Environmental Restoration/ Waste Management- APPLIED TECHNOLOGY

Semiannual Report for July 1992-June 1993

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Use of Ceramic Forms to Immobilize Residues from the Treatment of Mixed Wastes

Proposed Treatment of Sodium Nitrate-Based Wastes to Minimize Disposal Volume

Evaluating Actinide Volatility and Emissions during the Thermal Treatment of Mixed Wastes

In Situ Microbial Filter for Groundwater Remediation

Joint LLNL/Russian Cooperation in Environmental Technologies and Waste Management

Fiber-Optic Sensors for Characterizing Soil and Groundwater Contamination

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Applied Technology Semiannual Report**

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Environmental Restoration/Waste Management APPLIED TECHNOLOGY

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On the Cover

Typical compositions and activities of sodium nitrate-based DOE mixed wastes. The article beginning on p. 6 describes an innovative technique for processing and disposing of such wastes.

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Foreword

After the publication of the first issue of the *Environmental Restoration/Waste Management-Applied Technology (ER/WM-AT) Semiannual Report*—and when preparation of this issue was almost complete—the ER/WM-AT Program underwent further reorganization. The program as a whole has been taken into the Laboratory's newly formed Environmental Programs Directorate, and in the process it has been renamed the Environmental Technologies Program. Further, the Department of Energy's recent approval of the construction of the Mixed Waste Management Facility (MWMF, described in the Overview on p. v) has led to that project's being organizationally separated from the ER/WM-AT Program, in which it took shape.

The articles in this double issue complement those in the first issue by covering additional topics: ceramic final forms for residues of mixed waste treatment; treatment of wastes containing sodium nitrate; actinide volatility in thermal oxidation processes; *in situ* microbial filters for remediating contaminated soils; collaboration with scientists in the former Soviet Union on new ER/WM technologies; and fiber-optic sensors for chlorinated organic solvents.

Martyn Adamson
Scientific Editor

Overview

The Environmental Restoration/Waste Management-Applied Technology (ER/WM-AT) Program is developing restoration and waste treatment technologies needed for the ongoing environmental cleanup of the Department of Energy (DOE) complex and treatment technologies for wastes generated in the nuclear weapons production complex. These technologies can find application to similar problems nationally and even worldwide. They can be demonstrated at the Livermore site, which mirrors (on a small scale) many of the environmental and waste management problems of the rest of the DOE complex. Their commercialization should speed cleanup, and the scope of the task should make it attractive to U.S. industry. We are already working with industrial partners in many of our development programs.

Recent Highlights

Construction Approval for the Mixed Waste Management Facility

The Mixed Waste Management Facility (MWMF)¹ has received KD-1 (construction) approval from the Department of Energy (DOE), with about \$75 million budgeted for the entire project. Preliminary design of the MWMF began in July 1994, and initial operation is scheduled for 1997. The MWMF will be a fully integrated pilot-scale demonstration facility that will provide a bridge between technologies demonstrated at bench scale and full-scale mixed waste treatment facilities. The MWMF is a key element in the deployment of effective and environmentally acceptable alternative treatment processes to incineration for DOE's large inventory of low-level organic mixed waste.

The Mixed Waste Management Facility has received KD-1 (construction) approval from the DOE

Success in Dynamic Underground Stripping

Dynamic underground stripping, described in the first issue of this report,² far exceeded expectations in its first full-scale test, conducted at a location on the LLNL Livermore site where thousands of gallons of gasoline had leaked from an underground storage tank in the 1970s. In just a few months, 7800 gallons of gasoline were extracted from the ground, cleaning up essentially all the free gasoline from 300 m³ (80,000 cubic yards) of earth at depths of 18 to 43 m (60 to 140 ft). UC Berkeley researchers, who developed dynamic underground stripping, now plan to test it for cleanup of common chlorinated solvents, such as trichloroethylene and perchloroethane. The LLNL team working on the process plans to use it next to clean up spills of solvents at a military base slated for closure.

Summaries of Articles in This Issue

The first article, *Use of Ceramic Forms to Immobilize Residues from the Treatment of Mixed Wastes*, describes work on a proposed waste form using ceramic processing methods to immobilize treatment-process residues such as those expected from the Mixed Waste Management Facility, and therefore typical of residues from treating a large portion of the mixed wastes stored on DOE sites nationwide.

In *Proposed Treatment of Sodium Nitrate-Based Wastes to Minimize Disposal Volume*, we describe a multidisciplinary approach to the processing and disposal of radioactive, hazardous, and mixed wastes in which sodium nitrate is a major component. Several DOE sites, including Hanford, have large quantities of such wastes in storage.

In *Evaluating Actinide Volatility and Emissions during the Thermal Treatment of Mixed Wastes*, we describe studies aimed at determining the maximum amounts of uranium, plutonium, and americium that might volatilize and be emitted to the atmosphere during the treatment of mixed wastes in various thermal oxidation processes. Molten salt oxidation, one of the initial technologies selected for demonstration in the MWMF, is one of the technologies evaluated.

The article *In Situ Microbial Filter for Groundwater Remediation* describes a bioremediation method that can be engineered for specific field applications and that might cost only half as much as current pump-and-treat processes. Our first field test of the concept (jointly funded by the National Aeronautics and Space Administration and DOE) has been conducted at a TCE-contaminated site at the Kennedy Space Center in Florida.

Joint LLNL/Russian Cooperation in Environmental Technologies and Waste Management describes work by senior LLNL managers and scientists to establish alliances with their counterparts in the former Soviet Union through which new environmental restoration and waste management technologies can be explored. Visits in August 1993 to seven Russian technical institutes allowed them to evaluate laboratories, facilities, technical personnel, and analytical capabilities, identify opportunities for accessing environmental technologies and data sources and for conducting mutually beneficial research and development, initiate technology-development projects, and prepare a joint Russia/U.S. mixed-waste treatment demonstration proposal to the International Science and Technology Center (ISTC) in Moscow.

Fiber-Optic Sensors for Characterizing Soil and Groundwater Contamination describes the development and field-testing of a new technology for monitoring chlorinated organic solvents such as trichloroethylene (TCE) and chloroform. This rapid analytical technique could greatly reduce restoration costs at many DOE sites by reducing sampling and analysis expenses and by helping optimize the siting of measurement apparatus.

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*Dynamic
underground
stripping...
far exceeded
expectations
in its first under-
ground test.*

Use of Ceramic Forms to Immobilize Residues from the Treatment of Mixed Wastes

As part of a mixed waste management facility to demonstrate treatments that are alternatives to incineration, we are developing final waste forms using ceramic processing methods to immobilize treatment-process residues.

Introduction

In the early 1980s, LLNL developed a ceramic waste form for immobilizing reprocessing residues held at the Department of Energy's (DOE's) Savannah River Plant.¹ That waste form, Synroc D, is being used as a model for designing and demonstrating a ceramic waste form that can immobilize the residues resulting from the treatment of DOE hazardous and mixed wastes.

The Environmental Restoration/Waste Management-Applied Technology (ER/WMAT) Program is developing a mixed waste management facility (MWMF) to demonstrate a variety of technologies that can be used as alternatives to incineration in the treatment of mixed wastes. The waste streams at the core of the demonstration project are DOE waste codes 2110 (7.8% Trimsol in water), 2120 (aqueous/nonhalogenated organic), 2210 (halogenated organic liquids), 5300 (combustible), 5440 (predominantly combustible), and 6100 (lab packs—scintillation cocktails). The residues from treating the combustible waste streams (5300 and 5440) result in about 10% of the original weight of waste being recovered as ash. The ash composition of the LLNL combustible stream is dominated by mineral-forming oxides SiO_2 , Al_2O_3 , MgO , ZnO , CaO , and Fe_2O_3 , which together account for almost 90% of the ash. In contrast, the other waste streams result in a concentrated residue having very small amounts of the major mineral-forming oxides found in the combustible ash. The low-ash residues are dominated by antimony, zinc, and barium, with lesser amounts of beryllium, molybdenum, lead,

and uranium. Other metals (cobalt, cadmium, nickel, copper, manganese, silver, vanadium, thallium, and chromium) are present in trace amounts. All these elements, recovered as nitrate salts or as oxides after destruction of the organic liquid-waste streams, are also found in small amounts in the ash residues from processing the two combustible waste streams.

Designing the Waste Form

Our approach in designing a ceramic waste form for waste-treatment residues is to use the ash components from the combustible waste streams as the model for our base ceramic compositions, and adding small amounts of chemicals to produce a final phase assemblage of proven durability and known processing parameters. Adding NaOH , ZrO_2 , and TiO_2 to the combustible ash provides a phase assemblage similar to that found in Synroc D.

The major phases in Synroc D are nepheline, perovskite, spinel, and zirconolite. For Savannah River wastes, which are high in iron, there were two spinels— Fe_2TiO_4 and FeAl_2O_4 ; however, the common natural spinel has the composition MgAl_2O_4 and is capable of extensive solid solution. To immobilize residues from the treatment of hazardous and mixed wastes, we are using the phase assemblage of nepheline, perovskite, zirconolite, and MgAl -spinel as the major phases. Toxic metals and radioactive elements in the treatment residues will be incorporated into the waste form as solid solutions in the major phases. In some cases, elements such as mercury and silver (as AgCl) will be volatile under the conditions used to make the ceramic

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waste form. These elements will be condensed from the offgas line and converted into a suitable secondary waste form.

The process we are using to produce the final ceramic product differs substantially from the original flow sheet for Synroc D processing. We plan to use a rotary calciner operating at 600 to 750°C to calcine and denitrate the ceramic waste-form feed stream and to induce the formation of the primary bonds in the ceramic. This is the process used for Synroc C processing at the Australian Nuclear Science and Technology Organisation,² rather than the fluidized-bed calciner ultimately employed at LLNL for work on Synroc D. After calcination, the powder will be pressed at room temperature into 1-cm-diam pellets in a high-capacity commercial pellet press. The pellets will be sintered in air or in a controlled atmosphere at approximately 1200°C to densify them and to produce the desired phase assemblages.

Waste-Form Composition and Characteristics

We chose two basic compositions (representing low- and high-ash residues) for the waste forms we are using to develop process parameters and waste-form characteristics for the treatment process residues. The composition (illustrated in Table 1) represents the pure end-member composition for immobilization of low-ash residues. Rather than use the expected concentrations of waste elements, which are high in antimony, zinc, and barium, we used equal amounts of 10 elements at ~0.5% each, so that we have enough present in the waste form to characterize the product easily. We prepared samples of this synthetic waste form using both oxide materials (gibbsite and kaolin for aluminum and silicon oxides) and alkoxide preparations. For the alkoxide and one batch of oxide material, we also used 1.6% NaCl in the mixture to investigate the effects of chloride ions on the behavior of the waste elements and to determine whether sodalite could be formed as part of the phase assemblage.

For each mixture, we prepared samples by mixing the oxides or alkoxide precursors with the waste-element oxides (using water to facilitate mixing), dried the mixture in air at 90°C to remove most of the water, calcined it at 600°C for 1 to 8 hr, and cooled it to room temperature. We then mixed the resulting powder with a Carbowax binder, pressed it into pellets at 15,000 psi in tool-steel dies, and sintered the pellets for 1 hr at 1050 to 1250°C. The green density of pellets prepared from oxide starting materials is generally about 52 to 57% of the theoretical maximum density of the sintered product.

Figure 1 shows the density of samples as a function of sintering temperature. The five data sets marked Oxide + NaCl; Oxide, no NaCl; and Alkoxide + NaCl all had approximately the composition shown in Table 1. For pellets made from oxide starting materials, sintering at 1050°C drives off the Carbowax but does not appreciably densify the pellet; thus, the sintered density is a little lower than the green density. Sintering at 1100 to 1200°C produces an increase in density that is approximately linear with temperature. Samples sintered at 1200°C achieve about 90% of theoretical density.

Table 1. Compositions of ceramic mixtures with oxide starting materials used to simulate residues from treating low-ash streams and to investigate the volatility of waste elements.¹

Component	Weight %	Mineral-containing component
CaO	16.1	Perovskite, zirconolite
TiO ₂	29.9	Perovskite, zirconolite, rutile
ZrO ₂	10.8	Zirconolite
MgO	6.8	Spinel
Al ₂ O ₃	22.0	Spinel, nepheline
SiO ₂	5.7	Nepheline
Na ₂ O	3.0	Nepheline
Waste oxides	5.7	Various
Mineral phase	Weight %	Composition of end-member phase
Perovskite	29.5	CaTiO ₃
Zirconolite	31.2	Ca ₂ ZrTi ₂ O ₇
Spinel	25.1	MgAl ₂ O ₄
Nepheline	14.2	NaAlSi ₃ O ₈
Rutile	0	TiO ₂

¹Waste oxides are equal weight percents of oxides of Co, Cu, Sb, Cr, Zn, Mo, Ag, Cd, Na, and Pb.

Differential thermal analysis of our samples shows that the solidus is at about 1180°C, so these samples experience some melting. Scanning electron microscopy (SEM) and transmission electron microscopy do not reveal any significant evidence of melting, so it must have been confined to grain boundaries. Sintering an oxide mixture at 1250°C produced a sample with 97% of theoretical density and obvious signs of melting.

Samples produced from alkoxide precursors with the compositions given in Table 1 also had green densities of 52 to 55% of theoretical maximum density but showed considerable densification upon sintering at 1050°C, indicating that the alkoxide materials are more reactive than the oxide equivalents. Somewhat surprisingly, these samples did not reach more than 80% of theoretical density when sintered at higher temperatures. It has been suggested³ that this may be due to the high surface area of the alkoxide powders and adsorption of gases on the powders after calcination. These gases then may be trapped in the pellets after pressing and cause porosity in the sintered pellet. Alternatively, nitrates added with the waste elements may not have completely decomposed during calcination.

Table 2 shows the composition of a simulated waste form designed to represent the high-ash residues obtained by processing a mixture of combustible solids such as plastics, rubber, and paper products. We used the average of a one-year inventory of such wastes at LLNL to generate the composition of the waste stream. In the waste-form composition given, all of the silicon and magnesium, one-fourth of the aluminum, and most of the calcium come from the waste-stream residues. The waste loading in the simulated waste form is about 50%, and the waste stream is low in the components (e.g., antimony and barium) that are high in low-ash residues. The simulated waste form for the composition in Table 2 has a different proportion of phases than does the low-ash host, notably being high in both nepheline and spinel and having little perovskite. (The apatite is assumed to be present because of the phosphate content; it has not yet been positively identified, and the phosphate may be in another phase). Despite the gross differences in phase proportions and bulk composition of the two phase assemblages,

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Figure 1. Density of waste-form pellets as a function of sintering temperature. Samples marked A and B are duplicate pellets separately processed.

Table 2. Compositions of ceramic mixtures using oxide starting materials to simulate residues from processing combustible materials through the molten salt process (MS ox 50% in Fig. 1).^a

Component	Weight %	Mineral-containing component
CaO	4.4	Perovskite, zirconolite, apatite
TiO ₂	8.9	Perovskite, zirconolite, rutile
ZrO ₂	3.9	Zirconolite
MgO	7.4	Spinel
Al ₂ O ₃	40.2	Spinel, nepheline
SiO ₂	16.8	Nepheline
Na ₂ O	7.9	Nepheline
K ₂ O (waste only)	1.0	Nepheline
Fe ₂ O ₃ (waste only)	1.6	Spinel
ZnO (waste only)	3.7	Spinel
P ₂ O ₅ (waste only)	2.2	Apatite (with Ca, Ce, Sr, Ba ²)
Waste oxides	5.7	Various
Mineral phase	Weight %	Model composition
Perovskite, rutile, apatite	9	CaTiO ₃ , TiO ₂ , Ca ₅ (PO ₄) ₃ (OH, Cl, F)
Zirconolite	11	CaZrTi ₂ O ₇
Spinel	40	MgAl ₂ O ₄
Nepheline	40	NaAlSi ₃ O ₈

^aWaste oxides are 0.1% of oxides of Cu, Sr, Cr, Ce, Mo, Mn, Ni, and V, 0.05% PbO, 0.15% BaO, 0.2% each of oxides of B and Sb, and 0.6% sodium sulfate.

the processing characteristics for both are similar, and SEM images and energy-dispersive x-ray (EDX) characterizations indicate that they are similar. Because of these similarities, we anticipate that it will be possible to combine the low- and high-ash residues and produce a single waste form for both streams.

Characterization of Sintered Waste Forms

Each sintered sample is weighed and measured to determine density; x-ray diffraction (XRD) and x-ray fluorescence (XRF) are also done. Then, selected samples are examined by SEM. Samples sintered at 1200°C, with 90% of theoretical density, show porosity distributions that indicate the formation of gas bubbles inside the sample during sintering. Thus the porosity is largely not interconnected and should not greatly affect the leaching characteristics of the waste-form pellets. The SEM micrographs show that the grain size of the sintered pellets remains small—less than 1 μm on average—even at the highest sintering temperatures. Increasing the sintering time from 1 to 10 hr did not produce noticeable additional grain growth. Although the fine grain size makes identifying the mineral phases and characterization by SEM and EDX very difficult, we have obtained several EDX spectra that show nearly pure phase compositions for each of the major mineral phases.

The sample sintered at 1250°C was examined by SEM and EDX to determine the distribution of waste elements within the major mineral phases. Table 3 lists the elements and host phases for the cases in which clear identification was possible.

Because the chemical composition of the waste streams to be treated in the MWMF will not be uniform, and because other mixed-waste streams may eventually be treated in the MWMF, we are interested in identifying the chemical elements that may affect the processing characteristics and final quality of the waste form. We examined chloride first, because it will be present in the residues from the treatment of chlorinated hydrocarbon wastes and is readily soluble as NaCl. Addition of NaCl to the oxide and alkoxide mixtures with compositions given in Table 1 did not adversely affect the densifica-

Table 3. Distribution of waste elements in major phases for the sintered waste form (Sample sintered at 1250°C, at which melting occurred).

Waste element	Host phase
Molybdenum	Al ₂ SiO ₅
Antimony	Amorphous
Cadmium	Zirconia
Copper	Spinel
Zinc	Spinel
Cobalt	Spinel
Chromium	Spinel

tion of the waste form at any given sintering temperature. Examination by XRF showed that the composition of pellets formed from calcined powders was indistinguishable from that of pellets formed from uncalcined powders. Sintering at 1050°C caused most of the silver in the samples to be lost, presumably because of the volatility of AgCl (vapor pressure = 6.6 mm Hg at 1050°C [Ref. 4]). All silver was gone from samples sintered at 1200°C in the presence of chlorine. Ion microprobe analysis of these samples indicated that some lead and antimony might also be lost in the presence of chloride at the highest sintering temperatures.

Mixtures with the composition given in Table 1, but without added NaCl, also showed loss of silver at 1050°C, but no further loss occurred at higher sintering temperatures. Silver oxide decomposes at temperatures above about 160°C.⁵ Since the vapor pressure of silver metal at 1050°C is very low,⁴ we presume that trace chloride impurities in the materials used to make the simulated waste forms have combined with the silver released during Ag₂O decomposition and later volatilized. Because chloride could not be excluded in any practical waste-treatment operation, provisions for collecting silver from offgases will need to be included in the waste-form fabrication area for any processes operating above ~900 to 1000°C.

Conclusions

We have designed a ceramic waste form based on the phases nepheline, zirconolite, perovskite, and spinel to use for immobilizing residues from the treatment of organic mixed waste. Because the waste form is similar in composition and processing parameters to Synroc D, it would also be suitable for immobilizing sludges. We have shown that chloride causes silver to be lost during processing at 1050°C and may also enhance the volatility of lead and antimony. This fact must be taken into account in any treatment process that employs these temperatures.

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Proposed Treatment of Sodium Nitrate-Based Wastes to Minimize Disposal Volume

We are developing a multidisciplinary approach to the problem of processing and disposal of radioactive, hazardous, and mixed wastes in which sodium nitrate is a major component. Many DOE sites are storing such wastes, which were generated when nitric acid solutions containing the radioactive residues from fuel reprocessing to produce strategic nuclear materials were neutralized with sodium hydroxide before storage in mild steel tanks. Our approach is to separate the majority of the radioactive constituents and other cationic species from the sodium nitrate and other sodium salts, then to separate the sodium salts, which are predominantly nitrates, into their acid and base components by a state-of-the-art electrodialysis process, and finally to immobilize non-nitrate inorganic residues in a ceramic waste form.

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The DOE has very large volumes of radioactive and mixed wastes that are predominantly sodium nitrate. These wastes were created at Savannah River and Hanford when nitric acid solutions of separated fission products and residual actinides were neutralized with sodium hydroxide before storage of the neutralized wastes in tanks. One and one-half million gallons of acidic sodium nitrate wastes produced as the by-product of processing naval reactor fuels are also in storage at the Idaho Chemical Processing Plant. Figure 1 shows typical compositions and activities of these wastes.

Disposal of sodium nitrate presents a challenge because of its high solubility and mobility and because of regulatory limits on the accumulation of nitrate ion in groundwater and in sources of drinking water. Savannah River is immobilizing salt solutions and residues in "saltstone" (a mixture of salt solution, cement, and fly ash), with a volume increase of 1.7 in

going from the liquid salt solution to the solid saltstone. They plan to have a total of 15 vaults to accommodate the saltstone from processing about 150 million gallons of salt solution. Three vaults have been built that will accommodate the saltstone from processing about 20 million gallons of salt solution. The remaining 12 vaults, which will be double width, would cost \$249 million to build, according to a recent GAO audit report. Hanford tank farms hold 37 million gallons of waste in single-shell tanks, of which most of the volume is saltcake. The double-shell tanks hold an additional 20 million gallons of salt solutions. The baseline plan for treatment of the Hanford salt solutions is immobilization in concrete, with an anticipated volume increase of a factor of 4 to 10 depending on the waste compositions.

Proposed Scheme for Treating Nitrate-Based Wastes

The method we are developing for treatment of dissolved nitrate wastes holds promise as an alternative treatment strategy that will eliminate

the need for construction of vaults to hold concrete and saltstone. This will result in large savings in capital construction costs. In addition, the scheme will produce only relatively small volumes of material that requires disposal as radioactive waste. This material will contain

(a) Mass of dissolved species in waste tank supernates

(b) Activities in waste tank supernates

Figure 1. Total masses and total activities of various species in waste tank supernates (Ref: DOE/MWIP-10, March 1993).

the aluminum originally in the nitrate waste solutions and minor amounts of residual radioactivity present in solution.

The first step is to separate aluminum and highly radioactive species such as cesium, strontium, technetium, and actinide elements from the waste salt solutions. At Hanford, concentrated cesium will be sent to a high-level waste vitrification treatment line.

The salt solution will then be processed in a bipolar-membrane electrodialysis system to produce nitric acid and sodium hydroxide. These product streams will be analyzed to determine whether "polishing" is needed to remove any residual trace radioactive components or hazardous chemical elements. After purification, the sodium hydroxide can be recycled within the DOE complex. Nitric acid will be purified and recovered by distillation; the other acids will be recovered, if economically viable, or will be incorporated into the waste form. The waste materials, including residual radioactive species, aluminum hydroxide, and (possibly) phosphoric and sulfuric acids, will be immobilized in a ceramic waste form for disposal. The final waste form volume is expected to be 5 to 10% of that of the initial salt solution; the actual volume reduction depends mainly on the amount of aluminum in the wastes.

Pretreatment

Because the Savannah River, Idaho, and Hanford salt solutions and the Hanford saltcake residues all contain substantial amounts of aluminum, the wastes will require a precipitation step to remove non-alkali metal cations from the solutions. This is needed because of the requirements of the membrane systems used in the electrodialysis process. We have been investigating means of coprecipitating strontium, technetium, and various actinides along with the aluminum. The Savannah River and Hanford wastes are sufficiently basic that aluminum is dissolved as the soluble aluminate.

The aluminum is precipitated as aluminum hydroxide by adjusting the pH to neutral (pH = 7). Aluminum hydroxide characteristically forms a gelatinous precipitate that is difficult to separate from the supernatant liquid. We

therefore investigated the use of ferric ion to act as a flocculating agent. The precipitation step coprecipitated many of the surrogates for the radioactive species expected to be present in the salt solutions. However, the separation factors achieved through coprecipitation for strontium, technetium, uranium, and plutonium remain to be determined. Cesium, if present in large amounts, will be removed from the wastes by passing the salt solution through a column of resorcinol formaldehyde ion-exchange resin before precipitation. The precipitate can be separated from the salt solution using a combination of centrifugation and filtration as appropriate. After the pretreatment methods are fully demonstrated using nonradioactive analogs (such as rhenium for technetium), a demonstration of the method using a fully radioactive salt system must be conducted.

Electrodialytic Salt Splitting

Electrodialysis involves the use of electricity to convert a neutral salt into its respective acid and base. The recent development of bipolar membrane technology has allowed the construction of large stacks of electrodialysis cells, driven by just two electrodes on the extreme ends of the stack. Each cell is separated into salt, acid, and base compartments by three ion-selective membranes: a cation exchanger, an anion exchanger, and a bipolar membrane. The separation of salt into acid and base occurs in each cell; parasitic gas evolution reactions occur at the two electrodes (hydrogen is generated at the cathode and oxygen at the anode). The heart of the experimental system used in this study was a stack of four such cells. This state-of-the-art design is much more efficient than that of a conventional electrodialysis stack constructed with cation and anion exchangers alone, no bipolar membranes, and more than two electrodes.

Preliminary evaluations of the durability of membranes were conducted. After being exposed to acid and base at room temperature for 100 days, no significant degradation in the physical strength of the membranes was detected. The membranes tested were representative of those used in salt splitting processes and were either cation- or anion-selective. For each

type, three base materials were tested: polytetrafluoroethylene, a perfluorinated hydrocarbon polymer, and polypropylene. Cation-permeable membranes were exposed to the strong base NaOH; the anion-permeable membranes were exposed to the strong oxidizing acid HNO_3 . The regeneration of sodium hydroxide, nitric acid, and sulfuric acid from salt solutions containing 0.75 to 1 M sodium nitrate and 0.75 to 1 M sodium sulfate at pH 2 to 3 was studied systematically in a number of pilot-scale experiments of 160 to 410 min duration. Nitrate and sulfate anions were transferred into a stream of 0.5 M hydrochloric acid, while the sodium cations were transferred into a stream of 1 M sodium hydroxide. Each stream (salt, acid, and base) had an inventory of 5 L and a flow rate of 2 L/min (0.55 gal/min). Both platinized titanium electrodes had active areas of 96 cm^2 and were bathed in 5 L of 1 M sodium hydroxide flowing at 4.6 L/min (1.22 gal/min). The cell stack had perfluorinated anion- and cation-permeable membranes used in conjunction with proprietary bipolar membranes supplied by WSI Inc., the vendor of the cell stack. The temperature of the system was maintained at 35, 45, or 55°C. At each temperature the current was varied from 0.96 to 9.65 A. Figure 2 shows typical current and voltage transients for an experiment at 45°C. During steady state operation at 9.65 A, the potential difference across the membranes alone was ~15 V, and that across the electrodes was ~20 V. The average power consumed by the stack during operation was ~200 W. As shown in Fig. 3, the initial concentrations of nitrate and sulfate in the salt stream dropped to 0.5 and 0.15 M, respectively. As expected, the concentration of nitrate in the hydrochloric acid increased from zero to 0.55 M. The concentration of sulfate in the hydrochloric acid also increased, but only to 0.15 M. The fate of sulfate in the system is still being resolved. It appears that very little nitrate and sulfate was transferred into the sodium hydroxide stream. Figure 4 shows the pilot-scale salt-splitting system.

Purification of Product Acid and Base Streams

Most of the radioactive species and the non-alkali metal cations should be removed by the

pretreatment steps described above. Final purification may be needed to allow delisting of the sodium hydroxide product stream. We expect that only cesium and strontium (of the materials known to be present in the salt wastes) will be found in the sodium hydroxide product. All other impurities are expected to be anionic and therefore to be found in the acid stream. We will check the validity of our assumption by doing one or more electrodialysis runs doped with cesium, strontium, technetium, and uranium just before electrodialysis. Once the fate of any residual radioactive or metal ion species is established, we will evaluate methods

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Figure 2. Voltage and current transients during the electrodialysis of nitrate-sulfate solutions.

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Figure 3. Concentration transients during the electrodialysis of nitrate-sulfate solution.

Figure 4. Photograph of pilot-scale salt-splitting system (inset: electro dialysis cell stack, enlarged).

for removing these species from the sodium hydroxide product. We expect that the resorcinol formaldehyde resin intended for use in initial removal of cesium from Hanford tank wastes will be suitable for purifying the sodium hydroxide after electrodialysis.

The acid product from electrodialysis will be predominantly nitric acid, with other acids such as phosphoric and sulfuric making up less than 10% of the product. The acid stream will probably contain any residual uranium and technetium not removed from the salt during the initial precipitation. We intend to purify the acid stream by distillation. Nitric acid has a lower boiling point than sulfuric or phosphoric acids, so it can be easily purified by distillation. The metal ion impurities will remain in the still bottoms and can be combined with the precipitate recovered during pretreatment and immobilized in a ceramic waste form.

Other Applications

In addition to processing dissolved nitrate wastes stored in tanks for recycling, electrodialysis could be used for waste minimization in future processing plants. For example, sprays of sodium hydroxide solution are used in quench and scrubbing columns to remove acid gases such as hydrochloric acid and hydrofluoric acid from the exhaust of hazardous waste incinerators. During operation, these acid gases are converted into their respective sodium salts. Electrodialysis may be applied to convert these salts back into their constituent acids and bases.

Acknowledgments

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Evaluating Actinide Volatility and Emissions during the Thermal Treatment of Mixed Wastes

The ER/WM-AT Program is carrying out studies aimed at determining the maximum amounts of uranium, plutonium, and americium that might volatilize and be emitted to the atmosphere during the treatment of mixed wastes in various thermal oxidation processors.

Large quantities of untreated mixed wastes are stored, awaiting treatment, throughout the DOE Weapons Complex.* These wastes generally contain hazardous organics and small amounts of uranium and/or plutonium and americium and may also contain fission products and hazardous metals.

Limited storage space for organic-based mixed wastes has led the DOE and LLNL to study various high-temperature (thermal) treatment processes that accomplish the following:

- Completely destroy the organic component through oxidation.
- Substantially reduce the waste volume.
- Yield an ash residue that can be easily converted to a suitable waste form for storage. For example, the ash can be formed into a glass or ceramic or can be encapsulated in polyethylene.

The Environmental Protection Agency has identified incineration as the best demonstrated thermal technology for treating organic-based wastes. However, public concern over possible emissions of radioactive or other toxic gases from incinerators has led to the development of alternative thermal processes, including molten salt oxidation and supercritical water oxidation, that reduce the risk of radioactive and toxic gas releases to the atmosphere. Some nonthermal

processes, such as mediated electrochemical oxidation and wet chemical oxidation, are also being developed.

To help evaluate the risk of emissions from thermal oxidation processors, we have begun a series of experimental measurements of volatility for uranium, plutonium, and americium. Our data allow us to predict possible emissions of these actinides that can be expected if thermal oxidation treatment technologies are used to convert or destroy mixed waste.

Reducing the Risk of Toxic Emissions

Organic-based materials treated in thermal oxidation processors are primarily converted to carbon dioxide and steam, and any inorganic materials in the waste are converted to ash. In the case of halogenated organics, significant amounts of gaseous (g) HCl and HF are also generated during nonalkaline thermal treatment. If the treatment process is alkaline, as is the case in molten salt oxidation, the acid gases (including SO₂(g)) are neutralized to form NaCl, NaF, and Na₂SO₄.

Ash and aerosols produced in the treatment process must be removed from the gas stream before the offgas is released to the atmosphere. The ash is generally formed by particle

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* Typical organic-base mixed wastes are lab coats, rags, wipes, plastics (such as polyethylene and PVC), rubber gloves, paper, wood, filters (charcoal, paper, or fiberglass), machining and lubricating oils, transformer oils, fuel oils, spent organic solvents, scintillation cocktails, and sludges containing organic solvents.

entrainment in the gas flow, and the aerosols are generally formed by the recondensation of volatile material as the offgas cools. During condensation, volatile material also tends to concentrate on the fine ash particulates because of their high ratio of surface area to volume.

These offgas particulates are removed by several consecutive air-pollution-control devices before exiting the system. For example, a typical offgas treatment system for an incinerator may include the following:

- Fabric filters to remove ash particulates down to about 1 μm .
- Charcoal filters to remove mercury.
- Acid gas scrubbers to remove $\text{HCl}(\text{g})$, $\text{HF}(\text{g})$, and $\text{SO}_2(\text{g})$.
- High-efficiency particulate air (HEPA) filters to remove the remaining particulates smaller than 1 μm ash.

The HEPA filter, which is the most efficient means for removing fine particulates from the offgas, captures only 99.97% of the particulates of this size, however. Particulates smaller than 1 μm are primarily fine fly ash and aerosols, and both are composed primarily of volatile material that has condensed.

To reduce the risk of actinide release to the atmosphere, it is important to know the maximum actinide volatility that can be expected in each thermal process. If the volatility is very low in a particular process, the capture efficiency for fine particulates and aerosols is not important. However, if the volatility is relatively high, the offgas treatment system must be designed to capture the fine ash particulates and aerosols efficiently.

Predicting Potential Metal Emissions

Barton, Clark, and Seeker¹ have developed a metal emissions model for incinerators, and Rizeq et al.² have applied this model to the toxic metals silver, arsenic, barium, beryllium, cadmium, chromium, copper, mercury, nickel, lead, selenium, antimony, and thallium. Agreement between emissions predicted by the model and measurements made on incinerators is generally good. Where differences exist, the predicted values are on the high side. This model should apply equally well to uranium,

plutonium, and americium metals, but relevant thermodynamic information on vaporization from actinide oxides and mixed oxides is lacking.

Barton's model assumes that intimate mixing of constituents within the thermal oxidation chamber takes place and that chemical equilibrium is attained at the oxidation temperature. Thus, the metals of interest are converted to solid oxides or glasses in the oxidation process. Because of the presence of ash constituents, such oxides as silicates, chromates, and arsenates may be formed. Volatilization of one or more gaseous species for each of the metals then results in an equilibrium vapor pressure. In most cases, the presence of the reactive gases $\text{O}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{HCl}(\text{g})$, and $\text{HF}(\text{g})$ significantly influences the type and amount of gaseous species formed. The strength of the thermodynamic interaction of the metal oxide with the ash constituents also affects the volatility: the stronger the interaction, the lower the volatility. The model uses equilibrium thermodynamics to determine the stable form for each metal oxide and to calculate equilibrium vapor pressures for the volatilized gaseous species.

Because of kinetic limitations, the volatility for each metal is limited by the degree to which the equilibrium vapor pressure is reached during the residence time of the gas as it flows through the combustor. If the kinetics are too slow to attain the equilibrium concentration, the model will give too high a volatility, as was the case for some of the toxic metals examined by Rizeq et al.² If insufficient amounts of a volatile metal are available to form solid oxide phases, the metal will exhibit its full volatility for the amount present.

Volatility Measurements

The Transpiration Method

We are measuring the volatilities of uranium, plutonium, and americium using the transpiration method.³ In this method, a known amount of carrier gas is slowly passed over a solid or liquid in a furnace chamber picking up any volatilized gases produced and sweeping them out of the chamber into a collector tube where they are condensed and analyzed.

The carrier gas may contain reactive gases that contribute to forming the volatilizing gaseous species. For example, for the reaction

$\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are both reactive gases that contribute to the production of $\text{PuO}_2(\text{OH})_2(\text{g})$. The flow rate of the carrier gases must be low enough for equilibrium to be obtained but high enough for transport by gaseous diffusion to be insignificant.

The transpiration method can also be used to obtain information on the formula of the volatilizing species. To do this, we vary the partial pressures of the reactive gases at constant temperature and note the effects of the law of mass action on the volatilizing species. Thus, for reaction (1) above, we write the equilibrium constant K_1 at a given temperature as

$$K_1 = \frac{[p\text{PuO}_2(\text{OH})_2]}{[a\text{PuO}_2][p\text{O}_2]^{1/2}[p\text{H}_2\text{O}]}, \quad (2)$$

where p refers to pressures and a to thermochemical activity.

In our experiments, the activity of PuO_2 is unity. In a thermal processor, however, the activity of PuO_2 (and hence its volatility) may be reduced by reactions with the ash or process materials. If K_1 is to remain constant, the pressure of $\text{PuO}_2(\text{OH})_2(\text{g})$ must vary in proportion to $[p\text{O}_2(\text{g})]^{1/2}$ and $[p\text{H}_2\text{O}(\text{g})]$. If the volatilizing species were different than $\text{PuO}_2(\text{OH})_2(\text{g})$, the power dependences on $[p\text{O}_2(\text{g})]$ and $[p\text{H}_2\text{O}(\text{g})]$ would be different.

Transpiration Apparatus

Figure 1 shows a schematic of the apparatus used in our measurements. Mixtures of argon and oxygen are bubbled at controlled rates through a heated water bath to pick up water vapor, and the resulting gas mixture is passed over a powdered actinide oxide or actinide oxide/ash sample in a boat inside a furnace tube. The gas then flows through a collector tube that extends into the cold zone of the furnace. Volatilized actinides are condensed out in this

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Figure 1. Transpiration apparatus used for actinide oxide volatility measurements.

tube, which is then analyzed. The gas then passes out of the furnace and through a Drierite (CaSO_4) cartridge where the water is absorbed; the cartridge is later weighed to determine the total amount of water passed. Finally, the gases are exhausted to the atmosphere through a HEPA filter.

Results of Volatility Measurements

Uranium Volatility

Volatilization of uranium from $\text{U}_3\text{O}_8(\text{s})$ results in the formation of roughly equal amounts of $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ under our measurement conditions. The volatilization reactions and the corresponding equilibrium constants are given by

$$K_3 = \frac{[p\text{UO}_3]}{[a\text{U}_3\text{O}_8]^{1/3}[p\text{O}_2]^{1/6}}, \quad (3)$$

or

$$K_4 = \frac{[p\text{UO}_2(\text{OH})_2]}{[a\text{U}_3\text{O}_8]^{1/3}[p\text{O}_2]^{1/6}[p\text{H}_2\text{O}]}. \quad (4)$$

Figure 2 shows our results for volatilization to form $\text{UO}_3(\text{g})$ as a plot of $\log K_3$ vs $1/T$. The solid line represents a fit to our data based on the third law of thermodynamics. The dashed line represents published data^{4,5} for the reaction. The agreement is good. Figure 3 shows our

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Figure 2. $\log K_{\text{eq}}$ vs $10^4/T$ for the reaction $1/3 \text{U}_3\text{O}_8(\text{s}) + 1/6 \text{O}_2(\text{g}) = \text{UO}_3(\text{g})$. The solid line is obtained from a third-law treatment of our data; the dashed line represents published data.

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Figure 3. $\log K_{\text{eq}}$ vs $10^4/T$ for the reaction $1/3 \text{U}_3\text{O}_8(\text{s}) + 1/6 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{UO}_2(\text{OH})_2(\text{g})$. The solid line is obtained from a third-law treatment of our data; the dashed line is obtained from a third-law treatment of the data of Dharwadkar et al.⁵

results for volatilization to form $\text{UO}_2(\text{OH})_2(\text{g})$. The solid line is again a third-law fit to the data. The dashed line represents a third-law extrapolation from higher-temperature data for this reaction.⁵ These results are extended in Fig. 4 using the third-law treatment to give $\log p(\text{UO}_3(\text{g}))$ and $\log p(\text{UO}_2(\text{OH})_2(\text{g}))$ vs T for volatilization from $\text{U}_3\text{O}_8(\text{s})$ with 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, typical conditions for thermal oxidation.

Effects of Ash on Uranium Volatility

We studied the effectiveness of incinerator ash in lowering the volatility of uranium through chemical interaction. We reacted $\text{U}_3\text{O}_8(\text{s})$ at high temperature with several well-characterized coal fly-ash materials obtained as standard reference materials from the National Institute of Science and Technology (NIST).

These fly-ash materials had the approximate composition listed in Table 1.

We added Na_2O to one fly-ash sample to increase the Na_2O content to 8 wt%. Another sample had a high CaO content of 21 wt%. We added U_3O_8 to these samples at both 5 and 0.5 wt%.

The uranium volatility from typical ashes at 1400 K was only about 40% lower than that from $\text{U}_3\text{O}_8(\text{s})$. For the ash with Na_2O content enriched to 8 wt%, however, the uranium volatility decreased by a factor of 6; for the ash with 21 wt% CaO , the volatility decreased by a factor of 20. We see that typical ashes are not effective in reducing uranium volatility, but ashes with excess Na_2O or CaO significantly reduce uranium volatility.

Plutonium Volatility

We found very low volatilities in initial measurements on $^{239}\text{PuO}_2$. We made further measurements using more sensitive alpha counting techniques. In these experiments, we used $^{238}\text{PuO}_2$ because it has a higher specific activity for alpha decay than ^{239}Pu . We measured even lower volatilities for Pu with this technique, and found that the transport of very fine PuO_2 dust particulates exceeded the amounts of volatilized Pu. We set upper-limit volatilities of 1×10^{-13} atm for both $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ at 1326 K in the presence of 0.5 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.

Applying the third law of thermodynamics to these upper-limit values, we obtained upper-limit volatilities for $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ vs temperature, in the presence of 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, as shown in Fig. 4. Although we were not able to obtain definitive plutonium volatilities, setting upper limits is still useful, especially when the volatilities are extremely low.

Americium Volatility

We made volatility measurements for americium using a solid-solution sample of 2 wt% $^{241}\text{AmO}_2$ in $^{239}\text{PuO}_2$. Detection sensitivity was good for the ^{241}Am , but (as with the Pu) volatilities were so low that very fine dust transport exceeded the volatilities. We set an upper limit of 4×10^{-14} atm for both

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Figure 4. $\log p(\text{U})$ vs T for the species $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ and maximum $\log p(\text{Pu})$ and $p(\text{Am})$ vs T for $\text{PuO}_3(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, $\text{AmO}_3(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ above $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$, and 1000-ppm AmO_2 solid solution in $\text{PuO}_2(\text{s})$, where $p(\text{O}_2) = 0.1$ atm and $p(\text{H}_2\text{O}) = 0.1$ atm.

$p(\text{AmO}_3(\text{g}))$ and $p(\text{AmO}_2(\text{OH})_2(\text{g}))$ above the 2 wt% AmO_2 sample at 1329 K in the presence of 0.5 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. If we assume that the solution of AmO_2 in PuO_2 is ideal, then the pressures of $\text{AmO}_3(\text{g})$ or $\text{AmO}_2(\text{OH})_2(\text{g})$ will be proportional to the AmO_2 content in PuO_2 . Hence, for pure $\text{AmO}_2(\text{s})$, the pressures of $\text{AmO}_3(\text{g})$ or $\text{AmO}_2(\text{OH})_2(\text{g})$ will be 50 times higher than in the 2 wt% AmO_2 solid solution, which corresponds to a maximum of 2×10^{-13} atm for each species. This situation is very similar to that for the Pu species above $\text{PuO}_2(\text{s})$.

Applying the third law of thermodynamics to the upper-limit values for $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ species, we obtained upper-limit values vs temperature for the Am species. Further, knowing the Am content in Pu, we determined the proportionate reduction in Am volatility. Figure 4 shows maximum $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ volatilities vs temperature for a 1000-ppm (0.1 wt%) AmO_2 solid solution in PuO_2 in the presence of 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.

Predictions for Thermal Oxidation Processors

Volatility Induced by Oxygen and Steam

To apply actinide volatility data to thermal oxidation processors, we assume that thermodynamic equilibrium is attained at the process temperature. The actinide vapors then saturate the offgas and are swept out of the reactor.

For application to the rotary kiln incinerator, which can be used as a reference for other thermal oxidation processors, we assume that the actinides are present in sufficient amounts to form as $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$, and a 1000-ppm AmO_2 solid solution in $\text{PuO}_2(\text{s})$. The secondary combustor temperature is taken as 1100°C (1373 K), pressures of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are taken as 0.1 atm each, and the offgas flow rate is taken to be 40 kmol/h. Chlorine and fluorine are assumed to be present at negligibly low concentrations in the feed so as not to contribute to actinide volatility. Under these assumptions, we calculate the actinide volatilization rates shown in Table 2.

Table 2. Actinide Volatility Rates from a Rotary Kiln Incinerator

Actinide	Temperature (°C)	Volatility Rate (g/hr)
Uranium	1100	0.0001
Plutonium	1100	0.0001
Americium	1100	0.0001

The rates with a HEPA filter assume only a 99.97% collection efficiency, the minimum efficiency for fine particulates in a properly functioning HEPA filter. Except possibly for uranium, *these emission rates are low enough that no detectable actinide emissions are expected from volatility contributions.*

For fluidized-bed incinerators, the volatilities will depend on the process temperature used and on the reactivity of the fluidized bed itself. At 1100°C, for example, the actinide volatilities in a fluidized bed incinerator will be similar to those in the rotary kiln incinerator. However, the Rocky Flats Plant fluidized bed unit operates at only 550°C, and reaction of the waste feed material with the $\text{Na}_2\text{CO}_3(\text{s})$ particulates in the primary reaction chamber further reduces the actinide volatility. The actinide volatilities are therefore expected to be much lower in that unit. Actinide volatilities will also be low in the molten salt oxidizer, which operates at a maximum temperature of about 900°C, and in the supercritical water oxidizer, which operates at around 600°C.

Chlorine- and Fluorine-Induced Volatility

Thermodynamic data for the gaseous species $\text{UO}_2\text{Cl}_2(\text{g})$ (Ref. 6) and $\text{UO}_2\text{F}_2(\text{g})$ (Ref. 7) indicate that for an incinerator operating at 1100°C, the vapor pressures of $\text{UO}_2\text{Cl}_2(\text{g})$ or $\text{UO}_2\text{F}_2(\text{g})$ will exceed those of $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ if the chlorine or fluorine content in the gas stream exceeds ~1% of the gas content. We expect that plutonium and americium will form similar vapor species, but no thermodynamic data exist.

Since a number of organic-based mixed wastes (e.g., PVC and Teflon) contain substantial amounts of chlorine and fluorine, thermodynamic data for the oxyfluorides and

oxychlorides of plutonium and americium are needed to evaluate their volatilities. We are estimating thermodynamic data for the plutonium and americium oxychloride and oxyfluoride vapor species, but experimental work is needed to accurately determine the chlorine- and fluorine-induced volatility effects on these actinides. In two of the thermal oxidizers (the molten salt oxidizer and the Rocky Flats Plant fluidized bed unit), chlorine and fluorine would be removed from the gas stream by reaction with sodium carbonate, so that the chlorine- and fluorine-induced volatilization of actinides would be substantially reduced.

Conclusions

Of the three actinides (uranium, plutonium, and americium) most likely to be found in mixed waste, our results show that uranium is the most volatile in thermal oxidation processors—nearly six orders of magnitude more volatile than plutonium. As long as chlorine and fluorine are not present in the waste feed, the emission rates of volatilized uranium, plutonium, and americium in a typical incinerator using HEPA filters are expected to be <0.4 mg/h, <0.7 ng/h, and <0.7 pg/h, respectively. If chlorine and fluorine are present in the waste feed, the volatilities of all the actinides may be higher.

The focus of our current work is on estimating thermodynamic properties for plutonium and americium oxychloride and oxyfluoride vapor species. Eventually, we expect to measure and hence determine more accurately the chlorine- and fluorine-induced volatilities of actinide oxides.

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In Situ Microbial Filter for Groundwater Remediation

In situ microbial filters offer a simple solution to the problems encountered in other bioremediation methods. They can be engineered for specific field applications and might cost only half as much as current pump-and-treat processes.

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Remediation of contaminated groundwater at industrial and government facilities is expensive and is often unsatisfactory. In the standard remediation method, called pump-and-treat, the underground plume is penetrated by a number of wells, contaminated groundwater is extracted from the wells, and the water is treated and disposed of at the surface. Contaminants are often transferred either to the atmosphere or to a solid medium such as activated charcoal.¹ Pump-and-treat has great uncertainty in the ultimate level of decontamination, the time and cost required to achieve it, and the permanence of the decontamination.² Alternative technologies are needed to reduce costs, speed cleanup, and provide a more acceptable ultimate fate of the contaminants.

In situ bioremediation is an alternative to pump-and-treat for a wide range of toxic and hazardous compounds.³ It has the potential to be a rapid means of degrading contaminants to innocuous compounds without the expense of extracting large volumes of groundwater. Although bioremediation is an established technology for fuel hydrocarbons, it has not yet achieved its potential for other important classes of contaminants such as volatile organic compounds (VOCs) because of difficulties encountered in engineering predictable and reliable subsurface processes.

The most common approach to *in situ* bioremediation of VOCs has been to treat the entire volume of the plume by injecting nutrients to stimulate the growth of indigenous bacteria that naturally biodegrade the contaminants. Ideally, the resulting increase in the biomass of those bacteria increases the rate of the desired

biodegradation process to an acceptable value. This approach has proven to be unreliable because injection displaces contaminated groundwater, making it difficult to bring the contaminated groundwater and the stimulated bacterial population into satisfactory contact with one another. Contact between contaminants and bacteria could be reestablished by terminating injection and either relying on natural groundwater transport or actively withdrawing contaminated groundwater through the stimulated region. However, experiments at Moffett Naval Air Station, Mountain View, California, have demonstrated the inability of biostimulated bacterial populations to sustain their cometabolic capabilities for more than a few hours⁴; it appears that nutrients must be continuously supplied. This prevents establishment of contact except at thin zones at the boundaries of the injection package. The Moffett Field experiments avoided this contact problem by injecting the contaminants along with the nutrient stream, thereby ensuring contact but reducing the commercial value of the experiment.

An interdisciplinary ER/WM-AT Program research team has developed a new strategy that reduces these problems. The *in situ* microbial filter concept shows the potential of being a reliable and cost-effective field technology.

Concept

In situ microbial filters are a significant departure from current *in situ* bioremediation practices. The concept has two main components: (1) treatment of only the contaminant source region and selected portions of the

plume and (2) injection of resting (i.e., nondividing) bacterial cells into the subsurface, without nutrients. We selected trichloroethylene (TCE) as our target contaminant because of its ubiquitous occurrence, and *Methylosinus trichosporium* OB3b as our prototype microorganism because it catalyzes TCE breakdown with no hazardous or toxic by-products and because it can be easily grown to high densities on methane gas. These naturally occurring microbes are grown in surface bioreactors, separated from their growth medium, resuspended in groundwater from the site, and injected into the subsurface through an array of wells. Some of the injected bacteria attach to the soil or rock to form a fixed-bed biofilter. Contaminated water enters this region (either naturally or because of pumping), the contaminants are degraded as they flow through the filter, and the groundwater exits clean.

The main advantages of the approach are its simplicity and the ability to engineer field applications to specific sites. It eliminates the problems caused by nutrient injection because injection occurs for only a short time. Treatment of the pollutant source region(s) eliminates continued release of contamination; treatment of selected regions of the plume simplifies remediation by reducing the characterization effort while preventing further spread of the plume. Engineering control is achieved by designing a biofilter whose length and bacterial density are matched to the expected contaminant flux. The actual geometry of the biofilter depends on the injection pattern, but in general a thin region is formed that extends across the expanding contaminant plume.

The microbial filter concept can be generalized, even though our current focus is on intercepting chlorinated ethene plumes. It is possible to bioremediate many classes of contaminants, especially when suites of microbial species are considered.

Engineering Design

The design of an *in situ* biofilter depends on three parameters: filter residence time, filter degradation capacity, and enzyme longevity. We have completed a hierarchy of laboratory exper-

iments to measure each of these parameters under controlled conditions on a well-sorted medium-grained quartz sand.⁵

Filter residence time is the time the contaminant must remain in the filter to be degraded to the required concentration. Residence time depends on the subsurface contaminant flux, the intrinsic degradation rate, the attached population density, and the filter length. We have determined intrinsic TCE degradation rate coefficients in laboratory tests. The attached population density and the filter length can be designed for the specific application; a model for cell transport and attachment, confirmed in the laboratory, is used to predict the attached population density (typically about 10^9 cells per gram of sand); filter length is controlled by the well pattern used to inject microbes. The product of attached population density, filter sand volume, and sand density determines the total biomass in the filter. A scaled-aquifer experiment has demonstrated the effectiveness of a biofilter with sufficient residence time to remediate TCE-contaminated groundwater (Fig. 1).

Filter degradation capacity is the amount of TCE that can be degraded by the biofilter. Biodegradation of TCE causes a loss of key intracellular compounds required to oxidize the contaminant. Since nutrients are not supplied in the subsurface, the attached population density is fixed and gradually loses its TCE-degrading capabilities; a fixed population can degrade only a finite amount of TCE. We have accurately measured the specific degradation capacity for resting-state cells: 0.25 ± 0.05 g TCE per gram (dry weight) of bacteria. Filter degradation capacity is given by the product of specific capacity and filter biomass. The product of filter degradation capacity and contaminant flux determines how long a biofilter retains its degradation capabilities. The biofilter must be replenished by reinoculation to restore the required degradation performance.

Enzyme longevity is the time the microbial population can stay catalytically active in the resting state. Longevity appears to be independent of the *in situ* environment and to depend on the particular microbe used. We have made a major breakthrough in extending longevity from a few days to more than 4 weeks for

Figure 1. A 24-hr, 100-ppb TCE pulse is completely degraded by a 10-cm-thick biofilter in a scaled-aquifer experiment. The medium is homogeneous quartz sand; fluid flow velocity is 1.5 cm/hr; the contours represent attached bacterial population at 50, 100, and 200×10^6 cells per gram of sand. Closed and open circles in the test bed are microbe injection and sampling ports, respectively; data points are measured TCE values. Detection limit is 0.5 ppb.

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M. trichosporium OB3b by adjusting the growth chemistry in the bioreactors. This means that filter replenishments will occur at approximately one-month intervals when filter degradation capacity is not the limiting parameter.

Groundwater pH and dissolved oxygen content also influence filter performance. Groundwater pH must be in the 7.0 ± 0.5 range for these naturally occurring, but not necessarily indigenous, microbes to stay metabolically active. The constraint on dissolved oxygen content is less well known and depends, in part, on TCE concentration. It appears that a dissolved oxygen content of 0.4 ppm for every ppm of TCE will be adequate.

Field Scenarios

We envision three strategies for emplacing an *in situ* microbial filter, called huff-and-puff, sand-filled trench, and pattern floods (Fig. 2). The huff-and-puff approach uses individual wells and is an adaptation of a standard production process used in the petroleum industry. For each well selected, microbes are injected for a specified time. The microbe-laden fluid flows radially outward, and an attached *in situ* filter is thereby established in a region around the well

bore. The inoculation is terminated when the filter has the desired radial extent. When the well is pumped, groundwater is decontaminated as it flows through the filter, and clean water is extracted at the wellhead. This approach is applicable to slow-moving contaminant plumes and for uncommon media geometries in faster-moving plumes. It also offers a method for treating point or confined contaminant sources.

The sand-filled trench and pattern flood approaches are primarily for contaminant plumes with significant groundwater velocities. The sand-filled trench strategy includes digging a narrow trench at the expanding plume margins, filling it with a homogeneous medium, and inoculating the resultant porous medium with microbes through emplaced pipes. The approach is most suitable for shallow, fast-moving plumes. The pattern flood approach is for deeper plumes that can be reached only through wells. Here, a pattern of injection and withdrawal wells is drilled such that only a selected portion of the contaminant plume will be captured and drawn through the emplaced filter. A filter is established by injecting microbes into closed circulation paths between these wells. Once inoculation is complete, the flow field is reestablished, allowing contaminants to flow through the filter region.

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Figure 2. Three ways of implementing the *in situ* microbial filter concept. (a) Huff-and-puff is applicable to contaminant plume source regions and to slow-moving plumes. (b) Pattern flood (here, a line of wells) is used for deeper, faster-moving plumes. (c) The sand-filled trench approach can be a quick solution that ensures complete coverage of an expanding, fast-moving, shallow contaminant plume.

Cost comparisons between the biofilter approach and standard pump-and-treat for a large, deep, dilute, moderately fast-moving plume suggest that the biofilter approach is less expensive by at least a factor of 2.

Field Test

Our first field test of the concept, a jointly funded NASA-DOE project, was conducted in 1994 at the Wilson Corners site at the Kennedy Space Center in Florida. Groundwater contamination beneath Wilson Corners originated from degreasing operations using TCE; the groundwater is contaminated with vinyl chloride (VC) and cis-1,2-dichloroethylene (c-DCE) in addition to TCE, some fluorocarbons, and methane, suggesting that *in situ* anaerobic degradation of TCE by indigenous microorganisms has already occurred. Maximum total chlo-

rinated ethene concentration is about 15 ppm, with the contaminants varying in relative abundance.

Contamination extends from the water table, at about 3 ft, to the top of an aquiclude at about 50 ft. The plume extends over about 14 acres. The subsurface medium is a homogeneous mixture of quartz sand and shell fragments. Grain sizes range from silt to coarse sand; porosity is estimated to be about 40%. Although the hydraulic conductivity is high, natural groundwater velocities are exceedingly low (about 0.25 cm/day) because of the small natural hydraulic gradient.

Pump-and-treat plume remediation is already being carried out, under the auspices of the NASA Environmental Management Office. Contaminated groundwater is being withdrawn from 5 to 12 wells at about 3 gal/min and is being treated by air stripping. Low withdrawal

rates are required to prevent saltwater intrusion. It is estimated that plume cleanup using pump-and-treat will take more than 30 years.

We selected two wells for the field test. The low groundwater velocity precludes relying solely on the natural groundwater flow to transport contaminants through a biofilter, so we will use the huff-and-puff method. Biofilter performance will be assessed by preceding the experiment with baseline concentration measurements at this well.

We designed a down-hole column device that was used to evaluate site suitability. Results from this test indicated that 1 to 2 ppm of the total contaminant load was biodegraded. This is about 10 times the best previously reported results for bioremediation. But biodegradation of this 1–2 ppm reduced the dissolved oxygen content enough to prevent further remediation. Results from this test showed that the site was not suitable.

Large-Scale Bioreactor Facility

About 3 kg of *M. trichosporium* OB3b cells will be required for the pilot-scale study; this mass far exceeds the current biomass production capability of any DOE facility. We are constructing an Environmental Microbial Biotechnology Facility at LLNL to grow the cells for this and subsequent field applications. This pilot-scale facility will have a 1.5-kL bioreactor and a suite of smaller bioreactors. This unique DOE facility, which has many other potential uses, is scheduled to be operational by October 1994.

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Joint LLNL/Russian Cooperation in Environmental Technologies and Waste Management

The realignment of the former Soviet Union into the Commonwealth of Independent States created an excellent opportunity for us to establish mutually beneficial alliances through which to explore and implement new environmental restoration and waste management technologies.

In June 1992, seven senior managers and scientists from LLNL visited fourteen Russian institutes and identified several areas of common interest. We later placed more than twenty small procurements for state-of-the-art research reports, and we organized a joint CIS-LLNL workshop at Livermore in February 1993 to discuss potential collaborations.

As a follow-up, we visited eight institutes and facilities (Table 1) in Russia during a two-week trip in August 1993. Our objectives for this second trip were as follows:

- Evaluate CIS laboratories, facilities, technical personnel, and analytical capabilities.
- Identify opportunities for accessing key environmental technologies and data sources and for conducting mutually ben-

eficial research and development in ways that facilitate the conversion of Russian scientists and engineers from military to environmental endeavors.

- Initiate technology-development projects with various Russian institutions to assess the state of the art in selected waste-management technical areas.
- Discuss and finalize the scope of a joint Russia/U.S. mixed-waste (MW) treatment demonstration proposal to the International Science and Technology Center (ISTC) in Moscow.

Below we briefly evaluate each of the Russian institutes and facilities visited, describe the topics covered in our discussions, and specify any agreements reached for future work.

A. C. Heywood

M. G. Adamson

A. Kusubov

B. R. Myers

Table 1. Russian institutes and facilities visited by LLNL personnel in August 1993.

Institute of Catalysis, Novosibirsk
NOVOSELETT, Novosibirsk (a design institute)
Plant of Chemical Enterprises, Novosibirsk
Institute of High Current Electronics, Tomsk
Institute of Atmospheric Optics, Tomsk
Institute for Problems in Electrodynamics, St. Petersburg
General Physics Institute, Moscow
Institute of Spectroscopy, Troitsk

* Catalysis is a process in which an increase (or change) in the rate of a chemical reaction is induced by a material that is chemically unchanged at the end of the reaction.

Boreskov Institute of Catalysis (BIC), Novosibirsk

Since its establishment in 1958, BIC has become one of the world's largest institutes specializing in catalysis.* The Institute is organized into 10 departments and has 30 laboratories; its staff of over 900 includes about 400 technical personnel, of whom more than 120 are either doctors of science or candidates for that degree.

The BIC has a world-class capability for applying catalytic processes and techniques to environmental restoration/waste management (ER/WM) activities. A number of these processes and technologies are suitable for use in the ER/WM tasks facing the DOE Complex and could be important in developing new, environmentally attractive technologies to replace or improve current industrial processes and technologies. However, we were informed that Russian technologies are not easily accepted

in the West, even though BIC already has many contacts with Western companies. BIC's approach has therefore been to develop and commercialize in Russia first and then attempt to market to the West. As an example, BIC successfully developed a catalyst for recovering sulfur from H_2S in H_2S -rich natural gases, licensed the technology to Kazakhstan, and retained a 50% interest in a Kazakhstan company that markets the catalyst. This catalyst and the technology are patented in the West, but there has been no significant Western implementation so far.

The Institute also has advanced ceramic-fabrication capabilities, most clearly evident in its manufacture of two types of ceramic-based catalysts—impregnated (supported) and monolithic—in an impressive variety of shapes, sizes, and forms, including honeycombs (see Fig. 1). One application for monolithic, mixed-oxide, honeycomb catalysts promoted by BIC is a two-

Figure 1. Poster showing catalysts developed and marketed by BIC.

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stage filter used in diesel engine exhaust systems. In the first stage, a porous honeycomb catalyst loads up with tars and soot during operation and is periodically decoked by injecting oxygen at a higher temperature. In the second stage, NO_x and SO_2 removal/conversion is performed. It has been difficult to interest Western sponsors because development and commercialization of this technology will take longer than three years.

Professor Zinifer Ismagilov, head of BIC's Department of Environmental Catalysis, briefed us on major activities at the Institute, and explained how it participates in a regional environmental program, which includes the following features:

- Monitoring air and water quality.
- Treating organic waste from the various institutes.

- Developing catalytic converters for buses.
- Designing systems for removing volatile organic compounds (VOCs) from the air.

Ismagilov also described the various types of catalysts under development in his department and explained that, because of BIC's various commercial contacts and licensing agreements established over the past few years, it is not as economically impacted as most other institutes in Russia. To illustrate this, he told us how, in conjunction with a local company, BIC markets a small (2.5-kW) propane-fueled space heater based on a BIC-developed catalyst (see Fig. 2). The platinum-impregnated catalytic elements are prepared at BIC, whose share of the profits from about 3000 units sold per month supports about 10 Institute workers. Apparently, the complete cycle from concept to initial sales took

Figure 2. Poster showing catalytic heater marketed by BIC.

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only three years, including obtaining government permission not to recycle the small quantities of platinum used in the fibrous catalysts.

Facilities at BIC include several pilot-scale ceramic catalyst production systems and a pilot-scale, two-zone, catalytic, fluidized-bed reactor (used for oxidative destruction of organic wastes) capable of treating up to 5 kg/hr (see Fig. 3). This reactor, which consists of vertically stacked fluidized beds containing supported-catalyst alumina beads of different sizes, is specially instrumented for process development. Several laboratories are devoted to catalyst testing and characterization.

For rapid evaluation of catalysts, BIC has developed special reactor designs for simultaneously comparing several process variables and using vibrating reactors to achieve limiting reaction rates. The instrumentation on these

systems allows on-line measurement of nitrogen oxides by fluorescence, CO/CO₂ by gas chromatography/IR, and VOCs by gas chromatography/mass spectrometry. Figure 4 shows one of these systems. The Institute also uses an impressive variety of state-of-the-art physical examination techniques to characterize and understand catalysts: ion cyclotron mass spectrometry, pulsed NMR, ESR, LEED, ESCA, Auger-EXAFS, electron microscopy, automated spectrophotometry, and high-sensitivity systems that incorporate mass spectrometers for measuring surface area.

Topics covered in discussions at BIC included terms and conditions for three small research and development contracts. We presented BIC with requests for quotation, which had been prepared after discussions at the CIS-LLNL Workshop in Livermore in February 1993. Two

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Figure 3. Fluidized-bed reactor used for destruction of toxic compounds.

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Figure 4. Instrumentation system for testing and evaluating new catalysts at BIC.

of these contracts are funded by DOE/EM-50; the third is supported by an LLNL Laboratory Directed Research and Development Supporting Research (LDRD) project. The contracts supported by EM-50 cover the following:

- Development at BIC of environmentally benign honeycomb catalysts for selective reduction/destruction of NO_x in offgases from MW-treatment facilities.
- Disclosure of three innovative MW-treatment processes involving catalytic enhancements. The LDRD-supported contract requires BIC to perform scoping tests to identify an effective catalyst for oxidizing organic substrates in molten salts based on sodium carbonate.

NO VO VNIPIET Design Institute, Novosibirsk

The NO VO VNIPIET (short for Novosibirsk Department of Research and Design Institute of Complex Energy Technologies) Design Institute was established in the 1960s to design a variety of nuclear processing plants in Siberia and to design and build specific process systems such as those required for offgas treatment. The Institute is a subsidiary of another "VNIPIET" in St. Petersburg and has a staff of 470, of whom 340 are engineers and designers. The Institute has a particular interest in environmental process systems for industries such as uranium enrichment and nuclear power plants.

The NO VO VNIPIET Institute formerly designed, built, and operated large, two-stage incinerators for hazardous and radioactively contaminated organic wastes. Although incineration is not now completely prohibited in Russia, it is expected to be so eventually—hence the interest in the fluidized-bed catalytic unit for destruction of organic mixed wastes. Wastes of particular interest include oils, solvents, complexants such as tributyl phosphate, transformer oil, kerosene, and offgases containing VOCs.

Institute leaders showed us designs for a variety of thermocatalytic cleaning systems for VOC-contaminated gases. These systems handled gas flow rates from 150 to 3000 m^3/hr at VOC loadings of up to 6 g/m^3 . For lower VOC loading (50 to 100 mg/m^3), they designed a low-

temperature (60°C) catalyzed ozone reactor that handles gas flow rates up to 3000 m^3/hr .

Another low-temperature catalytic reactor is available to remove residual ozone from the processed gas. The influence of BIC is clearly evident in these systems, all of which contain catalyst-regeneration units. Versions of the ozone-removal system (KF-1000) are reportedly used on commercial aircraft and in factories where UV light processing is used. Other innovative systems we saw included the following:

- Jet scrubbers that use turbulent foams and suspended beads for cleaning particulates and impurities from ventilation and process gases (up to $5 \times 10^4 \text{ m}^3/\text{hr}$), a foam scrubber for very high flow systems (up to $10^6 \text{ m}^3/\text{hr}$), and a dry scrubbing process for P_2O_5 production that can handle up to $10^5 \text{ m}^3/\text{hr}$.
- Various "in place" filter systems, including filters based on activated charcoal; several back-flushable, high-temperature (400 to 500°C) filters based on ceramics or sintered nickel or stainless steel (we were shown a porous "ceramic" tube prepared by combustion synthesis of nickel and aluminum); and an iodine-impregnated charcoal filter used for removing mercury vapor from contaminated air.

Plant of Chemical Concentrates, Novosibirsk

This plant, which is the intended location of the ISTC catalytic fluidized-bed demonstration plant (discussed below), is on a large, secured site within the city boundaries. The site contains several factories; the one that we toured manufactures complete fuel assemblies for VV1000 pressurized-water nuclear power reactors, although the enriched UO_2 fuel pellets are manufactured elsewhere. It is an apparently clean, well-run, and efficient operation involving considerable automation and a comforting amount of quality control.

According to factory officials, the plant's principal wastes are uranium-contaminated vacuum oils and cutting and cooling fluids. Approximately 300 tons of oils and fluids are used per year, and some of these are decontaminated and reused. Formerly, contaminated oils

were incinerated at the plant's waste storage site, but now plant officials are looking for new ways to treat or dispose of them. Even with the present emphasis on recycling, some contaminated oils must be destroyed, and wastewaters contain traces of organics. They treat this wastewater much as we do at LLNL—the organics are separated, and then residual metals and radioactivity are adsorbed from water (e.g., by ion exchange and/or precipitation-filtration). We were told that the demonstration plant for oil destruction was to be installed in the same facility in which wastes are now stored and treated.

Institute of High-Current Electronics (IHCE), Tomsk

The IHCE employs approximately 400 people, about half of whom are technical professionals. It was launched in 1977 by Academician Gennadi Mesyats. The Institute's main mission is the development of pulsed power sources for high-current electron beams, microwave beams, and lasers. The principal purpose of our visit was to initiate a research contract with Dr. Victor Tarasenko, head of the IHCE's Optical Radiation Laboratory, for development and

delivery to LLNL of two high-power UV lamp prototypes. The lamps of interest are incoherent excimer sources that use triggered discharges in rare-gas mixtures such as KrF to produce narrow-band, high-intensity UV light. These sources might be of value in UV water treatment because of the variety of wavelengths available and because of the possibility of direct excitation of organic (contaminant) molecules.

During our tour of the Institute, we were shown several excimer-based UV sources, including an operating "Excilamp" (Fig. 5). We also were shown a variety of electron-beam guns and high-power microwave sources. Some of the electron-beam sources already have applications in materials processing (surface treatment) and medicine (surface sterilization). Should electron-beam processing of wastewater prove economical, the IHCE sources may be ideal candidates for this application as well.

Before we left the Institute, we agreed on the terms of a contract under which IHCE would construct two 100- to 200-W UV lamps for delivery to LLNL in approximately 12 months. After a joint lamp acceptance test at Tomsk, we plan to evaluate the lamps in wastewater treatability tests at LLNL.

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Figure 5. (right) V. Tarasenko shows the IHCE-developed "Excilamp" UV lamp partly disassembled (right and above).

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Institute of Atmospheric Optics, Tomsk

During the year preceding our visit, the Institute of Atmospheric Optics (IAO) underwent major changes, during which it lost almost all of its 28 largely military programs and replaced them with a variety of contracts and civilian programs, including several contracts with LLNL. Although none of these contracts are with the ER/WM-AT Program, we were shown two measurement techniques that could be of interest to atmospheric researchers.

The Institute of Atmospheric Optics has developed a portable mercury-vapor detector that uses optical absorption to measure extremely low concentrations of mercury vapor in the atmosphere (see Fig. 6). The detector has a lamp with a single mercury isotope in a 50-kG magnetic field (produced by samarium-cobalt permanent magnets surrounding the lamp). Spectral lines emitted from the lamp (wavelength unspecified) are split by the Zeeman effect and are then selected by a spike filter to measure the absorption of atmospheric mercury vapor. A 6-m path length (folded beam) is used for the measurement, and a detection threshold of a few nanograms per cubic meter is claimed.

We visited another facility at IAO, a large optical system used for measuring ozone in the upper atmosphere using a 2-m-diam reflecting telescope pointed vertically upward and connected by a flexible optical system to various laser and diagnostic systems in surrounding laboratories. By means of techniques devised at IAO, metal vapor lasers (mainly copper and gold) are used to measure ozone and aerosol concentrations to altitudes of 60 km. These measurements are used to study interactions between atmospheric aerosols and ozone.

Institute for Problems in Electrophysics, St. Petersburg

Like many of the Institutes of the Russian Academy of Sciences, the Institute for Problems in Electrophysics has been immersed in military work for several decades and is now struggling to survive in a free-market economy. This Institute consists of a physics department and an electrotechnical department. The physics department works on the physics of high-pressure discharges in gases and liquids (e.g., gas guns), the stability of discharges, the character of emitted spectra, plasma generators (e.g., plasmotrons for waste treatment), plasma

Figure 6. Portable mercury detector developed at the IAO, Tomsk.

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vitrification, pulsed-power systems, and various types of pulsed-plasma applications (e.g., ozone generators and water-purification systems). The electrotechnical department works on high-speed machinery, super- and hyperconducting generators, and control systems for industry, including rotating turbogenerators (e.g., flywheels for submarines), large switched capacitor banks, and small (50–60-MW) power plants.

During our visit, we extensively toured both of the Institute's sites—the older of which is in the basement of a former palace—and saw examples of many unique systems and machines. Of particular interest for environ-

mental applications were a prototype system for water purification that uses low-energy discharge pulses (see Fig. 7) and a prototype, stationary, ac plasma generator (see Fig. 8).

The water-purification system uses pulsed discharges with a steep current rise time and repetition rates of 50 to 100 Hz. The discharge takes place in severely contaminated water as it flows tangentially between a cylindrical anode and a set of point cathodes around the circumference. As a result of the pulse shaping, the discharge energy appears in the form of a shock wave with a steep front characterized by emissions in the UV range and by the production of ozone and hydrated electrons. The discharge voltage is 12 to 15 kV, current is 30 to 40 A, and energy emission is $\sim 1 \text{ J/cm}^3$. The coliform index of treated water drops from an initial value of 10^9 to between 10^4 and 10. The 1-kW installation, with a capacity of 120 m^3 per day, is suitable for both flow-through and storage applications. Researchers claim that the discharge-treated water preserves its purified properties for some time. Although they prefer the electrical discharge method for detoxifying water, they have built high-efficiency, low-volume ozonizers with outputs of 1 to 50 g/hr and are investigating ways to use ozone to decontaminate polluted water and shipping containers and to eliminate odors in various manufacturing shops.

The Institute has also constructed and operated various types of stationary ac plasma generators with power ratings of 10 kW to 3 MW, chamber pressures of 1 to 80 atm, and jet temperatures of 1000 to 12,000 K. Working gases are hydrogen, helium, xenon, argon, and air. Several techniques using plasmatrons are under development for the following environmental applications:

- Destruction of highly toxic wastes in plasma jets within a reaction chamber.
- Vitrification of solid radioactive wastes.
- Enhancement of fuel combustion in the combustion chambers of electric-power stations running on fossil fuels. This method enhances the efficiency and reliability of combustion plant systems and reduces their operating costs while reducing the emissions of NO_x and SO_x by several times.

Figure 7. Prototype electrical-discharge water purifier.

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Figure 8. Prototype stationary ac plasma generator.

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Professor Philip Rutberg, the head of the Institute, was our host for the visit, and we are continuing to discuss with him the possibility of collaboration in one or more areas.

General Physics Institute, Moscow

Work at the General Physics Institute on remote sensing has focused on sensing return signals from a Nd:YAG laser probe beam (laser illumination, detection, and ranging, or LIDAR) mounted on airborne platforms. Frequency doubling, tripling, and quadrupling have all been used, depending on the application. Return signals from fluorescence, Raman scattering, aerosols, and the surface have all been detected. The Institute's techniques have been applied to atmospheric monitoring, sea-surface measurements, and underwater sensing to depths of several hundred meters. Output LIDAR pulse energies of several tens of millijoules have been used, and detection systems typically monitor several hundred return pulses. Absorption cells and techniques using multiple laser wavelengths have been described as ways to increase detection sensitivity, and an acousto-optic sensor has been used in conjunction with the LIDAR. (A sensitivity of 1 to 30 ppm benzene in the atmosphere was claimed for this technique.)

Highlights of the techniques that we observed include the following:

- **Atmospheric measurements**—Systems deployed on helicopters have sensed path lengths of about 100 m and have detected atmospheric hydrocarbons of a few parts per million by weight (researchers at the Institute speculate that 0.1 ppm might be achievable).
- **Sea-surface measurements**—In measurements of oil slicks on the sea surface, systems have detected 1–5-ppm oil in seawater.
- **Undersea measurements**—Systems deployed on airborne platforms have made depth-sounding measurements that have yielded both bottom and thermocline returns to depths of several hundred meters, and plankton (chlorophyll) measurements have yielded profiles of plankton concentrations to depths of 100 m.

Supplementary funding of several hundred thousand U.S. dollars per year would be required to continue this research. Much of this cost is due to the high rental cost of helicopters, which are no longer available free of charge to the Institute.

ISTC Catalytic Fluidized-Bed Waste Treatment Project

We have been assisting BIC in preparing an ISTC proposal to fund the development and pilot-scale demonstration of a catalytic fluidized-bed organic mixed-waste destruction technology. In addition to BIC and NO VO VNIPIET, this project will involve the following Russian and U.S. processing plants:

- **Russian plants:** Tomsk-7, Krasnoyarsk-26, Krasnoyarsk-45, and the Angarsk Electrolysis and Chemistry Complex.
- **U.S. plants:** EG&G Rocky Flats Plant, Colorado School of Mines, and LLNL.

The U.S. participants will support the Russian project by providing consultation on fluidized-bed oxidation technology and by conducting separate assessments of catalyst efficiency. During our visit, we discussed the scope of the project with interested participants from BIC, the Plant of Chemical Concentrates, NO VO VNIPIET, and Tomsk-7.

At BIC, catalysts and processes are being developed for environmentally safe fuel combustion, gas-exhaust purification, organic-waste treatment, and industrial wastewater decontamination. In particular, BIC researchers are investigating the oxidative destruction of fuels and organic wastes in a fluidized-catalyst bed. A unique feature of the proposed method is the possibility of complete oxidation of organic compounds in stoichiometric mixtures with air at temperatures low enough (600 to 700°C) to prevent thermal NO_x formation. This is accomplished by means of active catalysts in a fluidized bed, which also effectively removes reaction heat. Testing of catalytic oxidation of various wastes, such as organic liquid solvents, chemical-industry wastes, nitrogen-containing compounds, and used liquid scintillators, has already been carried out in bench- and pilot-scale installations.

Russian project participants will inventory organic wastes, verify their compositions, prepare technical task plans for research and development, and deliver model mixtures of inactive waste to BIC for preliminary destruction tests in bench-scale setups. These studies will furnish new data on the catalytic oxidation of chlorine- and phosphorous-containing compounds necessary for preparing novel catalysts and optimizing the process. The NO VO VNIPIET Institute will develop an efficient gas-cleaning system downstream from the catalytic reactor that will incorporate new technical approaches to ensure the necessary purity of gaseous emissions.

On the basis of their results, BIC and NO VO VNIPIET will prepare a conceptual design for a plant, in response to which NO VO VNIPIET will prepare construction documentation for a demonstration plant with a capacity of 300 tons of waste per year. BIC will oversee the preparation of catalysts for use in the demonstration plant, to be constructed at the Plant of Chemical Concentrates. Tests of the plant will be conducted in the presence of American project participants. The resulting experience is expected to help introduce the improved destruction process at other Russian plants that must process wastes resulting from the processing of nuclear material, and the information should also be valuable to U.S. waste-processing specialists.

Institute of Spectroscopy, Troitsk

We briefly visited Professor Evgenii Vinogradov, Deputy Head of this world-famous institute, to discuss a multilaboratory environmental monitoring proposal submitted to the ISTC in Moscow. This project is intended to establish a "Russia-wide" network to monitor and characterize the sources and ultimate distribution of radioactive and other hazardous chemical contamination. The data generated by this network will be used as a resource to identify the sources of contamination and to design, implement, and manage cleanup efforts.

After validation, the data will be integrated into the global ENVIROTRADE database now under development in the DOE's Office of Environmental Restoration and Waste Management. The network will incorporate the existing infrastructure within the Russian Association of Spectroscopists and CIIEAS (The Center of Intellectual Initiative and Entrepreneurship), the Arzamas-16 and Chelyabinsk-70 nuclear laboratories, and Russian industrial and governmental facilities. The use of established laboratories is the quickest and cheapest way to establish this network. Experts from research institutes and government laboratories will train the personnel in the local laboratories. Using their special high-sensitivity equipment, they will also calibrate, standardize, verify, and provide quality control and assurance for the equipment in the local laboratories. They also will provide meteorological sampling and measurement expertise as required.

We and our hosts concluded the discussions by signing a request for quotation for the Institute to begin setting up the environmental monitoring network. This contract is being supported by funding recently received from the DOE Office of Technology Development (EM-50).

Summary and Prospects for Future Work

We achieved all four of the objectives we had established for our second visit. Since returning from that visit we have initiated four research contracts, which we hope represent the beginning of ER/WM endeavors that will benefit the environmental cleanup programs of both countries. In June 1994 the ISTC Board of Governors approved the fluidized-bed organic mixed-waste destruction technology proposal. We are now negotiating a new contract with the Arzamas-16 Laboratory, funded by the ILAB Stabilization Project.

Fiber-Optic Sensors for Characterizing Soil and Groundwater Contamination

Our fiber-optic chemical sensor for groundwater and vadose-zone monitoring uses a colorimetric detection technique. It is accurate and sensitive enough for environmental monitoring of trichloroethylene and chloroform. By assisting in optimizing the siting of monitoring wells, this sensor will significantly reduce remediation costs.

It is estimated¹ that soil and groundwater remediation problems at Department of Energy (DOE) facilities include at least 1.9×10^{11} gal of contaminated groundwater and at least 5×10^7 cubic yards of contaminated soils. More than 4800 individual hazardous waste and hazardous substance release sites on DOE properties (not including 24 designated inactive uranium processing sites and 5000 vicinity properties) have been identified.² Contaminants in soil and groundwater on DOE lands include organics (such as solvents and fuels), inorganics (such as salts and metals), radionuclides, and mixed wastes. Except for the radioactive materials, these contaminants are similar to those associated with common industrial practices throughout the industrial nations of the world.

DOE has begun an ambitious program to clean up these sites and to bring continuing activities into compliance with U.S. environmental regulations. Site restoration involves three major steps: (1) characterization; (2) evaluation, selection, and implementation of containment or restoration measures; and (3) performance monitoring during and after remediation. The ultimate cost of site remediation is strongly influenced by the number and cost of environmental samples needed for the characterization and monitoring steps of the cycle. There is, therefore, an urgent need for new analytical techniques that can provide rapid, inexpensive, and credible measurements of contaminant concentrations. A rapid analytical technique could greatly reduce restoration costs by significantly reducing sampling and analysis

expenses and by facilitating optimum placement of measurement locations (monitoring wells or soil vapor extraction points).

The ER/WM-AT Program is developing and field-testing a fiber-optic sensor technology for monitoring chlorinated organic solvents such as trichloroethylene (TCE) and chloroform. The sensor's design permits it to be placed into the subsurface solely with hydraulically driven penetrations (cone penetrometry).

Characterization and Monitoring

Characterization technology is used to identify and define soil and groundwater contamination problems. Site characterization depends on historical records and recollections (if available) and on sampling, testing, and analysis. Generally, state-of-the-practice methods can be effective in characterizing contaminant plumes if the contamination is simple, but heterogeneous physical or chemical subsurface conditions can make characterization more difficult and costly. Current practices usually require construction of wells with dedicated pumps, periodic sampling of the wells, and analysis of the samples. This approach requires capital investment for the wells and equipment and creates operational expenses for the skilled labor needed to draw and analyze the samples.

Monitoring schemes are designed to measure soil vapors or groundwater for contaminant concentrations to assess the performance of a remedial action or closure. Monitoring data can also be used to check assumptions developed for site characterization and remediation design. In

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Figure 1. Reagent delivery system and penetrometer cone. The reagent is connected to the sensor through microtubing. The syringe reservoirs are held in place with quick-disconnect clamps for easy servicing. The cone is made from corrosion-resistant steel tubing.

general, the technical requirements and limitations of monitoring schemes are similar to those for characterization (e.g., dedicated wells, equipment, labor, and sample analysis needs, with concomitant capital and operational costs). Postclosure or performance monitoring is generally performed at intervals over an extended time, making it a potentially large ongoing component of site remediation expense.

Sensor Design

The sensor operates on colorimetric principles. Optical fibers are used to remotely monitor a quantitative, irreversible chemical reaction that, upon exposure to various target molecules, forms products that absorb visible light. The primary chemical reagent used in the sensor is an outgrowth of early work³ that demonstrated that basic pyridine, when exposed to certain chlorinated compounds, develops an intense red color. We have shown that the absorption of 560-nm light by these colored products increases directly with the vapor-phase concentration of the contaminant and that some selectivity of target molecules is possible through modifications of the reagents and their relative proportions.⁴ We have evaluated the sensor against gas-chromatographic standards; its accuracy and sensitivity (<5 ppb by weight) are sufficient for monitoring the environmental contaminants TCE and chloroform.⁵

The sensor system has three major components: a miniature pumping and delivery system for renewing the chemical reagent, an electro-optic readout device for monitoring the transmission of the sensor, and the sensor itself. The system design allows consecutive, on-demand measurements to be taken at short intervals; control and monitoring are done remotely. The small reaction volume of the sensor allows a large number of measurements to be made before the reagent reservoir must be recharged. This allows the sensor to stay in place for a long time before it must be serviced.

Figure 1 shows the most versatile version of the reagent delivery system, which was designed to fit into a standard cone penetrometer system. (Cone penetrometers, used for many years in soils testing, are now in common use in DOE site characterization.) The high-aspect-ratio

design was achieved by placing the reagent supply into a gas-tight 5-mL syringe that is opposed to an identical, empty syringe. The syringe plungers are fixed with respect to one another and are simultaneously driven by a motor and drive screw. As fresh reagent is delivered to the sensor, spent reagent is thus captured in the empty syringe, making recovery and disposal easy. The motor is encoded to permit monitoring of the remaining reagent volume.

A custom penetrometer cone, also shown in Fig. 1, was designed by S. Cooper of the U. S. Army Corps of Engineers Waterways Experiment Station (COE/WES) and S. Brown of LLNL, and was constructed at LLNL. The cone (495 mm long, 44.5 mm o.d., 33.75 mm i.d.) is threaded to receive standard 1 m $\times$ 33.75 mm COE/WES push rods. The reagent delivery system and sensor are housed in the cone and are isolated from the environment until measurement depth is reached. The TCE sensor is exposed to soil vapors by means of a removable, disposable ground-penetrating tip. The cone is driven to the desired depth and then retracted by 15 cm, leaving the removable tip at depth while exposing the sensor to soil vapors and creating a void or "probed volume" of about 200 mm³. Communication from the ground surface to the sensor and support equipment housed in the cone is accomplished with a custom-built 60-m-long umbilical cord containing two optical fibers, a tube for vacuum evacuation of the probed volume, and a six-wire electrical cable for electronic instruction delivery and data acquisition.

Field Test

The DOE Office of Technology Development Integrated Demonstration at the Savannah River Site was chosen as the initial location for field demonstration and evaluation of the sensor technology. The objectives of the work

reported here were to deliver the sensor, using cone penetrometry, to multiple depths at multiple locations; to expose the sensor to a range of TCE concentrations; and to observe the effect of pumping, as in a vadose zone "grab sample" operation, on the measurement process.

Before the experiments, the umbilical cord was threaded through 47 1-m-long push rods, allowing us to reach depths of at least 41 m. Four separate "pushes" (to depths of 9, 14, 41, and 33 m) were accomplished over two days. The average push rate was 1 m/min. All pushes were carried out by COE/WES participants. Experiments were controlled from the surface by means of a portable optical sensor readout device and portable computer. Measurements were made in both a quiescent ("static") and vacuum extraction ("dynamic") mode. A total of 121 individual TCE concentration measurements were made during the four pushes; measured concentrations ranged from ~2 ppm by volume (static measurement at 9 m depth) to ~120 ppm by volume (dynamic measurement at 14 m).

Table 1 gives the results of an extended experiment performed after the sensor was pushed to 33 m, which placed it approximately 6 m above the water table. We made three measurements with the cone tip in place to zero the sensor, then removed the tip and made 15 consecutive static measurements. The measured TCE concentration was 18.8 ± 5.0 ppm. We then performed nine consecutive measurements under dynamic conditions. Here the concentration jumped abruptly into the 30-ppm range and remained stable for the duration of pumping, yielding a TCE concentration of 34 ± 1.3 ppm. When we discontinued pumping, the concentration almost immediately dropped back to the previous static values (average concentration 14.4 ± 1.8). This is identical to the initial measurements within experimental uncertainty.

Table 1. TCE concentrations measured *in situ* under static (unpumped) and dynamic (vapor extraction) conditions.

Pump	TCE concentration (ppm, by volume)											Mean
Off	29.8	26.9	20.2	18.2	18.0	16.6	16.7	15.8	15.2	13.0	14.6	18.8 ± 5.0
On	35.2	33.7	32.1	31.6	33.3	32.5	36.2	35.2	34.3			34.0 ± 1.3
Off	23.7	18.4	16.0	15.5	14.2	13.2	14.4	12.9	13.0	13.0	13.2	14.4 ± 1.8

The first three readings after tip retraction gave higher concentrations than the next eight measurements. This is probably attributable to the vacuum, and the resulting greater soil extraction, generated upon initial retraction of the cone to form the probed volume. Removing the first three measurements (29.8, 26.9, and 20.0 ppm) from the initial static set yields a mean TCE concentration of 16.1 ± 1.4 ppm, which agrees very well with the mean and uncertainty obtained during the second static set of measurements. The higher values obtained during pumping might be due to increased TCE volatility during flowing conditions.

Applications

The development, commercialization, and use of automated sensor systems to quickly and inexpensively measure contaminant concentrations *in situ* will benefit site investigation and monitoring by reducing costs and improving the quality and types of data available. A similar revolution in field measurement capabilities occurred in geomechanics several years ago, when automated piezoelectric measurement of hydraulic pore pressure in rock and soil began to replace conventional water level measurements made with tag lines in wells and standpipes. These improved, lower-cost measurements were

particularly valuable for projects such as dams, tunnels, and engineered slopes. The data supported better understanding of project performance and improved operational safety.

Automated systems for *in situ* measurement of contaminant concentration could have an even greater impact on site investigation and remediation applications for contaminated soil and groundwater. These systems could be used in several ways:

- Installation in advance of migrating plume or at site boundaries for contaminant detection or watchdog applications (see Fig. 2).
- Reducing characterization and monitoring costs associated with conventional well sampling and sample analysis.
- Monitoring concentrations during pump-and-treat and other groundwater cleanup operations (including new cleanup technologies) to support optimization of design and operations (Fig. 2).
- Investigating changes in spatial distribution of contaminants with time to verify effects of design assumptions on remediation.
- Providing "ground truth" measurements to verify geophysical remote sensing or underground imaging to detect non-aqueous phase liquids and to delimit plume boundaries.

Figure 2. Plan view of groundwater contamination plume, showing locations of penetrometer-installed sensors to measure contaminant concentration changes with time (within the plume) or to detect contaminant spread (along site boundary for watchdog applications).

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This technology for measuring contaminant concentrations *in situ* represents the most rapid and cost-effective means of obtaining initial survey information on subsurface contamination distributions for a variety of chlorinated solvents. Its impact on optimizing the siting of monitoring wells will significantly reduce remediation costs. With lower sensor and installation costs, this approach should provide better-quality and more complete data, thus improving understanding of *in situ* processes and phenomena during site characterization and remediation.

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