CONF-880510--1

DE88 007470

INNOVATIVE TECHNOLOGIES FOR THE TREATMENT OF HAZARDOUS AND MIXED WASTES

L. D. Eyman
Hazardous Waste Remedial Actions Program
Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee, USA 37831

T. D. Anderson
U.S. Department of Energy
DP-124(GTN)
Washington, D.C., USA 20545

HAZWRAP SUPPORT CONTRACTOR OFFICE
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

INNOVATIVE TECHNOLOGIES FOR THE TREATMENT OF HAZARDOUS AND MIXED WASTES

ABSTRACT

The treatment, storage, and disposal of hazardous and mixed wastes incur significant costs for Department of Energy (DOE) installations. These wastes must be managed under strict environmental controls and regulations to prevent the possibility of migration of hazardous materials to the biosphere. Through the Hazardous Waste Remedial Actions Program, the DOE is seeking to develop innovative ways of improving current treatment technologies to eliminate the hazardous components of wastes, reduce waste management costs, and minimize the volume requiring disposal as hazardous or mixed waste. Sponsored projects progress from research and development to field demonstration. Among the innovative technologies under development are supercritical water oxidation of hazardous chemicals, microwave-assisted destruction of chlorinated hydrocarbons, paramagnetic separation of metals from waste, detoxification and reclamation of waste acid, nitrate destruction through calcination, treatment/disposal of reactive metals, and methodologies for encapsulation. Technologies at a demonstration phase include detoxification of mixed waste sludge, microbial degradation of polychlorinated biphenyls in soil, and the remediation process for a hydrocarbon spill.

1. INTRODUCTION

The U.S. Department of Energy (DOE) has embarked on a program to minimize its production of hazardous wastes, including mixed hazardous and radioactive wastes. Through the Hazardous Waste Remedial Actions Program (HAZWRAP), the DOE is examining currently generated waste streams at its laboratories and fuel production and reprocessing facilities to reduce both the volumes and toxicity of the wastes [1].

Environmental protection requirements encompass all aspects of the treatment, storage, and disposal of hazardous and mixed wastes to ensure that hazardous chemicals are isolated from the biosphere. By minimizing the amount of waste requiring management as hazardous waste, the DOE installations realize not only economic savings in all areas of waste management but also potential reduction of future migration of contaminants and of remedial containment measures. Some of the current technical requirements for all hazardous waste facilities include controlled entry to the facility; personnel training, and fire, explosion, and release control measures. Land treatment facilities, surface impoundments, and land disposal units are subject to requirements for groundwater monitoring through properly designed monitoring wells, runoff prevention, double containment layers with leak detection capability, and facilities for leachate collection. The wastes and waste forms eligible for disposal are also subject to numerous requirements and prohibitions, including bans on disposal of liquids, dioxins, certain solvents, and -- at concentrations above specified limits -- toxic metals, polychlorinated biphenyls (PCBs), and halogenated organics. In addition, and compounding the need to reduce the production of hazardous and mixed wastes, there is a lack of availability of licensed disposal sites, especially for mixed wastes. Current DOE practice is to dispose of hazardous wastes at commercial facilities. The waste then leaves DOE control; however, another feature of environmental regulation is that the waste generator is ultimately responsible for cleaning up any migration of its waste from the disposal facility. Consequently, long-term liability remains with DOE even though its hazardous wastes are disposed of in licensed commercial facilities. No commercial facilities exist for mixed wastes. DOE is currently storing these wastes pending availability of permitted facilities owned by DOE. The volume of waste requiring storage and the long-term liability issues further create a need for hazardous and mixed waste minimization.

Current DOE hazardous and mixed waste operations have relied on traditional means of waste treatment and preparation of wastes for disposal. These treatment technologies include neutralization, chemical oxidation and reduction, high temperature thermal oxidation by incineration, solvent recovery, blending, encapsulation, mixing with inert matrices such as cement grout, and an array of biological methods. Based on analysis performed under HAZWRAP, it was apparent that these current methods could be improved upon to reduce the volume of hazardous effluents requiring disposal [2,3].

A search was initiated to locate treatment methods that would show promise in improving current hazardous waste management techniques. Existing treatment methods for other materials were surveyed for applicability to DOE hazardous waste effluents. The waste streams were surveyed to determine if changes in treatment methods or handling could reduce, recycle, or detoxify the resultant waste material. A key component of the survey was the Waste Information Network (WIN), a computerized communications and data retrieval system developed by HAZWRAP [4,5]. Several promising areas were identified for further research and development (R&D) and have been developed to the laboratory-scale development phase; other areas have progressed to a demonstration phase.

Among the innovative hazardous waste treatment technologies under development are supercritical water oxidation, microwave-assisted destruction of chlorinated hydrocarbons, paramagnetic separation of heavy metal waste, detoxification and reclamation of waste acid, nitrate destruction by calcination, treatment/disposal of reactive metals, and methodologies for encapsulation. Among the technologies at a field demonstration phase are detoxification of mixed waste sludge, microbial degradation of PCBs in soil, and remedial processes for a hydrocarbon spill. Through HAZWRAP, the DOE is investigating the feasibility of applying these innovative technologies to treatment of hazardous and mixed waste streams.

2. TECHNOLOGY DEVELOPMENT

The approach in these R&D projects involves a planned progression from research and development phase to pilot-plant phase to field demonstration phase. Demonstration consists of treatment of an actual DOE waste stream to show a practical application of the technology and the initiation of the solution of a real world problem. The final phase entails transfer of the technology to the scientific and engineering community, including other agencies and the commercial sector.

2.1. Supercritical water oxidation

This technology [6] uses the properties of water in its supercritical state (above 647°K and 22.13 MPa) to dissolve and oxidize organic hazardous wastes such as chlorinated hydrocarbons. The unique properties of water at a supercritical state include the ability to dissolve nonpolar, organic compounds, while inorganic salts exhibit greatly reduced solubility. Although the oxidation taking place is similar to combustion, it occurs at much lower temperatures than incineration (at about 650 to 800°K as compared with 2000°K or more), can be confined to a completely closed system, and produces no oxides of nitrogen. During combustion, the organic compounds are reduced to carbon dioxide and water, with the heat of oxidation having the potential for recovery to sustain the treatment reaction and even to produce net heat for other uses. Oxidation of halogenated hydrocarbon compounds also produces corresponding inorganic acids (e.g., HCl is produced during oxidation of chlorinated hydrocarbons), which may be neutralized as they are produced to form inorganic salts.

The relative insolubility of inorganic salts allows these components to be easily separated out as solids and reused or discarded. The combustion process is capable of high destruction efficiencies for the organics. The separation of inorganics and efficient oxidation of organics can result in clean water being the major product of the supercritical water oxidation treatment. The use of this process to treat aqueous effluents and even groundwater is intuitive. It also appears to have potential in treating soils, because water can permeate the soil and surround the soil particles.

Several commercial firms in the United States are also investigating applications of supercritical water oxidation. These efforts are focused on applied research and demonstration. Indications are that standard pressure-vessel technology can be used to construct plants with capacities in the 40,000 to 200,000 L/day range. The kinetics of the reactions taking place during supercritical water oxidation, though not well understood, are not being investigated to any extent by these firms. Part of the DOE-HAZWRAP-sponsored work is studying the basic chemical kinetics of the process. The consensus within the agency remains that -- in the long term -- time, energy, and funding are conserved with solid scientific understanding of the technological processes.

Although the oxidative process works at a wide range of concentrations of organics, from 2 to 100%, the operation of the reaction on a self-sustaining basis using the heat supplied by the process is optimized at about 10% concentration. The efficiencies of organic destruction at the small concentrations common to groundwater contamination problems (i.e., parts per million levels or less) are not well characterized, and the economics of supplying the heat required to oxidize such small levels of organics would make the process uneconomical at those levels. Further directions for HAZWRAP investigations include better understanding of the kinetics of the reactions, experiments at small concentrations of organic wastes, and pilot-scale and field demonstration of the technology.

2.2. Microwave-assisted destruction of hazardous waste

Because microwave oven technology is readily available and provides rapid and uniform heating, a study [7] was initiated to determine the feasibility of detoxifying liquid hazardous waste containing organic solvents. The investigation was conducted using trichloroethylene (TCE), a major constituent of DOE waste streams, heated by a commercially available microwave oven (2.45 GHz frequency) while passing through an activated carbon bed.

Destruction efficiencies in the 80% range in laboratory-scale experiments were encouraging. In this work, TCE was stripped from aqueous solution and passed through activated carbon, both with and without copper and chromium oxide catalysts, while being heated in a quartz reaction vessel by microwaves. The temperature during oxidation was determined to be about 350°C, which is significantly lower than that required for conventional incineration processes.

Investigation of microwave heating to regenerate the carbon beds was also conducted. Although some regeneration was possible, the adsorbed chlorine on the carbon bed was not easily removed. Regeneration of the beds is critical to the efficiency of the process, and further work in this area is needed.

2.3. Paramagnetic separation of waste

A key aspect of the DOE Defense Programs approach to the management of mixed and hazardous wastes is the development of substitute or modified processes resulting in a reduction of waste materials requiring treatment, disposal, and storage. Research and development studies involving the use of paramagnetic separations pointed to a potential waste minimization process [8]. Bench-scale tests of pretreatment by magnetic separation of process wastes containing magnesium fluoride contaminated with uranium have shown reduction in the level of contamination comparable with that obtained from the present chemical refinery process while generating no additional wastes. Although the remaining concentrated material must be further processed to obtain pure uranium for reuse, the quantity of magnesium fluoride/uranium to be chemically processed would be reduced and, thus, decrease the amounts of acid and organic wastes produced. Estimates show that for every pound of contaminated material entering the refinery, 26 to 37 kg (7 to 10 lb) of low-level radioactive waste requiring disposal are now generated. Thus, magnetic separation pretreatment could impact storage and disposal costs. Laboratory tests of the paramagnetic separations will be followed by pilot-scale testing and demonstration of the effectiveness of this technology.

Laboratory-scale tests using a superconducting-magnetic separation system to separate uranium from magnesium fluorides have been successfully performed. Actual samples of this waste were collected from the Feed Material Production Center at Fernald, Ohio. An existing, commercially available magnetic system specially made for dry open-gradient separation was utilized. Coiled wires immersed in a liquid helium bath provided a cylindrical magnetic field gradient separating particles that pass through the center into a spectrum representative of the magnetic susceptibilities of the particles. The paramagnetic materials are pulled toward the outer portion of the core while the diamagnetic materials are forced toward the center. The particles with a magnetic susceptibility near zero are unaffected.

Separations from magnesium fluoride were also studied on the bench-scale magnet in free-fall mode using regrinding techniques. Free-fall tests performed on a wire mesh feed with a concentration of 0.9% uranium resulted in a spectrum of concentrations from 8.5 to 0.4% uranium. The resulting fractions are not as pure as those obtained from open-gradient separations that have achieved as low as 0.04% uranium. This separation mode may be utilized, however, where a higher uranium concentration is tolerable.

Initial gradient tests have been performed on a calcium oxide/uranium mixture. Open-gradient chromium separations from a pond sludge were also attempted. The technology may have a number of applications as a tool for waste minimization.

2.4. Waste acid detoxification and reclamation

Because DOE nuclear fuel fabrication and reprocessing operations result in significant quantities of metal-bearing waste acid effluents, HAZWRAP initiated a project to detoxify waste acid by removing heavy metals and radionuclides and recovering the acid for reuse [9]. Where economically justified, the metals can also be recovered for reuse. As a result of these recycling efforts, acid waste streams can be greatly reduced in volume.

Bench-scale experiments were conducted using a waste stream from an actual DOE uranium fuel fabrication operation at the Hanford facility in Richland, Washington. Historically, the acid is discharged as waste when the concentration of metal impurities reaches a maximum limit. Three waste acid solutions were processed during the tests: a chemical milling solution containing nitric and sulfuric acid with uranium as the major metal contaminant, a strip solution containing nitric acid with copper as the major metal impurity, and an etch solution containing hydrofluoric and nitric acid with zirconium as the major metal impurity.

The milling is routinely neutralized and the uranium precipitated out as sodium diuranate for recovery. The strip and etch solutions are also neutralized for disposal, while the copper and zirconium precipitates are disposed of as waste. The reclamation of these acids would significantly reduce waste generation. In addition, the large volume of nitrates currently requiring disposal could be reduced or eliminated, removing a potential immobile contaminant from the environment.

The waste acid detoxification and reclamation project was only moderately successful with respect to the etch solution because of difficulty in removing the zirconate salt. Future plans include improvement in this process. Reclamation of the strip solution was more successful, with an average of approximately 75% of the nitric acid regenerated and an average of 88% of the copper removed. Distillation tests using the milling solution were somewhat successful, with the concentration of the recovered nitric acid related to the initial concentration and the addition of sulfuric acid to the waste stream.

The highly corrosive nature of the acids was considered in the testing of candidate materials, mainly plastics, for construction of a pilot-scale acid reclamation system. Many plastics survived an ambient temperature 76-day immersion test in the acids, while several survived a 10-day test at a temperature of 100°C, indicating the feasibility of constructing a reclamation system from readily available plastic materials. Future plans include refinement of the reclamation techniques investigated to eliminate problems encountered and additional work on materials survivability.

2.5. Nitrate destruction in an elutriated fluid-bed calciner

In neutralization and disposal of waste acids, sodium nitrate is a major constituent of the waste. The nitrate waste from DOE operations is often contaminated with other hazardous chemicals and toxic and radioactive metals. HAZWRAP determined that a cost-effective method of converting the nitrate ions to elemental nitrogen gas and water would not only reduce the volume of waste requiring disposal but would provide for an improved waste form when mixed with grout or glass.

The calcining of sodium nitrate waste was tested at the laboratory scale using a surplus calciner [10]. Although initial runs resulted in destruction of over two-thirds of the nitrate, the calciner became clogged when additional material was added in an attempt to increase the destruction efficiency. A test run with copper nitrate showed greater than 99% destruction efficiency. Future plans include redesign of the calciner configuration to enable greater efficiency in processing sodium nitrate waste.

2.6. Improved treatment/disposal of reactive metals

Another wide-ranging waste problem in the DOE Defense Programs has been the treatment and disposal of waste reactive metals, primarily sodium (a waste from sodium-cooled, fast-breeder nuclear reactors). The basic approach used in this

HAZWRAP-sponsored R&D project was to convert the reactive metal (in preliminary work, sodium contaminated with small quantities of both radioactive and nonradioactive materials) to a glass form by reacting it with silica sand along with additives to impart the desired mechanical and chemical integrity to the waste form [11]. A high soda silicate glass was initially selected with small quantities of additives to yield acceptable resistance to leaching by groundwater and other environmental stresses.

Various glass formulations were developed and subjected to testing. Differential thermal analyses with varying compositions of sodium dioxide, silicon dioxide, calcium dioxide, and magnesium oxide showed that the primary glass-forming reactions occur at less than 300°C. A suite of glass samples was produced in a laboratory furnace and qualitative glass characteristics were determined. Appropriate leaching tests were carried out.

Planning ahead to a pilot-plant and/or demonstration phase, the investigators have designed a conceptual process for waste reactive metal conversion, incorporating a high temperature cyclone. A commercial firm with considerable experience in such design has expressed interest in working with the DOE contractor to build and test a prototype demonstration system.

2.7. Innovative encapsulation methods

To protect public health and safety along with the environment in both the short and long terms, HAZWRAP has initiated R&D on technologies that approach hazardous chemical and mixed waste problems with chemical fixation and/or solidification methods [12,13]. The objective is to convert the hazardous waste to a form suitable for disposal in landfill sites or radioactive burial sites. The DOE researchers are looking at materials and processes that have the potential to encapsulate "problem" waste streams, employ simple and economical procedures, result in environmentally compatible forms during storage, transportation, and disposal, and demonstrate compliance with waste form performance and disposal criteria.

Solidification materials currently in use in commercial or DOE facilities include cement, asphalt, vinyl ester styrene, and gypsum. The R&D work considers various modifications or additions to these agents as well as an array of nontraditional agents such as polyethylene, sulfur cement, and polyester-styrene. In addition to the characterization of the materials under test in combination with various waste forms, the project also approaches the design and engineering of systems to deliver and mix the wastes and binders.

3. TECHNOLOGY DEMONSTRATION

When sufficient R&D on a new and innovative technology has progressed to the point where a demonstration with an actual waste stream can be accomplished, the DOE investigators, in collaboration with the commercial sector when applicable, plan and execute a full field experiment at the appropriate site. Planning includes completing the necessary permitting and documentation activities for technology transfer to all parties interested in waste management. Several demonstrations are already under way through HAZWRAP sponsorship [14]. In these initial demonstrations, much of the development work was available from ongoing DOE experience or from commercial vendors. In contrast, each of the development projects described in the previous section will progress and evolve into a similar demonstration phase.

3.1. Mixed waste sludge detoxification

The sludge detoxification demonstration is being conducted at Oak Ridge and constitutes the first technology demonstration selected by HAZWRAP. In this example, a private sector contractor with technology for the treatment of mixed waste sludges will actually carry out the work. The sludges result from treatment of various wastewater streams at the Y-12 Plant and the Oak Ridge Gaseous Diffusion Plant. The process involves thermal treatment of the sludge to remove water and organic materials followed by fixation of the dried solids in a cement-based grout matrix. Water separated from the organic material will be used in cement formulation. Disposal of the organic material is not a part of the demonstration at this stage. A key part of the project will be an attempt to "delist" the dried solids under applicable Resource Conservation and Recovery Act provisions through the U.S. Environmental Protection Agency. At this point a contract has been executed and the permitting activities are under way.

3.2. Biodegradation of polychlorinated biphenyls

The objective of this demonstration project (short term) is to determine the feasibility of using biodegradation as a treatment method for sites contaminated with PCBs at the Y-12 Plant in Oak Ridge. The study represents another aspect of the strategy involved in HAZWRAP-sponsored work, that is, cooperative efforts between DOE installations (Oak Ridge National Laboratory and the Y-12 Plant), universities (University of Tennessee), and the private sector (Oak Ridge Research Institute). Lysimeters have been installed along a PCB-contaminated creek bank for an in situ study of biodegradation. In addition, soil samples were collected for chemical and microbial analyses. A slurry bioreactor is being operated for the study of biodegradation under controlled conditions. In the field tests, the soil will be characterized for microbial population and community structure, levels of PCBs and other contaminants, and mobility of the contaminants. Controlled additions to the lysimeters will be monitored by leachate and soil analyses.

3.3. Gasoline spill remedial process

The objective of this project is to develop appropriate processes and process concepts to demonstrate the in situ mobilization and removal of volatile fuel hydrocarbons (gasoline) from both deep intervals of contaminated, saturated soils and the affected interstitial groundwater. The gasoline spill located at the Lawrence Livermore National Laboratory site (Building 403) has resulted in relatively high concentrations of fuel hydrocarbon contaminants trapped in the saturated soil. The selected remedial treatment processes for the contaminated soil and groundwater are (1) dewatering of the saturated soil, (2) induced soil venting, (3) air or vacuum stripping of the extracted groundwater, and (4) incineration of gaseous effluent from the venting and stripping operations. The investigators are attempting to develop a system capable of reducing volatile hydrocarbon levels to <1 ppb in the anticipated large volumes of groundwater. Two modifications were studied: spray aeration in a partial vacuum and stripping in a vacuum degasifier. Vacuum degasification yielded stripping efficiencies of about 99.99% when used with a packed tower of smaller volume than required for conventional air stripping. The demonstration is in progress.

4. CONCLUSIONS

The DOE-HAZWRAP approach attempts to solve waste treatment problems with a progression from the needed development work to actual on-site demonstration of the applicability of the technology. Information on the performance, acceptability, costs, and regulatory impact of innovative technologies will be gained. Significant environmental and health problems within the DOE Defense Programs will be impacted or solved. Technology transfer of this information to the scientific and engineering world forms the final and key aspect of this progression.

5. REFERENCES

[1] EYMAN, L.D., HAZWRAP Annual Report for FY 1986, Rep. DOE/HWP-25, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (1987).

[2] RODGERS, B.R., POJASEK, R.B., and SCHOENBERGER, R.J., Hazardous Chemical Defense Waste Management Program. Technology Review Report: Currently Available Technology, Rep. DOE/HWP-4, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (1985).

[3] DOE AD HOC WASTE OPERATING CONTRACTORS COMMITTEE, DOE Defense Waste Management Needs Assessment/Resolution Document, Rep. prepared by Maxima Corp., Oak Ridge, TN (1987).

[4] FORE, C.S., MASON, P.M., MOORE, R.S., BAYLESS, T.L., and DALFONSO, P.H., Hazardous Chemical Defense Waste Management Program. DOE Waste Information Network. Information Systems: Data Management and Analysis, Rep. DOE/HWP-10, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (1985).

[5] FORE, C.S., DOE Waste Information Network: A Summary Report of DOE-DP Hazardous and Mixed Wastes, Rep. DOE/HWP-17, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (1986).

[6] ROFER, C.K., Supercritical Water Oxidation of Hazardous Chemical Waste, Kinetics Experiments and Bench-Scale System, Background, Design and Preliminary Experiments, Rep. LA-11106-MS, DOE/HWP-42, Los Alamos National Laboratory, NM (1987).

[7] VARMA, R., NANDI, S.P., CLEAVELAND, D.C., Microwave-Assisted Chemical Process for Treatment of Hazardous Waste, Rep. ANL-87-120, DOE/HWP-28, Argonne National Laboratory, IL (1987).

[8] HOEGLER, J.M., Bench-Scale Magnetic Separation of Department of Energy Wastes, Rep. DOE/HWP-34, Oak Ridge National Laboratory, TN (1987).

[9] STEWART, T.L., Waste Acid Detoxification and Reclamation: Summary of Bench-Scale Tests for FY 1986 and FY 1987, Rep. PNL-6321, DOE/HWP-41, Pacific Northwest Laboratory, WA (1987).

[10] COWAN, R.G., CASH, R.J., OWEN, T.J., SHOOK, G.E., Nitrate Destruction in an Elutriated Fluid-Bed Calciner, Rep. WHC-EP-H0062, DOE/HWP-39, Westinghouse Hanford Company, WA (1987).

[11] RAJAN, J.B., KUMAR, R., and VISSERS, D.R., Improved Treatment/Disposal of Reactive Metals, Rep. ANL-87-39, DOE/HWP-29, Argonne National Laboratory, IL (1987).

[12] FRANZ, E.M., HEISER, J.H., and COLOMBO, P., Immobilization of Sodium Nitrate Waste with Polymers, Rep. BNL-52081, Brookhaven National Laboratory, NY (1987).

[13] EPLER, J.L., PARKER, J.C., and ROTHERMICH, N.E., HAZWRAP Fiscal Year 1988 Program Plan for Hazardous Waste Research and Development, Rep. DOE/HWP-44, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (IN PRESS).

[14] EYMAN, L.D., HAZWRAP Annual Report for FY 1987, Rep. DOE/HWP-XX, Martin Marietta Energy Systems, Inc., Oak Ridge, TN (IN PRESS).