Proceedings of the

Workshop on Cement Stabilization of Low-Level Radioactive Waste

Held at
Gaithersburg Marriott Hotel
Gaithersburg, Maryland
May 31 – June 2, 1989

ABSTRACT

The Workshop on Cement Stabilization of Low-Level Radioactive Waste was co-sponsored by the U.S. Nuclear Regulatory Commission and National Institute of Standards and Technology and held in Gaithersburg, Maryland on May 31-June 2, 1989. The workshop provided a forum for exchanging information on the solidification and stabilization of low-level radioactive waste in cement among federal and state regulators, nuclear power station operators, cement vendors, national laboratory researchers and consultants. The workshop was structured into a "Plenary" and four "Working Group" sessions. Each working group session discussed a set of specific issues as follows: Working Group 1."Lessons Learned from Small- and Full-Scale Waste Forms and Observations at Nuclear Power Stations", Working Group 2."Laboratory Test Experience and Application to Problem Waste Streams", Working Group 3."Stabilized Waste Form Testing Guidance", and Working Group 4."Waste Characterization, Solidification, and Process Control Programs(PCP)."

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EXECUTIVE SUMMARY

This report is a summary of discussions held at a Workshop on the use of cement in solidifying and stabilizing low-level radioactive waste. The Workshop was held from May 31, 1989, to June 2, 1989, at the Gaithersburg Marriott Hotel in Gaithersburg, Maryland. In attendance were federal and state regulators, cement system vendors, utility representatives, consultants and national laboratory researchers. Approximately 160 people attended.

The Workshop was structured into "Plenary" and "Working Group" sessions. In the opening plenary session there were presentations from representatives of the radwaste treatment vendors, national laboratory researchers, and utilities. Following the opening plenary session, and on each of the following days of the Workshop, there were Working Group meetings. Each of the four Working Groups addressed a specific set of issues, as follows:

Working Group 1.   Lessons Learned from Observations of Small/Full-Scale Waste Forms at Nuclear Power Plants.

Working Group 2.   Laboratory Test Experience and Application to Problem Waste Streams.

Working Group 3.   Stabilized Waste Form Testing Guidance.

Working Group 4.   Waste Characterization, Solidification, and Process Control Programs (PCPs).

The first two Working Groups were "problem identification" oriented, while the second two were intended to be "regulatory pathway" oriented. Whereas it would have been desirable to conduct the Working Group sessions consecutively, time constraints dictated that most of the discussions had to be held simultaneously. The Working Group sessions, which were open to all Workshop attendees, were conducted by designated participants. The remaining meeting attendees were invited to raise questions and voice comments at summary plenary sessions, which were held at the end of each working day.

The purpose of the Workshop was to obtain an improved understanding of the technical concerns involved in the use of cementitious materials, such as Portland and pozzolonic-type cements, to solidify and stabilize low-level radioactive wastes. Though such cements are widely used in the nuclear industry as agents that can be used to place the wastes in a stable state suitable for disposal in a low-level waste disposal facility, problems have been encountered in both laboratory testing of the simulated (and real) waste forms as well as in field observations of real wastes. Such experiences indicate that there are complex chemical and physical phenomena involved in the use of cement to solidify low-level radioactive waste materials. The Workshop, therefore, provided a means of exchanging information concerning these phenomena and to discuss approaches that can be used to mitigate their effects on the cement waste forms.

The requirements for low-level radioactive waste forms are spelled out in 10 CFR Part 61, the Nuclear Regulatory Commission's regulation for land disposal

of such wastes. As established in subsection 61.55 of Part 61, there are three classes of low-level radioactive wastes, called Class A, B, and C, respectively. While all three classes of wastes must meet certain "minimum" requirements (e.g., must not contain greater than 0.5% free liquid), Class B and Class C waste forms must possess long-term (e.g., 300-year) structural stability. Guidance on methods that can be used to demonstrate structural stability is provided in a Technical Position on Waste Form that was issued in May 1983 and which lists test methods and associated acceptance criteria that the NRC staff has used as indirect indicators of the required long-term structural stability. Typically, low-level waste processors perform the Technical Position tests to qualify recipes that can be used to stabilize specific waste stream compositions. The test results are usually submitted in the form of a topical report. After review and approval of the topical report, waste generators and processors who prepare their wastes in a manner described in the report may refer to the approved topical report as evidence that they have met the provisions of 10 CFR 20.311, which requires certification that the wastes satisfy the "minimum" and "stability" requirements of Part 61.

There are seven topical reports currently under review by the NRC that deal with cement stabilization of low-level wastes. At present, no commercial cement low-level waste formulations have been approved. The only formulation that has received approval is the West Valley Demonstration Project's (WVDP's) decontam-inated supernatant waste. That waste stream differs, however, from most com-mercial low-level radioactive waste streams in that the West Valley waste has a relatively uniform and well-characterized composition.

Some of the key issues and questions addressed at the Workshop were as follows:

    1.   Based on laboratory observations and field experience, what waste streams and compositions appear to be incompatible with cement?

    2.   Can (must) waste generators do a better job of characterizing their waste prior to processing the material?

    3.   What waste streams require pretreatment prior to solidification, and how should they be pretreated (chemically and/or physically)?

    4.   What changes, if any, should be made to the 1983 Technical Position on Waste Form?

    5.   What features should be included in a good Process Control Plan and how can the PCP be better coupled to the waste form qualification testing program?

    6.   What procedures and criteria should be used for post-solidification testing of full-scale cement waste forms?

Because the Workshop was not a "Consensus Conference" this report is not a consensus document that contains conclusions or recommendations. Rather, the report is in the form of a summarial document that, in addition to publishing the formal presentations made in the opening plenary session, also provides concise summaries of the discussions held in the Working Group sessions. Some additional background and supplementary information is provided in the appendices.

The report also contains a Closing Statement by the NRC Workshop Chairman. The Closing Statement provides a discussion of impressions received by the Chairman at the Workshop and some insight on ways that the information exchanged at the Workshop might best be used to resolve regulatory issues.

CEMENT WORKSHOP

MAY 31–JUNE 2, 1989

GAITHERSBURG MARRIOTT HOTEL
Gaithersburg, Maryland

WORKSHOP OBJECTIVES: To discuss and identify possible solutions that may be used by the Nuclear Regulatory Commission to resolve administrative and technical issues regarding the use of cement for the solidification and stabilization of low-level radioactive waste.

AGENDA

DAY 1 — Wednesday, May 31, 1989

PLENARY SESSION

7:00   Registration

8:00   Workshop Welcome: National Institute of Standards and Technology
                                                        Richard Wright

8:10   Welcome by NRC/NMSS Senior Management   John T. Greeves

8:15   Workshop Introduction   Michael Tokar

8:40   Remarks by DOE National Laboratories (BNL, INEL, SRL) and WVDP

        Brookhaven National Laboratory   Barry Siskind
        Idaho National Engineering Laboratory   John Mandler
        Savannah River Laboratory   Christine Langton
        West Valley Nuclear Services Co.   Charles McVay

9:45   BREAK

10:15   Remarks by Nuclear Utilities Representative   Les Skoski

10:30   Remarks by Cement Vendors

        Chem–Nuclear Systems, Inc.   Michael Ryan
        LN Technologies Corp.   Regan Voit
        Westinghouse Radiological Services, Inc.   Bryan Roy

11:15   Presentations by Technical Coordinator of each workshop working
          group

          Working Group 1—Lessons Learned from Small—and Full—Scale Waste
                         Forms and Observations at Nuclear Power Stations.
                              John Mandler, Idaho National Engineering Lab

          Working Group 2—Laboratory Test Experience and Application to
                         Problem Waste Streams.
                              Barry Siskind, Brookhaven National Laboratory

          Working Group 3— Stabilized Waste Form Testing Guidance.
                              Peter Soo, Brookhaven National Laboratory

          Working Group 4—Waste Characterization, Solidification, and
                         Process Control Program(PCP).
                              Biays Bowerman, Brookhaven National Laboratory

12:15   Closing Comments for the Morning Session   Michael Tokar

12:30   LUNCH

                              WORKSHOP

1:30   Working Group Discussions
          Working Groups 1 and 2 will begin discussions this afternoon.
          Working Groups 3 and 4 will begin discussions tomorrow morning.

3:15   BREAK

3:30   Continue Working Groups 1 and 2 Discussions (Closed Sessions)

4:00   Status summary by Technical Coordinators of Working Groups 1 & 2

          The rest of this afternoon will be open for discussions
          in the form of a question and answer session. Questions and
          comments will be directed to specific working groups. Unanswered
          questions will be taken up for discussions in the working groups
          on the following day. If there is no time for all of the
          questions to be answered, the attendees will be asked to give
          their questions in writing to the respective Working Group
          Chairman or Technical Coordinator and they will be discussed by
          the technical working group tomorrow morning.

5:00   Adjourn

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EVENING DINNER

6:00   Cash Bar

7:00   DINNER
          Dinner Speaker   Robert M. Bernero, Director
                                       Office of Nuclear Material
                                       Safety and Safeguards
                                       Nuclear Regulatory Commission

DAY 2 — Thursday, June 1, 1989

WORKSHOP

8:00   Continue Working Group Discussions
          All four working groups will be in session today.

10:00   BREAK

10:15   Continue Working Group Discussions

12:00   LUNCH

1:00   Continue Working Group Discussions

3:15   BREAK

3:30   Continue Working Groups Discussions (Closed Sessions)

4:00   Status summary by Technical Coordinators of each Working Group

          The rest of this afternoon will be open for discussions
          in the form of a question and answer session. Questions and
          comments will be directed to specific working groups. Unanswered
          questions will be taken up for discussions in the working groups
          on the following day. If there is no time for all of the
          questions to be answered, the attendees will be asked to give
          their questions in writing to the respective Working Group
          Chairman or Technical Coordinator and they will be discussed by
          the technical working group tomorrow morning.

5:00   Adjourn

Day 3 — Friday, June 2, 1989

WORKSHOP

8:00   Continue Working Group Discussions

10:00   BREAK

10:15   Continue Working Group Discussions

12:00   LUNCH

CONCLUDING SESSION

1:00   Summaries and remarks by the Technical Coordinators of each
        working group.

        After all the technical coordinators have presented their
        summaries to the attendees, the workshop will be open for
        comments by general members attending the workshop. Most of
        the comments, if of a question in nature, will be answered by
        the working group members. If not, they will be addressed prior
        to documenting the workshop proceedings.

3:45   Closing remarks   Michael Tokar

4:00   Adjourn

CEMENT WORKSHOP

WORKING GROUP AND DISCUSSION TOPICS

WORKING GROUP 1 – LESSONS LEARNED FROM SMALL–AND FULL–SCALE WASTE FORMS AND OBSERVATIONS AT NUCLEAR POWER STATIONS

Working Group 1 will address issues encountered in comparing small–and–full scale test results using laboratory and actual solidified low–level radaste as well as problems encountered with solidifying radwaste at the nuclear power stations. Some of the topics expected to be discussed include:

1. The relationship between small–and–full scale testing

2. Full–scale testing of solidified low–level radwaste

3. Additional testing to be performed on actual waste solidified at the nuclear stations

4. Problems encountered with solidifying actual low–level radwaste at nuclear power stations including problems identified with the verification samples

5. Small–scale testing at INEL on actual solidified radwaste collected from operating nuclear stations

6. Mechanisms, including chemical causes, for the observed deteriorations and unsuccessful solidifications

7. Testing solidified waste in drums and liners to be performed at the power stations to ensure complete solidification(e.g. nondestructive testing and archived samples)

CEMENT WORKSHOP

WORKING GROUP AND DISCUSSION TOPICS

WORKING GROUP 2 — LABORATORY TEST EXPERIENCE AND APPLICATION TO PROBLEM WASTE STREAMS

Working Group 2 will discuss laboratory tests and waste streams solidifications where problems with the solidification process have occurred. Topics to be discussed include:

1. Problems encountered with small laboratory tests performed at INEL using actual solidified LLW from power stations and BNL using simulated wastes

2. Identification of possible waste streams that perhaps should not be solidified or which waste loading should be limited

3. Experience with cement solidification of low—level radwaste from DOE's operations at the West Valley Demonstration Plant; lessons to be learned on the sensitivity of the effects of organic materials on the strength of the stabilized waste and the scope of testing performed

4. Experience with cement solidification of low—level radwaste from DOE's operations at the Savannah River Laboratory

CEMENT WORKSHOP

WORKING GROUP AND DISCUSSION TOPICS

WORKING GROUP 3 — STABILIZED WASTE FORM TESTING GUIDANCE

Working Group 3 will address regulatory concerns and technical information developed from laboratory testing programs for preparing Topical Reports. Items expected to be discussed include:

1. NRC Branch Technical Position (May 1983) waste form testing, revisions, and changes to the evaluation criteria

2. Modification and/or elimination of any tests

3. Proposed new tests that would address long—term stability concerns

4. Guidance on specimen preparation, present practices of using different sized specimens in different tests, test specimens from different batches of mix, minimum number of tests for the results to be statistically significant. (Define standard testing program to attain uniformity in testing so that data from different licensee programs and laboratories may be evaluated for a pattern in test results.)

5. Different waste streams from nuclear power stations solidified, including the use of ion—exchange resins solidified in cement

6. Quality control and assurance in laboratory testing

CEMENT WORKSHOP

WORKING GROUP AND DISCUSSION TOPICS

WORKING GROUP 4 -- WASTE CHARACTERIZATION, SOLIDIFICATION, AND PROCESS CONTROL PROGRAM(PCP)

Working Group 4 will address low-level radioactive waste stream characteristics and their impact on the cement solidification process at nuclear power stations. Issues expected to be addressed include:

1. Low-level radioactive waste stream characteristics, including chemical and radiological composition and other constituents present

2. Pretreatment of waste streams such as pH control, additives to the solidification process, and physical treatment to waste streams such as dewatering/decantation, volume reduction, and ion-exchange resin depletion.

3. Characteristics of decontamination wastes.(Decontamination wastes are uniquely chemically and radiologically different from routine low-level radioactive wastes agents because they contain activated metals, chelating agents, and metals removed from nuclear station piping and reactor components. These wastes are expected to increase in volume in the future as nuclear stations implement full-system decontamination practices.)

4. Adequate pretesting of the cement solidification formulations using actual wastes at the power stations

5. Parameters of the low-level radwaste to be monitored as part of the process control program for cement solidification at the nuclear stations

6. The effects of composition of the low-level radwaste streams that either accelerate or retard the setting of cement. Admixture effects to counter the above.

CHAIRMAN, TECHNICAL COORDINATOR AND MEMBERS
OF CEMENT WORKSHOP WORKING GROUPS

WORKING GROUP 1 — LESSONS LEARNED FROM SMALL—AND FULL—SCALE WASTE FORMS AND OBSERVATIONS AT NUCLEAR POWER STATIONS

CHAIRMAN: Phillip R. Reed,   Nuclear Regulatory Commission

TECHNICAL COORDINATOR: John Mandler,   Idaho National Engineering Laboratory

1.	Everett Wick	Nuclear Regulatory Commission
2.	Chuck McIsaac	Idaho National Engineering Laboratory
3.	John Remark	ARC, Inc.
4.	Regan Voit	LN Technologies Corp.
5.	James Jeffrey	Chem—Nuclear Systems, Inc.
6.	Paul Denault	PN Services
7.	John Bishop	Consultant
8.	Alan Campbell	Northeast Nuclear Energy Co.
9.	Steve Davis	Commonwealth Edison Co.
10.	Andy Young	New York Power Authority Fitzpatrick Nuclear Power Station
11.	Mike Dragoo	Philadelphia Electric Co. Peach Bottom Nuclear Power Station

CHAIRMAN, TECHNICAL COORDINATOR AND MEMBERS
OF CEMENT WORKSHOP WORKING GROUPS

WORKING GROUP 2 — LABORATORY TEST EXPERIENCE AND APPLICATION TO PROBLEM WASTE STREAMS

CHAIRMAN: Banad Jagannath, Nuclear Regulatory Commission

TECHNICAL COORDINATOR: Barry Siskind, Brookhaven National Laboratory

1. Derek Widmayer   Nuclear Regulatory Commission

2. Mark Fuhrmann   Brookhaven National Laboratory

3. John McConnell,Jr.   Idaho National Engineering Laboratory

4. Christine A. Langton   Savannah River Laboratory

5. Russ Stimmel   West Valley Nuclear Services Co.

6. John Carlson   Chem—Nuclear Systems Inc.

7. Gene Smeltzer   Westinghouse Electric Co.

8. Paul Piciulo   Ecology and Environment, Inc.

WORKING GROUP 3 — STABILIZED WASTE FORM TESTING GUIDANCE

CHAIRMAN: Michael Tokar, Nuclear Regulatory Commission

TECHNICAL COORDINATOR: Peter Soo, Brookhaven National Laboratory

1.	Jake Philip	Nuclear Regulatory Commission
2.	James Clifton	National Institute of Standards and Technology
3.	Wallace Y. Chang	Envirosphere Company
4.	Robert Neilson, Jr.	Idaho National Engineering Laboratory
5.	Robert Rogers	Idaho National Engineering Laboratory
6.	Gregory Boris	Westinghouse Radiological Services, Inc.
7.	William House	Chem–Nuclear Systems, Inc.
8.	Angela Valvasori	LN Technologies Corp.
9.	William Phillips	Stock Equipment Co.
10.	Richard Blauvelt	Mound Laboratory
11.	Russell Propst	Duke Power Co.

WORKING GROUP 4 — WASTE CHARACTERIZATION, SOLIDIFICATION, AND PROCESS CONTROL PROGRAM(PCP)

CHAIRMAN: Keith McDaniel, Nuclear Regulatory Commission

TECHNICAL COORDINATOR: Biays Bowerman, Brookhaven National Laboratory

1. Frank Cardile   Nuclear Regulatory Commission

2. Charles Willis   Nuclear Regulatory Commission

3. Geoffrey Frohnsdorff   National Institute of Standards and Technology

4. William Serrano   Idaho National Engineering Laboratory

5. Steve Duce   Idaho National Engineering Laboratory

6. Lynn Mayeaux   Chem-Nuclear Systems, Inc.

7. Rick January   LN Technologies Corp.

8. Bryan Roy   Westinghouse Radiological Services, Inc.

9. Tom Oliver   Pacific Nuclear Services

10. Charles McVay   West Valley Nuclear Services Co.

11. Bruce Watson   Baltimore Gas and Electric Co.
                          Calvert Cliffs Nuclear Power Station

12. Channing Gerber   Niagara Mohawk Power Corp.
                          Nine Mile Point Nuclear Power Station

OPENING PLENARY SESSION
MAY 31, 1989

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WELCOME TO THE CEMENT WORKSHOP

By

Richard Wright
National Institute of Standards and Technology

INTRODUCTION TO THE CEMENT WORKSHOP

I am Richard Wright, the Director of the Center for Building Technology of the National Institute of Standards and Technology, formerly the NBS. We are delighted to co-host the workshop with NRC, and look forward to interesting, important discussions.

We, at NIST, have for generations been engaged in research on durability of concrete. The topic fits the NIST role as the Nation's central engineering and physical sciences laboratory. It also fits the Center for Building Technology's role of improving the usefulness, safety and economy of constructed facilities through the improvement of methods for measuring, testing and predicting the performance of materials, components, systems and practices used in construction.

It is a challenging task to develop methods to predict the service lives of construction materials. It is challenging when you seek housing materials that will last as long as the mortgage. It is still more challenging to seek a 300 year service life for containment of radioactive wastes. Consequences of failure are more severe, reliability must be very high, failure modes must be fail-safe, and both intrinsic and extrinsic environments must be accounted for - with cognizance of uncertainties.

Our experience indicates that the mechanisms and rates of degradation must be understood quantitatively for reliable assessments of service life. Only with this understanding can accelerated test methods be identified to exercise the potential mechanisms of failure and give results that can be evaluated in terms of actual service life performance. For cement solidification of wastes, detailed knowledge is needed of the waste properties, the cement properties, interactions between the waste and the cement, and the external environment.

We have developed this approach into a general methodology and seen it adopted as an ASTM standard, and as an international recommended practice. This is not to say the problems are solved, rather, there is a rational approach to their solution which has been exercised successfully in other areas. Geoffrey Frohnsdorff and James Clifton of our Building Materials Division have been leaders in this work and will participate actively in the workshop. Your topic is of great national importance. You are the right group to tackle the work. We at NIST look forward to participation in the workshop and the research and development to follow.

INTRODUCTION TO CEMENT WORKSHOP

by

Dr. Michael Tokar, Section Leader
Engineering Section
Technical Branch
Division of Low-Level Waste Management
and Decommissioning
Office of Nuclear Materials Safety
and Safeguards (NMSS)

I. Welcome

Welcome to the Workshop on Cement Solidification and Stabilization of Low-Level Radioactive Waste. My name is Michael Tokar. I am the Section Leader of the Engineering Section in NRC's Division of Low-Level Waste Management and Decommissioning, and I will act as your main Master of Ceremonies for this and the other plenary sessions that will be held over the next three days.

This Workshop is being co-hosted by the Nuclear Regulatory Commission (NRC) and the National Institute of Standards and Technology (NIST). NRC Offices participating in this effort include the Office of Nuclear Materials and Safeguards (NMSS), the Office of Nuclear Reactor Regulation (NRR) and the Office of Research (RES). Because NMSS has the primary responsibility for implementing the provisions of NRC's regulation, 10 CFR Part 61, for the land disposal of low-level radioactive waste, that Office, which I and several others here represent, established the need for the Workshop and requested assistance from the other NRC Offices and NIST in setting up the Workshop. NIST, NRR, and RES have all played major roles in structuring this meeting, in setting up the logistics, and in identifying significant technical issues. I want express my gratitude for their hard work, the results of which are readily apparent here today. I anticipate that the representatives of these organizations will continue to make very significant contributions to the technical discussions that will take place over the next three days.

II. Purpose

Why are we holding this meeting? What is there about the use of cement to solidify and "stabilize" low-level radioactive waste that would lead us to convene this gathering of experts to discuss the technical issues involved? I believe I can best respond to these questions with a little demonstration.

Here is a specimen of mixed (40% cation/60% anion) bead resin solidified in Portland cement. The specimen was prepared approximately fifteen months ago in February 1988. As you can see, it is a perfectly intact, monolithic right cylinder. On the 6th of March 1989 (over one year after the specimen was prepared) I took a similar specimen (identical except for having a slightly

higher cement content) and placed it in a glass of water for a week. This is that specimen as it exists today. As you can see, it now consists of a loose granular mixture of resin beads and cement powder. Please note that this is a waste form recipe that had passed all the qualification tests called out in the 1983 Technical Position on Waste Form (which I will be speaking about in a little more detail in a few minutes). If this is what can happen to a supposed "stabile" waste form after one week of exposure to water, what does it portend with regard to the ability of a real cement waste form, contained in a carbon steel liner and disposed of in a shallow land burial disposal facility, to possess the long-term (300-year) structural stability required by 10 CFR Part 61?

This is but one illustration, albeit a rather dramatic one, of problems that have been encountered with cement-solidified low-level radioactive waste in laboratory testing as well as in the field. Many of you are already quite familiar (and if you are not already familiar with the details you will be by the time this Workshop is over) with reported cases of full-scale and lab-scale waste forms that have disintegrated like this one, or that did not fully solidify, or that foamed up due to an exothermic reaction, or that solidified too rapidly, or that swelled and bulged their liners, and so on. These cases demonstrate that there are complex chemical and physical phenomena involved in the use of cement to solidify low-level waste streams. A basic objective of this Workshop, therefore, is to exchange information concerning these phenomena and to discuss approaches that can be used to mitigate their effects on the cement waste forms.

III. Part 61 Requirements and the 1983 Technical Position on Waste
     Form

I have alluded to the Part 61 requirements for low-level waste forms. Those requirements, contained in subsections 61.56(a) and 61.56(b) (for "minimum" and "stability" requirements, respectively), are coupled to the waste classification system called out in subsection 61.55. As noted in subsection 61.55, there are three classes of low-level radioactive waste, called Class A, Class B and Class C. The minimum requirements apply to all three classes of waste while the stability requirements apply only to Classes B and C (unless Class A waste is comingled with Class B or Class C waste). One of the most pertinent minimum requirements for a cement-solidified waste form concerns the allowable amount of free liquid: in no case shall such liquid exceed 1% by volume (0.5% if the waste form is stabilized; i.e., Class B or Class C). Thus, cement is used to solidify liquids and slurries so as to satisfy the free liquid limit as well as to meet the long-term structural stability requirement of Part 61.

Waste form "structural stability" is intended to address two concerns in Part 61: (1) the need to minimize "access of water to the waste" so that "migration of radionuclides [to the environment] is thus minimized." (see 10 CFR 61.7), and (2) to need to limit exposure to an inadvertent intruder by providing a recognizable and nondispersible waste (see 10 CFR 61.56(b). A stabile waste

form contributes to the overall stability of the site by helping to preclude slumping, collapse, or other failure of the disposal unit. In so doing the waste form itself helps to minimize contact of water with the waste and migration of radionuclides off-site. The waste form's ability to contribute to the prevention of trench slumping and to be "recognizable" are characteristics that are relatively easy to attain in the sense that even a completely disintegrated waste form could possess those characteristics. However, a disintegrated waste form would not be expected to contribute effectively to the minimization of migration of radionuclides. This is true because the increased surface area of the disintegrated particulate material would, if it were in contact with water, be subject to increased leaching and release of the radionuclides contained in the material.

The "minimum" requirements for low-level waste forms are relatively straight-forward and require little elaboration. The main concern here is with the requirements for "structural stability." Though Part 61 provides the basic licensing requirements for structural stability, the regulation does not indicate in any detail how those requirements should be demonstrated to be met. That type of detailed guidance is instead provided in the "Technical Position on Waste Form" (TP), which was issued in May 1983. For solidified waste forms, the tests (see Table I) essentially involve subjecting the waste specimens to conditions of compression, irradiation, biodegradation, leaching, immersion, and thermal cycling. Most of the tests, which were selected for their relative simplicity and reproducibility, are based on American Society for Testing and Materials (ASTM) or American Nuclear Society (ANS) standard methods of test that were originally developed for specific non-radioactive material applications. Though it is not explicitly so stated in the TP, these methods of test are intended to provide confidence, by means of exposing test specimens to relatively short-term (minutes or weeks) conditions, that low-level radioactive waste forms will have the desired long-term (300-year) structural stability. It is important to remember in this regard that there is a major difference in time scale between the periods of time allotted for the tests and the period of time of concern for LLW disposal. Therefore, the test conditions cannot match, and are not intended to exactly duplicate, the conditions that might actually exist in the disposal facility at the time of disposal or which might exist at some point in time following placement of the waste in the facility. For example, the irradiation test calls for the specimens to be exposed to a minimum of 10E+8 rads, which is the maximum level of exposure for the waste forms after (300 years of) diposal; this requires the test specimens to be exposed to a much higher gamma flux than would actually be encountered under real exposure conditions. Thus, in some ways (some of) the TP tests can be considered to be accelerated tests, while in a more fundamental sense they are actually screening tests that are used to weed out material formulations and designs that do not exhibit sufficient assurance of long-term stability.

It will be noted that the principal acceptance criterion parameter for most of the tests is compressive strength. The compressive strength criterion and the tests are related to Part 61 through the statement [in 10 CFR 61.56(b)(1)] that "a structurally stable waste form will generally maintain its physical

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dimensions and its form, under expected disposal conditions, such as weight of overburden and compaction equipment, the presence of moisture ([a rationale for the immersion and leaching tests] and microbial activity [a rationale for biodegradation tests] and internal factors such as radiation effects [a rationale for radiation stability tests] and chemical changes." In the 1983 TP, a cover material density of 120 lbs./cu.ft. is assumed, which yields a pressure of approximately 37.5 psi at a burial depth of 45 feet (the then-maximum burial depth at Hanford). Taking into consideration potential additional loads from trench compaction equipment, waste contents, etc., the compressive strength criterion was set at 50 psi, which was raised to 60 psi when Hanford increased the depth of its trenches to 55 feet. Thus, the compressive strength criterion was not established as a result of some direct correlation of an intrinsic material property to long-term structural stability, but was instead intended to accommodate the environmental or in situ loads at the bottom of a disposal trench. For certain types of solidification media such as Portland or Pozzalonic cements, which typically have compressive strengths on the order of several thousand psi, a 60 psi compressive strength criterion does not appear to have a strong correlation to long-term structural stability. However, it should be noted that the waste form TP indicates that for solidification agents that are easily capable of meeting the 50 psi limit, process control procedures should be developed to achieve the maximum practical compressive strengths, not simply to acheive the minimum acceptable compressive strengths. This recommendation seems not to have received much attention (mainly because of economic considerations and competive factors that have led to lower and lower cement loadings), with the result that in some waste forms the waste loadings are so high that the radioactive waste ingredients comprise the overwhelming bulk of the material. In such cases there may be so little cementitious material in the waste forms that they may, because of physical and chemical interaction between the waste material and the cement, be intrinsically unstabile.

IV. The Topical Report Review Process

As noted earlier, the purpose of the 1983 Technical Position on Waste Form is to provide guidance on an acceptable approach for demonstrating compliance with 10 CFR Part 61 requirements for LLW structural stability. Under current procedures, the outlines of which were established in an agreement reached with the current-sited States (Nevada, South Carolina, and Washington) in late 1983, the NRC provides a "central" review of topical reports on waste form stabilization media and high integrity containers (HICs). The centralized review is intended to be generically applicable to all disposal sites.

Waste generators and processors must satisfy the provisions of NRC regulation 10 CFR 20.311 concerning the need to certify that the waste form requirements of 10 CFR Part 61 have been met. The most straight-forward way for a waste generator or processor to satisfy 10 CFR 20.311 is to use a stabilization medium (or high integrity container) that has been reviewed and approved by the NRC. In stating that an NRC-approved medium or HIC was used, the waste generator or processor also simplifies the task of the NRC inspector who audits

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the licensees' activites to ensure that they are safe and in compliance.

The current status of the topical report review program is shown in Table II. Since the program began in 1983, a total of 32 topical reports have been submitted for review. Of those, 7 are approved, 4 were disapproved, 3 reviews were "discontinued" (disapproved with the option of resubmittal), 7 were voluntarily withdrawn by the vendor, and 11 are currently under review. It will be noted that, while there are seven cement topical reports currently under review, no commercial cement formulations have received approval. In the six years that NRC has been reviewing cement-solidified LLW formulations and topical reports, the only formulation that has received approval is the West Valley Demonstation Project's (WVDP's) decontaminated supernatant waste. The WVDP decontaminated supernatant waste, which has a relatively uniform composition compared to typical commercial low-level waste streams) required a very extensive (and expensive) qualification program that received a rigorous review by the NRC staff and consultants. You will be hearing more about the WVDP cement qualification testing program and licensing review from Charley McVay of West Valley Nuclear Services later this morning. The point to be made here is that it required a massive testing and review effort to determine the acceptability of this cement-solidified, relatively uniform waste stream. It is, therefore, not surprising that no commercial waste formulations have yet received approval, and it raises questions concerning what can be done in a practical sense to qualify cement-solidified wastes.

The NRC topical report review program has two parts. The Office of Nuclear Materials Safety and Safeguards (NMSS) reviews the stabilization media and formulations from the standpoint of product compliance with the long-term stability requirements of Part 61. The Office of Nuclear Reactor Regulation, however, has been reviewing generic and Plant-specific Process Control Plans (PCPs). The generic PCPs are normally reviewed as topical reports in a manner analogous to the NMSS reviews of product topical reports. NRR's reviews tend to be focussed on the systems interactions of the solidification equipment with plant systems and operation. Inasmuch as the PCPs also address the procedures used to prepare the waste forms, we intend in the future to merge the process procedure reviews with the waste form product reviews; i.e., there would be only one topical report submittal that will address both product testing as well as the procedural recipe that is needed to ensure that the actual waste form will possess the qualities demonstated in the laboratory test program. Information on the details for the new PCP review procedure will be provided in the near future and is outside the scope of this Workshop. However, the relationship of the PCP procedure to the qualification testing used to demonstrate the adequacy of the waste formulation is an important issue that needs to be addressed in this Workshop.

V. Workshop Objectives, Structure, and Products

As noted in the announcement you all received concerning this Workshop, the overall objective of the Workshop is to exchange information on the technical issues in cement solidification of LLW and to develop initiatives that will

lead to regulatory resolution of those concerns. Thus, it is our hope and expectation that we will be able to use the information shared in this Workshop to make some near-term, perhaps interim, decisions on the issues involving cement stabilization of LLW (e.g., to approve, on at least an interim basis certain waste stream formulations and concentrations) while longer term solutions can be sought for the more difficult areas of concern.

The Workshop has been structured into "Plenary" and "Working Group" sessions. During this opening plenary session we will hear presentations from representatives of the radwaste treatment vendors, national laboratory researchers, and utilities. We will then break for lunch. After lunch we will reconvene with the start of Working Groups 1 & 2. There will then be a Status Summary Session later this afternoon. At that session the Working Group Chairmen and Technical Coordinators will report on the activities taking place during their sessions and will field questions and comments from members of the audience. There will be similar summary sessions at the conclusion of each day's Working Group meetings. Please check your copy of the agenda for the time and place of the planned sessions for each day of the Workshop.

You will note from the Meeting Announcement and Agenda that there will be four Working Groups, as follows:

1. Lessons Learned from Small/Full-Scale Waste Forms
2. Laboratory Test Experience and Application to Problem Waste Streams
3. Stabilized Waste Form Testing Guidance
4. Waste Characterization, Solidification, and Process Control Procedure

We have structured these Working Groups in such a way that the first two groups are intended to be "problem identification" oriented, whereas the second two are considered to be "regulatory pathway" oriented. Clearly, it would be desirable to conduct the problem identification sessions first, as the information received and "lessons learned" from such discussions could be factored into the regulatory pathway discussions. Unfortunately, time constraints do not allow us to run the sessions consecutively. The best we can do timewise is to initiate the discussions for the first two sessions first (this afternoon), and to start the second two Working Group (3 & 4) sessions tomorrow morning. Members of Working Groups 3 and 4 will, therefore, have the benefit of listening in to some of the "problem identification" discussions before undertaking their tasks tomorrow and the next day. And, should Working Group 1 & 2 members complete their activities before the wrap-up plenary session on Friday afternoon, they can listen in on the "regulatory pathway" discussions. In this way, we can make the best use of the time available and maximize the benefits that may accrue.

We envision that the Working Group session discussions will be conducted by designated members of the Working Groups. There will be ample opportunity for questions and comments for all attendees during the plenary summary sessions

each afternoon. I strongly urge all of you, whether you are a Working Group member or observer, to voice your opinions and to speak freely and openly about the issues at the appropriate time. The one thing we want to avoid is a situation where people are afraid or reluctant to speak candidly. If everyone simply sits and listens, hoping to obtain information without sharing any of their own, we will accomplish very little. Be aware that in general, the less information there is available upon which to base a regulatory decision, the more conservative that decision is likely to be.

The main product, in the sense of a document, that will ensue from this meeting will be a Summary Report. The report will contain the presentations made during this plenary session and will summarize the discussions, including the data presented and opinions expressed during the Working Group sessions. (Note that the sessions will not be transcribed, taped, or otherwise recorded). The most important benefit to be gained from this meeting will be the information shared that will provide the basis for resolving issues and reaching regulatory decisions concerning the use of cement in solidifying and stabilizing low-level radioactive waste. In this regard it must be recognized that this is not a "Concensus Conference." The intent is not to develop a Concensus Document, but is rather to share information, experience, and data that will enable the regulatory authority (i.e., the Nuclear Regulatory Commission) to reach decisions on how to deal with the use of cement to solidify and stabilize low-level radioactive wastes.

With regard to the issues, each Working Group member has received well in advance of this meeting a list of potential issues and questions to be addressed in his/her Working Group. In some cases, depending on the nature of the issue, more than one Working Group may be involved with a given issue. Different Groups may address different aspects of the issue. There are also certain issues or questions for which we would like input from all attendees to this Workshop. For those issues, we have provided you with questionaires that we would like you to fill out and return on your way out from this session to the cafeteria for lunch. We will tabulate the results. This is an opinion survey only and is intended only to serve as a means of ascertaining if there is a preponderance of opinion on some of the key issues.

Some of the key issues/questions that we would like you all to address are as follows:

1. (a). Based on laboratory observations and field experience, what waste streams or waste concentration levels appear to be compatible/ incompatible with cement?

1. (b). What additional R&D, if any, is needed to answer Question 1a?

2. (a). Can (must) waste generators do a better job of characterizing their wastes prior to solidifying the material?
   (b). If the answer to 2a is "yes," what ingredients should be checked (presence identified and quantified)?
   (c). if the answer to 2a is "yes," how should this be factored into

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the qualification and PCP programs?

3. What waste streams require pretreatment prior to solidification and how should they be pretreated (chemically and/or physically)?

4. What changes, if any, should be made to the 1983 Technical Position on Waste Form?

5. (a). What features should be included in a good PCP?
   (b). How should the PCP be related to the TP qualification testing?

6. What post-solidification testing procedures and criteria should be used?
   (a). For post-solidification/pre-shipment examinations;
   (b). For archival specimens.

The issues listed above are ones that will require regulatory decisions in the near future. It is our urgent hope and expectation that this conference will, at a minimum, help point the way to the regulatory pathways that can be followed to resolve these and other issues to be discussed over the next three days and that the information exchange during the conference will further our efforts to produce stabile waste forms that will allow safe operation of disposal facilities and the long term protection of the environment.

VI. Summary

In summary, this Workshop is being held because cement is known to interact adversely chemically and physically with some waste stream materials. Such interactions can be quite complex and can be adverse to the extent that the resultant waste forms cannot readily be demonstrated to have the long-term structural stability required by Part 61 for Class B and Class C wastes. And yet, cement is the medium most widely used to solidify and stabilize low-level radioactive wastes. In an effort to provide NRC licensees with a mechanism for demonstrating compliance with Part 61 and the provisions of 10 CFR 20.311 that require waste generators to certify that the Part 61 requirements have been satisfied, the NRC provides a centralized review of topical reports dealing with the stabilization medium or high integrity container. In performing the technical reviews NRC staff utilize acceptance criteria established in Technical Position on Waste Form that was issued in May 1983. The relevance and relationship of those tests and criteria to the need to ensure that the waste forms will possess long-term structural stability, the need to establish whether certain waste streams/compositions/concentrations are incompatible with cement, the need to address what, if any, pre- and post-solidification tests and criteria should be developed -- these will be among the major issues that we will be addressing over the next three days. I believe that this will be an interesting and productive workshop, and I thank you all for your active participation and cooperation in making it a success.

Table 1

Solidified product guidance

Tests	Methods	Criteria
1. Compressive Strength	ASTM C39 or D1074	60 psi (a)
2. Radiation Stability	(See 1983 TP)	60 psi comp. str. after 10E+8 rads
3. Biodegradation	ASTM G21 & G22	No growth (b) & comp. str.> 60 psi
4. Leachability	ANS 16.1	Leach index of 6
5. Immersion	(See 1983 TP)	60 psi comp. str. after 90 days
6. Thermal Cycling	ASTM B553	60 psi comp. str. after 30 cycles
7. Free liquid	ANS 55.1	0.5 percent
8. Full-scale Tests	(See 1983 TP)	Homogeneous & correlates to lab size test results

(a) The 1983 TP calls for a minimum compressive strength of 50 psi. This has been raised to 60 psi to accommodate an increased maximum burial depth at Hanford of 55 feet (from 45 feet).

(b) The 1983 TP calls for a multi-step procedure for biodegradation testing: if observed culture growth rated "greater than 1" is observed following a repeated ASTM G21 test, or any growth is observed following a repeated ASTM G22 test, longer term testing (for at least 6 months duration) is called for, using the "Bartha-Pramer Method." From this test, a total weight loss extrapolated for full-size waste forms to 300 years should produce less than a 10 percent loss of total carbon in the sample.

TABLE II

TOPICAL REPORT REVIEW STATUS SUMMARY
SOLIDIFIED WASTE FORM AND HIGH INTEGRITY CONTAINERS (HICs)
MAY 31, 1989

Office of Nuclear Material Safety and Safeguards

Vendor	Docket No.	Type	Disposition
Waste Chem	WM-90	Solidification (bitumen)	Approved.
General Electric	WM-88	Solidification (polymer)	Approved.
DOW	WM-82	Solidification (polymer)	Approved.
Chichibu	WM-81 Rev 2	HIC (poly impreg/concrete)	Approved.
Nuclear Packaging	WM-45	HIC (ferralium/FL-50)	Approved.
Nuclear Packaging	WM-85	HIC (ferralium/family)	Approved.
LN Technologies	WM-93 Rev 1	HIC (stainless/poly)	Approved.
Chem-Nuclear	WM-18	HIC (polyethylene)	Not Approved.
Hittman	WM-80	HIC (polyethylene)	Not Approved.
TFC Nuclear	WM-76	HIC (polyethylene)	Not Approved.
U.S. Gypsum	WM-51	Solidification (gypsum)*	Not Approved.
ATI (U.S.Ecology)	WM-91	Solidification (bitumen)	Discontinued.
VIKEM	WM-13	Solidification/oil (cement)	Discontinued.
Stock	WM-92	Solidification (cement)	Discontinued.
Nuclear Packaging	WM-71	Solid/Encap (cement/gypsum)	Withdrawn.
Chem-Nuclear	WM-19	Solidification (cement)	Withdrawn.
Chem-Nuclear	WM-96	Solidification (cement)	Withdrawn.
Hittman	WM-79	Solidification (SG-95)	Withdrawn.
Nuclear Packaging	WM-87	HIC (316-stainless/SDS)	Withdrawn.
LN Technologies	WM-57	HIC (polyethylene)	Withdrawn.
Chem-Nuclear	WM-47	HIC (fiberglass/poly)	Withdrawn.
Chem-Nuclear	WM-101	Solidification (cement #1)	Under review.
Chem-Nuclear	WM-97	Solidification (cement #2)	Under review.
Chem-Nuclear	WM-97 Rev 1	Solidification (cement #2)	Under review.
Chem-Nuclear	WM-98	Solidification (cement #3)	Under review.
LN Technologies	WM-20	Solidification (cement)	Under review.
LN Technologies	WM-99	Solidification (cement/decon)	Under review.
Hittman	WM-46	Solidification (cement)	Under review.
ATI (U.S. Ecology)	WM-100	Solidification (bitumen)	Under review.
Bondico	WM-94	HIC (fiberglass/poly)	Under review.
Babcock & Wilcox	WM-95	HIC (coated carbon steel)	Under review.

* Had been approved for single waste stream for one year ending March 3, 1989.

Remarks by the National Laboratories: Brookhaven National Laboratory

SOLIDIFICATION OF LOW-LEVEL WASTE IN PORTLAND CEMENT: A LABORATORY SCALE PERSPECTIVE

by

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1. INTRODUCTION

Good morning! In these introductory remarks I would like to present an overview of the solidification of low-level waste in portland cement from the perspective of testing and investigations in the laboratory. In the few minutes alloted to me, I can only present some of the highlights as I see them after Mel Cowgill and I conducted a review of laboratory-bench-scale cement solidification data for the NRC. At this point, let me add the usual disclaimer, namely, that my comments in this presentation represent my own viewpoint and are in no way to be construed as representative of the position of the Nuclear Regulatory Commission or of its Staff nor are they to be taken as the position of Brookhaven National Laboratory. Now, with the formalities out of the way, let us proceed.

Because of time constraints, in this presentation I will discuss only some qualitative aspects of studies of compressive strength for cement-solidified LLW from reports and technical articles. Although vendor topical reports constitute a major portion of our review, much of the information from vendor topical reports is proprietary and thus cannot be discussed in any detail. Perhaps some of the vendors will share the more interesting portions of their data during the course of this workshop.

I think I had better say a few words about the reason for our review of these cement solidification data. We needed as large a data base as possible consisting of compressive strength values for LLW solidified in cement in order to utilize this data base to characterize LLW streams, especially those waste streams addressed in the vendor's topical reports, as one of the following:

(1) a waste stream which can be successfully solidified in cement (up to some maximum loading);

(2) a waste stream which cannot be successfully solidified in cement; and

(3) a waste stream whose successful solidification in cement is still open to question.

"Successful solidification" means, in this context, that the final waste product meets the long-term structural stability criteria of 10 CFR Part 61 and the 1983 Technical Position on Waste Form (TP). Note that because of time constraints on this review, we did not explicitly address any of the TP requirements except immersion resistance, since we consider this requirement to be the most stringent. I will have more to say about the criteria we selected to indicate "successful solidification" later in this presentation.

This review which we undertook for the NRC was by no means the first. In a status report on cement solidification of one particular family of LLW streams, namely organic ion-exchange (IX) resins, Barletta et al. (1980) summarize the relevant literature available at that time. [Even then, it was realized that IX resins were somewhat of a "problem" waste stream.] Some of the conclusions from that review are of particular relevance here:

" Acceptable composites have been produced using anion exchange resins, cation exchange resins, and mixed bed resins. Conversely, composites made of all three types of resins have been known to exhibit poor mechanical properties [i.e., swelling, cracking, and, in extreme cases, complete disintegration of the composite, especially, but not only, when immersed in water]."

" For a particular resin (or resin mix) there exists a window of water cement ratios within which an acceptable composite may be produced. Water content either greater or less than this range produces composites exhibiting poor mechanical properties. This window is not the same for all resins or for all resins of a given type. ... Thus, in order for valid conclusions to be drawn concerning the mechanical properties of a given resin/cement composite, scoping experiments must be performed using resin or resin mix identical to that of interest."

" Since, in a water deficient environment, one might expect a competition for available water between ion exchange resins and cement, **curing conditions and most particularly those relating to water availability** (i.e., humidity, amount of free standing water during curing, etc.) might be expected to affect the mechanical integrity of the product. Indeed, improved strength has been noted for cement products when curing is done in the presence of a large excess of water. ... no systematic study of this variable has been undertaken, and it appears that, at best, composites were allowed to cure in water-saturated air ... Thus, **the effect of curing conditions upon the mechanical strength and integrity of ion exchange resin/cement composites is unknown.**" (Emphases added).

It would be interesting to see to what extent our understanding of solidification of IX resins in cement has advanced since the preparation of the status report.

2. AN OVERVIEW OF THE REPORTS AND TECHNICAL ARTICLES

While cement-based immobilization processes have been in use at nuclear power plants for several decades, the nature of the laboratory studies of solidification of LLW in portland cement or similar materials has depended on the perceived purpose of such solidification. At first, radwaste solidification seems to have been implemented primarily in order to simplify handling, storage, and transport of radioactive wastes, although reduction of release of radionuclides to the environment -- as indicated by the ease with which they could be leached from the cement matrix -- was also considered important. For example, according to Colombo and Neilson (1979), the mechanical properties of solidified waste forms (such as the compressive, tensile and impact strengths) "are important primarily during transportation [and] interim storage, but mechanical failure can also affect the disposal environment because it increases the effective waste form surface area and thus increases the rate of leaching and the potential waste form dispersibility." Burns (1971), Buckley (1982), and Brownstein and LeVesque (1978) also present versions of this viewpoint in their reviews of cement solidification. The last of these three reviews states explicitly that the "ideal solidified end product" of radwaste solidification is "a solid, free standing and inert monolith."

The earlier reports to be discussed in this section describe laboratory-bench-scale studies undertaken to identify compositions which result in free-standing monoliths. With the notable exception of the work by Bonnevie-Svendsen (1976), immersion resistance seems to have become a significant factor first in connection with leachability testing, when it became obvious that a leach test could not be meaningfully conducted on a specimen that disintegrated in water. Immersion resistance begins to be associated with structural stability during the development of 10 CFR Part 61 and the TP. Compressive strength as a measure of structural stability also seems to be associated with the development and issuance of the TP. Structural stability and, therefore, compressive strength were considered important largely because of concerns about subsidence and subsequent influx of water at disposal facilities.

The selection of the studies discussed in the remainder of this section is in no way meant to be exhaustive. Furthermore, in this selection we have emphasized cement solidification of IX resins because this waste stream appears to be one of the more difficult to solidify in portland cement and similar binder materials. Because of time limitations, I will not present any of the ternary composition diagrams from these studies, but if anyone is interested I have copies and would be willing to discuss them with you individually later.

In laboratory-bench-scale tests Bonnevie-Svendsen et al. (1976) investigated the performance of cement-solidified IX-resins. As already noted, they found that water-resistant products were obtained only within a narrow range of water/cement ratios. The lower limit of this ratio -- 0.45 to 0.5 for 4 to 20 weight percent dry resin -- is determined by the water necessary to give a workable mix, but the upper limit depends on the type of resin (cation- or anion-exchange), the depletion of the resin (the species of the depleting ion), the potential for resin swelling, and the water-retention properties of the resin. Depletion of the cation-exchange

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resins by replacing H^+ with Na^+ or Ca^{2+} improved the quality of the cement-solidified product. Depletion of the anion-exchange resins by replacing the OH^- with SiO_3^- or Cl^- allowed incorporation of the resin into a water-resistant cement product, but the OH^--form of the resin could not be incorporated into a water-resistant cement product. [Later studies would also show that the nature of the counter ions, i.e., the chemical species, oxidation states, and their relative proportions, can affect the performance of the final cement-solidified product.] The authors note that "cement products are easily impaired by small irregularities in process conditions," and present the narrow range of water/cement ratios as an example. They further conclude that product qualities can be improved and tolerance ranges increased by means of stabilizing additives.

Lerch et al. (1977) investigated cement solidification of IX resins at the Hanford Engineering Development Laboratory (HEDL) in order to identify the range of "workable" compositions. In this HEDL study, "workable" compositions seem to be those which form a free-standing monolith which does not swell and has sufficient water for mixability but no residual free liquid. This HEDL study did not report any data on stability during immersion. A report issued later (Greenhalgh 1977) noted that specimens of cement-solidified resin which were free-standing solids when dry expanded and fragmented when placed in water (as part of a leach test procedure).

Resistance of cement waste forms to immersion seems to have been an afterthought in other early cement-solidification work as well, since immersion stability is necessary for carrying out leaching studies. For example, Manaktala and Weiss (1980) in an NRC-sponsored study at BNL investigated a range of compositions for cement-solidified ion-exchange (IX) resin in order to establish a "window" of binder:water:waste ratios within which an "acceptable" waste form might be produced. In this study, an "acceptable" waste form was a free-standing monolith which did not swell or crack. In a follow-on study at BNL which focussed on leaching from such waste forms, Morcos and Dayal (1982) further limited the window of acceptability by requiring stability to immersion in order to conduct leaching measurements. The IRN-77 cation beads had been converted to the Na^+ form by treatment with NaOH solution. The immersion-resistant formulation established by Morcos and Dayal was used in some of the subsequent BNL studies, including the waste-form curing study to be discussed below, which terms it the "BNL reference formulation".

In studies at BNL sponsored by DOE, Neilson and Colombo (1982) determined a range of "acceptable" formulations for the solidification of IX resin waste in hydraulic cements. Once again "acceptable" meant that the waste form is a free-standing monolith with no drainable free liquid. In addition, the waste form was to maintain its integrity during a two-week immersion test in demineralized water. "The water immersion test is taken to be indicative of long-term waste form integrity," according to these authors, who reported the results of testing a large number of formulations in the form of ternary compositional diagrams. These diagrams presented envelopes for acceptable as well as for some unacceptable compositional formulations.

Because of the aforementioned concern that the performance of cementitious waste forms in the TP water immersion test might be dependent on the cure period prior to water immersion, NRC sponsored an experimental study at BNL of the effect of cure conditions on the stability of cement waste forms after immersion in water (Piciulo et al., 1987; Siskind et al., 1988). The test specimens consisted of partially depleted mixed-bed bead resins solidified in one of four Type I portland cement formulations -- the BNL reference formulation determined by Morcos and Dayal and three vendor formulations. The cation exchangers were partially depleted by expending about 40% of the exchange capacity with a mixture of various non-radioactive cations (Fe^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Cs^+) intended to simulate those actually found on PWR primary coolant clean-up resin. Two of the cement formulations exhibited apparent portland-cement-like behavior, i.e., compressive strength increased or stabilized with increasing cure time (7, 14, and 28 days), but the other two exhibited behavior unlike that of portland cement, i.e., compressive strength decreased with increasing cure time. Following the terminology employed by the NRC in letters sent to the four cement solidification vendors in November 1987, we are calling such a decrease in compressive strength with time "**atypical cement strength behavior**" and we note that it is correlated with higher waste loadings. Some physical deterioration (cracking, spalling) of the waste forms also occurred during immersion. This investigation, however, did not separate the effects of cure time on immersion resistance from the time-dependence of the compressive strength. The changes in compressive strength as a function of waste loading are given in Figure 1, which is taken from Jungling et al.(1987).

3. CRITERIA FOR SUCCESSFUL SOLIDIFICATION IN CEMENT

As I indicated in my introductory comments, I am employing the term "successful solidification" to mean that the final waste product meets the long-term structural stability criteria of 10 CFR Part 61 and the TP. The results of some of these laboratory studies indicate that laboratory-scale waste forms may exhibit what I have termed "atypical cement strength behavior," as well as visible surface and bulk degradation following immersion after cure times of varying lengths. Therefore I would consider "successful solidification" to be contingent not only upon data showing that the waste form meets the criteria of the TP but also upon data showing that the compressive strength increases as a function of time or, if it decreases, at the very least levels off to an acceptable value. Otherwise, I would be unable to conclude that there is reasonable assurance that the waste-binder formulation in question will maintain its long-term structural stability. Also, the time dependence of the compressive strength needs to be separated from the effects of cure time (and curing conditions) on immersion resistance although it was the cure-time investigations which flagged the time dependence of compressive strength as a potentially significant parameter. Both of these aspects of cement behavior are important. [Published data on the effects of curing on the performance of cement waste forms are minimal, e.g., Piculo et al. (1987), but published data on the time dependence of the compressive strength independent of immersion appear to be non-existent.]

I have not attempted to define an absolute "acceptable" value for the asymptotic value of the compressive strength with time, but I note that the NRC has specified that, in order to withstand the weight of the overburden at current disposal site burial depths, waste forms have a minimum value of 60 psi. Also, "typical cement strength behavior" should include a final compressive strength value in some way "typical" of values for portland cement. [Without quantifying such values any further, we would expect them to be well over 60 psi.] I would also like to note that any conclusions which might be made using this "typical cement behavior" criterion regarding the successful solidification of a waste stream concentration in cement would be based only on the laboratory testing; I leave it to Working Group No. 1 at this workshop to consider whether the applicability of these laboratory results to full-scale field samples has been established.

4. CONCLUSIONS

Unfortunately, we must conclude that the data base on cement solidification of the different kinds of LLW streams is still too limited to allow us to reach any but the most superficial conclusions regarding the relationship between successful solidification in portland cement and the various waste and binder parameters.

I will conclude with what might be called a "wish list" of the data I would like to see in order to characterize a LLW stream as amenable to solidification in a binder matrix consisting of a particular cement formulation. The major difficulty with the existing data is the lack of sufficient time-dependent compressive strength data. Ideally, I would like to see sufficient data to allow for statistically meaningful plots of the compressive strength as a function of time. Also, I would like to see some further work on the effects of cure conditions and cure time on the compressive strength of LLW/cement composites, especially in conjunction with immersion -- very likely the most severe of the TP tests. Also, we would have more confidence in particular waste-stream/binder formulations if envelopes of acceptable compositional formulations in ternary compositional diagrams similar to those utilized by Neilson and Colombo (1982) were available. Such envelopes of stability would indicate how much variation in composition could be tolerated without loss of stability of the waste form. They would also be of use in process control.

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FIGURE 1

% Change in Strength vs. % Loading

□ 4—wk vs 1—wk cure   + 2—wk vs 1—wk cure

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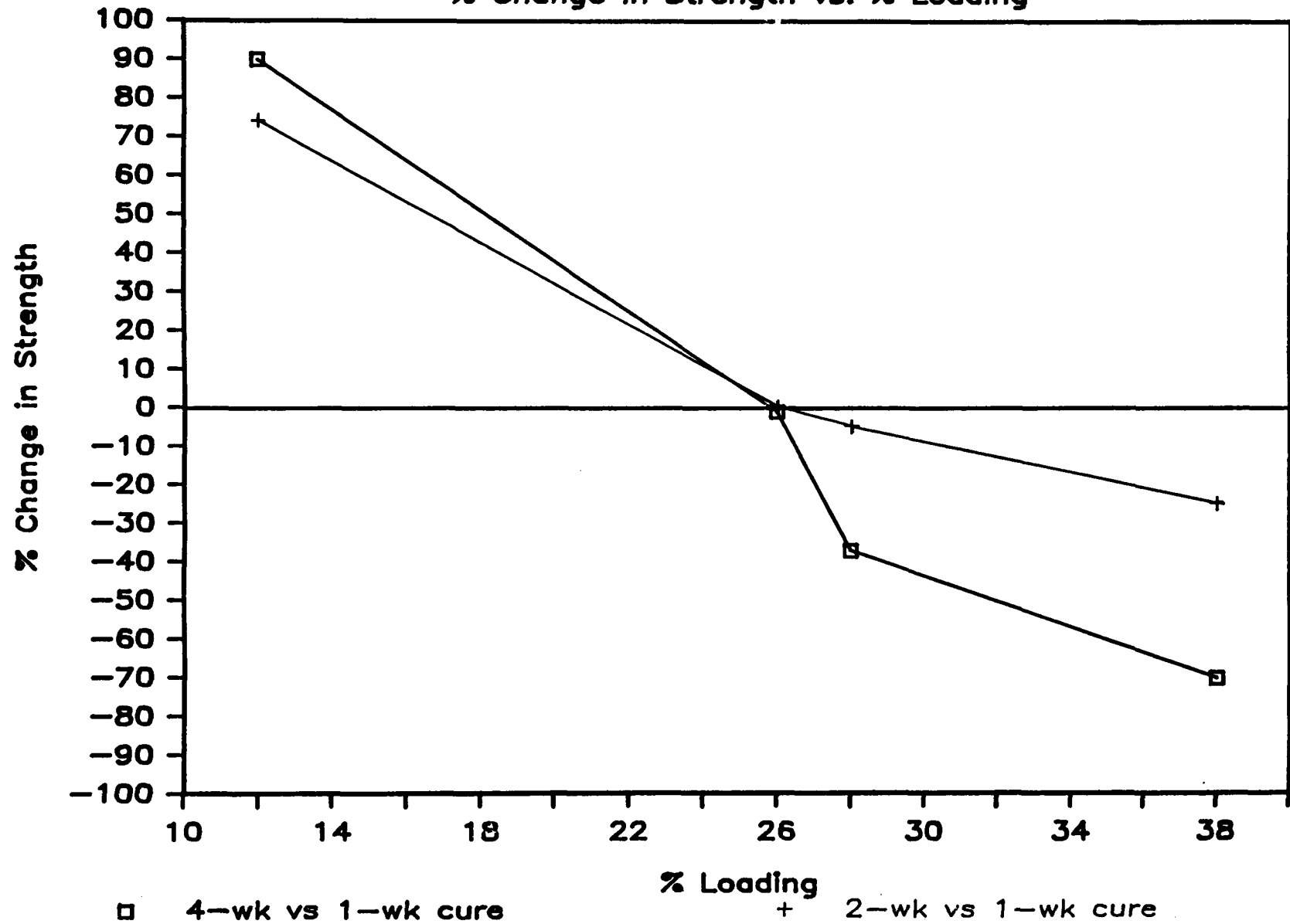
INEL STUDIES CONCERNING SOLIDIFICATION OF LOW-LEVEL WASTE IN CEMENT

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INTRODUCTION

The Idaho National Engineering Laboratory (INEL) has performed
numerous studies addressing issues concerning the solidification of
low-level radioactive waste in cement. These studies have been performed
for both the Nuclear Regulatory Commission (NRC) and the Department of
Energy (DOE). This short presentation will only outline the major topics
addressed in some of these studies, present a few conclusions, and
identify some of the technical concerns we have. More details of the work
and pertinent results will be given in the Working Group sessions.

The topics that have been addressed at the INEL which are relevant to
this Workshop include (1) solidification of ion-exchange resins and
evaporator waste in cement at commercial nuclear power plants,
(2) leachability and compressive strength of power plant waste solidified
in cement, (3) suggested guidelines for preparation of a solid waste
process control program (PCP), (4) cement solidification of EPICOR-II
resin wastes, and (5) performance testing of cement-solidified EPICOR-II
resin wastes.

SOLIDIFICATION OF POWER PLANT WASTE

The initial objectives of this program were to study the process of cement-solidification of evaporator wastes (boric acid and sulfate wastes) and the waste streams feeding this process at operating nuclear power plants. The solidification of several batches of boric acid and sulfate wastes were observed at two operating nuclear power plants. Samples of the solidified waste form ranging in size from 5 cm diameter x 10 cm long (2 inch x 4 inch) cylinders to 55 gallon drums were collected and leach tested using demineralized water. Leaching parameters and compressive strength were determined. Emphasis was placed on studying the effects of sample size and determining whether the behavior of small samples can be extrapolated to full-sized waste forms.

The focus of the studies then turned to the solidification of ion-exchange resin waste produced by chemical decontamination processes. The solidification of wastes from four decontamination processes (CAN-DECON, DOW NS-1, LOMI, and PNS CITROX A) were observed at operating nuclear power plants. Small samples (5 cm diameter x 10 cm long) of the waste form were collected. Subsequently, these samples underwent leaching and compressive strength testing. This work is still in progress with particular emphasis being placed on studying the effects of the chelating agents on the leach parameters.

During these studies, a number of problems were observed. One large batch of 55 gallon size waste forms failed to solidify. One set of samples, after appearing to solidify properly, disintegrated into a sand-like consistency during shipment to the INEL. Several solidifications failed to proceed as expected, the waste forms setting more rapidly than expected. In a few cases, the waste forms set so rapidly that all of the ingredients could not be added. One set of waste forms developed numerous cracks during leaching. Several sets disintegrated totally during leaching.

Because of these problems, we have several technical concerns regarding the cement solidification of low-level waste. These concerns include (1) adequacy of the solidification quality control program, (2) adequacy of the characterization of the waste stream to be solidified, (3) range of parameter values for which a solidification process is valid, (4) adequacy and applicability of PCP tests, (5) representativeness of the verification samples.

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SUGGESTED GUIDELINES FOR PREPARATION OF
SOLID WASTE PROCESS CONTROL PROGRAM

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Concurrent with our work on the cement solidification of low-level waste, we were involved with assisting the NRC in implementing Licensee radiological environmental technical specifications (RETS). This included review of Licensee process control programs (PCPs) for processing low-level waste into a form acceptable for disposal. Because of the problems we had observed during actual solidifications at power plants and the inadequacies of many of the PCPs submitted for our review, we were asked to develop guidelines for the preparation of a process control program for this activity. Topics addressed in these guidelines included system description, methods, operating procedures, waste characteristics, stability requirements, quality assurance, administrative controls, and the NRC Technical Position on Waste Form.

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EPICOR-II RESIN/LINER INVESTIGATIONS

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The INEL has also been heavily involved with the EPICOR-II Research and Disposition Program. Included in this program is the solidification of EPICOR-II resin waste forms and performance testing of these waste forms.

Formulations for cement-immobilization of EPICOR-II prefilter wastes were developed using simulated non-radioactive materials. Parameters studied during this phase of the work included waste/binder volume ratio, water content of the resin, pH adjustment, and the effects of immersion

testing. The selected Portland cement formulation was then used to solidify actual EPICOR-II wastes. Baseline/qualification and environmental testing of these samples were conducted to determine the adequacy of test procedures specified in the NRC Technical Position when applied to the case of the EPICOR-II resin wastes.

The baseline/qualification testing was performed on eight samples containing two types of waste and included (1) presence of any free-standing liquid, (2) as-prepared compressive strength, and (3) homogeneity. Eight samples containing two types of waste underwent environmental tests which included (1) thermal stability (thirty cycles in temperatures ranging from -40 C to 60 C), (2) leachability in demineralized water, (3) immersion stability (i.e, compressive strength after immersion in demineralized water for 90 days), (4) leachability and compressive strength after irradiation (5×10^8 rad of gamma radiation), and (5) biodegradability (fungi and bacteria).

Although this work is not yet completed, some conclusions have been reached. The Portland cement waste forms were found to meet the 10 CFR 61 waste form stability requirements for (1) free liquids, (b) homogeneity, (3) compressive strength, (4) resistance to thermal degradation, (5) leachability, (6) immersion, and (7) radiation stability. The formulations used, however, had low waste loadings compared to commercial practice. The procedures specified in the NRC Technical Position were found to be generally satisfactory for demonstrating compliance with 10 CFR 61 stability requirements, and the following potential improvements to the Technical Position were identified: (1) containerize the specimen for thermal stability testing to prevent evaporative water loss, (2) specify the leachant fluid type (i.e., demineralized water and/or sea water, or other), (3) provide guidance on radionuclides of interest for the leachability tests, (4) specify more completely the immersion test conditions, and (5) specify 10^8 rad (or higher if the waste form is expected to exceed this exposure) for the radiation stability testing.

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SOLIDIFICATION OF POWER PLANT WASTE
CURRENT STUDIES

- ION-EXCHANGE RESIN WASTES FROM FOUR DECON. PROCESSES
  - CAN-DECON
  - DOW NS-1
  - LOMI
  - PNS CITROX A

- OBSERVED SOLIDIFICATION PROCESSES

- MEASURED LEACHING PARAMETERS, COMPRESSIVE STRENGTH

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EPICOR-II RESEARCH AND DISPOSITION PROGRAM

- EPICOR-II PREFILTER WASTES

- DEVELOPMENT OF FORMULATION FOR CEMENT-SOLIDIFICATION
    - WASTE/BINDER VOLUME RATIO
    - WATER CONTENT OF THE RESIN
    - PH ADJUSTMENT
    - IMMERSION TESTING

- BEHAVIOR OF ACTUAL SOLIDIFIED EPICOR-II WASTE
    - BASELINE/QUALIFICATION TESTING
    - ENVIRONMENTAL TESTING

PROBLEMS OBSERVED

- MANY SOLIDIFICATIONS DID NOT BEHAVE AS
  EXPECTED
  - WASTE FORMS DID NOT SOLIDIFY
  - WASTE FORMS SOLIDIFIED TOO QUICKLY

- ONE SET OF WASTE FORMS DISINTEGRATED DURING
  SHIPMENT TO INEL

- CRACKING OF WASTE FORMS DURING LEACHING

- COMPLETE DISINTEGRATION OF WASTE FORMS DURING
  LEACHING

SOLIDIFICATION OF POWER PLANT WASTE
CURRENT STUDIES

- ION-EXCHANGE RESIN WASTES FROM FOUR DECON. PROCESSES
    - CAN-DECON
    - DOW NS-1
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- OBSERVED SOLIDIFICATION PROCESSES

- MEASURED LEACHING PARAMETERS, COMPRESSIVE STRENGTH

TECHNICAL CONCERNS

- ADEQUACY OF QUALITY CONTROL PROGRAM

- ADEQUACY OF CHARACTERIZATION OF WASTE STREAM

- RANGE OF PARAMETER VALUES FOR WHICH PROCESS IS VALID

- ADEQUACY AND APPLICABILITY OF PCP TESTS

- REPRESENTATIVENESS OF VERIFICATION SAMPLES

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GUIDELINES FOR LICENSEE PREPARATION OF PCP

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- METHODS
- OPERATING PROCEDURES
- WASTE CHARACTERISTICS
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- QUALITY ASSURANCE
- ADMINISTRATIVE CONTROLS
- NRC TECHNICAL POSITION ON WASTE FORM

BEHAVIOR OF ACTUAL EPICOR-II WASTE

- FREE-STANDING LIQUID

- AS-PREPARED COMPRESSION STRENGTH

- HOMOGENEITY

- THERMAL STABILITY

- LEACHABILITY

- IMMERSION STABILITY

- LEACHABILITY AND COMPRESSION STRENGTH AFTER
  IRRADIATION

- BIODEGRADABILITY

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TENTATIVE CONCLUSIONS FOR EPICOR-II STUDIES

- CEMENT WASTE FORMS MET 10CFR61 REQUIREMENTS

- WASTE LOADING LOW COMPARED TO COMMERCIAL PRACTICE

- NRC TECH POSITION PROCEDURES GENERALLY SATISFACTORY FOR DEMONSTRATING COMPLIANCE WITH 10CFR61

- POTENTIAL IMPROVEMENTS TO THE NRC TECHNICAL POSITION
  - CONTAINERIZE SPECIMEN FOR THERMAL STABILITY TESTING
  - SPECIFY LEACHANT FLUID TYPE
  - PROVIDE GUIDANCE ON RADIONUCLIDES OF INTEREST
  - SPECIFY MORE COMPLETELY THE IMMERSION TEST CONDITIONS
  - REQUIRE 10^8 RAD (OR HIGHER) FOR RADIATION STABILITY TESTING

SOLIDIFICATION OF POWER PLANT WASTE
INITIAL STUDIES

- BORIC ACID AND SULFATE EVAPORATOR WASTES
- OBSERVED SOLIDIFICATION PROCESSES AT POWER PLANTS
- MEASURED LEACHING PARAMETERS, COMPRESSIVE STRENGTH
- STUDIED EFFECTS OF SAMPLE SIZE

SOLIDIFICATION OF LOW-LEVEL RADIOACTIVE WASTE AT THE SAVANNAH RIVER SITE

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CEMENT SOLIDIFICATION OF LOW-LEVEL RADIOACTIVE WASTE
AT THE SAVANNAH RIVER SITE
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INTRODUCTION

Research on cement solidification of low-level radioactive waste has been carried out at the Savannah River Site since about 1980. As a result of these efforts, aqueous-based process waste from the Defense Waste Processing Facility, (DWPF), Separation Effluent Treatment Facility, (ETF), and the Fuel Production Facility, (FPF), and sludge from the Manufacturing Facility settling basin, are currently being solidified in inorganic cement-based wasteforms. In addition, cement stabilization of SRS mixed wastes, such as F006-low-level electroplating sludge and incinerator ash and liquid TRU wastes is planned.

In general, wastes considered for cement stabilization at SRS are relatively well defined with respect to composition and volume. For example, the three major process waste streams contain about 30 wt% sodium salts of which sodium nitrate is the primary constituent. Spent ion exchange resins and contaminated organic liquids, charcoal, and reactive metals, such as aluminum, are currently not solidified in cement at SRS. In addition, disposal of low-level radioactive waste at SRS is also well defined and will consist of direct or containerized emplacement into engineered vaults (except TRU wastes) starting in 1992. This disposal method is consistent with the Final Environmental Impact Statement issued on groundwater protection and waste management activities at SRS[1] and the DOE Record of Decision for the EIS[2].

Consequently, performance criteria for all SRS cement wasteforms can be generalized as follows: Contain contaminants so that groundwater quality at the landfill boundary is maintained; prevent disposal facility subsidence; and prevent direct disposal of liquids.

DISCUSSION

Waste Characterization

Waste streams considered for cement stabilization are characterized with respect to bulk composition, pH, activity, and metal and organic concentrations. Physical properties which will affect processing such as specific gravity, temperature, rheology, and solids content are measured. Properties of any precipitated solids are also determined including solubility over the pH range 5 to 14. In addition, the EPA hazardous characteristics, toxicity, ignitability, reactivity, and corrosivity are evaluated prior to developing specific pre-treatment and solidification processes.

Cement Wasteform Preparation and Testing

Sample mixing is carried out to simulate actual process mixing. At SRS, high volume, high speed mixing is used for the DWPF saltstone process, whereas, in-drum paddle mixing is used for the FPF saltstone process. These are simulated by Waring blender and Hobart mixer preparations, respectively. The resulting slurries are tested for rheological properties, set time, and free liquid. Specifications are determined for each process.

Samples are cast for evaluation of EPA hazardous characteristics, compressive strength, ANS 16.1 leach testing and waste cement compatibility (soak test). Adiabatic temperature rise is also measured for each wasteform. In addition to calculating a leach index or effective diffusion coefficient from the ANS 16.1 test, information on the mechanism of stabilization for each contaminant of concern is also obtained.

Field Testing

Field testing of three 30 ton monoliths and several 1000 pound monoliths in lysimeters has been in progress since 1985. In addition, 55 gallon drums of DWPF saltstone were tested at Brookhaven National Laboratory as part of the scale-up process from laboratory to full scale operations. Results of these intermediate size experiments track the bench top studies. The lysimeters, in particular, have been useful for testing and supporting performance modeling predictions for the saltstone disposal facility.

SUMMARY

Aqueous-based process waste and other small volume wastes including basin sludge and incinerator ash will be solidified in cement-based wasteforms at SRS. A variety of inorganic solidifying agents are used depending on the chemistry, contaminants, and processing characteristics of the waste. In some cases, pre-treatment of the waste is used to reduce the activity of the waste and/or to remove the hazardous characteristics of the waste.

In the case of DWPF saltstone, pretreatment is used to reduce 137 Cs and 90 Sr concentration to Class A levels and in-situ treatment (chemical reactions between the cementitious solids and waste) is used to remove the toxic metal characteristic of the waste. Chemical reduction of the Cr^{+6} to Cr^{+3} and subsequent precipitation of $Cr(OH)_3$, (low solubility) occurs as the result of reactions between the cementitious raw materials and the waste liquid.

In summary waste treatment and solidification used at SRS is designed to meet both South Carolina and Federal requirements for maintaining the quality of the groundwater at the disposal site boundary.

REFERENCES

1. U.S. Department of Energy, Final Environmental Impact Statement: Waste Management Activities for Groundwater Protection Savannah River Plant Aiken, South Carolina, U.S. Department of Energy (December 1987).

2. U.S. Department of Energy, Waste Management Activities for Groundwater Protection, Savannah River Plant, Aiken, South Carolina; Record of Decision, Federal Register, V. 53, No. 48, page 7557, Wednesday, March 9, 1988.

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WVNS EXPERIENCE WITH CEMENT
SOLIDIFICATION OF DECONTAMINATED SPENT FUEL WASTE

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ABSTRACT

This report provides a summary of work performed to develop a cement-based, low-level waste (LLW) formulation suitable for the solidification of decontaminated high-level waste liquid produced as a by-product of PUREX (Plutonium Uranium Reduction Extraction) spent fuel reprocessing. The resultant waste form is suitable for interim storage and is intended for ultimate disposal as low-level Class C waste; it also meets the stability requirements of the Nuclear Regulatory Commission (NRC) Branch Technical Position on Waste Form Qualification, May 1983, and the requirements of 10 CFR 61.

A recipe was developed utilizing only Portland Type I cement based on an inorganic salts simulant of the PUREX supernatant. The qualified recipe was tested full scale in the production facility and was observed to produce a product with entrained air, low density, and lower-than-expected compressive strength. Further laboratory-scale testing with actual decontaminated supernatant revealed that set retarders were present in the supernatant, precluding setting of the product and allowing the production of "bleed water." Calcium nitrate and sodium silicate were added to overcome the set-retarding effect and produced a final product with acceptable performance when compared to the original formulation.

This report describes the qualification process and qualification test results for the final product formulation.

INTRODUCTION

The West Valley Demonstration Project Act of October 1, 1980, (Public Law 96-368) directs The Department of Energy (DOE) to carry out a high-level radioactive waste (HLW) management demonstration project at the former Western New York Nuclear Services Center site located in West Valley, New York. Under the Act, the Department is responsible for removing the liquid HLW from underground storage tanks and solidifying it into a form suitable for long-term storage and transportation to a federal repository for final disposal of HLW. The facility at West Valley, New York, was formerly operated by Nuclear Fuel Services, Inc. (NFS) as a commercial nuclear fuel reprocessing plant. West Valley Nuclear Services Co., Inc. (WVNS), a subsidiary of Westinghouse Electric Corporation, was selected to be the prime contractor for site operations and assumed control of the site in February 1982.

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The West Valley site was the location of the only operating commercial nuclear fuel reprocessing plant in the United States. NFS operated this facility from 1966 to 1972, processing 640 metric tons of commercial and defense fuels using the PUREX process. Approximately 2.1 million litres of fuel reprocessing waste resulted from this operation. The major portion (~98 percent by volume) of these wastes are stored in an underground storage tank designated 8D-2. The bulk of the tank's contents was formed by adding excess caustic (NaOH) to a nitric acid-based stream originating from essentially the first solvent extraction cycle (although other additions of decontamination and cleanup waste have been made). The neutralization of the solution has resulted in the formation of a sludge layer at the bottom of the waste tank, consisting of insoluble oxides, hydroxides, and carbonates at a pH of 10.

Early in the Project, two decisions were made which determined the major thrust of the HLW solidification effort:

1. The HLW alkaline supernatant would be separated from the sludge, and the major radioactive component in the supernatant would be chemically separated and combined with the sludge into a terminal HLW form. The treated (or decontaminated) supernatant would be processed into a suitable LLW form (the separated salt/sludge option of the Phase I Final Environmental Impact Statement, reference 1).

2. The terminal HLW form would be borosilicate glass.

The decision on the processing scheme was based on chemical, radiochemical, and physical properties characterizations performed on samples of the PUREX HLW.

This report provides a summary of work done at the Westinghouse Research and Development (R&D) Center in Pittsburgh, Pennsylvania, and the Analytical and Process Chemistry Laboratories of the WVNS at West Valley, New York. This work was performed to develop a cement-based formulation suitable for the solidification of the decontaminated supernatant waste produced as a by-product of PUREX spent fuel reprocessing. The waste has been well characterized radiochemically and was reported on in reference 2. Table I presents a summary of its inorganic composition and Table II presents its radiochemical properties as reported in reference 3. Prior to solidification in cement, the waste will be decontaminated in the Supernatant Treatment System (STS) to remove the cesium. The purpose of the cement waste form is to solidify the resultant decontaminated salt solution in a medium suitable for interim storage and ultimate disposal as low-level Class C waste which meets the stability requirements of 10 CFR 61 and the NRC Branch Technical Position on Waste Form Qualification.

CEMENT WASTE FORM DEVELOPMENT

A formulation for the solidification of the decontaminated supernatant was developed by the Westinghouse R&D Laboratories using Portland Type I cement.

The formulation which was developed and ultimately recommended for use was supernatant and Portland Type 1 cement at a water-to-cement ratio of 0.61 with a range from 0.54 to 0.70. This basic formulation was tested at Westinghouse R&D against the requirements of reference 4 and was qualified. With a salt concentration of 39 weight percent, equal weights of supernatant and cement were to be used.

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TABLE I: 8D-2 SUPERNATANT CHEMICAL COMPOSITION

Compound	Wt. % Wet Basis	Wt. % Dry Basis	Total Kg in Supernatant
$NaNO_3$	21.10000	53.3800	602659
$NaNO_2$	10.90000	27.5700	311326
Na_2SO_4	2.67000	6.7600	76261
$NaHCO_3$	1.49000	3.7700	42557
KNO_3	1.27000	3.2100	36274
Na_2CO_3	0.88400	2.2400	25249
$NaOH$	0.61400	1.5500	17537
K_2CrO_4	0.17900	0.4500	5113
$NaCl$	0.16400	0.4200	4684
Na_3PO_4	0.13300	0.3400	3799
Na_2MoO_4	0.02420	0.0600	691
Na_3BO_3	0.02090	0.0500	597
$CsNO_3$	0.01870	0.0500	534
NaF	0.01760	0.0400	503
$Sn(NO_3)_4$	0.00859	0.0200	245
$Na_2U_2O_7$	0.00808	0.0200	231
$Si(NO_3)_4$	0.00806	0.0200	230
$NaTcO_4$	0.00620	0.0200	177
$RbNO_3$	0.00416	0.0100	119
Na_2TeO_4	0.00287	0.0070	82
AlF_3	0.00271	0.0070	77
$Fe(NO_3)_3$	0.00152	0.0040	43
Na_2SeO_4	0.00054	0.0010	15
$LiNO_3$	0.00048	0.0010	14
H_2CO_3	0.00032	0.0008	9
$Cu(NO_3)_2$	0.00022	0.0005	6
$Sr(NO_3)_2$	0.00013	0.0004	4
$Mg(NO_3)_2$	0.00008	0.0002	2
TOTAL	39.53000	100.0000	1129038

H_2O (by difference)   60.47   1727164

TABLE II: RADIOCHEMICAL COMPOSITION OF 8D-2 SUPERNATANT (T° 1983)

Species	1 ft*	5 ft	15 ft -	% RSD**
	mCi/gm			
Cs-137	2.86 E0	2.80 E0	2.84 E0	0.2
Cs-134	2.36-E2	2.32-E2	2.35-E2	3.0
Sr-90	1.14-E3	1.13-E3	1.12-E3	1.0
Sb-125	5.70-E5	5.50-E5	5.40-E5	12.0
Ru-106	<1.50-E5	<1.50-E5	<1.50-E5	NA
Ce-144	<7.60-E7	<7.60-E7	<7.60-E7	NA
Rare Earth B⁻	2.10-E4	1.50-E4	2.70-E4	3.0
Am-241	<1.50-E5	<1.50-E7	<1.50-E7	NA
Am-243	<2.00-E7	<2.00-E7	<2.00-E7	NA
Cm-244	<6.00-E8	<6.00-E8	<6.00-E8	NA
	µgm/gm			
Pu-238	0.0024	0.0031	0.0027	3.0
Pu-239	0.1302	0.1545	0.1461	3.0
Pu-240	0.0251	0.0307	0.0301	3.0
Pu-241	0.0051	0.0066	0.0060	3.0
Pu-242	0.0021	0.0025	0.0024	3.0
U-233	0.0170	0.0190	0.0180	8.0
U-234	0.0140	0.0170	0.0160	8.0
U-235	0.9670	1.1010	1.0440	3.0
U-236	0.0970	0.1080	0.1050	8.0
U-238	55.1450	63.1820	59.8650	0.3

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*   Samples taken at three levels: 1, 5, and 15 feet below the surface
     of the liquids.
** Percent relative standard deviation.

High air entrainment in the simulated waste slurry (without chromates), was discovered during full-scale testing at West Valley using the Portland Type I formulation. Similar foaming was reported to have been observed at the Westinghouse R&D Laboratories and was removed by vibration. The capability to vibrate the waste product to remove air in the full-scale system does not exist. Testing was conducted at the West Valley laboratories in an attempt to duplicate the foaming seen in the full-scale system using samples of the simulated supernatant and cement being used in the full-scale system. It was found that the type of mixer blade and mixing speed were critical in reproducing the foam. The low-shear impellers available at the West Valley laboratories and turned with drill motors at 1000 to 1700 rpm were not capable of reproducing the foaming observed in the plant. A commercially available, high-speed blender was obtained and produced a mixture on its lowest speed (not measured directly) which approximated the amount of foam seen in the waste form produced in the Cement Solidification System (CSS). The simulated supernatant used in the test was carefully analyzed in parallel with the mixer study, and the analysis showed that the simulated supernatant used for testing was acceptably close to the simulant used in Portland Type I recipe development.

The verification of the supernatant recipe and the ability of the laboratory to reproduce the foaming allowed the testing of various additives to reduce the amount of foam in the final product without agitation. The best candidate of the additives investigated at WVNS was GE AF-9020 antifoam (a silicon-based, food-grade additive); the amount of AF-9020 to be added to the mixture was optimized with further testing. This revised recipe was then applied in full-scale simulant testing using the CSS high-shear mixers.

A full-scale test of the recommendations derived from the lab-scale testing was performed by single batch processing in the full-scale system. The antifoam was added by hand to the mixer after the addition of the simulated supernatant, the mixer started, and the solids were added. The mix times were varied over a range from one-half to three minutes following cement addition. The Portland Type I cement mixture processed as expected; the one-half minute mix was homogeneous and contained little entrained air as shown by the density of the mixture. Longer mix times decreased the gelation times and increased the amount of entrained air.

To verify that the Portland Type I recipe would produce an acceptable waste form, it was tested using actual decontaminated supernatant. Three 2-inch cubes were prepared from the decontaminated supernatant using the proper ratios of supernatant, antifoam, and cement. The mixtures formed an excellent low-viscosity slurry during mixing with little entrained air observed on pouring. The cubes experienced a phase separation after approximately one-half minute. The amount of bleed water increased until approximately 5 percent of the supernatant in the waste form was evident as bleed water. The reason for the bleed water separation was a slow gelation time which permitted the cement solids to precipitate from the slurry production. The cause of the slow gelation time was thought to be a set retarder present in the decontaminated supernatant which was not present in the simulant. Some organic materials are set retarders, so an attempt was made to determine the amount of organics which had been added to Tank 8D-2 during previous operations. During the records search, organics known to be used in the process, including kerosene, tributyl phosphate, mono- and dibutyl phosphate (degradation products of tributyl phosphate), and decontamination reagents such as oxalate, tartrate, and citrate were tested for their effect on the

setting of cement. A small amount (approximately 0.3 grams) of each was added
to a lab-scale batch of simulated supernatant and processed in the
laboratory. The kerosene and tributyl phosphate had negligible effects; the
mono- and dibutyl phosphates were a strong set accelerator; and the citrate,
oxalate, and tartrate were observed to be set retarders.

The search for organics added to the 8D-2 tank showed that approximately
30 thousand pounds of citrate, oxalate, and tartrate had been used during
plant decontamination (reference 5). The only organic analyzed for during
supernatant analysis was oxalate, which was reported to be below a detection
limit of 39 micrograms per gram of filtered supernatant (reference 2). The
lack of detectable oxalate in the supernatant was considered to support the
assumption that the organic input to the tank had decomposed radiolytically
during HLW storage (reference 2). The results of the waste form
solidification test indicated that there may be an organic acid salt or
residue remaining in the supernatant.

With the presence of citrate, tartrate, and oxalate suspected in the waste and
causing severe set retardation, a literature search and questioning of DOE
contractor experts in the cementation of waste were conducted.
Laboratory-scale testing of possible recipe modifications was initiated.
Several of the additives recommended were tested. They included; bentonite
clay, attapulgite clay, calcium chloride, hydrated lime, calcium nitrate,
sodium silicate, and blends of calcium chloride or nitrate and sodium
silicate, with both chromated and nonchromated synthetic supernatant with
organic acid salts added.

The conclusions reached at that time were:

o   The salt concentration was too high for the high-surface-area adsorbants,
    attapulgite, bentonite and calcium hydroxide, to be effective.

o   The chromate and the organic acid salts act in a synergistic manner as the
    amount of bleed water increased markedly when chromates were added to the
    organic acid doped simulated supernatant.

o   The calcium salts by themselves were not adequate due to the adhesive
    nature of the resultant slurry and attendant processing difficulty.

The calcium-nitrate/sodium-silicate mixture was the most likely candidate for
further development. The order of addition and amount of each additive
required was determined. The commercial availability of the additives was
also investigated.

The objectives of the study were to produce a recipe which would be acceptable
for disposal and full-scale processing using the CSS with as few modifications
as possible. The major assumptions made were:

o   The Lab Master mixer and high-shear impeller simulates the full-scale,
    high-shear mixers sufficiently for continued lab-scale development work.

o   Both chromates and organic acid salts are necessary in the simulant to
    accurately represent the decontaminated supernatant.

o   Liquids could be added to the mix at any time during the mix cycle.

o   Solids would preferably be premixed with the cement, but could be added at
    any time.

o   The set retardants in the actual supernatant are suspected to be citrate,
    oxalate, and tartrate at the concentrations added in 1971 to 1972. These
    residues alone do not account for the full, set-retarding effect, but
    appear to enhance the retardation caused by the high-salt concentration in
    the waste stream.

The variables identified which required further investigation were the order
of addition of the additives, amount of additive, the range of organic-acid
concentration for which the formulation produced acceptable results, and the
increase (if any) in the total volume of cement to be produced during
full-scale production caused by reduced waste loading.

Eight different orders of addition were investigated. The most effective
order for the elimination of bleed water is supernatant, antifoam, calcium
nitrate, cement, and sodium silicate. This mixture was difficult to mix and
did not transfer well. The second best mixture for elimination of bleed water
was supernatant, antifoam, cement, and calcium nitrate preblend, then sodium
silicate. This mixture was processed easily and transferred well.

The mixing of the calcium nitrate and the cement presented the least impact to
the mechanical system in the CSS, and the addition of the liquid
sodium-silicate solution required a relatively simple liquid addition system
to be added. This was the minimum impact which could be expected by the
required process changes, so the preblend of cement and calcium nitrate with
the addition of the sodium silicate near the end of the mix cycle was chosen
for optimization.

The amount of sodium silicate and calcium nitrate to be added was determined
by trial and error to be within the range of 7.0 to 9.0 grams of calcium
nitrate and 8.4 to 11.2 grams of sodium silicate per 100 mL batch of simulated
supernatant. All of the mixtures from this region showed very little bleed
water at any time during gelation, and all of the bleed water which did form
was reabsorbed in less than 24 hours. The processibility of all these
mixtures was good with the optimum mixture of 8.0 grams calcium nitrate and
9.8 grams of sodium-silicate solution showing the best processibility of any
mixture made in the laboratory.

The optimum recipe was tested for flexibility by reducing organic acid salts
concentration in the simulated supernatant. When the concentration was
reduced by half, there was no change in the processibility, or bleed water
characteristics of the waste form produced.

To determine the acceptable range of the recipe, 41 test specimens were
produced. The specimens were observed for free-liquid formation after pouring
and were allowed to cure for 7 days. After 7 days, the samples were crushed
to determine compressive strength per ASTM C109. The parameters that were
varied included:

o   Total Solids (TS)   35.900 to 42.000   weight percent
o   Water/Cement Ratio (W/C)   0.537 to   0.709
o   Calcium Nitrate   3.800 to   7.700   percent
o   Sodium Silicate   7.800 to 12.600   grams per 100 mL of
                                                        decontaminated supernatant

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As a result of varying the TS, water-to-cement ratio, calcium nitrate, and sodium silicate concentrations, the compressive strength varied from 355 to greater than 750 psi. These data were then utilized to establish processing limits. The limits, as a result of this testing, are as follows for the processing of decontaminated supernatant in the full-scale solidification system:

	Acceptable Range	
Parameter	Low	High
Total Solids (wt%)	37.000	41.000
Water-to-Cement Ratio	0.550	0.700
*Calcium Nitrate (%)	4.100	7.300
Sodium Silicate (lbs)	12.500	20.500
approximate wt%	3.100	5.100

A small amount of waste form using the actual decontaminated 8D-2 supernatant was produced. The waste form was processible, had no bleed water, a high density and compressive strength greater than approximately 600 psi after 8 days of curing. The conclusion of this work was that the waste form produced on the laboratory scale showed merit for full-scale testing and qualification. The full-recipe scale for a 19-gallon batch compared to the original formulation is shown below: (Note that 2 batches are required to fill one 71-gallon drum)

Constituent	R&D Recipe	Improved Recipe
Supernatant	19.0 gal	19.0 gal
Cement	211.0 lb	211.9 lb
Antifoam	10.8 mL	10.8 mL
$CaNO_3 \cdot 4H_2O$	----------	12.8 lb
Sodium-Silicate Solution	----------	15.8 lb

FULL-SCALE TESTING

Following resolution of the recipe at the laboratory-scale, full-scale testing using the actual solidification equipment was performed. The purpose of these tests was to:

o   Confirm recipe performance in scale-up to full-scale;

o   Produce full-scale drums for further qualification testing to confirm product performance at full scale and to develop a correlation with laboratory-scale data; and

o   Evaluate the extent of the exotherm at full scale to better understand the hydration rate and to evaluate peak centerline temperature in a well-insulated drum.

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*   Calcium nitrate is preblended with Portland Type I cement. The calcium nitrate is preblended at a nominal 5.7 weight precent of the cement/calcium-nitrate mixture.

The CSS was operated using the enhanced recipe to produce several drums of full-scale product with accurate simulant (contains chromates and total organic carbon in the correct ratio). During production, excellent correlation between laboratory and full-scale system performance was observed. Several drums were pulled from the production run to use in further testing. Thermocouples were installed on the longitudinal centerline of one drum at three positions (top, center, and bottom) and the drum insulated on the sides and top with 12 inches of fiberglass insulation. The thermocouple output was collected by a digital data logger and data was collected at approximately 15-minute time intervals. The insulation was removed after the peak exotherm was reached to provide an indication of cool-down rate. The temperature profile was as expected, reaching a peak centerline temperature of 173°F approximately 18 hours after mixing. Transport time to the drum cell from the completion of mixing is about 2 hours, indicating that the drum will be in final position well in advance of the hydration phase and avoiding transport during setting. The insulated condition very conservatively represents the exotherm since the drums will be subject to convection cooling in storage. The cement surface was inspected following cool down; neither bleed water nor water of condensation was observed on the surface.

QUALIFICATION TESTING

To assure that the use of admixtures did not adversely affect the performance of the original R&D formulation, a supplementary qualification test program was developed and implemented. The following additional tests were performed:

o   Leach testing of specimens using actual cemented decontaminated supernatant;

o   Compressive-strength testing of specimens produced from actual decontaminated supernatant;

o   Thermal-cycle testing of cores removed from full-scale production drums produced with accurate simulant (containing chromates and organic acids),

o   Immersion testing of specimens produced from actual decontaminated supernatant;

o   Compressive-strength testing of cores removed from full-scale production drums produced with accurate simulant; and

o   Measurement of the effect of cure time vs. immersion duration on compressive strength.

This section presents a discussion of the test methods, procedures and the results.

LEACH TESTING

The cemented waste specimens were prepared as follows. Each cylinder used for leach testing was produced in the laboratory using a Lightning Lab Mixer equipped with a high-shear impeller. A mixing vessel was selected that had a diameter slightly larger than the impeller to closely approximate the

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full-scale, high-shear mixer. Added to the mixing vessel was 24.50 mL (32.00 grams) of decontaminated 39 w/o supernatant. The mixer was run at 1,000 rpm for 10 seconds while 0.74 mL of antifoam was added. Mixer speed was increased to 2,000 rpm and 2.06 grams of calcium nitrate, preblended with 32.41 grams of Portland Type I cement, was added to the liquid while the mixer was running. The mixture was mixed for 3 minutes and 2.45 grams of sodium silicate was added; this was mixed for an additional 30 seconds prior to pouring into the cylinder molds. The cylinders were then placed into plastic bags, sealed, and allowed to cure for 28 days prior to starting the leach test. Leach testing was performed in accordance with ANS 16.1.

The results of the leach testing are summarized below:

Nuclide of Interest	Leach Index, Σ x	
	Sample A	Sample B
Cs-137	7.1	7.1
Sr-90	8.8	8.8
Pu	14.1	14.0
Tc-99	7.3	7.2

The results of the leach test for each nuclide exceed the minimum requirements, a leach index of 6.0, of reference 4. For Cs-137, the leach index for the WVNS waste formula was 7.1. Since the leach indices are an exponential function, the leach index of 7.1 is over 10 times the required minimum. The reported leach index for Cs-137 tested on the original Portland Type I recipe was 6.6. It was, therefore, concluded that the new formulation had a better leach index for Cs-137 (the most leachable species) than the original formulation. The leach index for plutonium, strontium, and technetium also exceed the minimum requirement of a leach index of 6.0.

COMPRESSIVE-STRENGTH TESTING

Compressive-strength testing was conducted per ASTM C109 for 2-inch cubes. The samples were made in the laboratory using a Lighting Lab Mixer. A total of 350 mL of actual decontaminated supernatant was used to prepare four 2-inch cubes; two were used for compressive-strength testing, and two were reserved for immersion testing.

The cubes were allowed to cure for 40 days and then were tested for compressive strength per ASTM C109. The compressive strength of each cube (Sample A & B) was greater than 750 psi. The minimum requirement per the NRC Branch Technical Position is 60 psi.

THERMAL-CYCLE TESTING

Six cores were shipped to the Westinghouse R&D Center in Pittsburgh for thermal-cycle testing. One core was damaged in shipment. The cores were taken from full-scale production drums made with accurate simulant. Prior to thermal-cycle testing, the cores were allowed to cure for 40 days. Each core was subjected to thirty 24-hour thermal cycles ranging from -40° to 60°C in an environmental control chamber.

The results of the thermal cycling are as follows:

Drum Number	Compressive Strength
52	902
55A	953
57	815
58	1130
55B	1010
Avg.	961 psi

The average compressive strength was 961 psi compared to an average of 560 psi obtained with the original Portland Type I recipe. Reference 4 requires that the cylinders have a compressive strength as great as possible, but exceeding 60 psi. All of the tested cores exceed the 60 psi value by a large margin.

IMMERSION TESTING

Two 2-inch cubes were prepared as for compressive-strength testing. The cubes were placed into a 2.0-litre beaker and covered with 1.5 litres of deionized water. The cubes were immersed for 90 days and crushed per ASTM C109 to determine compressive strength. Visual observation indicated that no spalling, cracking, or degradation of the cubes had occurred during the immersion cycle.

The results of the 90-day immersion and compressive strength on the two 2-inch cubes is the following:

Cube A	633.0	psi
Cube B	754.0	psi*
Average	693.5	psi

Reference 2 requires, as a minimum, a compressive strength of 60 psi. The average compressive strength for the two cubes of 693.5 psi is 11.5 times greater than the minimum required 60 psi.

FULL-SCALE, COMPRESSIVE-STRENGTH TESTING

To test the process performance using the enhanced formula containing the admixture, 8 full-scale, single-mixer batches of drums (normally two-mixer batches per drum) were produced. The drums were produced using accurate simulant.

The drums were cured at ambient temperature for six days and then cored either from the top or the bottom of the drum. Two cores from different locations were taken from each drum. The drums were cured for an additional 33 days for a total cure of 39 days. The drums were then cored from the top in two new locations. For each drum, a total of four cores were taken from two different locations to test for compressive strength.

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* 754 is an estimated value. The scale on the cement-cube tester only goes up to 750 psi.

Full-scale cores were tested for compressive strength per ASTM 39 and the results are tabulated below:

Compressive Strength for Full-Scale Cores in psi

	7-DAY CURE			40-DAY CURE		
DRUM #	A	B	AVG	A	A	AVG
51	620	610	615.0	840	900	870.0
52	660	650	655.0	780	810	795.0
53	760	740	750.0	1,100	1,040	1,070.0
54	580	570	575.0	820	760	790.0
55	550	650	600.0	830	820	825.0
56	690	670	680.0	900	850	875.0
57	620	680	650.0	850	890	870.0
58	850	770	810.0	1,040	1,080	1,060.0
	AVERAGE		666.0			894.0

Several observations from the compressive-strength data can be made:

o   Compressive strength on cores from the same drum are very similar, indicating that the as-poured cement matrix is quite homogeneous;

o   There is a 34-percent increase in compressive strength from a 7- to a 40-day cure;

o   The relatively tight distribution of compressive-strength data from one drum to the next indicates the full-scale system can produce a homogeneous product repeatedly;

o   Compressive strengths on the average were 10 times the required minimum, 60 psi, after curing for 7 days per reference 4;

o   The enhanced formula reached a compressive strength of about 890 psi compared to original Portland Type I recipe values at 453 psi following 40-days curing; and

o   At no time were voids or water-filled pockets observed in the full-scale cement product during coring.

At the same time the eight drums were produced, 2-inch standard-cube molds were filled from the drum contents. Two cubes were collected from each drum produced and were cured for 7 and 40 days, respectively. Compressive strengths were measured per ASTM C109. The results are tabulated below:

DRUM #	7-DAY CURE	40-DAY CURE
51	760	1,120
52	730	990
53	980	1,410
54	900	1,140
55	N/A	1,290
56	880	1,240
57	870	1,160
58	1,040	1,410
AVERAGE	880	1,220

Several observations can be made from the compressive-strength data for the cubes:

o 39-percent increase in compressive strength from a 7- to a 40-day cure; and

o Low variation in compressive strength for the cubes from different waste batches (drums) indicating that a homogeneous product is produced.

CURE TIME VERSUS IMMERSION AND THE EFFECT ON COMPRESSIVE STRENGTH

Cores in this test were prepared as described in full-scale, compressive-strength testing.

Three cylinders, cored from full-scale production drums, were placed into a 5-gallon pail and completely covered with deionized water. A total of six 5-gallon pails, three cores per pail, were used. A lid was placed on the pail and samples were allowed to immerse undisturbed for the desired time interval. The immersion time intervals and times allowed for curing were selected based on a test design reported to the NRC by LN Technologies, Inc. These periods were selected to provide a basis for comparison with visual observation data previously submitted to the NRC by LN Technologies, Inc. Although compressive-strength data are reported for the WVNS specimens, these data are not available for the LN Technologies, Inc. tests.

Time Period	Cure Time (days)	Immersion Time (days)	Immersion Date	Drum Cores*
1	22	69	4/07/88	58, 57, 55
2	28	63	4/13/88	57, 55, 52
3	42	49	4/27/88	57, 55, 52
4	56	35	5/11/88	52, 55, 52
5	70	21	5/25/88	52, 55, 55
6	84	7	6/08/88	52, 53, 58

* Cored from full-scale production drums.

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The cores (18 cores, three for each of the six periods) are nominally
3- by 6-inch right circular cylinders. After the 91-day cure/immersion
period, the samples were removed and brought to Empire Soils Investigation,
Inc. for compressive-strength testing per ASTM C39. It should be noted that
the cylinders were trimmed to maintain a length-to-diameter ratio of 2 by
Empire Soils investigation personnel. The results are as follows:

VARIATION OF COMPRESSIVE STRENGTH WITH WATER IMMERSION

Drum #	Period	Time Time	Cure Time	Immersion Strength in psi	Compressive Average for Time Period; psi
57	1	22	69	845	
56	1	22	69	970	985
58	1	22	69	1140	
57	2	28	63	1080	
55	2	28	63	1010	1060
52	2	28	63	1090	
52	3	42	49	1060	
55	3	42	49	1085	1071
57	3	42	49	1060	
52	4	56	35	1060	
55	4	56	35	1080	1057
52	4	56	35	1030	
52	5	70	21	1050	
55	5	70	21	1050	1037
55	5	70	21	1010	
54	6	84	7	795	
53	6	84	7	950	931
58	6	84	7	1050	
				Overall Average	1023 psi

Several conclusions can be drawn from the results.

o All of the cores exceeded the reference 4 minimum requirement of 60 psi.
   The average compressive strength was 1023 psi, which is 17 times greater
   than the minimum requirement.

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o The average compressive strength for the 40-day cure from section 4.5 was
   894.4 psi. The average compressive strength after the 91-day
   cure/immersion was 1023 psi. This represents a 14.4-percent increase in
   compressive strength during the immersion cycle when compared to dry-cured
   specimens.

o Variance of the compressive-strength data about the mean was statistically
   evaluated to determine its significance. It was determined that the
   observed variance in the data is within the expected variance as indicated
   by a T-test.

Reference 4 contains no acceptance criteria for this test. It is, therefore,
assumed that the criteria for acceptance is the compressive strength of the
cores following immersion. All of the cores exceeded the 60 psi requirement
by a large margin.

SUMMARY AND CONCLUSION

A formulation for solidification of decontaminated PUREX supernatant using
Portland Type I cement was developed by the Westinghouse R&D Center using an
inorganic salt simulant to represent the supernatant. As reported, use of the
recipe at full scale resulted in processibility difficulties with air
entrainment and accelerated hydration of the product in the high-shear
mixers. Further laboratory-scale testing indicated that bleed water was
produced when the recipe was tested with actual decontaminated supernatant.
Laboratory investigations showed that the bleed water resulted from set
retardants or an enhancement of the set-retarding effect produced by the salts
present in the supernatant. The agent producing the effect is believed to be
residues of organic acids which were added to the HLW tank during plant
decontamination.

Further laboratory work was conducted to modify the original Portland Type I
recipe using additives routinely used in the cement-product industry.
Antifoam (AF-9020), calcium nitrate, and sodium silicate were selected after
both laboratory- and full-scale testing. A target formulation and an
acceptable operating range were developed for use. The final product
elemental composition varied from the Portland Type I recipe by less than
2 percent and is within the allowable variance for ASTM Portland Type I
cement. The reformulation produced a product with substantially improved
processibility, high density, reduced porosity, and higher compressive
strength than the Portland Type I formulation.

As a result of the change in formulation, supplementary testing was conducted
to demonstrate that the additives did not degrade the performance
characteristics of the Portland Type I product. The results of the testing
indicate that product performance is improved with respect to compressive
strength, thermal-cycling resistance, and compressive strength following water
immersion. The improved performance is attributed to the addition of excess
calcium, which improves the product's compressive strength, and sodium
silicate, which acts to close the cement-product pores.

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A TECHNICAL BASIS FOR MEETING THE STABILITY
REQUIREMENTS OF 10 CFR 61

Presentation to NRC Workshop on Cement Waste Forms
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INTRODUCTION

The NRC finalized the Branch Technical Position on Waste Form (BTP) in May, 1983. In their continuing effort to provide technical guidance in this area, the NRC has informally issued two "Preliminary Draft" Regulatory Guides (DRGs) in February 1985 and November 1986, for industry review and comment.

Under the sponsorship of AIF(NUMARC), Envirosphere Company, an Ebasco subsidiary prepared a report "A Technical Basis for Meeting the Waste Form Stability Requirements of 10 CFR 61" to respond to the proposed testing procedures and acceptance criteria in the latest DRG (November, 1986). This report reviewed the link between the BTP and the DRG testing requirements and the 10 CFR 61 regulation and the majority of test results available to date (April, 1987). Some of the review findings and test data pertinent to cement solidification contained in that report are excerpted for this presentation.

WASTE FORM STABILITY AND PART 61

The NRC's effort to formulate a set of specific regulations and guidelines to address shallow land burial of low level waste (LLW) began in late 1970s. The timing and circumstances surrounding the NRC decision to develop LLW disposal regulations and the availability of technical information for regulation development are important to the understanding of the current requirements contained in the 10 CFR 61 and regulatory guidance documents. Following the closure of three disposal sites in the late 70s and increased concerns about the environment and safety of nuclear related activities, the NRC began formulating a set of specific regulations to address shallow land disposal of LLW.

Although the NRC supported waste form research since 1976, little of that technical research was directed to the stability requirement defined in the 10 CFR 61. This research did however identify, in general, certain parameters which should be considered to ensure structural stability over the 300-year period required of certain waste. It was not until the issuance of the BTP that the NRC identified specific technical criteria addressing specific parameters as indicators of waste form stability. The NRC-sponsored research that predated the BTP provided little or no support to either the criteria or any of the testing procedures in the BTP.

Regulatory Framework

The relevance of the testing requirements in the BTP were also determined by reviewing these requirements against the performance objectives and the specific technical requirements of the 10 CFR 61. Results of this review indicated that the intent of the BTP testing requirements should not aim to simulate the disposal environment and conditions. Rather, the testing requirements should function as screening tests to identify and eliminate inappropriate waste forms. These tests can also be used as a framework for a preliminary evaluation of various binder and waste form on a common basis.

10 CFR 61 Performance Objectives

The BTP prescriptive requirements for waste form stability were compared to the four performance objectives of 10 CFR 61. This comparison leads to the following:

o   Waste form stability is related to long term site stability as an additional support system for the protection of the general population from releases of radioactivity (61.41). Lack of waste form stability can lead to closure cap failure, water infiltration and subsequent radionuclides release.

o   Stability is related to protection of individuals from inadvertent intrusion (61.42) as the last protective measure in any intrusion scenario, i.e., recognizing that contact had been made with radioactive wastes.

o   Protection of individuals during operations (61.43) has little relation to waste form stability.

o   Long-term stability of the disposal site after closure are primarily dependent on the site characteristics, site design and operation. Stability of the waste form is a secondary consideration to the stability of the engineered closure cap and its long-term ability to minimize infiltration.

This review of the BTP stability testing requirements against the 10 CFR 61 Performance Objectives leads to the conclusion that waste form stability only indirectly supports the achievement of the performance objectives. With the exception of protection of the inadvertent intruder, waste form stability becomes significant only if the other parts of the systems approach fail.

10 CFR 61 Technical Requirements

A review of the 10 CFR 61 Subpart D, Technical Requirements, indicated that a link exists between the BTP requirements and 10 CFR 61.56b. Extrapolating this linkage to the tests however was not always appropriate.

For example, comparing the phrase "presence of moisture" with the leachability and immersion testing requirements shows these tests to be an extreme condition regarding the intent of the regulation. Similarly, thermal degradation test while a consideration for transport has little relation to already buried waste. Radiation effects have their counterpart in the radiation stability test as does "microbial activity" with the biodegradation test, however, these tests reflect

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extreme conditions not those typically encountered.

Presented in Table 1 is a point-by-point comparison of the testing requirements of the BTP against the 10 CFR 61 regulation.

In summary, a stronger relationship exists between the BTP and the 10 CFR 61.56b (Waste Characteristics) than existed for the Performance Objectives. However a comparison of each of the tests in the BTP and regulation shows that the intent of the regulation bears little relation to many of the required tests.

However, these tests can provide a framework for a preliminary evaluation of cement additives and waste forms on a common basis. It should also be noted that the systems approach explicit in the 10 CFR 61 assumes shallow land burial as the disposal technology of choice. With the national movement toward using other engineered disposal technologies, waste stability and its importance is further reduced as are the tests.

STABILITY TESTING PROCEDURES

The applicability of the BTP recommended test procedures and their suitability as a reasonable indicator of waste form stability for the six criteria, i.e., leachability, compressive strength, immersion, thermal stability, radiation stability and biodegradation were reviewed and are presented below.

Leachability Testing Procedure ANS 16.1

The ANS 16.1 procedure is a reasonable method for determining the leachability of stabilization media or waste forms and the leachability indices (LIX) are reasonable indicators of the leach characteristics of the waste form sample.

Compressive Strength Testing Procedure ASTM C39

The NRC recommended the use of ASTM C39 procedure, "Compressive Strength of Cylindrical Concrete Specimens," as the method for determining compressive strengths of cement solidified waste form specimens. Although this procedure does not contain a precision statement, the precision statements in other similar test procedures offer an indication of the accuracy of the C39 test. In general, this type of testing procedure permits an error bound of plus or minus 10 percent for single laboratory testing and a plus or minus 20 percent for multi-laboratory testing. Compressive strength can be a reasonable indicator of the waste forms' ability to maintain their structural integrity under pressure.

Immersion Testing Procedure

The recommended 90-day immersion in demineralized water test procedure is a test of extreme condition. The post-test compressive strength of the waste form is a reasonable indicator of the waste form sample's ability to continue maintaining structural integrity after being exposed to an extreme condition.

Thermal Stability Testing Procedure ASTM B553

The intent for conducting thermal cycling testings is to protect the waste forms against degradation resulting from thermal cycling during storage and transportation. The requirements for storage of radioactive wastes are governed by other NRC regulations and the requirements for assuring safe transportation of radioactive wastes have been traditionally governed by DOT regulations as reflected in NRC regulation 10 CFR 71. No specific linkage of the thermal stability testing requirement to the regulatory or technical basis of 10 CFR 61 regulation can be identified. In any case, the intent and testing conditions of ASTM B553 procedure are not applicable to waste form stability testing.

Radiation Stability Testing Procedure of Using 100 Megarads

The value of 100 megarads should be retained.

Biodegradation Testing Procedure ASTM G21 and G22

These test procedures are for detecting microbial growth and are not for the determination of biodegradation. Other experts in the testing field have also indicated that ASTM test procedures are not appropriate for measuring biodegradation.

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"WASTFORM" DATA BASE

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The prior material focused on the basis of the BTP tests and their relationships with the regulations. In this section and that follows, is a brief review of a data base (WASTFORM) used to collect and evaluate waste form data followed by the results of the evaluation on cement waste forms.

Date Base Framework

The WASTFORM data base was constructed using three major parameters: waste streams, the six NRC stability criteria and stabilization media. All data set were grouped to six basic categories of waste streams: (1) Mixed-Bed Resins, (2) Mixed Powdered Resins, (3) BWR Filter/Precoat Media, (4) PWR Evaporator Concentrates, (5) PWR Evaporator Concentrates and (6) Decontamination Solution. To better characterize each of the waste stream categories, the data base also included data on the weight percent (w/o) concentration of the principle substances in the waste streams, waste loading ratio and vendor additives where available.

Table 1

Relation of 10 CFR 61.56b Regulation to BTP Testing Requirements

10 CFR 61.56b Regulation	BTP Testing Requirements (5/83)
"...provide stability of the waste..."	"To the extent practical Class B and C waste forms should maintain gross physical properties and identify over a 300 year period:"
"maintain its physical dimensions and its form, under the expected disposal conditions such as weight of overburden and compaction equipment,..."	"...compressive strength of at least 50 psi..."
"...the presence of moisture..."	"...leach testing and immersion testing..."
"...and microbial activity..."	biodegradation testing
"...internal factors such as radiation effects..."	exposure to 100 megarads
"...and chemical changes..."	----
----	thermal degradation
"...but in no case shall the liquid exceed 1% of the volume of the waste when the waste is in a disposal container designed to ensure stability, or 0.5% of the volume of the waste for waste processed to a stable form."	"...should have less than 0.5 percent by volume of the waste specimen as free liquids as measured using the method described in ANS 55.1. Free liquid should have a pH between 4 and 11."

The six stability criteria are, of course, leachability, compressive strength, immersion, radiation effect, thermal stability and biodegradability.

The stabilization media consist of those commercially available at that time which included cement, bitumen, gypsum and polymer. For this presentation, only data related waste forms solidified using cement are considered.

Other data and information stored in the data base included the physical parameters of the test specimens, such shape and dimensions, volume weight surface area and volume to surface area ratio of the test samples.

Source of Data

Three major sources were identified for the collection of waste form stability test data relevant to the BTP:

    o Government-Sponsored (NRC and DOE) Research
    o Vendor-sponsored Testings

The source materials reviewed for collecting test data included primarily research reports prepared for the NRC and DOE by the Brookhaven National Laboratory (BNL), Oak Ridge National Laboratory (ORNL) and EG&G Idaho. The earlier government sponsored research focused primarily on leachability of the waste form using a wide rage of boundary conditions and parameters. There was little consistency or compatibility in those data to allow meaningful evaluation. Consequently, only minimal data sets were obtained from the review of the government sponsored research reports.

Most of the existing data sets in WASTFORM related to cement solidification consists primarily results of waste form stability testing performed by commercial vendors. These vendors include

    o Chem-Nuclear Services, Inc.
    o London Nuclear Services
    o Stock Equipment Company
    o Westinghouse Electric Company

The type of information furnished by the vendors varied, which included their topical reports and supplements, internal reports on media-specific performance, and unpublished data. This information was further supplemented by personal interviews conducted with some of the vendors. All of these tests were conducted consistent with the procedures recommended in the May, 1985 BTP.

CEMENT DATA EVALUATION

As of April 1987, the WASTFORM data base contains 960 records with each record containing one or more data sets. There are in total 1229 data sets for the four stabilization media. Of these, about 45% or 555 data sets are related to cement waste form, as shown in Table 2. Presented below are evaluations of the cement waste form test data for the six stability criteria.

Table 2

Cement Waste Form Data

Stability Criteria	No. of Data Sets
o Leachability	
Demineralized Water	212
Synthesized Sea-Water	57
o Compressive Strength	59
o Immersion	50
o Radiation Stability	51
o Thermal Stability	52
o Biodegradation	
Fungal Growth	41
Bacterial Growth	33

Table 3

Review of Leachability Index By Waste Streams

Waste Streams	Total No. of Data Sets	No. of Data Sets 6 < LIX < 7	7 < LIX
BWR Evap. Conc.	10	4	6
PWR Evap. Conc.	18	3	15
BWR Filter/Precoat	13	2	11
Decon Solution	14	3	11
Mixed Bead Resins	24	2	22
Mixed Powdered Resins	18	7	11

Leachability

There is a total of 269 leachability test data sets available in the WASTFORM data base. Initial review of the 97 of the 269 data sets indicated that cement solidified waste forms possess acceptable to excellent leach resistant characteristics. All of the 97 data sets reviewed attained the minimum NRC leachability index (LIX) requirement of 6 with more than half of those samples achieving leachability indices in a range between 7 and greater.

A closer examination of the leachability indices according to the embedded waste streams shows that only a small fraction of the samples have leachability indices in the lower range of the acceptable leachability indices of between 6 and 7. Table 3 below presents a tabulation of the leachability indices for each of the waste stream categories.

Compressive Strength

The 59 data sets demonstrates that cement waste forms possess more than adequate structural strength to maintain waste form stability. The compressive strength of cement waste forms are in the range from several hundred to several thousand psi. Table 4 presents the compressive strength of cement waste forms by waste stream categories.

Immersion

Of the 50 cement samples tested, 43 samples show a less than 15.6 percent change (i.e., both increase and decrease) from pre-test compressive strength. A comparison of the range of post-test to pre-test compressive strengths for each of the waste stream categories is shown in Table 5.

The post-test strengths for most of the samples were high. With the exception of one data point (which showed a post-test strength of 70 psi) the lowest post-test strength was 211 psi. This represents a safety factor of 3.5 when compared to the 60 psi requirement. The rest of the test specimens showed post-test strengths ranging from several hundreds to several thousands psi, indicating that water immersion has little or no impact on the structural stability of the cement waste form. Due to an absence of complete waste to binder ratio data, no correlation could be made between compressive strength loss and the percentage loading of waste streams.

More recent test results have indicated that rapid curing of cement can increase post-immersion compressive strength.

Thermal Stability

Although the overall effects of continuous freeze-thaw cycles are presumed to be damaging to the structural integrity of cement, most of the cement samples evaluated show an increase in post-test compressive strength.

There are in total 52 cement waste form samples tested for thermal stability. Of the 52 data sets, 32 show an increase in the post-test compressive strength, while 20 show a decrease. The change in compressive strength for eight (8) of the data sets showing a decrease in compressive strength were within the bounds

64

of the variability of the ASTM C39 test procedure. Table 6 presents comparisons of the range of the post-test to pre-test compressive strengths for each of the waste stream categories.

Radiation Stability

Of the 51 cement data sets, 25 show a decrease in compressive strength, while 26 showed an increase. The maximum increase was over 400 percent, while the maximum decrease is about 90 percent. The waste stream contained in the test sample with the maximum percent decrease is mixed bead resins. The test result for this sample also represents the lowest absolute value for post-irradiation strength - 70 psi. Of the 25 data sets that show a decrease, 19 of them are samples containing organic resins either as mixed bead or mixed powdered resins. The samples showing a decrease also include two samples containing BWR evaporator concentrates, two samples containing decon solutions, and one containing PWR concentrates. Table 7 presents a comparison of the range of pre-test to post-test compressive strergths for each of the waste stream category.

While all samples satisfied the 60 psi minimum strength requirement, it appears that waste forms solidified with organic ion exchange media exhibited degradation due to radiation effects. This is consistent with past findings of the degradation associated with organic resins when exposed to high doses of radiation.

Biodegradation

There are 41 data sets in the WASTFORM data base for fungal tests and 33 data sets for the bacterial tests. None of the data sets indicated fungal or bacterial growth on the test samples. The post-test compressive strength was compared to the pre-test compressive strength. Table 8 is a tabulated summary of the number of data sets associated with the percent changes.

Among the records for bacterial tests, only four show a greater than +/-50 percent change from the pretest compressive strengths. For the fungal tests, 25 out of the 41 data sets showed a less than +/-20 percent change from the pre-test compressive strengths. The other 16 data points showed a wide range of changes from a decrease of 93 percent to an increase of 212 percent in compressive strength. Since there was no fungal growth reported on any of the specimens, the large magnitude of changes in the specimen's post-test compressive strength could not have been caused by fungal attack. These changes are therefore attributed to the statistical variation of the ASTM C39 test procedure.

CONCLUSION

Results of this review indicate that the BTP testing requirements should not simulate the disposal environment and conditions. Rather, these testing requirements should function as screening tests to identify and eliminate inappropriate waste forms. The current testing requirements exceed and have extended beyond the intent of the 10 CFR 61 regulation on stability.

The review of the BTP stability testing requirements against the 10 CFR 61
Performance Objectives confirms that waste form stability only indirectly
supports the achievement of the performance objectives of 10 CFR 61.
Stability of the waste form is a secondary consideration to the stability
of the cap and its long-term ability to minimize infiltration. Comparison of
the BTP testing requirements against the Technical Requirements of 10 CFR 61
indicate that the basis for these testing requirements are at best based on a
very liberal interpretation of the 10 CFR 61 regulation.

Regarding the testing procedures, it is concluded that a number of them are
either irrelevant, or inappropriate for determining the parameters being
measured.

Nevertheless, test data obtained from the various vendors indicate cement as a
viable stabilization medium. Review of the cement waste form test data showed
an overwhelming success of this binder material to maintain its physical
dimensions and form after being exposed to severe and beyond expected disposal
conditions.

Table 4

Cement Waste Form Compressive Strength

Waste Streams	No. of Data Sets	Range of Compressive Strength (psi)		
BWR Evap. Conc.	6	530	-	3110
PWR Evap. Conc.	15	130	-	2113
BWR Filter/Precoat	6	710	-	3738
Decon Solution	3	340	-	1250
Mixed Bead Resins	14	140	-	1850
Mixed Powdered Resins	15	300	-	1925

Table 5

Summary of Immersion Test Data

Waste Streams	No. of Data Sets	Pre-test Strength Range (psi)	Post-test Strength Range (psi)
BWR Evap. Conc.	5	530 1525	540 1063
PWR Evap. Conc.	7	130 1170	330 1963
BWR Filter/Precoat	6	710 3738	1200 5400
Decon Solution	3	340 1250	460 1738
Mixed Bead Resins	13	140 1850	280 2625
Mixed Powdered Resins	16	300 1925	70 2250

Table 6

Summary of Thermal Stability Testing Data

Waste Streams	No. of Data Sets	Pre-test Strength Range (psi)	Post-test Strength Range (psi)
BWR Evap. Conc.	6	530 1525	540 1063
PWR Evap. Conc.	9	130 1170	330 1963
BWR Filter/Precoat	6	710 3738	1200 5400
Decon Solution	3	340 1250	460 1738
Mixed Bead Resins	14	140 1850	280 2625
Mixed Powdered Resins	14	300 1925	70 2250

Note: One test specimen with initial strength of 4117 psi failed the compressive strength test following exposure to thermal test.

Table 7

Summary of Radiation Stability Testing Data

Waste Streams	No. of Data Sets	Pre-test Strength Range (psi)	Post-test Strength Range (psi)
BWR Evap. Conc.	5	530 3110	630 2025
PWR Evap. Conc.	8	130 2113	160 2263
BWR Filter/Precoat	6	710 2500	670 4125
Decon Solution	3	340 1250	200 2169
Mixed Bead Resins	14	140 1850	70 2313
Mixed Powdered Resins	15	360 1925	310 1650

Table 8

Summary of Biodegradation Test Results

	No. of Data Sets	
	Bacterial Test	Fungal Test
Less and 10% change	21	19
Less than 20% change	27	25
Greater than 20% change	6	16
Greater than 50% change	4	8
Total Records	33	41

CHEM-NUCLEAR SYSTEMS, INC.

WASTE PROCESSING PERSPECTIVE

By

Michael T. Ryan
Chem-Nuclear Systems, Inc.

Chem-Nuclear Systems, Inc. (Chem-Nuclear) is a waste management company providing a full range of waste management services to the nuclear industry, and has operated the Barnwell burial facility without interruption since 1971. We own and operate the world's largest fleet of licensed shipping casks for transport of various radioactive materials, including radioactive waste. Decontamination and decommissioning services have been provided to the nuclear industry since 1978.

Radioactive waste solidification operations at customer facilities began in 1974 and dewatering services were added in the following year. Since that time more than half a million cubic feet of waste has been solidified, representing service to most of the commercial nuclear power plants in the country. We have processed every type of low-level radwaste generated by these power plants and have developed more than 50 formulas meeting NRC and state stability requirements.

Just as the waste streams and regulatory requirements have changed over the years, Chem-Nuclear's waste formulations have evolved and improved significantly and continue to do so.

Chem-Nuclear's Portland cement formulas served the industry well during the late seventies and early eighties after urea-formaldehyde was no longer considered an appropriate binder. Portland cement was effective for the waste being generated during this period and continues to work well for certain wastes today. Chem-Nuclear certified five generic waste forms using Portland cement binder to meet the Branch Technical Position (BTP) requirements. Documentation on these five waste forms was submitted in a topical report[1] to the NRC in 1983.

Along with development of certified waste forms, Chem-Nuclear improved processing equipment to provide sufficient energy and agitation to consistently form homogeneous monolithic waste products. The NRC accepted our cement solidification system topical report[2] as appropriate for referencing in future licensing actions at commercial nuclear power plants. This topical report included the process control program used at all full scale solidification projects to verify the adequacy of the formulations to be used. Our philosophies concerning solidification equipment and process control methods remain essentially unchanged today.

During the mid-eighties, different approaches were sought to low-level waste management in the industry. Rising costs, increased competition, greater radionuclide concentrations, and increased concerns for ALARA demanded waste volume minimization. Therefore, waste formulation techniques had to be improved so that Branch Technical Position requirements could still be met. Chem-Nuclear began testing and developing waste formulas using superior pozzolanic cements and specialized additives with Portland cement to provide acceptable waste product characteristics. As recent reports from the cement and concrete construction industry have documented, pozzolan modifiers have provided an entirely new perspective to the cement industry for improved product performance. Chem-Nuclear has used pozzolanic cementitious binders to upgrade the stability and leach resistance of many waste forms during the past 5 years. We have documented these improvements in our recently submitted waste form certification topical reports[3].

As we move into the next decade with the advent of engineered barrier disposal technology and multiple levels of waste containment, the industry must reevaluate waste form stability requirements. The decisions we make as cognizant members of the nuclear industry must ensure that current and future disposal requirements are met for the long-term protection of our environment.

The sponsors of this workshop have brought together a team of experienced individuals to discuss issues of concern for low-level radioactive waste stability using cementitious materials. The Chem-Nuclear personnel here are prepared for full and open participation in each panel discussion group. We hope to gain resolution in the following areas:

o   The finalizing and promulgating the criteria which constitute a stable waste form.

o   Establishing meaningful and universal methods to be used in meeting the criteria.

o   Identifying the parameters which must be determined for proper waste stream characterization.

o   Establishing appropriate formula variations with respect to waste loadings and compositions.

Certain specific areas should also be addressed and resolved. We would like to:

o   Establish a common technical basis for measuring waste loading.

o   Establish the extent of full scale solidification testing necessary for correlation with laboratory test data.

o   Establish the criteria for identification and quantification of chelating agents.

o   Discuss the various concerns for processing decontamination solution wastes.

o   Demonstrate that for specific waste forms the general assumption that decreased waste loadings do not necessarily make more stable products.

This is a unique technical setting for consideration of the issues surrounding low-level waste stability using cementitious materials. Thank you for the opportunity to provide this perspective of waste processing from a concerned vendor.

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OPENING REMARKS FOR NRC WORKSHOP
ON CEMENT SOLIDIFICATION OF RADIOACTIVE WASTE
May 31 - June 2, 1989

by
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Vice President, Operations
LN Technologies Corporation

I was asked to comment about my perspective on the use of cement for
solidification and stabilization of low level radioactive waste, field
experience using cement and finally what expectations I have about this
workshop. I will summarize my views on each of these subjects in the short
time provided this morning.

Perspective on Cement for Solidification and Stabilization

Cement is a very desirable medium. Experience using cement for various
applications is well documented and dates back several hundred years. This
significant data base is valuable when attempting to project stability
characteristics to 300 years. However, limitations when using cement must be
recognized.

The radwaste industry has been using cement in a different way from the
more traditional construction industry. Strength is important but so is the
ability to contain radioisotopes within the cement matrix in a water
environment. This industry currently has five years experience in using cement
this way. Over these next three days we'll hear a lot of details about that
experience - some very good - some indicating that there may be limitations to
how much waste can be contained for a given waste type or whether cement is a
suitable medium for all waste types. It is very important for us to understand
the limitations of this medium based on our experience.

Knowing the waste make-up is important to the successful use of cement for
waste stabilization. Like any other chemical reaction the active ingredients
must be identified to properly predict the product of the reaction. Even when
all the ingredients are known it is not always apparent which way the reaction
will go.

The detailed chemical make-up of radioactive waste is not always well
known. There is evidence that waste make-up at nuclear power plants varies
depending upon plant corrosion chemistry, operations vs. shutdown conditions
and operating practices. For example, some plants remove resins from service
because of high differential pressure across the vessel while others remove
resins from service because of chemical depletion.

For cement or any other solidification media, the risk of not knowing the
exact chemical make-up of waste must be considered acceptable given the
conservatism provided for in the application of the waste processing chemistry.

Finally, it is important to recognize the difference between solidification and stabilization. Solidification provides a hard product with no free water while stabilization provides the same plus a product that is capable of passing the tests specified in 10CFR61.56b. Less than 10 percent of the waste processed today must meet 10CFR61.56b criteria specified by the NRC. However, the agreement States which currently have burial sites have more conservative requirements than the NRC. In general they require stabilization at greater than 1 uci/cc for isotopes with half lives of 5 years or more. That conservatism results in about 30 percent of the waste requiring stability. The importance of this meeting is enhanced because of this large percentage of waste requiring stability.

Field Experience with Cement

Field experience with cement solidification/stabilization has been good. Better than 95 percent of the liners processed do not display any problems. However, since inspections of the top of solidified liners and proper cure indications are the only practical inspection that can be done on radioactive liners, it is difficult to detect subtle problems with the stability of a liner.

Actual field experience has shown us that the following situations do occur.

o   Cure time variations - Cure time is dependent upon ambient conditions (summer to winter), whether the cure occurs inside or outside a shipping cask or what active ingredients are in the waste. Cure times have varied between 2 days which is typical to 6 weeks which is very unusual.

o   Temperature profile difference - Temperature profiles are sometimes sharp distinct peaks and other times gradual small peaks. The time to reach peak temperature also varies.

o   Total unexpected waste behavior - We will hear a lot of details about isolated problems today. There has been gas generation in resins resulting in bulging liners. When investigated the source of the problem was an undetected chemical spill in the plant. Resins have coagulated into jelled pockets and never mixed with cement in solidified liners. Cement solidified liners have setup rapidly before all cement material could be added resulting in an unstable product. These unexpected occurrences have taken place using formulations which were successfully tested to 10CFR61.56b requirements on generic waste streams. They were also successfully used on supposedly identical waste streams at the same plants in the past.

These are isolated cases and represent a very small percentage of the waste that is processed using cement. In contrast, there has been some

very good experience showing that cement can be used and give repeatable and consistent products. This is especially true when the waste is well characterized and all waste constituents are known. Under such circumstances, surrogate waste can be tested on small scale and actual full scale waste can be processed with predictable and repeatable times to temperature peaks, peak temperatures, and cure times.

Expectations from the Workshop

There are several expectations that I have for this workshop. These are listed here.

o   An understanding of the limitations on waste characterization - Regulatory decision makers need to understand what operational limitations exist at plant sites. Time for analysis, ability to segregate waste streams and rate of waste processing to keep a plant operating are all real world situations that must be considered.

o   An acceptance of the generic waste form testing concept - Regulatory, plant and vendor personnel must recognize that waste is not the same from plant to plan and from time to time within a plant. There are conservative steps built into process control test programs on generic surrogate waste to account for such changes. We must accept that situation.

o   Obtain a commitment for the NRC to provide clear documented requirements for certification of waste formulations - Currently the 10CFR61 regulation and the Branch Technical Position do not address sea water leaching, 28 day curing, 90 day immersion or guidance on extended cure requirements. Better guidance is necessary to ensure everyone is implementing the intent of 10CFR61 correctly.

o   Re-evaluate the 10CFR61 tests - some tests such as biodegradation and thermal cycling are not considered meaningful.

I expect this to be a very beneficial meeting for all present. We all have the same goal, we just have to pull it all together.

REV/sab

OPS Rpts 5

PERSPECTIVE ON CEMENT FOR SOLIDIFICATION AND STABILIZATION

o   Cement is very desireable medium

o   Recognize limitations

o   Known waste makeup is important

o   Solidification vs. Stabilization

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FIELD EXPERIENCE

o   Problems difficult to identify

o   Batch to batch differences

   -   Cure time

   -   Temperature profile

o   Variations in generic waste streams

o   Predictable processing with no
   variations

LN

EXPECTATIONS

o   Constraints on Waste Characterization

o   Generic waste form testing concept

    acceptance

o   Real world variations in waste

o   Clear requirements for certification

o   Reevaluation of 10CFR61 tests

LN

WESTINGHOUSE PERSPECTIVES AND OBJECTIVES

Presented at the

Cement Solidification Workshop

Gaithersburg, Md.

May 30, 1989

Bryan Roy

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1256 North Church Street

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WESTINGHOUSE COMMERCIAL PLANT EXPERIENCE

o 10 YRS. MOBILE AND IN-PLANT CEMENT SOLIDIFICATION

o 7 YRS. PER 10CFR61 AND BTP REQUIREMENTS

o 5000 SIMULATED AND ACTUAL TEST SOLIDIFICATIONS

o 2000 FULL-SCALE SOLIDIFICATIONS AT 30 PLANTS

o 100 WASTE STREAM COMBINATIONS EVALUATED

o FOUR MAJOR DESIGN EVOLUTIONS OF MOBILE SYSTEMS

WESTINGHOUSE PERSPECTIVES

o CEMENT USAGE

o SOLIDIFICATION ISSUES AND CAUSES

o COMMERCIAL PLANTS AND DOE FACILITIES

o SERVICE SUPPLIER-GENERATOR WORKING TOGETHER

o FUTURE

WESTINGHOUSE WORKSHOP OBJECTIVES

o MAINTAIN PERSPECTIVE

o SHARE POSITIVE AND NEGATIVE WESTINGHOUSE EXPERIENCES

o FOCUS ON THE ACTUAL CAUSES

o DEVELOP SPECIFIC RECOMMENDATIONS TO PARTICIPANTS

o IMPROVE WESTINGHOUSE PROCESS AND SERVICE

WORKING GROUP 1 - LESSONS LEARNED FROM SMALL- AND FULL-SCALE WASTE FORMS AND OBSERVATIONS AT NUCLEAR POWER STATIONS

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OBJECTIVE

The objective of Working Group 1 is to address current issues encountered in comparing small-scale and full-scale waste form test results using laboratory and actual solidified low-level radwaste as well as problems and concerns identified with cement solidification of radwaste at nuclear power stations.

CURRENT ISSUES, PROBLEMS, AND CONCERNS

A number of cement solidifications at nuclear power stations either have not behaved as had been expected or have produced a waste form that did not behave as expected. For example, there have been cases where the waste form set up more quickly than expected, sometimes before all the ingredients had been added. In other cases, the liner bulged or cracked, or the waste form was found not to have been completely solidified. In addition, some samples taken from waste forms have deteriorated when subjected to leaching. These observations have raised questions concerning the relationship between small-scale and full-scale testing, adequacy of the verification testing, and mechanisms that could be causing the observed unsuccessful solidifications and waste form deteriorations. These issues form the basis of the topics that will be discussed in detail by Working Group 1.

The following topics will be discussed by Working Group 1. Because of the large number of topics and the limited time available during the workshop, the topics have been organized into three priority groupings, with Priority 1 as the highest. Priorities within the groupings have not been established. Although we hope to address all the topics, the discussions will proceed according to the priority groupings.

Priority 1 Topics

1. <u>Solidification at Nuclear Power Stations - Review of Recent Events</u>
   a. Currently used solidification methods/techniques.
      i. Mixing.
      ii. Chemical addition sequence.
      iii. Horsepower.
      iv. Range of waste loading.
   b. Examples of unsuccessful solidifications.
      i. Bulging of liners (e.g., TMI-2, Millstone-1).
      ii. Premature solidifications (e.g., Quad Cities-2, Peach Bottom).
      iii. Incomplete solidifications (e.g., J.A. FitzPatrick).
   c. Causes of problems - known causes, possible causes.
      i. Chemical (e.g., formation of calcium picolinate and other chemical processes that occur during the cement solidification of actual LLW).
      ii. Physical (e.g., lack of proper mixing, presence of mixing blades).
      iii. Use of simulated rather than actual waste for preparation of PCP samples.
      iv. Lack of knowledge of properties of actual waste (e.g., presence of unidentified chemicals that hindered solidification).

d. Solutions to solidification problems.

   i.   Technical.

   ii. Procedures.

   iii. Management.

   iv. Equipment (e.g., Is current equipment sufficiently versatile? Does equipment take varying field conditions into account? Are blades optimized for the different kinds of wastes?).

   v.   Field conditions (e.g., temperature).

   vi. Better, more complete characterization of waste to be solidified.

   vii. Preventive measures (e.g., pretreatment of waste stream).

2. **Relationship Between Small- and Full-Scale Testing**

   a. Results of laboratory testing.

   b. Full-scale test results.

      i.   Evaporator concentrates.

      ii. Ion exchange resins.

      iii. Decontamination radwaste.

      iv. Other LLW.

   c. Results of testing of solidified LLW waste forms collected from nuclear power stations.

   d. Certification testing - relationship between small- and full-scale certification testing.

   e. Verification testing - purpose, methods, problems with small-scale testing.

   f. Hydration exotherm - impact on small-scale test results.

   g. Impact of differences in the rates binder materials are added to small-scale samples vs full-size liners.

3. **Full-Scale Testing**

   a. Methods - current and proposed.

      i.   Immersion.

      ii. Leaching.

      iii. Compressive strength.

      iv. Other NRC Technical Position tests.

b. Parameters (e.g., composition, compressive strength, etc.).

    i. Ranges.

    ii. Sample-to-sample variations.

    iii. Variations within waste form.

    iv. Variations of test parameters as a function of time, waste content.

    v. Homogeneity.

    vi. Porosity.

c. Curing time.

d. Potential problems.

    i. Logistical.

    ii. Handling of large radioactive waste forms.

e. Costs.

4. **Sampling of Solidified Waste at Nuclear Power Stations**

a. Grab samples before setting.

b. Coring after setting.

c. Representativeness of samples.

5. **Methods to Verify Proper Solidification of Actual LLW in Liners**

a. Puncture.

b. Accoustic.

c. X-ray.

d. Other.

<center>**Priority 2 Topics**</center>

1. **Comparison of Test Results Using Simulated vs Actual LLW**

a. Analytical capability to accurately characterize actual evaporator and decontamination ion-exchange resin LLW.

b. Comparison of waste loadings and waste-to-binder ratios used in laboratory studies vs those typically used at nuclear power stations.

c. Are surrogate wastes representative of actual waste?

2. __Quality Control of Full-Scale Solidification at Nuclear Stations__

3. __Utility and Vendor Field-Verification Test Samples__

4. __Parameters that Affect Stability and Effects of These Parameters__
   a. Waste loading.
   b. Curing time.
   c. Radiation (effects on ion-exchange resin).

Priority 3 Topics

1. __Preparation of Verification Samples at Nuclear Power Stations__
   a. Sample preparation methods/procedures.
   b. Representativeness of samples.
   c. ALARA considerations.
   d. Problems identified.

2. __How Does a Utility Intelligently Select a Solidification Process or Vendor?__

WORKING GROUP 1

LESSONS LEARNED FROM SMALL- AND FULL-SCALE WASTE FORMS AND OBSERVATIONS AT NUCLEAR POWER STATIONS

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OBJECTIVES

- COMPARE SMALL-SCALE AND FULL-SCALE WASTE FORM
  TEST RESULTS

- ADDRESS PROBLEMS AND CONCERNS IDENTIFIED WITH
  SOLIDIFICATIONS AT NUCLEAR POWER STATIONS

ISSUES, PROBLEMS, CONCERNS

- SOME SOLIDIFICATIONS HAVE NOT BEHAVED AS EXPECTED
  - WASTE FORM SET UP TOO QUICKLY
  - LINER BULGED
  - LINER CRACKED
  - INCOMPLETE SOLIDIFICATION

- SAMPLES HAVE DETERIORATED WHEN LEACH TESTED

- RELATIONSHIP BETWEEN SMALL-SCALE AND FULL-SCALE TESTING

- ADEQUACY OF VERIFICATION TESTING

- MECHANISMS CAUSING UNSUCCESSFUL SOLIDIFICATIONS, WASTE FORM DETERIORATIONS

WORKING GROUP 1 TOPICS

GROUPED BY PRIORITY

PRIORITY 1
PRIORITY 2
PRIORITY 3

PRIORITY 1 TOPICS

- SOLIDIFICATION AT NUCLEAR POWER STATIONS - REVIEW OF RECENT EVENTS

- RELATIONSHIP BETWEEN SMALL- AND FULL-SCALE TESTING

- FULL SCALE TESTING

- SAMPLING OF SOLIDIFIED WASTE AT NUCLEAR POWER STATIONS

- METHODS TO VERIFY PROPER SOLIDIFICATION OF ACTUAL LLW IN LINERS

PRIORITY 2 TOPICS

- COMPARISON OF TEST RESULTS USING SIMULATED VS ACTUAL LLW

- QUALITY CONTROL OF FULL-SCALE SOLIDIFICATION AT NUCLEAR STATIONS

- UTILITY AND VENDOR FIELD-VERIFICATION TEST SAMPLES

- PARAMETERS THAT AFFECT STABILITY AND EFFECTS OF THESE PARAMETERS

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PRIORITY 3 TOPICS

- PREPARATION OF VERIFICATION SAMPLES AT NUCLEAR POWER STATIONS

- HOW DOES A UTILITY INTELLIGENTLY SELECT A SOLIDIFICATION PROCESS OR VENDOR?

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Introduction to Working Group 2

LABORATORY TEST EXPERIENCE AND APPLICATION TO PROBLEM WASTE STREAMS

by

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1. INTRODUCTION AND PURPOSE

Good morning! In this presentation I would like to give you an overview of what we hope to accomplish as a result of our deliberations and discussions in Working Group 2 during the course of this workshop. As you know, the overall objective of this workshop is to obtain an improved understanding of the technical concerns and issues in cement solidification of low-level radioactive waste (LLW) and to develop initiatives that will lead to their regulatory resolution. As the title of Working Group 2, "Laboratory Test Experience and Application to Problem Waste Streams," indicates, the primary objective of this working group is to discuss potential problems with cement solidification of low-level radioactive waste which may be inferred from laboratory test experience. Another objective is to determine possible causes or reasons for these problems.

2. ORGANIZATION OF DISCUSSIONS

We have requested that the members of Working Group 2 who are familiar with applicable laboratory test experience to prepare brief summary presentations (say, about ten minutes -- no slides or viewgraphs) as opening statements to "kick off" the subsequent discussion. We expect to have opening presentations this afternoon by appropriate participants on the following topics:

Problems encountered with small-scale laboratory testing of cement solidification of LLW performed at the national laboratories and sponsored by either DOE or NRC using either simulated or actual LLW.

Identification of possible waste streams which as a result of the testing should be considered either unsuitable for solidification in cement or suitable only at very limited loadings.

Vendor experience with laboratory testing of cement solidification of power reactor wastes.

Experience with cement solidification of LLW at DOE's operations at the West Valley Demonstration Project and at Savannah River Laboratory.

We have requested that the Working Group 2 participants limit these opening statements to brief summary presentations of about ten minutes each, no slides or viewgraphs. Each presenter has an abundance of information to share, so keeping these opening presentations short will be a challenge, but time is limited.

On Thursday morning, we expect to address the following issues and concerns:

1. The implications of data from the cement solidification of low-level waste from DOE operations at the West Valley Demonstration Project and at Savannah River Laboratory. We are especially concerned with the implications for the cement solidification of power reactor radwaste.

2. Problems associated with radwaste characterization as it affects solidification with cement, e.g., organic impurities at ppm concentrations in the West Valley supernatant waste and the possible implications for solidification of decontamination waste streams in cement.

3. The significance of laboratory data on the effects of the degree of depletion of ion-exchange resins as well as the effects of particular species of depleting cations and anions on the properties and performance of the resulting cement-solidified waste forms.

4. The significance of the effects of curing times and curing conditions on laboratory-scale test specimens.

After lunch tomorrow, we expect to address the following issues and concerns:

5. The feasibility of using laboratory research or exploratory testing to identify waste streams that cannot be solidified in cement.

6. The feasibility of using laboratory research or exploratory testing to establish the maximum waste loading for a specific waste stream in an actual full-scale waste form.

During the final working group session on Friday morning, we expect to address the following issue/concern:

7. The feasibility of using laboratory research or exploratory testing to develop means of solidifying "problem" waste streams and/or increased waste loadings in cement.

We expect to use any remaining time to tie up any "loose ends."

3. SUMMARY

I have attempted in this presentation to provide you with an overview of what we plan to discuss in Working Group 2 and of how we will organize these discussions. We expect that the "kick-off" presentations by some of the working group participants to consist of relatively straightforward descriptive accounts of laboratory work already accomplished. Following those, however, we expect some very interesting and, we hope, fruitful discussions and deliberations about the issues and concerns which I outlined a few minutes ago. At the close of this working group's deliberations, we expect to have a better understanding of the application of laboratory test experience to problem waste streams, namely, those which exhibit adverse and complex chemical and physical interactions with cement.

Evaluation of NRC Staff Technical Position (TP) Qualification Tests for Cementitious Waste Forms

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1. INTRODUCTION

In order to minimize the release of radionuclides from a shallow land burial trench, the NRC has developed guidelines and criteria on waste packages and the burial site itself. These are described in 10CFR61, the Technical Position, and the Draft Regulatory Guide, all of which are familiar to the low-level waste community. Perhaps the most important strategy regarding the burial of Class B and Class C wastes is that they be "stable" so that deleterious changes from their original condition are reduced.

Table 1, taken from reference 1, lists the TP tests which are currently in use to qualify a waste form with respect to stability. The tests are usually short-term ones and are not always of an accelerating nature. Because of this, there is uncertainty in their capability to predict long term properties.

In addition, there has been criticism of some of the tests by ACRS in a letter dated November 10, 1987, and by NUMARC [2]. In particular, they question the usefulness of the tests on the basis of:

(a) their rationale and technical connection with NRC stability requirements described in 10CFR61;

(b) their applicability to real waste behavior; and

(c) the choice of test methodologies and test conditions.

It is with these concerns in mind that the NRC decided to hold a workshop on low-level cementitious wastes to further study the need to modify or eliminate individual TP tests. This will be considered in Working Group 3 (Stabilized Waste Form Testing Guidance) to be chaired by M. Tokar. Technical coordination will be provided by this writer.

2. GUIDANCE FOR WORKSHOP DISCUSSIONS

In order to systematically address the usefulness of each TP test, the following questions, as a minimum, will be asked and discussed:

(a) Is there a defensible rationale for each test? If not, should it be eliminated?

Table 1

Solidified product guidance

Tests	Methods	Criteria
1. Compressive Strength	ASTM C39 or D1074	60 psi (a)
2. Radiation Stability	(See 1983 TP)	60 psi comp. str. after 10E+8 rads
3. Biodegradation	ASTM G21 & G22	No growth (b) & comp. str.> 60 psi
4. Leachability	ANS 16.1	Leach index of 6
5. Immersion	(See 1983 TP)	60 psi comp. str. after 90 days
6. Thermal Cycling	ASTM B553	60 psi comp. str. after 30 cycles
7. Free liquid	ANS 55.1	0.5 percent
8. Full-scale Tests	(See 1983 TP)	. Homogeneous & correlates to lab size test results

(a) The 1983 TP calls for a minimum compressive strength of 50 psi. This has been raised to 60 psi to accommodate an increased maximum burial depth at Hanford of 55 feet (from 45 feet).

(b) The 1983 TP calls for a multi-step procedure for biodegradation testing: if observed culture growth rated "greater than 1" is observed following a repeated ASTM G21 test, or any growth is observed following a repeated ASTM G22 test, longer term testing (for at least 6 months duration) is called for, using the "Bartha-Pramer Method." From this test, a total weight loss extrapolated for full-size waste forms to 300 years should produce less than a 10 percent loss of total carbon in the sample.

(b)   If the test is useful, should:

    *   the rationale be strengthened?
    *   the acceptance criteria be changed?
    *   the test methodology and test conditions be modified?
    *   the data analysis be improved to eliminate uncertainty?

(c)   What approaches are recommendable for full-size specimen testing?

Working Group members will discuss these issues during the workshop.

    The individual TP tests are listed below together with selected reports that have a bearing on their usefulness and limitations. It is recognized that much additional literature is available, but the reports listed were prepared at Brookhaven as part of an extended program to evaluate various characteristics of the TP tests.

Compression Strength	Thermal Cycling	Radiation Testing
NUREG/CR-2813	NUREG/CR-2813	NUREG/CR-2969
NUREG/CR-3444 (Vol. 5)	NUREG/CR-3444 (Vol. 5)	NUREG/CR-3812
NUREG/CR-3829	NUREG/CR-3829	NUREG/CR-3829
NUREG/CR-5279	NUREG/CR-4201	NUREG/CR-5279

Biodegradation Tests	Leaching and Immersion Tests
NUREG/CR-3829	BNL-51517
	NUREG/CR-2813
	NUREG/CR-3829
Free Liquid Test	NUREG/CR-3909
	NUREG/CR-4756
NUREG/CR-2813	NUREG/CR-5153

3.   PROPOSED NEW TESTS AND CRITERIA

    To help ensure that waste forms are fully characterized with respect to failure/degradation modes that could reduce stability and cause increases in radionuclide release, completely new tests to measure relevant properties may need to be devised. Any new test will need:

(a)   a defensible rationale for its use;
(b)   ability to predict long term performance; and
(c)   a defined acceptance criterion.

Working Group members will consider what new tests should be implemented.

4. OTHER ISSUES

The following additional issues will be addressed at the workshop:

(a)   Qualification of Combined Radioactive Waste Streams;

(b)   Specimen Scale-up Effects;

(c)   Accelerated Tests;

(d)   Minimum Numbers of Specimens;

(e)   Specimen Preparation, Curing, Etc.; and

(f)   General QA/QC Procedures, Archival Specimens.

5. SUMMARY

Although the tests to qualify solidified waste forms have been in use for many years, they remain the subject of much controversy. Their applicability and usefulness in predicting long term stability are the main areas of concern. This workshop will address a broad range of technical issues pertinent to individual tests with the focus on cementitious wastes.

Appendix 1 is an agenda for the Working Group 3 deliberations over the 3-day workshop. It is hoped that through the participation of individuals working for organizations involved in different aspects of the low-level waste field (NRC, utilities, solidification vendors, and National Laboratories) that the limitations in the TP tests will be more clearly defined and that modifications may be considered along with the implementation of completely new tests to characterize relevant waste form properties.

6. REFERENCES

1.   "Report to the Director, Office of Nuclear Materials Safety and Safeguards, Regarding Current Status and Proposed Action for Regulation of LLW Stability," May 31, 1988.

2.   NUMARC/NESP-002, "A Technical Basis for Meeting the Waste Form Stability Requirements of 10CFR61," Nuclear Management and Resources Council, Inc., W. Chang, et al., April 1988.

3.   BNL-51517, "Waste Form Development Program - Annual Progress Report," R. M. Neilson, Jr. and P. Colombo, January 1982.

4.   NUREG/CR-2813, "Development of Low Level Waste Form Criteria Testing of Low Level Waste Forms," R. E. Davis and E. P. Gause, November 1983.

5.   NUREG/CR-3812, "Assessment of Irradiation Effects in Radwaste Containing Organic Ion-Exchange Media," K. J. Swyler, et al., May 1984.

6. NUREG/CR-3444, Vol. 5, "The Impact of LWR Decontaminations on Solidification, Waste Disposal and Associated Occupational Exposure," J. W. Adams and P. Soo, June 1988.

7. NUREG/CR-3829, "An Evaluation of the Stability Tests Recommended in the Branch Technical Position on Waste Forms and Container Materials," B. S. Bowerman, et al., March 1985.

8. NUREG/CR-3909, "Solidification and Leaching of Boric Acid and Resin LWR Wastes," H. Arora and R. Dayal, June 1984.

9. NUREG/CR-4201, "Thermal Stability Testing of Low-Level Waste Forms," P. L. Piciulo and S. F. Chan, May 1985.

10. NUREG/CR-4756, "Leaching Studies of Cement-Based Low-Level Radioactive Waste Forms," H. Arora and R. Dayal, October 1986.

11. NUREG/CR-5153, "The Leachability and Mechanical Integrity of Simulated Decontamination Resin Wastes Solidified in Cement and Vinyl Ester-Styrene," P. Soo, et al., May 1988.

12. NUREG/CR-5279, "Sulfate-Attack Resistance and Gamma-Irradiation Resistance of Some Portland Cement Based Mortars," P. Soo and L. W. Milian, March 1989.

APPENDIX 1

Agenda for Working Group 3 Discussions

DAY	MORNING	AFTERNOON
Wednesday, (5/31)	Plenary Session	
Thursday, (6/1)	Compressive Strength; Leaching/Immersions; Scale-up Effects; Free Liquids.	Numbers of Test Specimens; Curing Procedures; Thermal Cycling; Biodegradation.
Friday, (6/2)	Combined Waste Streams; QA/QC; Archival Specimens; New Tests; Left-over Business; Summary of Findings.	Tech. Coordinator Summary of Findings to NRC.

Introduction to Working Group 4

WASTE CHARACTERIZATION, SOLIDIFICATION,

AND

PROCESS CONTROL PROGRAMS

by

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1. INTRODUCTION AND PURPOSE

Good morning and welcome to the Cement Solidification and Stabilization Workshop, especially those of you who will participate in or observe Working Group 4. Group 4 will discuss what goes on at the plant, focusing on practical problems that arise when real waste streams are processed for disposal. Overall, Group 4 will attempt to answer the following:

Since real waste seldom has the exact same composition as "qualified" waste, how does one assure that a specific batch of real LLW solidified with cement is stable as required by 10 CFR Part 61?

Group 4 will attempt to address this issue by confining most of its discussions to technical problems associated with full-scale waste form production. The technical problems will be discussed within the following framework:

* What is being done (current practices);
* What should be done (requirements for stability);
* What can be done (technological, ALARA, or other limits).

2. ORGANIZATION OF DISCUSSIONS

The emphasis on the in-plant technical aspects of LLW cement stabilization means that there will be a wide range of topics to cover. The topics will be categorized according to where they fit in the generic process diagram shown in Figure 1. To cover them all in the limited time available, we will adhere to a tight agenda, as shown in Figure 2.

Thursday morning we will consider waste characterization, starting with listing the most common waste types solidified in cement, and their properties as determined in the field. Discussion topics will include the sampling and analytical methods for determining waste stream chemical and physical properties, methods for tracking waste in the plants, and procedures followed when tank and pipe residues contaminate a particular waste stream.

After lunch Thursday, we will discuss pretreatment and small-scale recipe verification testing before full-scale solidification. The subject of pretreatments may only include identifying those waste streams that can be pretreated, since actual pretreatment processes may involve proprietary information. Discussions of recipe verification will involve identifying waste sampling methods and frequency, sample preparation procedures, and what tests to perform on the small samples to confirm that the recipe can be used to make a stable waste form. We will also consider how waste sampling and small-scale sample preparation and testing affect ALARA principles in this session.

In our final session Friday morning, we will discuss process monitoring and post-solidification testing or monitoring of the solidified waste product. Process monitoring includes such items as waste and binder feed parameters, and mixing parameters such as speed and time of mixing. For post-solidification monitoring and testing, we will consider controlling curing conditions as well as non-destructive tests that can provide data on product characteristics such as hardness, set time, and homogeneity.

3. REGULATORY IMPLICATIONS

The technical topics to be discussed in Group 4 have significant regulatory implications which may need to be resolved at some time. Specific items which might be included in a guidance document will be discussed in our working group as we are covering the technical issues. Some of these items are shown in Figure 3.

However, the actual development of regulatory guidance will necessarily rest on resolving the issue of what constitues reasonable assurance. The resolution could consist of specifying how much sampling and analysis is required for the waste streams, the number of recipe verification samples needed, or what testing and acceptance criteria should be applied to waste products after the process is complete and before shipment to the disposal site.

Overall, the topic for Working Group 4 falls into the realm of product quality control. This concept of quality control applied to treating "garbage" may seem out of place, but it is completely appropriate when one remembers that the QC is being applied to materials that may be hazardous for several hundred years.
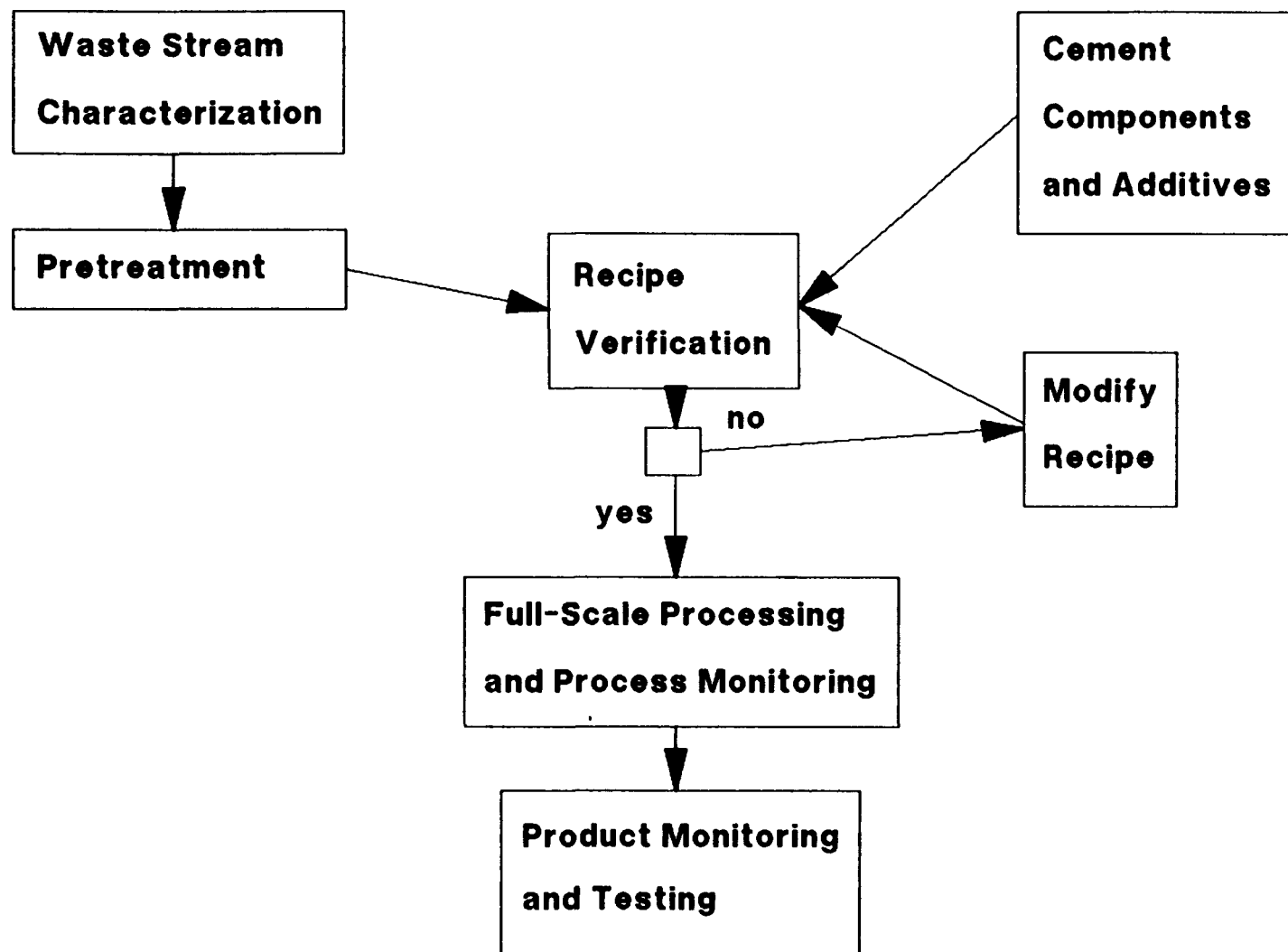
Figure 1. Elements of Process Control

FIGURE 2

AGENDA FOR WORKING GROUP 4

A. Technical Issues (Elements that can contribute to waste stability, or as an alternative viewpoint, to produce quality control. These could be elements of generic and plant specific PCPs.)

Thurs. A.M.

1. Waste characterization

    * sampling method (where obtained, size of sample)
    * qualitative (waste id, well-segregated or combined with others)
    * quantitative (concentrations of total solids, main constituents)
    * acceptance criteria (procedures for out-of-spec wastes)

Thurs ⌐.M.

2. Pretreatment and recipe verification

    * what waste stream materials can (must) be pretreated (neutralize pH, precipitate)
    * sampling method (where, how big)
    * sample prep (controlled mixing, curing)
    * tests to perform (set time, hardness)
    * limitations due to ALARA

Fri. A.M.

3. Process monitoring and pre-transport storage/handling

    * waste stream homogenized and at temperature
    * mixing characteristics (speed, time)
    * monitor/control cure conditions
    * nondestructive tests of final waste form
    * small sample for archival storage

FIGURE 3

B.   Regulatory Issues (Process Control Programs, their purpose and use. How much should be required in a PCP?)

1. Waste characteristics, specifications for:

    * chemical analysis vs. waste tracking, record-keeping
    * allowable ranges of composition for each waste stream
    * acceptance criteria

2. Recipe verification samples, specifications for:

    * number of samples made and tests applied
    * acceptance criteria

3. Process monitoring, specifications for:

    * equipment mixing characteristics for a given waste

4. Pre-transport storage/handling, specifications for:

    * cure conditons (time, temperature)
    * nondestructive test acceptance criterion

5. Record-keeping

WORKING GROUP SESSIONS
MAY 31 - JUNE 2, 1989

WORKING GROUP 1 DISCUSSIONS:

Technical Coordinator: John W. Mandler
Science and Technology Division
Physics and Mathematics Group
Idaho National Engineering Laboratory

Working Group Chairman: Phillip R. Reed
Division of Engineering Safety
Office of Nuclear Regulatory Research
U. S. Nuclear Regulatory Commission

1. LESSONS LEARNED FROM SMALL- AND FULL-SCALE WASTE FORMS AND OBSERVATIONS AT NUCLEAR POWER STATIONS

The U. S. Nuclear Regulatory Commission (NRC) regulation 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste," establishes a waste classification system based on the radionuclide concentrations in the wastes. The regulation requires that high-activity wastes, which are designated Class B and C wastes, be stabilized prior to disposal at a land burial site. Lower-activity waste, designated Class A waste, may be disposed of without having been stabilized. According to 10 CFR Part 61, low-level radioactive waste may be stabilized by dewatering it and placing it in a high-integrity container or by solidifying it in a binder material such as cement inside a steel liner. However, state regulations require that low-level radioactive wastes containing chelating agents be solidified and wastes having radionuclide concentrations greater than 1 $\mu Ci/cm^3$ be stabilized prior to burial. Consequently, ion-exchange resins used to process decontamination reagents at nuclear power stations following chemical decontaminations of primary coolant system components are routinely solidified at reactor sites using Portland cement or a mixture of Portland cement and flyash. And because it is impractical to dewater certain types of low-level wastes, wastes such as evaporator concentrates are also solidified at reactor sites prior to shipment to disposal sites.

The discussions of Working Group 1 were focused on issues related to laboratory testing of small- and full-scale waste form samples and observations of solidifications performed at operating commercial nuclear power stations. During the past several years, a number of solidifications which were performed at reactor sites did not go as planned. In one case, ion-exchange resin waste solidified prematurely and in another case ion-exchange resin waste failed to completely solidify. At other times, the liners used to solidify wastes bulged during the hydration of the cement binder. The Working Group attempted to define explanations for these unusual occurrences in light of what has been demonstrated in laboratory experiments conducted at DOE facilities and in the

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laboratories of the solidification vendors. The Working Group suggested improvements in the methods used to prepare and evaluate process control program (PCP) specimens and also suggested possible diagnostic techniques that could be used following solidifications to assure that the waste forms were, in fact, acceptable for burial.

1.1 Introduction

The objective of Working Group 1, titled "Lessons Learned from Small- and Full-Scale Waste Forms and Observations at Nuclear Power Stations", is to address current issues encountered in comparing small-scale and full-scale waste form test results using laboratory and actual solidified low-level radwaste as well as problems and concerns identified with cement solidification of radwaste at nuclear power stations.

1.1.1 Current Issues, Problems, and Concerns

A number of cement solidifications at nuclear power stations either have not behaved as had been expected or have produced a waste form that did not behave as expected. For example, at Quad Cities Station- Unit 2, LOMI decontamination ion-exchange resin waste that was being solidified with cement in a solidification liner set up prematurely. Only about one-third of the quantity of cement that was intended to be added to the liner was in the liner when the waste solidified. Two liners containing Submerged Demineralizer System waste bulged and cracked following their solidification at Three Mile Island- Unit 2 (TMI-2). A liner containing LOMI decontamination ion-exchange resin waste bulged after it was solidified in cement at the Millstone Station- Unit 1. In another case, a liner containing LOMI decontamination ion-exchange resin wastes that was solidified at the J. A FitzPatrick Station was puncture tested prior to burial at the Barnwell, SC disposal site. The liner was found to contain regions that had not completely solidified. In addition, some small-scale decontamination ion-exchange resin waste-form specimens that have been collected from solidification liners at nuclear power stations have deteriorated when immersed in demineralized water leachant in the laboratory. These observations have raised questions concerning the relationship between small-scale and full-scale testing, the adequacy of the process control program (PCP) verification testing, and the mechanisms that could be causing the observed unsuccessful solidifications and waste form deteriorations. These issues form the basis of the topics that were discussed in detail by Working Group 1.

1.1.2 Working Group 1 Topics

The following topics were discussed by Working Group 1. Because of the large number of topics that the Working Group had intended to cover and the limited time available during the workshop, the topics were organized into three priority groupings, with Priority 1 as the highest. Priorities within the groupings were not established. All topics were expected to be addressed (and all were addressed except for one Priority 3 topic), and the discussions proceeded according to the priority groupings.

1.1.2.1 Priority 1 Topics

1. Solidification at Nuclear Power Stations - Review of Recent Events

   a. Examples of unsuccessful solidifications.

      i. Premature solidifications (e.g., Quad Cities-2).
      ii. Incomplete solidifications (e.g., J.A. FitzPatrick).
      iii. Postponed solidifications (e.g., Peach Bottom)
      iv. Bulging of liners (e.g., TMI-2, Millstone-1).

   b. Causes of problems - known causes, possible causes.

      i. Chemical (e.g., formation of calcium picolinate and other chemical processes that occur during the cement solidification of actual LLW, chemical addition sequence).
      ii. Physical (e.g., lack of proper mixing, presence of mixing blades, horsepower).
      iii. Use of simulated rather than actual waste for preparation of PCP samples.
      iv. Lack of knowledge of properties of actual waste (e.g., presence of unidentified chemicals that hindered solidification).
      v. Range of waste loading.

   c. Solutions to solidification problems.

      i. Technical.
      ii. Procedures.
      iii. Management.
      iv. Equipment (e.g., Is current equipment sufficiently versatile? Does equipment take varying field conditions into account? Are blades optimized for the different kinds of wastes?).
      v. Field conditions (e.g., temperature).

      vi.   Better, more complete characterization of waste
to be solidified.

     vii. Preventive measures (e.g., pretreatment of
waste stream).

2.   Relationship Between Small- and Full-Scale Testing

    a.   Results of laboratory testing.

    b.   Full-scale test results.

        i.   Evaporator concentrates.
       ii.   Ion exchange resins.
      iii. Decontamination radwaste.
       iv.   Other LLW.

    c.   Results of testing of solidified LLW waste forms
collected from nuclear power stations.

    d.   Certification testing - relationship between small-
and full-scale certification testing.

    e.   Verification testing - purpose, methods, problems
with small-scale testing.

    f.   Hydration exotherm - impact on small-scale test
results.

    g.   Impact of differences in the rates binder materials
are added to small-scale samples vs full-size
liners.

3.   Full-Scale Testing

    a.   Methods - current and proposed.

        i.   Immersion.
       ii.   Leaching.
      iii. Compressive strength.
       iv.   Other NRC Technical Position tests.

    b.   Parameters (e.g., composition, compressive strength,
etc.).

        i.   Ranges.
       ii.   Sample-to-sample variations.
      iii. Variations within waste form.
       iv.   Variations of test parameters as a function of
time, waste content.
        v.   Homogeneity.
       vi.   Porosity.

c. Curing time.

    d. Potential problems.

        i.   Logistical.
        ii. Handling of large radioactive waste forms.

    e. Costs.

4. Sampling of Solidified Waste at Nuclear Power Stations

    a. Grab samples before setting.
    b. Coring after setting.
    c. Representativeness of samples.

5. Methods to Verify Proper Solidification of Actual LLW in
    Liners

    a. Puncture.
    b. Accoustic.
    c. X-ray.
    d. Other.

1.1.2.2 Priority 2 Topics

1. Comparison of Test Results Using Simulated vs Actual LLW

    a. Analytical capability to accurately characterize
        actual evaporator and decontamination ion-exchange
        resin LLW.
    b. Comparison of waste loadings and waste-to-binder
        ratios used in laboratory studies vs those typically
        used at nuclear power stations.
    c. Are surrogate wastes representative of actual waste?

2. Quality Control of Full-Scale Solidification at Nuclear
    Stations

3. Utility and Vendor Field-Verification Test Samples

4. Parameters that Affect Stability and Effects of These
    Parameters

    a. Waste loading.
    b. Curing time.
    c. Radiation (effects on ion-exchange resin).

1.1.2.3 Priority 3 Topics

1. Preparation of Verification Samples at Nuclear Power
    Stations

a. Sample preparation methods/procedures.
    b. Representativeness of samples.
    c. ALARA considerations.
    d. Problems identified.

    2. How Does a Utility Intelligently Select a Solidification Process or Vendor? (This topic was intended to be discussed, but due to time constraints it was not discussed.)

1.1.2.4 Presentation of Results of Working Group 1 Discussions

    The following presents a summary of the Working Group 1 discussions. This summary does not present items in the chronological order in which they were discussed by the Working Group; rather, for purposes of clarity, it groups them into the general topic areas presented above in Section 1.1.

1.2 **Priority 1 Topics**

1.2.1 Solidification at Nuclear Power Stations-Review of Recent Events

1.2.1.1 Examples of Unsuccessful Solidifications

    Several examples of unsuccessful solidifications were discussed by Working Group 1. Most members of the Working Group believe that the vast majority (i.e., greater than 95%) of solidifications have been successful. The focus of the discussions, therefore, was on the few problem solidifications in order to make the technology even better than it currently is.

    The following are brief outlines of these events. For purposes of clarity and completeness, supplemental information about these events, which was obtained from the utilities and/or solidification vendors, has been added to that discussed by the Working Group. This additional information includes certain details concerning the decontamination operation which produced decontamination ion-exchange resin waste and the scenario of events during solidification of the waste.

1.2.1.1.1 Premature Solidification (Quad Cities Station- Unit 2). LN Technologies Corp. (LN) performed a LOMI decomtamination of the primary coolant recirculation system (PCRS) at Quad Cities Station-Unit 2 during April, 1988[1,2]. During the same month, Chem-Nuclear Systems, Inc. (CNSI) performed the solidification of the decontamination ion-exchange resin waste using a mixture of Portland Type I cement and flyash. This particular solidification was the eleventh solidification of decontamination resins performed by CNSI for Commonwealth Edison Company.

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Phase 1 of the LOMI decontamination included the discharge piping of both loops, the pipe header, and the jet pump risers up to approximately three feet above the vessel penetration. Phase 2 included the suction piping and the reactor annulus filled to the top of the suction nozzle. Phase 1 was completed by recirculation of the spent LOMI solution through a bank of ion-exchange resin columns containing strong acid cation (SAC) resin and weak base anion (WBA) resin. The columns were arranged in series with a SAC column upstream of a WBA column. Recirculation was continued until greater than 95% of the chemicals were removed.

During the transfer of the hot process water from the discharge side to the suction side in preparation for Phase 2, a high level was noticed on the suction side with water levels substantially above the suction nozzles. Since this water was mildly contaminated with LOMI chemicals, it was decided to lower the water level by passing it through a mixed-bed resin of SAC and strong base anion (SBA) resin before sending the water to radwaste. After this exercise, all ion-exchange columns were emptied by sluicing to a carbon steel solidification liner. The ion-exchange resin beds were then refilled with SAC and WBA resin for Phase 2 and with SAC and SBA resin for the final polishing of the water inventory in both the suction and discharge loops.

Once the rough cleanup of the spent reagents in the piping on the suction side had occurred, the final cleanup or polishing of the water was performed. At this point, the filled resin columns were sluiced to the same solidification liner.

A total of 119 ft^3 (3.37 m^3) of ion-exchange resin was sluiced into the solidification liner, and this resin filled about 70% of the total usable volume inside the liner. A summary of the quantities of the different types of ion-exchange resin that were solidified is given in Table 1.

Following the final transfer of ion-exchange resin to the liner, excess water was pumped out of the liner until about 2 in (5 cm) of water remained standing over the surface of the settled

Table 1. Mixture of resins solidified at Quad Cities Station- Unit 2

Resin Type	Volume		Brand
	(ft^3)	(m^3)	
Strong acid cation	53	1.50	Rohm and Haas IR-120
Strong base anion	26	0.74	Dowex SBR
Weak base anion	40	1.13	Ionac A-365

resin beads. The decision was made to delay the solidification until the following morning. In order to reduce the radiation exposure rate above the liner, water was added to the liner from the decontamination skid. On the following morning, the liner was again dewatered until about 2 in (5 cm) of free-standing water remained above the surface of the resin.

Process Control Program (PCP) verification samples were prepared prior to initiation of the solidification. These were prepared using simulated decontamination resin waste with LOMI reagent loadings similar to those of the decontamination resins. Two PCP verification samples were prepared - one using a pH adjustment step and one not using a pH adjustment step. Because both PCP verification samples (including the one prepared without a pH adjustment step) seemed to solidify properly, the full-scale solidification proceeded without a pH adjustment step. The utility questioned the procedure revision (i.e., elimination of the pH adjustment step); however, the utility's staff did not have the expertise in the area of waste solidification to understand the possible consequences of such a revision.

The total quantity of cement that was to be added to the liner was about 7500 lb (3400 kg). Although the cement addition hopper had adequate capacity for the entire process, the technician did not fill the hopper completely (only to about 2400 lb (1089 kg)) because of transfer problems experienced previously due to packing of the material. (This problem was later corrected). The cement, therefore, was going to be added in three stages. The addition of one hopper load of cement normally took about one hour, and about 20 minutes was required to reload the cement hopper between additions. The solidification process began, and after about one hour about one-third of the cement had been added, and the cement hopper required filling. At this time, the hydraulic pressure on the mixer motor was about 1600 psi, which is normal operating pressure. Because the cement hopper had to be filled from the top of the control truck, the solidification operators were not able to monitor the mixer motor pressure during the time they were filling the cement hopper. When they returned to the control panel, the mixer motor hydraulic pressure was 2700 psi and climbing, an indication that the mixture was setting. The mixer motor upper limit set-point was 3300 psi. At this point the operators realized that the cement-resin mixture was beginning to set up. Within 10 minutes the mixer hydraulic pressure exceeded 3000 psi, and the mixer seized and ceased to run due to high viscosity. No more cement could be added to the mixture. Because the waste solidified prematurely, the liner was encapsulated in cement inside another larger liner before it was shipped to a disposal site.

1.2.1.1.2 Incomplete Solidification (J. A. FitzPatrick Station). Pacific Nuclear performed a decontamination on the fuel pool cooling/residual heat removal (RHR) crosstie, the RHR/RHR service

water crosstie, and the PCRS at the J. A. FitzPatrick Nuclear Station during September, 1988 using a LOMI-NP-LOMI process with oxalic acid rinse after the NP (nitric permanganate) step[3]. LN was contracted to perform the solidification of the ion-exchange resin waste. The resins were solidified in three separate liners.

The transfer of the decontamination ion-exchange resins from the Pacific Nuclear ion-exchange columns to two of the three solidification liners commenced the evening of September 22, 1988 and continued during the morning of September 23. Initially, about 30 ft^3 (0.85 m^3) of LOMI SAC resin and 75 ft^3 (2.12 m^3) of LOMI WBA resin were sluiced to the first liner. The total mass of these resins was 4875 lb (2211 kg), and they were loaded with 402 lb (182.2 kg) of picolinic acid. Following the completion of this first transfer of resins, the liner fill-head was removed, and the liner was capped and moved to a location outside the truck-bay.

A second liner was then moved into the reactor building truck-bay, and the transfer of ion exchange resin continued. During this transfer, high radiation readings were measured at the surface of the liner, which prompted plant personnel to halt the transfer. At the time the sluicing of the resin was discontinued, this second liner contained 60 ft^3 (1.70 m^3) of cation resin and 15 ft^3 (0.42 m^3) of anion resin. These resins were loaded with 78 lb (35.2 kg) of picolinic acid. Station personnel were concerned that the addition of the resin from the final anion column might raise the liner radiation level above the limit required for shipping. The decision was made to complete the filling of this liner using relatively low activity mixed-bed ion-exchange resin from the plant radwaste treatment system and charcoal from a plant air purification system. A total volume of 32 ft^3 (0.91 m^3) of mixed-bed resin and charcoal was added to the second liner so that the total waste volume was 107 ft^3 (3.03 m^3). This second liner was the first to be solidified.

During the morning of September 23, the mixing apparatus on the second liner was turned on to homogenize the ion-exchange resin and charcoal waste in the liner. After about 40 minutes of mixing, a 3 in^3 (50 cm^3) sample of the wet waste was obtained from the liner by dipping a plastic vial below the surface of the waste. Additional resin samples were collected at this time which were later used to prepare PCP samples. The solidification of the second liner took place the morning of September 24. The solidification was performed by LN personnel. The total quantities of ion-exchange resins, charcoal, slaked lime, and cement that were added to the second liner are given in Table 2.

Table 2.   Composition of waste form that was sampled at the J. A.
            FitzPatrick Station

Type of Material	Volume (ft³)	(m³)	Mass (lb)	(kg)
LOMI cation	60	1.70	3000	1361
LOMI anion	15	0.42	675	306
Radwaste ion-exchange resin and charcoal	32	0.91	1500	680
Picolinic acid		----	78	35.2
Cement		----	6428	2915
Slaked lime		----	208	94.3
	Total:		11888	5391.5

The third liner contained 28 ft³ (0.79 m³) of decontamination
ion-exchange resin having a mass of 1260 lb (571.5 kg) and 105 ft³
(2.97 m³) of ion-exchange resin from a plant clean-up system.
Thus, two of the three liners contained significant quantities of
waste other than decontamination ion-exchange resin waste, and just
one of the liners contained only LOMI decontamination ion-exchange
resin waste.

Samples of ion-exchange resin waste were collected from each
of the three liners after the waste had been thoroughly mixed, and
these waste samples were subsequently used to prepare PCP
verification waste forms. Nothing unusual was noticed during the
preparation of the PCP verification specimens. They appeared to
solidify normally. In addition, nothing unusual was noticed during
the solidification of the liner loaded with a mixture of LOMI
resin, mixed-bed resin, and charcoal. However, during the
solidification of the liner containing only LOMI resin, the
technician saw potential problems on the video monitor which showed
the mixing vortex inside the liner. When about 1/3 of the cement
had been added, the general appearance of the mixing vortex
indicated that the waste form might solidify prematurely. Liquids
and cement were added to completion, although the final level was
higher than was expected.

Following the completion of the solidification operation, the
liner containing only LOMI ion-exchange resin waste was probed and
it exhibited a hardness that was typical of other liners that had
been solidified. Since the composition of the waste form met the
acceptance criteria and the liner's temperature exotherm was
normal, it was sent to Barnwell along with the other two liners.
Because the resin in the liner that contained only LOMI
decontamination waste was loaded with a realtively high

concentration of picolinic acid (7.6 wt%), this liner was chosen for puncture testing when it arrived at the Barnwell, SC, disposal site. The punctures revealed that the waste form had not completely solidified. At two different locations the material in the liner was gelatinous. A thick, redish colored mixture of resin beads and water oozed out through the punctures. Upon drying, the material looked and behaved like ordinary resin beads. This liner was subsequently returned to the J. A. FitzPatrick Station where it was eventually encapsulated in cement inside another larger liner in order to make it acceptible for burial.

1.2.1.1.3 Postponed Solidification (Peach Bottom Atomic Power Station). Pacific Nuclear performed a LOMI-NP-LOMI decontamination of the PCRS and the reactor water clean-up system (RWCS) during December, 1987 at the Peach Bottom Atomic Power Station[4]. The decontamination ion-exchange resins, consisting of Ionac A-365 anion resin and Rohm and Haas Amberlite IRN-77 cation resin, were transferred to three liners in preparation for solidification. Table 3 presents the compositions of the wastes in the three liners.

On November 30, 1988, PCP verification specimens were prepared using actual decontamination resin waste that had been collected from liner 446692-1. These PCP specimens appeared to set up correctly, and the solidification of the waste in the corresponding liner was scheduled for the following day. However, the next morning it was discovered that the liner being prepared for solidification was liner 446828-10 rather than liner 446692-1. So that morning three PCP verification specimens were prepared using resin waste from liner 446828-10, which contained resins loaded with 4.5 wt% picolinic acid. Each of the PCP verification specimens was prepared by first mixing slaked lime into the resin waste sample. Before cement could be added to the neutralized resin waste, it was observed that the resin in each PCP specimen was covered with a layer of white material that had the consistency

Table 3. Compositions of resin wastes in the three Peach Bottom liners

Liner ID	Anion Resin		Cation Resin		Picolinic Acid Loading
	(ft^3)	(m^3)	(ft^3)	(m^3)	(wt%)
446692-1	42	1.19	42	1.19	1.5
446828-15	59	1.68	61	1.72	5.5
446828-10	59	1.68	33	0.94	4.5

of pudding. When tapped with a glass rod, this material seemed rubbery. Below this layer, the resin appeared to be uniformly dispersed in material having the same color as the segregated layer on top of the resin. No free-standing water was visible in any of the three PCP containers. Another PCP specimen was prepared using a sample of resin from liner 446828-15 and this specimen exhibited the same features. Solidification of all three of the LOMI liners was postponed.

1.2.1.1.4 Bulging of Liners.

1.2.1.1.4.1 Millstone Station- Unit 1. During June, 1987 LN decontaminated the PCRS and the RWCS at Millstone Station- Unit 1 using the dilute LOMI decontamination process[5]. A total volume of 243 ft^3 (6.87 m^3) of ion-exchange resin waste was generated. The resin waste was slurried into two 182-ft^3 cpacity liners (liners 6291-034 and 6291-035) for solidification and disposal. LN then prepared PCP verification specimens using actual waste, and when these set up properly, they performed the solidifications.

The total mass of the resins in liner 6291-034 was estimated to be 8238 lb (3736 kg) and that in liner 6291-035 to be 8408 lb (3813 kg). The activities loaded on the resins were 1.39 Ci (0.4 uCi/cm^3) for liner 6291-034 and 67.6 Ci (19.9 uCi/cm^3) for liner 6291-035. On a weight percent basis, the concentrations of formic and picolinic acids on the resins were 6.2 wt% for liner 6291-034 and 4.6 wt% for liner 6291-035. Liner 6291-034 contained a 2:1 anion-to-cation ratio, and liner 6291-035 contained a 2:1 cation-to-anion ratio. Table 4 lists the contents of the two liners following solidification.

Following the completion of the hydration exotherm, the vertical wall of liner 6291-034 (which was solidified second) was observed to have bulged below about 2 feet from the top of the liner. The swelling was estimated to be 1-2% of the liner's original volume.

1.2.1.1.4.2 Three Mile Island Station- Unit 2. On August 9, 1985, Hittman Nuclear began solidifying five HN-200 liners containing EPICOR-II mixed-bed ion-exchange resins and sand from the Submerged Demineralizer System and filters. Following solidification, two liners (designated as liners 19 and 23) exceeded the low specific activity (LSA) shipping limits. Hittman applied to the NRC for an exemption to transport the liners to a disposal site, and the exemption was granted on June 11, 1986. On July 8, 1986, while removing liner 23 from storage in preparation for shipment, it was observed that the liner wall had bulged. The following day, liner 23 was removed from storage for further inspection. Photographs were taken that showed a bulge in the liner wall that started at the top of the solidified matrix. Measurements indicated that the diameter of the liner in the region of the bulge was 6 ft 3 in (190

Table 4. Composition of the Millstone Station- Unit 1 waste forms

| Type of Material | Liner 6291-034 | | | | Liner 6291-035 | | | |
| | Volume | | Mass | | Volume | | Mass | |
	(ft³)	(m³)	(lb)	(kg)	(ft³)	(m³)	(lb)	(kg)
Ionac A-365 resin	60	1.70			40	1.13		
R-78 resin	28	0.79						
(?) -10 resin	32	0.91			80	2.27		
Cement			5182	2350			NA	NA
Slaked lime			220	99.8			NA	NA
Formic acid			105	47.7			61	27.5
Picolinic acid			404	183.0			331	150.0
Metals			1	0.5			24	10.7

NA - data not available at this time.

cm), about 3 in (7 cm) larger than the normal diameter of a HN-200 liner.

On July 9, 1986, liner 19 was removed from storage for examination. This liner had also swelled, the maximum diameter being about 6 ft 2 in (189 cm). In addition, one of the vertical welds on the liner was found to have been breached. The weld was part of a rectangular patch that had previously been used for access to modify the liner internals. The cement matrix was visible through the crack in the weld. Table 5 lists the measured diameters of the two liners at various locations.

On December 18, 1987, liner 19 was being removed from storage so that the matrix material inside the liner could be sampled. As the liner was being lifted, it was observed that the original crack had expanded and now extended from the top of the liner to the bottom. In addition, the crack was more

Table 5. Diameters of TMI-2 liners 19 and 23

| | Diameter | | | |
| | Liner 19 | | Liner 23 | |
	(in)	(cm)	(in)	(cm)
Top of cement matrix	73.8	187.4	73.7	187.2
Maximum bulge	74.4	189.0	74.8	190.0
Bottom	74.2	188.4	74.7	189.7

than 1 in (2.5 cm) wide over most of the height of the liner. The liner was returned to storage.

During March, 1988, liner 23 was transferred to the auxiliary building, and during March and April the matrix material inside the liner was removed and placed into six high integrity containers (HICs). The liner was cut up and placed into a LSA box for disposal.

On May 4, 1988, liner 19 was removed from storage. When the liner was lifted, it was observed that the bottom plate had been detached from the vertical wall along most of its circumference. The liner was subsequently moved to the auxiliary building, and on June 2, 1988, the matrix material inside the liner was removed and placed into six HICs. The liner was cut up and placed into a LSA box.

1.2.1.1.4.2 Waste Form Failure During Immersion Tests. The INEL has a program, sponsored by the NRC, in which samples of actual waste forms have been collected from nuclear power stations and have been subjected to leach testing and compressive strength testing both prior to and following leach testing.[6,7] The types of wastes that have been solidified for which waste-form specimens have been collected include: (1) PWR boric acid evaporator concentrate, (2) BWR sulfate evaporator concentrate, and (3) PWR and BWR decontamination ion-exchange resins. Samples which have been leach tested and tested for compressive strength have ranged in size from 2 in x 4 in (5 cm x 10 cm) to 55-gallon size. The 55-gallon samples were full-size waste forms containing boric acid evaporator concentrate solidified in cement at a pressurized water reactor (PWR). The smaller samples were obtained from various full-size liners after mixing of neutralizing agents and binder materials was completed but prior to setting of the mixture.

While collecting samples for this program, INEL personnel have observed a number of solidification problems[6,7]. In one case, during 1982, a whole batch of 55-gallon drums of evaporator concentrate waste containing borates from Prairie Island Station, which is a PWR, failed to solidify, even though the PCP verification sample behaved normally. One set of samples of solidified evaporator concentrate waste containing sulfates collected from the J. A. FitzPatrick Station, which is a BWR, appeared to solidify properly but disintegrated into a sand-like consistency during shipment to the INEL. Several premature solidifications involving evaporator concentrate wastes were also observed from 1982 to 1984.

Immersion and leach tests of samples of solidified LLW obtained from nuclear power plants were conducted at the INEL.[6,7] All the samples of boiling water reactor (BWR) evaporator concentrate waste containing sulfates cracked during the

immersion tests, but all maintained their structural stability (i.e, they did not fall apart). The compressive strength of one of the cracked samples was measured. It was found to be 100 psi after immersion in demineralized water.

The INEL has observed several problems involving decontamination ion-exchange resin waste solidified in cement. Samples of cement-solidified ion-exchange resin waste were collected from the Cooper and Brunswick Stations during November, 1984 and December, 1987, respectively. The PCRS at each station had been decontaminated using the Citrox process, which employs citric and oxalic acids. All of these waste form specimens disintegrated rapidly after being immersed in demineralized water and other leachants. These Citrox waste-form specimens completely disintegrated into loose rubble within eight hours of the initiation of leach testing. Cement-solidified waste-form specimens which were collected from the J. A. FitzPatrick Station during September, 1988, following a LOMI decontamination of the PCRS, also deteriorated while immersed in demineralized water and other leachants. But the disintegration of these waste form specimens was more gradual than that observed for the specimens of solidified Citrox resin waste. These LOMI waste-form specimens cracked and eventually crumbled over a period of 90 days.

It has been observed[7] that crumbling upon immersion in a leachant did not seem to drastically alter the rates at which radionuclides were released from waste-form specimens. The releases of radionuclides from waste-form specimens that fell apart during leaching were comparable to the releases of corresponding radionuclides from specimens that maintained their physical integrity during leach testing. Leachability indexes of all radionuclides, except ^{137}Cs, were all greater than 6, the minimum value considered acceptable according to the NRC Branch Technical Position. A member of the Working Group pointed out, however, that if the resin in the specimens that disintegrated had been anion rather than cation and mixed-bed, the leach rates of radionuclides would have been higher because anion resin is regenerated at the pH levels found in cement mixtures.

1.2.1.1.5 What Is Currently Being Solidified. The Working Group desired to look at the different categories of waste being solidified and to identify solidification problems encountered with each of these groups. Before this could be done, however, the specific categories of waste being solidified had to be identified and discussed. This section summarizes the discussions on this topic.

Little ion-exchange resin regeneration is currently being done. The industry trend is to go away from regeneration (e.g., sulfate waste) and away from evaporators. Some power stations, however, still regenerate ion-exchange resins.

The Hanford and Barnwell disposal sites' state licenses require waste greater than 1 uCi/cm^3 to be stabilized. Stability may be achieved by either dewatering or solidifying the waste. Most spent ion-exchange resin and evaporator concentrate waste is Class A with some Class B. Evaporator bottoms, filter sludge, etc. are being solidified because they normally cannot be conveniently dewatered. Because of the low activities in these wastes, they are not required to be stabilized according to NRC requirements. Decontamination ion-exchange resin wastes are being solidified because they contain chelating agents and because of state requirements on stability of LLW.

Some encapsulations of particulate filters are being performed. Most PWRs use cartridge filters which are dried and put in HICs. Most BWRs dewater the filter demineralizer media. Ion-exchange resins from plant cleanup systems are not solidified; they are dewatered and placed in HICs.

CNSI reported the following estimated fractional breakdown of the types of waste they solidified from 1983 to 1988:

45%   - Resins (PWR letdown system, decon., etc.)
22%   - Boric acid evaporator waste
 4.5% - Oil
15%   - Sludges
11%   - Concentrator wastes
 1%   - Encapsulations (e.g., filters)

They further stated that only about 5-10% of solidified waste requires stabilization. Most of the waste that is solidified is Class A, but it is solidified because it is greater than 1 uCi/cm^3. There is very little Class B waste generated.

Northeast Nuclear Energy Company, which operates the Connecticut Yankee and Millstone Stations, reported that they solidify or dewater about 57 liners per year at their four power stations. The following is an approximate breakdown of the solidified and dewatered wastes they normally generate in one year:

16 - PWR polishing demineralizer media (2-3 are Class B): dewatered
 2 - decontamination ion-exchange resin waste (every 2 years): solidified
 2 - BWR sludges: solidified
25 - BWR condensate polishing demineralizer media: dewatered
12 - PWR filters (of which 4-5 are Class B): dewatered.

Solidifications of unknown or out-of-specification waste seldom happens, but it was noted that it could be a problem when it does happen.

1.2.1.1.6   Solidification Problems Encountered with Various Waste Types

The Working Group identified the following problems as having occurred during the solidification of different categories of wastes:

Ion-exchange resins other than chemical decontamination resins:

> The vendors initially had a mixing problem, but a redesign of the mixer blades solved it.
>
> Ammonia generating compounds (e.g., sewage waste) slow the setting of cement (i.e., longer than normal setting times are required), but the cement ultimately does cure. However, the ammonia problem has been very infrequent.
>
> Longer than expected curing times have sometimes been required when solidifying bead resins used to remove activation products from reactor coolant following reactor shut down. The PCP verification samples took a little longer than normal to set up - but it was nothing significant.

Borated waste:

> Standard cement does not work well, but the mix has been reformulated successfully. No problems have been encountered after the change to the new formulation.

Oil:

> Oily sludges are usually preprocessed to either remove the oil or homogenize the waste if an oil problem is expected. When the waste stream is itself contaminated liquid oil, it is either solidified or decontaminated for unconditional release. When oil is decontaminated, the residual
>
> contamination is a dry powder that can be easily disposed of.

Sludge:

Only a small percentage of sludge waste requires stabilization. Most unidentified sludge is associated with floor drains and sumps which are designed to receive only very low activity media. Therfore, sludges very rarely require stabilization. If a waste that requires stabilization is encountered, as might be the case when tanks or other components are desludged, the vendors will do certification tests for that specific waste. It was noted that some nuclear stations include filter media and pre-coats in the sludge category.

Evaporator waste:

Only a small percent of nuclear stations regenerate ion-exchange resin media. The regeneration of ion-exchange resins involves passing a solution of reagents through the ion-exchange resin bed. Following the completion of regeneration, the spent reagents are normally concentrated using an evaporator. The likely solution to the problems that have been encountered when trying to solidify evaporator concentrates is to identify the chemicals that adversely affect solidification, have nuclear stations analyze for them, and formulate recipies for the specific waste streams.

Flash set has been seen with sulfate wastes, where waste is kept at a high temperature prior to and during solidification. The high temperature of the waste has occasionally caused waste forms to set up very rapidly.

Unknown organics in the waste have caused solidification problems. Tartaric and citric acids were specifically mentioned as having the ability to retard the setting of cement.

Combining ion-exchange resin and evaporator concentrates used to create problems but the practice is no longer used.

INEL saw all sulfate waste forms crack upon immersion in demineralized water leachant, however, the types of cement and additives that are used have changed since that work was done.

Encapsulation:

> Flotation problems have been encountered when trying to encapsulate a liner inside another liner because buoyancy calculations were not performed. (The encapsulation of the liner that failed to completely solidify at the Quad Cities Station - Unit 2 is an example.) Buoyancy calculations are now being performed. Filters that are used to remove particulates from the decontamination reagent slurry during chemical decontamination operations are routinely solidified with the spent ion-exchange resin waste. Current practice is to enclose these filters in metal cages inside the liner to prevent them from floating out of the matrix during the addition of cement.

1.2.1.2 Causes of Problems

1.2.1.2.1 Quad Cities Station- Unit 2. The Working Group discussed a number of factors which may have contributed to the premature solidification that occurred at Quad Cities Station- Unit 2. Some of the factors that were identified as possible causes are itemized below:

> Calcium picolinate formed after the cement was added,
> Surrogate waste rather than the actual waste was used to prepare PCP verification samples,
> The solidification formula was not sufficiently tested,
> The cement addition hopper ran out of cement before a l l of the cement was added to the liner,
> The waste resin had a relatively low pH (i.e., 4),
> On the day of the solidification the weather was relatively warm, and
> The liner was inside a shipping cask during the solidification so the cask may have acted as a thermal barrier.

The Working Group did not unanimously agree on a primary cause of the premature setting that occurred at Quad Cities- Unit 2. CNSI used a PCP procedure at Quad Cities- Unit 2 which called for the PCP specimen to be prepared and then placed in an oven for curing. The procedure did not specify that the specimen was to be periodically checked to determine whether or not it had solidified prematurely. Thus, it is the position of CECO that even had an actual waste sample been used to prepare the PCP specimen, and had a premature solidification occurred, it would not have been detected because the sample would not have been examined during the first several hours of curing. CECO believes that the primary causes of this premature solidification were (1) the pH adjustment step was eliminated

and (2) the PCP procedure did not specify that the PCP specimen be examined to determine if the sample solidified prematurely.

The position of some Working Group members was that the only cause of the premature solidification at Quad Cities- Unit 2 was the formation of calcium picolinate following the addition of cement to the liner. Calcium ions in the cement are believed to have combined with picolinic acid on the resin beads to form a viscous calcium picolinate gel. The position of some Working Group members was that this same compound would have formed even if slaked lime ($Ca(OH)_2$) had first been added to adjust the pH of the resin waste, since the slaked lime rather than the cement would have provided the source of calcium to form the calcium picolinate gel.

Still other Working Group members felt that the basic causes of the premature solidification were (1) the elimination of the pH adjustment step in preparing the waste formulation and (2) the use of surrogate waste rather than the real waste to verify solidification. They believed that because of the low pH of the LOMI resin and the elimination of the pH adjustment step, the cement had to do the job of neutralizing the acidic resin waste. The heat of neutralization (when the high pH cement neutralized the low pH resin mixture) and heat of hydration caused an early, rapid temperature increase (exotherm) which, in turn, caused premature solidification. It is likely that a similar temperature increase did not occur in the PCP verification step because simulated resin was used for the PCP sample. However, this cannot be confirmed since the temperature of the specimen was not monitored. The small size of the PCP sample and the fact that the PCP container was not insulated would have made detecting the early exotherm difficult. The actual resin waste had not been analyzed and, therefore, its low pH was not known at the time of the solidification.

Although the cement formulation is not altered to take environmental conditions into account, the environmental conditions at Quad Cities- Unit 2 are believed to have been a contributing factor, but were of secondary importance. The warm ambient temperature and the insulation provided by the shipping cask did not cause the problem, but likely added to it. Although of secondary importance, operators should be aware of the effect of environmental conditions.

The Working Group members generally agreed that the recurrence of the premature solidification problem cannot be eliminated by simply using actual waste. The use of actual waste will not by itself solve the problem because the methods that are now used to prepare PCP specimens are not specifically designed to detect premature solidification. PCP specimens are now normally prepared in small plastic containers that have no thermal insulation. Accurately monitoring the neutralization

and hydration exotherms of a sample prepared in such a container is not possible. If the PCP container was properly insulated, a more rapid than usual exotherm, perhaps having a higher than usual exotherm peak temperature, might be symptomatic of a premature solidification. Another consideration is that the rates at which chemicals are usually added to the PCP specimen containers are normally not the same as the rates they are added to the solidification liner. If the chemical reaction rates in the PCP specimens are different from those in the full-scale liner, the symptoms of a premature solidification might not be detected in the PCP specimens. Methods should be devised that make the chemical addition rates more nearly the same. In addition, because a chelating agent (e.g., picolinic acid) is concentrated near the influent surface of a decontamination anion-exchange column, when the anion resin is first sluiced to the solidification liner the concentration of the chelating agent in any given volume of resin will vary widely. The samples of ion-exchange resin waste that are used to prepare PCP samples must be representative of the entire volume of resin that is to be solidified, and therefore, must be collected only after the resin in the liner has been completely homogenized.

1.2.1.2.2   J. A. FitzPatrick Station.   Laboratory tests[8] were performed to determine the cause of the incomplete solidification that occurred in one of the LOMI resin waste liners solidified at the J. A. FitzPatrick Station. These tests showed that the incomplete solidification was caused by picolinic acid reacting with calcium in the slaked lime $(Ca(OH)_2)$ used to adjust the pH of the resin waste prior to the addition of cement. When slaked lime is used for pH adjustment, the high pH achieved can cause resin regeneration. Since Ionac A-365, which was the anion resin used at the J. A. FitzPatrick Station, is a weak base resin, it can be regenerated at a lower pH than strong base resins. When regenerated, the Ionac A-365 anion resin releases picolinic acid out of the bead. The acid can combine with calcium from the slaked lime to form calcium picolinate. This compound forms a sticky gel hydrate which coats the surface of the anion resin beads and causes them to lump together, thereby inhibiting the mixing action of the liner mixing blades. The concentration of picolinic acid in the resin waste is critical as is how heavily the resin is chemically loaded. The formation of calcium picolinate is not a problem when slaked lime is added to resin wastes having low picolinic acid loadings. Also, the ratio of anion resin to the cation resin is important.

The formation of calcium picolinate interferes with the normal mixing that occurs in a liner. Mixing is very important. Mixing in a liner is not the same as mixing in a beaker. Lab simulations of liner stirring indicate that you can have a solid top but still have loose resin beads on the bottom.

Ionac A-365 anion resin was been successfully solidified
many times since 1986 when mixed with an equal proportion of
cation resin. The resin waste in the J. A. FitzPatrick liner,
however, had a relatively high anion-to-cation ratio. Ionac
A-365 resin has a higher exchange capacity than strong base
anion (SBA) resin, and as a result, higher concentrations of
picolinic acid can be obtained. The formation of calcium
picolinate is not expected to be a problem with SBA resins
because of the lower concentrations of picolinic acid that are
typical for SBA resins.

Potential solutions to the type of problem encountered at
the J. A. FitzPatrick Station include:

Reducing the picolinic acid loading on the resin.
Achieving a more even distribution of chemicals throughout
    the resin waste.
Maintaining a lower pH during the pH adjustment.
Reducing the anion resin concentration in a liner.
Using a non-calcium chemical rather than slaked lime to
    adjust the pH of the resin waste (CNSI has certified
    such a formulation in order to solidify LOMI resin
    wastes).

1.2.1.2.3 Peach Bottom Atomic Power Station. The cause of the
problem with the PCP samples at Peach Bottom was the same as the
cause of the incomplete solidification at the J. A. FitzPatrick
Station - the formation of a calcium picolinate gel when slaked
lime was added to the resin waste. The formation of calcium
picolinate removes interstitial water from the resin that is
required to hydrate the cement. The results of laboratory
tests[8] performed following the incident at the J. A. FitzPatrick
Station had been made available to the Philadelphia Electric
Company and to the solidfication vendors prior to the attempted
solidfication at the Peach Bottom Station. Personnel involved
with the solidfication at the Peach Bottom Station were
specifically looking for calcium picolinate in the PCP
specimens. Subsequent laboratory tests have indicated that a
revised procedure with a pH adjustment ingredient that does not
contain calcium solves the problem. LN performed a
solidification of LOMI decontamination ion-exchange resin waste
at LaSalle prior to the attempted solidfication at the Peach
Bottom Station. They were able to successfully solidify the
waste by keeping the adjusted pH of the waste below 10 and by
keeping the concentration of picolinic acid relatively low by
diluting the WBA resin, which contained the vast majority of the
picolonic acid, with SBA and SAC resins that contained little
or no picolinic acid.

Since the formation of calcium picolinate was identified
at the Peach Bottom Station at the PCP verification stage, this
shows that the PCP verification sample is valuable and can

identify problems if you pay attention or if you know what to look for. The Working Group believes the problem may not have been so easily recognized if information concerning problems at other nuclear stations (e.g., Quad Cities- 2 and J. A. FitzPatrick) and the results of subsequent laboratory experiments had not been known.

1.2.1.2.4 Millstone Station- Unit 1. The utility personnel believed that the liner bulged because of a mechanical tolerance problem (i.e., overfill). There was little reserve volume in either of the two liners, and the expansion accounts for a 1-2% volume change. The second liner may have had a few ft^3 of excess resin. It is difficult to know accurately how much resin is in the liner because the level is determined by visual sighting of the 120 ft^3 level in a 6 ft diameter liner, and liners are sized to negative tolerances to ensure fitting in casks.

CNSI stated that they frequently fill a liner to the top and have not had a bulging problem. They suggest that the problem was due to the resin itself expanding. However, a utility representative responded that manufacturer's information indicates that if the expansion were chemical in nature, the beads would have expanded 40 to 100% by volume. One of the Working Group members suggested that the liner could have been faulty or not constructed properly. The Working Group suggested that INEL could provide a more definitive answer since the liner has already been shipped to the INEL for examination.

1.2.1.2.5 Three Mile Island Station- Unit 2. Resin bead expansion (about a 16% volume expansion) is believed to have been the cause of the TMI-2 liners bulging and splitting. The liners had head space, but expanded horizontally. There is no apparent explanation for this expansion or the extremely high pressures that had to have been generated in order to bulge and split the liners. Resin beads can generate pressures up to 1800 psi upon expansion. Calculations indicate that pressures greater than 10,000 psi were required to bulge the liners.

Freeze-thaw was investigated and then eliminated as a cause, as was non-homogeneous mixing. Also resin bead dehydration and subsequent hydration were considered but were ruled out.

1.2.1.2.6 INEL Experiences. To date, the only solidification problem which INEL personnel observed that has been investigated to determine the cause has been the failure of the batch of solidified borated evaporator waste to solidify[6]. The cause was determined to be the procedures the nuclear power station used. The procedures did not require the feed tank to be isolated prior to collection of the waste for the PCP verification test. Because of this ommission, more waste was allowed into the tank,

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changing its makeup. When the cause of the failure to solidify was identified, the station procedures were modified to preclude this problem in the future.

The reasons for the disintegration of the evaporator sulfate waste during shipment and the cracking of the evaporator sulfate waste samples during immersion tests were not investigated by INEL. Members of the Working Group, however, stated that these problems have been identified and solved by altering the solidification formulation. The Working Group noted that it is well known that high concentrations of sulfate in cement cause cracking in waste forms.

The reasons for the deterioration of solidified waste-form samples during immersion tests have not yet been investigated by the INEL.

1.2.1.2.7 General. The Working Group examined some general causes of solidification problems that have been observed:

> PCP verification specimens have occasionally been prepared using surrogate wastes. This practice is no longer being used by the solidification vendors (although we cannot be sure that nuclear power stations doing their own solidifications do not still use surrogate wastes).

> The preparation of the PCP verification specimens has at times not closely enough represented the actual solidification process in a liner, and there have been cases where chemical interactions occurred in the solidification liner that were not observed during the PCP verification tests. For example, stirring may not have been the same in the two cases; demineralized water has been used for the PCP verification specimen rather than the water in the liner; ingredients have been added faster during the preparation of the PCP samples than during the liner solidification (e.g., cement is added slowly over a several hour period during actual liner solidifications); if ammonia, which retards solidification, is present, it volatilizes and is lost from the PCP sample but it is retained by the full-size waste form in the liner; foaming does not always show up in the PCP sample container in cases where it later occurs in the liner; the oven environment in which the PCP verification specimen is cured does not exactly duplicate the conditions under which a full-size waste form is cured; over time the types of resins used in decontamination

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operations have been changed, but the solidification formulations may not have been altered to reflect this.

Inadequate or incomplete characterization of the waste to be solidified can be a major cause of solidification problems. Although this is not a problem for some waste streams (because with time more waste streams have been well characterized), many waste streams have not been completely characterized chemically. Some waste streams have had to be characterized because of the potential of being mixed waste. There have been cases, however, where unknown chemicals have apparently caused solidification problems (e.g., an unknown organic constituent caused a waste form to swell and ooze out the top) and where the unexpected presence of particulates has caused solidification problems because the particulates displaced water that otherwise would have been available for cement hydration.

Picolinic acid is always distributed chromatographically through an ion-exchange resin column; that is, resin beads near the influent surface of the column will be loaded to nearly 100% of their exchange capacity while resin beads near the effluent end of the column will contain little or no picolinic acid. Beads that are loaded uniformly in a batch operation in a laboratory test may well give different results than beads that are loaded chromatographically. The formation of calcium picolinate has not been a problem with low picolinic acid loadings, but with high picolinic acid loadings calcium picolinate forms on the surfaces of the resin beads and removes interstitial water from the resin that is needed for the hydration of cement[3]. The ratio of anion-to-cation resin beads in a liner will affect how the waste solidifies with cement. Cation resins tend to require higher water-to-cement ratios and more slaked lime. Since the resins generated differ from decontamination to decontamination and from vendor to vendor, it is fair to assume that the amount of calcium picolinate gel formed and the extent of loss of mixibility will vary with each solidification.

Foaming (often caused by the presence of detergents in the waste) has caused some solidification problems.

Field conditions, while not the primary cause of solidification problems, have exacerbated the situation. For example, high temperatures can promote a premature solidification and cold temperatures can delay the complete hydration of cement for as long as several weeks.

The Working Group noted that some of the solidification problems have been solved, but many are still being studied. The Working Group recommended that these ongoing studies be continued and the results be made available to interested parties.

1.2.1.3   Solutions to Solidification Problems

The Working Group discussed the number of solidification failures. Representatives of the solidification vendors stated that the number of solidification failures that have occurred represent a very small fraction of the total number of solidifications that have been performed. Over a period of 7-1/2 years at Barnwell, the number of liners shipped back to the generator has been less than 10. About two liners per week have been punched. Only about 1 liner in 400 has been returned to the waste generator. In addition, new cement formulations have come into use, such as mixtures of Portland Type I cement and fly ash, which provide reduced permeability and greater strength compared to pure Portland Type I cement.

The results of recent laboratory studies, which were performed at a Department of Energy (DOE) laboratory, that used simulated rather than actual radwaste were also discussed. The position of the Working Group was that a very close look must be taken at the materials used for these laboratory studies before conclusions relating to the "real world" should be drawn. Using the results of laboratory studies that have been performed with non-representative binder materials or non-representative waste-to-binder ratios and with surrogate waste instead of actual radwaste to predict the behavior of currently generated waste forms may not be valid. It is like comparing apples and oranges. The evaluation of technical solutions to today's solidification problems must be based on currently used solidification formulations and procedures. The Working Group felt that surrogate waste should not be used to perform performance evaluation studies.

Better or more complete chemical characterization of the waste stream to be solidified may help to eliminate some solidification problems. Although it is a practical impossibility to fully chemically characterize every waste stream and every waste to be solidified, the Working Group believes a better job could be done using more sophisticated chemical analyses than are currently used. The solidification

vendors are already measuring the following parameters to help characterize waste streams:

pH,
Particulate loading on resin beads (some estimate is taken
        into account),
Visual examinations for oils, etc,
Boric acid, and
Total solids.

The possibility of identifying ranges of constituents that will ensure solidification was discussed. The Working Group was of the opinion that this would not be feasible because of the high cost and the time required. There is no known way to develop a complete list of chemicals that will inhibit cement solidification and then to eliminate these chemicals from the stations. It is possible, however, to identify and control the worst offenders. It was suggested that the solidification vendors could identify chemicals that hinder solidification and have the stations analyze for them. The vendors agreed to work together to come up with such a list. A report[9] published in the United Kingdom in 1986 discusses the effects of various substances on the hydration of cement, and provides a rather exhaustive listing of both inorganic and organic chemicals that either retard or accelerate the setting of cement.

The possibility of increasing the safety margin by increasing the compressive strength criterion from 60 psi to maybe 500 psi was suggested. A limited amount of experimental data indicates that this may require lowering the waste-to-binder ratio of waste forms. More experimental work needs to be done to determine if, in fact, lower waste loadings significantly increase compressive strength. On the other hand, if this course were taken, the volume of waste for burial would be increased, which would impact utility waste volume reduction and ALARA goals.

Improvements in the preparation of the PCP verification specimens were suggested by the Working Group as potentially helping to eliminate some solidification problems. For example, surrogate waste should not be used, and any water added to the PCP cup should be water from the liner and not demineralized water. Mixing procedures could be designed that more accurately simulate mixing in a liner, and PCP specimen curing conditions (e.g., temperature gradient inside the sample) could be designed to be more representative of those of the liner.

Procedures used in the liner solidification itself could be improved. For example, procedures which contain checks for premature solidification can be developed (some now have such procedures). One Working Group member suggested segregating cation and anion resin into different liners for solidification.

Improved personnel training and experience and administrative improvements were suggested as a means to prevent solidification problems. For example, use a limited number of trained, experienced personnel (say one with one backup), and use management oversight during the preparation of the PCP verification sample if the personnel are not too knowledgeable. To ensure that the PCP verification sample does not solidify too quickly, a member of the station's management or a representative of the solidification vendor should be responsible for preparing the PCP verification specimen.

Preventive measures such as improved binders and waste pretreatment were discussed briefly. The British are going away from Portland Type I cement because many ion-exchange resins and Portland Type I cement are not compatable; the U.S. vendors have also done this, although certain vendors still use Portland Type I cement to solidify specific waste streams. Additives and cement substitutes such as blast furnace slag have improved the long-term stability of solidified waste. Studies[10] are currently under way in the U.K. and the U.S. to explore the use of a process that destroys organic resins and chelating agents and yields a liquid waste that can be handled by evaporators.

1.3 Relationship Between Small- and Full-Scale Testing

1.3.1 Results of Laboratory Testing

Studies reported in the literature[6,11,12,13,14] indicate that releases of radionuclides and chelating agents from cement-solidified waste forms closely follow predictions based on classical diffusion models. They show that for cylindrical samples, the effective diffusivities derived by using the semi-infinite plane source diffusion model do not depend on sample size. The widest range of sample sizes (2 x 4 in to 22 x 30 in (5 x 10 cm to 56 x 76 cm)) was investigated in the work done at the INEL[6]. BNL performed some tests on surrogate ion-exchange resin waste forms ranging in size up to about 15 in (38 cm) diameter, and found similar results.

1.3.2 Full-Scale Test Results

The solidfication vendors have performed tests on full-scale waste forms made using surrogate ion-exchange resin waste. Because of ALARA concerns, similar tests have not been performed on full-scale waste forms prepared using actual waste. Core samples have been obtained from the bottom, side, middle, and top of the solidified waste forms, and dip samples have been taken from below the top surface prior to solidification of the waste form. These samples have been subjected to compressive strength and immersion testing.

Full-scale waste forms have been cut apart by CNSI to determine if proper mixing was being achieved. For these tests, resin beads having different colors were added to the waste to facilitate investigations of resin bead mixing. Results indicated that the mixing was very good.

The vendors have not performed tests on real full-scale waste forms nor leach or compressive strength tests on intact full-scale waste forms (neither real nor surrogate). They have pulled samples out of real liners by submerging a closed container a couple of feet below the surface of the unsolidified waste form and then opening the container and collecting a sample. Compressive strength tests were then run on these dip samples. Core samples have also been taken from full-scale liners containing solidified surrogate waste, and these samples have been subjected to immersion and compressive strength tests.

The INEL has performed leach tests on full-scale 55-gallon (210 L) size borate waste forms and on sulfate waste forms up to 13.4 in diamter x 21.3 in long (34 cm diameter x 54 cm long) which were solidified at power stations.[6] Compressive strength tests were performed on 2 in diamter x 4 in long (5 cm diameter x 10 cm long) samples that were dipped from the full-scale waste forms following the addition and thorough mixing of cement.

The vendors have some experimental data that indicates that dip samples have lower compressive strengths than core samples. These data imply that the temperature the waste form experiences as a function of time (perhaps both peak temperature as well as average temperature over the exotherm) affects the waste form's final compressive strength. LN feels that dip samples are conservatively representative since core samples (and the actual full-scale waste form) can be expected to have higher compressive strengths. CNSI feels similarly. This is consistent with Stock's results. The consensus of the Working Group was that dip samples should be cured at elevated temperatures that simulate the exotherm experienced in a full-scale waste form.

The acquisition of core samples from an actual full-scale waste form poses serious personnel exposure problems. Although members of the Working Group have never compared dip samples with cores obtained from an actual full-scale waste form, they feel that a dip sample can be a good representative sample and will be comparable to core samples in composition if cured properly (but may have a lower compressive strength). Use of dip samples, therefore, has the potential of providing the required information (with a conservatively low compressive strength) without the exposure problems inherent in obtaining core samples.

Some members of the Working Group felt that it is best to stick a pipe in the unsolidified waste form and get a full height core sample. CNSI, however, said that from their mixing experience, you do not need a full height core sample; but you must get a sample from at least a few inches below the surface of the matrix. CNSI feels that the liner is sufficiently homogeneous so that a dip sample from 3-4 inches below the top surface is representative of various internal locations.

A member of the Working Group suggested that a modified liner be developed with a displaced opening that would accommodate INEL's sampling tube.

1.3.3 Full-Scale Testing

Increasing the amount of full-scale testing and expanding the scope of these tests were discussed. It was concluded that, although the solidification vendors would like to perform tests on full-scale waste forms, testing of full-scale waste forms containing radioactive waste is difficult and expensive due to ALARA concerns, which require remote handling and extensive shielding. In addition, the unavailability of sufficiently large equipment, compressive strength tests cannot be performed on full-scale waste forms.

It was suggested that more studies be performed, possibly using surrogate waste, to check diffusion coefficients and to show that tests on small waste samples give results indicative of the behavior of full-scale waste forms. To date, this has been shown for waste forms up to 210 L in size (the INEL studies did this using real power plant waste), but not for full-scale liners. In addition, results using dip samples and core samples should be compared to show that representative (or at least conservative) results are obtained using dip samples. Once we know that we can extrapolate from small samples to full-scale waste forms and that dip samples give adequate results, then tests like the INEL has performed using small samples of real waste dipped out of a liner prior to solidification can be used in lieu of tests on full-scale waste forms.

Although leach testing of full-scale waste forms may be logistically difficult and, therefore, expensive to do, it is possible, at least on a limited basis, to perform full-scale experiments to verify models. Because of ALARA considerations and the large number of different wastes, it is impractical to do full-scale certification testing. It may be possible to use modeling and then to verify the models on a limited basis using real full-scale waste forms. The Working Group believes that decontamination waste with ion-exchange resins should be a top priority due to the radionuclide and chelating agent content.

Both CNSI and LN have liners that can be removed from the solidified waste matrix, and they are willing to make these liners available for tests of full-size waste forms. Terry Reckart (TARCO) stated that he has a place where he can get 55-gallon drum and full-size liners from the same system and same waste.

1.3.4 Sampling of Solidified Waste at Nuclear Power Stations

The subject of sampling solidified waste at nuclear power stations was discussed. To date, most of the sampling has been by collection of dip samples from a liner after mixing has ceased but prior to solidification, although some core samples have been obtained. It was suggested that special plugs could be put in a liner to accommodate obtaining core samples. CNSI puts in special plugs in a liner when they want core samples. Collecting core samples, however, would require lifting the liner out of its cask, and some stations do not have the overhead space to allow lifting the liner out of the cask. Dose expenditure is another drawback.

Collecting dip samples seems to be a better alternative, although dip samples tend to have less compressive strength than core samples and can now only be obtained from near the central axis of the liner (although the solidification vendors suggested that more openings could be put on the top of the liner). Dip samples are easier to obtain, and workers would get lower radiation doses than they would if they collected core samples.

1.4 Methods to Verify Proper Solidification of Actual LLW in Liners

The various methods (both currently used methods and potentially useful methods) were discussed. The following briefly summarizes the results of these discussions.

1.4.1 Procedure Check

The first and foremost check should be to see if the solidification followed the PCP formulation (i.e., all ingredients were added in the proper amounts and in the proper sequence), the mixing and the vortex during mixing (as seen by the video camera) looked normal, the hydraulic mixing pressure was normal, and the expected exotherm was attained.

1.4.2 Dose Rate

Measuring the dose rate profile may provide information concerning the success of the solidification. At least it may be a good screening technique for detecting mixing/solidification problems. Dose rates around a liner or cask are typically uniform. Radiation levels, therefore, can

give an indication of proper or sufficient mixing and solidification. The LOMI liner at the J. A. FitzPatrick Station that was rejected by the Barnwell disposal site did not exhibit a uniform dose rate.

Care must be taken when using this method to indicate solidification problems because filters which are used to remove activation products from the decontamination slurry are often solidified in the same liner used to solidify the decontamination ion-exchange resin waste. These filters, which may contain significant quantities of ^{60}Co, are normally enclosed in metal cages near the bottom of the liner and remain at fixed locations following solidification.

1.4.3 Accoustic Method

The hardwood pick handle method (i.e., tapping the liner with a hardwood pick handle and listening for indications of voids or changes in density) seems to work very well. After the fact, it worked very well at the J. A. FitzPatrick Station on the liner which was rejected by the Barnwell, SC disposal site. Since the method must be performed on the liner, an ALARA dose committment must be considered. It could be used as a second method if the dose rate method indicates a potential problem. It could be a high radiation exposure job. Normally, however, it takes less than 1 minute per liner, so the radiation exposure probably would not be a great problem. It would be more of a problem for stations which solidify inside casks because it would require removal of the liner from the cask.

An accoustic method like oil companies use in exploration for petroleum deposits, where a sound is injected into the top of the waste form and the reflected signal is monitored, was discussed. None of the Working Group members knew much about this type of a technique, so it should be investigated further.

1.4.4 Ultrasonics

An ultrasonic technique was suggested. CNSI has tried this technique but has had problems with reproducability using commercial gear. The feeling of the Working Group was that this technique would probably be impractical if the liner was in a shipping cask. The general feeling was that this technique would be difficult to perform at an operating station. Some Working Group members, however, did not fully agree that the technique was impractical; they felt that it should be studied further.

1.4.5 Inspection via Punching or Coring

This could be done at the plant, but ALARA radiation exposures must be considered. The solidification vendors are

willing to put in inspection plugs anywhere a utility wants them. These plugs could be removed and either a penetrometer could be used (a puncture-type test is usually performed at the Barnwell, SC disposal site on liners containing higher than 7 wt% chelates) or core samples could be obtained.

1.4.6 Radiography

Interrogation by x-rays may be practical for 55-gallon drums but may not be practical for 6-ft diameter liners. This may not be practical at a station because the liner must be taken out of its shipping cask.

Neutron radiography would be better than using x-rays for full-scale waste forms, but it would have the same disadvantages at a station as the x-ray technique.

1.4.7 Infrared

The use of an infrared temperature profile has been investigated by Stock, but the members of the Working Group had no details of the results of these investigations.

1.4.8 Pressure Testing of Cask

This method was discussed, and it was concluded that it had numerous drawbacks. If there is incomplete solidification, this test may dimple the liner. In addition, it is not a good idea for routine use because it could damage a liner (remember head space) or make handling impossible. It probably is a last resort sort of test.

1.4.9 Extra Instrumentation of Liner

Extra thermocouples placed at various locations in a liner might give some useful information, but exactly how useful these temperature data would be is questionable.

Placing some sort of a sacrificial transmitter in the waste form, maybe inside the mixing blade drive shaft, and looking at the signal coming from the transmitter was a potential method that seemed to intrigue the Working Group members. No details of such a technique, however, were available.

1.4.10 Archive Samples

The suggestion to sample every liner, store the waste-form samples, and randomly test a sufficient number of them using the NRC Branch Technical Position tests to get adequate statistics was discussed at length.

It was recognized that when performing an out of the ordinary solidification, it is good practice to keep a sample of the waste for future tests should something go wrong. Experiments and/or analyses performed on the waste sample could help answer questions about the stability of the full-scale waste form in the liner. It was also recognized, however, that to collect waste-form specimens from every liner for future testing has many drawbacks. The following issues and concerns were readily apparent to the Working Group:

> ALARA (i.e., excessive radiation exposure).
> Cost.
> Who would keep them? Where would they be kept?
> Establishing and controlling curing conditions.
> Transporting a lot of waste samples.
> Quality control would be difficult.
> Sampling procedures and documentation.
> Management risk - legal liability.
> The possibility of retrieving liners may arise.

The Working Group suggested that, rather than sampling every liner and archiving the samples for future tests, more sampling of liners and testing of these samples using methods similar to what the INEL is currently doing would be a better alternative.

1.5 Priority 2 Topics

1.5.1 Comparison of Test Results Using Simulated vs Actual LLW

The question of whether surrogate wastes are representative of actual wastes was discussed. The Working Group concluded that it is practically impossible to make surrogate wastes that simulate every waste. However, becasue many waste streams at nuclear stations are well characterized chemically, it was felt that the overt characteristics of many wastes could be reasonably duplicated using simulated wastes. At many nuclear power stations, most of the Class B waste comes from pretty well-characterized waste streams. Wastes in floor and equipment drains are beginning to be better characterized to make sure that they are not mixed waste. However, the Working Group felt that the use of surrogate wastes to evaluate the performance of solidification formulations should be discouraged. It has been shown that certain attributes of actual waste, which may be quite subtle, can serioulsy affect the outcome of a solidification.

The waste loadings and the waste-to-binder ratios used in studies conducted at the DOE laboratories were discussed vis a vis what is commonly used in the real world. It was concluded that there should be more, and better, interface between the laboratories and industry so that the parameters used in the

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laboratory studies have a better correspondence to the solidification parameters that are used in the real world. Because this has not generally been the case in the past, the applicability of many of the laboratory results to the real world has been questioned.

The binder materials used in the laboratory studies were compared with what is now used in actual solidifications of real waste at power stations. It seems that there are major discrepancies. For example, the binder material frequently used in laboratory studies is Portland Type I cement while the binder used by some solidification vendors at power stations is a pozzolanic material consisting of a mixture of Portland Type I cement and fly ash[15,16,17].

The West Valley experience was discussed. At West Valley, laboratory studies using simulated waste were conducted to determine a mixture that would solidify. When applied to the real waste, the formulation proved to be inadequate. The cement set up, but there was bleed water on the top of the waste form. It was suspected that 150 ppm of total organic carbon (TOC) retarded the solidification. Subsequently, ORNL confirmed that individually oxalic, citric, and tartaric acids (all of which the waste could have contained) in concentrations of 50-75 ppm each can affect solidification of Portland Type I cement. In addition, it is known that the petroleum industry uses small amounts of organics to retard cement solidification during drilling operations. A working Group member mentioned that at an operating commercial power station, Class B waste streams are associated with the reactor coolant system, where TOC is maintained in the ppb range.

1.5.2 Quality Control of Full-Scale Solidification at Nuclear Stations

The Working Group discussed the current quality control of full-scale solidifications at nuclear stations and concluded the following.

In general, the industry feels that the quality control of full-scale solidifications has been good. There have been a few problems with liners, but the reward-to-risk ratio does not warrant spending a lot of money to eliminate the few problems that do occur. Other than ion-exchange resins, there have been no instances of shipping questionable material offsite. All members of the Working Group did not agree with this position. Some felt that the problems that have been seen indicate that the quality assurance program should be improved.

The PCP verification stage is where solidification problems and unusual situations should be caught. A good example of where this worked is the West Valley experience,

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where the excess bleed water, which was probably caused by the presence of trace amounts of organic compounds, was noticed and determined to indicate a problem. A potential problem was caught at the Peach Bottom Station because personnel involved with the solidifciation carefully examined their PCP verification samples using information learned following the incomplete solidification at the J. A. FitzPatrick Station.

The Working Group felt that the PCP verification procedure does not always identify problems that are encountered when solidifying full-scale liners. For example, the ammonia problem is not detected by the PCP; foaming does not always show up in the PCP container; and the problem with using slaked lime to adjust the pH when picolinic acid is present is not always readily apparent during the PCP test. The PCP tests typically show standing water and indicate whether the waste form will harden at all. If a PCP verification test indicates a formulation adjustment is required, this adjustment can be implemented only if it falls within the certification limits for the waste stream. Changing the solidification recipe outside the certification limits requires recertification.

During a typical liner solidification operation, a video monitor is mounted on top of the liner such that the solidification operator is provided a view of the vortex around the mixing blade drive shaft. The pitch of the mixing blades is such that the material in the liner flows down near the center of the liner and up along the vertical wall of the liner. An experienced operator can judge whether mixing is typical based on the appearance of the vortex around the mixing blade drive shaft.

The hydraulic pressure required to turn the mixing blade drive shaft is also monitored and used as an indicator of how the solidification is progressing. A normal drive shaft hydraulic operating pressure is about 1600 psi, and when the mixture begins to set up the hydraulic pressure increases. The normal upper limit set point for the mixing motors is about 3300 psi, and when the hydraulic pressure reaches this set point mixing is discontinued.

The temperature in the liner is measured using a single temperature probe located about 4 to 6 inches below the surface. The exotherm is monitored during chemical addition and during the setting process. Monitoring of the exotherm is important. A crusting problem was noticed at the J. A. FitzPatrick Station because the hydration exotherm was not right. A liner was found to have a crust about a foot thick. Later, another crust approximately one foot thick formed beneath the first crust. This solidification problem would probably not have been detected if the exotherm had not been monitored.

The solidification vendor does a limited characterization of the waste to be solidified. It is not economically or technically practical, however, to fully characterize the waste quantitatively prior to solidification in order to identify anything that might affect solidification. We do not know enough yet. It is very difficult, expensive, and costly in terms of man-rem to chemically characterize the waste. Methods must be sophisticated, simple, and timely to determine the chemical content. Within the time frame that is practical, probably little more can be done. All we can do is to list the chemicals as we identify those that adversely affect solidification. It is relatively easy to come up with the list of chemicals that we know of so far, but developing the total list is not easy because we do not know all the chemicals present in the waste stream. Once a list is developed, then, if feasible, the stations can control these chemicals, not use them, or perhaps use pretreatment.

The question was asked whether additional tests can be recommended. It was concluded that there are various QC hold points which can probably be used as checks, but no other tests were identified. It must be remembered that additional testing/characterizations will increase costs and exposure. Can this additional exposure be justified by the unfavorable experience that we have had with just a few liners? This question must be addressed.

1.5.3 Utility and Vendor Field-Verification Test Samples

The PCP verification specimens are prepared as a field-verification test that the waste form will solidify correctly. This test was really not designed to identify all problems that might occur in a full-scale solidification; it was designed to identify only the more obvious symptoms of an improper solidification. Hence, it does not always pick up problems before full-scale solidification.

Attempts have been made to improve the PCP verification test to enable it to identify more potential problems. For example, one vendor adjusted the chemical addition rate in the PCP and adjusted the oven temperature used during curing. As a result of the premature solidification at the Quad Cities Station- Unit 2, CNSI incorporated a procedure in the PCP verification test to monitor the specimen setting time. Advanced knowledge or lessons learned previously are also used, when possible, in the PCP verification test. At the Peach Bottom Station, prior knowledge of what had happened at the J. A. FitzPatrick Station was used to alert the operators to more carefully inspect the PCP verification samples and to look for the presence of a gel-like substance. As a result, the operators were able to identify a potential problem before a full-scale solidification was attempted.

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Quality control during the PCP verification specimen preparation is very important. The waste used should be from the actual liner to be solidified, not surrogate waste. The operators should be well-trained and have sufficient experience to be able to evaluate the PCP verification test results. Management oversight is important to ensure that procedures are followed correctly, indications of potential solidification problems are recognized, and proper ALARA guidelines are maintained.

1.5.4 Parameters that Affect Stability and Effects of These Parameters

1.5.4.1 Mixing

Mixing in the full-scale waste forms has been shown to be excellent (by coring and/or sectioning surrogate waste forms and by measuring dose rates around real waste forms). Mixing was a problem earlier for the case of ion-exchange resin waste. The design of the mixing blades was changed to solve these mixing problems with resins. The new blade is a universal blade, which contains a blending blade and a pumping blade, that is designed for the worst case. A problem in mixing, therefore, would only be expected if there was an equipment breakdown so that all additives could not go into the liner on schedule.

Mixing in PCP verification samples (i.e., in a beaker or cup) is not the same as the mixing that occurs in full-scale liners. The PCP verification sample is often mixed with a spatula that will mix viscous material that would stop the mixing blades in a liner. It is possible that a liner would have better mixing than the PCP verification sample and would, therefore, out-perform the PCP verification sample. A design for a mixer for PCP verification samples should be developed which better simulates the mixing in a real liner.

1.5.4.2 Chemicals

It is well known that certain chemicals adversely affect the solidification of a cement mixture. It was recognized that it would be ideal if all waste streams could be 100% characterized so that any chemical present that could adversely affect solidification would be identified. This, however, is not possible. Although some waste streams are well characterized, many are not well-characterized chemically, and all cannot be 100% characterized. In addition, since the number of different chemicals is growing rapidly each year, it is a practical impossibility to identify every individual chemical that could have an adverse effect on cement solidification. The solidification vendors (CNSI and LN) have agreed that they will collaborate and come up with a list of chemicals that adversely affect cement solidification. This will be a living list to

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which additional troublesome chemicals will be added as they are identified. The mechanism by which this information will be collated and transmitted to interested parties on a routine basis was not specifically defined.

1.5.4.3 Waste Loading

In the past, the objective of the utilities and solidification vendors has been to use the highest practical waste loadings in order to maximize volume reduction. Recently, however, the concern has shifted to enhanced stability, and lowered waste loadings have been suggested by the NRC as a means of enhancing stability.

Waste loading tests were recently performed at BNL to determine the effects of waste loading and cure time on waste form compressive strength, but they have not yet used real waste generated at operating power stations. In addition, the BNL extended cure tests used only Portland Type I cement and did not use any pozzolanic mixtures. The solidification vendors have done some limited tests using lower waste loadings. For example, LN has performed some tests whose results tend to indicate that the compressive strength of a waste form increases at lower waste loadings. The Stock Equipment Owners Group has done extended cure time tests with simulated depleted resin waste. This came about because they found that samples that passed with short cure times did not pass after a 28-day cure. TARCO, a consultant to Dusquene Power and Light, which operates the Beaver Valley Station, reported that they are having "great results" on some samples of cement-solidified borated mixed resins waste from Beaver Valley. These mixtures contained 20 volume percent resin (weight percent would be lower still). These samples were hermetically sealed and oven-cured in drums at Beaver Valley for 30, 60, or 90 days, or 1 year and then they were immersed in demineralized water. The compressive strengths were measured before and after immersion. With immersion times as long as 1 year, compressive strengths as high as 2000 psi were measured and were still increasing as cure times were increased. Although TARCO had success with somewhat higher waste loadings than did the Stock Equipment Owners Group, both the Stock and TARCO formulations used waste loadings that were much lower than the waste loadings used by the solidification vendors. BNL came to their conclusions based on tests performed at high waste loadings.

Some major concerns were voiced relative to lowering the waste loading. Since the total heat generated during cement hydration is proportional to the cement content, lowering the waste content might increase the exotherm and increase the possibility of premature solidification. A one-half waste loading was successfully performed on decontamination resin at LaSalle during the fall of 1988, and the product appeared to

have a higher compressive strength than waste forms with normal waste loadings. In addition, with a lower waste content and higher cement content, the resin beads could dehydrate. This could cause the waste forms to break up during the immersion test when the resin beads expand as a result of absorbing water. It was agreed that more testing needs to be done before a decision regarding lowering the waste loading is formally proposed.

1.5.4.4 Field Conditions

High ambient temperatures may accelerate the hydration of cement. They are not the root cause of premature solidification, but will add to the problem (e.g., Quad Cities Station- Unit 2). Cold temperatures will cause no problems other than possibly delaying the complete curing of a full-scale waste form by several weeks.

1.5.4.4 Formulation

The British are going away from Portland Type I cement because many ion-exchange resins and Portland Type I cement are not compatible. They are now adding up to 90 wt% blast furnace slag to their cement. Some U.S. vendors have discontinued the use of Portland Type I cement for the solidification of certain types of resins and have begun using pozzolanic mixtures as well as selective additives. (LN still uses pure Portland Type I cement to solidify some waste streams). Some laboratory tests, however, are still being made using only pure Portland Type I cement.

1.5.4.5 Exotherm

It is known that a high hydration exotherm temperature can cause premature solidification. The normal peak exotherm temperature is below 165 F. (A Working Group member calculated a maximum temperature rise of 51 F for the J. A. FitzPatrick liner). Anion resins do not decompose at these temperatures and generate ammonia (which only retards solidification but has not caused any other problems).

1.5.4.6 Other

Leaving the mixer blades in place tends to strengthen the cement waste form like reinforcing bars do in structural cement.

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1.6   Priority 3 Topics

1.6.1   Preparation of Verification Samples at Nuclear Power Stations

The purpose of the PCP verification samples is to provide some assurance that a waste form will set up. There is a desire to enhance this test to enable it to identify additional potential problems before the actual full-scale solidification is attempted. To begin to accomplish this, most vendors have implemented the following changes to their PCP verification specimen preparation procedures:

Surrogate waste is no longer used by the vendors. They either take a small amount of waste from the liner after it has been mixed, which is the most widely used method, or they draw a sample from a transfer line or tank after the contents of the tank have been mixed.

They now have time delays in the chemical addition to account for the time required for addition of ingredients to the liner and to better simulate the actual liner solidification.

The specimens are cured in an oven at between 120 and 145 F to simulate the exotherm experienced by the full-scale waste form.

More experienced persons now perform the PCP verification tests.

The following are potential improvements to the PCP verification test which were suggested by members of the Working Group:

If they have not already done so, all solidification vendors and utilities performing their own solidifications should add procedures which contain checks for premature solidification.

Demineralized water should not be used when liquid is needed for the PCP sample; water from the liner should be used instead.

Mixing in the PCP sample container may be different from the mixing that occurs in the liner. Therefore, improved methods of stirring the PCP specimens should be developed to better simulate the stirring in the actual liner. One suggestion was to develop a small mixer for the PCP containers that would simulate the mixing in a liner.

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The quantity of insoluble fines in the resin waste should be determined as part of waste characterization.

It was recognized by the Working Group members that more extensive PCP tests will increase personnel exposure. Therefore, personnel exposure must be considered before any additional PCP verification tests are required. Maintaining ALARA guidelines is extremely important, and any proposed modifications to existing PCP tests must not require excessive radiation exposure.

To enhance quality assurance, a limited number of trained, experienced personnel, say one with one backup, should be used to prepare the PCP verification specimens. Management oversight is necessary to ensure strict adherence to procedures and prompt recognition of indicators of potential solidification problems. This is especially true if the personnel preparing the PCP specimens are not too knowledgeable.

1.7 Summary

1.7.1 Solidification Experiences

Most members of Working Group 1 believed that greater than 95% of solidifications of radwaste have been successful, but a few members thought more data should be made available to support this claim. The focus of the discussions, therefore, was on the few problem solidifications in order to make the technology even better than it currently is.

Experiences of unsuccessful or unusual solidifications at nuclear power staions (i.e., Quad Cities- Unit 2, J. A. FitzPatrick, Peach Bottom, Millstone- Unit 1, and Three Mile Island- Unit 2) were reviewed as were the experiences at West Valley and the leaching tests performed by the Idaho National Engineering Laboratory (INEL) and Brookhaven National Laboratory (BNL). The events and the probable causes of the solidification problems were reviewed.

1.7.2 Types of Solidifications Being Performed

The Working Group discussed the types of solidifications currently being performed at nuclear power stations. A list was generated, but it was recognized that this list was incomplete because the data came from only one vendor and only one utility.

1.7.3 PCP Verification Tests

The Working Group concluded that the PCP verification tests are valuable if attention is paid to them so that problems can be identified. There are too many variables to depend on

vendor certification tests to identify all potential problems. Certification testing can never bracket every situation; there is a possibility that the surrogate waste used in the certification tests will be different from the actual waste. Therefore, the PCP verification test can be very important in discovering potential problems prior to attempting an actual liner solidification.

For the PCP verification test to be useful, actual waste must be used rather than surrogate waste, and the PCP specimens must be prepared in a way that is analogous to the way the actual liner is solidified. Quality control and operator experience are also very important. If potential problems are to be identified during the preparation of the PCP specimens, a trained, experienced person must participate in preparing the samples.

1.7.4 Important Parameters

The following parameters were identified as being of prime importance in obtaining a successful solidification:

Chemical loading and distribution on ion-exchange resin
Waste pH
Mixing
Distribution of ion-exchange resin in the waste form

In addition, the ambient temperature in the area in which the solidification is performed must be considered, but it is of secondary importance.

1.7.5 Relevance of Laboratory Studies

The results of laboratory studies were discussed. The position of the Working Group was that the materials and methods used for these laboratory studies must be closely examined before conclusions are drawn regarding actual solidifications at nuclear power stations. The Working Group felt that future laboratory studies should be performed with actual radwaste, not surrogate waste, and cement formulations that are currently used for actual liner solidifications.

1.7.6 Solutions to Solidification Problems

The Working Group discussed potential solutions to solidification problems, including improvements in the PCP verification tests and methods to verify proper solidification in liners. The following were identified as being important in solving solidification problems:

Better chemical characterization of the waste to be solidified.

Improved personnel training and experience.

Improved procedures for PCP verification tests to more closely simulate liner solidificationa (e.g., more representative mixing and oven temperatures).

The suggestion to sample every liner, store the samples, and, at a later time, subject a number of these samples to the NRC Branch Technical Position tests was discussed. The Working Group felt that this suggestion has both merits and drawbacks. The merits, although not specifically discussed, included the following:

The chance for acquittal of suspect liners.

The drawbacks identified included the following:

Increased radiation exposure (ALARA consideratons).

Cost.

Transportation and storage of a large number of samples.

Quality control would be difficult.

Management risk and legal liability.

The possibility of retrieving liners may arise.

1.7.7 Full-Scale Test Results

The Working Group reviewed the full-scale testing that has been performed and the results of this testing. It was found that only a limited amount of full-scale testing has been performed using actual waste. The vendor's full-scale tests were performed on waste forms made from surrogate waste. It was concluded that increasing the amount of full-scale testing and expanding the scope of thes tests was probably not practical. Rather, it was suggested that (1) more studies be performed, possibly using surrogate waste, to show that tests on small samples give results indicative of the behavior of full-scale waste forms and (2) leach testing of full-scale waste forms be performed on a limited basis to verify models.

1.7.8 Methods to Verify Proper Solidification of Actual LLW in Liners

The various methods (both currently used methods and potentially useful methods) to verify proper solidification of actual LLW in liners were reviewed. It was felt that a number of these methods were promising and should be investigated further. In addition, the suggestion to sample every liner and store these samples for possible future testing was discussed at length. A number of advantages and drawbacks to this proposal were identified.

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WORKING GROUP 2 DISCUSSIONS:

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2. LABORATORY TEST EXPERIENCE AND APPLICATION TO PROBLEM WASTE STREAMS

This portion of the workshop proceedings provides an overview of our deliberations and discussions in Working Group 2. As you know, the overall objective of this workshop is to obtain an improved understanding of the technical concerns and issues in cement solidification of low-level radioactive waste (LLW) and to develop initiatives that will lead to their regulatory resolution. As the title of this working group indicates, its primary objective is to consider potential problems with cement solidification of low-level radioactive waste which may be inferred from laboratory test experience. Another objective is to determine possible causes or reasons for these problems.

We requested that the members of Working Group 2 who are familiar with applicable laboratory test experience prepare brief summary presentations as opening statements to initiate the subsequent discussion. On the first afternoon of the workshop we had opening presentations by appropriate participants on the following topics:

Problems encountered during the course of laboratory-bench-scale testing of the procedures for LLW solidification in cement and of the solidified waste-form product performed at the national laboratories. Such testing may have been conducted with either simulated or actual LLW and may have been sponsored by either DOE or NRC.

Vendor experience with laboratory-bench-scale testing of cement solidification of power reactor wastes and of the solidified waste-form product.

Experience with cement solidification of LLW at DOE's operations at the West Valley Demonstration Project (WVDP), at the Savannah River Site (SRS), and at the Idaho National Engineering Laboratory (INEL).

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During the next day of the workshop, we addressed the following issues and concerns:

(1)   The implications of data from the cement solidification of low-level waste from DOE operations at WVDP, SRS, and INEL. We were especially concerned with the implications for the cement solidification of power reactor radwaste.

(2)   The need for detailed radwaste characterization, since minor constituents may affect solidification with cement (e.g., the organic impurities present at low (~100 ppm) concentrations in the West Valley supernatant waste) and the possible implications for solidification of decontamination waste streams in cement.

(3)   The significance of laboratory data on the effects of the degree of depletion of ion-exchange resins as well as the effects of particular species of depleting cations and anions on the properties and performance of the resulting cement-solidified waste forms.

(4)   The significance of the effects of curing times and curing conditions on laboratory-scale test specimens.

(5)   The feasibility of using laboratory exploratory testing to identify waste streams that cannot be solidified in cement.

(6)   The feasibility of using laboratory exploratory testing to establish the maximum waste loading for a specific waste stream in an actual full-scale cement-solidified waste form.

(7)   The feasibility of using laboratory exploratory testing to develop means of solidifying "problem" waste streams and/or increased waste loadings in cement.

We used remaining time on the final day of the workshop to tie up any "loose ends."

This account of the activities of Working Group 2 is broken down into ten sections. The following eight sections provide an overview of our discussions. The first seven of these sections are organized by issue or concern in accord with the above list rather than chronologically. For example, the highlights of the opening presentations by working group participants are included in this account of our discussions under the appropriate issue or concern. The eighth section summarizes other topics which came up during the

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working group discussions. The ninth section presents the results of our discussion of the issues and concerns as we summarized them in our report to the closing plenary session. The tenth section is a bibliography of relevant reports and articles; the "General" and "BNL" references constitute a list which was distributed to the working group participants before the start of the workshop in order to provide a common technical basis for the discussions while the remainder of the bibliography was compiled during or after the workshop.

2.1 Implications of the Cement Solidification of LLW at DOE Facilities

2.1.1 Implications of the Cement Solidification of LLW at WVDP

The major LLW stream at WVDP is the decontaminated Plutonium Uranium Reduction Extraction (PUREX) reprocessing waste supernatant, which is an aqueous solution whose major components are $NaNO_3$ and $NaNO_2$. This is a well-defined waste stream when compared to typical nuclear reactor LLW. In our discussions, we considered certain highlights of the experience with cement solidification of this waste at WVDP. For example, control of the conditions during the addition of the various ingredients and also during mixing is important when preparing solidification specimens, whether they are laboratory-scale samples or full-scale waste forms. In addition, mixing speed, speed of addition of ingredients, and the order of addition of ingredients are all important for solidification of the waste.

One of the most significant lessons to be learned from the cement solidification of the decontaminated supernatant at WVDP is the potential for drastic effects of some minor constituent of the waste on the solidification process. In the present case it appears that organic constituents (perhaps including a proprietary "EDTA-like" chelating agent) interfered with the setting of the initial cement waste formulation. This problem was discovered by laboratory investigations of the real waste. (Note: EDTA refers to ethylene-diaminetetraacetate.).

Based on the studies at WVDP, the laboratory-scale solidifications should simulate all the details of the full-scale solidifications to the extent practicable. For example, at one point in these WVDP studies, excessive entrained air (i.e., foaming) was removed from lab specimens by vibrating them. Since there was no way to similarly vibrate the full-scale specimens, foaming remained a problem for that particular formulation.

The experience at WVDP with the solidification of the PUREX supernatant as described in the plenary paper indicates that, in addition to qualification testing on surrogate waste forms, lab-scale solidifications of actual waste stream samples are

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necessary to verify whether a given waste stream encountered in the field can be solidified in cement.

It was also emphasized during this discussion that qualification and process testing should be carried out by qualified personnel.

("They should know what they are doing and be able to identify a problem when they see one.")

Solidification of the decontaminated reprocessing waste supernate at WVDP is described in more detail in one of the Opening Plenary Session papers.

2.1.2 Implications of the Cement Solidifications of LLW at SRS

At SRS, the waste streams are relatively well defined when compared to commercial power reactor waste streams. The major process wastes contain about 30 wt.% sodium salts, largely sodium nitrate. Other wastes considered for cement solidification include concentrates, spent processing chemicals, electroplating sludge, incinerator ash, and seepage basin sludges. Pretreatment of the wastes prior to solidification may be required in order to render the waste less leachable and/or chemically and physically compatible with the cement matrix. Organic resins, reactive metals, and organic liquids are not solidified in cement at SRS.

In some cases the solidification system stabilizes the waste during formation of the waste form matrix, a process referred to as *in-situ* treatment. The preferred *in-situ* treatments for reducing the mobility of soluble waste constituents are two chemical stabilization processes, namely, precipitation of low-solubility compounds and incorporation into the lattice structure of hydrated cementitious phases. However, since certain ions in the SRS waste streams, notably NO_3^-, do not readily form insoluble precipitates, the mobility of such constituents is controlled by physical adsorption onto the internal surface area of the matrix pore structure and by physical entrapment within this pore structure. Other soluble species whose retention in the waste form may depend on physical entrapment include Cs^+ and tritium. Control of constituent mobility by physical entrapment requires a monolithic waste form. Consequently, waste forms which depend on entrapment to control waste mobility are evaluated for physical integrity.

Wastes which are dimensionally unstable, i.e. they expand or shrink due to changes in moisture or chemistry, must be carefully evaluated for compatibility with a rigid matrix since stress caused by expansion can crack the matrix. At SRS, evaluation of cracking caused by expansive matrix phases (which are formed by secondary reactions between cement and waste) is done by visual examination of aged samples.

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SRS experience indicates that the compressive strength requirement should be based on adequate support of the weight of the overburden by the buried waste form. However, cement waste forms at SRS are designed as part of an engineered disposal system which includes concrete vault containment. Although the written specifications on the waste form product are 50 psi after a 28-day cure in sealed containers, the "informal" in-house specifications are stricter, namely, 500 psi. This latter value has no necessary relationship to stability, since waste form performance as measured by leachability and durability does not necessarily improve as compressive strength increases.

Experience at SRS indicates that scale up of processing from laboratory scale through pilot scale to full scale can be accomplished if chemistry and processing are adequately simulated. Mixing action, waste chemistry, temperature, cement type, and processing time are among the variables which must be simulated. Scale up of the SRS leaching performance of defense waste saltstone material, a large volume waste which is relatively well defined compared to reactor wastes, has been carried out in laboratory-size samples, in 55-gallon-drum-size samples (evaluated at Brookhaven National Laboratory (BNL)), and in lysimeters.

2.1.3 Implications of the Cement Solidifications of LLW at INEL

The EPICOR II prefilters constituted the first stage of the demineralization system used to decontaminate contaminated water resulting from the March 1979 incident at Three Mile Island Unit 2. Many of the prefilters were loaded with radioactivity to six times the TP-recommended amount (60 Ci/ft^3). Samples of organic ion-exchange resins from two of the prefilters were examined for evidence of radiolytic degradation by a variety of techniques such as infrared spectroscopy, gas chromatography, scanning electron microscopy, and barium chloride precipitation. Degradation has been observed at less than 10^8 rad. Samples of ion-exchange resins from two other prefilters, one consisting entirely of organic resins and the other of an organic resin and an inorganic zeolite were solidified in cement (and in vinyl-ester styrene).

Much of the formulation development for those waste forms was done with simulated EPICOR II resin waste, i.e., unirradiated resin material from the supplier. (The EPICOR II resins themselves are proprietary.) Many of the waste forms tested during the formulation development phase disintegrated rapidly on immersion, but a formulation consisting of 24 wt.% waste (which consists of decanted resin with about 10% by volume of additional standing water above the resin bed), 63 wt.% cement (with no additives), and 13 wt.% water resulted in an "excellent" waste form.

One goal of this program was to obtain and test real ion-exchange resin waste in accord with the TP tests. The waste forms were subjected to all the tests specified in the TP. Another

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goal was to obtain real waste for field testing in lysimeters. Waste forms were fabricated for and installed in field lysimeters which have been operating for four years.

2.2 Radwaste Characterization

One very basic goal of radwaste characterization is to establish the compatibility of the particular kind of waste with cement, i.e., whether the waste-cement mixture will solidify and whether the resulting composite resists immersion. For example, during small-scale and full-scale leaching tests at BNL, some cement-solidified wastes degraded (e.g., Na_2SO_4/ion-exchange resin waste) while others held together fairly well. In one case, real Na_2SO_4 waste solidified in cement resisted immersion longer than the simulated waste solidified in cement, possibly because of the presence of iron in the real waste. Investigations of cement-solidified Na_2SO_4 with the Scanning Electron Microscope (SEM) indicated the presence of new mineral phases. There was no impact on leaching despite a decrease in surface porosity. At WVDP, zeolite waste was found to perform like a pozzolan when solidified in cement; the compressive strength was too high for the measuring device. In any case, the formulation for solidification will generally have to be changed for different waste streams. As an example, a specific formulation may be needed to solidify the waste resulting from the use of any given decontamination reagent. Appropriate radwaste characterization, by indicating the presence of constituents which can react with cement, may indicate the relative difficulty of solidification of the radwaste in cement.

Based on experience with laboratory-scale investigations and tests at BNL, at WVDP, and at a cement-solidification vendor laboratory, a small amount of either a set retardant or a set accelerator can result in unsatisfactory solidifications. For example, at BNL even simulated borate waste was found to set (although borates are notorious set retardants), but real borate waste with 100ppm EDTA had not set even after several months. The experience with solidification of the decontaminated supernatant at West Valley also shows that small quantities of chelating agents can affect the setting of cement. This kind of problem with solidification may be detected by the normal process control program (PCP) testing of samples taken from the actual waste prior to solidification. For example, if a waste form made from such a sample does not set at room temperature after 18 to 24 h (even if one heated in an oven has set), there is a possible problem with a set retarder in the waste. By means of such pre-solidification verification testing, potential problems with cement solidification of LLW have been avoided at WVDP, SRS, and commercial reactors.

A cement solidification vendor participant in our working group presented an overview of the laboratory operations which his firm typically conducts in order to characterize the radwaste before proceeding with the solidification.

The first consideration in characterizing the waste stream, since it determines the binder formulation to be used, is the kind of waste stream (e.g., bead resin, borate, Na_2SO_4). For example, this vendor maintains that ion exchange resin bead waste forms made from pozzolanic cement binders have permeabilities at least one order of magnitude less than ones made from ordinary portland cement binders and thus will yield waste forms with better leach properties.

Several properties may be measured by the vendor as part of the waste characterization for any given kind of waste stream. The wt.% of the dissolved solids (such as Na_2SO_4) is determined from the specific gravity or, in other cases, by evaporation of the liquid in an oven. The pH is another important parameter.

Once the total formula is established for any particular solidification campaign, a PCP "set" sample is prepared which is oven cured for 18-24 h and examined for free liquid and hardness.

2.3   Depletion of Ion-Exchange Resins

The degree of depletion of the ion-exchange resin as well as the chemical species of the depleting ions, i.e., the nature of the counter ions, has been found to affect the stability of the cement waste form incorporating the resin, especially with regard to immersion. For example, at Westinghouse R & D Center, cement waste forms incorporating some types of cation-exchange resins in the as-received Na^+ form had much poorer immersion resistance than waste forms incorporating the same resin depleted with a mixture of bivalent cations. For other cation-exchange resins, the Na^+ form resin did not pose a problem for immersion resistance of the resulting cement waste form. The degree of exhaustion of the resin, namely, the number of times it had been recycled, and its physical form -- bead, granular, or powdered -- were also contributing factors to the effects of the counter ion on the stability of the cement waste form.

The poor immersion resistance of the cement-solidified Na^+-form (or in some studies, H^+-form) cation-exchange resin beads has generally been explained by the following mechanism:

The resin beads exchange cations with the surrounding cement matrix and are thus converted from the Na^+ (or H^+) form to the Ca^{2+} form. The Ca^{2+}-form resin beads can have a larger volume than the Na^+ (or H^+) form, thus disrupting the cement matrix.

BNL studies utilizing energy-dispersive analysis of X-rays (EDAX) and scanning electron microscopy (SEM) have found the aluminum content of the cement adjacent to the resin beads depleted as well as indications of calcium uptake by the resins. These observations suggest an alternative mechanism, as follows:

The resin beads are degrading the cement in their immediate vicinity by depleting it of calcium and aluminum, thus causing structural instability of the cement matrix.

SEM observations of the degradation of the resin beads themselves, e.g., pitted surfaces, have also been made at BNL. Similar SEM observations of resin beads have been made at Westinghouse R&D.

We discussed whether pre-treatment of the ion-exchange resin prior to solidification could be utilized to minimize the potentially deleterious effects of resin depletion. We considered the following pre-treatment techniques:

(1)   heating of the resins (which is believed to result in thermal decomposition of the organic resin matrix, especially of the functional groups directly involved in ion-exchange);

(2)   coating of the resin beads with a polyester (which is supposed to form a barrier between the resin and cement matrices which is impermeable to water and ions);

(3)   pre-treating the resins with lime (CaO) (in order to "pre-deplete" them before solidification and also to provide some pH control); and

(4)   pre-treatment by unspecified means to increase the moisture content. [See Section 2.7, Solidification of Problem Waste Streams, below.]

The pre-treatment will have to be tailored to the particular resin-cement system since the relative effect of a particular depleting species will depend on the particular kind of ion-exchange resin as well as on the binder and waste constituents present.

2.4 Curing Conditions and Curing Times

At BNL, investigations had been conducted of the release of organic chelating agents from solidified decontamination wastes. This investigation included studies of the effect of immersion in water on the solidified waste forms. Cement waste forms incorporating certain chelating-agent/ion-exchange-resin combinations exhibited so-called "aging" effects when immersed in water, i.e., a longer cure period prior to the immersion period resulted in improved immersion resistance. When the waste forms did not fall apart during immersion they had compressive strengths much greater than 50 psi [which is the minimum compressive strength specified in the May 1983 Technical Position on Waste Form]. Depending on the particular chelating-agent/ion-exchange-resin

system, the post-immersion compressive strength was greater, about the same, or less than the pre-immersion value.

Another study at BNL specifically addressed cure-time effects in waste forms consisting of ion-exchange resins solidified in cement. In this study, BNL utilized several vendor formulations as binders and mixed-bed ion-exchange resins (in order to simulate power-plant-coolant clean-up resins) as the wastes. BNL found that the waste forms with lower waste loadings exhibited "typical" portland cement behavior, i.e., the compressive strength increased with cure time, while the waste forms with higher waste loadings exhibited "atypical" portland cement behavior, i.e., the compressive strength decreased with cure time. These results may consist of two distinct processes which still need to be separated out with further work, namely, the effect of cure time and curing conditions on the immersion resistance of the cement waste forms and the change with elapsed time of the compressive strength of these waste forms apart from immersion.

The question arose whether there is some minimum curing time for laboratory specimens. Tests based on partially cured samples may give misleading results which are only of academic interest. "Real" samples need longer times (months) to cure. It was noted that longer cures generally result in a finer pore structure and thus in a higher leach index.

We considered several possible reasons for the loss of durability of cement waste forms. One cause is dimensional instability of the waste, such as the potential for swelling of ion-exchange resin beads by absorption of water. Expansive reactions may occur in the cement paste itself, e.g., ettringite formation due to reaction with sulfates. (Note: "Ettringite" is the name commonly given to a sulfate reaction product in portland cement, namely 6-calcium aluminate trisulfate 32-hydrate, which may be written as $Ca_3Al_2O_6$ • $3CaSO_4$ • $32H_2O$. Ettringite is a naturally occurring mineral of the same composition.) It was also noted that under wet-dry cycling cement paste is subject to expansions and contractions which decrease with progressive curing.

Leveling off of the compressive strength is usually indicative of approach to complete (i.e., 100%) curing. Only then are the results of immersion testing other than of academic interest. 100% cure means that 100% of the anhydrous cement grains have reacted to be in equilibrium with the pore solution. In actual cement specimens curing may still be in progress years after setting, but in many practical situations of interest in a radwaste context, the specimens are "essentially cured" -- i.e., the overwhelming majority of the cement grains are in equilibrium with the pore solution.

We noted that laboratory tests could be carried out on samples cured under conditions simulating field conditions from a

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time/temperature standpoint (which takes note of transport, storage, handling, and disposal). For example, 140°F for several days is <u>not</u> an accelerated cure -- it is an attempt to simulate the average temperature of the "real world" exotherm. The oven cures at West Valley are also an attempt to simulate the full-scale exotherms. However, temperature gradients in real world liners cannot be rigorously duplicated on a laboratory scale, but according to some working group participants the oven-heating utilized at the start of the laboratory cures should be close enough. It was thought that in most cases the cement/waste product would be the same whether the laboratory heating regime utilized the temperature-vs.-time profile at the center of a cemented-waste liner or near an outer surface. In support of this contention, vendor experience has generally found that lab-scale compressive strengths correlate with those of liner cores.

There was some discussion of the "Tokar kitchen test," i.e., Dr. Michael Tokar's presentation during his plenary session introduction to this workshop of a waste form which had disintegrated after a week of immersion in water even though the recipe had passed all the qualification tests of the TP. We recognized during our discussions that this specimen had probably dehydrated over the year it had been stored in a cracked plastic container. We also noted that such conditions must be avoided when conducting long-term tests on cured samples.

2.5 Identification of Unsolidifiable Waste Streams

We addressed and dismissed this issue relatively quickly after two participants presented actual samples of 50 to 60% borate solutions solidified in cementitious binders. In principle, there is probably no LLW stream which cannot be solidified in cement, especially if cost is no object. We also noted, however, that a <u>solidified</u> waste stream is not necessarily <u>stable</u> over the long term. Therefore, we must distinguish between <u>solidification</u> and <u>stabilization</u>. The former term refers to the setting of the cement paste in a waste form into a hardened matrix; the latter refers to the long-term maintenance of dimensions and form.

2.6 Determining Maximum Waste Loadings

Laboratory investigations have been extensively employed to establish compositional envelopes of solidifiability and stability. The stability referred to here is stability towards immersion although stability towards thermal cycling was also mentioned. As a practical matter, according to some of the working group participants, the water/cement ratio is the first delimiting factor -- excess bleed water being the upper bound and mixability or workability being the lower bound. Then, the waste loading is increased to the maximum level which does not fail during immersion.

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In connection with maximum waste loadings, it was noted that lower w/c ratios correlate with higher compressive strength. Unfortunately, they also were said to correlate with lower waste loadings and higher exotherms -- even to boiling. The water-reducing admixtures (e.g., surfactants) designed to address the problem of high exotherms resulting from the heat of hydration in concrete are not applicable to waste forms because they interact with the wastes.

It was also noted by our group that establishment of maximum waste loadings on a weight basis would require an approved, industry-wide test procedure that uniformly characterizes the weight percent solids of any particular waste stream. Only in this way can comparable test data be generated by the various participants.

2.7 Solidification of Problem Waste Streams

The discussion of this issue focussed on the mechanisms of leaching and of loss of monolithic integrity of waste forms.

It was noted that the mechanism of radionuclide retention is important in determining whether a monolith is needed for the purpose of tying up the particular species of radionuclide. For example, Cs-137 and H-3 are physically entrapped in the pore solutions of the cement matrix, so they can diffuse out. Therefore, a monolith is required for retention of these radionuclides. In order to reduce or prevent leaching of contaminants, an alternative to a monolith is chemical stabilization, for example, by incorporating as many contaminants as possible in insoluble phases.

Since the loss of monolithic integrity of cement-solidified ion-exchange resins has been attributed to expansion of the resin beads, several methods of reducing or eliminating such expansion were discussed. [Note that an alternative mechanism was discussed. See Section 2.3, Depletion of Ion-Exchange Resins, above.] It was stated that appropriate pre-treatment of resin beads can render them dimensionally and chemically stable after solidification in cement. For example, pretreatment to increase the moisture content of the resins will result in greater immersion resistance since drier resins have a greater tendency to swell by absorbing water and thus disrupt the cement matrix. Additional ingredients may be used as well. For example, pozzolans remove the lime (CaO) before it can cation-exchange with the resin.[1]

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[1]It was noted in a dissenting comment after the workshop that (1) resin beads pre-treated to increase their moisture content may still be "sucked" dry by the cement during the curing period and (2) the rate of uptake of Ca^{2+} by the resin bead may be "essentially instanteous" when compared with the rate of reaction of pozzolans with lime.

It was pointed out by a solidification vendor representative that none of the resin bead references included with this summary involve pozzolanic binder systems. Such modified resin bead waste forms have not as yet been evaluated by the principal independent laboratories. It was reported that this vendor has used pozzolanic binders for solidification of resin bead wastes almost exclusively since 1984, accounting for a substantial number of commercial operations.

The physical form of the resin is also important; powdered resins are easier to solidify into a more immersion-resistant cement waste form because of their higher surface-to-volume ratio so that the volume increase on absorption of water distributes the resulting stresses over a larger surface area.

2.8 Additional Items

We compared the terms "stability" and "durability". The term "stability" refers to general maintenance of physical dimension and form [specifically, stability in the 10 CFR Part 61 sense] while the term "durability" refers to the performance of the design function for the design lifetime [specifically, durabilty in the civil engineering sense].

We also discussed some of the reasons for conducting laboratory scale testing. We came up with the following list:

- To explore the mechanisms of degradation and contaminant release, e.g.,

  • SEM and EDAX studies have already been utilized in the waste management arena for ion-exchange-resin/cement systems and for sulfate-waste/cement systems. They have been employed by the concrete industry to investigate degradation of pozzolanic building materials.

- To conduct formulation development and optimization. (As one participant said, "Don't stop at portland-cement/water investigations.")

- To flag potential problems (but be cautious regarding scale-up to full-size specimens), e.g.,

  • Chemical form of resin,
  • Effects of cure time and cure conditions,
  • Effects of small quantities (ppm) of organics.

- To identify key parameters for process control. In this connection, it was noted that one must pay closer attention to detail during process development. The final stage in the bench-scale phase of process development before scale-up is pre-testing in the laboratory with actual waste.

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- Investigate the compatibility of wastes and binders. (As someone said, "Problem wastes depend on the binder system used.")

We also addressed how to better link the results of laboratory tests on surrogate wastes with the performance of real solidified wastes. We considered the following possibilities:

- Taking small-scale archival samples of real wastes during the PCP and performing tests on them after some time.

- Conducting much more detailed correlations of real wastes with surrogate wastes than are now done in order to provide test results which are more representative.

- Doing chemical analyses of real wastes during the PCP sample set time (say, 24 hours) in order to ascertain that there are "no surprises" in the real wastes, i.e., that the information on waste composition given by the utility to the vendor was adequate for formulation development.

2.9 Summary of Working Group 2

In our report to the closing plenary session we summarized our discussion of the Working Group 2 issues and concerns as follows:

(1a) Implications of the West Valley solidifications:

- Current waste management practice at commercial nuclear power plants does not link the qualification tests and the actual process waste forms. Lab-scale solidification of the actual waste stream is necessary to verify that the actual waste when processed in accord with a PCP will solidify. Such testing is in addition to qualification testing of surrogate waste forms.

- The details of the lab-scale testing should simulate the full-scale testing (e.g., air entrainment during mixing).

- Qualification and process testing should be carried out by personnel with appropriate experience and training. (Typical statements: "They should know what they are doing." "Hands-on training is necessary because there are no textbooks or courses.")

(1b) Implications of the SRS solidifications:

- All of the implications of the West Valley solidifications are applicable.

- Immersion testing was very useful in development of suitable formulations.

- The "qualification testing" phase established a wide range of concentra-tions which bracket expected compositions for actual nitrate waste. Current QA/QC procedures involve testing grab samples of waste as well as testing the other ingredients (cement and additives) to ascertain whether the composition is within the range which results in a solidified product whose properties are within permitted ranges. The grab samples of the mix are allowed to solidify and are tested. It is found that the properties and performance of laboratory samples correlate with the properties and performance of the process product samples. This can be generalized to power plant situations by appropriate attention to detail.

(1c)   Implications of the INEL solidifications:

- All of the implications of the West Valley solidifications are applicable.

- Correlations between lysimeter field studies and laboratory tests for a few representative systems would be useful.

- Immersion testing was very useful in development of suitable formulations.

(2)   Radwaste characterization:

- Small-scale waste/binder PCP samples shall be examined for processing abnormalities, e.g.,

  . set retardation
  . set acceleration
  . bleed water
  . rheology

(3)   Depletion of ion-exchange resins:

- The effect of a particular species of depleting ion will depend on the kind of ion-exchange resin.

- Pre-treatment to control the inherent dimensional instability of the ion-exchange resins currently in use must be tailored to the particular resin cement system. These changes in size result from changes in the species of counter ion as well as from changes in moisture content of the resin bead. The binder system should not dehydrate the beads during processing.

(4) Curing conditions and curing times:

- The most meaningful qualifications testing results are obtained from essentially fully cured waste forms. Curing should be carried out at 100% relative humidity (e.g., in sealed containers). Essentially complete curing correlates with leveling off of the compressive strength.

(5) Laboratory work to identify unsolidifiable waste streams:

- In principle, none of the low level waste streams from commercial power reactors are unsolidifiable. See item 7 below.

(6) Laboratory work to establish maximum waste loadings:

- It is frequently done by using immersion resistance as the final limiting parameter after the range of water/cement ratios has been defined by bleed water and mixability considerations.

(7) Laboratory work to solidify "problem" waste streams:

- It is likely that solidification of any "problem" waste stream from commercial power reactors is feasible. Two examples of 50 to 60% borate solutions solidified in cementitious binders were presented. We must distinguish, *however, between set and stability. Only by addressing credible degradation mechanisms can we provide reasonable assurance of long-term stability.

- With relatively minor modifications to the 90-day immersion test, much additional useful information could be obtained indicating the trends toward product stability. However, short-term laboratory test programs, while necessary, are insufficient to demonstrate long-term stability.

- In order to provide reasonable assurance of long-term stability for low-level waste solidified in cementitious binders, it may be necessary to conduct performance-based evaluations of the solidified waste product similar to those described in the May 1983 TP for qualification of high integrity containers.

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WORKING GROUP 3 DISCUSSIONS:

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3. TECHNICAL POSITION TESTS FOR CEMENTITIOUS WASTE FORMS

In order to minimize the release of radionuclides from a shallow land burial trench, the NRC has developed guidelines and criteria on waste package performance and the burial site itself. These are described in 10 CFR 61 and the Technical Position (TP), both of which are familiar to the low-level waste community. Perhaps the most important strategy regarding the burial of Class B and Class C wastes is that they be "stable" so that deleterious changes from their original condition are reduced.

Table 3.1 taken from an NRC report (1988) lists the TP tests which are currently in use to qualify a waste form with respect to stability. The tests are usually short-term ones and are not always of an accelerating nature. Because of this, there is uncertainty in their capability to predict long-term behavior.

In addition, there has been criticism of some of the tests by the Advisory Committee on Reactor Safeguards in a letter to NRC dated November 10, 1987, and by Chang and others (1988). In particular, they questioned the usefulness of the tests on the basis of:

    (a) Their rationale and technical connection with NRC
         stability requirements described in 10 CFR 61;

    (b) Their applicability to real waste behavior; and

    (c) The   choice   of   test   methodologies   and   test
         conditions.

It is with these concerns in mind that the current Working Group addressed the need to modify or eliminate individual TP tests.

Table 3.1

Solidified product guidance

Tests	Methods	Criteria
1. Compressive Strength	ASTM C39 or D1074	60 psi (a)
2. Radiation Stability	(See 1983 TP)	60 psi comp. str. after 10E+8 rads
3. Biodegradation	ASTM G21 & G22	No growth (b) & comp. str.> 60 psi
4. Leachability	ANS 16.1	Leach index of 6
5. Immersion	(See 1983 TP)	60 psi comp. str. after 90 days
6. Thermal Cycling	ASTM B553	60 psi comp. str. after 30 cycles
7. Free liquid	ANS 55.1	0.5 percent
8. Full-scale Tests	(See 1983 TP)	Homogeneous & correlates to lab size test results

(a) The 1983 TP calls for a minimum compressive strength of 50 psi. This has been raised to 60 psi to accommodate an increased maximum burial depth at Hanford of 55 feet (from 45 feet).

(b) The 1983 TP calls for a multi-step procedure for biodegradation testing: if observed culture growth rated "greater than 1" is observed following a repeated ASTM G21 test, or any growth is observed following a repeated ASTM G22 test, longer term testing (for at least 6 months duration) is called for, using the "Bartha-Pramer Method." From this test, a total weight loss extrapolated for full-size waste forms to 300 years should produce less than a 10 percent loss of total carbon in the sample.

In order to systematically address the usefulness of each TP test, the following questions were asked and discussed:

(a) Is there a defensible rationale for each test? If not, should it be eliminated?

(b) If the test is useful, should:

   *   The rationale be strengthened?
   *   The acceptance criterion be changed?
   *   The test methodology and test conditions be modified?
   *   The data analysis be improved to reduce uncertainty?

(c) What approaches are suitable for full-size specimen testing?

Also, the Working Group addressed the need for completely new tests and acceptance criteria to help ensure that waste forms are fully characterized with respect to failure/degradation modes that could reduce stability and cause increases in radionuclide release. Any new test would need:

(a) A defensible rationale for its use;
(b) Ability to predict long-term performance; and
(c) A defined acceptance criterion.

Finally, the following additional issues were addressed:

(a) Qualification of combined radioactive waste streams;
(b) Specimen scale-up effects;
(c) Accelerated tests;
(d) Minimum numbers of specimens;
(e) Specimen preparation, curing, etc.; and
(f) General QA/QC procedures, archival specimens.

In the sections that follow, details are given of the discussions of Working Group 3 regarding current TP tests, new tests, and the additional issues listed above.

3.1 Compressive Strength Test

The compressive strength test is the most important TP test to characterize the structural integrity of a waste form. Not only is it used to quantify the strength of a standard as-cured material, but it is also used after the water immersion, thermal cycling, irradiation, and biodegradation tests to measure strength changes that may have resulted from these events. Currently, the

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acceptance criterion for compressive strength is 60 psi which is based on estimates of soil overburden stresses for a maximum burial depth at Hanford, WA, of 55 feet, plus additional stresses that would likely arise from waste with high density, and from the stresses caused by soil compaction machinery. For soil alone, assuming a density of 120 lbs/ft^3, the compressive stress at 55 feet is 45.83 psi. The anticipated additional stresses from waste packages that are denser than soil (cement is about 12% denser) and compaction machinery are assumed to be accounted for by the overall 60 psi stress level.

It was pointed out by several of the Working Group that the compressive strength changes after the waste form is made. Therefore, the test is usually done after samples had been cured for 28 days. This length of time is generally taken by the construction industry to represent the minimum required for hydraulic cement to achieve a large fraction of its ultimate strength. Longer curing does not usually cause additional large strength changes. In general, the test was thought to be valuable and necessary. However, its use as an indicator of long-term structural stability was questioned on the basis of its short-term nature, especially in regard to possible slow, long-term degradation from irradiation, biodegradation, sulfate attack, etc. These factors will be discussed later.

Also discussed was the validity of the 60 psi acceptance criterion. Little or no safety margin appears to be included to take into consideration extra heavy waste packages such as those containing contaminated metal components. These could cause cement waste forms on the bottom of a trench to be subjected to stresses in excess of 60 psi. Moreover, because a compressive strength value of 60 psi is only about one one-hundredth of the strength achievable with a typical cement mortar, there is a fundamental question of whether cement waste forms possessing strengths as low as 60 psi could reasonably be expected to exhibit structural stability for time periods on the order of 300 years. Recognition of this issue is provided in the Technical Position which contains the statement that, "Many solidification agents will be easily capable of meeting the 50 [now 60] psi limit for properly solidified wastes. For those cases, process control parameters should be developed to achieve the maximum practical [emphasis added] compressive strengths, not simply to achieve the minimum acceptable compressive strength."

Owing to the considerable strength of cementitious materials used in construction, some DOE projects, e.g. those at the West Valley Demonstration Project and at the Savannah River Plant, arbitrarily specify 500 psi as a minimum guideline for an acceptable compressive strength. Some Working Group members believe that such a high value would be useful since, if it were met, it would increase the confidence that a waste form will withstand overburden loads and it will possess sufficient bonding

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strength between the microconstituents to remain intact and resist disintegration over time.

The participants addressed the scatter in measured strength values. This would lead to controversy if the majority of the test specimens exceeded the 60 psi limit, whereas a small number fell below this value. The Working Group felt that better guidance was needed on the numbers of tests to be carried out and the procedures to be used in analyzing uncertainties in the data.

One participant questioned the need to be concerned about structural stability of waste forms inasmuch as some of the new regional compacts were going to use engineered structures, which could be relied on for structural stability. In response, it was pointed out that most agreement-state compact authorities were indicating a desire to use a "belt and suspenders" approach, wherein both the waste form and the engineered structure would be required to be stable. Thus, any expectation or hope for relief from the States from the requirement of long-term structural stability for waste forms is, in all likelihood, taken in vain even if the States opt for an engineered structure-type of disposal.

The recommendations made by NUMARC (Chang, and others, 1988) based on their review of the Draft Regulatory Guide recommendations on acceptable strength losses were discussed. They believe that a maximum allowable percent decrease from the original compressive strength would be a good approach to assure long-term stability. They recommend that the post-immersion compressive strength for brittle materials (e.g., cement) should decrease by no more than 20 percent or that the minimum value reached be in excess of 90 psi.

Some Working Group members felt that these were not adequate acceptance criteria since they still did not address long-term decreases in strength. A distinction was made between strength values that showed a continuing decrease with time, and those where the strength tended to stabilize at some value above the acceptance limit.

At the end of the discussions on the compressive strength test, it seemed that most Working Group members felt that the test was valuable even if, at a minimum, it was used for general quality assurance or screening purposes to separate good waste forms from poor ones. It was pointed out, however, that improvements in the acceptance criteria were desirable since some vendors may opt to increase the waste loading in a waste form to the point where they would just meet the minimum strength requirement. Guidance from NRC could ensure that adequate safety margins were maintained.

In defining how long-term changes in strength may be approached in a generalized and conservative way, it was suggested that this could be achieved by first adding a safety factor on the

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60 psi limit, say, for example, a two-fold increase. This would make the acceptance criterion 120 psi which, hopefully, would be more than sufficient to accommodate anticipated and unanticipated loads experienced by waste forms in the bottom layer of a trench. The uncertainty in measuring the compressive strength of a waste form as it is degraded with exposure to Technical Position test conditions may be quantified by testing sufficient samples such that sigma limits about the mean trend curve could be determined. Any waste form whose lower sigma limit line (1σ, 2σ; whatever is deemed acceptable) falls below the 120 psi limit, would be unacceptable. Very long-term testing for strength changes would not be needed, if the strength showed a tendency to increase with time or, if an early stable strength plateau was attained.

A more comprehensive approach for predicting service life in building materials from accelerated tests was briefly outlined by a Working Group member. It is formulated in ASTM Standard E632-82 (Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials). It was thought to be valuable since it seeks to identify degradation modes, and designs test methodologies to quantify them. Through mathematical modeling, the rates of change in properties are quantified and validated against in-service tests. From established performance criteria, the service life may then be predicted.

There would be some problems involved, however, in attempting to develop a mechanistic approach, based on first principles of materials science, to qualify low-level waste. One of the most important problems is that it is estimated that a period of three to five years would be required to develop an accelerated test to predict the "structural stability life" of a cement-solidified waste form. Inasmuch as low-level wastes requiring long-term stability are being generated and disposed of continuously, the waste generators expressed a genuine concern about creating a situation of "constipation," wherein waste would backup because it had not been qualified to some new criteria.

3.2   Leaching and Immersion Tests

According to the Technical Position:

"Leach testing should be performed for a minimum of 90 days in accordance with the procedure in ANS 16.1. Specimen sizes should be consistent with the samples prepared for the ASTM C39 or ASTM D1074 compressive strength tests. In addition to the demineralized water test specified in ANS 16.1, additional testing using other leachants specified in ANS 16.1 should also be performed to confirm the solidification agents leach resistance in other leachant media. It is preferred that the synthesized sea water leachant also be tested. In addition, it is preferable that radioactive tracers be

utilized in performing the leach tests. The leachability index, as calculated in accordance with ANS 16.1, should be greater than 6."

It was generally regarded by the Working Group that the release of radio-nuclides was of fundamental importance, since it provided a mechanism for the transport of activity to the general public. However, most felt that there was not a clear connection between leachability and structural stability, which is the basis for virtually all of the TP tests. No specific mention of leachability requirements are given in 10 CFR 61, although it may be inferred from Section 61.51 which states:

"(a) covers must be designed to minimize to the extent practicable water infiltration, to direct percolating or surface water away from the disposed waste, and to resist degradation by surface geologic processes and biotic activity, (b) surface features must direct surface water drainage away from disposal units..., and (c) the disposal site must be designed to minimize to the extent practicable the contact of water with waste during storage, the contact of standing water with waste during disposal, and the contact of percolating or standing water with waste after disposal."

Clearly, contact of the wastes by water is recognized as being potentially detrimental. In addition, it was stated by a Working Group member that the leaching of radionuclides and other constituents from a waste form reflects "chemical instability." This, in turn, could influence structural stability.

With respect to the acceptance criterion (leachability index of greater than 6) few participants had a clear understanding of its significance and defensibility. [Note that the leachability index for an element is the logarithm of the inverse of its diffusivity in the waste form. Hence, the higher the index, the slower the release rate.] One Working Group member, however, believes that the value of 6 was derived from early leaching experiments. Based on such work, it appeared that the value of 6 was a practical value which separated "good" waste form binders from "bad" ones. The observations that justified such a distinction, however, were not clear.

Further discussion by the Working Group revealed that modeling of the leach rates, that would give legally acceptable releases at a site boundary, were subsequently used to justify the value of 6. It seems that an early Dames and Moore study showed that a leachability index of 4 would give rise to the maximum permissible release. By adopting a two-order-of-magnitude safety margin, the acceptable leachability index became 6 or greater.

The procedures for leachability testing also were the source of criticism by some of the participants. Findings of the NUMARC study were cited to support the proposition that:

(a) Leach tests should last up to 5 days and not 90 days, and

(b) Only one leachant (seawater) need be used.

Some Working Group members countered by stating that it was long-term behavior that was important and that 5-day tests, notwithstanding the fact that the leach rates are conservatively higher during this initial time period, could not detect increases in leach rates that may occur at long times. These could be present as a result of changes in the leaching mechanism. It was rebutted to some extent by the fact that most changes in leach rate that were identified in the literature usually occurred after a 90 day test period. Eventually, after much discussion, many Working Group members appeared to agree that a 5 day leach test gives conservative values for the leachability index and will quickly indicate whether a waste form meets the acceptance criterion. However, the 90 day immersion test, which may be run as an integral part of the 90 day leaching test, was thought to still be very valuable as a structural integrity test and should be maintained as is. If no signs of cracking or spallation are observed after 90 days, one could make the assumption that gross increases in the leach rate also would not occur. However, several Working Group members believe that long-term leaching tests should not be abandoned completely, since changes in leaching mechanisms are a distinct possibility. Therefore, research in this area may be desirable as a check on whether, and under what circumstances, changes in the mechanism might occur.

With respect to the use of two leachants, one participant stated that both should be used since one could not initially predict which leachant would be more aggressive. The counterargument given was that some preliminary tests could be run first to identify the most aggressive leachant (NUMARC believes this to be seawater) and then more comprehensive testing should be done with that leachant. Few Working Group members appeared to object to this strategy, provided that the more aggressive leachant is clearly identified first.

3.3 Scale-up Effects

A basic concern with waste form characterization centers on the ability to use small test samples to predict full size waste form behavior. Because of the expense that it would entail, vendors are not expected to run all qualification tests on full size waste forms. However, a quantitative relationship must be

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established between smaller laboratory specimens and prototypic ones before the former can be used as indicators of anticipated behavior.

It was stated by one Working Group member that, in many cases, standard ASTM tests will specify a range of acceptable specimen sizes that will yield results that are not affected by size considerations. In addition, he cited some leaching data from Brookhaven National Laboratory that quantified releases from cement forms of varying size. The results showed that there was excellent agreement between measured release rates and those theoretically predicted based on sample size (i.e., surface area to volume ratio).

Two vendors described their approach for scale-up effects. They stated that TP tests had been carried out on core samples taken from prototypic waste forms. The samples were taken from regions throughout the monolith to check for differences in properties that could be attributed to thermal gradient effects and/or poor mixing procedures. Both stated that although there were some differences in properties, based on location, they were not considered important. All samples, regardless of the location from which they were taken, met homogeneity requirements.

Other considerations that were addressed centered on the curing procedure for small samples prior to testing. Full size forms are usually subjected to higher temperatures because of hydration effects during mixing. One vendor maintains the waste temperature at 120 - 130°F maximum, in order to prevent boiling during solidification. He felt that a temperature history should be obtained and this should be administered to small laboratory specimens to ensure that these high temperatures are taken into account during the pre-test curing period.

Oven curing using an arbitrary time and temperature were found by some Working Group members to yield results that did not conservatively reflect prototypic waste form strength. In particular, one vendor stated that for waste compositions that his company had studied, oven-cured samples had superior strength than those which had been cured at ambient temperatures for 28 days. He stated that some of the data that had been compiled by other organizations using oven-cured samples could, therefore, be suspect.

Other vendors countered this assertion by saying that some of their tests showed that oven-cured material often had lower strength than ambient-cured specimens. After much discussion, it appeared that the chemistry of the waste form was important. Some additives, for example pozzolanic materials, are very sensitive to temperature and could cause accelerated curing compared to cement cured at ambient temperatures. It was for this reason that it became clear that a prescribed standard curing procedure would not

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be advisable; each vendor should have the latitude to adopt a curing procedure that will reflect the actual performance of his particular waste form.

An additional important point made with respect to comparing small and large samples is that one vendor found that he often had to adjust the waste form composition depending on the size of the form in order to achieve an acceptable product. This applied only to boric acid type wastes. Evidently, the problem centers on poor mixability which is overcome by making compositional changes. Since the prototypic forms have a different composition, this vendor was obliged to more comprehensively test core samples taken from his full size forms. The other vendors in the Working Group, however, did not apparently experience such problems and stated that no compositional differences existed between prototypic forms and smaller laboratory samples.

An important comment made by an NRC Working Group member concerned the roles of the Office of Nuclear Reactor Regulation (NRR) and the Office of Nuclear Materials Safety and Safeguards (NMSS) in waste regulation. It was NRR's responsibility to certify the process control plan (PCP) that defines a vendor's solidification procedure and NMSS' responsibility to certify the waste form produced, using information that is usually obtained from laboratory-scale samples. It was stated that it was likely that NMSS would assume overall responsibility for the product acceptance and associated recipes for the PCP specimens and full-scale waste forms. This would help to more clearly define a uniform set of guidelines for solidification and waste form qualification. This could include, for example, a clearer definition of acceptable processing temperatures to assure consistency with curing temperatures used in smaller samples used for qualification tests.

In general, it appears that the vendors do not have any significant problems regarding scale-up effects. They feel that they can adequately correlate the results taken from full-size and smaller samples so that most qualification tests can be conducted on the latter.

3.4 Free Liquids

Section 61.56 of 10 CFR 61 states that, "...liquid wastes, or wastes containing liquid, must be converted into a form that contains as little free standing and noncorrosive liquid as is reasonably achievable, but in no case should the liquid exceed 1% of the volume of the waste when the waste is in a disposal container designed to ensure stability, or 0.5% of the volume of the waste for waste processed to a stable form." Also, it states that, "Void spaces within the waste and between the waste and its package must be reduced to the extent practicable." Futhermore, the Technical Position states that, "the free liquids should have

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a pH between 4 and 11," presumably to minimize container corrosion from extremely acidic or alkaline solutions.

No Working Group members appeared to have any significant criticisms of the rationale for the free liquid TP test or for the 0.5% acceptance criterion for free liquid.

At the West Valley site, the procedure for free liquid testing involves perforating the top of a container and inverting it to allow free liquid to drain. Apparently, there is little difficulty in meeting the acceptance criterion.

One vendor described a non-destructive procedure for measuring free liquids, involving infrared scanning. This technique detects temperature differences on the surface of a container that are caused by voids (presumably liquid filled) between the cement and the container. The temperature variations occur as a result of differences in thermal conductivity for the liquid filled cavities and for cement.

Another participant stated that ultrasonic testing procedures are also available for estimating free liquid content. However, the details were not given at that time.

3.5 Numbers of Test Specimens

In demonstrating compliance with a performance requirement, many vendors expressed the need for guidance concerning the minimum acceptable number of test specimens. Some felt that three or more replicate tests should be sufficient to establish sigma limits. In some tests, however, duplicate tests were often used for measuring properties with good reproducibility, e.g. leaching tests. For compressive strength testing, a larger number of samples is often used because of the larger degree of scatter in the data, ease, and low cost of testing compared to leaching.

One Working Group member stated that guidance on the numbers of specimens to be tested are often given in the ASTM/ANS standard procedures recommended in the Technical Position. However, it was recognized that the TP tests are just recommendations. Vendors may use alternative tests for waste form qualification, if they so wish. Hence, the testing of fewer specimens than recommended by the ASTM/ANS procedures is a frequent occurrence.

Although most vendors want more definitive guidance on the numbers of test specimens, it became clear during the discussions that even when such guidance is given in ASTM procedures, they were not always adequate since waste form characteristics could show large variability caused by deficiencies in process control procedures. In these situations, more tests would be needed to establish confidence limits.

Another factor was discussed by the Working Group with respect to quantifying trends in properties with time. For example, in considering strength degradation caused by water immersion, measurement of the strength after 90 days' immersion will not necessarily give an accurate estimate of strength changes for longer periods of immersion. At best, one could only draw a straight line between the starting strength and the strength after 90 days, and linearly extrapolate to longer times. Information on long-term trends would be needed if the strength after 90 days immersion showed a significant drop from pre-immersion strength values. In that case, longer immersion times (e.g., 120, 150, 180 days) might be used in addition to the standard 90 day period to ensure that the strength was not monotonically decreasing with time. This would more clearly determine whether a property was continuously changing with time, or whether it was tending to a stable value.

3.6 Curing of Cement Test Specimens

Much of this topic was discussed earlier in Section 3.3 on scale-up effects. However, it was reiterated during these discussions that the curing of small scale specimens prior to testing should follow the expected time-temperature history that a prototypic form would encounter. After general discussion, it seemed that most Working Group members did not wish to endorse a single curing schedule for all small scale specimens since some forms, depending on composition, would have properties quite different from prototypic waste forms. The most important guideline would be to administer to the laboratory test specimens a temperature-time profile that simulated actual conditions.

3.7 Thermal Cycling

The rationale for the test was discussed by Working Group members. In the NUMARC study it was pointed out that the ASTM B553 test, recommended in the Technical Position, is basically a quality control test to check the adhesion of metal plating to plastic automobile parts. The specified test temperature extremes (-40°C, +60°C) were originally intended to not only address damage from thermally-induced stresses but also stresses originating from dents and scratches. Only four thermal cycles are required in ASTM B553.

Although there was an understanding by most participants that some type of thermal-cycling test was desirable, some believe that the temperature extremes were excessive, based on anticipated temperature changes during the waste storage and transportation periods. Also, the 30 test cycles, based on an assumption of one month of thermal cycles, was thought by some to be excessive. In addition, some participants thought that guidance was needed with respect to spalling and cracking that could occur during cycling. This is not discussed in the Technical Position. It only recommends a post-cycling compressive strength of 60 psi. This

means that, according to the Technical Position, a specimen could be heavily cracked and spalled but would be deemed satisfactory, if it had a compressive strength greater than this value.[1]

With regard to the actual performance of the test, the following features were thought by several Working Group members to be important:

(a) Ensure that sufficient time is given to allow test specimens to achieve a uniform temperature at the specified limits (40°C and +60°C).

(b) Use a capped test container to ensure that moisture evaporation does not occur. It was pointed out that some experiments at Brookhaven National Laboratory showed that during the hotter parts of the cycle, moisture evaporation occurred. This water was able to fall under gravity during cooler periods and be absorbed in the lower part of the cement. Upon freezing, this excess of moisture caused the bottom half of the specimen to disintegrate first. Sealing the test vessel simulates the behavior of a waste form in a closed drum.

Several participants felt that thermal-cycling could have wider applicability than merely checking for freeze-thaw damage. Since cycling is a severe challenge to the integrity of the cement structure, they suggest that it could be used as a general accelerated test for structural integrity and allow the elimination of some of the other structural integrity tests. However, it was pointed out by another participant that the mechanism of structural degradation for freeze-thaw cycling was different from those caused by immersion, irradiation, etc. Therefore, a single test could not be used to study the effects of all failure modes.

3.8 Biodegradation

The biodegradation tests specified in the Technical Position are ASTM G21 and G22 for fungal and bacterial attack, respectively. These tests were devised for use on synthetic polymeric materials, with the extent of biodegradation being determined visually. An additional test may be used to more quantitatively estimate microbial degradation based on measurements of CO_2, which is

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[1] A "no-cracking, no-spalling, no-atypical strength behavior" criterion has been adopted and used by the NRC for the past two years for cement waste form reviews, though the Technical Position has not yet been revised to include this.

generated from microbial respiration. This is the Bartha-Pramer test (1965).

Most Working Group members were generally familiar with limitations in these tests. The main problem with the G21 and G22 tests is the selection of inappropriate fungal and bacterial strains to estimate the degree of biode-gradation. An expert microbiologist in the group stated that biodegradation can be expected if the test materials are exposed to fungi/bacteria that normally utilize such materials as a food source. As he pointed out, "You don't try to feed a cow hamburger," meaning that cementitious wastes cannot be assimilated by the microbes specified in the TP tests.

Some participants felt that all biodegradation tests should be eliminated for cement waste forms since they were never found to support microbial growth. This, however, was challenged by others who gave case histories of catastrophic degradation of concrete sewer systems, buildings, and monuments in Germany and throughout Europe. In the case of the sewer systems, sulfuric acid was formed by microbial action on H_2S in the sewage, and the concrete failed by acid attack. In several other cases, nitric acid microbiologically produced from air- and water-borne nitrogen compounds, has been shown to damage buildings and monuments. Some recent work by Bowerman (1988) was also cited in which simulated decontamination waste resins were found to be susceptible to attack by microbes isolated from resin wastes from the Brookhaven High Flux Beam Reactor. This lends support to the theory that, under appropriate conditions, both the cement and ion-exchange resin wastes can be degraded by microbial action.

It became apparent during the deliberations that improved tests would be needed if biodegradation studies of a meaningful nature were to be conducted on cement-solidified wastes. The current tests have no ability to check for the biodegradability of cementitious materials since the microbes used in the test are not associated with cement degradation. However, nitrates and sulfates that may be present in low level wastes do provide sustenance for some microbes that exist in natural environments. Metabolic activity by these organisms together with growth in cement-waste micro-sites could lead to the degradation of cement waste forms. There appeared to be a clear need to specify more appropriate microbes for such tests. This might require a substantial research effort. Until more improved tests could be developed, most Working Group members felt that further G21 and G22 testing was unwarranted, at least for waste forms that do not contain organic or other carbonaceous materials.

3.9 Combined Waste Streams

A useful discussion concerned the ways in which "combined waste streams" could be processed. For this topic, a combined

waste is defined as one made up from different radwaste components. This makes their composition, processing, and behavior more difficult to determine. One vendor cites the possibility of diluting a Class B or C waste stream with Class A wastes to obtain an overall Class A composition. This allows disposal under far less stringent regulations.

Another participant suggested that the key to maintaining high quality in a combined waste was more detailed chemical characterization of the waste stream to detect deleterious constituents. This was illustrated by the problem encountered at West Valley, where the presence of about 150 ppm of certain organics prevented cement from setting. By placing a maximum allowable concentration on constituents that are known to compromise waste form stability, it was thought that good quality products could be assured. However, most vendors did not relish the prospect of any major increases in the chemical characterization of waste streams. They feel that most waste streams are routinely produced, and their chemistries are sufficiently well understood for them to be satisfactorily solidified. They indicate that problem waste streams that may be contaminated with constituents that could create problems usually are Class A. This allows more flexible procedures to be used for their processing and disposal.

3.10 Quality Assurance/Archival Samples

The use of archival specimens for monitoring the integrity of buried wastes over long time periods was next discussed. Such a quality assurance procedure was thought by some to be very useful since the TP tests only measure short-term characteristics.

Of particular relevance to this discussion was a description by Dr. M. Tokar during his Plenary Session presentation in which he showed a resin/cement waste form that had disintegrated to granules after it had been immersed in water for 1-2 days. Material from the same batch had successfully passed the TP test for immersion about a year ago. It was speculated that during one year of storage in a capped container, that moisture from the resins had been removed by cement undergoing hydration. Upon rewetting, the resins reswelled and caused the cement to disintegrate. The periodic testing of archival specimens would provide indications of the performance of buried wastes.

The question was raised about the implications of archival specimens failing an immersion test. Would this mean that wastes would need to be retrieved from a trench for reprocessing? The general point of view was that it would be impractical and unnecessary since the volume of affected waste would most likely be small. No significant impact would be expected on overall radionuclide release from a site. The main benefit of an archival specimen program is that it would identify poorly performing cement

wastes and allow additional analyses to be performed to pinpoint causes of the problem. Lessons learned would help prevent future problems.

During the deliberations, it was stated that the NRC had discussed with various States the possibility of developing archival trenches at waste sites. Wastes would be buried for extended periods and retrieved for testing. At this time, no formal responses had been received from the States.

The technical benefits of an archival specimen program did not seem to be questioned by the Working Group. However, how it should be implemented, including locations for storing specimens and the responsibilities for testing them, was thought likely to create problems.

3.11   Radiation Damage

Radiation damage to waste forms is discussed in Section 3 of the Technical Position. It refers specifically to ion-exchange resin stability and specifies a maximum allowed gamma dose of 10^8 rad. It states that chemical and radiological conditions should be simulated and that there should be no adverse swelling, acid formation or gas generation which could be detrimental to the proposed final waste product. The acceptance criterion is for the compressive strength to be at least 60 psi after an irradiation of 10^8 rad. However, the Technical Position also requires a waste form to remain stable after being exposed in a radiation field equivalent to the maximum level of exposure expected from the wastes being solidified. This could cause a contradiction if a cement waste form initially had a strength of, say, 3000 psi, and a post-irradiation strength of 60 psi. On the one hand, it is clearly unstable in an irradiation environment but, on the other, it passes the radiation stability test.

Nevertheless, few participants thought that cementitious wastes could be significantly degradated by gamma irradiation. Doses of 10^{10} rads, at least, were usually needed to cause degradation. Some data from Idaho National Engineering Laboratory on the leachability of Three Mile Island resins solidified in Portland I and Portland II cements was cited to support this. At the 18 percent resin loading level, there was only a slight increase in the leachability of cesium/strontium for forms subjected to gamma irradiation up to 10^8 rad during leaching compared to non-irradiated specimens. Some other data from Brookhaven National Laboratory were also described for Portland cement mortars subject to gamma doses up to 10^9 rad. Two dose rates were used and it was stated that even though some decreases in compressive strength were discernable, especially for the slower dose rate, the strength seemed to become stable after a small decrease of about 15 percent.

Because of these relatively minor radiation damage effects, many participants felt that additional radiation testing of cement forms could be safely held in abeyance.

3.12 New Tests for Waste Forms

Discussion briefly focused on the need for any new additional tests to add to current TP tests. Some of them are outlined below.

3.12.1 Biodegradation Tests

These may be necessary for some cementitious waste forms containing nitrates or sulfates since it is known that appropriate organisms are able to assimilate these constituents. Moreover, the microbes specified for the G21 and G22 tests are not considered to be appropriate for cementitious wastes in general. Most participants believe that significant research with respect to microbe selection and testing procedures will be needed if viable tests are to be developed.

3.12.2 Lysimeter Tests

One participant recommended that lysimeter tests be performed in order to obtain realistic long-term data on waste performance.

3.12.3 Sulfate Attack Tests

Such tests were discussed more than once during this Workshop. The rationale is that sulfate may be leached from sulfate wastes in a trench and will attack cement wastes not formulated to withstand sulfate degradation. In discussing an accelerated procedure to quantify sulfate attack by wet/dry cycling of specimens in sulfate solutions, one cement expert stated that care should be used in interpreting such results. The problem lies in the possibility that other salts, such as chlorides, could also deposit in cement during the drying cycle and cause cracking not associated with classical sulfate attack. However, no participant objected to sulfate attack testing,
perse.

3.12.4 Advanced Structural Stability Tests

The possibility was again discussed for the development of an "advanced" structural stability test that would take the place of some of those currently specified in the Technical Position. The thermal-cycling test was proposed earlier, but was not felt by many to be defensible as a single test that could replace all others (see Section 3.7). Again, the possible use of the ASTM E632 methodology was proposed as a means to develop such a test. It outlines a procedure to determine cement failure modes and to model them against laboratory tests. If the procedures were carried out successfully, it would be possible that some new general structural

integrity test can be specified for future use. At this time, however, it does not appear practical to defer the use of cement for a 3 to 5 year period while tests to develop a mechanistic understanding of the failure process are developed.

3.13 <u>Summary Comments by Working Group Members</u>

At the end of the formal deliberations, general comments were solicited from participants regarding their impressions of the Workshop. Individual comments are summarized below.

o   One participant stated that during the deliberations there was an identification of paths to follow for future waste form testing. However, he believes that the burden on the vendor to perform these tests is likely to be too heavy. He suggested that comprehensive testing of waste forms, which involves many variables, could be greatly reduced if supplementary concrete barriers, whose long-term properties are much better known, could be placed around waste forms to achieve waste/trench stability.

o   Another participant reiterated earlier thoughts that the current TP tests were mainly of use for screening purposes to separate good from poor waste forms. New tests were needed to determine long-term performance and to establish service life.

o   One group member felt that a great deal of progress had been achieved in two days. It was felt that we were proceeding in the right direction. This member felt that some performance criteria were less important than long-term materials-property trends.

o   Another participant hoped that if the Technical Position is revised, it will more clearly differentiate between screening tests and "scenario-based" tests.

o   One participant said he now better understood the rationales for the TP tests. Extra assurance of long-term stability could be gained if additional safety margins were placed on some acceptance criteria, such as compressive strength.

o   Another Working Group member endorsed the need for new tests for waste form evaluation. The need to consolidate tests was emphasized. He asked whether a single hi-tech test for structural stability could be developed.

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o   One participant stated that this Workshop was two
     years overdue. He said that it was long known that
     the TP tests could not demonstrate 300-year
     stability.   The need for mechanistic models for
     predicting long-term behavior was clear.

o   One person said that he believes that waste is
     currently being buried safely and that cement is an
     excellent solidification medium. He has concerns
     that there are too many variables to accurately
     characterize all types of wastes. Thus, he requests
     a definition of what is "acceptable confidence" in
     a waste form as opposed to "absolute confidence"
     (which seems to be what is required).

o   Another participant compared the current state of
     the art for low-level waste management with that
     for nuclear reactor technology. He surmised that
     many years ago, in the early reactor programs, some
     of the test requirements were also of a simple
     scoping nature. Nowadays, with reactor technology
     in an advanced state, sophisticated tests for
     materials were available. He felt that the next
     stage of test development for waste forms will have
     to reach a higher plane to achieve an understanding
     of long-term behavior.   It was felt that the
     Workshop had provided a convergence of ideas for the
     tests that will need to be developed.

o   Another participant stated that some TP tests could
     be modified and acceptance criteria changed. One
     underlying problem is to coordinate the requirements
     of TP testing and the Process Control Plan for
     solidifying waste.   It was stated that some power
     plant personnel were not as qualified as
     solidification vendors because of their more limited
     involvement in waste solidification and testing.
     This commentator specified a 4-pronged approach to
     achieve this goal:

     a)   Improve waste characterization;
     b)   Improve testing procedures;
     c)   Test archival specimens; and
     d)   Improve the Process Control Plan and make it
          consistent with the Technical Position.

At this point, the formal deliberations for Working Group 3
were completed.

3.14 References

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WORKING GROUP 4 DISCUSSIONS:

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4. WASTE CHARACTERIZATION, SOLIDIFICATION, AND PROCESS CONTROL PROGRAMS

The purpose of Working Group 4 (Group 4) was to discuss waste stabilization at nuclear power plants, focusing on practical problems that arise when real waste streams are processed for disposal. Overall, Group 4 attempted to answer the following:

Since real waste seldom has the exact same composition as "qualified" waste, how does one provide reasonable assurance that a specific batch of real LLW solidified with cement is stable as required by 10 CFR Part 61?

Group 4 attempted to address this issue by confining most of its discussions to technical problems associated with full-scale waste form production. The technical problems were discussed within the following framework:

* What is being done (current practices);
* What should be done (requirements for stability);
* What can be done (technological or other limits, for example, the as-low-as-reasonably-achievable (ALARA) principal.)

The emphasis on the in-plant technical aspects of LLW cement stabilization resulted in a wide range of topics categorized according to the generic process diagram shown in Figure 4.1. To cover them all in the limited time available, the Group adhered to the agenda shown in Figure 4.2.

The technical topics discussed in Group 4 have significant regulatory implications which may need to be resolved at some time. However, the actual development of regulatory guidance will necessarily rest on resolving the issue of what constitutes reasonable assurance. The resolution could consist of specifying how much sampling and analysis is required for the waste streams,
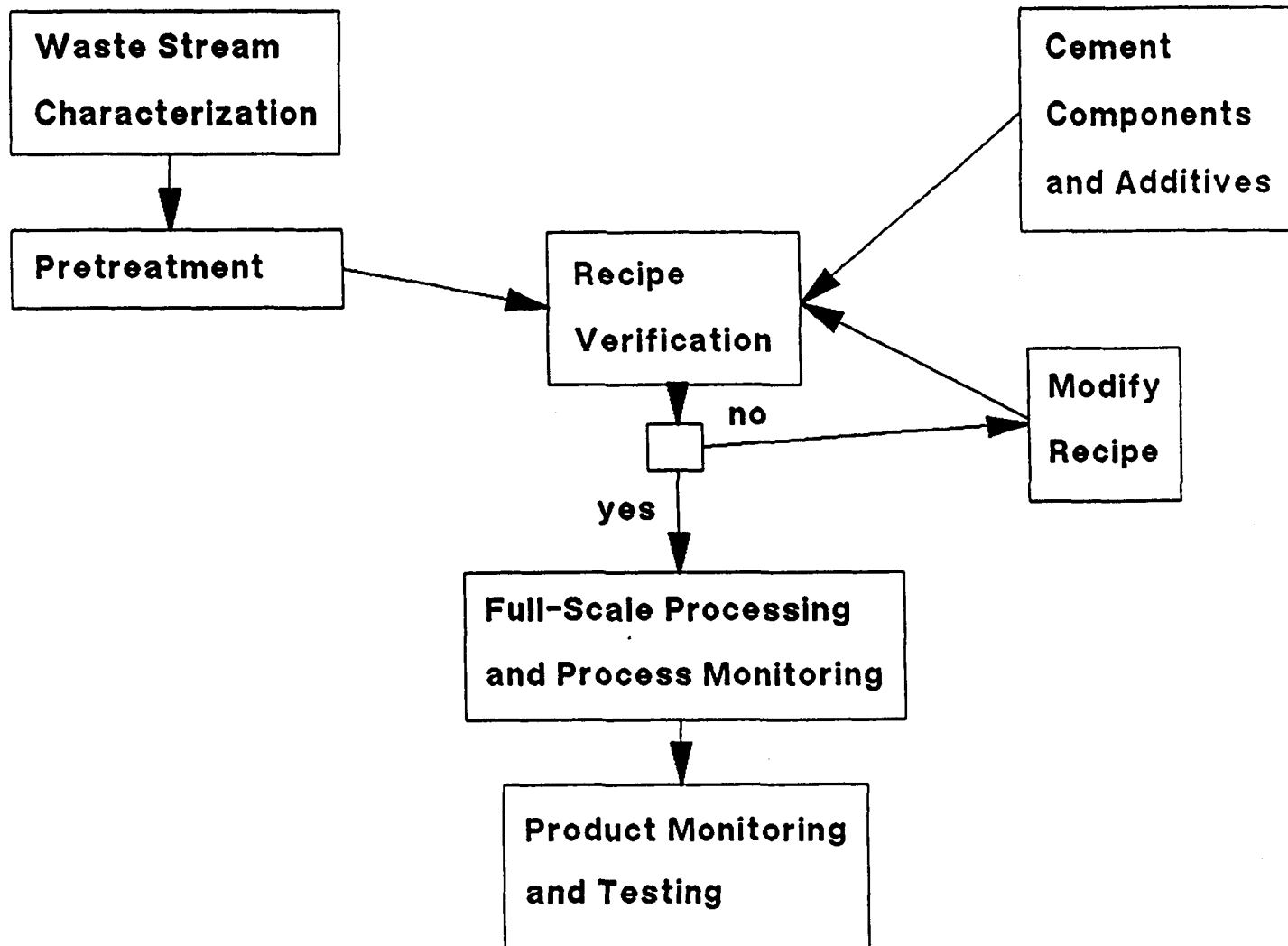
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Figure 4.1 Elements of Process Control

Figure 4.2.   AGENDA FOR WORKING GROUP 4

List of technical issues and elements that can contribute
to waste stability, or as an alternative viewpoint, to
product quality control.   These could be elements of
generic and plant specific process control programs
(PCPs).

Thursday A.M.

    1. Waste characterization
       * sampling method (where obtained, size of sample)
       * qualitative (waste id, well-segregated or
          combined with others)
       * quantitative (concentrations of total solids,
          main constituents)
       * acceptance criteria (procedures for out-of-spec
          wastes)

Thursday P.M.

    2. Pretreatment and recipe verification
       * what can be pretreated (neutralize pH,
          precipitate)
       * sampling method (where, how big)
       * sample prep (controlled mixing, curing)
       * tests to perform (set time, hardness)
       * limitations due to ALARA

Friday A.M.

    3. Process monitoring and pre-transpo:t storage and
       handling
       * waste stream homogenized and at temperature
       * mixing characteristics (speed, time)
       * monitor/control cure conditions
       * nondestructive tests of final waste form
       * small sample for archival storage

the testing and acceptance criteria required of recipe verification samples, or testing and acceptance criteria applied to waste products after production and before disposal.

Overall, the topic for Working Group 4 fell into the realm of product quality control. This concept of quality control applied to treating "garbage" may seem out of place, but it is completely appropriate when one remembers that the QC is being applied to materials that may be hazardous for several hundred years.

Group 4 consisted of 14 members, including the Technical Coordinator and Chairman. Six were from the commercial sector, including two from utility owned nuclear power plants (a BWR and a PWR), and four from vendors offering nuclear waste solidification and packaging services. The remainder were from the government or from government-funded enterprises, including three NRC staff members and five researchers or scientists from national labs or federally sponsored projects. The members were sent a list of issues and a bibliography of reports and publications so they could prepare for Working Group 4. A copy of the bibliography is appended to this chapter (Section 4.6.1).

The Working Group 4 Chairman opened the actual working group session with his summary of Group 4's objectives and a listing of approaches to meeting them. The Chairman stressed the need to link the Technical Position qualification tests to full-scale waste solidification and waste form production. The areas where approaches could be developed to demonstrate the link between a qualified recipe and the actual waste solidification in a liner are as follows:

1) Waste characterization (within a range of values determined for each plant),

2) Qualification testing and improved waste simulation,

3) Waste management practices in the plant, especially segregation of different waste streams,

4) Verification tests in process control programs (ᴾCPs),

5) Storage of solidified wastes and/or collection of archival samples for subsequent monitoring and testing,

6) Pretreatment to make adverse constituents inert or compatible with the cement solidification process, and

7) Limit waste loadings in final waste form.

After this introduction, discussions followed the agenda mentioned earlier.

4.1 Waste Characterization

The Technical Coordinator suggested limiting the discussion to Class B and C wastes that are generated on a routine basis. This would eliminate discussions of decontamination wastes, which were being covered in Working Group 1 in some detail. Encapsulation of mechanical filter cartridges in cement was removed from consideration as well, since the process is very different from mixing a waste stream with cement. One of the vendor representatives pointed out that some States may require some Class A wastes to be stabilized, even if they are not co-disposed with B and C Wastes.

There are some general comments and trends worth noting about waste streams, their characteristics, and stabilization methods applied to them. First, most Class B and C wastes are ion-exchange bead resins. Second, power plants are moving away from using evaporators for waste stream treatment. Instead, plants are using demineralizer systems, and expending the resins to higher loadings than they did in the past by using them in several systems. The latter approach involves first using the resins in high-purity systems. Then, when breakthrough, pressure drops or, more frequently, primary system chemistry requirements dictate bed changeout, the resins are used to process "dirtier" liquids in other systems.

Finally, another trend is that bead and powdered resins and filter media are being dewatered more often than solidified in cement. At present this is for economic reasons. One Group 4 participant at the table noted that HICs would not be able to compete with cement solidification if waste loading increased dramatically. A utility representative stated that his plant's filter media wastes were solidified in cement to meet transportation requirements that limit dose rates for shipping casks.

One aspect of waste characterization applies to both resin and filter media wastes. "Hotter" wastes from primary (and more closely controlled) systems can be well characterized, while those wastes from cleaning up liquids from floor drains, etc., are more difficult to characterize because a variety of wastes and materials can go down floor drains.

Another important factor affecting waste characterization lies with holdup tank capacity. For instance, the BWR utility representative noted that filter media from all filter operations at the plant were stored in a single holdup tank until enough had accumulated to begin a solidification campaign. He didn't mention whether records were kept of the amounts of filter wastes from

different sources. However, a sample for istopic characterization and solidification recipe verification would be taken routinely. Waste stream segregation and characterization are significantly dependent on installed plant waste systems and tankage. Proper batching was also identified as an important aspect of characterization and affected by plant equipment and procedures. An isolated, well-mixed batch is essential to proper waste characterization. If plant systems do not ensure this, a waste sample is drawn from the liner prior to solidification.

One utility representative present in the audience indicated that the only bead resins solidified in cement were reactor water cleanup (RWCU) system resins. All other resins are dewatered. The utility developed its own cement process and presented to the NRC a qualification test program for solidification.

One vendor representative noted that they have specific requirements for and need utility information about plant-specific bead resin wastes before beginning their solidification operations. Resins must be mixed cation/anion and expended (about 60 to 70% of exchange capacity), otherwise a pretreatment is needed.

Typically waste streams are routinely characterized as follows prior to solidification: identify major constituents (resin type, diatomaceous earth, crud), weight percent primary ions/salts (boron, sodium) and other solids, density, pH, temperature, identify radioactive elements (isotopic analysis), and presence (or lack thereof) of detergents and immiscible fluids (oils). Some vendors use an abbreviated series of the qualification tests as a screening test to ensure that specific chemicals identified by the plant characterization program are innocuous contaminants.

Several members of the group concluded that it would be pointless to try to bound certain concentrations of contaminants (e.g., organic acids, detergents, other "bad actors") generically in the qualification testing. Such a specific set of chemicals is not common among plants. If present individually or in other combinations in the actual wastes, the qualification testing would not necessarily be indicative or conservative.

4.2 Pretreatments and Recipe Verification

All the solidification vendors represented in Group 4 perform a small-scale test solidification with actual waste before beginning with full-scale processing as part of their PCP. The sample, procedure and program were all identified as the "PCP" by some members. This small-scale recipe verification test was seen by everyone as a very important point for providing assurance of waste form stability.

The vendors have standardized their own procedures for preparing and testing PCP samples. All use actual wastes that may

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have up to 1 rad/hr dose rates. Hot samples are usually scaled down to reduce worker exposure. Pretreatments such as pH adjustment that may be needed are included, and the characteristics of solidification are observed to verify behavior in accordance with expected characteristics (from experience and qualification testing). All the vendors cure the PCP samples in an oven within 18-24 hours. (Specific temperatures were not given.)

Vendor tests of the PCP samples include checking for such properties as mixability, time to solidify, physical appearance, presence of free liquid, whether it is a solid monolith, volume changes, and hardness at the end of the specified cure time. The hardness test consists of a technician probing the sample with a metal or wooden rod. One vendor representative indicated that they monitor thermal behavior, in order to detect heat spikes larger than the normal exotherm. They also look for oil and foaming. When questioned about quantitative measures of the waste samples properties, one of the vendor representatives noted that only trained and experienced technicians conduct the verification tests. Because they are experienced, they will know when the sample isn't quite typical. An atypical sample may prompt further or recharacterization of the waste, and a recipe adjustment. Recipe adjustments, if required, are made within the bounds established by the waste qualification tests.

There were several suggestions for improving assurance of final waste stability by using quantitative tests, and even a modified immersion test. The possible quantitative tests included using a calibrated penetrometer, monitoring cure temperature of an unheated sample kept in an insulated flask, and compression tests after a one-day cure. Participants expressed two views about the compression test. One opinion was that the test should not be considered, because compressive strengths of samples cured for such a short period exhibit a broad distribution. The other opinion held that the test would be useful and build confidence in the process, provided a data base on the distribution of compressive strengths were established.

One researcher from a government funded project stated that their PCP for waste solidification required compressive strength testing after a 7 day cure. Utility representatives pointed out that curing samples for compression tests could be a problem. The maximum time they believed it would be practical to wait before proceeding with full-scale solidification would be one day due to tankage and storage limitations and exposure concerns. It was suggested that accelerating the curing process in an oven for one day might reduce the scatter and lend credence to a one-day compressive strength test.

One of the researchers in Group 4 stated that without thorough knowledge of degradation mechanisms that occur over the long term, you couldn't prescribe short term tests that provided a significant

level of long-term assurance. This sparked a discussion about options for assessing long-term degradation, including the use of archival specimens, obtained and prepared as PCP verification samples, then served for future testing. Further discussion of archival specimens is summarized in Section 4.4.4.

4.3 Process Monitoring and Solidified Waste Storage and Handling

Discussions during the last session of Group 4 Friday morning covered full-scale processing and handling of the waste forms from in-plant processing to burial at the disposal site. Waste form stability is assured currently by utilities or vendors monitoring different aspects of the solidification process and inspection of the product, and some limited testing of the wastes at the disposal site.

After a satisfactory small PCP verification sample is obtained and full-scale processing is approved, process parameters are monitored to make sure the waste is solidifying as it should. Process parameters include proper amounts of cement, additives, and waste and equipment parameters such as mixer speed and torque. (Torque provides a measure of the viscosity of the cement-waste mixture.) At least one vendor monitors temperature of the waste during solidification. After mixing and solidification are completed (the latter usually a day or so after mixing) vendors inspect the liner to make sure no liquids are present and probe the surface of the waste form to make sure it is hard.

The Technical Coordinator questioned how mixing equipments' ability to achieve homogeneity was evaluated and approved. Vendor representatives pointed out that the main approval came with the qualification test program, since the preparation and destructive examination of a full-scale waste form is called for in the NRC Branch Technical Position on Waste Form (TP). The representatives also noted that in the development of the solidification and disposal containers, mixer blade design was a major consideration.

The burial sites inspect waste packages routinely. At Barnwell, at least 10% of the waste liners have holes punched in their sides to look for drainable water and solidified material that failed to harden. Waste containers from generators who have had problems with solidification or free water in the past are checked more frequently. Random liners are weighed to check for consistency with the manifest and with a cement waste form weight. Inspectors at the site also test random liners by hitting them with a stick. (The acoustic response can indicate the presence voids, free liquids, or inadequate solidification.)

The Group 4 Chairman suggested that an overall approach to improving assurance of long-term stability should combine possible improvements in "front-end" activities related to solidification with improvements in "back-end" activities. Front-end activities

include qualification tests, waste characterization, waste segregation, waste pretreatment, and plant chemical control programs. Back-end activities include PCP verification tests, archival test samples, and burial site inspections. Each of these activities is considered an "element of assurance," and the Chairman requested that the discussion cover current practices and options for added assurance of stability for each of these elements.

A lively debate about front-end versus back-end testing followed. Suggestions for providing added assurance of waste stability included taking "dip" samples from the liner before the waste had set, and saving the sample for archival purposes and/or for testing such as immersion or compressive strength measurements. Restricting collection of dip samples to "dirty" or poorly characterized wastes was suggested to meet ALARA requirements. Possible uses for archival samples are for longer term verification research on mechanisms of degradation.

Additional testing or inspection practices at the burial sites were not considered in great detail, since current practices appeared to be adequate. One suggestion was to use the impact echo technique as a nondestructive test to confirm homogeneity of full scale liners. (A list of references on the impact-echo technique is in Section 4.6.2.) In addition it was suggested that burial site data as well as plant processing data on waste solidification problems could be analyzed to determine whether there was a real need for concerns about stability.

4.4 Summary

During its last hour together, Working Group 4 jointly prepared Table 4.1 to summarize its discussions. The table lists elements that can be used to provide assurance that full-scale waste production yields stable waste forms. For each of these elements, current practices are shown as well as suggested options for providing additional assurance of stability to supplement current practices should these practices be judged inadequate. Options for more assurance were included in Table 4.1 without an in-depth evaluation of whether or not current practice provided reasonable assurance of long-term stability.

The elements of assurance can be separated into two groups: those at the front-end before full-scale mixing with cement, and those associated with the back end, beginning with PCP verification samples. The following sections provide a summary of some of the elements listed in Table 4.1.

4.4.1 Qualification Program

A major element of long-term assurance involves a qualification test program, such as that outlined in the Branch

Technical Position on Waste Form (TP). Since the TP tests were evaluated in Group 3, discussing them was avoided in Group 4.

There was a suggestion that qualification test programs should include generic waste streams containing "bad actors" (chemicals that are known or suspected to degrade waste form properties). A vendor representative pointed out that this is done to a limited extent for specific plants that are known to have "bad actors" in their waste streams. Effects on compressive strength and immersion resistance are determined. The full range of TP tests are not necessarily carried out. However, a generic qualification test program for all "bad actors" in all generic waste streams was not considered helpful.

4.4.2 Waste Characterization

The need for good waste characterization arises because power plants do not generate wastes with the same characteristics all the time. Unknown materials are always present in some of the wastes. Group 4 members agreed that many materials are inert or compatible with cement binders, and that only suspect and proven "bad actors" are the primary concern and reason for additional characterization. In most cases, the "bad actor" components only present a problem if they are not properly identified prior to processing.

Some pretreatments are available to "neutralize" the effects of bad actors in wastes. When this was mentioned, there was some discussion about differences between the waste and the waste without "bad actor" components that had been qualified. It was suggested that resulting waste should be evaluated to determine whether it was a "new" waste stream that should undergo qualification testing.

In-plant chemical control and utility management attitudes were considered very important for characterization of routinely produced wastes. Standards for chemical control programs have been developed by the Institute for Nuclear Power Operations (INPO) and generally focus on the safety impacts of chemical use, especially as they may affect primary systems in the plant. Added assurance of waste stability could result from adjusting the focus of chemical control programs to include consideration of chemical's effects on solidification. This would be especially appropriate when changes in chemical use at power plants are anticipated.

Several participants stressed that utility management can influence waste characteristics as much or more than other factors. Some plants emphasize good housekeeping, tracking of wastes sent to holdup tanks, segregating "clean" wastes from "dirty" wastes (i.e., wastes which are not well-characterized because inputs, such as floor drains, are difficult to control), and cleaning out holdup tanks routinely. Those plants generally have better characterized waste streams. Plants with these elements in their waste

management practices have fewer problems with solidifications. INPO encourages waste stream segregation. For added assurance of waste stability, further encouragement of waste segregation practices was suggested, for example, by NRC endorsement of the INPO policy.

Current practices for characterizing wastes generally depend on the utility actions. Normally, the utility identifies primary chemical constituents, radio-active elements and also such properties as pH, density, and solids content. Vendors usually do limited testing for waste constituents at the plants, depending more on the utilities analyses because the plant laboratory is better equipped for this. Vendors normally prescribe the analyses to be conducted to support execution of the test and full-scale solidifications. Usually, the vendor will check the results of the more basic utility analyses (e.g., pH, weight percent solids, density) and/or work closely with plant chemistry personnel to arrive at a characterization that is mutually agreed upon. Vendor representatives indicated that they have developed lists of chemicals which can cause problems with cement solidification. Vendors provide utilities with the checklist, and the utilities certify that the "bad actors" are not in the waste stream. In some cases, the certification may be based on cross-referencing the vendor's list with the plant's chemical inventory list. Chemical analyses specifically to identify the "bad actors" are normally not performed.

An option for providing more assurance of stability would be for the NRC to publish an information notice compiling a list of all known bad actors identified by the solidification vendors. [Some of the solidification vendors provided their lists for publication in these proceedings. These lists are at the end of this Chapter in Section 4.6.3.] In addition, utilities could devote more efforts to characterizing their waste streams that are not well characterized. This could be accomplished to some extent by better waste tracking and segregation practices, as well as personnel training and administrative controls.

4.4.3 Process Control Program

Overall, the process control program (PCP) was considered the prime means of assuring waste form stability. It documents the procedures to be followed and the quality control practices on a generic and plant-specific basis. It also serves as a manual of operating procedures. During the Group 4 sessions, an unpublished INEL report entitled "Guidelines for Preparation of a Solid Waste Process Control Program" was mentioned frequently. The report had been prepared for NRR in 1986 and had industry input. Group 4 members agreed that publication of the report by NRC would be useful to vendors and utilities, since the format and elements of a good PCP have not been collected in a single document before.

The most important elements for a PCP include waste characterization procedures (including sampling practices and batch control), preparation and monitoring of small-scale verification test samples, and adequate process monitoring throughout the full-scale solidification process.

Several participants stressed that the utility and vendor should include in the applicable PCP special recognition of those cases where an element of "routine" waste generation and solidification has been changed or is altogether new. In other words, the PCP should anticipate changes in vendor, operator personnel (and experience level), equipment and chemistry policies, new plant or equipment start-up, new waste stream being solidified, and plant operation methods.

4.4.4 PCP Verification Sample Tests and Archival Samples

Some Group 4 members felt that improvements in back-end activities by additional, quantitative tests on actual waste would provide added assurance of cement solidified waste stability. Suggested tests included compressive strength and hardness (or penetrometer) testing of PCP verification samples.

Another means of achieving added assurance was the collection or preparation of specimens to be saved for later testing, the "archival" samples. Two sources of archival samples were considered: extra PCP verification specimens, and "dip" samples obtained from the disposal container after mixing but before the waste had set. Restricting collection of dip samples for archival specimens to "dirty" or poorly characterized wastes was suggested to meet ALARA requirements.

Archival samples could provide data about the full-scale waste properties and behavior over the long term. Because of utility concerns about recalling wastes that were already shipped and buried, Group 4 arrived at several possible uses for archival specimens. The first was that poor performance of the archival specimen should not immediately result in a recall (although this may be a point for developing some sort of acceptance criterion). The archival specimen could be tested for stability, and the information from the test could be used as feedback for improving the solidification process. Another possible use for the specimens would be to use them in a research program to identify degradation modes that operate over the long term. Other aspects of an archival sample program that must be resolved include: where are samples stored (under what conditions, how long), what tests should be done on the samples, which waste stream should be part of the program and whether an archival program conforms to the principle of ALARA.

4.5 Concluding Remarks

As Working Group 4 concluded its meeting, there were several opinions prevailing. Some felt that stable waste forms were already being produced and that there was already adequate assurance of stability if the entire system of qualification testing, PCPs, and burial site inspections are considered. There was general agreement that the role of utility and plant management was extremely important. Where management shows an interest in and support for radwaste control, problems are few and short-lived. Conversely, without management support, added regulatory requirements may not accomplish all they were expected to.

One researcher recommended getting the involvement of a standards organization such as ASTM. Although such organizations often work slowly, the development of standards can be expedited when necessary. The researcher felt that the development of voluntary consensus standards applicable to waste form stability would benefit NRC, waste generators, and vendors.

Given the limited time and format for Group 4, it was impossible to judge on the adequacy of current waste solidification practices. Options for improving assurance of waste form stability were identified which could be added to operating procedures. The judgement as to the need for (and adequacy of) the options will have to be to the NRC or another forum.

4.6 Addenda

4.6.1 Bibliography (sent to Group 4 Members before workshop)

B. S. Bowerman and B. Siskind, "Evaluation of Solidification of Decontaminated Tank 8D2 Supernatant at West Valley Demonstration Project, Staff Evaluation Memorandum" WM-3175-1, Brookhaven National Laboratory, 1988

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O.E. Ekechukwu, et al, "Pretreatment and Bed Materials for Improved Liquid Radwaste Processing, EPRI Project RP 2424-2," Waste Management '88, Tucson, AZ, 1988

A. A. Moghissi, et al, eds., Radioactive Waste Technology, American Society of Mechanical Engineers, New York, 1986

T. E. Phillips, et al, "Virginia Power Liquid Radwaste Characterization Program," Waste Management '88, Tucson, AZ, 1988

R. F. Tucker, JR., et al, "Low-Level Radwaste Solidification," EPRI-NP-2900, March, 1983

U.S. Nuclear Regulatory Commission, Branch Technical Position ETSB 11-3, "Design Guidance for Solid Radioactive Management Systems Installed in Light Water Cooled Nuclear Power Plants," NUREG-0800, Rev. 2, July, 1981

U.S. Nuclear Regulatory Commission, "Standard Review Plan, Office of Nuclear Reactor Regulation, Section 11.4, Solid Waste Management Systems," NUREG-0800, Rev. 2, July, 1981

U.S. Nuclear Regulatory Commission, "Branch Technical Position on Waste Form, Rev. 0," May, 1983

Staff of Waste Management and Decommissioning Division, "Report to the Director, Office of Nuclear Materials Safety and Safeguards, Regarding Current Status and Proposed Action for Regulation of LLW Stability," June 21, 1988

4.6.2 Additional References

Sansalone, Mary and Carino, N.J., "Detecting Delaminations in Concrete Slabs With and Without Overlays Using the Impact-Echo Method," ACI Materials Journal, Detroit, V. 86, No. 2 (1989).

Sansalone, M. and Carino, N.J., "Impact-Echo Method: Detecting Honeycombing, the Depth of Surface-Opening Cracks, and Ungrouted Ducts," Concrete International, V. 10, No. 4, pp. 38-46, Detroit (1988).

Sansalone, M. and Carino, N.J., "Laboratory and Field Studies of the Impact-Echo Method for Flaw Detection," Nondestructive Testing, ACI SP112, pp. 1-20 (1988).

4.6.3 Vendor Lists of "Bad Actors"

Chem-Nuclear Services, Inc.

LIST OF CHEMICAL CONSTITUENTS WHICH REQUIRE IDENTIFICATION

AND PRETREATMENT PRIOR TO CEMENT SOLIDIFICATION

1) Ammonia
2) Organic Acids
3) Nitrates
4) Phosphates
5) Borates
6) Chelates
7) Sulfates
8) Aromatic Oils
9) Soaps/Detergents

Westinghouse Radiological Services, Inc.

CHEMICAL INCOMPATIBILITIES WITH CEMENT SOLIDIFICATION

I. Chemicals that at ppm concentrations are known to cause problems to cement solidification operations and product acceptance and must be precluded from waste streams unless specific counteractive steps are taken.

    Benzene   Nitrates
    Toluene   Acetone
    Hexane

II. Chemicals that are known to cause problems to solidification operations and product acceptance unless characterized/quantified and appropriate formulations are used.

    Potassium Permanganate (e.g., Turco Decon
    Solution 4324-NP)
        Paint thinners
        Oils
        Boric Acid Loaded onto Bead Resin

III. Families of chemicals that should be regarded as potentially incompatible with certain wastes and solidification formulae. Plant's chemical control program and administrative procedures should be used to preclude or minimize their introduction (in uncharacterized quantities) into the waste streams.

    Organic Hydrocarbons   Decon Solutions
    Organic Solvents   Detergents
    Petroleum Products/Lubricants   Oxidizing Agents

LN Technologies Corporation

List of chemicals that have created problems with solidifications of radio-active waste in the past. Problems have only occurred when concentrations of these chemicals are unusually high. In other words, trace amounts are not a concern.

    Dry cleaning solvents from laundry facilities
    Sodium Hypochlorite
    Ammonia
    Ionic Soaps
    Oils
    Industrial Cleaners

TABLE 4.1

Compare Current Practices with Possible Additional Options
to Assure Waste Form Stability

Element to Provide Assurance	Current Practice	Option for More Assurance
Front-End Elements		
Qualification test program	* BTP tests discussed in Group 3	* BTP tests discussed in Group 3.
	* Qualify adverse chemicals (bad actors) known to be in _specific_ plant's waste	* Qualify plant-specific "bad actors." Generic "bad actor" testing not helpful.
PCP: general		* Publish Draft INEL guidelines on PCPs.
		* Guidelines can vary for difficult ("clean" vs. "dirty") wastes.
Plant chemical control program	* Focus is on each chemical's effects to primary system and safety impacts	* Adjust focus to include impacts on solidification and disposal, especially for new or changed waste streams.
PCP: Waste characterization, sampling, and batch control	* Some waste segregation ("good" plants)	* Implement segregation at all plants. NRC should endorse practice.
	* There are "clean" and "dirty" waste streams. "Dirty" wastes are more variable and not well characterized.	* Plants could devote more attention to characterizing "dirty" or poorly characterized streams.
	* Vendors provide plants with list of "bad actors"	* NRC could publish Information Notice about "bad actors."
	* Utility analyses for chemicals in wastes as directed by vendors or their experience	
	* Pretreatments for plant-specific bad actors are sometimes used	

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TABLE 4.1 (cont.)

Element to Provide Assurance	Current Practice	Option for More Assurance
Back-End Elements		
PCP: Verification Sample	* Check for free water, solid monolith, hardness with hand-held rod, other parameters during preparation	* Add quantitative tests, such as penetrometer or compressive strength.
		* Add other tests, such as immersion or monitor exotherm.
		* Archival samples.
Processing, on-site handling, shipping	* Monitor process equipment parameters	* Dip samples from liners for some BTP tests.
	* Inspect liner for free liquid and surface hardness test with stick or pipe	* Dip samples for archival samples, especially applied to less well characterized wastes.
Burial Site	* Random selection of at least 10% of all liners (SC includes dewatered wastes), test weight and "sounding" for hardness, punch holes in liner to look for liquids	* Add impact echo technique.

GENERAL SESSION
JUNE 2, 1989

Michael Tokar - NRC

The following remarks concerning the Cement Workshop are in the form of initial perceptions rather than final conclusions. Conclusions and recommendations must await further analysis and assimilation of the material covered in the working group and plenary sessions.

As noted in the opening plenary session presentation, "Introduction to the Cement Workshop," this meeting was <u>not</u> intended to be a "consensus conference" that would produce a consensus report. The meeting was instead meant to serve as a vehicle for information exchange. And yet, it is clear from the dialogue heard in the working group discussions and summary plenary sessions that there was a coming together of the views and opinions of the participants, regardless of their affiliation. Therefore, while the statements that follow represent only the perceptions of one NRC representative (M. Tokar), it is believed that they, in most cases, and except where indicated otherwise, reasonable represent the views of the workshop participants as a whole.

The first "perception" is that the Workshop was an unqualified success! Much useful information was exchanged. There were frank and open discussions between the vendor, utility, researcher, regulator, etc., representatives. The meeting also went well logistically. For example, the time periods set aside for the plenary and working group discussions seemed to be just about right. The credit for this overall success belongs to (1) the participants, who through their willing and enthusiastic support ensured that things would go well technically and (2) the NRC, NIST, and Marriott staff who, in their pre-meeting activities established the groundwork for a successful meeting and whose diligent attention during the meeting avoided the creation of any unsurmountable logistical problems.

To this observer/participant, the discussions clearly established that cement is a viable stabilization medium, from a technical standpoint, for low-level radioactive waste. That cement can be used successfully to stabilize low-level waste is undeniably true, for two reasons: (1) there is an excellent example of a qualified cement-solidified waste form in the presence of the West Valley Demonstration Project decontaminated supernatent waste; and (2) stability of the cement-solidified waste form is to a large extent a function of the concen-tration (i.e., volume fraction) of the waste ingredients in the waste form. Thus, just about any waste stream ingredient can be incorporated into a stable cement waste form if the concentrations of waste are low enough--the issue, rather, is one of commercial, not technical, viability.

To the question of whether the waste generators can (must) do a better job of characterizing their wastes prior to processing with cement, it appears that most Workshop participants would answer "yes." Characterization can be improved through (a) improvements in knowledge of process and (b) improved methodologies. The vendors have lists (provided elsewhere in this summary report) of chemicals that can adversely affect the solidification of cement. From these lists poten-tial problem waste streams that might contain the troublesome ingredients can be identified. and appropriate steps can be taken to mitigate or avoid their

deleterious effects. For those waste streams that may contain the troublesome
secondary ingredients, a variety of solutions are available, including limiting
the waste concentrations to provide added margin for assuring satisfactory long-
term performance. Other alternative or complementary approaches are addressed
below.

The central question remains of how to relate laboratory qualification testing
on simulated waste compositions to real wastes in the field. The Process Control
Program (PCP) specimens that are prepared by the waste generator/processor prior
to proceeding with solidification do not ensure that the ensuing full-scale waste
forms will possess long-term structural stability. The PCP samples simply pro-
vide some indication of whether or not the full-scale waste forms will solidify
at the desired rate (or at all). In cases where the PCP specimens do not solid-
ify properly, the waste processor may modify the PCP. Thus, waste forms can be,
and, in fact, are sometimes produced in accordance with recipes that have not
been qualified by the testing called for in the 1983 Technical Position on Waste
Form. In such cases, and in the absence of other controls or provisions, it
cannot be said that there is reasonable assurance that such waste forms will be
structurally stable for 300 years.

There is apparently a widely-shared opinion in the industry that it is not
possible to treat satisfactorily in the qualification testing all the potential
variables important to the cement solidification process (because there are
simply too many variables involved). It has, therefore, been suggested that the
only recourse is to rely on the PCP samples for confirmation that the recipes
will work. But inasmuch as the PCP samples merely show whether or not the full-
scale waste forms will solidify in an acceptable manner, some other means must
be used to obtain reasonable assurance that the waste forms will be stable as
well as solid. As noted earlier one approach that could be followed would
involve setting arbitrary upper limits on waste concentration. This would, in
an indirect fashion, provide some margin, or cushion, against the potentially
deleterious effects of secondary ingredients or chemicals. But this approach
appears not to be attractive to most waste generators or solidification system
vendors, who prefer instead to establish a compressive strength criterion sig-
nificantly higher than the current 60 psi. Thus, there appears to be a fairly
widely held opinion that, by raising the acceptance criterion to several hundred
psi from the current 60 psi, desirable reductions in waste loadings, concomitant
increases in margin to "failure", and resultant improvements in stability would
follow. In the opinion of this observer this suggestion, along with possible
improvements in waste characterization as addressed above, are particularly
worthy of further consideration. In addition, the use of archival specimens
(discussed in more detail below) should provide a further contribution to
assurance that the Part 61 requirements for structural stability will be met.

Potential improvements in waste form testing guidance were discussed by Working
Group 3. The most convenient means for providing that guidance would be through
a revision to the Technical Position on Waste Form, which was issued in May 1983.
Several good suggestions were received concerning ways to improve the Technical
Position tests and criteria. For example, some tests (such as the irradiation
tests) could be entirely eliminated while others (such as the leach tests) could
be modified for cement-solidified waste forms, and improvements can be made in
the compressive strength criteria. Guidance on specimen preparation and statis-
tical analysis (areas which are not addressed in the current Technical Position)
could also be made available. It would be desirable to implement any changes

to be made in the Technical Position as soon as possible. In that regard, this writer has established a personal target for a draft revision by the end of calendar year 1989. That target is subject to adjustment, however, based on the availability of resources and prioritization of agency work. In addition, it is not possible to predict the length of time required for NRC management review and approval of a revision to the Technical Position.

There are two additional important points to note concerning potential revisions to the Technical Position: (1) a new test, based on first-principles of material science mechanistic analysis, could, if substituted for the current indirect screening-type tests, provide direct assurance of a long-term structural stability, and (2) some decision would have to be made concerning how such revisions would be factored into the reviews of the existing docketed topical reports on cement stabilization. Though the National Laboratory representatives, in particular, appeared to favor the development of a mechanistic performance-based evaluation approach over the current process of using indirect measures (i.e., short-term "screening" tests) to obtain the necessary "reasonable assurance" of long-term structural stability, an extensive R&D program would be needed to develop the mechanistic relationships and criteria. It was estimated that 3 to 5 years might be needed to achieve useful results. That length of time might be acceptable for a situation such as exists in the high-level waste program, where commercial wastes will not be disposed of in a repository for at least another decade. However, for low-level radioactive wastes, which are currently being placed in disposal sites on a routine basis (and have been for several years), a 3 to 5 year disposal hiatus would not be tolerable. During the Workshop summary plenary sessions, several utility representatives expressed a legitimate concern about potential "constipation" that could cause a backup of waste due to an inability to dispose of the material off-site. For these reasons, it is this observer's opinion that the topical report review program should continue, with determinations of reasonable assurance of long-term structural stability made on the basis of an appropriate combination of better qualification testing (using modified versions of the current tests and criteria, as discussed earlier), improved waste characterization, implementation of more rigorous PCP recipes, and the use of archival specimens for verification examinations.

With regard to archival specimens, the NRC waste management technical staff has for quite some time held the view that an archival specimen program was a necessary part of the process of ensuring that Class B and C wastes would possess the long-term structural stability required by Part 61. The basic reason that the use of archival specimens is an important concept is that it would provide a final verification that the qualification testing, waste characterization, and PCP efforts were successful in producing a structurally stable waste form. An archival specimen program is in principle equivalent to the surveillance specimen program used for several years for reactor fuel assemblies. As noted at the Workshop final plenary session, there are several potential drawbacks associated with an archival specimen program, including concerns related to ALARA, cost, storage, specimen preparation, quality control, transportation, and management risk. However, in the final analysis, none of these areas of concern appear to this writer to present insurmountable obstacles. For example, it would be a relatively simple, safe, and inexpensive matter to prepare, as part of the Process Control Program, a few extra samples that could be set aside and checked (visually, by immersion testing, and/or compression testing) at six or twelve month intervals to determine that the samples are not degrading over time. A somewhat more complex and longer range program would involve the disposal of

surveillance specimens in assigned archival trenches set aside for such purpose at the disposal sites. The details of any archival specimen program would obviously take some time to work out, but should be developed without further delay.

In summary, the information exchanged in the Workshop, together with the information presented in the submitted topical reports and additional data being generated by the vendors, should enable the NRC staff to cut the Gordian knot that has hindered progress in this area for so long. The staff intends to work closely with the waste processing vendors, waste generators, researchers and Advisory Committee on Nuclear Waste to capitalize on the momentum that has been achieved from the Workshop and to ensure that there will be satisfactory progress leading to NRC approval of specific cement-solidified low-level waste formulations.

APPENDIX

List of Attendees

Cement Solidification of Low-Level Radioactive Waste Workshop

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