CONF-930205--17

U.S. DEPARTMENT OF ENERGY, OFFICE OF TECHNOLOGY DEVELOPMENT, MIXED-WASTE TREATMENT RESEARCH, DEVELOPMENT, DEMONSTRATION, TESTING, AND EVALUATION

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ABSTRACT

Department of Energy (DOE) mixed waste is contaminated with both chemically hazardous and radioactive species. The DOE is responsible for regulating radioactive species while the Environmental Protection Agency (EPA) is responsible for regulating hazardous species. Dual regulations establish treatment standards and therefore affect the treatment technologies used to process mixed waste. This duality is reflected in technology development initiatives. Significant technology development has been conducted for either radioactive or hazardous waste, but limited technology development, specifically addressing mixed waste treatment issues, has been completed. Technology has not been designed, developed, demonstrated, or tested to produce a low-risk final waste form that increases the probability that the final waste form will be disposed.

Throughout the DOE complex, the mixed-waste problem is significant because definitive treatment standards have not been established and few disposal facilities are available.[1,2] In addition, the treatment that is available is limited in its capability and capacity.[3] These constraints have led to the storage of mixed waste at DOE sites for future disposal. One driving force for the development of mixed-waste treatment technology is provided by EPA regulations. Both the Land Disposal Restrictions (LDR) within the Resource Conservation and Recovery Act (RCRA) and the new Federal Facility Compliance Act of

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1992 (FFCA) have mandated schedules for treatment regardless of whether treatment standards or applicable treatment technologies exist. Site-specific solutions to the management of mixed waste have been initiated; however, site-specific programs result in duplication of technology development effort between various sites. There is a clear need for technology designed to meet the unique requirements for mixed-waste processing and for a system-wide integrated strategy for to develop treatment technology and manage mixed waste.

In response to the need for a comprehensive and consistent approach to this complex issue, the Office of Technology Development has established the Mixed Waste Integrated Program to ensure that treatment capability is developed. This program supports the national DOE waste management needs identified by the Mixed Low-Level Waste Program which includes the Mixed Waste Treatment Project. The Mixed Waste Treatment Project has defined baseline treatment steps that will be required for a prototypical treatment of both present and estimated future mixed wastes at DOE sites. The Mixed Waste Integrated Program, in turn, is evaluating the gamut of treatment technologies that correspond to each treatment step and assessing their appropriateness for the treatment of mixed waste. The Mixed Waste Integrated Program is also providing technical data to contribute to the resolution of mixed-waste processing issues such as the lack of acceptance criteria for waste disposal, limits on the recycle of decontaminated material, and public acceptance of incineration. The status of the technical initiatives in destruction/stabilization technology, off-gas treatment, and final waste form production/assessment are described in this paper.

INTRODUCTION

A comprehensive and consistent approach to the complex issue of mixed-waste management has been established by the DOE Office of Environmental Restoration and Waste Management. The Office of Waste Management established the Mixed Low-Level Waste Program with the primary objective of identifying and implementing the optimum treatment, storage, and disposal options for mixed waste.[4] The Office of Technology Development established the Mixed Waste Integrated Program to develop mixed-waste treatment technology in support of the Mixed Low-Level Waste Program.

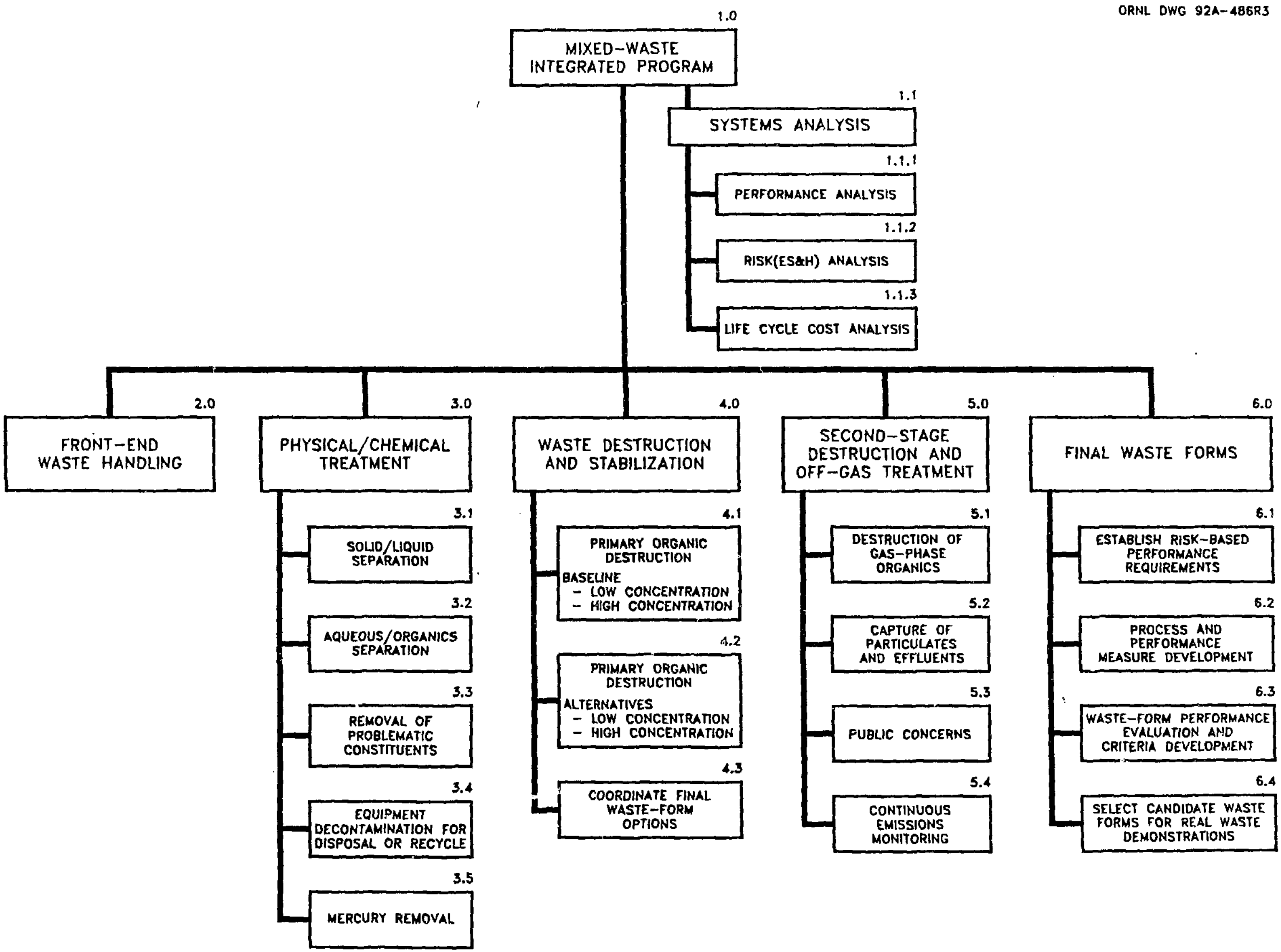
A driving force for the development of mixed-waste treatment technology is provided by EPA regulations. The primary purpose of the LDR is to prohibit the placing of untreated wastes in or on the land when there is a better treatment alternative. EPA has established treatment standards for all characteristic and listed wastes that either require the use of specified treatment technologies or require that the wastes be treated to EPA-established concentration limits for the hazardous constituents.[5] The concentration limits are based on the use of the best demonstrated available technology (BDAT) even though the waste can be treated by any technology (as long as the waste is treated to the same or lower levels as the BDAT).

After EPA established the BDAT for a waste, it then established an effective date for the LDR based on a nationwide availability of BDAT capacity.[6] Based on this assesment, DOE mixed wastes were placed in category of waste that were given until May 8, 1992 to comply with LDR. However, several issues have delayed DOE compliance with the LDR schedule. These issues include, but are not limited to, transportation of waste to distant treatment sites, the matrix within which the hazardous components are found, and complications of treatment due to presence of the radioactive components. Further, dispoal criteria and capacity have not been established for many mixed waste streams. The problem has been summarized as "a lack of existing proven technology to treat and dispose of . . . mixed waste to meet treatment standards".[7] Without capability and capacity to treat mixed wastes, DOE sites have been forced to store untreated waste. However, the LDR also prohibits the storage of restricted wastes except when necessary to accumulate sufficient quantities to properly treat, recover, or dispose. Therefore, the sites that have not or are not pursuing a Federal Facility Compliance Agreement with the EPA and their state may be in violation of the LDR.

The Federal Facility Compliance Act of 1992 amends RCRA, among other conditions, to waive sovereign immunity for federal facilities permitting the assessment of fines and penalties on DOE for violations of RCRA. Several of the provisions of the Act address violations of the LDR storage prohibition for mixed wastes by federal facilities.[8] The Act does not invalidate existing agreements but does establish a three year timeframe for facilities to establish plans to come into compliance with the LDR. The items these plans must contain include: the treatment technologies that exist for the mixed wastes in question and if none exists, the schedule for identifying and developing the needed technologies. A national approach to developing the needed technology can draw the resources of the DOE-complex and industry together thus significantly reducing costs.

A total of approximately 179,000 m^3 of mixed waste is being stored at DOE sites[9] but such storage does not comply with specific requirements established by EPA. In addition, the generation of mixed waste continues at the rate of 81,000 m^3/year. DOE wastes cover the spectrum of possible waste management concerns. In fact, DOE has classified 751 individual waste streams from 34 sites into 9 broad waste matrix categories.

The strategy being used by the Mixed Low-Level Waste Program is to "establish a standardized approach to mixed waste management activities throughout the DOE system that is cost effective, and sets a technically sound standard of excellence for environmental protection in the DOE waste management programs".[10] To implement this strategy, the Mixed Waste Treatment Project has combined waste streams that require similar processing steps to establish a generic baseline mixed-waste treatment scheme using currently available technologies. The logic for processing mixed waste is comprehensive and covers the range of wastes requiring treatment within the DOE complex. By using a comprehensive national approach to the mixed waste problem rather than focusing on a specific site, the major treatment needs have been identified


ORNL DWG 92A-486R3
1.0
MIXED-WASTE INTEGRATED PROGRAM
1.1
SYSTEMS ANALYSIS
1.1.1
PERFORMANCE ANALYSIS
1.1.2
RISK(ES&H) ANALYSIS
1.1.3
LIFE CYCLE COST ANALYSIS
2.0
FRONT-END WASTE HANDLING
3.0
PHYSICAL/CHEMICAL TREATMENT
3.1
SOLID/LIQUID SEPARATION
3.2
AQUEOUS/ORGANICS SEPARATION
3.3
REMOVAL OF PROBLEMATIC CONSTITUENTS
3.4
EQUIPMENT DECONTAMINATION FOR DISPOSAL OR RECYCLE
3.5
MERCURY REMOVAL
4.0
WASTE DESTRUCTION AND STABILIZATION
4.1
PRIMARY ORGANIC DESTRUCTION
BASELINE
- LOW CONCENTRATION
- HIGH CONCENTRATION
4.2
PRIMARY ORGANIC DESTRUCTION
ALTERNATIVES
- LOW CONCENTRATION
- HIGH CONCENTRATION
4.3
COORDINATE FINAL WASTE-FORM OPTIONS
5.0
SECOND-STAGE DESTRUCTION AND OFF-GAS TREATMENT
5.1
DESTRUCTION OF GAS-PHASE ORGANICS
5.2
CAPTURE OF PARTICULATES AND EFFLUENTS
5.3
PUBLIC CONCERNS
5.4
CONTINUOUS EMISSIONS MONITORING
6.0
FINAL WASTE FORMS
6.1
ESTABLISH RISK-BASED PERFORMANCE REQUIREMENTS
6.2
PROCESS AND PERFORMANCE MEASURE DEVELOPMENT
6.3
WASTE-FORM PERFORMANCE EVALUATION AND CRITERIA DEVELOPMENT
6.4
SELECT CANDIDATE WASTE FORMS FOR REAL WASTE DEMONSTRATIONS

The Mixed Waste Integrated Program is clearly defining the mixed-waste processing technology development needs and providing data to resolve key issues that affect the ability of DOE to assign definitive treatment plant requirements such as the lack of acceptance criteria for waste disposal, limits for recycle of decontaminated material, and public acceptance of incineration.

Commercially available equipment has been identified for the majority of processing steps; however, no currently available techniques were found for some steps in the processing logic. Further, this baseline treatment scheme includes disposal of radioactive material, recycle of decontaminated material, and incineration — activities for which system requirements have not been established. Technology development is required to investigate the application of existing technologies to the treatment of mixed waste and to the development of integrated treatment modules. Further development is required to obtain data to support the establishment of system requirements and to meet the identified needs of the treatment scheme. Additionally, there are opportunities to improve upon the baseline treatment process by applying innovative waste treatment operations. New technologies under development have the potential for major process impacts by simplifying and increasing the throughput rate of the baseline treatment process. Technologies will be developed to enhance or improve the baseline technologies such that the implemented treatment scheme is more cost-effective, has better performance, and has lower risk than the baseline.

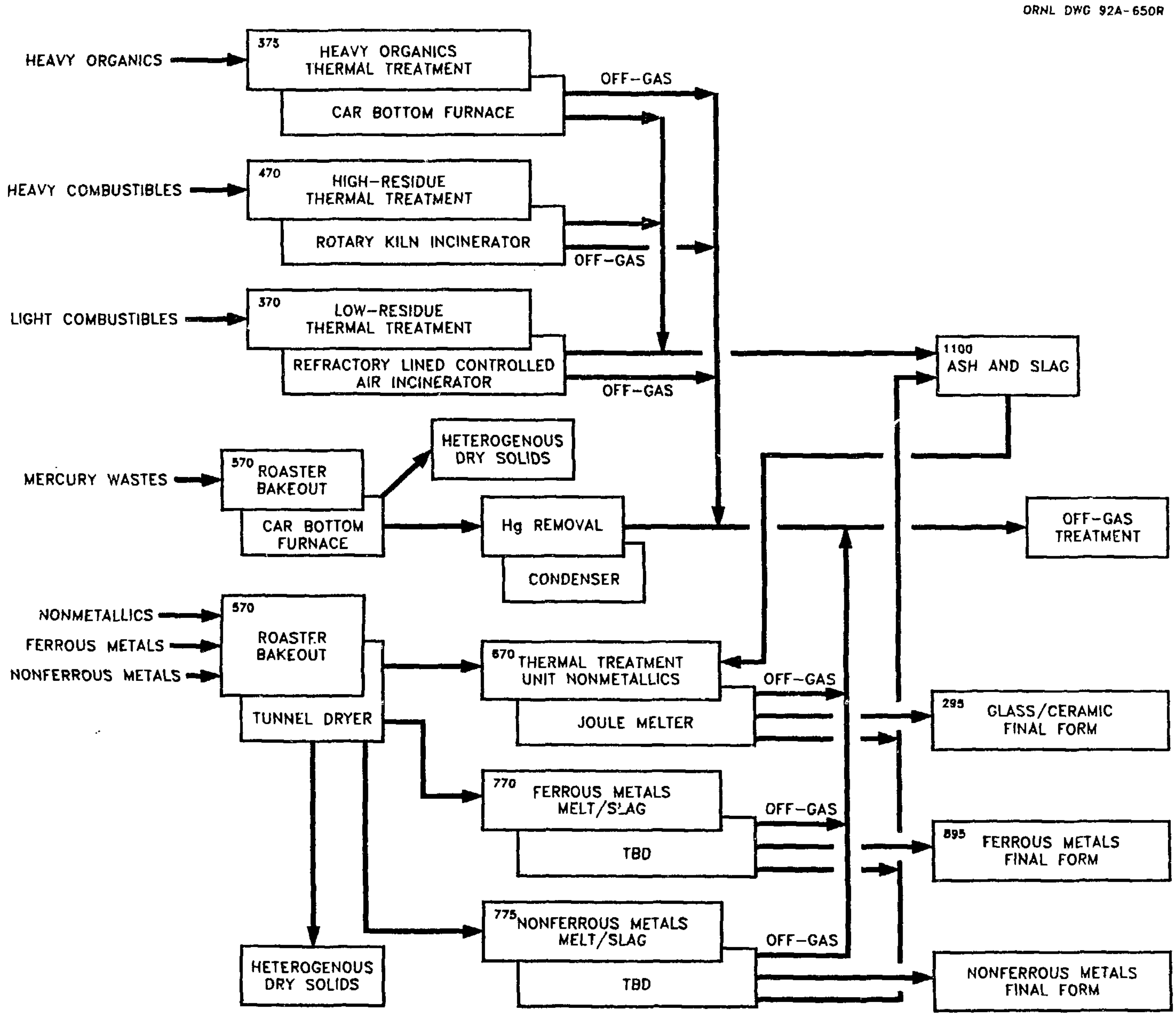
A systematic approach is being employed to determine how the baseline treatment scheme should be modified to incorporate innovative technologies. An example of the application of this systems approach is seen by comparing Figs. 2 and 3. Figure 2 illustrates the baseline flow sheet for thermal treatment technologies. An innovative alternative to this baseline thermal treatment system includes a plasma-arc furnace that has the potential to treat numerous waste streams in one unit operation (see Fig. 3). The two systems are being compared for performance (i.e., material and energy balance, operability, maintainability, reliability); risk (i.e., environmental, health, and safety); and life-cycle cost. Those subsystems that are superior to commercially available subsystems will be included in mixed-waste treatment facility design.

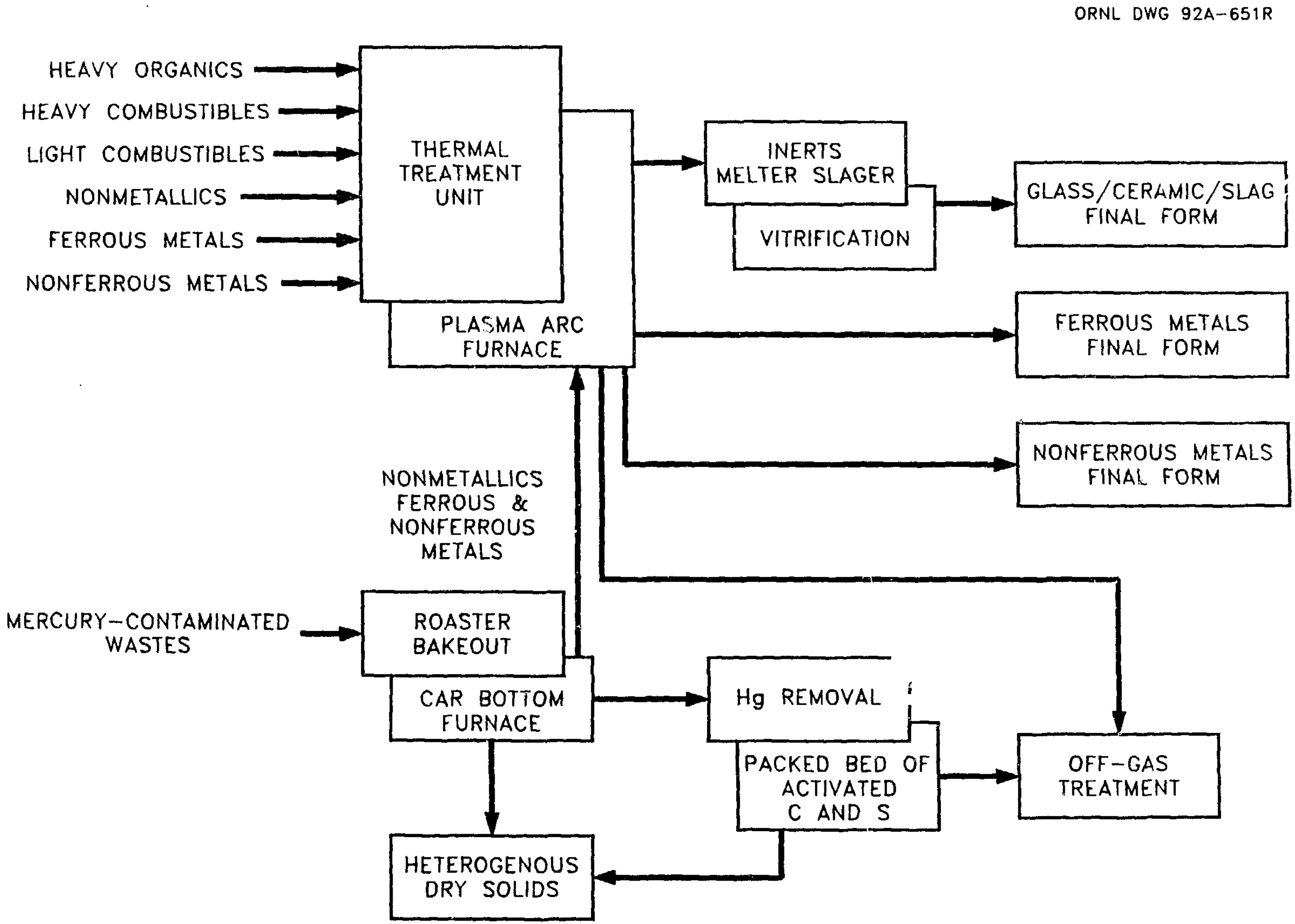
Needs for technology development have been broadly categorized into the following technical areas: front-end waste handling, chemical/physical treatment, destruction/stabilization technology, off-gas treatment, and final waste form production/assessment. Specific technology development needs have been identified by analyzing the Mixed Waste Treatment Project baseline flow sheet as described above. The goal of the Mixed Waste Integrated Program is to develop a suite of appropriate technologies that will treat mixed waste to acceptable disposal criteria and provide design and reliability data on the schedule required to support implementation of mixed-waste treatment. The status of the technical initiatives in the technical areas of destruction/stabilization technology, off-gas treatment, and final waste form production/assessment are described below.[11,12]

DESTRUCTION/STABILIZATION TECHNOLOGY

DOE is investigating the use of thermal treatment technologies for waste destruction and stabilization.[13] Innovative technologies, loosely defined as those technologies that are not currently being used on a large scale to treat wastes, are being demonstrated, and issues regarding full-scale operation are being resolved. Development of the following processes is currently in progress: metal-melting technologies, photochemical organic destruction processes, thermal reactors, and plasma-arc incineration. Metal-melting technologies are basically adapted from the metals industry (e.g., induction furnaces and plasma-arc melters) and the glass industry (e.g., fuel-fired and joule-heated melters). Although the operating principles for these processes are not new, there is only limited operational experience in the waste management area. In addition, new concepts in melting processes are being researched as waste management tools (e.g., the microwave melter).[14]

Melter technologies hold the promise of being highly effective for waste treatment because the ash residue may not require additional treatment prior to disposal. The final waste form is physically and chemically stable and will likely pass regulatory performance standards. Because of the


ORNL DWG 92A-650R
HEAVY ORGANICS
375 HEAVY ORGANICS THERMAL TREATMENT
CAR BOTTOM FURNACE
OFF-GAS
HEAVY COMBUSTIBLES
470 HIGH-RESIDUE THERMAL TREATMENT
ROTARY KILN INCINERATOR
OFF-GAS
LIGHT COMBUSTIBLES
370 LOW-RESIDUE THERMAL TREATMENT
REFRACTORY LINED CONTROLLED AIR INCINERATOR
OFF-GAS
1100 ASH AND SLAG
MERCURY WASTES
570 ROASTER BAKEOUT
CAR BOTTOM FURNACE
HETEROGENOUS DRY SOLIDS
Hg REMOVAL
CONDENSER
OFF-GAS TREATMENT
NONMETALLICS
FERROUS METALS
NONFERROUS METALS
570 ROASTER BAKEOUT
TUNNEL DRYER
670 THERMAL TREATMENT UNIT NONMETALLICS
JOULE MELTER
OFF-GAS
295 GLASS/CERAMIC FINAL FORM
770 FERROUS METALS MELT/SLAG
TBD
OFF-GAS
895 FERROUS METALS FINAL FORM
775 NONFERROUS METALS MELT/SLAG
TBD
OFF-GAS
NONFERROUS METALS FINAL FORM
HETEROGENOUS DRY SOLIDS


ORNL DWG 92A-651R
HEAVY ORGANICS
HEAVY COMBUSTIBLES
LIGHT COMBUSTIBLES
NONMETALLICS
FERROUS METALS
NONFERROUS METALS
THERMAL TREATMENT UNIT
PLASMA ARC FURNACE
INERTS MELTER SLAGER
VITRIFICATION
GLASS/CERAMIC/SLAG FINAL FORM
FERROUS METALS FINAL FORM
NONFERROUS METALS FINAL FORM
NONMETALLICS FERROUS & NONFERROUS METALS
MERCURY-CONTAMINATED WASTES
ROASTER BAKEOUT
CAR BOTTOM FURNACE
Hg REMOVAL
PACKED BED OF ACTIVATED C AND S
OFF-GAS TREATMENT
HETEROGENOUS DRY SOLIDS

high temperature of melting operations, melters can be used to destroy residual organics. Process modifications will be required to ensure the destruction of organic material during the metal-melting process.

Melters are ideally suited for inorganic waste streams such as inorganic oxides and elemental metals. Furthermore, the chemistry in the melt can be reducing or oxidizing depending on the type of waste form desired. When processing oxides, the final waste form will be a glass or a ceramic, primarily depending on the rate of cooling. When processing metals, the melt will form a top layer of slag and a bottom layer of molten metal. The slag can then be separated from the molten metal, allowing for the recycle of the molten metal. Depending on operating parameters, it is possible to oxidize the majority of the radionuclides in the waste so the radionuclides become part of the slag, resulting in a decontaminated molten metal.

Research and development are needed in the waste destruction area. Generally, these needs can be classified as requiring more operational experience, better materials of construction, improved materials handling techniques, less waste pretreatment, control of the chemistry in the process, and detailed analysis of the resulting residue and off-gas to determine the constituents that are in the process effluent streams.

OFF-GAS TREATMENT[15]

DOE is evaluating air pollution control equipment for use in treatment of gaseous effluent from mixed-waste stream processing based on criteria generally relevant to DOE facilities. These criteria include primary pollutant removal, secondary waste stream generation, safety, versatility, experience, simplicity, and cost. The preliminary evaluation resulted in ranking the spray dryer absorber best for acid-gas removal, high-efficiency particulate air filters best for particulate removal, activated carbon adsorption best for removal of both toxic metals and residual hydrocarbons, and selective catalytic reduction best for nitrogen oxide abatement. However, selection of off-gas components for a given application is highly dependent on waste streams, location, and thermal technology.

A systematic analysis is used to select the appropriate off-gas system for a given waste stream. For the purpose of illustration, the expected performance of two hypothetical DOE waste streams and thermal treatment technologies is presented here.

The first waste stream is defined to contain a large variety of waste types (i.e., solids, sludges, and liquids) and is, therefore, suitable for processing in a rotary kiln, which is a versatile thermal treatment device. The rotary kiln process is mated with wet and semidry off-gas systems in series. The wet off-gas system is designed with a rotary atomizer as the principal component and will accomplish excellent removal of acid gases and good removal of particulate. Other pollutants would either not be affected, or the removal efficiency for such pollutants is not known. The semidry off-gas system for the rotary kiln is designed with a spray dryer absorber/baghouse combination for good removal efficiency of acid gases and excellent removal efficiency of particulate and toxic metals.

The second waste stream is defined to contain a large percentage of contaminated soils and inorganic constituents, making it amenable to the plasma-arc system, which will not only destroy the organic constituents but also vitrify and stabilize the inorganic constituents. The plasma-arc process is mated with wet and dry off-gas systems in series. The wet off-gas system incorporates a venturi/packed-bed scrubber combination to accomplish excellent acid-gas and nitrogen oxides removal and moderate removal of particulate and toxic metals. The dry off-gas system incorporates selective noncatalytic reduction followed by dry sorbent injection and a baghouse. This system accomplishes moderate acid-gas and NO_x removal and excellent removal of toxic metals.

Particular areas in which further research and development are necessary include treatment and disposal of secondary wastes, ability to remove multiple pollutants, mass-transfer rates, optimization of multiple air pollution control devices used in an integrated off-gas train, process control, catalyst activity and resistance to degradation, and materials of construction for air pollution control devices.

FINAL WASTE FORM PRODUCTION/ASSESSMENT

Treatment of mixed waste is intended to protect human health and the environment from risks associated with the release of hazardous and radioactive components from the waste. DOE Order 5820.2A requires a performance assessment for each disposal site, which shows by analysis that the waste treatment process and other disposal controls adequately meet this objective. At present the assessment does not credit the waste form with any capacity to restrict contaminant mobility; all containment is attributed to physical barriers such as vaults. In order to rate the waste form as a physicochemical barrier to contaminant release, performance criteria must be developed. Criteria can be based solely on regulatory requirements, solely on technical parameters, or combination of both. The latter approach has been selected, recognizing that current regulatory criteria do not address all of the properties of a waste form that determine its ability to reduce contaminant mobility and acknowledging that the properties measured may not, in fact, be indicative of the performance of the waste form in the specific disposal setting. The most important technical requirement affecting whether a waste form can be disposed of is the long-term stability of the waste form in the disposal setting. This information is critical in developing the performance assessment, which documents the ability of the entire waste control system to prevent unacceptable releases. Tests to measure and predict release rates of hazardous and radioactive constituents need to be developed and verified for long-term stability. There is a need to establish uniform testing requirements for waste form performance for both short- and long-term stability. Compositional flexibility, minimal volume increase, and low unit cost are all desirable properties of waste forms. Difficulties experienced with the long-term integrity and performance of traditional waste form technologies (e.g.,cementation and grout) have led DOE to consider evaluation of technologies for production of enhanced waste forms (e.g., glass and ceramics) with the expectation that these waste forms will exhibit comparatively superior performance characteristics (e.g., leach resistance and durability), which will facilitate eventual disposal.

DOE is evaluating the use of the following groups of final waste forms for mixed waste disposal: hydraulic cement, sulfur polymer cement, glass, ceramic, and organic binders. The current status of the development of enhanced waste forms has been determined, gaps and deficiencies in what is known about technologies have been identified, and a course of action to alleviate these deficiencies has been recommended.[16]

Evaluation of vitrification processes for mixed-waste streams is in progress in an attempt to assess alternative technologies for inclusion in the proposed prototype treatment plant for mixed waste. Vitrification-related treatability studies include the following waste streams: incinerator ash (including air pollution control equipment sludge), wastewater treatment sludge, soils, and off-specification cemented wastes. The treatability studies will involve: (1) characterization of the wastes, laboratory-scale or "crucible" studies to identify appropriate glass compositional formulations and additive requirements; (2) engineering-scale process studies (e.g., steady-state operation) of small-scale melters to identify process concerns; and (3) pilot-scale demonstrations of the process in an integrated fashion including feed and air pollution control system evaluation.

CONCLUSION

The DOE Office of Technology Development has established a national approach to technology development for mixed waste treatment. This multi-functional approach reduces duplication of technology development effort as compared to a site-specific approach. A comprehensive approach to the solution of DOE mixed radioactive and toxic waste problems includes an analysis of alternative waste treatment systems. The implemented treatment schemes will be more cost effective, have better performance, and have lower risk than baseline technologies.

The regulatory drivers found in the LDR and the FFCA of 1992 have mandated treatment/ development schedules that will be difficult for all the sites to achieve on an individual basis. A coordinated effort among all the sites will be required where each site can take advantage of the efforts taking place at other sites.

Technology development for mixed waste treatment has been categorized by evaluating the required treatment steps. A prototypical mixed waste treatment scheme includes unit operations in the following technical categories: front-end waste handling, chemical/physical treatment, destruction/stabilization technology, off-gas treatment, and final waste form production/assessment. DOE has initiated technology development activities in each of these technical areas. This paper describes significant progress to date and additional research needs in the areas of waste destruction/stabilization technology, off-gas treatment, and final forms production/assessment.

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