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Development and Demonstration of Treatment Technologies for the Processing of U.S. Department of Energy Mixed Waste

G. A. Bloom
J. B. Berry

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Chemical Technology Division

**DEVELOPMENT AND DEMONSTRATION OF TREATMENT TECHNOLOGIES
FOR THE PROCESSING OF U.S. DEPARTMENT OF ENERGY MIXED WASTE**

G. A. Bloom
J. B. Berry

January 1994

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ACRONYMS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CO	carbon monoxide
CO ₂	carbon dioxide
CPTS	Chemical Physical Treatment System
dc	direct current
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
FCTAC	Freeze Crystallization Technologies Acquisition Corporation
FFCA	Federal Facilities Compliance Act
H ₂	hydrogen gas
HEPA	high-efficiency particulate air (filter)
LVFTDS	Large Volume Flow Thru Detector System
MBE	moving bed evaporator
MWIP	Mixed Waste Integrated Program
MWTP	Mixed Waste Treatment Project
NO _x	oxides of nitrogen
OTD	Office of Technology Development
OWM	Office of Waste Management
PA	Performance Assessment
ppb	parts per billion
RCRA	Resource Conservation and Recovery Act
RDDT&E	research, development, demonstration, testing, and evaluation
SO _x	sulfur oxides
SPC	sulfur polymer cement
TDL	tunable diode laser
TTP	Technical Task Plan
uv	ultraviolet
WD/S	Waste Destruction and Stabilization

ABSTRACT

Development and Demonstration of Treatment Technologies for the Processing of U.S. Department of Energy Mixed Waste

G. A. Bloom

J. B. Berry

Mixed waste is defined as “waste contaminated with chemically hazardous and radioactive species.” The Mixed Waste Integrated Program (MWIP) was established in response to the need for a unified, DOE complexwide solution to issues of mixed waste treatment that meets regulatory requirements. MWIP is developing treatment technologies that reduce risk, minimize life-cycle cost, and improve process performance as compared to existing technologies. Treatment for waste streams for which no current technology exists, and suitable waste forms for disposal, will be provided to improve operations of the DOE Office of Waste Management.

MWIP is composed of six technical areas within a mixed-waste treatment system: (1) systems analysis, (2) materials handling, (3) chemical/physical separation, (4) waste destruction and stabilization, (5) off-gas treatment, and (6) final waste form stabilization. The status of the technical initiatives and the current research, development, and demonstration in each of these areas are described in this paper.

1. INTRODUCTION

The Mixed Waste Integrated Program (MWIP) is sponsored by the U.S. Department of Energy (DOE) Office of Technology Development (OTD). MWIP oversight and direction are provided by the OTD Program Manager. Program coordination is the responsibility of the Integrated Program Coordinator.

MWIP was established in response to the need for a unified, DOE complexwide solution to the issues of mixed waste treatment that meets regulatory requirements. MWIP has the responsibility for research, development, demonstration, testing, and evaluation (RDDT&E) of new and emerging technologies for application to treatment and permanent disposal of mixed low-level waste generated by DOE. MWIP has identified technology areas that correspond to the treatment steps required to process mixed waste (Fig. 1). A systems approach to technology development in these areas is being employed to determine how modification to the baseline mixed waste treatment plan [being developed by the Office of Waste Management (OWM)] by incorporating new or emerging technologies would improve life-cycle cost, reduce risk, and improve performance.

The technical areas consist of a technical area leader and principal investigators who are responsible for technology development and implementation. These technical areas are as follows: systems integration, materials handling, chemical/physical treatment, waste/destruction and stabilization, off-gas treatment, and final waste forms. The technical areas establish system requirements based on Waste Management and Environmental Restoration needs, evaluate and rank alternative technologies, assist in monitoring RDDT&E activities, and recommend priorities for technologies worth developing to treat mixed low-level wastes. Principle investigators within each functional area research, develop, and demonstrate the new and emerging technologies. This paper describes the mixed waste problem within DOE and gives a technical overview of treatment technologies being developed by MWIP.

2. PROBLEM STATEMENT

DOE has identified over 1,478 mixed waste streams currently in storage or that will be generated in the next 5 years at 50 DOE sites in 22 states (Fig. 2). Table 1 provides a national overview of DOE mixed waste by volume per state, and Fig. 3 provides an overview by waste stream matrix category. The total mixed waste volume currently in storage is approximately 589,481 m³, and the volume projected to be generated for the next 5 years is approximately 297,932 m³.^[1] Waste streams currently in storage with treatment capacity are being treated. The waste volume is being updated to more accurately reflect the mixed-waste inventory. Mixed waste, as defined by the Federal Facilities Compliance Act (FFCA) of 1992, is "... waste that contains both hazardous waste and source, special nuclear, or by product material subject to the Atomic Energy Act of 1954 (42 U.S.C. 2011 et seq.)." As defined by the Atomic Energy Act, "source material" includes uranium, thorium, and ores containing one or more of the foregoing materials. "Special nuclear material" includes plutonium, uranium enriched in the isotope 233 or in

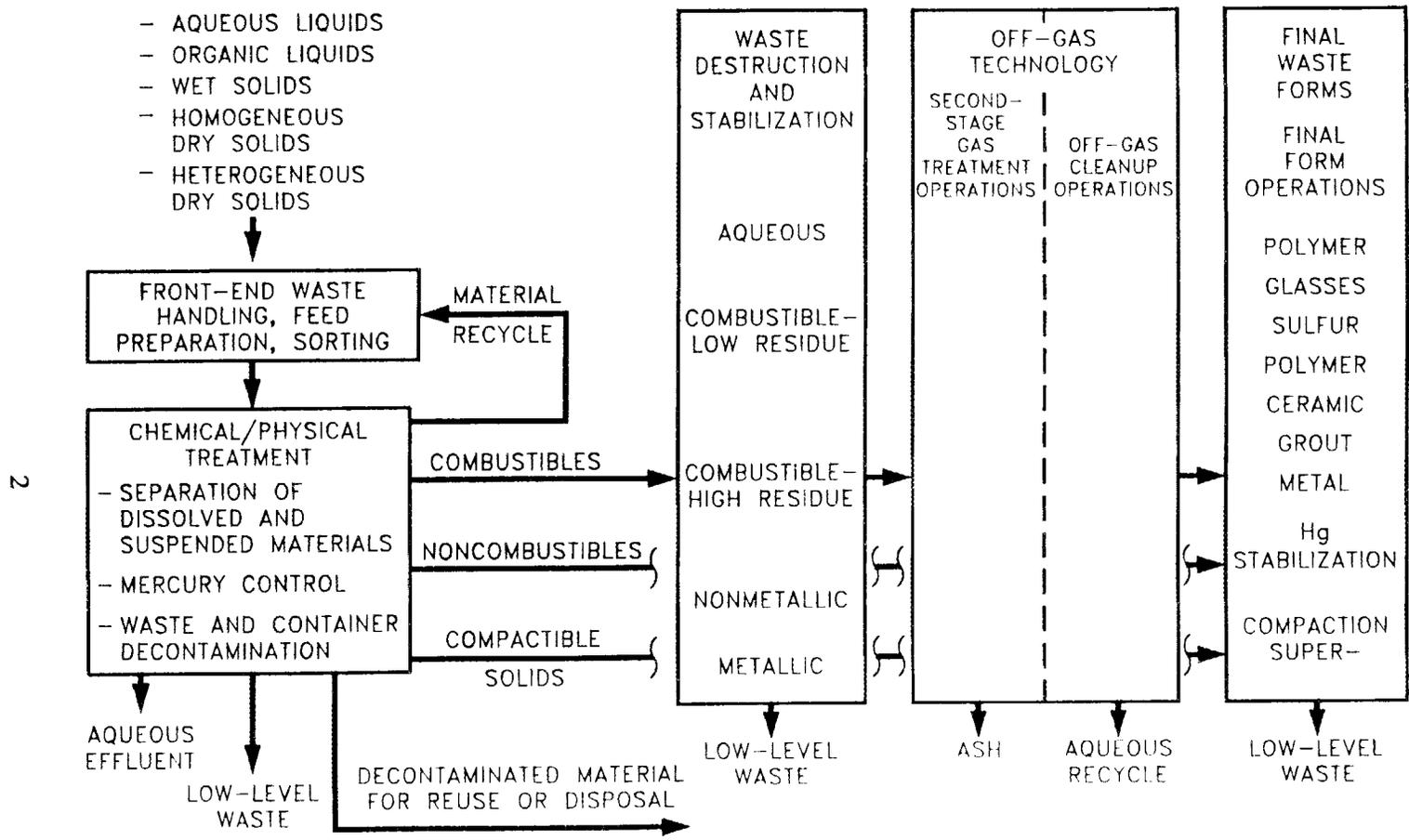


Fig 1. Mixed Waste Integrated Program technology areas.

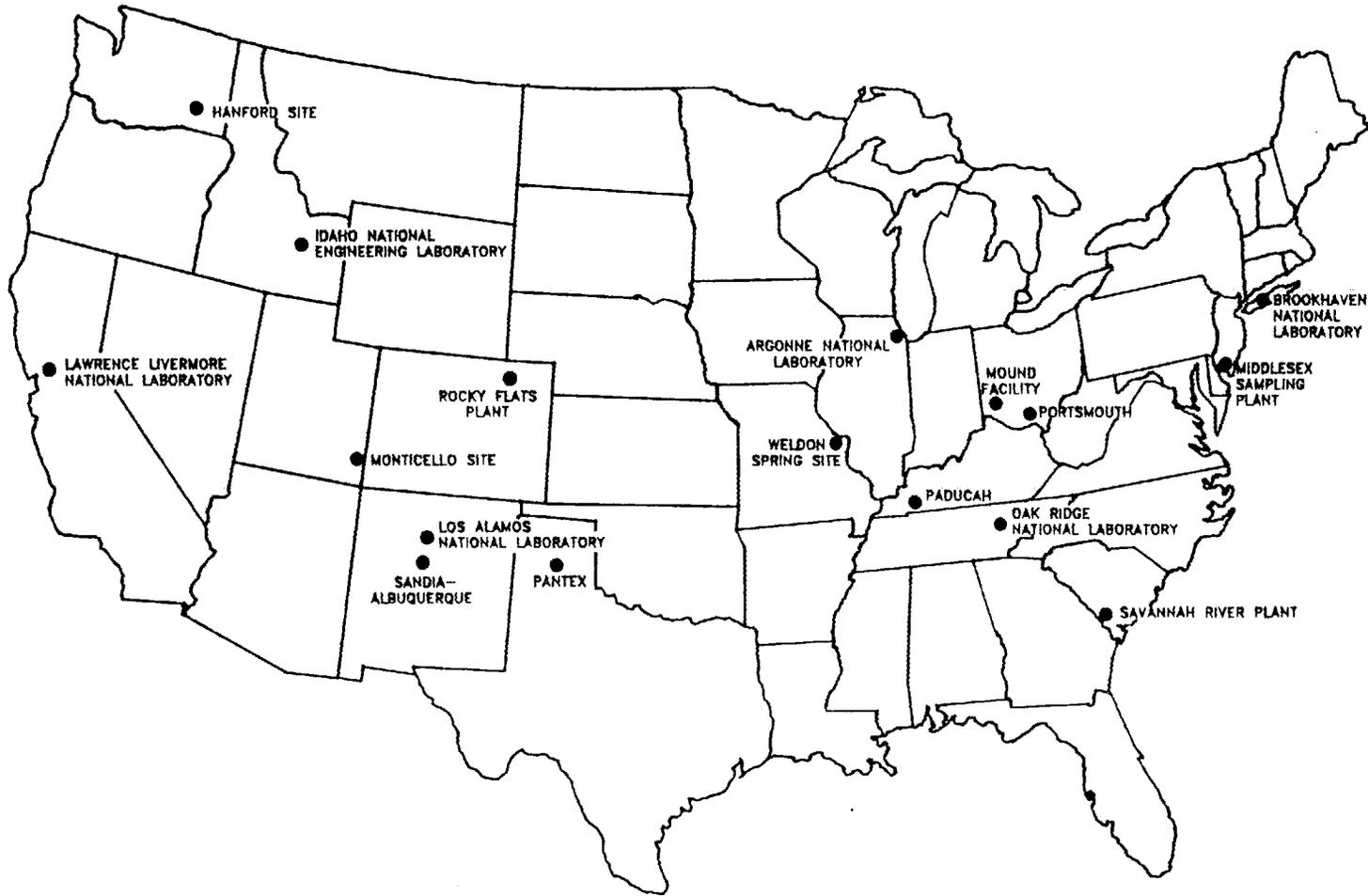


Fig. 2. U.S. Department of Energy sites.

Table 1. U.S. Department of Energy mixed waste volume per site by state

State	No. of sites	Mixed waste inventory (m ³)	Five-year projection (m ³)
California	8	878	541
Colorado	2	57,506	2,914
Connecticut	1	0	10.1
Florida	1	0	0
Hawaii	1	1.5	0.9
Idaho	2	72,748	8,484
Illinois	2	97	31
Iowa	1	0.2	0
Kentucky	1	200	380
Maine	1	0.1	0.2
Missouri	3	92	0
Nevada	1	612	0
New Jersey	2	24,468	0.5
New Mexico	4	8,946	1,260
New York	5	400	59
Ohio	5	8,705	4,764
Pennsylvania	1	28	5
South Carolina	2	136,590	24,000
Tennessee	3	44,370	17,369
Texas	1	88	195
Virginia	1	0	1.5
Washington	2	233,749	237,916
National total	50	589,479	297,932

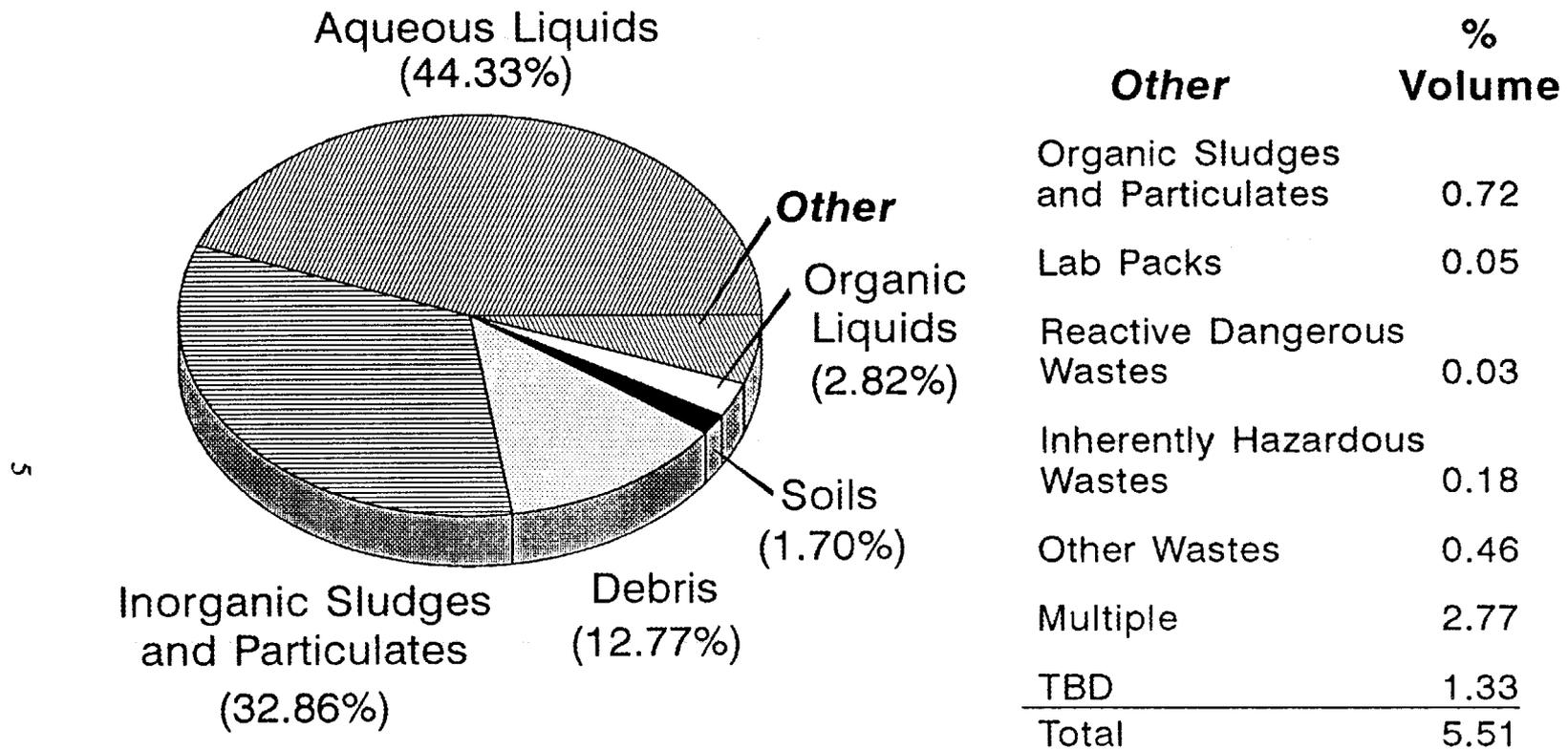


Fig. 3. Waste matrix categories.

the isotope 235, or any material artificially enriched by any of the foregoing, but does not include source material.

“Byproduct material” includes any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material, and the tailings or waste produced by the extraction or concentration of uranium or thorium from any ore processed primarily for its source material content.^[1]

Mixed wastes have been categorized based on their physical/chemical matrix, Resource Conservation and Recovery Act (RCRA) hazardous components, and radioactive characteristics. Waste streams are then categorized into “treatability groups” based on distinct combinations of these characteristics. The radioactive and physical/chemical categories are summarized in Tables 2 and 3.^[1]

The major issues concerning mixed waste technology development include the following items.^[2]

- The capability and acceptability of existing proven technologies to be effectively implemented in systems that treat a diversity of DOE waste streams have not been demonstrated.
- Federal and state laws and DOE compliance agreements require rapid commitment to plans for schedules, technologies, and facilities for treating mixed waste. Waste minimization measures are also often required.
- Major industry concerns regarding the treatment of DOE mixed waste include the lack of knowledge of market size, of the path of regulatory acceptance once a technology is demonstrated, and of mechanisms for limiting liability.
- Stakeholder input to strategic plans and the decision-making process has been limited.
- The cost of treating and disposing of mixed low-level waste and transuranic waste is estimated to be in the multibillion dollar range. This cost provides incentives to develop versatile treatment capabilities that can be standardized to assist with regulatory and public acceptance and that do not require excessive characterization costs for safe and effective operations.

3. REGULATORY SITUATION

Stored and to-be-generated mixed low-level waste must be treated according to RCRA guidelines covered in the FFCA or in other existing compliance agreements. The FFCA requires DOE to meet a constrained schedule to achieve compliance within a complex regulatory situation. Regulatory requirements are conflicting. RCRA is prescriptive, while the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) allows risk-based decisions. Further, DOE orders for implementing waste

Table 2. Mixed waste radioactivity categories

High-level wastes (48.3%)

Reprocessing of spent nuclear fuel

- Uranium
- Plutonium
- Irradiated targets

Mixed-TRU wastes (9.8%)

Remote handled
Contact handled

Mixed low-level waste (41.9%)

Remote handled

- Require transuranic alpha radionuclides containment (Alpha)
- Do not require transuranic alpha radionuclides containment

Contact handled

- Require transuranic alpha radionuclides containment (Alpha)
- Do not require transuranic alpha radionuclides containment

Table 3. Physical/chemical matrix categories

Category	Subcategory	Percent
Organic liquids		2.8%
Aqueous liquids		44.3%
Organic sludges and particulates		0.72%
Inorganic sludges and particulates	Including cemented soils	32.8%
Soils	Including soils with <50% debris	1.7%
Debris	Organic debris	12.7%
	Inorganic debris	
	Heterogenous debris	
Lab packs	With metals	0.05%
	Without metals	
Reactive/dangerous wastes	Reactive metals	0.03%
	Explosives	
	Compressed gases	

Table 3. (Continued)

Category	Subcategory	Percentage
Inherently hazardous wastes	Liquid mercury Elemental lead Beryllium dust Batteries	0.18%
Other wastes	Other, mixed, or unknown physical/chemical form	0.46%
To be determined		1.3%

treatment require interpretation, and the FFCA requires that plans and schedules for treating mixed waste be developed by October 1995.^[2]

4. MWIP MISSION

The mission of MWIP is to identify, develop, and demonstrate technologies that treat DOE mixed low-level wastes into forms suitable for disposal. These technologies must have improved performance, reduced risk, and minimized life-cycle costs over existing technology or provide treatment for waste streams for which no current treatment technology exists.^[3]

5. SYSTEMS INTEGRATION

MWIP will apply a systems approach that considers the integrated waste management process (i.e., characterization, retrieval, material handling, pretreatment, treatment, storage, and disposal).^[2] Applicable baseline technologies will be improved, new technologies will be developed, and technology transfer will be pursued.

The combination of mixed-waste characteristics highlights the need for treatment trains (i.e., series of unit operations). The performance requirements for and capacity of treatment trains will vary because of the wide spectrum of waste volumes, packaging, chemical matrices, containments, and extent of waste-stream characterization. Therefore, a systems approach is being implemented to develop mixed-waste treatment systems.

5.1 SYSTEMS ANALYSIS

Systems analysis includes the selection of alternative treatment technologies, as well as modification and evaluation of treatment flowsheets. The systems analysis includes performance assessment, risk assessment, and life-cycle costs analysis for modified or alternative technologies.

5.1.1 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.^[4]

5.1.2 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.^[5]

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. 4).

6. MATERIALS HANDLING

Materials handling includes the movement of materials from the receiving area to the process unit, into and out of the unit process, between process treatment lines, and through final waste-form packaging. The baseline technology for material movement is bidirectional conveyors; alternatives include rail transport, manual segregation, and forklift.^[6] A materials-handling technical area status report is being developed to identify processes and schemes for the movement of material from the front end of a processing facility or unit operation, throughout the facility, and through shipping. The materials-handling technical area is investigating methods to remove the contents of mixed-waste containers, to sort contents, to repackage wastes (if necessary), and to transport materials between treatment lines.^[7]

The materials-handling technical area is currently assisting the plasma hearth process team to develop flowsheets for the transfer of material into and out of the plasma hearth unit. The Materials Handling Research Center, participant in the National Science Foundation Industry/University Cooperative Research Centers Program, is being solicited for assistance in developing material-handling systems for the plasma hearth, as well as vitrification technologies.

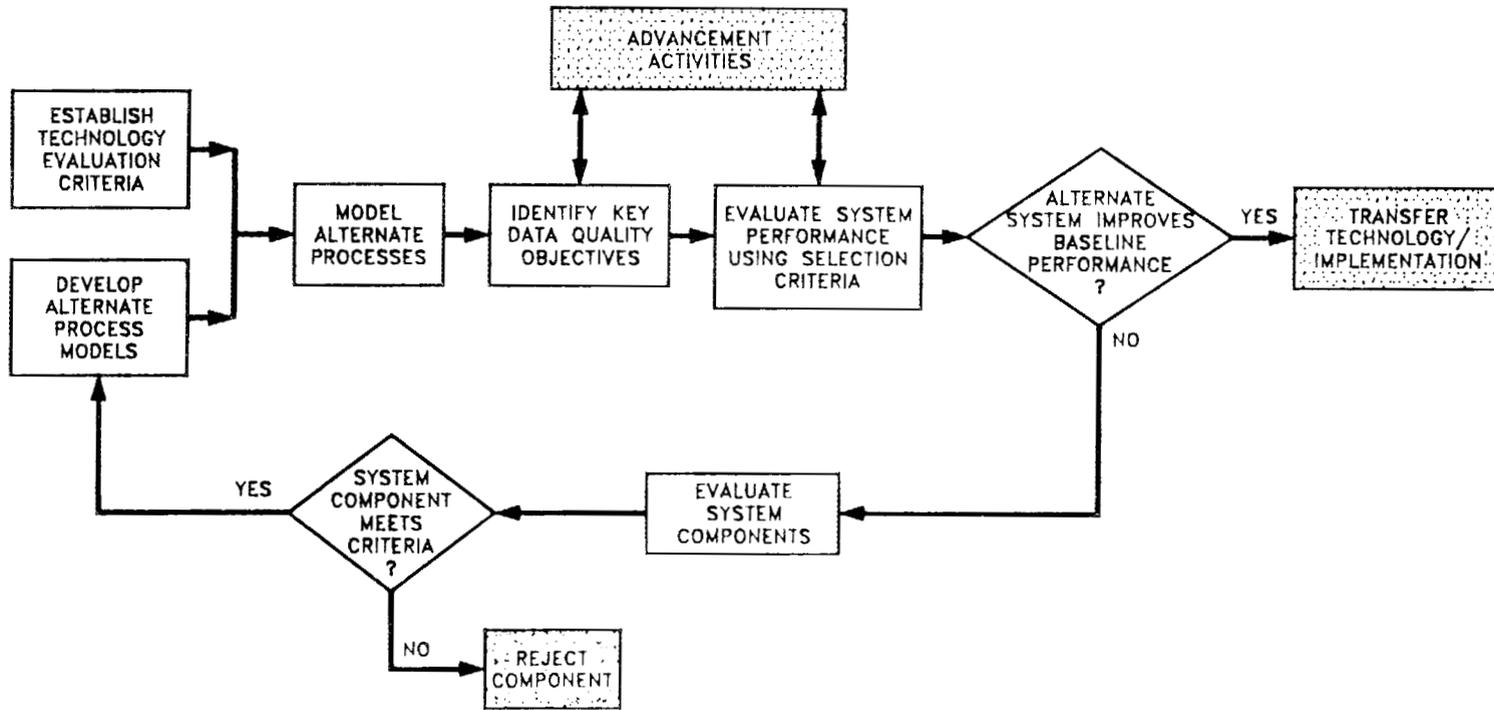


Fig. 4. Systems analysis flowsheet.

7. CHEMICAL/PHYSICAL TREATMENT

The Chemical Physical Treatment System (CPTS) performs the required pretreatment and separations on the waste streams passing through the system for discharge to the environment or efficient downstream processing. The primary separations being considered by the CPTS 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, including separation into constituents as required for subsequent thermal treatment and final form processing; (4) mercury removal and control; and (5) decontamination of waste classified as debris.^[6] Potential problem areas include processing chlorides, nitrates, high sulfur, phosphorus, and chromium-bearing salts.

The FY-94 projects being funded 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.

7.1 FREEZE CRYSTALLIZATION

Freeze crystallization is an alternative to the aqueous treatment baseline because it is a process for separating pure solvents such as water from dissolved solids, undissolved solids, and organic contaminants. The OWM baseline is 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.^[6] Freeze crystallization has significantly lower operating costs and operates at low temperatures. The low temperatures keep 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 freeze crystallization: direct contact and indirect contact. Crystals of the different solutes are formed separately and 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.

In direct-contact freeze crystallization, a compressed refrigerant is injected as a liquid and is mixed with the aqueous waste solution. The refrigerant has a lower vapor pressure than the system and therefore boils up through the solution, transferring heat directly from the aqueous solvent to the refrigerant. This heat transfer causes the solvent to form ice crystals. The ice/slurry solution is then pumped to a settling chamber where the less dense ice crystals are separated from the concentrated waste stream.

Another major type of direct-contact freeze crystallization is a vacuum process. This process uses a volatile or semivolatile component (e.g., ammonia, ethanol, or water-soluble ketone) that is either added to or is already present in the waste stream to increase the volatility of water. The process operates at or near the triple point (at or below 4-mm Hg absolute pressure) of the major solvent (water). The process produces a large volume of

vapor, which is condensed or absorbed into a suitable fluid with a lower vapor pressure than that of the solvent. If the vapor is absorbed into another fluid, it can then be boiled out and condensed in a flash evaporator or distillation column. If the vapors condense on a surface at a lower temperature than the solvent, the surface can then be washed or scrapped, and the crystals can be removed by gravity.^[8]

The other major method of freeze crystallization is the indirect-contact process. This process uses a heat exchanger in which a refrigerant gas is introduced into the heat exchanger and flows concurrently to the waste stream. After passing through the heat exchanger, the ice/slurry is pumped into a settling chamber where the less dense ice crystals are separated.

Researchers at the Westinghouse Hanford Company are currently developing this technology with Freeze Crystallization Technologies Acquisition Corporation (FCTAC) for the treatment of wastewater and groundwater treatment applications. Bench-scale and small pilot-scale studies and process development will be conducted using simulated target waste streams. A small-scale pilot-plant system will be tested by FCTAC to demonstrate the process and obtain data for designing and developing a larger pilot-plant for field testing. Based on the treatability studies and pilot-plant testing functional requirements, design specifications will be developed during FY-94.

7.2 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 of the waste forms. Nitrate destruction prior to solidification of waste would therefore be beneficial.^[9] 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 to efficiently destroy nitrate/nitrite. Immobilizing reductase enzymes on a solid support enables large specific catalytic activity to be obtained 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 inactivation. The reducing equivalents are provided by a low-voltage current, which transfers electrons from the cathode to the enzymes via an electron transfer dye.^[10]

The biocatalytic destruction of nitrate to nitrite focuses on demonstrating immobilization techniques to retain enzyme activity. This research will provide data to estimate the reactor throughput and stability towards varying feeds. The proof-of-concept efforts will provide data to determine whether studies should proceed. 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 .^[10]

7.3 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.^[11] 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 will be 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/I² 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.^[11]

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 will be gathered, and column breakthrough experiments will be conducted to provide design data.

The Efficient Separations/Processing 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.^[12] This membrane has the potential for better separations than packed columns in a more compact apparatus.^[11] Mercury removal efficiencies will be studied.

8. WASTE DESTRUCTION/STABILIZATION

The waste destruction and stabilization (WD/S) technical area develops thermal treatment technologies capable of treating a wide variety of DOE mixed waste.^[13] The WD/S technical area is also investigating emerging technologies that are alternatives to thermal treatment. Nonthermal treatment is defined as a treatment option that treats one or several DOE heterogeneous wastes at low temperature (< 300°C) and converts hazardous organics and organic matrices into gaseous products or inorganic salts.^[14] Studies have been completed to identify potential alternatives to thermal treatment. The technologies must destroy the hazardous constituents so that the enhanced final waste form will pass the EPA leach test and meet the RCRA Land Disposal Restrictions. Public acceptance

and permissibility must be taken into account, especially for thermal treatments, and minimizing secondary waste generation and releases to the off-gas system is desirable.

The FY-94 projects being funded in the WD/S technical area include fixed-hearth plasma treatment and steam reforming of mixed waste. Official mechanisms to involve stakeholders in the permitting and development of thermal treatment processes are being improved.

8.1 PLASMA ARC

MWIP is adapting the plasma torch, developed for use in metals processing, for the treatment of mixed low-level wastes. This robust technology is advantageous due to the possible acceptance of a wide range of heterogeneous waste streams with minimal prior characterization. The plasma process is a fixed-hearth process in which whole drums are fed into the stationary hearth.^[15] This high-temperature process destroys organics and stabilizes the residuals into a nonleaching, vitrified waste form. Off-gas systems ensure complete destruction of organics and removal of particulates before atmospheric discharge.

The system consists of a material-handling system for moving wastes into and out of the hearth, a primary combustion chamber, a secondary combustion chamber, and an off-gas treatment system. The volatilization of organics occurs in the primary chamber along with combustion of inorganic material; the products of incomplete combustion will be fed into the secondary combustion chamber operating with excess air above stoichiometric levels and a natural-gas burner to maintain temperatures above 980°C. The off-gas treatment system for the proof-of-principle unit consists of an air-atomized water quench, a high-temperature pulse-jet baghouse filter, and an induced air draft fan to maintain a slightly negative air pressure in the system.^[15]

Plasma refers to a highly energized gas. In the plasma hearth system, the plasma is contained within a dc torch with power levels up to 1.2 MW and nitrogen as the primary plasma gas.^[15] The torch uses the flowing gas to stabilize an electrical discharge between two electrodes. One of the electrodes is contained within the torch, and the other electrode is solid material being treated.^[16]

The ability of the system to accept poorly characterized wastes (including full 55-gal drums), the high-efficiency destruction of organics, the resulting volume reduction, and the high integrity of final waste forms make this technology very promising in the treatment of many heterogeneous waste streams. The current pilot-scale efforts are intended to provide design data for future upgrades to the hearth and off-gas system, baseline the process for comparison to future system upgrades, provide information to other key activities such as cost/risk/performance analysis, and provide overall direction for the development of the plasma hearth process.

8.2 STEAM REFORMING

The destruction of organics and nitrates in aqueous waste streams will be demonstrated by a commercially available steam reforming system. The system is provided by Synthertica Technologies, Inc., and consists of an appropriate feed system for gasification of the organic components and a subsequent high-temperature reaction chamber.^[17]

Aqueous mixed-waste simulants will be fed to a moving bed evaporator (MBE), soil simulants will be fed to heated screw feeder, and debris will be fed to a heated shredder for gasification of organics. Mineral acids produced in the gasification process will be neutralized by a moving bed containing ceramic spheres coated with an alkali base. The gaseous effluent will then be fed to a high-temperature steam reforming reactor for final organic destruction.^[17]

The appropriate feed system operates at 300–500°C with the introduction of superheated steam to gasify the organic components. Mineral acids released by the feed system gasification will be scrubbed by the MBE operating at 500°C with alkali-coated ceramic spheres. The effluent stream from the MBE will contain principally H₂, CO, CO₂, oxygenated hydrocarbon fragments, and oxides of nitrogen. Remaining organic fragments will be destroyed by steam reforming in the high-temperature (1200°C) reaction chamber of the detoxifier. Acids that were not neutralized by the MBE or that were produced in the detoxifier will be neutralized by a commercial adsorbent.^[17]

Steam gasification detoxifiers achieve high destruction rate efficiencies and have low off-gas volume consisting of NO_x, SO_x, products of incomplete combustion, and particulates. Downstream off-gas treatment units ensure that the stack gas meets environmental requirements. The current technology development includes six full-scale simulant destruction tests on aqueous organic waste simulant, high organic sludge waste simulant, ashes and solids simulant, lab packs stimulant, and a Trimsol-coated machining waste.^[18]

9. FINAL WASTE FORMS

The final waste form technical area is currently developing waste forms with sustained durability in the final disposal setting and data on waste forms to support a Performance Assessment (PA). The PA required by DOE Order 5820.2A is intended to show by analysis that the waste treatment process, the processed waste form, and disposal controls adequately protect human health and the environment.^[19] The final waste forms technical area is currently developing vitrification process limits, thermoplastic waste forms, and phosphate-bonded ceramics.

9.1 THERMAL VITRIFICATION PROCESS

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. Thermally formed glasses are produced by melting materials and cooling the liquids to form a solid without crystallization. The waste form (glass) usually contains less than 30 wt % of waste solids; however, the thermal treatment process reduces the waste volume significantly. Specific waste streams can be added at higher temperatures, and under conditions where the waste contains sufficient glass formers, a glass containing only waste can be produced.^[19]

Glass has the ability to accept a wide variety and amount of radioactive and hazardous materials. Because its physical properties are relatively constant with time, glass has been selected to stabilize a variety of waste streams. 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.^[19] Currently, vitrification and plasma arc melting (see Sect. 8.1) are being developed under MWIP.

9.2 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).^[20] 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 to 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.^[19]

SPC is an encapsulating waste-immobilization material. The wastes are encapsulated in the sulfur matrix with the exception of a few sulfide-forming metals.^[21] SPC has a high mechanical strength in a short period of time, high resistance to many corrosive environments, and low porosity.^[21] 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.^[19]

10. OFF-GAS TREATMENT

10.1 CONTINUOUS MONITORING USING TUNABLE DIODE LASER

This project will develop and demonstrate near-infrared tunable diode laser (TDL) spectroscopy^[22] 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 (all information from TTP).

10.2 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

This project will develop and demonstrate an instrument system to continuously measure total, elemental, and speciated mercury in effluent from DOE waste treatment units.^[23] 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 ppb (by volume).

10.3 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.^[24] 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 μm down to about 0.001 μm . The porous filter elements will have pore

diameters of about 0.25- μm to provide surface filtration and will have complete surface capture of particles with diameters of 0.3 μm or larger. Using filter elements with 0.25- μm diameter pores, particles with a diameter of 0.3 μm 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.

10.4 DEMONSTRATION OF PROOF-OF-PRINCIPLE 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^[25] will demonstrate that the steel HEPA filter made with 0.5- μm steel fibers meets both efficiency and pressure drop requirements for HEPA filters. Steel fibers with a 0.5- μm 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.

10.5 CONTROL AND RECOVERY OF VAPOR-PHASE MERCURY AND PARTICULATE USING A REGENERABLE GOLD-PLATED POROUS SUBSTRATE IMMOBILIZED IN A CERAMIC FILTER

A patented technology which uses a thinly gold-plated, regenerable ceramic filter to capture vapor-phase mercury and particulate will be developed and demonstrated.^[26] 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.

10.6 DEVELOPMENT OF A 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.^[27] 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.

11. FUTURE NEEDS

MWIP is problem oriented and supports DOE waste management needs and environmental restoration needs. MWIP has identified technology areas, as discussed, including systems analysis, material handling, chemical/physical treatment, waste destruction and stabilization, off-gas treatment, and final waste forms. Improved technologies must be demonstrated on hazardous and radioactive constituents before being accepted as the treatment technology of choice.^[14]

Significant problem-oriented technology development is in progress. A list of current principle investigators with phone numbers is given in Table 4. Technology development opportunities exist within the following technology areas: chemical/physical treatment, waste destruction and stabilization, off-gas treatment, and final waste forms production and assessment. For a more complete description of the mixed waste technology development needs for DOE waste streams, contact the Environmental Restoration and Waste Management Office of Technology Development.

Table 4. FY-94 MWIP projects and principal investigators

Technical Task Plan title	Principal investigator	Telephone number
Systems Analysis Area		
MWIP Program Support	Jan Berry	615-574-6907
Systems Analysis	J. J. Ferrada	615-574-4993
Emerging Technology Systems Integration	J. J. Ferrada	615-574-4993
Risk Assessment of MWIP	R. Ragaini	510-423-8877
Cost Savings Support to MWIP	S. Booth	505-667-9422
Waste Stream Diagnostic and Control	W. D. Bostick	615-574-6825
Process Monitoring and Control	L. C. Walters	208-533-7384
MWIP Support of FFCA Compliance	Jan Berry	615-574-6907
Front-End Handling (FEH) Area		
FEH Technical Area Leader	C. Ward	803-725-5891
Characterization to Treat for PHP	G. C. McClellan	208-533-7257
Chemical Physical Area		
Chem/Phys Technical Area Leader	C. Brown	303-966-3667
Mercury Control	J. Perona	615-576-9280
Biocatalyst Destruction of Nitrate	D. Chaiko	708-252-4399
Freeze Crystallization Technology	J. Wong	509-372-2464
Decontamination of Containers Equipment	C. Brown	303-966-3667
Waste Destruction and Stabilization (WD/S) Area		
WD/S Technical Area Leader	J. McFee	505-262-8740
Fixed-Hearth Plasma Treatment Process	C. Bonzon	208-526-0614
PHP Radioactive Waste Test-Idaho	S. Bates	208-528-6790
Steam Reforming of Organics and Nitrates	J. Sprung	505-844-0234
Alternatives to Thermal Treatment	J. McFee	505-262-8740

Table 4. (Continued)

Technical Task Plan title	Principal investigator	Telephone number
Off-Gas Treatment Area		
Off-gas Technical Area Leader	N. French	505-294-3185
Monitoring Using Tunable Diode Laser	D. Ottesen	510-294-3567
Elemental, Total, Speciated Mercury	J. Wang	510-294-2783
Hg Vapor Removal and Control	M. Hardwick	510-294-2157
Real-Time Monitoring of Alpha Emissions	R. Gritzso	505-667-0481
Off-Gas Treatment using Steel HEPA Filter	W. Bergman	510-422-8203
HEPA Filter Membrane	D. Fain	615-574-9932
Final Waste Forms (FWF) Area		
FWF Technical Support	J. Mayberry	208-528-2116
Vitrification Process Limits	D. Bickford	803-725-3737
Vitrification Process Limits/Treatability Studies	R. Peters	509-376-4579
Chemically Bonded Ceramics	A. Wagh	708-252-4295
Performance Criteria	E. Franz	516-282-3045
MW Treatability-Thermoplastic Final Forms	P. Kalb	516-282-3045

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