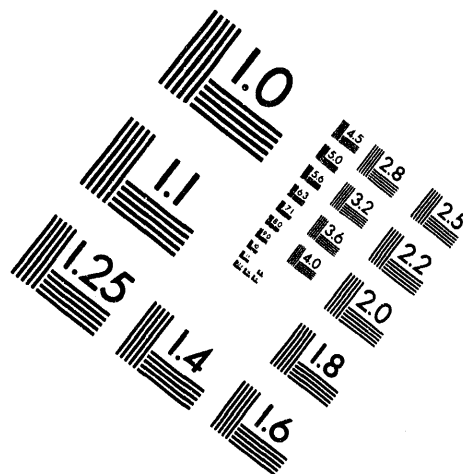


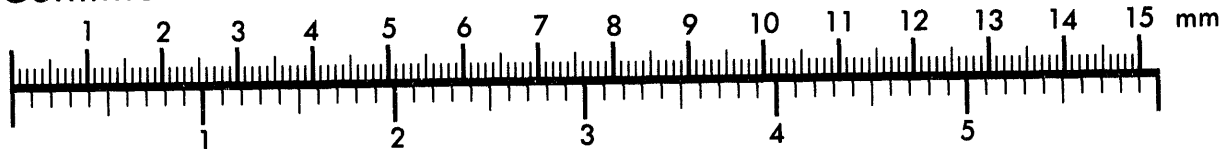
**AIM**

**Association for Information and Image Management**

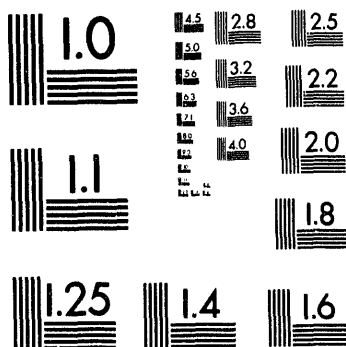
1100 Wayne Avenue, Suite 1100  
Silver Spring, Maryland 20910  
301/587-8202



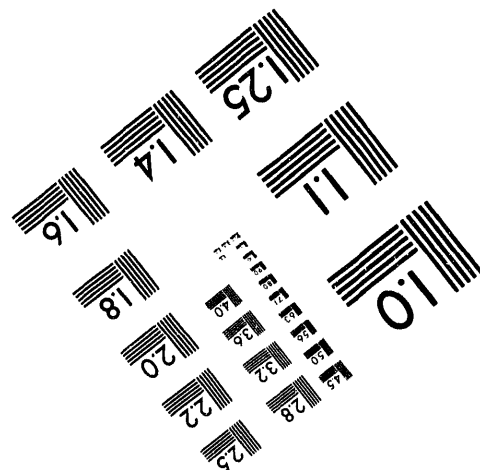
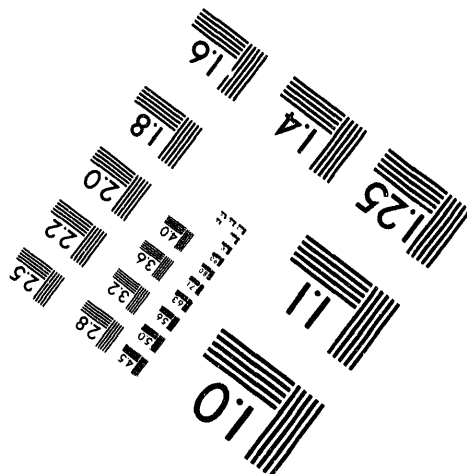
**Centimeter**



**Inches**



MANUFACTURED TO AIM STANDARDS  
BY APPLIED IMAGE, INC.



**1 of 1**

# ASSESSING MIXED WASTE TREATMENT TECHNOLOGIES

Jeanette B. Berry, Integrated Program Coordinator  
 Gary A. Bloom, Program Coordination  
 Oak Ridge National Laboratory  
 Oak Ridge, Tennessee 37831

Paul W. Hart, Ph.D.  
 Program Manager  
 U.S. Department of Energy  
 Washington, D.C. 20874

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## INTRODUCTION

The U.S. Department of Energy (DOE) is responsible for the management and treatment of its mixed low-level wastes (MLLW). As discussed earlier in this conference MLLW are regulated under both the Resource Conservation and Recovery Act and various DOE orders. During the next 5 years, DOE will manage over 1,200,000 m<sup>3</sup> of MLLW and mixed transuranic (MTRU) waste at 50 sites in 22 states (see Table I). The difference between MLLW and MTRU waste is in the concentration of elements that have a higher atomic weight than uranium. Nearly all of this waste will be located at 13 sites. More than 1400 individual mixed waste streams exist with different chemical and physical matrices containing a wide range of both hazardous and radioactive contaminants. Their containment and packaging vary widely (e.g., drums, bins, boxes, and buried waste). This heterogeneity in both packaging and waste stream constituents makes characterization difficult, which results in costly sampling and analytical procedures and increased risk to workers.

MASTER

**TABLE I**

**DOE-Managed Mixed Low-Level Waste and Mixed Transuranic Waste Volumes**

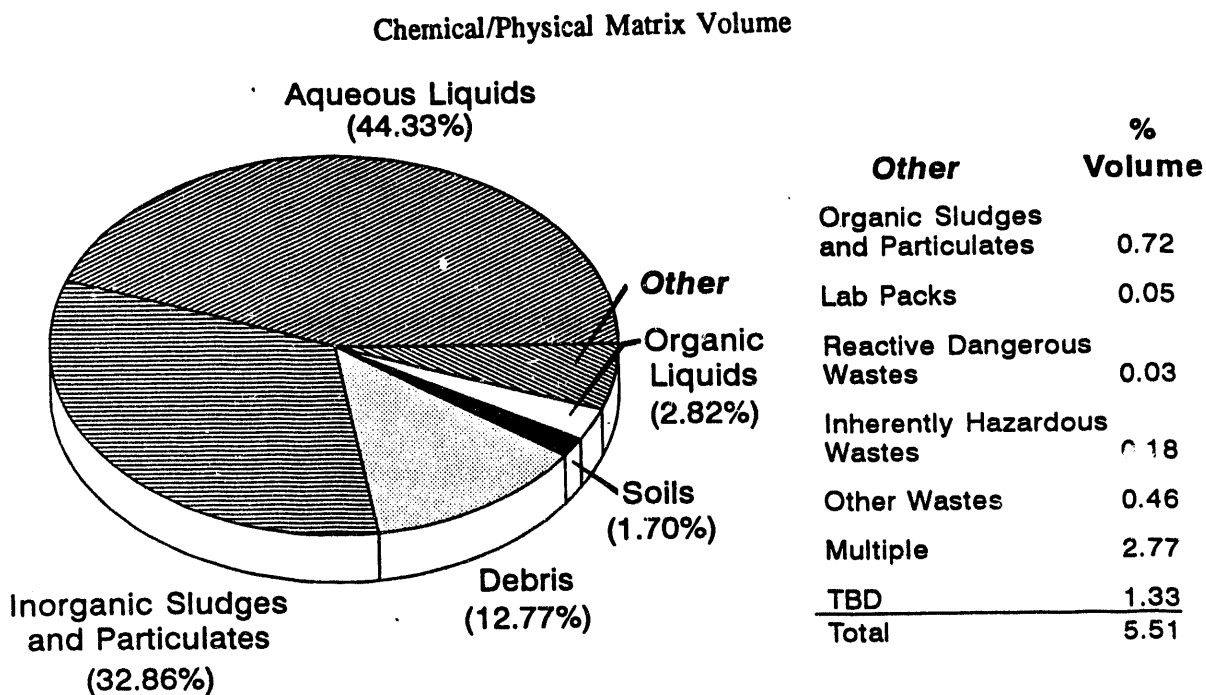
Source of Mixed Waste	Volume (m <sup>3</sup> )
<b>Current Site Inventories</b>	
Mixed Low-Level Waste	247,000
Mixed Transuranic Waste	58,000
<b>Operations Generated (Five-Year Projection)</b>	
Mixed Low-Level Waste	280,000
Mixed Transuranic Waste	2,800
<b>Environmental Restoration (Five-Year Projection)</b>	
Mixed Low-Level Waste	620,000
Mixed Transuranic Waste	300
<b>Total</b>	<b>1,208,100</b>

NOTE: Information from the Interim Mixed Waste Inventory Report

Based on radioactive characteristics, hazardous components, and physical/chemical matrices, DOE has grouped its wastes to reflect salient treatment considerations for each waste stream. These "treatability groups" relate waste streams to treatment facilities and to technology development needs [1]. Aqueous liquids include all pumpable aqueous liquids which may have total or settled solid levels as high as 40%. Organic liquids, sludges, and solids are primarily treated by incineration; however, considering the inventoried and projected quantities of organic liquids, solids, and sludges to be generated, DOE estimates that there is insufficient capacity for treating these mixed wastes to Land Disposal Restriction (LDR) standards. Inorganic sludges and solids are generally stabilized prior to disposal. Again, DOE does not have the treatment capacity to handle this treatability group. Soil and debris present a distinct problem to DOE. Other wastes include several distinct categories (e.g., laboratory packs, reactive metals, elemental mercury, elemental lead, explosives, and compressed gasses). Figure 1 illustrates the volume of each of these treatability groups stored

throughout the DOE complex.

FIGURE 1



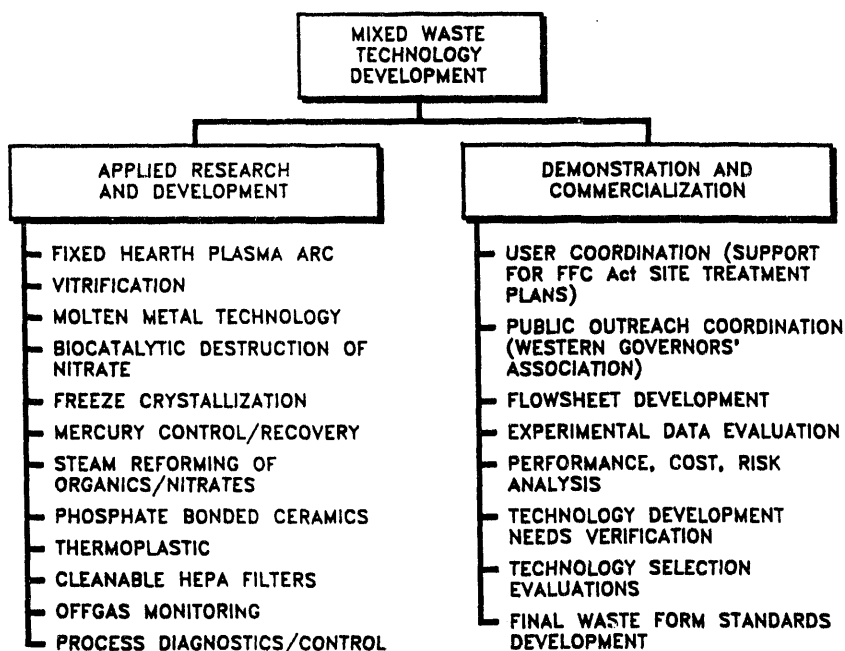
In order to successfully manage and treat these mixed wastes, DOE must adapt and develop characterization, treatment, and disposal technologies which will meet performance criteria, regulatory approvals, and public acceptance. Although technology to treat MLLW is not currently available without modification, DOE is committed to developing such treatment technologies and demonstrating them at the field scale by FY 1997.

The Office of Research and Development's Mixed Waste Integrated Program (MWIP) within the DOE Office of Environmental Management (EM), Office of Technology Development, is responsible for the development and demonstration of such technologies for MLLW and MTRU wastes. The Office of Technology Development advocates and sponsors expedited technology development and demonstrations for the treatment of MLLW. Further, appropriate public participation in the development and demonstration of technologies should be encouraged. Therefore, a two-pronged approach is required for mixed waste technology development: (1)

demonstration/commercialization – user, stakeholder, and regulator interfaces facilitate technology demonstration and support implementation in a systems context; and (2) technology development – unit operations are tested to collect data for technical evaluations (Fig. 2). Mixed waste treatment process development is unique because regulatory, stakeholder, and user requirements and needs provide the driving forces for technology selection. The Federal Facility Compliance Act of 1992 (FFCA) provides for the inclusion of stakeholders, [e.g., the Western Governor's Association (WGA), state and local governments, environmental groups, and key members of the general public] in DOE's technology development and demonstration process. Timetables for establishing site treatment plans were published in the Act. Technology selection, development, and implementation must be provided in a manner and a time frame which is acceptable to the stakeholders and which meets the requirements of the Act. Therefore, steps to support demonstration/commercialization must be clearly defined and implemented.

FIGURE 2

NO TITLE

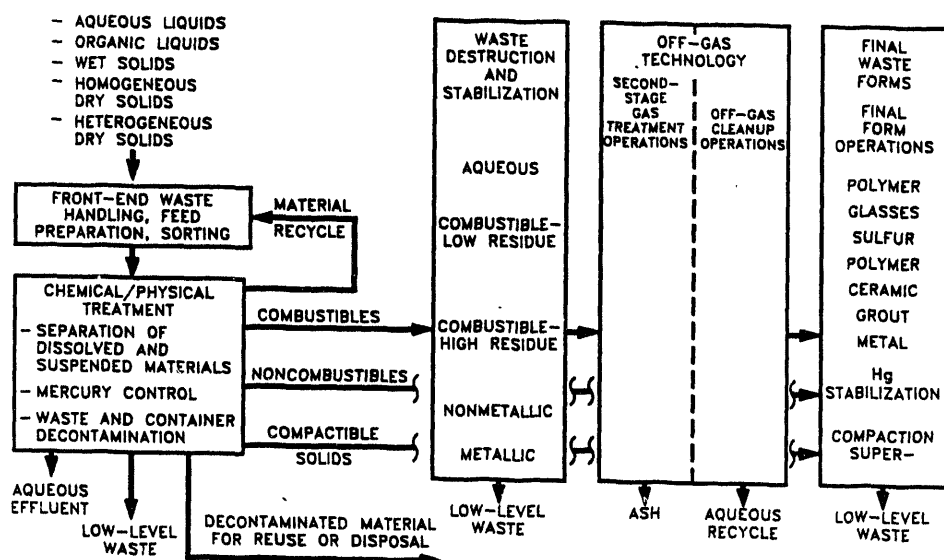


Technology development is ongoing in technical areas required to process mixed waste:

materials handling, chemical/physical treatment, waste destruction, off-gas treatment, final forms, and process monitoring/control (Fig. 3).

FIGURE 3

Technical Areas Cover Steps Required in Mixed Waste Treatment Train



Expediting the development of a suite of technologies to process heterogeneous waste is necessary to meet FFC Act deadlines. One robust process is the fixed-hearth plasma-arc process that is being developed to treat a wide variety of contaminated materials with minimal characterization. Additional processes include steam reforming and a catalytic extraction process that uses molten metal technology. Both processes are being demonstrated by the commercial developer of the technology. Advanced off-gas systems are also being developed.

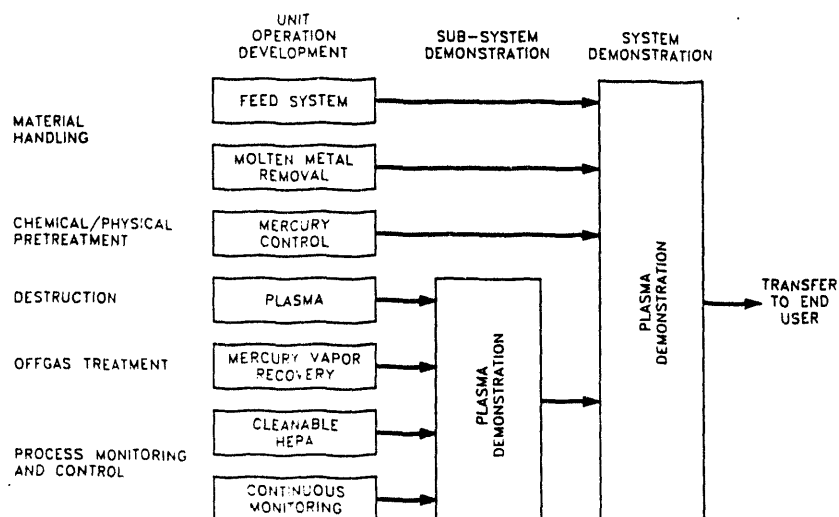
Vitrification technologies are being demonstrated for the treatment of homogeneous wastes such as incinerator ash and sludge. An alternative to conventional evaporation for liquid removal—freeze crystallization—is being investigated. Since mercury is present in numerous waste streams, mercury-removal technologies are being developed.

Moving technologies from basic research and development to system demonstration takes several steps. Unit operations are developed at the bench-scale where basic chemical and kinetic data

Are collected using both surrogate and actual waste. Unit operations are then combined into subsystems where mass and energy balance data are refined. The results of the sub-system demonstrations and unit operational data are combined to support demonstration of a complete system. Figure 4 illustrates this process for development of the fixed-hearth plasma arc process.

FIGURE 4

Technology Development Progresses From Demonstrating Unit Operations to System Demonstration



## MWIP DEMONSTRATION/COMMERCIALIZATION INITIATIVES

### Stakeholder Participation

Public and regulator participation in development of emerging and/or innovative technologies is necessary to obtain acceptance. This plays a major role in specific technologies being selected for implementation. Consensus building between numerous stakeholders is the preferred method of determining those technologies that will be developed and deployed. The need for public acceptance of emerging technologies is being addressed by Western Governors' Association-Development On-Site Innovative Technologies Committee's Mixed Waste Working Group. Technology demonstrations, funded by DOE, were identified by the committee because they appear to have a favorable climate for innovation (e.g., committed regulatory them, willing site manager, interested local stakeholder group). Those demonstrations relevant to mixed waste treatment are:



- Plasma Hearth Process
- Minimum Additive Waste Stabilization
- Thermal Desorption
- Two-stage Advanced Oxidation/Reduction Unit
- Microwave Solidification

Incorporating the interests and needs of regulators and the public is accomplished by initiating the permitting process during early stages of technology development. This stakeholder involvement is expected to ease implementation of innovative and emerging technologies.

Development of waste form performance criteria and standardized test methodologies is critical to the resolution of mixed waste problems. Neither disposal criteria nor uniform test methods have been established. Consensus of the technical community, regulators, and stakeholders is necessary to establish these criteria. As the technical arm of EM addressing mixed waste, MWIP has documented test methods and is proposing revisions to the DOE performance assessment methodology [2]. An objective of MWIP is that these data will be used in establishing waste acceptance criteria for disposal.

#### **Systems Analysis**

The cost of treating and disposing of MLLW and MTRU waste is estimated in the multibillion dollar range. This cost provides incentives to develop versatile treatment capabilities that do not require excessive characterization costs for safe and effective operations and that can be standardized to assist with regulatory and public acceptance. OWM and the Office of Environmental Restoration, are responsible for treating mixed waste and for selecting treatment technologies. A consensus has not been reached regarding the acceptability of existing, proven technologies and their effective implementation in systems to treat a wide diversity of DOE waste streams. Incentives for use of evolving and/or innovative technology are dependent upon the potential for reduction in life-cycle cost, reduction in risk, and improved performance.

System analysis, founded on technical rationale, should identify deficiencies and gaps in present technologies that prevent fast and effective implementation of waste treatment systems.

Baseline flowsheets, developed by the Office of Waste Management's Mixed Waste Treatment Project, [3] have served as the basis for technology development needs identification and selection of projects for development. This has resulted in focusing technology development activities on overcoming major obstacles to progress in mixed waste treatment to ensure that treatment leads to disposal. Major needs include (1) robust treatment processes, (2) enhanced waste forms to facilitate disposal, and (3) a systems approach to the mixed waste problem to ensure development of technology with improved cost/benefit over existing technologies.

One component of the systems analysis is to ensure that data are comparable when they are collected from experiments conducted at various locations by researchers with diverse backgrounds. To this end, surrogate formulations have been devised that represent major categories of waste throughout the DOE complex [4,5,6]. For more waste stream-specific applications, stimulants have been developed [7]. An additional factor that contributes to data comparability is the specification of the parameters of importance for which data must be collected [8,9].

### **Multicriteria Analysis**

A multicriteria analysis has been developed as an instrument for a systematic evaluation of distinct alternative technologies. The evaluation of alternative technologies for the treatment of mixed waste requires a logical ranking procedure that accounts for nontraditional evaluation criteria (such as social cost-benefit analysis and cost-effectiveness analysis) and regulatory and public acceptability, as well as traditional monetary-based criteria [10].

### **Performance Analysis**

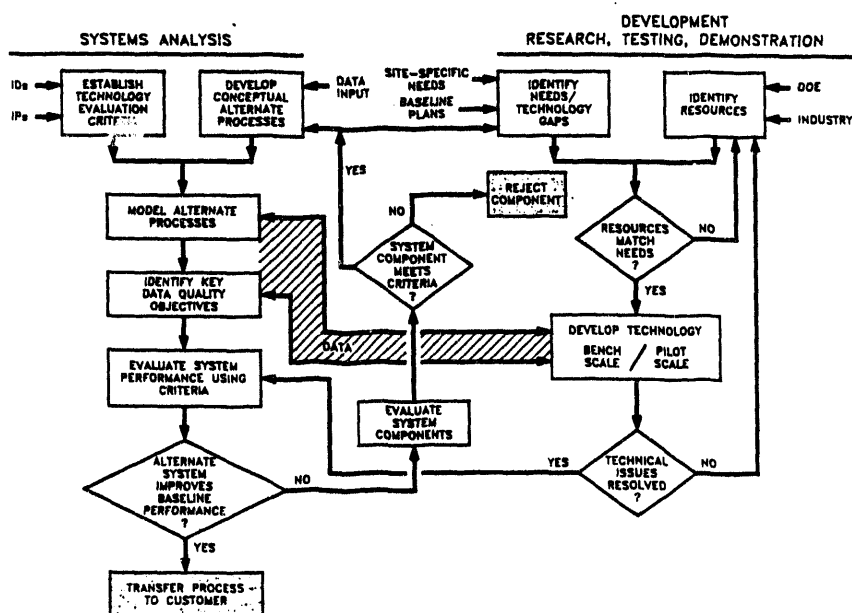
Methodologies for systems analysis are concerned with interactions among units within a larger system and how the units should be established and organized so that the whole system operates in the best possible manner. Systems analysis is a formal method for optimizing the interconnections and compatibility of system components, the effect of one component upon the other, the objectives of the whole, the relationship of the system to its users, and the system's economic feasibility [11].

Results of systems analyses conducted under MWIP have been documented [12,13,].

The integration of unit operations consists of developing flowsheets for treatment trains for individual or groups of waste streams. This is an iterative process as data from demonstrations become available. After identifying needs and resources, the alternate process is modeled and developed, and information from trial tests is used to improve the performance models. The treatment technology is then evaluated using performance analysis to determine if the technology improves baseline performance. If the baseline performance is improved, then the technology is transferred to the customer; if the baseline performance is not improved, then the system components are reevaluated (Fig. 5).

FIGURE 5

### The Potential for a Technology to Succeed is Continuously Evaluated

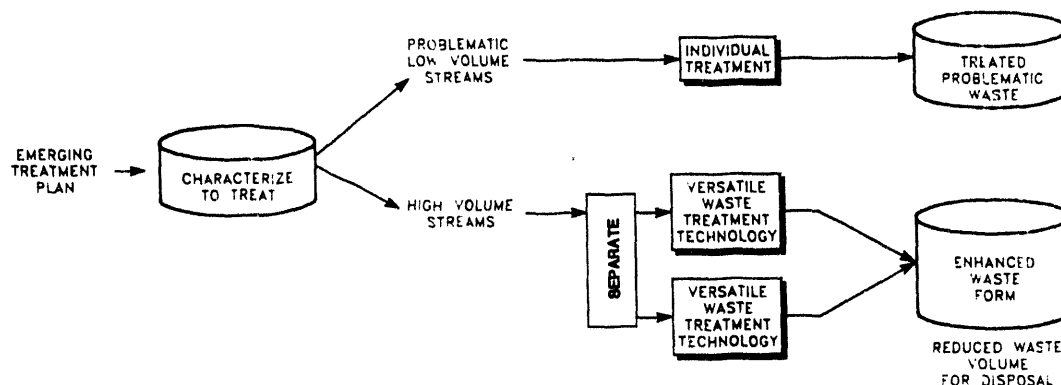


### MWIP TECHNOLOGY DEVELOPMENT INITIATIVES

Analysis of the mixed waste inventory makes clear that the majority of the waste is heterogeneous and will require robust treatment processes. Reduced characterization with production of enhanced waste form(s) are additional benefits of robust treatment processes.

FIGURE 6

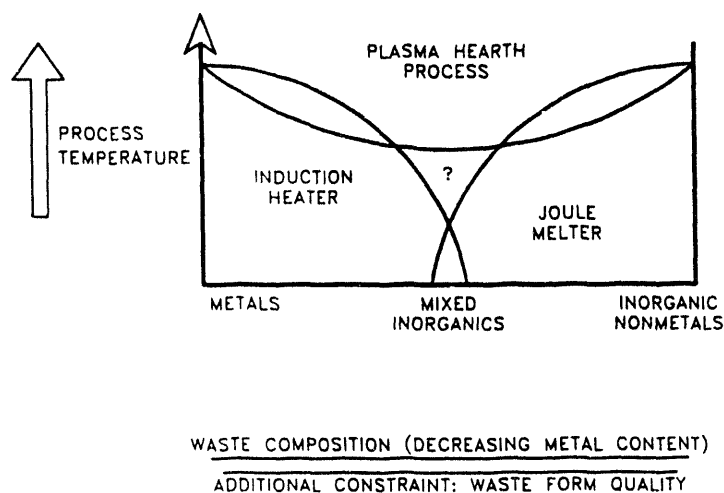
Flexible Treatment Processes that Produce Enhanced Waste Forms are Emphasized



Process envelopes are being defined for robust treatment processes to ensure that the range of waste matrices can be treated.

FIGURE 7

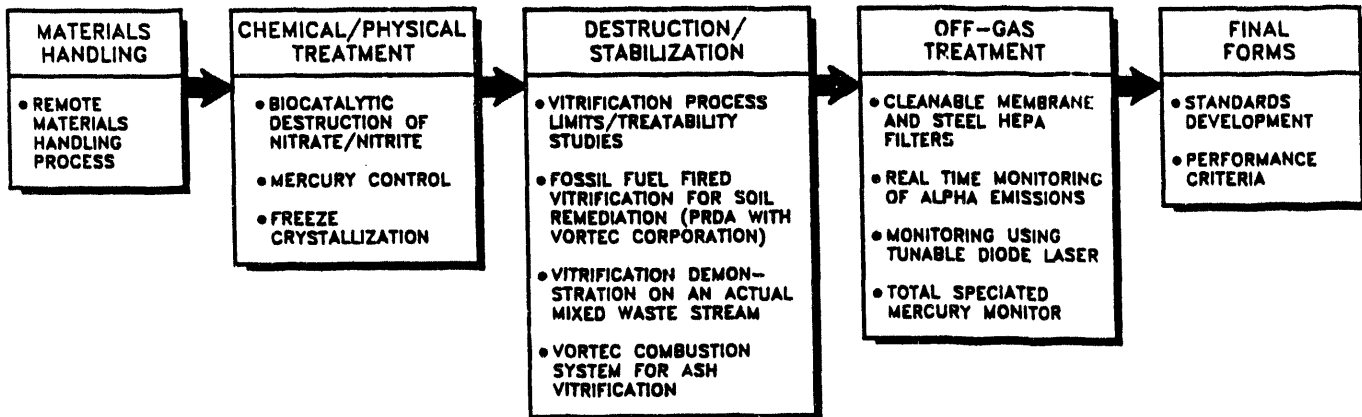
Process Envelopes are Being Defined for Versatile Thermal Treatment Systems



Systems using robust treatment technologies are being developed [14,15]. The first such system includes vitrification as the waste stabilization unit operation.

FIGURE 8

Development of Vitrification Treatment System



CHEMICAL/PHYSICAL TREATMENT

Waste streams must be treated prior to vitrification to ensure efficient downstream processing. Primary separations are (1) removal of suspended and dissolved solids from aqueous organic streams; (2) separation of water from organic liquids; (3) treatment of wet and dry solids; (4) mercury removal and control; (5) decontamination of waste classified as debris [16]. Potential problem areas include processing chlorides, nitrates, high sulfur, phosphorus, and chromium-bearing salts.

Technologies being developed in the chemical/physical treatment technical area are freeze crystallization, biocatalytic destruction of nitrate and nitrite, and mercury control and removal. These technologies have been identified as alternatives to the OWM treatment baseline.

Freeze Crystallization

Freeze crystallization is an alternative to the aqueous treatment baseline because it separates pure solvents such as water from dissolved solids, undissolved solids, and organic contaminants. The OWM baseline includes primary treatment by activated carbon, secondary treatment by membrane separation or evaporation, and tertiary treatment by a specialized, final polishing process dependent upon specific ions in the feed [17]. Freeze crystallization has significantly lower operating costs.

The process operates at low temperatures keeping volatile organics from vaporizing, thereby minimizing the need for off-gas systems.

The process separates water from solutions by cooling the solution until ice crystals begin to form. Crystals can be formed by two different methods of crystallization: direct contact and indirect contact. Various solutes form different crystals that can be separated from the solution by gravity. In most waste applications, the solvent is water, and ice crystals are less dense than the solutions; therefore gravimetric separation is easy.

### **Biocatalytic Destruction of Nitrate**

Nitrate-containing aqueous mixed wastes with high concentrations of either sodium nitrate or nitric acid are produced or stored at various DOE facilities. Nitrates in the waste will generally increase the volume or reduce the integrity of all forms. Nitrate destruction prior to solidification of waste would therefore be beneficial [18]. Several nitrate-destruction technologies are being investigated by DOE, each having advantages and disadvantages. Biocatalytic destruction of nitrate to nitrite to  $N_2$  and  $H_2O$  is being investigated to prove the validity of using immobilized reductase enzymes coupled with biphasic partitioning. Immobilizing reductase enzymes on a solid support results in large specific catalytic activity without the need for additional chemical reagents or the production of secondary waste streams. An aqueous biphasic system of wastewater and immiscible liquid phase in contact with the enzymes will be used to protect the enzymes from excessive concentrations of electrolytes, especially  $H^+$  and  $OH^-$ , which would result in enzyme deactivation. The reducing equivalents are provided by a low-voltage current, which transfers electrons from the cathode to the enzymes via an electron transfer dye.

The biocatalytic destruction of nitrate to nitrite focuses on demonstrating immobilization techniques to retain enzyme activity. Proof-of-principle research will provide data to estimate the reactor throughput and stability towards varying feeds. If the studies are successful, then the researchers will proceed to immobilize additional enzyme systems necessary to reduce nitrate directly

to  $N_2$  and  $H_2O$  [19].

### **Mercury Removal**

Mercury-containing mixed wastes occur in a number of physical forms, such as aqueous and organic liquids and combustible and noncombustible solids. The current U.S. Environmental Protection Agency (EPA) treatment standard of 0.03 mg/L is based on the performance of sulfide precipitation for wastewater and retorting/roasting for nonwastewater [20]. The MWIP Mercury Control task is developing two solids-leaching technologies for an alternative to thermal treatment of noncombustible solids and aqueous sludges, as well as two methods for mercury removal from aqueous liquids.

Acid leaching for noncombustible solids and aqueous sludges are being investigated to separate mercury from solids into liquid or gas from which mercury can then be concentrated. Acid leaching may be the preferred technology for highly insoluble matrices such as glass or plastics. Researchers will also investigate a process developed by General Electric Corporation that contacts the mercury-bearing mixed waste with  $KI/I_2$  solution to form soluble mercury iodide complexes that are precipitated in the form of metallic mercury, followed by an electrolytic membrane process for iodine recovery and recycle. This process was tested on leach solutions from mercury-containing soil and was the only process to achieve a satisfactory level of decontamination [20].

Mercury removal from aqueous streams by sorbents and ion exchange materials will also be investigated. A commercially available activated carbon impregnated with sulfur has been shown to have a high equilibrium distribution coefficient and high capacity for mercury. Kinetic uptake data are being gathered, and column breakthrough experiments are being conducted to provide design data.

The Office of Technology Development's Efficient Separations Integrated Program is sponsoring a collaboration between 3M Company, IBC Advanced Technologies, Inc., and Pacific Northwest Laboratories to develop membrane systems that will selectively remove various species including mercury from DOE wastes. IBC has developed a method of making highly selective, non-

ion exchange, organic ligands chemically bonded to solid supports such as silica particles. A 3M method has been developed for incorporating these particles into matrices, resulting in membranes that are highly porous, to afford very high flow rates [21]. This membrane has the potential for better separations than packed columns in a more compact apparatus [20]. Mercury removal efficiencies will be studied.

## DESTRUCTION/STABILIZATION

Grouting is a commonly used process for stabilization of waste. However, the ultimate disposition of grouted waste is highly uncertain due to the lack of disposal requirements or disposal sites. The volume increase associated with grouting conflicts with waste minimization policies and makes the final product costly to store or dispose of. A viable alternative to waste grouting (especially sludges, soils, ashes, filter aids, and resins) is vitrification. Glass waste forms are normally obtained by mixing one or more waste streams containing radioactive and hazardous inorganic chemical compounds with glass-forming materials and melting these materials during a high-temperature thermal process. Glasses formed at  $\sim 1,100^{\circ}\text{C}$  are produced by melting materials and cooling the molten liquid to form a solid without crystallization.

Thermal vitrification resulting in a glass final waste form can be accomplished in a variety of ways. Vitrification processes include fossil-fuel combustion, electric heating (joule), plasma arc melting, in situ vitrification, and induction and microwave heating [22].

Building on in-depth data generated for high-level waste vitrification has contributed to the success of glass formulations, and bench-scale and pilot-scale experiments. Typically glass formulations consist of (1) calcia-alumino-silicate glass formers processed at high temperatures (refractory lined furnaces) resulting in high waste loadings ( $\sim 50$  wt%); and (2) borosilicate glass formers processed at lower temperatures (metal alloy furnaces) resulting in lower waste loadings. Significant volume reduction is possible while producing a very stable waste form — a glass matrix.



Glass formulation tests for surrogate wastewaters and incinerator ashes using surrogate wastes have been successfully completed. Sample data are shown in Table II.

**TABLE II**  
**Surrogate Oak Ridge West End Treatment Facility Test**  
**Results Using CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> Glasses.**

RCRA Metal	Surrogate Feed Concentration (ppm)	TCLP Limit (ppm)	TCLP Results Waste Loading (wt%)	
			45	50
Ba	600	100.0	pass	pass
Cd	54	1.0	pass	pass
Cr	470	5.0	pass	pass
Ni	1,300	0.32	pass	0.448
Pb	280	5.0	pass	pass

Tests have been conducted using pilot-scale vitrifiers to obtain operational data. For example, a vitrification demonstration of surrogate incinerator ash was completed in December 1993 [22]. Tests of actual waste streams using a pilot-scale joule-heated ceramic melter are scheduled for FY 1994. Demonstrations of a field-scale (1000kg) mobile melter using actual wastewater sludge and/or incinerator ash are scheduled for completion during FY 1995.

**FIGURE 9**

**Vitrification Process Development**

	FY 1994	FY 1995	FY 1996	FY 1997
NONRADIOACTIVE TESTING AT CLEMSON UNIVERSITY				
INITIAL TEST PHASE PROCESS LIMITS	██████████			
SUPPORT RADIOACTIVE OPERATIONS		██████████		
BENCH-SCALE RADIOACTIVE TESTING (CRADA WITH SEG AND STIRRMELTER)				
DESIGN SYSTEM	██████████			
RADIOACTIVE TESTING		██████████		
FIELD-SCALE RADIOACTIVE TESTING (ASH VITRIFICATION CRADA WITH SEG AND ENVHCO)				
SYSTEM DESIGN	██████████	██████████		
TESTING		██████████	██████████	
FIELD-SCALE RADIOACTIVE TESTING (MODULAR SYSTEM)				
SYSTEM DESIGN	██████████	██████████	██████████	
TESTING			██████████	
FIELD-SCALE RADIOACTIVE TESTING (SOLID WASTE VITRIFICATION)				
			██████████	

9

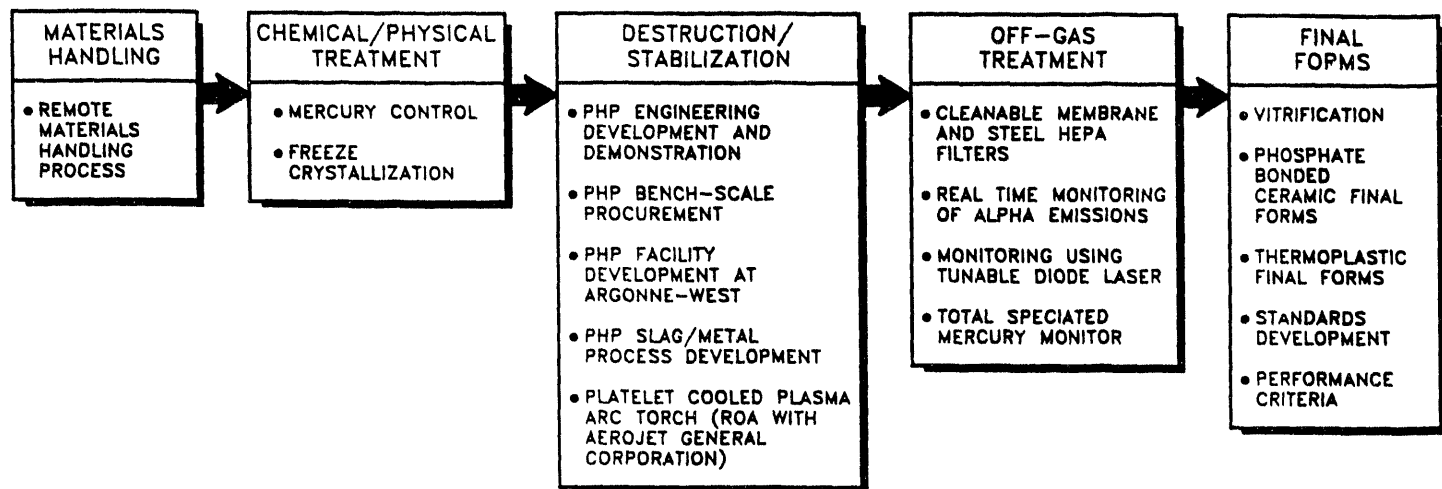
Data will be available to design and support the operation of full-scale units. These data will include the limits of vitrification equipment for destruction of some RCRA organic constituents [23,24,25,26,27].

#### Fixed-Hearth Plasma Arc Furnace

Another robust treatment process includes a fixed-hearth plasma arc furnace as the waste stabilization unit operation.

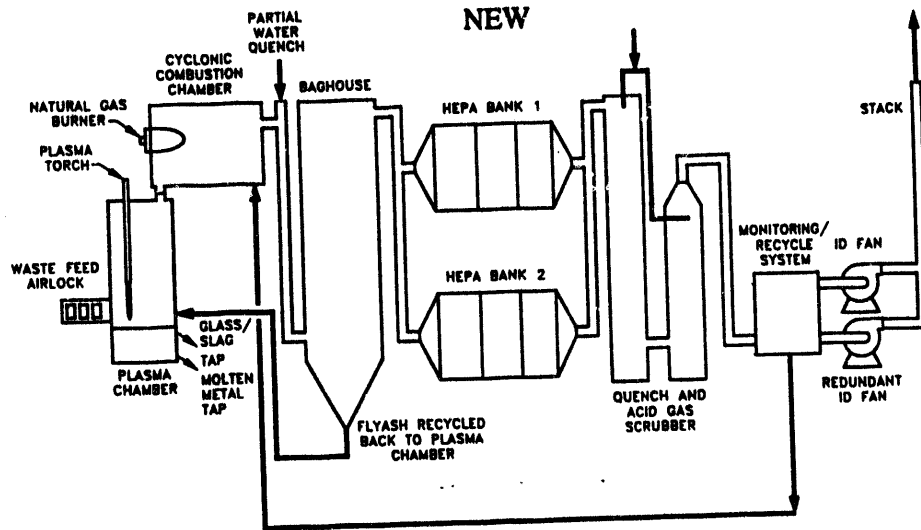
FIGURE 10

#### Development of Plasma Treatment System



Incineration is applicable for treatment of many mixed waste streams, but it has limited public acceptance. Other waste destruction technologies have been evaluated [28]. The fixed-hearth plasma-arc furnace is being demonstrated using a variety of mixed wastes [29,30]. This process offers benefits of direct production of enhanced final waste forms.

FIGURE 11



The process also has potentially reduced waste feed characterization, potentially reduced off-gas volumes, and the ability to treat a broader array of waste streams.

FIGURE 12

NO TITLE

	FY 1994	FY 1995	FY 1996	FY 1997
NONRADIOACTIVE TESTING				
PROOF-OF-PRINCIPLE TESTS	■			
DESIGN PILOT-SCALE SYSTEM TESTING	■	■		
BENCH-SCALE RADIOACTIVE TESTING				
DESIGN SYSTEM	■	■		
RADIOACTIVE TESTING		■		
FIELD-SCALE RADIOACTIVE TESTING				
DESIGN SYSTEM	■	■	■	
COMPLIANCE TESTING				■
INITIAL WASTE OPERATIONS				■

The process, designed to accept unopened/unsorted drummed wastes, recently underwent a series of surrogate tests. The principal objectives were to establish the treatability of priority mixed waste streams and to generate off-gas composition data to aid in off-gas component selection and design.

Three simulated mixed waste types — an organic sludge, an inorganic sludge, and a heterogeneous combustible debris (wood, paper, rubber, steel, etc.) — were spiked with hazardous components (heavy metals and organics) and radionuclide surrogates. A total of six tests, two replicates for each waste type, were successfully completed.

Preliminary results indicate that all the tests were very successful. All test materials were converted to a dense, vitrified monolith that is expected to test favorably for leach resistance using the toxicity characteristic leaching procedure and the product consistency test. Off-gas samples are currently being analyzed for particulate loading, particle-size distribution, and total metals content at the secondary stage outlet (prior to off-gas equipment) and for particulate loading, total metals content, HCl, and organics destruction at the off-gas system outlet (stack).

Table III  
TCLP Results — Slag

	Leach Rate (mg/l)					Limit
	SI	1&2	3	5	6	
Chromium	0.06	0.13	0.44	<0.05	<0.05	5.0
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	5.0

Total Leaching Potential (mg/l)					
Chromium	2200	300	900	34	43
Lead	1.7	4.1	0.60	0.35	0.45

### Thermoplastic Encapsulation

The thermoplastic encapsulation process can be effective for treating chloride salts (concentrates and dewatered salt cakes), secondary chloride streams (resulting from the thermal destruction of halogenated organics), mercury wastes (liquid mercury-contaminated solids) and tritium wastes (liquid and contaminated solids) [31]. The thermoplastic encapsulation processes being

developed involve polyethylene and sulfur polymer cement (SPC). Polyethylene has been successfully loaded with nitrates in the range of 5 - 70 wt %. Polyethylene loaded with 60 wt % sodium nitrate has shown that leaching of criteria metals is well within the EPA concentration by the Extraction Procedure and Toxicity Characteristic Leaching Procedure. Polyethylene has met the Nuclear Regulatory Commission criteria for compressive strength, radiation stability, thermal stability, and biodegradation with various simulated wastes [2].

SPC is an encapsulating waste-immobilization material. The wastes are encapsulated in the sulfur matrix with the exception of a few sulfide-forming metals [37]. SPC has a high mechanical strength in a short period of time, high resistance to many corrosive environments, and low porosity [32]. One restriction of SPC is that the prospective waste must contain less than 1% water. The promising characteristics of strength and resistance to corrosion, along with ability of the material to meet the criteria for radiation stability, compressive strength, and the EPA leachability tests, make this a promising final waste form [31].

## **OFF-GAS TREATMENT**

Off-gas systems are commercially available for particulate capture, destruction of products of incomplete combustion, and abatement of nitrogen oxides. However, improvements in off-gas treatment are needed including continuous monitoring, cleanable high-efficiency particulate air filters, and methods to capture mercury [33].

### **Continuous Monitoring Using Tunable Diode Laser**

This project will develop and demonstrate near-infrared tunable diode laser (TDL) spectroscopy [34] as a continuous monitor for trace amounts of toxic air species in the effluent gases from DOE hazardous and mixed-waste treatment processes. The method detects molecular gas-phase species by optical absorption using vibrational transitions in the near-infrared region. Initial efforts will determine the spectroscopic, optical, and electronic specifications for TDL instrumentation for

target molecular species. Laboratory research will identify the optimum absorption lines for detectability, which lie in the laser tuning range and are free from spectral interference from other molecular species that may be present in the waste stream. Differential optical absorption by trace species will be enhanced using wavelength or frequency modulation, as well as phase-sensitive detection.

Principle benefits of near-infrared TDL spectroscopy for waste-stream monitoring applications are (1) low-cost optical and electronic hardware for trace detection limits, (2) physically robust components that do not require cryogenic temperature control, (3) unambiguous identification of individual gas-phase molecular species, (4) rapid data acquisition and analysis for process control, and (5) the possibility of remote and in situ sampling.

#### **Continuous Monitor to Measure Total, Elemental, and Speciated Mercury**

This project will develop and demonstrate an instrument system to continuously measure total, elemental, and speciated mercury in effluent from DOE waste treatment units [35]. The principle objectives of the program are to use a commercially available elemental mercury analyzer in conjunction with a technique to convert speciated mercury into elemental mercury, and then use difference measurements to determine total, elemental, and speciated mercury. Techniques are being developed to improve the sensitivity of existing commercial elemental mercury analyzers, which are based on uv absorption; sensitivity is primarily a function of path length. A multipath cell is being developed by selecting a mirror coating that does not react with Hg (gold, a typical mirror coating, does react with Hg). The project will be successful if mercury measurements can be demonstrated at or below 0.1 parts per billion (by volume).

#### **Real-Time Monitor for Airborne Alpha Emissions**

The Large Volume Flow Thru Detector System (LVFTDS) provides real-time, on-line measurement of alpha activity from elements such as Pu, U, and Am at picocuries per liter levels. The LVFTDS uses parallel plates of scintillating plastic fabricated such that the entire stack gas

stream flows directly through the interplate volume. Light from the scintillations produced by the alpha particles striking the plates is collected and processed to determine the concentration of alpha-emitting radionuclides present in the air.

The detector consists of a large array of thin scintillating plates, aligned parallel to the flow of gas, arranged such that an alpha particle generated by decay anywhere in the active region of the detector has a high probability of striking a plate [36]. If the alpha particle strikes the plate with enough energy, a light pulse is produced and can be collected, converted to an electrical pulse, and processed.

#### **Cleanable High-Efficiency Particulate Air (HEPA) Filter**

Inorganic membrane technology will be used to fabricate long-life metal filter elements that will meet HEPA requirements [37]. The inorganic membrane technology has been used to produce porous materials from a wide variety of metals and ceramics. Tightly controlled pore-size distributions have been demonstrated over a range of mean pore sizes from about 20  $\mu\text{m}$  down to about 0.001  $\mu\text{m}$ . The porous filter elements will have pore diameters of about 0.25- $\mu\text{m}$  to provide surface filtration and will have complete surface capture of particles with diameters of 0.3  $\mu\text{m}$  or larger. Using filter elements with 0.25- $\mu\text{m}$  diameter pores, particles with a diameter of 0.3  $\mu\text{m}$  or larger cannot penetrate into the interior of the filter. As particles collect on the outer surface of the filter, a filter cake of these particles will be formed on the filter element. This collection of particulate will not reduce the pore size of the filter. Because the filter cake on the surface tends to form a relatively high void fraction cake, it will have a substantially smaller effect on permeability, and the filter can operate for longer periods of time before an increase in pressure drop. Because the velocity of the particles approaching the filter surface is small, the particles will form a very low density filter cake at the outer surface of the filter. The low density filter cake can be more easily removed or cleaned than if the particles are collected within the interior of the filter (as occurs with a depth filter). The filter will be cleaned periodically when the pressure drop across the filter reaches a

predetermined value. This cleaning will be accomplished by techniques such as vibration or reverse air pulsing.

#### **Cleanable Steel HEPA Filters**

The present air-cleaning technology is based on HEPA filters made from glass fiber media held together by glue. These filters do not have sufficient reliability for use in the off-gas treatment system. The filters may be destroyed by high temperature, moisture, or over-pressure conditions. In addition, glass HEPA filters cannot be cleaned, and recovery of radioactive dust is not possible without destroying the filter.

This project will demonstrate that the steel HEPA filter made with 0.5- $\mu$ m steel fibers meets both efficiency and pressure drop requirements for HEPA filters [38]. Steel fibers with a 0.5- $\mu$ m size will be sintered into a filter mat and configured into a single element of a full-scale HEPA. A filter will be fabricated, and the efficiency and pressure drop will be measured.

#### **Control and Recovery of Vapor-Phase Mercury**

A patented technology which uses a thinly gold-plated, regenerable ceramic filter to capture vapor-phase mercury and particulate will be developed and demonstrated [39]. This filter relies on the well-proven amalgamation process to separate mercury from the off-gas waste stream. The thinly gold-plated porous material backed by a ceramic filter captures vapor-phase mercury and particulate.

Mercury readily dissolves in many metals, including gold, to form a solution in mercury. This process of amalgamation has been used for several hundred years to purify gold ores. Amalgamation is a surface phenomenon, and therefore the gold layer can be extremely thin (only a few atomic layers). The gold releases the mercury when heated to approximately 350°C, thus allowing regeneration of the gold. The mercury is then collected in a nitrogen or air stream and subsequently condensed and collected as a liquid metal. The ceramic filter on which the gold-plated porous media is supported will be a commercially available ceramic filter membrane. Two candidates of the porous support material are activated carbons and sintered metals.



## **CONCLUSION**

DOE faces major technical challenges in the management of low-level radioactively contaminated mixed waste. Several conflicting regulations and lack of definitive mixed waste treatment standards hamper implementation of mixed waste treatment technologies. Disposal capacity for mixed waste is also expensive and severely limited. DOE now spends millions of dollars annually to store mixed waste because of the lack of accepted treatment technology and disposal capacity. Currently available waste management practices require extensive, and hence expensive, waste characterization before treatment. Therefore, DOE must pursue technology that leads to better and less expensive characterization, retrieval, handling, treatment, and disposal of mixed waste.

Selection of technologies that are acceptable and have improved cost/benefit over existing technologies will be accomplished by using the following approach:

- teaming with the customers in EM to identify, develop, and implement needed technology;
- focusing technology development activities on major problems such as heterogeneous waste destruction and homogeneous waste stabilization;
- involving industry in developing and implementing solutions including both technology transfer to the Department and technology transfer from DOE to the private sector;
- enhancing mechanisms for regulator and stakeholder involvement; and
- enhancing mechanisms for commercializing technologies and systems.

## **REFERENCES**

1. "U.S. Department of Energy Interim Mixed Waste Inventory Report: Waste Stream Treatment Capacities and Technologies, Vol. I - Overview," DOE/NBM-1100 (April 1993).
2. J. L. MAYBERRY, L. M. DEWITT, and the Final Waste Forms Working Group, "Technical Area Status Report for Low-Level Mixed Waste Final Waste Forms," DOE/MWIP-3 (August 1993).
3. T. K. THOMPSON, "Mixed Waste Treatment Project, Functional and Operating Requirements for an Integrated Facility," Los Alamos National Laboratory, New Mexico (August 30, 1992).
4. J. A. D. STOCKDALE, W. D. BOSTICK, and D. P. HOFFMANN, "Surrogate Formulation for Thermal Treatment of Low Level Mixed Waste: Part I -- Radiological Surrogate," DOE/MWIP-15 (September 29, 1993).
5. W. D. BOSTICK, et al., "Surrogate Formulation for Thermal Treatment of Low Level Mixed

Waste: Part II – Selected Mixed Waste Treatment Project Waste Streams," DOE/MWIP-16 (September 30, 1993).

6. J. M. CHAING, et al., "Surrogate Formulation for Thermal Treatment of Low Level Mixed Waste: Part III – Plasma Hearth Process Testing," DOE/MWIP-17 (September 29, 1993).

7. W. D. BOSTICK, et al., "Surrogate Formulation for Thermal Treatment of Low Level Mixed Waste: Part IV – Waste Water Treatment Sludges," DOE/MWIP-18 (September 29, 1993).

8. D. P. HOFFMANN, et al., "Guidelines for Benchmarking Thermal Treatment Systems for Low Level Waste," DOE/MWIP-19 (December 21, 1993).

9. D. P. HOFFMANN, et al., "Data Quality Objectives: Evaluation of Thermal Treatment Processes," to be published as DOE/MWIP-22 (December 21, 1993).

10. J. J. FERRADA and J. B. BERRY, "Multicriteria Decision Methodology for Selecting Technical Alternatives in the Mixed Waste Integrated Program," ORNL/TM-12480, Oak Ridge National Laboratory, Oak Ridge, Tenn. (November 1993).

11. J. J. FERRADA and J. B. BERRY, "MWIP Performance Systems Analysis," DOE/MWIP-23 (January 1994).

12. M. AYCOCK, et al., "Preliminary Hazards Analysis Plasma Hearth Process," DOE/MWIP-13 (November 1993)

13. P. BARNES-SMITH and S. BOOTH, "Mixed Waste Integrated Program Life Cycle Cost Analysis of Plasma Arc Furnace," DOE/MWIP-25 (October 1993).

14. J. B. BERRY, G. A. BLOOM, and D. J. KUCHYNKA, "Development and Demonstration of Treatment Technologies for the Processing of U.S. Department of Energy Mixed Waste," Waste Management '94, Tucson, Arizona (February 27 - March 3, 1994).

15. FY94 Program Summary Book, Ref. # on book - DOE/EM

16. C. H. BROWN, et al., "Treatment Technology Analysis for Mixed Waste Containers and Debris," DOE/MWIP-20 (November 1993).

17. J. J. WONG, "Freeze Crystallization Technology for Concentration and/or Partitioning of Liquid Waste Streams," prepared for the U.S. Department of Energy by Westinghouse Hanford Corporation (June 17, 1993).

18. P. A. TAYLOR, D. E. KURATH, and R. GUENTHER, "Evaluation of Nitrate Destruction Methods," DOE/MWIP-10 (March 30, 1993).

19. D. J. CHAIKO and T. R. KRAUSE, "Bio-Catalytic Destruction of Nitrate and Nitrite," Technical Task Plan CH-188, prepared for the U. S. Department of Energy (June 14, 1993).

20. J. J. PERONA and C. H. BROWN, "A Technology Assessment for Mercury-Containing Mixed Wastes," DOE/MWIP-9 (March 1993).

21. W. E. SCHWINKENDORF and C. H. BROWN, "Mixed Waste Separations Technologies," 8th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., October 24 1993.
22. Personal communication with Mike Barton of Vortec, Collegeville, Pennsylvania (December 1993).
23. J. R. COOK and D. F. BICKFORD, "Preliminary Assessment of Disposal Limits for Vitrified Low-Level-Mixed Waste in RCRA Landfills," Ceramics in Waste Management, Ceramic Transactions, American Ceramic Society (1993).
24. D. M. BENNETT, et al., "Pilot Scale Vittrification Studies on Hazardous and Mixed Waste," Proceedings of the 2nd International Symposium on Mixed Waste, Baltimore, Maryland (August 17-20, 1993).
25. K. L. COMPTON, D. M. BENNETT, and D. F. BICKFORD, "Regulatory Issues in Vittrification Research," Proceedings of American Ceramics Society Annual Meeting, Cincinnati, Ohio (1993).
26. R. PETERS, J. LUCERNA, and J. M. PLODINEC, "Vitrification Development Plan for DOE Mixed Waste," DOE/MWIP-11 (October 1993).
27. E. M. STEVERSON, "Vitrification Treatability Study and Process Demonstration Capabilities Assessment," to be published as DOE/MWIP-12.
28. J. D. DALTON, T. L. HARRIS and L. M. DEWITT, "Technical Area Status Report Waste Destruction and Stabilization," DOE/MWIP-4 (August 1993).
29. R. GEIMER, J. BATDORF, and P. WOLFE, Test Results from the Demonstration of the Plasma Hearth Process, 1993 Incineration Conference, Knoxville, Tennessee (May 1991).
30. R. GEIMER, J. BATDORF, and P. WOLFE, Plasma Arc Treatment of TRU and Mixed TRU Waste, 1991 Incineration Conference, Knoxville, Tennessee (May 1991).
31. P. KALB, "Mixed Waste Treatability Using Alternative Polymer Final Waste Forms," Technical Task Plan CH342004, prepared for the U.S. Department of Energy by Brookhaven National Laboratory (June 17, 1993).
32. C. H. MATTUS and A. J. MATTUS, "Evaluation of Sulfur Polymer Cement as a Waste Form for the Immobilization of Low-Level Radioactive or Mixed Waste," ORNL/TM-12657 (December 1993).
33. N. FRENCH, et al., "Offgas Treatment Technical Area Status Report," to be published as DOE/MWIP-5.
34. D. OTTESEN, "Continuous Monitor Using Tunable Diode Laser to Measure Ammonia, Acid Gases, and VOC's in effluent from DOE Waste Treatment Units," Technical Task Plan AL342003 prepared for the U. S. Department of Energy (July 2, 1993).
35. J. WANG, "Continuous Monitor to Measure Total, Elemental, and Speciated Mercury in

**Effluent Gases or on Solid Surface from DOE Treatment Process for Hazardous and Mixed Waste Destruction," Technical Task Plan AL342004 prepared for the U.S. Department of Energy (March 9, 1993).**

**36. R. E. GRITZO, "Development of a Real Time Monitor for Airborne Alpha Emissions," Technical Task Plan AL142017, prepared for the U.S. Department of Energy (July 2, 1993).**

**37. D. E. FAIN, "Cleanable HEPA Filter," Technical Task Plan OR142019, prepared for the U.S. Department of Energy (July 20, 1993).**

**38. W. BERGMAN, "Demonstration of Proof of Principle Steel HEPA Filters," Technical Task Plan SF242001, prepared for the U.S. Department of Energy (July 7, 1993).**

**39. M. F. HARDWICK, "Control and Recovery of Vapor-Phase Mercury and Particulate Using a Regenerable Gold-Plated Porous Substrate Immobilized in a Ceramic Filter," Technical Task Plan AL342007, prepared for the U.S. Department of Energy (June 15, 1993).**

**DATE**

**FILMED**

**7/12/94**

**END**

