TECHNOLOGY NEEDS FOR TREATMENT OF DOE'S LOW-LEVEL MIXED WASTES

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Mixed Waste Treatment Project

ABSTRACT

The US Department of Energy (DOE) stores and generates significant amounts of low-level mixed wastes (LLMW) consisting of radioactive materials mixed with hazardous chemical substances. Many of these wastes are regulated under the US Environmental Protection Agency (EPA) Land Disposal Restrictions and must be treated and disposed in compliance with applicable state and federal requirements. In general, treatment requirements include elimination of organic hazardous constituents and stabilization of inorganic hazardous constituents. Final waste forms must meet both EPA leach testing and DOE disposal acceptance criteria. The DOE currently does not have an adequate capability to meet these treatment objectives.

The Mixed Waste Treatment Project has been established by the DOE to define needed LLMW treatment capabilities as a basis for either a prototype plant design or an existing facility modification. Existing DOE mixed waste data bases were analyzed to identify the range of waste quantities and types and to define broad treatment categories needed to bring these wastes into compliance. Using these treatment categories as a starting point, we constructed a baseline flow sheet defining process steps from receipt through final form. From this baseline flow sheet, we developed functional and operational requirements (F&ORs) for each process train. An initial set of near-term technologies was identified for each process step, and alternative near- and long-term options were listed. Based on these analyses, we identified technology gaps and improvement needs in the areas of characterization, waste handling, segregation and sorting, size reduction, decontamination, materials recycle, primary and secondary treatment for RCRA compliance, offgas treatment, and final waste forms.

BACKGROUND

Over the years, some 30 Department of Energy (DOE) sites scattered around the country have generated substantial inventories of low-level mixed wastes consisting of radioactive materials mixed with other hazardous substances. Several of these sites continue to generate mixed wastes, and these mixed wastes must be managed in compliance with both DOE radioactive waste management requirements (per DOE Order 5820.2A) and Environmental Protection Agency (EPA) hazardous waste management requirements. EPA has promulgated a set of land disposal restrictions (LDRs) governing the management of mixed wastes. In May 1990, the EPA issued specific requirements and a schedule for compliance with these regulations (1,2). Depending on the particular waste, EPA regulations either prescribe a specific treatment technology or set a permissible concentration level, with the particular treatment technology left optional.

The DOE currently does not have an adequate capability to treat many of the wastes covered by the May 1990 ruling. To define the need for appropriate technologies and capacities, the DOE's Office of Waste Operations established a Mixed Waste Treatment Project (MWTP), which is responsible for identifying existing and needed mixed waste treatment technologies, evaluating these technology applications in system studies, and indicating further needed development and demonstration for potentially applicable technologies. The goal of the MWTP is to demonstrate effective treatment of mixed waste in a full-scale prototype plant.

Two early activities of the MWTP in support of identifying technologies for the prototype design included evaluation and upgrade of DOE's low-level data bases (3) and examining pertinent regulatory requirements.

Our evaluation of DOE data bases included reviewing the 1990 Integrated Data Base (4), the National Report on Prohibited Waste (5), and the Waste Management Information System (WMIS) data base as configured in April 1991. Although the data contained in each of these sources were useful, the objective for gathering the information was regulatory or for planning purposes, not the selection and design of process systems and facilities. Of the three sources, the WMIS proved the most current and applicable to MWTP needs; however, we determined that additional information was needed to support process design. A major requirement is a better understanding of the matrix composition of the wastes. Other needs included improved definition of several waste descriptors as well as resolution of site-to-site inconsistencies in reporting some categories of waste. MWTP analyses of existing data bases and supplemental data-gathering efforts are summarized in another paper presented in this symposium (3).

Review of the regulations identified EPA treatment requirements that must be met before the wastes can be placed in land disposal facilities. EPA has adopted three alternative approaches in establishing treatment standards: (a) specific treatment technologies must be used for some of the wastes, (b) a maximum concentration level is designated for some regulated constituents, and (c) a concentration limit is established by a leach test procedure. Key to satisfying LDR requirements is the implementation of appropriate treatment capability for individual hazardous wastes. The objective of treatment standards is either (a) the removal/destruction of the hazardous characteristic or constituent or (b) the stabilization/immobilization of toxic materials in a durable matrix. The assumption is that waste residue thus treated can be placed safely in a land disposal facility.

MWTP FLOW SHEET DEVELOPMENT

Based on early review of the three DOE databases, the MWTP staff established six major treatment categories: aqueous, organic liquid, wet solids, dry homogeneous solids, and large and small heterogeneous solids. The aqueous wastes include salt solutions, slurries, and aqueous wastes with trace organics. Organic liquids range from solvents to oils and heavy organic sludges. Wet solids contain inorganic and organic sludges, absorbed liquids, resins, and cemented sludges. The dry homogeneous solids category comprises ashes, concrete, asphalt, soils, salts, and a full range of combustibles (paper, rags, plastics). The heterogeneous solids category is a "catch-all" containing equipment, gloveboxes, construction debris, filters, glass, and associated combustible materials.

Each of the streams in the mixed waste data base was assigned to one of these six treatment categories. The data were sorted further by site and aggregated as total current inventory, expected total annual generation rate, and expected processing rate. The processing rate is based on the assumption that the current inventory will be processed over 10 years, that a processing facility will be available in about 10 years, that the annual generation rate will continue for the next 20 years, and that the waste will be processed uniformly over time. Algebraically, this means that the processing rate is 10% of the current inventory plus twice the annual generation rate.

Before categorizing the data, we removed several large, unique streams from consideration, for example, the fraction of Hanford tank waste that is low-level mixed and totals some 218,000 m^3 and the K-25 partially cemented waste pond sludge with a volume of 30,000 m^3. These streams and others will be treated in dedicated facilities independent of the MWTP.

Analyses of the data bases as configured in April 1991 indicated that the mixed waste inventory at the 30 DOE sites totals some 63,600 m^3, the continued generation rate is 7050 m^3, and the cumulative processing rate required to process low-level mixed waste is 20,500 m^3/year. The reader should note that these waste volumes and processing rates are changing significantly as the data bases are reviewed with individual sites. Figure 1 shows the distribution of waste volumes among the six treatment categories on the basis of processing rate. On a volumetric basis, the system is dominated by the wet solids, aqueous wastes, and small heterogeneous solids categories. Because of the small amount of waste included in the large heterogeneous solids category, the large and small categories were combined.

The MWTP flow sheet was developed as a grid to encompass the full range of treatment needs for low-level mixed wastes. Figure 2 shows the structure of this grid, which begins downstream of waste assay and characterization and terminates with the waste in a final form immediately before disposal. This base-line flow sheet has been critically reviewed by DOE site operations personnel as well as by MWTP staff. The complete base-line flow sheet is too detailed for inclusion in this paper; therefore, only the wet solids process train is shown in Fig. 3 to indicate the level of detail in each generic process train.

FUNCTIONAL AND OPERATIONAL REQUIREMENTS

After completing the flow sheet, we began work on the next level of detail, namely, preparation of functional and operational requirements (F&OR) documents for defined segments of the flow sheet. These documents were completed with significant contract support from T. K. Thompson, Inc. The overall configuration of these F&ORs is shown in Fig. 4. Basically, these documents are preconceptual design reports that indicate the sequence and nature of process operations required to process each waste stream. In addition, a material balance has been calculated for each process unit along with a preliminary layout of the specified equipment. The design-basis process rate shown in Table I is a median set of feed rates based on an early site-by-site analysis of the seven sites with the majority of mixed wastes: Idaho National Engineering Laboratory, K-25, the Portsmouth Gaseous Diffusion Plant,

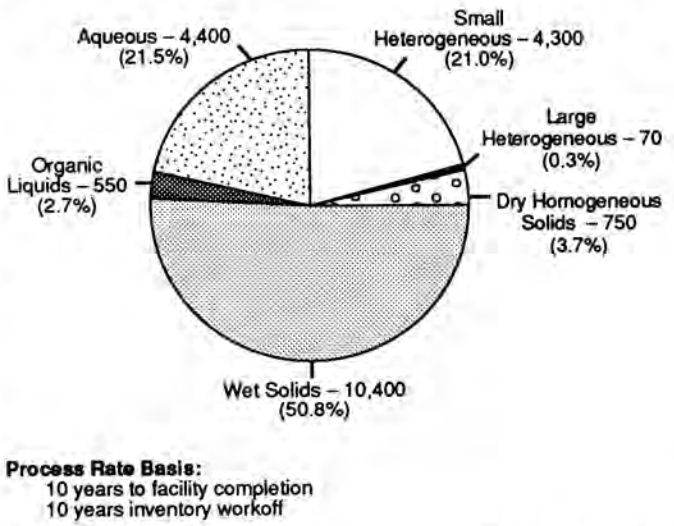

Fig. 1. Distribution of low-level mixed waste by type (processing rates, m^3/yr).

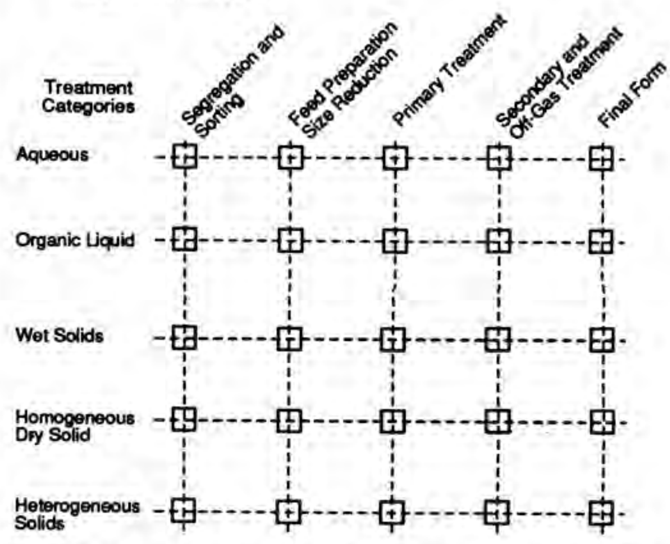

Fig. 2. Reference grid for mixed waste treatment project flow sheet.

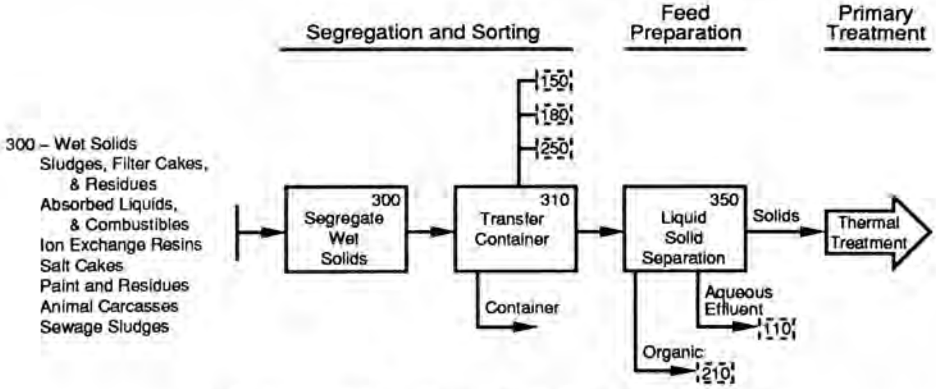

Fig. 3. Generic flow sheet for wet solids treatment.

the Richland Site, the Rocky Flats Plant, the Savannah River Site, and Y-12. Together, these seven sites account for about 94% of the DOE's total volume of mixed wastes.

The technologies specified for each primary treatment step correspond with EPA's Best Demonstrated Available Technologies (BDATs). More detailed flow sheets were developed for each F&OR segment. As an example, Fig. 5 contains the F&OR flow sheet for the Wet Solids segment. Each discrete flow sheet unit includes a description of generic technologies needed at that point. Table II shows the list of technologies selected for the base-line wet solids flow sheet together with the alternative technologies. The selected technologies reflect MWTP staff judgment regarding the best demonstrated available technology for a particular unit operation involving mixed wastes.

The F&ORs provide us with a more detailed flow sheet, material balances, and equipment layout. They also represent a structured indication of the technology needs for the overall mixed waste treatment project. We summarize technology strengths and gaps in the next section.

MIXED WASTE TREATMENT TECHNOLOGY NEEDS

Following completion of the baseline F&ORs, the MWTP project subdivided the overall flow sheet into nine technology areas. These areas cross several or all of the five treatment process trains.

- Front End Waste Handling
- Size Reduction Sorting and Separation
- Mercury Control
- Decontamination and Material Recycle
- Destruction and Stabilization
- Separation of Dissolved and Suspended Materials

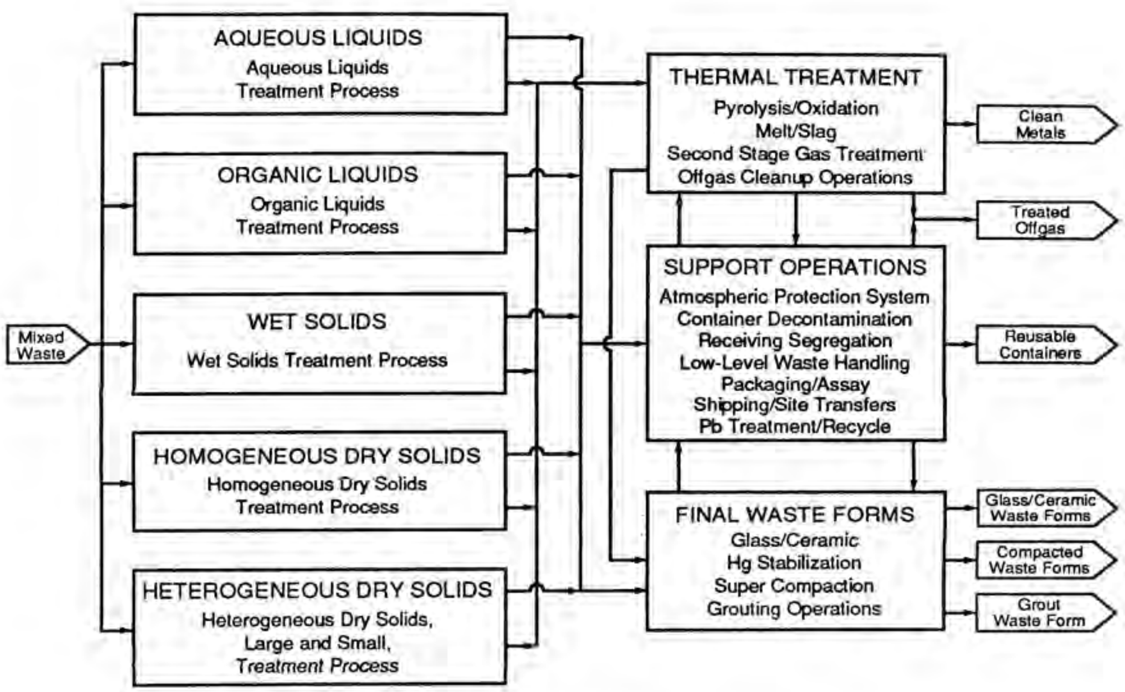

Fig. 4. Overall F&OR flow sheet configuration.

TABLE I

F&OR Design-Basis Process Rates

Waste Stream	Process Rate m^3/yr	Process Rate kg/yr
Aqueous	100	104,900
Organic Liquids	60	52,900
Wet Solids	750	957,200
Homogeneous Solids	75	88,600
Heterogeneous Solids-Large	100	150,500
Heterogeneous Solids-Small	400	466,600
Totals	1485	1,820,700

- RCRA Second Stage
- Offgas Cleanup
- Final Forms

Two additional technology areas, (a) Robotics and (b) Characterization, Assay, and Monitoring, complement the flow sheet activities. A preliminary set of technology needs and gaps developed on the strength of DOE site operations input, technology working groups, and an assessment of existing DOE development programs is described in the following paragraphs. These data have been transmitted to the DOE Office of Technology Development (OTD). As a starting point, OTD plans to develop status reports for each technology area.

Robotics

Remote or automated methods are needed for handling waste feed streams, solids, side streams, emptying containers, waste treatment operations, packaging, and transporting packages. The objectives are to increase throughput while enhancing operator safety by reducing exposure to radiation, hazardous chemicals, and other industrial hazards. A program has been initiated under the OTD Robotics Integrated Program)Waste Facility Operations.

Characterization, Monitoring, and Assay

Better methods of characterizing the incoming waste both for regulatory compliance and appropriate processing are needed for all kinds of wastes.

Better capabilities to monitor the plant operation are needed, both to improve conduct of operations and to ensure compliance with safety and the applicable environmental requirements. Real-time monitoring appears to be the keystone for public acceptance of many critically important treatment processes, specifically the thermal processes.

Methods are required for assaying the final effluents and disposal forms resulting from the treatment of mixed wastes. Final forms require quality assurance monitoring for uniformity and compliance with disposal facility and EPA permit conditions. Effluent assay requirements can include real-time monitoring to background levels.

Waste Handling

Much of the stored waste identified in the databases and during site visits is contained in 208-L (55 gal.) drums. Each of these drums must be moved and opened at the process receiving areas. In addition, the wastes must be segregated according to chemical compatibility to ensure safe storage.

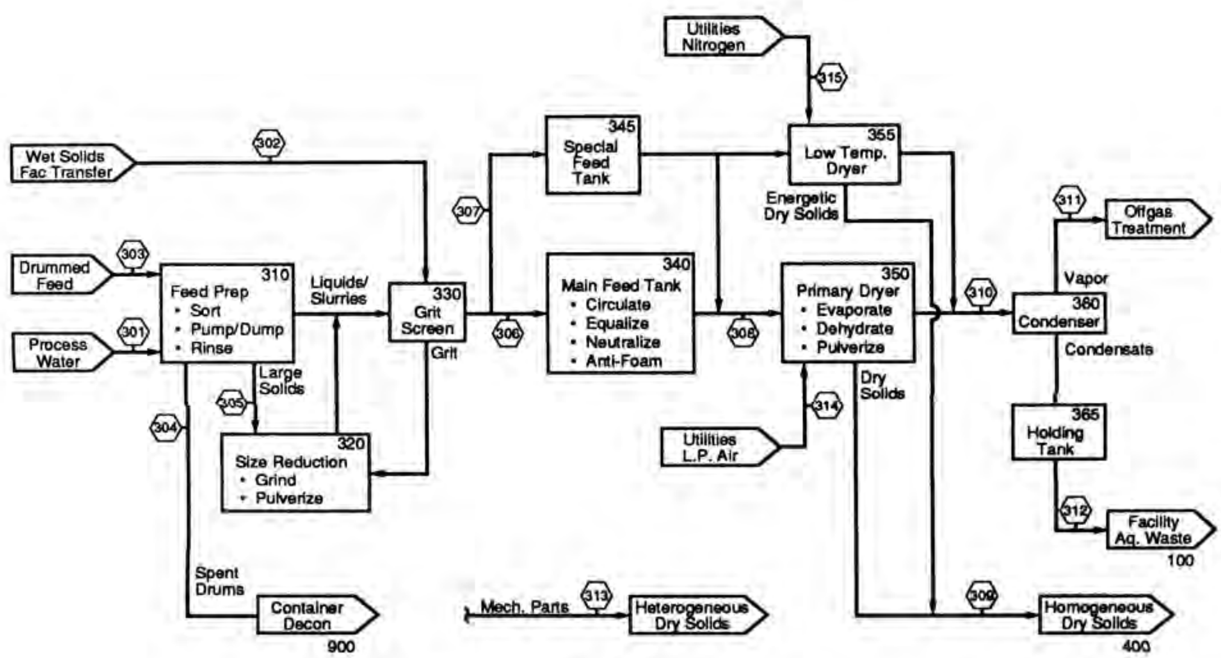

Fig. 5. F&OR flow sheet-wet solids treatment.

TABLE II

Base-Line and Alternative Technologies-Wet Solids Treatment

Function	Selected Technology	Alternative Technology
Feed Prep	Auto. drum handling; remote inspection (CCTV)	Manual Handling
Size Reduction	Wet grinding	Dry grinding; ultrasonic grinding
Grit Removal	Traveling screen	Centrifugation
Primary Dryer	Indirect heated rotary; air purge	Direct heated conveyer or drum type
Low-Temperature Dryer	Indirect heated; N_2 purge	Directed heated conveyor or drum type

The bottom line is that extensive waste handling and segregation are anticipated as a necessary precursor to mixed waste treatment. To minimize worker exposure to both radioactivity and chemical hazards, improved methods of unpackaging, manipulation, and transfer of waste containers are needed. Worker exposure can be reduced effectively by implementing more automated methods (including robotics) of handling waste.

Size Reduction, Sorting, and Separation

Size reduction will be required to feed many waste forms to RCRA compliance technologies. The need is to identify and develop reliable reduction technology that minimizes particulate and other hazardous emissions during the sizing of both metallic and nonmetallic solids.

Sorting will be required as pretreatment for technologies that are applicable only to a narrow stream composition or physical form. Remote capabilities using automatic equipment and robotics are vital to minimizing personnel exposure while maintaining needed feed rates.

Metal treatment processes require separation of ferrous, lead, and other nonferrous streams. Separation technologies also should consider the potential for recycle of any or all of these materials. The project has established a 95% separation criterion for the sorting of combustibles, metals and nonmetallic wastes.

Mercury Control

Mercury occurs as a contaminant in many waste materials from experimental and production operations. An engineering assessment should be prepared to evaluate the status of the technologies applicable to mercury control. Bakeout and recovery of mercury from DOE's wide array of waste matrices needs to be demonstrated. Capture of mercury vapors present in offgas streams also requires demonstration. Processing steps for refinement of recovered mercury need to be demonstrated and catalogued. Similarly, stabilization for mercury disposal, e.g., cinnabar formation, require evaluation and demonstration to ensure acceptable final form performance.

Decontamination and Material Recycle

There is a need to demonstrate new decontamination technologies that generate smaller volumes of secondary wastes. These technologies need to be tested on a broad range of DOE wastes and containers.

Large quantities of metals, both ferrous and nonferrous, exist in the DOE inventory. Much more metal will be generated by future remediation and decontamination and decommissioning activities. The potential for recovery and recycle of these metals needs to be fully understood. With a well-developed melt-slag process and enhancement of slag fluxing, most corrosion products, regulated materials, and radionuclides should be incorporated in the slag phase. The residual metal eventually may be decontaminated for recycle or direct land disposal. The quality of metal produced by both ferrous and nonferrous melt-slag processes needs to be established adequately to define the tradeoffs between minimum treatment for disposal and treatment for recycle.

Lead management is a significant issue in mixed waste processing concepts. The effect of lead on waste treatment and final waste forms requires study and demonstration. We anticipate that massive lead shapes will be decontaminated for recycle but that lead mixed with other waste forms will be incorporated into final waste forms. Disposal site performance analyses must be completed to establish acceptable concentrations of lead in final forms.

Destruction and Stabilization

The requirement to destroy the hazardous organic constituent of mixed waste is one of the two primary objectives of treatment. Incineration is currently the most prominent technology within this area, but there is a need to develop alternatives that may be more acceptable to the public. However, among all thermal treatment systems, incinerator and alternatives alike, there is a need to demonstrate effective destruction and absence of hazardous emissions in the effluent streams.

When applied to the DOE's wastes, low-temperature distillation, wet oxidation, and/or pyrolytic destruction systems may provide the basis for systems that are better accepted by the public than are incinerators. We need to know how the various waste matrices behave in these alternative thermal treatment systems, how well the processes meet regulatory compliance requirements, and what the robustness of these alternatives is.

Vitrification systems heated by any of several different means have been proposed for treatment of unsorted wastes.

Although it is of fundamental importance, the ability of these systems to handle the waste matrices and feed stream variations from day to day is currently not known. We need to understand the behavior of the wastes in the molten glass medium, how combustibles are destroyed or volatilized, the behavior of metals introduced with the waste, and the nature of the product glass or slag material resulting from various feed streams.

Sludges, both grouted and ungrouted, are a major mixed waste stream for DOE. These wastes often contain regulated inorganics and radionuclides. The ability of microwave technology to process these materials over a wide range of compositions to achieve drying, organic volatilization, melting, and finally vitrification requires study and demonstration. Microwave technology also should be evaluated for the treatment of organic sludges and adsorbed organics.

A number of alternative plasma concepts has been tested for various waste treatment applications. An engineering assessment of the status and potential for each concept needs to be conducted.

Dissolved/ Suspended Material Separation

There is a need for development of more effective techniques for separation of solutes and suspended materials from both aqueous and organic liquid streams. Improved liquid filtration, precipitation, centrifugation, evaporation, and ion exchange demonstrated with actual DOE mixed wastes and process secondary wastes will support progress toward the goal of zero discharge.

RCRA Second Stage

Most organic destruction systems create an offgas that contains trace volatile and partially oxidized organics that require subsequent secondary oxidation. Alternative low-temperature systems often generate an offgas that contains substantially higher concentrations of volatilized organics. These substances, now volatilized, may be destroyed in a conventional liquid or fume burner. However, these secondary products also may be destroyed effectively by some of several low-temperature organic destruction technologies, including catalytic conversion, ultraviolet photolysis, molten salt, silent plasma discharge, Brehmstrahlung, and plasmas. To fully evaluate the ability of the various candidate processes to destroy volatilized organics, the nature of those organics generated by the primary treatment process needs to be completely defined. A broad scoping evaluation of the ability of the primary and secondary treatments to achieve the required hazardous organic destruction on actual wastes is needed.

Offgas Cleanup

Effective removal of pollutants from the offgas generated by the full range of treatment processes is central to successful mixed waste treatment. Radionuclides, toxic metals, hydrocarbons, particulates, and acid gases must, as a minimum, be controlled to a level that meets Federal, state, and local requirements. A wealth of experience exists in private industry and within government agencies that should be drawn together in an engineering assessment of these technological alternatives. We need to understand the behavior of these technologies when processing mixed wastes in a variety of thermal and nonthermal systems.

Final Forms

Final waste forms must be produced that meet the requirements for control of inorganic constituents and radionuclides. Currently, grout forms are accepted for disposal, but there is dissatisfaction over the performance of this final waste form. Formulations and the performance of the grout forms should be quantified in an engineering assessment. An exploratory analysis of Portland cement grouts is justified because of the relative simplicity of grouting technology. The alternative sulfur polymers need to be assessed systematically.

Ceramic or glass final waste forms generally are considered more desirable and more effective than grout for control of the contained constituents. We need to understand the process requirements for production of ceramic or glass from the residues for the range of technologies applicable to DOE mixed wastes.

CONCLUSIONS

In progressing toward the goal of constructing and operating a prototype mixed waste treatment plant, the Mixed Waste Treatment Project has developed a base-line flow sheet that has identified a broad set of technology needs and gaps. Clearly in evidence is the requirement that development efforts address a broad range of process needs rather than solely focus on the development of the primary treatment technologies. An early project need is completion of status reports within each defined technology area. MWTP analyses show that existing technologies can meet many of the treatment objectives. However, applications engineering projects are needed to fill the gaps and enhance the capabilities of near-term technology. Parallel development efforts are needed to provide the improved technology to support the long term goal of enhanced mixed waste treatment effectiveness.

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