessing of old spent fuel to obtain repository-grade plutonium differs in two important respects from reprocessing of fresh spent fuel. First, the radioactivity of old spent fuel is much lower, which reduces shielding requirements, allows extensive direct-contact handling and maintenance, and hinders remote detection of reprocessing activities. Second, recovery of uranium in the spent fuel will not be required, simplifying the chemical processes required for plutonium separation. The technology employed for chemically separating repository-grade plutonium will be important, because separation rather than mining will most likely determine the maximum plutonium production rate.

The gamma dose rate from a typical 15-year old spent fuel assembly is 2000 rad/hr at 1 meter from the center of the assembly.[3] This gamma radiation level makes substantial shielding and remote handling necessary. Radiation levels drop substantially, however, as spent fuel ages. For young (15 years to 400 years) spent fuel the dose comes primarily from the decay of the fission product ^{137}Cs which generates hard 0.662 MeV gamma photons. Because ^{137}Cs decays with a 30-year half life, for the first several hundred years the gamma dose rate from a spent fuel assembly decreases by 50% every 30 years. Eventually the activity of ^{241}Am exceeds that of ^{137}Cs, emitting 0.059 MeV gamma photons. However, at this point the total gamma activity has dropped by almost four orders of magnitude from the activity of the 15 year old spent fuel. Then the gamma dose rate from spent fuel is under 1 rad/hr at one meter.

Several significant advantages accrue from the reduced radiation levels in old spent fuel compared to young spent fuel. The first is the potential for direct contact handling of the spent fuel itself, which will emit under 1 rad/hr. The duration of direct contact and the efforts to minimize doses will depend on the total doses the workers are willing or required to accept. Workers willing to accept these doses could perform direct contact work on old spent fuel for periods approaching 100 hours per year. With modest automation this would permit a single worker to cut open many spent fuel canisters and manually transfer fuel assemblies, particularly if rudimentary precautions were taken to minimize doses to the worker.

Reduced radiation levels also eliminate the need for massive shielding of reprocessing equipment for operation and maintenance. Reprocessing plants for young spent fuel use massive concrete walls over 1 m thick and remotely operated cranes to minimize worker doses, each contributing substantially to the cost of a reprocessing facility. With old spent fuel some direct contact work on equipment could be permitted, particularly if rudimentary measures were taken to reduce doses. Cold startup testing using simulated, nonradioactive materials could also be reduced or eliminated. Reprocessing equipment could be housed in standard industrial buildings, reducing costs and making it substantially easier to keep reprocessing activities covert. The absence of significant quantities of 10.76-yr half-life ^{85}Kr would further complicate efforts to detect covert reprocessing. Releases of ^{85}Kr from reprocessing plants have, in the past, provided considerable information on production of separated plutonium.[3]

The cost of a reprocessing facility devoted to separating plutonium for weapons can be lower than for a commercial reprocessing facility as noted in an Office of Technology Assessment (OTA) proliferation study, because of simpler design, particularly when health and safety standards are reduced.[6] Their cost estimate for a small dedicated reprocessing facility was $25 million (1977 dollars), from a range of estimates from one million to $70 million. This plant would have limited capacity, tens of kilograms of plutonium per year. The cost of a similar facility for old spent fuel would be significantly lower due to the lower radiation levels and the capability for more direct contact maintenance. Alternatively, an old-spent-fuel reprocessing plant of significantly greater capacity could be built for the same cost as the smaller facility studied by the OTA.

The low radioactivity of old spent fuel increases the probability that a group would remove old spent fuel not to separate the plutonium, but rather to sell directly to another group. Several countries have demonstrated the willingness to spend large sums of money to acquire fissile materials for covert weapons programs. It would not be unreasonable to expect that a market for illicit old-spent-fuel assemblies could exist in the future.

Comparisons to Dedicated Reactors and Enrichment Facilities

As discussed here, plutonium can be mined at rates as high as several hundred kilograms per day. By contrast, a small 25MW_t graphite-moderated reactor, like that used by the North Koreans, can produce 5.0 kg of plutonium per year at a 60 percent capacity factor.[7] The 200MW_t North Korean reactor, not yet operational, could produce about 40 kg per year of plutonium. The OTA estimated that a dedicated 400 MW_t reactor, capable of producing about 100 kg/year of plutonium, with an associated reprocessing facility, would require 50 to 75 engineers, 150 to 200 skilled technicians, 5 to 7 years from start of design to first output of plutonium metal, and capital costs from $175 million to $350 million (1977 dollars).[6]

Four primary techniques are available for isotope separation: gaseous diffusion, centrifuge, calutrons, and laser isotope separation. Gaseous diffusion plants are very large, require the largest energy input per SWU, and require a massive industrial infrastructure. Centrifuges require smaller energy input per SWU, and can be smaller in scale than diffusion plants. Laser isotope production can be very efficient and can greatly reduce the number of stages required for separation, however the technology is also difficult and has not been implemented commercially. The nominal mass of highly enriched ^{235}U required for an explosive is roughly three times the mass of ^{239}Pu, about 15 kg, requiring between 3000 and 3500 SWU to produce, depending on the depleted uranium tails assay. The OTA estimated the cost of a 60,000 SWU/yr centrifuge plant to be $120-$240 million (1977 dollars).[6]

COMPARISON OF IMMOBILIZED w-Pu AND OLD COMMERCIAL SPENT FUEL

The incremental proliferation risks from adding immobilized weapons plutonium to a much larger quantity of commercial plutonium in a U.S. repository depend primarily on the relative ease of recovery and chemical processing of the two waste forms, and the relative utility of the recovered plutonium for weapons use.

As discussed by others in the workshop, the chemical separation of plutonium from an immobilization waste form is relatively straight-forward, for a national group. The difficulty is of similar magnitude to that for spent fuel (if radiation barriers are present, it becomes substantially easier otherwise), so this paper reaches the preliminary conclusion that the relative difficulty of chemical separation would not influence any U.S. political decision to break out and rebuild nuclear weapons.

The isotopic composition of the plutonium in reactor-grade plutonium differs significantly from that in weapons-grade plutonium. A more difficult question is whether the higher quality of the immobilized weapons plutonium, compared to commercial plutonium, would significantly affect any political decisions related to proliferation. This question can not be answered definitively here, but the relevant information available in the open literature is summarized.

Isotopic Compositions of Commercial and Weapons-Grade Plutonium

The isotopic composition of commercial plutonium mined from a repository will differ substantially from the composition of plutonium generated expressly for weapons use. Weapons-grade plutonium is generated by neutron capture in ^{238}U during a relatively short residence in a nuclear reactor, giving the approximate isotopic composition shown in Table II. Spent fuel from power reactors typically remains in the reactor for much longer time periods, so that neutron capture generates significant quantities of the higher plutonium isotopes, while (n,2n) reactions create small but important amounts of ^{238}Pu. The recovery of plutonium by reprocessing and recycle of plutonium in light water reactors as mixed oxide fuel (MOX) further increases the fractions of higher plutonium isotopes for MOX-grade plutonium.

A spontaneous fission reaction of an even plutonium isotope releases about 3 neutrons, and likewise, reactions of plutonium alpha decay particles with light elements can generate neutrons. Spontaneous fission occurs at higher rates in reactor-grade plutonium, over six times the rate for weapons-grade plutonium. Figure 1 shows that spontaneous fission neutron generation rates per unit mass of total Pu decline only slightly before 20,000 years as ^{240}Pu decays, and then begin to increase substantially as ^{239}Pu decays and the remaining fraction of long-lived ^{242}Pu grows.

In plutonium separated from spent fuel, the radioactive decay of the plutonium isotopes, in particular ^{238}Pu, creates an internal heat source. The accumulation of ^{241}Am from decay of ^{241}Pu gradually increases the internal heat generation, balanced by the decay of ^{238}Pu and the eventual decay of ^{241}Am. For instance, the heat generation from spent fuel reprocessed at 10 years (with isotopic composition in Table III) is initially 10.5 W/kg, grows to 13.7 W/kg at 10 years, and peaks at 16.8 W/kg at 45 years. For weapons-grade plutonium the effect of ^{241}Am peaks at 64 years. Figure 3 shows that the heat generation is substantial for reactor-grade plutonium, but for plutonium separated after spent fuel ages the heat generation declines, eventually dropping below the value for new weapons-grade plutonium. Here such old plutonium from spent fuel is referred to as "repository-grade" plutonium (i.e. over 300 years old).

Table II Isotopic composition of various plutonium grades[3].

Grade	Isotope				
	Pu-238	Pu-239	Pu-240	Pu-241[a]	Pu-242
Super-grade	-	.98	.02	-	-
Weapons-grade	.00012	.938	.058	.0035	.00022
Reactor-grade[b]	.013	.603	.243	.091	.050
MOX-grade[c]	.019	.404	.321	.178	.078
FBR Blanket[d]	-	.96	.04	-	-
Repository-grade[e]	.0013	.676	.266	10^{-8}	.057

[a] ^{241}Pu plus ^{241}Am

[b] Plutonium from low-enriched uranium PWR spent fuel with 33 megawatt-days/kg burn up, stored 10 years before reprocessing

[c] Plutonium from 3.64 percent fissile plutonium mixed-oxide (MOX) spent fuel produced from reactor-grade plutonium, with 33 megawatt-days/kg burn up and 10 years storage before reprocessing.

[d] Fast breeder reactor.

[e] Plutonium from low-enriched uranium PWR spent fuel with 33 megawatt-days/kg burn up, stored 300 years before reprocessing

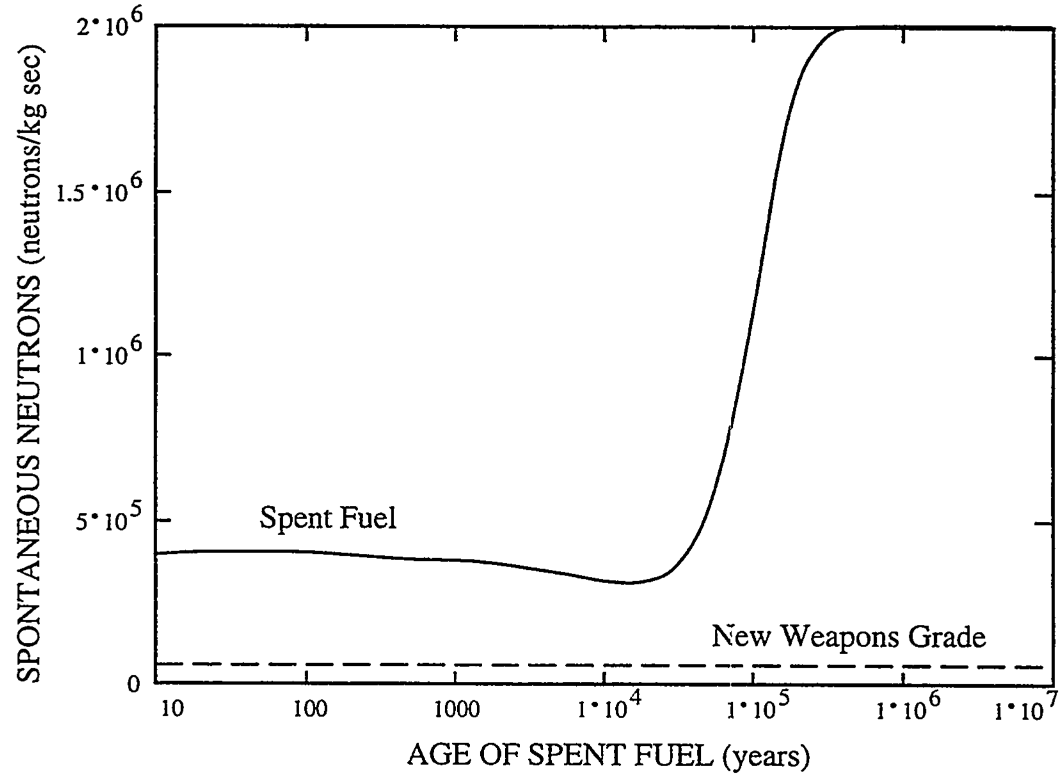

Fig. 1 - Spontaneous fission neutron rate from aged reactor-grade plutonium. Jump at 10^5 years occurs due to decay of Pu^{239}.

Relative Utility For Use In Nuclear Explosives

This section summarizes the information on nuclear explosive design which is available in the open literature and is relevant to the comparison of the utility of plutonium from commercial spent fuel and immobilized weapons-grade plutonium. Different grades of plutonium have different isotopic compositions (Table II), which modify their utility for use in nuclear explosives.

The probability that a neutron will cause fission of an isotope is proportional to the fission cross section of the isotope. Nuclear explosives are designed to rapidly assemble a sufficiently dense and large mass of fissile material to be supercritical with fast neutrons. The only uranium or plutonium isotope with a fast neutron fission cross section too small to be useful in nuclear explosives is ^{238}U. When enriched to 20% ^{235}U, the bare sphere critical mass for U is 850 kg, which is considered too large to construct a nuclear explosive of practical weight. All of the isotopes of plutonium have similar fission cross sections for fast neutrons, and the bare-sphere critical mass of any mixture of isotopes of plutonium is relatively small. Therefore, in principle, plutonium of any isotopic composition can be used for nuclear explosives.

The primary difficulties in nuclear explosive design introduced by the use of plutonium from commercial spent fuel arise from higher spontaneous neutron generation rates, higher heat generation rates, larger critical masses, and increased gamma radiation from the ^{241}Pu decay product ^{241}Am. The problems of high heat generation rate and ^{241}Am gamma radiation disappear as reactor-grade plutonium ages to become repository-grade plutonium.

To employ plutonium in a nuclear explosive, chemical high explosive (HE) is typically used to rapidly implode a solid sphere or hollow spherical shell of plutonium from a subcritical to a supercritical geometry. The amount of plutonium required is less than the amount required to create a critical mass with a bare sphere, both because any materials surrounding the core can reflect neutrons back, and because higher than normal plutonium densities can be achieved. Compared to the 10-kg bare-sphere critical mass for plutonium-239, the fully-tamped critical mass is 4.4 kg.

Premature Initiation

Neutrons generated by spontaneous fission or by alpha reactions with light elements after an imploding plutonium pit reaches a critical configuration, but before the pit reaches the full design density, have some probability of initiating a chain reaction prematurely, before an intentional pulse of neutrons is released to initiate the chain reaction. Premature initiation reduces the yield of the nuclear explosive below the design value, though simple analysis shows that the energy release is still substantial, and at worst the yield is likely to be in the kiloton range.[8] Such crude explosives would still be dangerous in the hands of subnational groups. For a national group a high probability of premature initiation would likely be considered unacceptable for weapons, particularly if the fission explosive was being used to drive a fusion-fission secondary explosive.

For a national group, however, implosion designs are likely available that are sufficiently fast to reduce the probability of premature initiation to an acceptable level. The recent NAS study on weapons plutonium disposition, citing a classified study,[9] states explicitly that "with a more sophisticated design, weapons could be built with reactor-grade plutonium that would be *assured* of having higher [than fizzle] yields" (italics added).

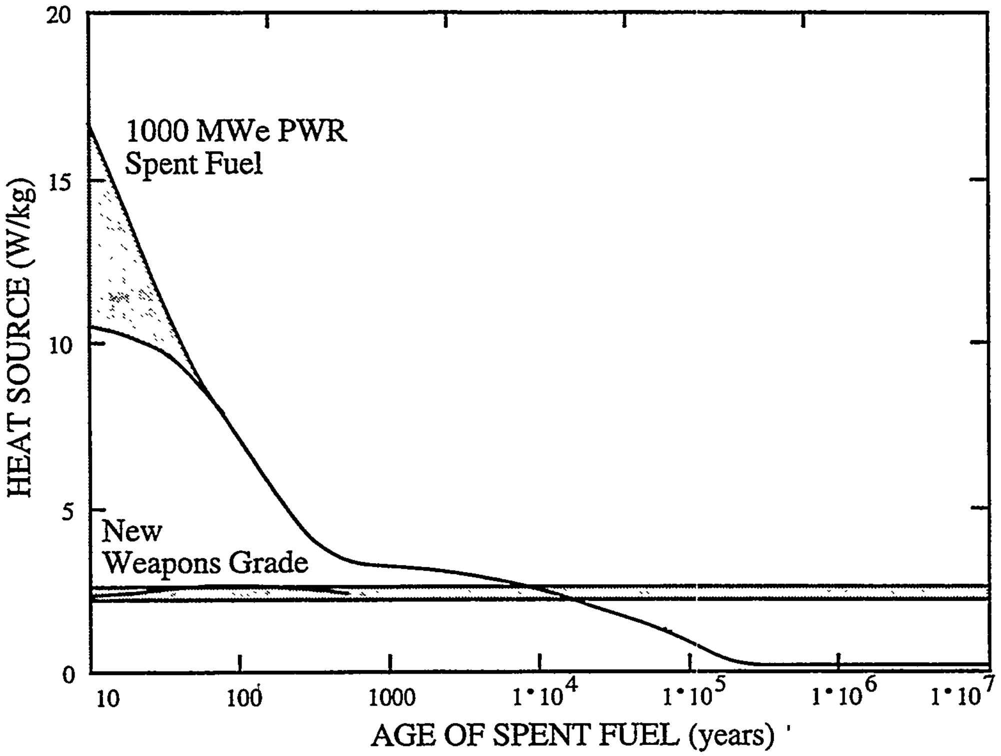

Fig. 2 - Heat generation rate from repository-grade plutonium (actual heat generation lies in shaded region and depends on the spent-fuel age when reprocessed).

Heat Generation

The radioactive decay of the plutonium isotopes creates an internal heat source substantially larger in reactor-grade plutonium than weapons-grade. For instance, a 4 kg weapons-grade plutonium pit would generate around 10 W, while an 8 kg reactor-grade plutonium pit (heavier to compensate for slightly smaller fission cross sections) would initially generate 85 W, increasing to 135 W at 45 years and then declining. This difference in heat generation presents a significant design problem, due to the relatively low thermal conductivity of the high explosive which surrounds the pit. Steady-state heat removal requires a substantial temperature difference between the pit and the surrounding environment. For a 10-cm-thick high-explosive shell an acceptable 26°C is required for weapons-grade plutonium, but the temperature difference would rise to between 225 and 360 °C for reactor-grade plutonium, an unacceptable value. Technical means can be envisioned to mitigate the problem of heat removal, such as using high-conductivity metal like aluminum to create a heat bridge across the high explosive [8], but it is reasonable to expect that current weapons designs would require significant modification to cope with the heat generation. The heat generation problem disappears within 300 years as shown in Figure 2, and becomes insignificant for most of the 200,000 year period that proliferation risks persist.

Gamma radiation

A final concern for handling plutonium centers on the shielding requirements for the 0.059 MeV gamma photons emitted by ^{241}Am. This gamma radiation builds up after plutonium is chemically separated, as 14.4-yr half-life ^{241}Pu decays, at substantially higher rates in reactor-grade plutonium due to higher initial ^{241}Pu concentrations. However, repository-grade plutonium has negligible concentrations of ^{241}Pu compared to weapons-grade plutonium (Table III), so that contact gamma radiation from repository-grade plutonium would be less hazardous than for weapons grade plutonium. For either plutonium grade, as long as weapons fabrication is performed shortly after reprocessing, the gamma radiation is not a significant problem.

Performance and Testing Requirements

Though the primary disadvantage of reactor-grade plutonium--large internal heat generation--disappears as it ages to become repository-grade plutonium, it is important to note some of the other potential liabilities to the use of repository-grade plutonium that arise from the substantial concentrations of even isotopes of plutonium. An implosion design that provides a given implosion velocity and degree of compression will reach a lower maximum multiplication factor k_{max} with repository-grade plutonium than with an equal mass of weapons-grade plutonium due to the smaller neutron fission cross sections. Put another way, similar implosion designs will provide a somewhat lower yield using repository-grade plutonium than weapons-grade plutonium, even if preinitiation is avoided.

A second disadvantage relates to testing requirements. It is generally agreed that fission weapons can be designed to have high reliability, though uncertain yield, without testing. Only testing of the HE implosion system is required, with appropriate x-ray diagnostics, to confirm that the desired compression and geometry of the core material is achieved.[6,10] However, for national groups reconstituting a stock of thermonuclear (fission-fusion) weapons which had originally been designed to use weapons-grade plutonium to drive the secondary fusion reaction, testing of the fission triggers could likely be required if repository-grade plutonium were substituted in the design. Such testing would slow down the introduction of repository-grade plutonium-based thermonuclear weapons, although national groups could conceivably conceal the tests of the fission triggers.[§§] A third disadvantage with repository-grade plutonium is the probability that the isotopic composition will likely be heterogeneous between batches, varying with the degree of burn up in the spent fuel assemblies processed, whereas weapons-grade plutonium is produced to have uniform isotopic composition.

CONCLUSIONS

Plutonium stored in concentrated forms (either spent fuel or immobilized w-Pu) remains a proliferation risk for a very long time period, due to the long (24,400 year) half life of ^{239}Pu. For national groups repository access requires several weeks to several months for tunneling activities, at a cost of a few tens of millions of dollars. Subsequent plutonium production rates are limited primarily by chemical separation capacity, which becomes progressively less expensive and easier to conceal as radiation levels decline. Because production rates are significantly higher and costs lower than for dedicated reactors or enrichment facilities, geologic repositories will provide attractive sources of fissile materials for nuclear explosives for roughly 200,000 years.

Proliferation risks from stored fissile materials (i.e. in repositories, monitored retrievable storage, and at operating and decommissioned power reactor sites) will depend primarily on the number and location of storage sites, rather than the absolute quantities of fissile material, due to the very large quantity of plutonium generated by even a single power reactor. Immobilized excess U.S. weapons plutonium will create only a small perturbation to the plutonium inventory in the U.S. repository, which will hold approximately half of the world's commercial spent fuel.

[§§] The Department of Energy declassified a large quantity of previously secret information on nuclear weapons in 1993, including data on 252 secret nuclear tests. "One point of concern is that the 18 unannounced tests that were made during the Reagan and Bush Administrations do not seem to have registered on the sensitive seismological monitoring equipment then in place." [11]

Preliminary Conclusions for Subnational Groups

- The U.S. spent-fuel repository containing immobilized weapons plutonium will likely be only one of many locations where long-term storage of plutonium occurs, thus contributing only a small fraction of the total risk of theft by subnational groups.

- Nuclear explosives of significant energy release can be constructed from either weapons, reactor, or repository-grade plutonium, reducing further the incremental risk from storage of immobilized weapons plutonium in the spent-fuel repository.

Preliminary Conclusions for National Groups

- Any future U.S. effort to manufacture nuclear weapons would likely use plutonium from the U.S. repository, rather than restarting or building new dedicated production reactors.

- Functional weapons can be fabricated from immobilized w-Pu, and likely from reactor-grade Pu.

- Use of reactor-grade plutonium would likely require modification of current weapons designs, and nuclear testing.

- The incremental effort to use repository-grade plutonium to reconstitute a large weapons stockpile would likely be relatively small compared to the overall effort required to rebuild the weapons and delivery systems.

- The availability of immobilized weapons-grade plutonium would not likely be a significant influence in any U.S. political decision to break out and rebuild a large weapons stockpile.

DISCLAIMER

The views expressed in this paper are those of the author(s) and so not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

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A Perspective on the Proliferation Risks of Plutonium Mines

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ABSTRACT

The program of geologic disposal of spent fuel and other plutonium-containing materials is increasingly becoming the target of criticism by individuals who argue that in the future, repositories may become low-cost sources of fissile material for nuclear weapons. This paper attempts to outline a consistent framework for analyzing the proliferation risks of these so-called "plutonium mines" and putting them into perspective. First, it is emphasized that the attractiveness of plutonium in a repository as a source of weapons material depends on its accessibility relative to other sources of fissile material. Then, the notion of a "material production standard" (MPS) is proposed: namely, that the proliferation risks posed by geologic disposal will be acceptable if one can demonstrate, under a number of reasonable scenarios, that the recovery of plutonium from a repository is likely to be as difficult as new production of fissile material. A preliminary analysis suggests that the range of circumstances under which current mined repository concepts would fail to meet this standard is fairly narrow. Nevertheless, a broad application of the MPS may impose severe restrictions on repository design. In this context, the relationship of repository design parameters to ease of recovery is discussed.

INTRODUCTION

According to current plans, U.S. surplus weapons plutonium will be converted to a form as inaccessible as the plutonium contained in commercial spent fuel (the "spent fuel standard") and will eventually be disposed of, together with a much larger quantity of commercial spent fuel, in a mined geologic repository, when (or if) one becomes available. [Note: for the purposes of this paper, all materials meeting the "spent fuel standard" will be referred to as "spent fuel."] The repository will be maintained in a "retrievable" state for 100 years. After this period, all access tunnels and ventilation shafts will be backfilled and sealed, and all supporting facilities will be decommissioned and dismantled. The repository will then be considered "irretrievable," in the sense that recovery of the emplaced material would then require much greater cost and effort.

The concept of geologic disposal of wastes containing plutonium has come under increasing criticism by some analysts from a non-proliferation standpoint, who argue that repositories will become attractive sources of large amounts of weapons-usable fissile material in the future. [1] This argument has two main components:

- The plutonium emplaced in repositories will be recoverable assuming sufficient time, effort and financing, even after the repository has been made "irretrievable." Repositories therefore will have to be safeguarded for hundreds of thousands of years, until the plutonium has decayed to a very low concentration. However, it is impossible to guarantee that safeguards can be maintained over such a long time frame. Furthermore, the ability to employ material accountancy, a cornerstone of International Atomic Energy Agency (IAEA) safeguards, will effectively be lost following closure of the repository.

- The attractiveness of repository spent fuel to a proliferant will increase with time in several ways. First, the penetrating radiation barrier that renders spent fuel extremely hazardous to handle will decay to a very low level after a few centuries of cooling, so that the material can be reprocessed for much lower cost than spent fuel of more recent vintage. Second, the time and effort necessary to recover the fuel from the repository will decrease as mining technologies improve. Third, the isotopic quality of the plutonium in commercial spent fuel will approach (although never quite reach) that of "weapons-grade" with time.

While this issue has been raised most often by promoters of reprocessing, such as an American Nuclear Society (ANS) special panel on the "Protection and Management of Plutonium, [2] it has also been noted in less partisan analyses. The National Academy of Sciences (NAS) recommended that "follow-on studies should continue on the longer-range questions of whether and how the residual security risks of ... plutonium should eventually be reduced beyond the spent fuel standard," though it also emphasized that this endeavor should not distract attention from the more immediate problem of reducing the risks posed by separated plutonium.[3]

Some observers have argued that this problem can only be avoided by foregoing geologic disposal of plutonium entirely and maintaining it in retrievable storage, while redirecting resources toward the development of technologies that can achieve the near-total "destruction" of plutonium.[4,5] Others argue that disposal in deep boreholes, rather than in mined repositories, can provide a more effective impediment to future recovery.[6]

However, replacing the current plan for geologic disposal of spent fuel with one of these even less well-established approaches would represent a drastic response to a highly uncertain future risk. Furthermore, some of the proposed cures would be worse than the "disease"; for instance, the plutonium "destruction" schemes require the large-scale separation of plutonium from spent fuel and would result in a dramatic increase in proliferation risks in the near-term. Clearly, some objective means are needed for evaluating whether the prospect of future "plutonium mines" really poses an unacceptable long-term risk and, if so, for determining how current plans for geologic disposal of spent fuel must be modified to achieve a reasonable level of security.

The Material Production Standard

As a first step, we propose a benchmark for analyzing the proliferation risks of spent fuel disposal, the *material production standard (MPS): any long-term plan for management of nuclear wastes with fissile content should be designed so that, under a set of plausible demand scenarios, a proliferant group (either national or sub-national) would find it essentially as difficult to recover the fissile material as to obtain it from the least accessible alternative source (e.g. new production).*

This definition is conceptually similar to the idea of the "spent fuel standard," introduced by the NAS to evaluate disposition options for separated plutonium.[7] It can be used as a basis for rejection of costly spent fuel disposition options which would render plutonium recovery far more difficult for a proliferant than new production, and therefore would achieve only a marginal increase in overall security. Similarly, it can identify options that, if pursued, would leave spent fuel relatively vulnerable to diversion.

In defining the MPS, one must determine which alternative source of fissile material is the most appropriate for comparison to repository mining. This depends to some extent on the future of commercial nuclear power, as the following discussion illustrates.

The standard that a repository must meet can be less stringent if one assumes that a nation will continue to operate nuclear reactors and other nuclear fuel cycle facilities. Such a nation will always have a ready supply of spent fuel available, either in retrievable storage or in the reactor cores. (If the nation operates commercial reprocessing plants as well, it will also possess stockpiles of separated plutonium.) Under these circumstances, it is apparent that spent fuel in a sealed geologic repository would be relatively unattractive with respect to both state-sponsored and sub-national diversion, assuming that repositories were safeguarded at a level consistent with other stages of the fuel cycle.

On the other hand, the relative attractiveness of spent fuel in a repository would be greatest in the context of a "nuclear-free" future, in which nuclear power had been phased out and neither operable reactors nor retrievable spent fuel storage facilities existed. In this case, the only means of acquiring spent fuel other than mining the repository would be the construction and operation of production reactors and associated front-end facilities (e.g. uranium mining and fuel fabrication) from scratch. The assumption of a nuclear-free future is therefore the most conservative one and is adopted here.

The most difficult part of this analysis, as in other aspects of repository performance assessment, is the task of making reasonably credible observations while minimizing speculation about the future, such as technological advances, political systems and human behavior. Use of a relative standard (e.g. the MPS) may be more sensible than an absolute standard (the IAEA's "practicable irrecoverability" criterion, discussed below), because any assumptions one makes about the future must apply equally to both pathways. For instance, one cannot expect that technological improvements that may reduce the difficulty of the mining route will occur without commensurate technical advances that may be useful for the new production route, such as the development of advanced materials.

Because of the need to avoid excessive speculation about the future, this analysis must necessarily be limited in scope. However, it can be used to provide insight into some questions, including:

- From a non-proliferation standpoint, how long after reactor discharge should spent fuel be kept in monitored retrievable storage?
- Is it indeed necessary to maintain long-term safeguards on spent fuel, and if so, does this constitute a "fatal flaw" of the geologic repository concept?

- Under what circumstances will spent fuel repositories pose unacceptably high proliferation risks? Are there ways of mitigating those risks?

Resource Needs for New Production

The development cost of a dedicated plutonium production capability from scratch depends on the size of program desired. For reference purposes, one may define three categories of plutonium production (all costs are given in 1992 dollars):

- A "minimum acquisition" plutonium program, based on a gas-graphite production reactor rated at 30 MW-thermal (MWt) and capable of producing around 8 kg of plutonium per year. This program is estimated to require a capital cost of $120 - $300 million, of which $35 - $100 million is the construction cost of the reactor.[8] The average cost of the reprocessing component is $15 - $40 million, or about 12% of the total. The time for construction of this project is estimated to be 3-4 years, with a crew of 100.

- An "intermediate acquisition" program capable of producing around 100 kg of plutonium per year. One program, based on a 400 MWt reactor, was estimated to require a capital investment in the range of $400 million to $1 billion (for the reactor alone), with a cost overrun of up to 100% possible in the event of delays. The construction time for this reactor is estimated to be 5-7 years, requiring a staff of 200-300.[9] The cost of the reprocessing plant in this case was not given; scaling from the previous example (40% of the reactor cost) yields a value of $160 - $400 million.

Actual construction times could be considerably shorter than these estimates, as is apparent from the original historical example of "new production." The 250 MWt B-Reactor at Hanford, the first plutonium production reactor of the Manhattan Project, was completed in about a year; 15 months later, two other reactors had begun operation as well. Together, these three reactors were producing plutonium at a rate of about 100 kg per year within two years after the start of construction.[10] Thousands of workers, however, were employed in these projects.

- A "maximum acquisition" plutonium program, in which the desired production rate is limited only by the resources available. For example, during the Cold War, multiple 2150 MWt reactors were constructed at the Savannah River Site, each capable of producing about 600 kg of plutonium per year. Scaling the previous cost estimates with a factor of 0.7 implies that the cost of each reactor of this size to be between $1.3 billion and $3.2 billion. The average time between start of construction and startup of these reactors was under three years.[11]

Capital Costs and Development Times for Repository Mining

During the period that a mined geologic repository is maintained in a retrievable condition, the spent fuel it contains will be approximately as accessible as spent fuel located in interim, above-ground storage sites. After the repository is closed, however, the effort necessary to regain full access to its contents will be, in general, on the order of the effort that was originally required to construct and load the repository (although specific design choices may make retrieval either easier or harder than emplacement, as discussed below). Retrieval of spent fuel from a closed repository would entail assembly of the necessary equipment on-site, construction of new surface support and material handling facilities, and reexcavation of the geologic formation.

Large underground mining operations today typically require capital investments on the order of a few hundred million to well over one billion dollars (with the higher figure reflecting isolated sites and/or difficult climates),[12] and development times of 2-5 years before production can begin.[13]

Excavation of a spent fuel repository would require a similar level of investment. For example, the development costs of the original (1988) design of the Yucca Mountain repository include $200 million for preparation of the site, $320 million for constructing the shafts and ramps, initial excavations at the repository level, and underground service systems, and $510 million for construction of surface facilities, for a total of over $1 billion (all costs in undiscounted 1992 dollars).[14] (Lest one think that these values are artifacts of fiscal inefficiencies of the U.S. radioactive waste program, it should be noted that the estimated underground costs in the U.S., when normalized to the volume of rock excavated, are the lowest among six countries surveyed.[15])

One may argue that these costs are based on rigorous standards for occupational and environmental safety which would probably not be observed by those seeking to acquire fissile material rapidly. However, there are limits to the extent to which one can skimp on mine safety and still guarantee a given level of productivity. A catastrophic accident could lead to extensive loss of personnel and set back the project by several years. Even if the cost were reduced by a factor of two or three, it would still exceed a few hundred million dollars.

Although the theoretical maximum advance rates of modern drilling methods are quite high, the minimum time necessary to gain access to a repository will probably be determined by the significant effort involved in the on-site assembly and preparation of equipment. For example, the tunnel boring machine (TBM) being used to drill the Exploratory Studies Facility (ESF) at the Yucca Mountain site was brought there in 52 separate truckloads. One engineer has estimated that one to two years would be needed to assemble a large TBM and auxiliary equipment, and to prepare a platform to launch the drilling.[16]

Furthermore, these costs and advance rates do not reflect the unusually harsh conditions that may be experienced when mining a filled spent fuel repository, as opposed to a conventional mineral deposit. Even after a few hundred years, when the gamma radiation levels have dropped substantially, the thermal conditions may remain severe. For instance, in the "extended hot, dry" scenario being considered for a repository at the Yucca Mountain site, waste package surface temperatures would remain above 100 C for several thousand years, and near-field rock temperatures would remain above 80 C for 10,000 years.[17] The maximum ambient temperature that could be tolerated by workers is about 35 C. Temperatures in the deepest mines today reach 55 C, and therefore extensive ventilation and cooling systems must be employed, capable of discharging several megawatts of heat. The additional infrastructure necessary will increase both the capital outlay and the detectability of the operation by providing both visual and thermal signatures (as discussed below).[18]

The above analysis suggests that for the "minimum" and "intermediate" acquisition scenarios, both the spent fuel mining route and the new production route would require capital investments in the range of several hundred million to over one billion dollars, and a development time of 1-5 years. In these cases, therefore, the mining route does not appear to have a decisive advantage with respect to these criteria.

Repository Production Rates

If one considers scenarios in which the demand for plutonium increases above one tonne a year, the capital cost of new production will rise as a function of demand much more rapidly than that of mining, increasing the relative attractiveness of the latter route.

The rate of removal of spent fuel from a repository, which will be on the order of the rate of emplacement, is controlled by the inventory of each waste canister and the spacing between canisters. Because of the high concentration of plutonium in commercial spent fuel and the limited space available for emplacment, production rates from a large plutonium mine could be quite high. For example, the rate of loading of the planned Yucca Mountain repository is currently anticipated to be 3000 tHM of spent fuel a year. Assuming equal rates of retrieval and emplacement, this mine could produce 25 tonnes of plutonium per year. More than forty large Savannah River-type reactors would have to be built to attain a level of production equivalent to the mining route, at a much greater capital cost. Therefore, current repository designs would fail to meet the MPS under scenarios in which a nation in a "nuclear-free world" suddenly wants to begin accumulating nuclear weapons at a rate of thousands per year. However, it remains to be determined whether this scenario is sufficiently credible to warrant concern.

The Attractiveness of Aged Spent Fuel

The "self-protecting" field of penetrating radiation emitted by spent fuel decreases steadily with time, and effectively disappears after several hundred years of cooling. After this period, spent fuel could be processed in a contact-handled glovebox facility, rather than in a shielded, remotely-operated reprocessing plant. It has been suggested that this would provide a strong incentive for a proliferant to mine long-cooled spent fuel from a repository.

However, when compared to new production, this advantage is not as overwhelming as it may first appear. The burnup of spent fuel from dedicated gas-graphite weapons-grade plutonium production reactors is typically quite low, below around 800 MWD/t.[19] This is around fifty times smaller than the typical burnup of commercial fuel.

For low and intermediate production rates, low-burnup fuel can be processed in small, rudimentary reprocessing cells known as "caves," provided the operators are willing to accept high but not debilitating radiation doses. These cells, which date from the 1950s, utilize primitive, mechanically operated remote-handling devices known as ball-joint manipulators.[20] The difference in cost between a small cave and a glovebox facility would probably not be great enough to influence the decisions made by a proliferant group.

The highest whole-body radiation dose that employees could tolerate without a significant loss of efficiency, taking into account the effect of fractionated dose, is around 3 Gy/yr, or about 15 mGy/hr for a standard work-week. This level of exposure is an order of magnitude below that at which acute prodromal symptoms would appear.[21] However, an operator in this environment will receive just under the LD_{10} dose annually, which means that on average, ten percent of those exposed will succumb to radiation sickness each year. (Whether or not this is an acceptable loss depends on the total number of available personnel).

After two years of cooling, each tonne of uranium gas-graphite reactor fuel, irradiated to a burnup of 800 MWD/t, will contain about 720 grams of weapons-grade plutonium and about 4000 curies (Ci) of hard (greater than 0.4 MeV) gamma activity. In order to produce 100 kg of plutonium per year, about 0.5 tonnes of fuel would have to be reprocessed per day (assuming 80% plant availability). This quantity of fuel could be subdivided into five batches per day, each containing about 400 Ci of hard gamma activity. The unshielded exposure from a point source of this strength at a distance of 50 cm is over 5 Gy/hr; to reduce this to the target value of 1.5 mGy/hr would require attenuation by a factor of 3300. This can be achieved with 8 cm of lead or 15 cm of dense lead glass. These dimensions are well within the constraints of process cells of the type described above.

At higher production rates, small, locally-shielded caves would no longer be feasible for reprocessing production-reactor fuel, and larger plants, utilizing remote operation and maintenance, would have to be employed. Thus the comparative attractiveness of repository-grade spent fuel is maximized under these circumstances. However, at high production rates, the cost of a facility for reprocessing aged spent fuel would increase as well, because of the need to provide greater containment of alpha particles and to mitigate the increased risk of a criticality accident.

Dectectability and The Role of Long-Term Safeguards

According to INFCIRC/153, the model safeguards agreement for NPT-member states, safeguards can be terminated on fissile material only if the IAEA determines that the material has been "diluted in such a way that it is no longer useful for any relevant nuclear activity or has become `practicably irrecoverable'."[22] For the plutonium contained in unreprocessed spent fuel, the issue is whether it can be considered practicably irrecoverable after it is emplaced and sealed in a geologic repository. The IAEA, which has been examining this question for many years, is expected to formally determine that this is not the case, and therefore that safeguards must be maintained on repositories containing spent fuel.[23]

On the other hand, the IAEA intends to terminate safeguards on vitrified high-level wastes (VHLW) with a fissile content of less than 2.5 kg per cubic meter (a concentration of about 0.1 weight-percent for a typical HLW glass of density of 2.5 g/cm3). Adoption of this threshold also implies that safeguards can eventually be terminated on spent fuel as well, since the concentration of plutonium will decrease with time. The plutonium concentration in a commercial PWR spent fuel assembly upon discharge (including the internal void volume) is approximately 25 kg/m^3; the concentration will fall below the IAEA threshold after decreasing by a factor of ten, which will occur after approximately 80,000 years (in the absence of geochemical concentration mechanisms).*

Techniques that could be employed in a repository safeguards program include seismic monitors to detect unauthorized drilling, satellite reconaissance to observe hard-to-conceal surface activities, and random on-site inspections.[24] These methods are neither technically challenging, intrusive or

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* However, the proposed 2.5 kg/m^2 threshold has an unclear technical basis and may have to be revised.

resource-intensive. In addition to visual cues, repository mining may also have a thermal signature, as ventilation and cooling systems may have to be employed in order to permit tolerable working conditions. The ground resolution available from commercial satellite reconaissance data (5-10 m visual, 120 m infrared) is more than adequate to detect repository mining activities.

It appears that the necessity of maintaining long-term safeguards on spent fuel repositories is inconsistent with one of the fundamental principles of geologic disposal; namely, that a repository, after it is sealed, should not require active monitoring for any purpose. However, one can argue, using the logic of the material production standard, that this issue does not compromise the validity of the concept of spent fuel disposal.

Recently, in view of the events in Iraq and North Korea, the IAEA has acknowledged the inadequacy of the current safeguards system, which focuses primarily on inhibiting the diversion of weapons-usable fissile materials from declared fuel cycle operations, in the absence of additional mechanisms for verifying the absence of clandestine material production.[25] In an attempt to rectify this situation, the IAEA Board of Governors is considering an array of expanded verification activities, known as the 93+2 program. This program would include enhanced access to all sites where nuclear materials are present, greater authority to inspect undeclared sites and the use of supplemental techniques such as environmental monitoring. Although the sharing of national satellite reconaissance data is not currently contemplated, it may very well become part of a future verification regime.

The threat posed by mining of a geologic repository will be maximized in the context of a world in which there are no operating nuclear reactors or retrievable spent fuel storage facilities, as discussed above. However, without an effective mechanism for verifying the absence of clandestine fissile material production, the notion of a "nuclear-free" world is not meaningful from a non-proliferation standpoint. If we cannot guarantee that safeguards on spent fuel repositories will remain in place indefinitely, then we also must assume that safeguards on clandestine production also cannot be guaranteed. In such an environment, it is far from clear that spent fuel repositories would pose the greatest proliferation risks.

On the other hand, if one assumes that a means of detecting clandestine production is in place, then such techniques could be extended quite simply to safeguard geologic repositories. For example, assume that a satellite system for the detection of thermal output from production reactors is deployed. This system could equally well be applied to the monitoring of repository sites for the presence of unauthorized mining activities. Furthermore, the task of monitoring a series of known sites would be far more straightforward than the task of verifying the absence of clandestine activities, which could occur anywhere (and in particular, in industrial areas where the visual and thermal signals could be camouflaged). This suggests that in the presence of a monitoring regime, a covert proliferation program would be more likely to escape detection if the clandestine production route, rather than the repository mining route, were employed.

Modifications to Repository Design Parameters

The difficulty a proliferant would face in attempting to remove spent fuel from a repository can be greatly affected by repository design choices; some examples are given below. It is not clear that this issue is being addressed substantively by groups engaged in repository design. However, as emphasized above, modifications to current repository designs need only be considered if "worst-case" proliferation scenarios are judged to pose credible future risks.

Backfill

Backfilling all drifts and shafts in a repository would ensure that regaining access would be as difficult and costly as originally excavating the site. However, in one design being proposed for the U.S. repository at Yucca Mountain, shielded canisters would be brought into repository drifts and simply left sitting on rail cars; no backfilling of the drifts would take place (the access shafts would, however, be backfilled). It is clear that this approach would permit rapid retrieval of spent fuel, once the repository horizon were reached. Eventually, the drift walls would collapse and bury the canister; but a densely packed backfill would provide a more reliable barrier in the near-term.

Canister inventory and spacing

To lower the rate of plutonium removal possible from a repository, the spent fuel inventory of disposal canisters could be reduced and the canisters placed farther apart. However, in order to do this effectively, spent fuel would have to be distributed at a very low emplacement density in a repository, substantially raising the cost of geologic disposal. Also, the thermal loading of such a repository would be very low, eliminating the deterrent effect of high temperature.

Repository depth

The risk involved in underground mining increases with the depth of the operation. The casualty rates in the very deep South African gold mines (over 2,300 m deep) are very high. Locating repositories at these depths would increase the cost of both retrievability and emplacement.

Composition of plutonium glass

It is apparent that if one takes the long-term proliferation problem seriously, then weapons-grade plutonium (W-Pu) vitrified with radioactive wastes does not meet the spent fuel standard. This follows from the fact that Pu-239 decays to U-235, another fissile isotope. The uranium in spent fuel, however, will remain low-enriched even after all the Pu-239 has decayed. In WPu-glass, however, the plutonium content of the glass will eventually become highly-enriched uranium with a few percent U-236 admixture. This can be easily corrected by denaturing the product, e.g. adding 5 weight-percent U-238 to the glass, assuming a WPu loading of 1 weight-percent (this may need to be adjusted to accommodate differential leaching that may occur). This will ensure that the U-235 concentration never exceeds the HEU threshold of 20%. Borosilicate glass compositions can easily be adjusted to accept a 5% U-238 loading.

CONCLUSIONS

The notion of a "material production standard" is introduced to argue that spent fuel emplaced in a repository is not likely to be more attractive as a source of plutonium for weapons than new production, except under a very narrow range of scenarios. One scenario involves a national group with no access to operating nuclear facilities which desires to amass a stockpile of nuclear weapons at a rate comparable to the highest rate of production achieved by the superpowers during the Cold War. It is possible to design a repository which would not be attractive even under these circumstances, but it would be much more costly than current repository designs.

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DISCLAIMER

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Long Term Performance Session Summary
Stephen Hanauer, US DOE Office of Civilian Waste Management

The session consisted of a technical introduction and 6 technical papers. Because of time lost as a result of audio system problems, no time was available for discussion.

1. A brief introduction to performance assessment was given by S. H. Hanauer, the session chairman. Geologic disposal of radioactive materials, such as immobilized plutonium waste forms, is intended to provide containment for a long time, and to limit the rate of any release after containment can no longer be assured. Several performance criteria have been adopted and others are being proposed. Since the relevant period of performance is many thousands of years, and repository safety and environmental protection decisions are to be made in the next few decades, compliance can be assessed only by modeling and calculation. Uncertainties in long-term prediction dictate the use of probabilistic analysis. Some results of recent performance assessments were reviewed. Factors, related to immobilized plutonium waste forms that appear significant to long-term repository performance, include waste package and waste form degradation and dissolution rates, solubility of plutonium and its daughters in the ground water, and potential for differential transport of fissile and neutron absorber materials.

2. John Bates presented the paper, "Glass Leaching and Irradiation Damage". The borosilicate glass being used in the United States for high-level waste vitrification does not appear to be particularly suitable for plutonium stabilization: [1] aluminum interferes with plutonium stability; and [2] the leaching rate for boron neutron absorber is about 1000 times the leaching rate for plutonium. A new glass is being developed for possible use in plutonium vitrification with gadolinium added for neutron absorption to control criticality. Leaching rates are controlled by the temperature, pH, and concentration of silicic acid and other silicon-bearing solutes in the water. An initial period of high leaching rates is followed by a stable rate, which can be followed by a period of much higher rates. Most of the existing leaching and radiation effects data is for the borosilicate glass, which will not be used for plutonium disposition. Data and improved models are needed on glasses to be used for plutonium disposal.

3. The paper, "Ceramic Leaching and Irradiation Damage Performance", was presented by Werner Lutze. Ceramic materials are characterized by mechanical durability, thermal stability and slow chemical reaction rates. Natural analogs show the geologic stability of ceramics, including thorium and uranium compounds. Radiation transforms crystalline ceramics to amorphous forms, which are stable but have 10 to 50 times higher leaching rates. Transformation of ceramics has been studied by looking at products of natural irradiation over hundreds of millions of years, studying plutonium-bearing samples, and by accelerator bombardment. The rate of amorphization depends on the temperature, the dose, and dose rate. Additional data and model improvement are needed. Natural and plutonium-doped zircon are predicted to be fully amorphized at 10^{19} alpha decays per

gram, and appear to be suitable for long-term geologic storage. Other plutonium- and curium-doped ceramics have also been studied.

4. Lonnie R. Moore presented "Safeguards and Security/Retrievability by Host Nation or Sub-National Group: Non-proliferation, Safeguards and Security for the Fissile Materials Disposition Program Immobilization Alternatives". This was a general outline of the domestic safeguards and security and international nonproliferation criteria, as they affect the DOE surplus weapons materials disposal program. The steps from surplus weapons through immobilization to geologic disposal involve materials with decreasing attractiveness and correspondingly decreasing requirements for safeguards and security. U. S. Department of Energy, U. S. Nuclear Regulatory Commission, and International Atomic Energy Agency requirements may all be relevant at the various stages of the program.

5. K. K. S. Pillay's paper was entitled, "Safeguardability of the Vitrification Option for Disposal of Plutonium". Both the neutron absorber and the radioactive "spike" prevent nondestructive measurement of the plutonium content of a glass or ceramic waste form or waste package using present technology. The plutonium immobilization process must, therefore, be safeguarded as a bulk handling facility. Implementing safeguards requirements could, in principle, be built into a new vitrification facility, but we have no experience in doing so. Retrofitting existing waste vitrification facilities to accomplish plutonium immobilization would make safeguards implementation very difficult.

6. The paper, "Long-Term Retrievability and Safeguards for Immobilized Weapons Plutonium in Geologic Storage" was presented by Per F. Peterson.

7. Edwin S. Lyman presented "A Perspective on the Proliferation Risks of Plutonium Mines".

Both Peterson's and Lyman's papers are based on the idea that attractiveness of plutonium in a closed and sealed geologic repository as raw materials for future weapons will be determined by the cost and effort to "mine" it, compared to the cost and effort to obtain nuclear weapons in alternative ways. A "materials production standard" is proposed based on this relative cost and effort. Alternatives considered include a "minimum" reactor making 8 kg/yr, an "intermediate" large single production reactor, and a "maximum" Manhattan Project. The analysis depends on assumptions: a nuclear-free world, present-day technology, willingness to incur substantial radiation exposure.

There is much more plutonium in spent commercial fuel than in surplus weapons material. However, in the very long term, when the plutonium-239 has decayed [24,000-year half-life] to fissile uranium-235, the weapons-origin material will be highly enriched, suitable for weapons development, whereas the spent fuel-origin material will be low enriched because the uranium-238 originally in the fuel will still be there.

Peterson concluded that geologic repositories will require safeguards, for example, intrusion detection, for a long time, and that the number of repository locations should be minimized. Immobilized weapons plutonium is comparable to spent-fuel plutonium in usefulness in weapons for nations and subnational groups. Cost and effort data are needed on the cost of "plutonium mining".

Lyman concluded that current repository concepts are assessed to meet the proposed standard. A possible scenario deserving attention is a single nation with access to technology--and a repository--desiring fast production of multiple weapons.

DISCLAIMER

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PLUTONIUM STABILIZATION & IMMOBILIZATION WORKSHOP

DECEMBER 12-14, 1995

CONCURRENT BREAK-OUT SESSIONS

Vitrification for Stabilization of Scrap and Residue
Breakout Session #1
Charles W. Forsberg, Oak Ridge National Laboratory

INTRODUCTION
A conference breakout discussion was held on the subject of vitrification for stabilization of plutonium scrap and residue. This was one of four such sessions held within the vitrification workshop for participants to discuss specific subjects in further detail. The questions and issues were defined by the participants. This summary of the session is organized by subjects that were discussed.

"Stabilization" refers to conversion of plutonium scrap and residue to more chemically stable forms for safe storage. Significant quantities of plutonium are currently in forms not suitable for safe long-term storage. The Defense Nuclear Facilities Safety Board has recommended stabilization of some materials on a 3-year schedule and other materials on an 8-year schedule.

BENEFITS OF VITRIFICATION FOR STABILIZATION
Several incentives for conversion of plutonium scrap and residue to glass were identified. Glass is a chemically inert, nonsoluble, stable form of storage for plutonium. This technology is based on experience with conversion of high-level wastes to glass. Proposed plutonium-containing glasses contain sufficient neutron absorbers that nuclear criticality cannot occur. These multiple glass characteristics minimize the safety concerns for plutonium in glass compared with those for plutonium in most other chemical forms. The glass form creates the first barrier to the release of plutonium to the environment.

Plutonium glass also minimizes long-term storage costs. The glass form eliminates nuclear criticality as a vault requirement and thus minimizes storage costs by reducing vault size. Homogeneous glass minimizes costs of safeguards compared with those of heterogeneous plutonium scrap and residue.

MEETING MULTIPLE OBJECTIVES
There is a major complication in using vitrification for stabilization. Four different sets of goals can be defined: (1) safe short-term storage, (2) safe long-term storage, (3) waste disposal in the Waste Isolation Pilot Plant (WIPP) or an equivalent facility, and (4) plutonium disposition by one of the options defined by the DOE Office of Fissile Materials Disposition. Each goal could imply different glass compositions. Plutonium scrap and residues may require stabilization to address short-term safety issues before longer-term goals are agreed upon.

In the discussions of these multiple objectives, several conclusions were reached by the participants:

- If scrap and residue are vitrified, the goal should be to produce a high-quality glass that meets the first three objectives. The costs of glove box operations are high and are almost independent of the glass produced. There are no incentives to produce poor-quality glass and little difference in costs of different glasses.

- The uncertainties associated with what plutonium scrap and residue can be accepted by WIPP and the associated waste acceptance criteria should be resolved as soon as possible.

- The possibility that it may be desirable to recover the plutonium in the future should not be a major factor in determining whether or not plutonium scrap and residue are vitrified. Although the procedure is complicated, plutonium can be recovered from glass. Vitrification is not an irreversible process. There are near term safety issues and high storage costs associated with plutonium in its current forms that must be addressed.

PROCESS RECOMMENDATIONS

There was general agreement on several process issues associated with vitrification:

- Vitrification can be used to address longer-term (8 year) stabilization issues. The time required for implementation indicates that vitrification is unlikely to be useful to address short-term safety concerns.

- There are strong incentives to test multiple competing vitrification technologies.
  - Multiple technologies increases the probability of success.
  - The optimum vitrification technologies for different scrap and residue streams may be different.
  - The practical knowledge gained with multiple vitrification options would create the experience base needed if it was decided to vitrify a significant fraction of the U.S. plutonium inventory as part of the Fissile Materials Disposition Program.

- For all vitrification options, better chemical characterization of the scrap and residue is required.

- Disposal standards for plutonium vitrification do not exist in the United States or elsewhere. Glass selection should be based on the best available glass currently existing. Producing a good glass in the near future and addressing current safety issues is a better choice than waiting for the optimum glass far into the future.

CONCLUSIONS

Vitrification offers multiple advantages in solving plutonium storage problems. It creates a storage form, which itself provides a barrier against plutonium release to the environment. This, in turn, minimizes long-term storage costs. The experience base with high-level-waste glasses provides reasonable confidence in the durability of plutonium storage forms, although processing uncertainties remain.

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Plutonium Inventories for Stabilization and Stabilized Materials Characteristics Breakout Session #2

Alan K. Williams, Science Applications International Corporation

INTRODUCTION

The objective of the breakout session was to identify characteristics of materials containing plutonium, the need to stabilize these materials for storage, and plans to accomplish the stabilization activities. All current stabilization activities are driven by the Defense Nuclear Facilities Safety Board Recommendation 94-1 (May 26, 1994) and by the recently completed Plutonium ES&H Vulnerability Assessment (DOE-EH-0415). The Implementation Plan for accomplishing stabilization of plutonium-bearing residues in response to the Recommendation and the Assessment was published by DOE on February 28, 1995. This Implementation Plan (IP) commits to stabilizing problem materials within 3 years, and stabilizing all other materials within 8 years. The IP identifies approximately 20 metric tons of plutonium requiring stabilization and/or repackaging. A further breakdown shows this material to consist of 8.5 metric tons of plutonium metal and alloys, 5.5 metric tons of plutonium as oxide, and 6 metric tons of plutonium as residues. Stabilization of the metal and oxide categories containing greater than 50 weight percent plutonium is covered by DOE Standard "Criteria for Safe Storage of Plutonium Metals and Oxides" December, 1994 (DOE-STD-3013-94). This standard establishes criteria for safe storage of stabilized plutonium metals and oxides for up to 50 years. Each of the DOE sites and contractors with large plutonium inventories has either started or is preparing to start stabilization activities to meet these criteria.

The DOE is also preparing criteria for Interim Storage of Plutonium Bearing Materials (paper presented at the workshop and criteria issued on January 25, 1996 as an addendum to the Implementation Plan for Defense Nuclear Facility Safety Board Recommendation 94-1). This document addresses storage of plutonium bearing materials for an interim duration (5-20 years), including residues. Final disposition of residues has not been decided, but may include one of the following:

- processing to a form meeting the plutonium metal and oxide standard (DOE-STD-3013-94),
- disposal to the Waste Isolation Pilot Plant or to a waste repository,
- further storage until final decisions are made regarding plutonium disposition.

GROUP DISCUSSION

The group discussion began with a presentation by A.K. Williams, in which he provided the information shown above, and suggested that the discussion concentrate on residues, where most of the problems in materials stabilization remain. However, plutonium oxides were also discussed briefly. The requirement for stabilizing plutonium oxides at 1000° C as required by the current standard was questioned. A large amount of plutonium oxide has been stored for more than 5 years with no adverse effects at Hanford. It was also mentioned that more recent experimental data from Los Alamos National Laboratory indicate that a lower calcining temperature and higher moisture content may be adequate for stabilizing plutonium oxides containing 80% or more plutonium. Consideration is being given to revising DOE-STD-3013-94 for plutonium oxides.

Plutonium residues contain up to 50 weight percent plutonium, although the bulk of the residues are in the 1-10% range. The residues consist of a large variety of materials (Rocky Flats has more than 400 item description codes). Full characterization of these materials has not been attempted, and to do so will be costly. Requirements for characterization will depend on the disposition option. For example, declaring many of these residues as waste or processing them to metal or oxide may simplify characterization requirements, while treatments such as immobilization will increase these requirements. Some frustration was expressed by members of the group with the lack of policies to address residues issues. For example, many of the residues can be processed to a metal or oxide form for long-term storage, but they cannot be shipped from one site to another. Sites which can process substantial quantities of residues (e.g., Savannah River), do not include processing residues from another site in its Environmental Impact Statement (EIS), and although there is capacity and capability to perform the work, it cannot be executed in a timely manner. The separation and purification of plutonium for long-term storage does not appear to be a politically acceptable option for residue stabilization.

1. Russian Activities

Russian representatives in the group stated that they do not have a residue inventory, since plutonium is not recycled. A waste program was initiated in 1965 to recover plutonium from sludge, fuel waste, pulp, liquid wastes, and solids on site. The program was completed in 1975.

The Russian attendee suggested that the Department of Energy should start with classification of waste based on chemical composition. The first step is to identify the different technologies available for each residue. This includes selection of the extraction/dissolution method, the purification method, and then other issues. Decisions on how to proceed can then be made when final disposition is known. In Russia, products containing less than 200 milligrams plutonium per kilogram (200 grams per ton) material were found to be non economical for plutonium recovery. Much of the work suggested by the Russian representative has already been completed; however, the final disposition alternative has not been decided. The Research Committee established by DOE for addressing residues covered by DNFSB Recommendation 94-1 identified those residues and materials where research and development is needed. For long-term disposition, processing of residues to an oxide in existing facilities would require little or no additional R&D. For immobilization alternatives, considerable R&D may be required.

2. Site Activities

Each site has been required to work independently, since plutonium cannot be easily transported from one site to another. Waivers on shipping to ease this problem would allow a better chance of optimizing capabilities at each facility. An example is shipping plutonium solutions from Hanford to Savannah River for processing. However, it was recognized that the transportation infrastructure is not in place, and that cost savings (including NEPA) and schedule savings may be minimal. The stabilization end-state needs to be determined. Until final disposition is decided, stabilization activities will continue to proceed for meeting DNFSB Recommendation 94-1. If glass/ceramic becomes the end point, then the approach to stabilization will be different than meeting DOE-STD-3013-94 and the Criteria for Interim Storage of Plutonium Bearing Materials.

All materials, regardless of plutonium content, can go to any end-state. Cost benefit analyses can determine which materials go which route; however, other issues/ drivers (e.g., political) may eliminate some options which otherwise would be economical.

Terms used for treating residues need to be defined. Separation can sometime imply purification, when it really involves only concentration. For example, the many tons of chloride salts containing plutonium can be processed, where the bulk of the salt is removed from the plutonium by distillation. Another example is incineration of combustibles, where plutonium is concentrated in the ash.

Concern was expressed that some stabilization activities (e.g. microwave calcining activities at Rocky Flats Environmental Technology Site) would create a form which is not compatible with those processes being considered for final disposition. The Record of Decision (ROD) for the Storage and Disposition of Weapons-Usable Materials Programmatic Environmental Impact Statement (PEIS) is scheduled for September, 1997. This ROD should determine ultimate disposition of surplus plutonium. In the meantime, sites are continuing efforts to meet DOE-STD-3013-94 and DNFSB 94-1 implementation schedules.

It was unclear if plutonium residues are covered in the Storage and Disposition of Weapons-Usable Materials PEIS. If they are not included, then disposition of residues to some end-state needs to be addressed.

MAJOR IDENTIFIED ISSUES

1. Avoid double processing. Materials that appear to be stored safely for an interim period may continue to be stored until the Storage and Disposition of Weapons-Usable Materials PEIS Record of Decision is made.

2. The PEIS may not include lean plutonium residues. The end-state for all plutonium materials needs to be addressed.

3. Information on material characteristics for residues such as salts, sludges, combustibles and non combustibles is documented, if processing in existing facilities is allowed. (See, for example, Research and Development Plan issued by the Nuclear Materials Stabilization Task Group in November, 1995 in response to the DNFSB Recommendation 94-1). For new processes such as those required for immobilization waste forms, additional characterization studies will be needed.

Technical Viability and Development Needs for Waste Forms and Facilities
Breakout Session #3
Dr. Ian Pegg, Catholic University of America and
Thomas Gould, Westinghouse Savannah River Company

INTRODUCTION

The objective of this breakout session was to provide a forum to discuss technical issues relating to plutonium-bearing waste forms and their disposal facilities. Specific topics for discussion included the technical viability and development needs associated with the waste forms and/or disposal facilities. The expected end result of the session was an in-depth (so far as the limited time would allow) discussion of key issues by the session participants. The session chairs expressed allowance for, and encouragement of, alternative points of view, as well as encouragement for discussion of any relevant topics not addressed in the paper presentations. It was not the intent of this session to recommend or advocate any one technology over another.

GROUP DISCUSSION

The session began with the presentation of a slide by the co-chairs proposing a flow for the discussion. The major issues listed on the slide included: waste form, the forming technology, disposal facilities (e.g. the disposal repository or borehole), and waste form performance within disposal facilities. Within each major issue discussed, specific criteria, technology and status, development needs, pros and cons, and issues were considered.

Ideally, the group could have discussed each of these points at length. However, the time allowance for the session was prohibitively short for this topic and did not permit the desired extent of discussion. The initial and recurring interest of the group related to the disposal facility and waste form performance requirements within the disposal facility. Many of the session participants were knowledgeable of waste form types and the associated forming technology (where certainly much knowledge exists). There was general agreement that the required technologies either exist or could be developed *provided* that the problem is sufficiently well-defined, particularly in the area of waste form performance requirements.

The discussion of disposal facilities was limited to considerations of either a geologic repository, such as Yucca Mountain, or disposal into a deep borehole. Discussion of concepts, such as above-ground storage, was not pursued. The audience was cautioned that the discussion would assume that deposition into a repository implies permanent (e.g., unrecoverable) disposal. The following is a summary of the various topics that were discussed, issues that were identified, and conclusions made by the group.

1. Health, Safety, and Environment: Major areas needing better understanding, as identified in this discussion, include: criticality (particularly the potential for long-term selective leaching of neutron absorbers), leachability (and subsequent migration), potential for human exposure, and the stability of fission products as deterrents.

2. Non-Proliferation: Recoverability of Pu was identified as the key issue.

a. The reversibility of the formation of the waste form was discussed as a sociological issue and not a technical problem. Even with a ceramic, Pu could be recovered if enough effort was put into releasing the Pu. A participant commented that considering any waste form as permanent, in this sense, is arrogant. Another question discussed was whether or not vitrified Pu really meets the Spent Nuclear Fuel standard, since the Pu would be present at higher concentrations and be more easily extractable.

b. One area of discussion was dubbed the "Pu mine" issue. The basic concern related to the period after the decay of fission products. The Pu is potentially left available for recovery in the distant future by simply mining the repository. The question was raised as to whether or not the repository would have to be guarded forever to prevent such access and, if so, then what useful function does it perform? Why not simply "Get another guard and another gun?" An argument in favor of the repository approach was that it would be constructed for the disposal of spent fuel and vitrified HLW anyway.

3. Waste Form Issues:

a. Performance: Much of the discussion focused on the issue of waste performance with respect to long-term leaching behavior and release to the environment. It was clear from the discussion that there is a pressing need for a consensus on the "specifications" or requirements on the waste form in this area. It was argued that, other things being equal, there may be a preference for a waste form whose behavior is easily modeled over one that is less easily modeled, or even for a "poorer" waste form with a well-known degradation mechanism over a "better" waste form with a poorly known mechanism. Other issues related to the extent of the performance burden for a repository *system* that should be placed on the waste form, especially since untreated Spent Nuclear Fuel (SNF) would also be disposed of in the repository, and to the general uncertainties associated with key factors (e.g., geologic and climatic). involved in performance assessments which could render waste form performance essentially irrelevant. The feasibility of projecting long-term waste form behavior within a repository was questioned by the audience, but at least one participant expressed the view that behavior for glass in a wet environment can be both modeled and projected.

b. Formulation: The discussion of the suitability of specific waste forms was limited by the lack of performance specifications. The group was asked to consider the present HLW repository criteria, with an additional criticality requirement, for use as "straw-man" waste acceptance criteria for Pu-bearing waste forms. Approximately 50% of the participants thought that this would be satisfactory, whereas about 50% did not. The group was asked whether glass or ceramics would make "acceptable" waste forms. The general consensus was that it is reasonable to assume that either form could be made to be acceptable with existing technology. Specific formulations would still have to be developed in concert with the development of performance specifications. The formulation development process is also complicated by the lack of detailed characterization data for many of the residue materials.

c. Reversibility: This issue came up again in discussions of waste form characteristics. However, it is ultimately a government policy issue. The group generally agreed that recovery of Pu from any waste form is, in principle, technically feasible but could be rendered extremely difficult in practice. The extent to which the task should be made more difficult or less difficult is a policy decision. The "SNF standard" has been proposed as a bench-mark in this area.

MAJOR IDENTIFIED ISSUES

These can be summarized as follows:

- Retrievability vs. permanent disposal.
- Pu "mine" and the utility of fission products as additives.
- Waste form performance requirements are undefined, especially interaction with water
- Criticality avoidance.

CONCLUSIONS

1. Major uncertainties exist regarding performance and performance criteria for waste forms in the disposal environment. Decisions on the functional intent of the repository (permanent or retrievable disposal) will drive the R&D needs for waste form formulation.

2. Pu feed materials need to be better defined (characterized), especially for residues.

3. The group was of the opinion that system requirements (i.e., waste form plus repository) must be defined in order to assess the adequacy of waste form behavior with respect to characteristics such as durability.

4. The current state of science and technology for Pu immobilization gives reasonable confidence that either glass or ceramic waste forms should be feasible.

5. Significant R&D gaps remain in areas such as the specific immobilization form and composition, and the optimal formation technology.

DISCLAIMER

The views expressed in this report are those of the author(s) or the individuals identified as making the remarks, and do not necessarily reflect any biases, proposed actions, or decisions of the United Stated Government or any agency thereof.

Safeguards and Retrievability from Waste Forms
Breakout Session #4
William Danker, US DOE, Office of Materials Disposition

BACKGROUND

On December 14, 1995, one of the four concurrent "breakout" sessions at the Plutonium Stabilization and Immobilization Workshop discussed technical issues related to safeguards and retrievability from these immobilized forms. Building on questions raised during the four safeguards and retrievability papers presented during the preceding plenary session, the following two technical issues were posed to the breakout group as a starting point for discussion:

- Does immobilization render retrieval more or less attractive (e.g., than commercial spent fuel)?
- Does immobilization limit the applicability of current safeguards tools and technologies or require significant new developments?

While the group developed an additional list of 25 comments/ideas/areas of interest, most of the discussion related at least indirectly to the above two issues.

At the outset, the group agreed to focus on the "incremental" effects introduced by immobilization, rather than dwelling on more fundamental issues associated with high-level waste repositories and international safeguards. Much of the initial discussion "scoping" dealt with perceived threat over time introduced by these immobilized material forms. Again, given limited time, the group decided to focus discussion on the time period preceding repository closure, based on a sense that uncertainties associated with the postclosure period reduced the significance of "incremental" discussions.

SUMMARY

Throughout the discussion, the group probed the goals of disposition efforts, particularly an understanding of the "spent fuel standard", since the disposition material form derives from these goals. The group felt strongly that not only the disposition goals but safeguards to meet these goals could affect the material form. Accordingly, the Department was encouraged to explore and apply safeguards as early in the implementation process as possible. It was emphasized that this was particularly true for any planned use of existing facilities. It is much easier to build safeguards approaches into the development of new facilities, than to backfit existing facilities. Accordingly, special safeguards challenges are likely to be encountered, given the cost and schedule advantages offered by use of existing facilities.

During discussions focused on whether particular material forms might meet the spent fuel standard ("as inaccessible and unattractive as the plutonium in commercial spent fuel"), it was agreed that proliferation resistance is not just a function of the material form. Proliferation resistance (e.g., the time and effort need to divert weapons-usable fissile material) is a function of the material form, its location, and applied safeguards and security measures. Accordingly, an assessment of the adequacy of proliferation resistance offered by certain material forms (e.g., the can-in-canister, the "hot can", etc.) needs to evaluate threat over time, including "windows of vulnerability" (e.g., time until weapons-usable form is altered, time until geologic disposal, etc.).

That portion of the plutonium determined to be excess to national defense needs and which is in classified shapes was identified as a key consideration in the initiation of international safeguards, and would require continuing discussions between the Department and the International Atomic Energy Agency to clarify appropriate interfaces and verification measures.

It was generally concluded that disposition through immobilization processes could offer "adequate" nonproliferation, but that the application of safeguards will not be "trivial". To date, vitrified high-level waste is treated as a "measured discard" and falls outside of the international safeguards regime. Additionally, discrimination of significant quantities (i.e., 8 kg Pu) in "bulk handling" immobilization processes operating at production rates will require resources and attention. While existing safeguards tools and technologies offer a substantial basis for adaptation and application, significant research and development is expected to be required for these applications.

DISCLAIMER