K--2073-Vol.3B

DE93 009488

**Oak Ridge K-25 Site
Technology Logic Diagram**

**Volume 3
Technology Evaluation Data Sheets**

**Part B
Remedial Action • Robotics/Automation • Waste Management**

Prepared for the Office of Technology Development
U.S. Department of Energy

Published: February 26, 1993

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U. S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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FOREWORD

The Oak Ridge K-25 Technology Logic Diagram (TLD), a decision support tool for the K-25 Site, was developed to provide a planning document that relates environmental restoration (ER) and waste management (WM) problems at the Oak Ridge K-25 Site. The TLD is based on the Strategic Road Map for the Oak Ridge Reservation. The TLD technique, developed by the U.S. Air Force, applied new innovative technologies to problems specific to the K-25 Site.

The TLD technique identifies the research necessary to develop these technologies to a state that allows for technology transfer and application to waste management, remediation, decontamination, and decommissioning activities. It is essential that follow-on engineering studies are conducted to build on the output of this project. These studies will begin by selecting the most promising technologies identified in the TLD and finding an optimum mix of technologies that will provide a socially acceptable balance between cost and risk.

The Oak Ridge K-25 Site TLD consists of four separate volumes—Vol. 1, Vol. 2, Vol. 3A, and Vol. 3B. Volume 1 provides introductory and overview information about the TLD. Volume 2 contains logic diagrams. Volume 3 has been divided into two separate volumes to facilitate handling and use.

This volume provides the Technology Evaluation Data Sheets (TEDS) for ER/WM activities (Remedial Action, Robotics and Automation, Waste Management) that are referenced by a TEDS code number in Vol. 2 of the TLD for the K-25 Site (K-2073). Each of these sheets represents a single logic trace across the TLD. These sheets contain more detail than each technology in Vol. 2. The TEDS are arranged alphanumerically by the TEDS code number in the upper right corner of each data sheet.

Volume 3 can be used in two ways: (1) technologies that are identified from Vol. 2 can be referenced directly in Vol. 3 by using the TEDS codes, and (2) technologies and general technology areas (alternatives) can be located in the index in the front of this volume.

The technology evaluations that are contained in this volume are based on the best information available during the TLD compilation. New or more accurate information is solicited to improve the TLD data base. Please FAX comments (615-576-8558) to R. L. Fellows, Editor, Technology Logic Diagram for the K-25 Site, Martin Marietta Energy Systems, P.O. Box 2003, Oak Ridge, TN 37831-7274.

ACKNOWLEDGMENTS

The authors acknowledge the significant contributions made by the DOE Overview Team for the Technology Logic Diagram Review and Development: Robert Benedetti, Holmer Dugger, Mitchell Erickson, Ned Hutchins, William Schutte, and Randall Snipes.

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- Ultrasonic Extraction CHAR-20-OG
- Ultrasonic Leak Detection CHAR-70-OG
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- Voice Control ROBA-35-OG
- Wall Thickness Measurements ... ROBA-68-OG
- Waste Curie Monitor (Bag or
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- Waste Isolation Pilot Plant WDIS-105-OG
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- Water-Jet Cutting of Steel, High-
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- Water-Jet Cutting, Thermal Arc ... DISM-61-OG
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- X-Ray Diffraction, Powder (XRD) .. CHAR-31-OG
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REMEDIAL ACTION

CHEMICAL EXTRACTION OF URANIUM IN SOIL USING WATER EXTRACTANT

REMA-1-OG

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Chemical separation

Technology: Chemical extraction of uranium in soil using water

Technology Status: Demonstration. This technique has been used in the field for cleaning soluble uranium salts from soils and mill tailings, often as a pretreatment process to other physical or chemical treatments.^{1,2} This technique is included in the Fernald Integrated Demonstration. Note that water alone will only remove soluble uranium, that is, uranium that is highly mobile in the soil. There may not be much uranium in soluble forms in K-25 soils. The addition of chelating agents and oxidizing agents may increase the solubility of the uranium, but that extends the complexity of the approach. Costs could be moderate (<\$100/t) if the uranium is sufficiently soluble (not expected to be the case). Development and demonstration costs could be <\$10M.

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CHEMICAL EXTRACTION OF URANIUM IN SOIL USING WATER EXTRACTANT

REMA-1-OG

Science/Technology Needs: Further characterization of uranium solubilities in soils at K-25 is necessary. Characterization should determine the oxidation state of the uranium and identify those fractions present as insoluble compounds and those adsorbed. Because of the high rainfall in the K-25 region, most uranium is expected to be insoluble, either as uranium (IV) or adsorbed on clays (See Characterization). We need determination of the usefulness of this technique via bench- and pilot-scale testing for mixed waste contamination.

Large-scale testing and demonstrations. No large-scale testing strictly for uranium leaching with water should be considered unless there is indication that sufficient uranium will be soluble. However, the characterization (solubility) studies could be helpful because of their importance in other separation techniques.

Implementation Needs: The principal implementation problem is the doubt that sufficient uranium will be removed. Acceptable treatment levels have not been established. Leaching can be combined with soil washing. Dispersion of soils will be crucial to reaching practical leaching times. Maximum recycling of reagents will be required. Acceptable leach targets need to be established, presumably based upon the risk of leaving some uranium in the soil. Equipment will consist largely of dispersion units, vats, and reagent recycling equipment. The vats may be the largest items. Serious questions remain about the effectiveness of this treatment approach, while cost considerations are not as significant.

Authors: G. Macklin, W. Harwood, J. Watson

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1. E.R. Landa, "Geochemical and Radiological Characterization of Soils from Former Radium Processing Sites," *Health Physics*, **46**, 1984, pp. 385-394.
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February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Chemical separation

Technology: Electrokinetic removal of uranium from soil

Status: Predemonstration. Exploratory studies have moved toxic metals through soil under electrostatic potential.¹ A DOE-sponsored workshop was held recently in Atlanta to evaluate the potential of this concept. Much remains to be understood about the concept before it can be applied to uranium contamination. For instance, does the uranium have to be oxidized to the more soluble VI state before it becomes mobile? Uranium IV can form complexes with chloride, carbonate, or sulfate to form anions and neutral specie as well as cations; which way(s) will the uranium go under an electric field? How will the uranium be recovered from the electrodes as migration is completed? How far apart can the electrodes be spaced? This appears to be a concept, not a proven technology. Costs are very uncertain at this time because the concept is not sufficiently defined. The costs are not expected to be low once the

entire removal scheme is defined. Costs could still exceed \$100/t. Development and demonstration costs probably will be moderate, perhaps \$1M to \$10M.

Science/Technology Needs: As noted above, much remains to be learned about this concept before its applicability can be evaluated. There is a need for study of uranium solution chemistry in soils and soils with humus and other organic materials (such as those found near the soil surface). The questions listed above should be addressed. The technology, if operated in situ in shallow soils (near the surface) as expected, would have to operate under conditions ranging from drought to heavy rainfall. The role of acid formation from electrolyte electromigration on uranium movement needs to be understood. Although the technique could also be considered as an ex situ method, excavation and placement in treatment bins will increase the cost and the need for more rapid treatment rates. Concepts need to be developed and tested for recovering the uranium from the electrodes (of the electrode region).

Large-scale testing and demonstrations. Large-scale testing in situ will be needed to show how the technology can handle the heterogeneity usually found in K-25 soils. Such tests should also demonstrate that uranium moves principally along the electric field lines, and the electrokinetic treatment does not free the uranium so it can be "washed" from the soil and spread the contamination. The rate of treatment should be confirmed.

Implementation Needs: Much needs to be learned about this technology before all implementation needs can be assessed. It is too early to assess costs, but one would expect in situ costs to be moderate if the uranium can be removed from the electrode regions at moderately high concentrations and easily concentrated for disposal. Ex situ costs might be excessive if the rates are low and treatment facilities are not sufficiently inexpensive. Treatment levels are also not yet established.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. Y. Acar, et al., *Electrokinetic Soil Processing: Project EKSITE*, EK-BR-008-079, 1991.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils, groundwater, and surface water

Problem Area/Constituents: Dense nonaqueous-phase liquids (DNAPLs)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Vacuum extraction (only for volatile DNAPLs located above the water table)

Technology: Surfactant flushing

Status: Predemonstration. Field tests of this approach have been conducted, but the highly fractured and complex soil structure at the K-25 Site is believed to be sufficiently different from most deserts that the technology should be considered "demonstrated." Surfactant flushing itself may not be a very expensive operation, but extensive characterization is likely to be needed before surfactant flushing can be applied. It will be necessary to get the surfactant to the DNAPLs and to recover the DNAPLs effectively in recovery wells. Because much of the characterization cost may be incurred before decisions are made on treatment, the total cost for this technology may not be evident from the operating costs alone. The time of operation also will depend on the "solubility" of the DNAPLs with the surfactants present and, thus, the treatment time required. The total cost for treatment is likely to be high, probably several hundred dollars per ton, even if operating costs are moderate. Development costs are likely to be high, especially if development of new characterization methods is required. Even with suitable characterization methods available, in-field tests and demonstrations will require costly characterization to evaluate performance and gain the needed understanding of the technology. Development and testing are likely to cost several million dollars, perhaps even several tens of millions of dollars. Wastes will consist of the recovered DNAPLs and surfactants. Reuse of the surfactants may be possible but, because they will almost certainly contain some residual contaminant, reinjection of the materials may not be permitted.

Science/Technology Needs: The greatest need is for better ways to detect the presence of DNAPLs and to define the treatment region. A need also exists to understand underground structure and for methods to use this knowledge to design surfactant flushing treatment and predict the behavior of the treatment. Most important is to predict the movement of DNAPLs caused by reductions in interfacial tension. It is also important to be able to design a reliable recovery (extraction) well system. Slightly less important is the need to predict DNAPL "solubility" with surfactant addition, thus, the time required for treatment.

Implementation Needs: Acceptable treatment levels need to be defined and, in this case, this also means that a method for determining the contamination level needs to be defined. Treatment of any DNAPL-contaminated region will require approval and assurances that little chance exists for spreading the contamination. Because surfactant flushing intentionally mobilizes the contaminant so that it can be removed, it is especially important to ensure that the recovery system is good enough that the merits of removing the DNAPLs exceeds the risk of spreading some small fraction of the DNAPLs.

Authors: J. Watson

References:

1. Consultations with MMES staff.

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternatives: Physical separation

Technology: Solids separation techniques for segregating and concentrating soil particles: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques

Status: Demonstration. All of the above physical separation processes are used extensively in uranium extraction and are commercially available within the mining industry.¹ An integrated demonstration of soil separations is proposed for the Fernald Plant. The wastes produced are the rejected contaminated soil fractions. These contaminated fractions will require further treatment. The advantage of this technology is the potential reduction in the volume of waste that needs treatment.

Costs for most physical separations are likely to be moderate (<\$100/ton). The success or performance of the technology depends on the nature of the uranium contamination. For physical separations to be useful, the contamination must be concentrated in only a small fraction of the soil particles. This distribution can be a function of the way the uranium was introduced into the soil and the composition of the soil, especially the presence of materials that could adsorb or reduce soluble uranium.

Development and demonstration costs could range from a few million dollars to perhaps \$10M. Because of the wider interest in these problems, some or much of the development/demonstration costs may be carried in other programs, such as the Fernald Integrated Demonstration. Several industrial firms are also developing and testing soil washing and various solids separations equipment at their own as well as government expense.

Science/Technology Needs: The textural classes (i.e., sand, silt, and clay fractions) of K-25 soils and the distribution of uranium between the textural classes must be determined to establish the maximum separation that is possible. The density, size, and other properties of uranium-contaminated particulate must be established to identify suitable separation methods. Identification of appropriate combinations of bench- and pilot-scale testing for separation techniques will likely accommodate K-25's soil contamination problems. Determination of ultimate disposal or treatment of process end-products ("clean soils" and highly concentrated radioactive sediments) is necessary.

Large-scale testing and demonstrations. The technologies developed and demonstrated at Fernald should be tested with K-25 soils.

Implementation Needs: Physical separation methods often use significant quantities of water. Recycling the water is essential for waste minimization. Equipment is likely to be uncovered or in simple shelters rather than in enclosed buildings. Portable equipment may be available, but the equipment may be relatively large. Physical separations may be combined with chemical leaching. Costs for physical separation alone are currently low, but this technology is likely to be combined with leaching or other chemical treatments that may prove to be expensive. The important economic factor is likely to be the cost savings that can be realized by reducing the volume of material that requires chemical treatment via physical separation. Waste volume depends upon acceptance of the soil residue for return to the ground and the techniques used to concentrate the uranium bearing particles or leach solution. The waste volume could be large.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. U.S. Environmental Protection Agency, *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002, Office of Research and Development, Washington, D.C., 1988.

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Treatment. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternatives: Physical separation

Technology: Soil washing. Techniques using additives such as surfactants, chelates, bases, or acids for removing uranium.¹

Status: Demonstration. Conceptual-, bench-, pilot-, and large-scale testing of soil washing has been performed for various organic compounds and metals but not for uranium. "Soil washing" usually refers to separation of soil fractions by size. Thus, "soil washing" can be viewed as a subset of "solids separation." This technology involves the excavation of contaminated soil and subsequent washing of the soil with water in combination with additives. The treated soil can then be returned to the site or disposed of while the elutriate is collected along with the solvent, which also requires disposal. This process can be conducted on site or performed at remote facilities after excavated soil is removed and transported for treatment.¹ Soil washing has been used to effect several full-scale remedial

actions on a variety of substances such as herbicides, tetrachloroethylene, and metals.¹⁻³ Water used in combination with a chelate seems most effective on metals in sandy, low clay soils.²⁻⁵ Soil washing technologies are being considered for the Fernald Uranium in Soils Integrated Demonstration. Costs will depend strongly on subsequent treatment, leaching, disposal, etc. Cost for washing alone (no subsequent treatment) could be <\$100/ton. Waste volumes are likely to be large.

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, extraction with mineral acids, extraction with complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; and storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Science/Technology Needs: Laboratory-scale testing should be implemented with uranium-contaminated soil from the K-25 sites to determine the effectiveness of the technology with these particular soils. It is important to characterize the different soil fractions that can be separated by size, density, etc., to determine how the uranium is distributed in these fractions.

Large-scale testing and demonstrations. Tests are in progress to remove plutonium from soils. Large-scale tests for uranium in the Fernald soils are likely through the Uranium in Soils Integrated Demonstration. Several manufacturers provide equipment for soil washing. The performance of these equipment designs may be different and should be evaluated using K-25 soils.

Implementation Needs: Suitable treatment levels need to be established. The usefulness of size separations for K-25 soils must be determined, and suitable subsequent treatment steps need to be developed and assessed. Equipment for soil washing can be relatively large, but individual items are often portable, which means they can be moved from site to site. The merits of soil washing over more conventional leaching are seen only when the separation of the different soil particles reduces the quantities of soil to be leached. Characterization of the soils should reveal significant differences in the uranium concentration in the different soil fractions. Costs can vary widely depending upon the extent of uranium contamination, soil conditions, excavation costs, and the type and quantity of additives used. Additional expense can occur if other additive-consuming materials are present in the soil to compete with the uranium. Development and demonstration costs could be a few million dollars (perhaps

<\$5M). Current development and testing for other DOE programs and in commercial firms could represent much of the development cost.

Authors: G. Macklin, W. Harwood, J. Watson

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1. U.S. Environmental Protection Agency, *Handbook on In Situ Treatment of Hazardous Waste Contaminated Soils*, EPA/540/2-90/001, Office of Research and Development, Cincinnati, Ohio, 1990.
2. K. Stief, "Remedial Action for Groundwater Protection: Case Studies Within Federal Republic of Germany," 5th National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., November 7-9, 1984.
3. J.B. Truet, et al., "In Situ Treatment of Uncontrolled Hazardous Waste Sites," Proceedings of the 3rd National Conference, The Hazardous Materials Research Institute, Silver Springs, Maryland, 1982, pp. 451-457.
4. U.S. Environmental Protection Agency, *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002, Office of Research and Development, Washington, D.C., August 1988.
5. P. Esposito, et al., *Results of Treatment Evaluations of a Contaminated Synthetic Soil*, JAPCA, 39(3), March 1989, pp. 294-304.
6. K.W. Tsang, P.R. Dugan, R.M. Pfister, "Extraction of Bismuth Cadmium, Lead, and Uranyl Ions from Contaminated Soil and the Influence of Bacteria on the Process," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Ga., September 21-23, 1992, Vol. II*, D. William Tedder, ed., American Chemical Society, Washington, D.C. 1992, pp. 597-600.

EM Problem: Remedial Action

K-25 Site Problems: Soil Contamination

Problem Area/Constituents: Uranium in Soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ oxidation state, spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Chemical separation

Technology: Mobile soil washing unit using a combination of physical separation, washing, and chemical extraction techniques for treating uranium contamination. This is a combination of solids separation and soil leaching that are discussed separately elsewhere.

Status: Predemonstration. The EPA Mobile Soil Washer Pilot Plant was used to remove nonradioactive contaminants from selected soil.^{1,2} A demonstration of soil separation, washing, and leaching is expected to be made for the Fernald Integrated Demonstration. Costs depend strongly on the leaching step used in the unit, both on the leaching fluid used and the rate of leaching. Operating costs could be a few hundred dollars per ton. Development and demonstration costs could be a few million dollars. Much help could come through development of the size separation and leaching operations separately and from other activities such as the Fernald Integrated Demonstration.

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, extraction with mineral acids, extraction with complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; and storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete vaults, underground concrete vaults, and underground mine repository, underground deep well injection.

Science/Technology Needs: Characterization data will be needed for the K-25 soils to enable rational designs and evaluation of the technology. Leachability of uranium will depend on the chemical form of the uranium. Distribution of uranium in different soil fractions should be determined.

Large-scale testing and demonstrations. Specific tests will be needed on K-25 soils. A mobile soil washing unit could be easily moved to a K-25 application. Selection of ligands and treatment of concentrated uranium products will be important considerations.

Implementation Needs: Equipment may be uncovered or in light shelters; few buildings are likely to be required. Power (electrical or internal combustion), water, and waste collection/treatment facilities will be needed. Recycling of all water and reagents will be necessary. Costs will vary widely depending on unit configuration and ease of uranium leaching. Costs are likely to be moderate to high. Waste volume could be large.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. U.S. Environmental Protection Agency, *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002, Office of Research and Development, Washington, D.C., 1988.
2. R.D. Traver, "In Situ Flushing and Soil Washing Technologies for Superfund Sites," RCRA/Superfund Engineering, Technology Transfer Symposium, 1986.

ACID LEACHING OF URANIUM IN SOIL USING MINERAL ACIDS

REMA-14-OG

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Chemical separation

Technology: Acid leaching of uranium in soil using mineral acids

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, extraction with mineral acids, extraction with complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

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ACID LEACHING OF URANIUM IN SOIL USING MINERAL ACIDS

REMA-14-OG

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; and storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Status: Conceptual/predemonstration. This technique has been demonstrated for use on mineral ores for extracting radioactive metals. Laboratory experience suggests that the process may be applicable for contaminated soils.¹⁻³ It has been considered for the Fernald Integrated Demonstration. The high limestone content of some K-25 soils may make this approach impractical unless the limestone can be separated by soil washing. Costs are uncertain but could be high (>\$100/t). Development and demonstration costs could be several million dollars, perhaps <\$10M.

Science/Technology Needs: Evaluation of common mineral acids and concentrations for their effectiveness with K-25 soil contamination problems is necessary. The condition of the soil and the concentration/recovery of uranium need to be determined. This technique may be most effective for only a fraction of separated soils. Treatment method needed for leach liquor.

Large-scale testing and demonstrations. This technology might be an alternative to carbonate leaching. Acid recovery might be an important factor in designing large-scale treatment units. Leaching rates will be important and could be affected significantly by the degree of soil dispersion achieved before the addition of acids. Removal of acid-consuming carbonate rock may be necessary.

Implementation Needs: Treatment levels need to be established, and processes must be available for recovering uranium from the leach liquors. Acid leaching has been used in the uranium mineral industry, but its application to soils will depend, in part, on the following: (1) the ability to handle the fine fraction of the soils and (2) the ability to remove acid-consuming limestone from the soil without removing significant uranium before leaching. Dispersion equipment is not always easy to scale to larger sizes, and this factor could affect performance of large facilities. Large equipment may be required, depending upon leach rates. Recycling unconsumed acid and minimization of wastes will be required. Costs will be strongly affected by the presence of limestone or other acid-consuming materials in the soil. Leach times and the remediation level will also affect costs significantly. Cost data are not available in the cited references and probably will be high.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. U.S. Environmental Protection Agency, *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002, Office of Research and Development, Washington, D.C., 1988.

February 26, 1993

**ACID LEACHING OF URANIUM IN
SOIL USING MINERAL ACIDS**

REMA-14-OG

2. A.E. Torma, et al., "Sodium Carbonate—Bicarbonate Leaching of a New Mexico Uranium Ore and Removal of Long Half-Life Radionuclides from Leach Residue," *Uranium*, 2, 1985, pp. 17-36.
3. A.E. Torma and S.Y. Yen, "Uranium Ore Leaching with Brine Solutions Containing Hydrochloric Acids," *Erzletall*, 37, 1984, pp. 548-554.

February 26, 1993

EM Problem: Remedial action

K-25 Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Chemical separation

Technology: Alkaline leaching. Chemical extraction of uranium contamination in soils using alkaline inorganic salts and other selected ligands.

Status: Predemonstration. No field demonstration of soil cleaning using this extraction process has been attempted; all research consists of laboratory experiments.¹ However, this is a proven technology in the uranium ore industry. The research has concentrated primarily on the extraction of radium and thorium.^{2,3} This technique is included in the Fernald Integrated Demonstration. This is most likely to be the preferred leaching method for soils containing limestone. It is also expected to be more selective than acid leaching and to dissolve fewer metals other than uranium. Tests at the Fernald Integrated Demonstration will provide a basis for determining meaningful cost estimates. The cost may be a few hundred dollars per ton. Development and demonstration costs could be a few million dollars,

probably <\$10M. Much of the development cost may be covered by existing programs, mostly for Fernald.

Science/Technology Needs: Only recently have efforts been made to apply these techniques to uranium-contaminated soils. The oxidation and chemical state of the uranium contaminate is important to the approach and possibility of success for this method of extraction. Carbonate-leaching technology can be adapted from the ore industry relatively quickly. More innovative ligand leachates may require significantly more development. Recovery and concentration of uranium must be considered as part of the application of this technique.

Large-scale testing and demonstrations. Initial demonstrations are expected to come from the Fernald Integrated Demonstration; however, further tests will be needed with actual K-25 soils. Leaching rates will be important and could be affected significantly by the degree of soil dispersion achieved before feeding the soil to the leach vats.

Implementation Needs: Suitable treatment levels need to be established. Leaching can be combined with soil washing. Dispersion of soils will be crucial to reaching practical leach times. Maximum recycling of reagents will be required. Acceptable leach times need to be established, preferably based on target levels for residual uranium. Equipment will consist largely of dispersion equipment, vats, and reagent recycling equipment. Costs are likely to be similar to those encountered in ore processing, although leach times may be different and thus affect costs, probably moderate to high (a few hundred dollars per ton). Leach times may be affected by remediation levels as well as soil properties. The volume of solution to be processed for uranium concentration/recovery will also depend on remediation levels. Cost data are not available in the cited references and probably will be moderate to high. Waste volume will depend upon the state of the treated soil; volume could be large.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. U.S. Environmental Protection Agency, *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002, Office of Research and Development, Washington, D.C., 1988.
2. A.E. Torma, et al., "Sodium Carbonate—Bicarbonate Leaching of a New Mexico Uranium Ore and Removal of Long Half-Life Radionuclides from Leach Residue," *Uranium*, 2, 1985, pp. 17-36.
3. E.R. Landa, "Leaching of Radionuclides from Uranium Ore and Mill Tailings," *Uranium*, 1, 1982, pp. 53-64.

EM Problem: Remedial Action

K-25 Site Problem: Soil Contamination

Problem Area/Constituents: Uranium in Soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Fixation

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, mineral acids, complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete

vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Technology: In situ solidification of radiologically contaminated soils using cement-based grouting

Status: Accepted. In situ grouting with cement-based materials has been used at Oak Ridge National Laboratory (ORNL) Solid Waste Storage Area 6 as a field demonstration for long-term remediation.¹⁻⁴ Suitably prepared grout will pass the TCLP test. Costs are likely to be moderate, perhaps \$30-70/m³.²

Science/Technology Needs: Detailed characterization of waste matrix is required to determine suitability of cement-based grout as a solidifying agent for specific sites. We need long-term assessment of the ability of grouting technology to maintain the pH necessary for retention and containment of uranium contamination. Continued research might explore grout formulations that limit or reduce the volume of the final solidified product. Reliability of operations need to be determined.

Large-scale testing and demonstrations. High confidence in grouting is not universal. More careful demonstrations and operations are needed to create a higher level of confidence in the long-term performance of cement-based grouting.

Implementation Needs: Future uses of soils will be severely affected by significant grouting; therefore, solidification has to be an acceptable final condition for the site. Costs are likely to be moderate, perhaps \$30 to \$70/m³.² Waste volumes will be high.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. R.D. Spence, T.T. Godsey, and E.W. McDaniel, *In Situ Grouting of a Low-Level Radioactive Waste Trench*, ORNL/TM-10462, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1987.
2. T. Tamura and W.J. Boegly, Jr., *In Situ Grouting of Uranium Mill Tailings Piles: An Assessment*, ORNL/TM-8539, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983.
3. E.C. Davis and B.P. Spalding, *Field Evaluation of a Cement-Bentonite Grout and a Chlorosulfonated Polyethylene Fabric Liner in Hydrologically Isolating Low-Level Radioactive Solid Waste*, ORNL/TM-9742, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1986.
4. C.W. Francis, R.D. Spence, T. Tamura, and B.P. Spalding, *In-Situ Grouting of Low-Level Burial Trenches with a Cement-Based Grout at Oak Ridge National Laboratory*, ORNL/TM-11838, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1992.

EM Problem: Remedial action

K-25 Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Fixation

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, extraction with mineral acids, extraction with complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete

vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Technology: In situ polymer grouting. In situ solidification of radiologically contaminated soils using chemical/ polymer-based grouting.

Status: Demonstration. In situ grouting with polyacrylamide (polymer) has been used at Oak Ridge National Laboratory (ORNL) Solid Waste Storage Area (SWSA) 6 in the absence of radioactive contaminants.¹ Additional field demonstrations using polyacrylamide to ensure hydrological isolation of mixed waste materials in an inundated trench are currently proposed at the same ORNL site.² The costs for implementing this technology could be high ($> \$100/\text{m}^3$).³ The remaining development and demonstration costs could be low, principally for a selected demonstration; cost could be $< \$1\text{M}$.

Science/Technology Needs: Detailed comparative analysis of SWSA 6 and K-25 disposal site characteristics is required to determine the suitability of the grout materials as a solidifying agent for K-25 soil contamination problems. Preliminary laboratory experimentation is needed to determine whether K-25 site leachates inhibit grout composition and solidification. Long-term assessment of the ability of the grouting technology to contain migration of contamination is necessary.

Large-scale testing and demonstrations. Large-scale test data are not available. Such tests with long-term evaluation of the results are needed for K-25 soils before this approach can be considered seriously.

Implementation Needs: The needs are uncertain at this time. Cost and performance need to be compared with alternate soil treatment methods. The acceptability of removing large quantities of soil from future use would be a serious question if large portions of the K-25 Site were to be treated by this method. This may be more appropriate for the most seriously contaminated soils. Most other contaminants would also be retained by this grouting approach.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. B.P. Spadling, G.K. Jacobs, and E.C. Davis, *Demonstrations of Technology for Remediation and Closure of Oak Ridge National Laboratory Waste Disposal Sites*, ORNL/TM-11286, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
2. B.P. Spadling, *Task Plan for TARA—II Compaction and Grouting Demonstration*, ORNL/ER-25, Environmental Sciences Division Publication 3808, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1991.
3. T. Tamura and W.J. Boegly, Jr., *In Situ Grouting of Uranium Mill Tailings Piles: An Assessment*, ORNL/TM-8539, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983.

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Fixation

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, extraction with mineral acids, extraction with complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete

vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Technology: In situ vitrification of radiologically contaminated soils using resistance heating

Status: Demonstration. In situ vitrification has been demonstrated with field-scale tests at Pacific Northwest Laboratory and Oak Ridge National Laboratory.¹⁻⁵ Uranium was not a major contaminate of any field tests to date. Test areas with tanks and other severe heterogeneities have had problems. This technology currently looks promising only for relatively homogenous media without significant size metal components. Costs need to be compared with other alternatives. The costs are likely to be high ($> \$100/\text{m}^3$).⁵ Development and demonstration costs are likely to be moderate, perhaps only a few million dollars if uranium is the only contaminant of concern. If Tc or other potentially volatile components are also in the soil, the development work would have to consider off-gas treatment more seriously. The high cost of this approach and the effect on future uses of the soil will limit the use of this technology to only the most seriously contaminated soils.

Science/Technology Needs: Determination of volatilization characteristics of contaminants in K-25 soils is required along with methods to control and treat off-gases. Better evaluation of leachability and long-term stability of vitrified solids is necessary. We need to make a determination of the solid-waste compositions necessary for effective vitrification.

Large-scale testing and demonstrations. Demonstrations need to show that volatile compounds can be recycled to other portions of the vitrification operation. Demonstrations should also establish whether vitrified solids (consolidated blocks) can be coupled into continuous units within a waste disposal trench. Further testing should establish if boundaries at the vitrified product and soil face are leachable and/or contain contaminants.

Implementation Needs: Field tests need to include identification of suitable sites, effective off-gas treatment facilities, and effective postvitrification characterization equipment.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. J.L. Buelt and T.G. Carter, *In Situ Vitrification Large-Scale Operational Acceptance Test Analysis*, PNL-5828, Pacific Northwest Laboratory, Richland, Washington, 1986a.
2. J.L. Buelt and T.G. Carter, *Description and Capabilities of the Large-Scale In Situ Vitrification Process, Test Analysis*, PNL-5738, Pacific Northwest Laboratory, Richland, Washington, 1986b.
3. B.P. Spalding and G.K. Jacobs, *Evaluation of an In Situ Vitrification Field Demonstration of a Simulated Radioactive Waste Disposal Trench*, ORNL/TM-10992, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
4. B.P. Spalding and G.K. Jacobs, *Demonstration of Technology for Remediation and Closure of Oak Ridge National Laboratory Waste Disposal Sites*, ORNL/TM-11286, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.

5. L.L. Cole and D.E. Fields, *In Situ Vitrification: A Review*, ORNL/TM-11293, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
6. C.L. Timmerman, J.E. Hansen, "Planned Applications of *In Situ* Vitrification Technology to Contaminated Soil Site Remediation," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Ga., September 21-23, 1992, Vol. I*, D. William Tedder, ed., American Chemical Society, Washington, D.C. 1992, pp. 181-184.

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Uranium in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Total concentration. Radiation detectors with detection limits in situ and with detection limits in laboratory, ICP with detection limits in laboratory, and XRF with detection limits in laboratory
- Enrichment. Mass spectrometry with detection limits in laboratory, neutron activation with detection limits in situ
- Oxidation state. Spectrometry with detection limits and problems, electrochemical measurements of surrounding media
- Compound. X-ray diffraction
- Adsorbed or in solution. Chromatographic methods
- pH and buffer conditions. pH in surrounding solutions
- Redox condition. Electrochemical potentials
- Heterogeneity of contamination. Sample size/procedures, radiophoto imaging
- Transport in environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Mechanical excavation, pneumatic excavation, electrokinetic removal

Alternative: Fixation

Treatment techniques. Physical separation: screening, classification, flotation, gravity concentration, sedimentation, filtration, combinations of physical separation techniques; soil washing: surfactants, chelates, acid or alkaline solutions, combinations of soil washing reagents; chemical extraction/leaching methods: extraction with water, extraction with inorganic salts, mineral acids, complexing agents; in situ stabilization/solidification: cement-based grouting, chemical/polymer-based grouting, bitumen (asphalt)-based grouting; vitrification: in situ, ex situ; and electrokinetic treatment: in situ, ex situ.

Deposition. Recovery/reuse: precipitation and coprecipitation, solvent extraction, ion exchange membrane filtration; packaging: drums, cylinders; storage/disposal (on-site or off-site). Aboveground covered and uncovered containment pads, aboveground concrete

vaults, underground concrete vaults, underground mine repository, underground deep well injection.

Technology: Ex situ vitrification of radiologically contaminated soils using resistance heating

Status: Conceptual. Ex situ vitrification has been successfully applied to high-level wastes (spent fuel and process wastes) in large-scale units for several years.^{1,2} However, applications for low-level contamination in soils have been addressed recently.³ Because of the high costs associated with ex situ vitrification systems, this technology may prove unjustifiably expensive for K-25 soil contamination problems. Costs are likely to be very high ($> \$100/\text{m}^3$). This approach is expected to be considered only for the most serious contamination problems. Cost data are not available for ex situ applications on low-level wastes in the cited references. Development and demonstration costs are likely to be a few million dollars.

Science/Technology Needs: Determinations of process modifications necessary to accommodate K-25 soil contaminants are needed. A comparative analysis of ex situ vs in situ vitrification technologies would be needed to assess the appropriate applications at the K-25 Site. A significant issue is the relative cost of installing and operating systems capable of meeting specific stabilization criteria. Off-gas treatment and the safety and cost of handling the materials captured by the off-gas treatment need to be assessed; the vitrified solids are not the only waste produced.

Large-scale testing and demonstrations. Large-scale testing is needed only if less costly alternatives begin to look unattractive.

Implementation Needs: Immediate needs are limited to cost/performance comparisons. Costs are likely to be very high³ ($\$400\text{--}600/\text{ton}$). This approach is expected to be considered only for the most serious contamination problems. Cost estimates do not include handling of residual wastes.

Authors: G. Macklin, W. Harwood, J. Watson

References:

1. L.L. Cole and D.E. Fields, *Radioactive Waste Vitrification: A Review*, ORNL/TM-11292, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
2. L.L. Cole and D.E. Fields, *In Situ Vitrification: A Review*, ORNL/TM-11293, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
3. U.S. Environmental Protection Agency. *Babcock and Wilcox Cyclone Furnace Vitrification Technology: Application Analyses Report*. EPA/540/AR-92/017, August 1992.

EM Problem: Remedial action

K-25 Site Problem: Groundwater contamination

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Chemical absorption

Technology: Coagulation/filtration

Status: Predemonstration. Several laboratory tests and small-scale pilot plant studies have been successful in varying degrees of removal efficiency for drinking water and pond water samples.¹⁻³ Coagulant treatment efficiencies are directly affected by the initial uranium concentration in raw water source.¹ Choice of coagulant and optimal pH range remain the most significant factors in demonstrating effective uranium removal.⁴

Although the potentially large waste volumes from this technology may make this unattractive for removing uranium, it could be important because it is standard technology for removing a broad spectrum of contaminants. Costs of the water treatment alone could be low, perhaps <\$1/1000 gal. However, additional costs for handling contaminated precipitates could be large and could dominate overall costs. Development and demonstration costs (including waste handling) could be several million dollars.

Science/Technology Needs: Proper supervisor characterization of uranium species is critical to any groundwater remediation system, particularly at K-25, where mixed waste contamination poses a problem. Candidate coagulants for K-25 groundwater must be evaluated for removal efficiency and cost effectiveness using laboratory- and bench-scale tests. A series of experiments is required to determine the optimal pH value to which K-25 groundwater must be adjusted for actual uranium removal to occur and the accumulation of other contaminants in the precipitate.

Large-scale testing and demonstrations. Before any large-scale demonstrations are attempted, a definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. A significant effort must be made to plan and design a system which will meet K-25 groundwater treatment needs without risking disruption or further contamination of downstream groundwater flows. Final disposal of filtrate should be considered in demonstration plans.

Implementation Needs (Facility Needs): Such systems will appear and operate much like conventional water treatment systems and could involve moderately large equipment. The merits of such systems need to be evaluated carefully because there are uncertainties in the ability of these methods to reduce the uranium to extremely low concentrations. The volume of waste produced and the disposition of that waste must be assessed carefully. Costs are likely to be similar to those for wastewater treatment plants plus the substantial cost for contaminated sludge disposal. Cost data are not available in cited references. Operating costs will be low, but waste handling costs will probably be high. Waste volume will be large.

Author: G. Mackin, W. Harwood, J. Watson

References:

1. S.Y. Lee, and S.K. White, E.A. Bondietti, *Methods of Removing Uranium From Drinking Water: II. Present Municipal Water Treatment and Potential Removal Methods*, EPA/570/9-82/003, U.S. Environmental Protection Agency, Washington, D.C., 1982.
2. S.Y. Lee, and E.A. Bondietti, "Removing Uranium From Drinking Water by Metal Hydroxides and Anion Exchange Resin," *Journal AWWA*, **75**(10), October 1983, p. 536.
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ION EXCHANGE (REMOVAL OF URANIUM FROM GROUNDWATER)

REMA-22-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Related to the CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Chemical separation

Technology: Ion exchange

Status: Demonstrated. Ion exchange techniques for recovering uranium are well established within the mining industry.¹ Several pilot-plant and full-scale systems have been utilized for treating water supplies, consistently achieving high removal efficiencies.^{2,3} Most ion exchange systems are pH dependent and somewhat sensitive to media clogging. Both anion and cation exchange resins are commercially available. One study² suggested operating costs (in 1998) of \$6.70/1000 gal. Waste disposal costs will depend upon the rate of uranium recovered from regeneration. It may be concentrated sufficiently that recovery is practical. Development and demonstration costs could be a few million dollars to improve the current resins and processes. Workable systems probably could be established for less.

Science/Technology Needs: Laboratory- and bench-scale testing of K-25 groundwater samples must be conducted to determine the removal efficiency and cost effectiveness of the various exchange systems. A key issue is the selectivity of the resin for uranium; selectivity affects the volume of waste produced. Appropriate pH values must be determined for optimal uranium removal; major pH changes will not be practical for most groundwater applications. Tests should evaluate the rate processes involved and thus the role of column height on column performance. Pretreatment sediment filters should be considered in designing bench- and pilot-scale tests. Thorough characterization of samples should be developed for evaluating the initial and post-treatment water quality.

Large-scale testing and demonstrations. A definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. A significant effort must be made to plan and design a system which will meet K-25 groundwater treatment needs without risking disruption or further contamination of downstream groundwater flows. Ultimate disposal of regenerant solution and waste minimization must be considered when developing a regeneration regime for exchange columns.

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ION EXCHANGE (REMOVAL OF URANIUM FROM GROUNDWATER)

REMA-22-OG

Implementation Needs (Facility Needs): Ion exchange requires only modest size facilities, depending upon the size and composition of the water stream to be processed. Regeneration reagents and uranium recovery (or concentration) may add to the equipment requirements.

Author: G. Mackin, W. Harwood, J. Watson

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2. R.T. Jelinek and T.J. Sorg, "Operating a Small Full-Scale Ion Exchange System for Uranium Removal," *Journal AWWA*, 80(7), July 1988, p. 79.
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February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Groundwater contamination

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Chemical analyses. ICP (laboratory) detection limits, concentration and analysis
- Enrichment. Mass spectrometry [see U in soils]
- Oxidation state. Spectrometry, electrochemical, chromatography
- pH of groundwater. Glass electrode pH meters
- Soluble or adsorbed. Ultrafiltration
- Transport in the environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Drilling methods. Well construction, well configuration, groundwater control

Alternatives: Chemical separation

Technology: Biosorption

Status: Predemonstration. The literature offers a fair list of laboratory-scale tests using biomass and spiked contaminant concentrations for uranium adsorption capacities. Several species of microbes exhibit particularly high adsorptive capabilities and warrant additional experimentation.¹⁻³ Temperature, pH, cell preparation, culture age, and uranium concentration/cell mass ratio have been identified as factors that influence biosorptive uptake. Pilot-scale biosorption reactor designs have been developed for treating mill process wastewaters, though their use is currently not well documented.^{4,5}

Science/Technology Needs: Laboratory- and bench-scale tests must be conducted using K-25 groundwater samples. These tests should include only those species with the highest adsorptive capabilities. A range of pHs, temperatures, dissolved solids, and uranium concentrations that represent conditions occurring in K-25 groundwater should be explored. Further development of biosorption substrate (gelatinous beads or resins) should be encouraged to improve the possibilities of large-scale demonstrations and, ultimately, commercial availability of this technology. Costs could be low (< a few dollars/1000 gal) if regeneration or other methods for reducing waste volume are effective and inexpensive. If the

sorbents are not regenerated, the waste volume would be inversely proportional to the maximum loading that can be achieved on the sorbent. Development and demonstration cost should be a few million dollars, perhaps \$1M to \$3M.

Large-scale testing and demonstrations. A definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. A significant effort must be made to plan and design a system that will meet K-25 groundwater treatment needs without risking disruption or further contamination of downstream groundwater flows. Further analysis of existing systems and continued development of pilot plant units are necessary. Search and/or development of a full-scale biomass source should be implemented. Destruction and final disposal of spent biomass should be considered in designing and implementing a large-scale system.

Implementation Needs: Equipment and facility needs are modest. The reliability of many bioprocesses have been questioned, but because living organisms may not be required for biosorption, instabilities from organism "die off" should not be a serious issue. Costs are expected to be low (less than a few dollars per 1000 gal), but treatment of "loaded" biosorbent must be established before meaningful cost estimates can be made.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Groundwater contamination

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Chemical analyses. ICP (laboratory) detection limits, concentration and analysis
- Enrichment. Mass spectrometry [see U in soils]
- Oxidation state. Spectrometry, electrochemical, chromatography
- pH of groundwater. Glass electrode pH meters
- Soluble or adsorbed. Ultrafiltration
- Transport in the environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Drilling methods. Well construction, well configuration, groundwater control

Alternatives: Chemical separation

Technology: Adsorption with titanium oxide

Status: Predemonstration. Titanium has been utilized to successfully remove uranium compounds from contaminated pond water samples.¹ This method is pH dependent and is influenced by concentrations of free carbonate anions in the solution. The technology has not been optimized for use with high volumes of groundwater. It may prove to be desirable to recover the uranium and reuse the titanium dioxide to reduce waste volume. Both cost and waste volume depend upon the loading capacity of the titanium dioxide for uranium at the concentrations found in the groundwater and in the presence of all other materials dissolved in the groundwater. Costs could be \$10/1000 gal. Development and demonstration costs should not be more than a few million dollars.

Science/Technology Needs: Proper characterization of uranium species is critical to any groundwater remediation system, particularly at K-25, where mixed waste contamination poses a problem. The characterization should include determining the chemical forms of uranium and the presence of other solutes that could affect adsorption performance. Laboratory- and bench-scale tests with K-25 groundwater samples are needed to determine the effectiveness of this treatment method. Selectivity will be an important parameter.

Regeneration and waste volumes generated will also have to be evaluated. Rate information (or the effect of column height on performance) will need to be determined. Experimentation might involve carbonate removal and sediment filtration before adsorption on titanium oxide.

Large-scale testing and demonstrations. Before any large-scale demonstrations are attempted, a definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. A significant effort must be made to plan and design a system that will meet K-25 groundwater treatment needs without risking disruption or further contamination of downstream groundwater flows. Adsorption tests need to be continued to approach breakthrough to fully evaluate column performance. Final disposal of contaminated waste titanium oxide should be considered in the demonstration plans.

Implementation Needs: Adsorption units can be incorporated into relatively small field units, but regeneration equipment may become more complex. The technology is not sufficiently well developed to obtain meaningful cost estimates. Waste volume could be high, depending upon the adsorption capacity of the titanium oxide.

Author: G. Mackin, W. Harwood, J. Watson

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1. S.Y. Lee, S.K. White, and E.A. Bondietti, *Methods of Removing Uranium From Drinking Water: II. Present Municipal Water Treatment and Potential Removal Methods*, EPA/570/9-82/003, U.S. Environmental Protection Agency, Washington, D.C., 1982.

EM Problem: Remedial action

K-25 Site Problem: Groundwater contamination

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Chemical analyses. ICP (laboratory) detection limits, concentration and analysis
- Enrichment. Mass spectrometry [see U in soils]
- Oxidation state. Spectrometry, electrochemical, chromatography
- pH of groundwater. Glass electrode pH meters
- Soluble or adsorbed. Ultrafiltration
- Transport in the environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Drilling methods. Well construction, well configuration, groundwater control

Alternatives: Chemical separation

Technology: Adsorption with granular activated carbon (GAC)

Status: Predemonstration. GAC has been used to successfully remove uranium compounds from drinking water and pond water samples.^{1,2} Varying degrees of removal efficiency have been demonstrated through the research. The GAC technique is pH dependent and is influenced by concentrations of free carbonate anions in solution. This treatment method appears limited in that breakthrough uranium in effluents was experienced at concentrations greater than those reported before GAC adsorption.³ This could mean that the uranium is being displaced by another component in the groundwater. It is, thus, clear that much remains to be learned about uranium adsorption on carbon. There are too many uncertainties for meaningful cost estimates, but the cost depends on the waste volume and the capacity of the carbon for uranium from K-25 groundwater. The costs could range from a few dollars per 100 gal to \$10/1000 gal. Development and demonstration costs could be a few million dollars.

Science/Technology Needs: Proper characterization of uranium species is critical to any groundwater remediation system, particularly at K-25, where mixed waste contamination poses a problem. The characterization should include quantification of carbon properties

before experimentation. Laboratory- and bench-scale tests with K-25 groundwater samples must be attempted to determine the effectiveness of this treatment method. Experimentation might involve pretreatment to remove carbonate and other components that may hinder uranium adsorption and sediment filtration before GAC adsorption.

Large-scale testing and demonstrations: A definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. A significant effort must be made to plan and design a system that will meet K-25 groundwater treatment needs without risking disruption or further contamination of downstream groundwater flows. Maximum uranium loadings and thus the minimum waste volumes need to be determined. Final disposal of the contaminated waste GAC should be considered in the demonstration plans.

Implementation Needs: Limited efficiency appears to be the most serious problem with this technology. Equipment requirements could be modest, but waste volumes could be high if the capacity of the GAC for uranium is not high. Regeneration is not likely to be practical; oxidation of uranium may affect the GAC performance. Disposal costs for spent GAC are likely to be significant. Cost data are not available in the cited references. Capital and operating costs should be moderate, but waste handling costs could be high.

Author: G. Mackin, W. Harwood, J. Watson

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2. S.Y. Lee and E.A. Bondietti, "Removing Uranium From Drinking Water by Metal Hydroxides and Anion Exchange Resin," *Journal AWWA*, **75**(10), October 1983, p. 536.
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REVERSE OSMOSIS TO REMOVE URANIUM IN GROUNDWATER

REMA-26-OG

EM Problem: Remedial action

K-25 Site Problem: Groundwater contamination

Problem Area/Constituents: Uranium in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Chemical analyses. ICP (laboratory) detection limits, concentration and analysis
- Enrichment. Mass spectrometry [see U in soils]
- Oxidation state. Spectrometry, electrochemical, chromatography
- pH of groundwater. Glass electrode pH meters
- Soluble or adsorbed. Ultrafiltration
- Transport in the environment. Solubilities, leaching methods, chromatographic methods

Retrieval:

- Drilling methods. Well construction, well configuration, groundwater control

Alternatives: Chemical separation

Technology: Reverse osmosis

Status: Demonstration. Reverse osmosis (RO) has been successfully employed for removing uranium from drinking water and pond water samples using commercially available membrane systems within laboratory-scale experimentation.^{1,2} Pilot-plant systems have also been utilized to remove natural uranium from groundwater sources.² All of the research indicates very high removal efficiencies for the various reverse osmosis systems investigated. RO is most likely to be attractive when there are a variety of toxic contaminants dissolved in the groundwater. Because of RO can remove most dissolved materials, it will not separate contaminants from other dissolved materials. Large concentrations of nontoxic materials dissolved in the groundwater could result in more materials in the reject stream (a concentrated liquid) than from alternate processes. RO units are sold commercially, and costs for the units alone are moderate. Even with operating costs included, the total costs for osmosis alone could be moderate, perhaps a few dollars per 1000 gal. However, RO does not produce a solid product suitable for disposal, and treatment of the concentrate could add significantly to the overall costs. RO is not a selective process and usually removes essentially all dissolved matter. A lot of mineral content in the groundwater limits the amount of waste

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REVERSE OSMOSIS TO REMOVE URANIUM IN GROUNDWATER

REMA-26-OG

concentration that can be achieved without including an additional chemical separation step. The cost for demonstrating RO with K-25 groundwater should be low, perhaps less than \$1M. This cost could include some testing of different membranes. Greater costs would be required to develop chemical separation systems to remove uranium from other minerals dissolved in the concentrate.

Science/Technology Needs: Laboratory- and bench-scale testing of various commercially available membrane systems must be attempted with K-25 groundwater samples to assess the viable systems. In evaluating each membrane system, cost and removal efficiencies should be considered along with life expectancy and the throughput volume capacity of the membrane. The effects of other solutes (toxic and nontoxic) must be considered. Further separation of the uranium and other toxic materials from the concentrate may be required to minimize the waste volume. Studies of such separations may be needed.

Large-scale testing and demonstrations. A definitive set of treatment criteria and water quality objectives must be established upon which to evaluate test results. Relationships between uranium removal efficiency and the concentration of the reject stream must be established. Effects of cross flow and other methods for reducing concentration polarization need to be evaluated. Effects of membrane fouling and membrane lifetime will need to be established. Final disposal of concentrated contaminants, cleaning solutions, and membrane apparatus must be considered in the demonstration plans.

Implementation Needs: RO can be carried out using relatively compact field equipment. Recovery (concentration) of the uranium from the reject stream may require more complex facilities, but the reject stream should be relatively small. The cost for RO is likely to be moderate (a few dollars per 1000 gal), but RO only produces a concentrated solution that will require further treatment. The waste volume will depend upon the total dissolved material removed by RO. Waste volume depends upon treatment of uranium concentrate.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Soils, buried waste

Problem Area/Constituent: Chlorinated volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Field analyses, laboratory analyses, sampling

Retrieval:

- Pumping, drilling

Alternatives: Physical separation

Technology: Vacuum extraction techniques (soil venting). Remediation of soil contaminated with VOCs using vacuum extracting techniques.

Status: Demonstration. Vacuum extraction technologies have been used for removing VOCs from contaminated Superfund sites under a variety of conditions.¹⁻⁴ The technique is applicable to VOC contamination above the water table. Full-scale demonstrations of in situ vacuum extraction, also known as soil venting, have been performed at spill sites containing jet fuel.⁵ This approach works by applying a vacuum at extraction wells within the contaminated soil profile. Generally, the contaminant must be above the water table. The negative pressure produced by the vacuum helps to volatilize the VOCs and move them out of the soil pores and into the extraction wells for recovery. The vented gas containing VOCs is usually treated (carbon filtered or incinerated) to destroy toxins. However, new membrane separation techniques can be applied to capture and concentrate the volatiles for reuse. Operating costs depend upon the permeability of the soil, the volatility of the contaminant, and the interactions between the soil and the contaminant. Costs are usually low for high permeability soils, usually less than \$100/ton, perhaps much less. Few development expenses are needed for highly permeable soils, where vacuum is usually applied. Waste volumes are limited to the condensed product or carbon beds used to remove the VOC contaminants from the off-gas.

Science/Technology Needs: Characterization of soil conditions and contaminants is needed to determine if vapor extraction would be applicable at K-25. Mixed waste contamination could be a problem that might limit applications of this technology or require specialized procedures and equipment modifications to achieve adequate treatment objectives. In situ

approaches such as vacuum extraction do not remove soil and avoid important questions about the disposition of treated soils.

Large-scale testing and demonstrations. Any large- or full-scale tests of soil vapor extraction at K-25 can be patterned around existing designs and should clearly demonstrate target treatment objectives. Such tests may be part of an integrated demonstration whereby remediation alternatives are applied. This approach should allow for a comparative evaluation of two or more soil treatment technologies. The porosity of the soil and the location of the contamination.

Implementation Needs: The required treatment level needs to be established for each contaminated site. A significant amount of information is available to support further development of vacuum extraction technologies. Process applications and equipment systems are also readily available to facilitate additional experimentation/implementation of this method of treating VOCs in soil. The major uncertainties are in the soil itself. The costs can be low (<\$100/ton). This technology is usually not considered for materials that are difficult to vaporize.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Soils, buried waste

Problem Area/Constituent: Volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Sampling, field analyses, laboratory analyses

Retrieval:

- Drilling, injection wells, extraction wells

Alternatives: Physical separation

Technology: In situ steam extraction. Remediation of soil contaminated with VOCs using steam extraction.

Status: Demonstrated/accepted. In situ steam extraction removes volatile and semivolatile hazardous contaminants from soil and groundwater without excavation of the hazardous waste. The use of steam enhances the stripping of volatile contaminants from soil and can be used to displace contaminated groundwater under some conditions. Generally, the contaminant must be above the water table, but the process may be used below the water table. Waste constituents are removed but not actually destroyed using this approach. Steam extraction displaces the VOCs from the soil/gas matrix and captures them in extraction wells. The contaminated emissions can be treated before disposal.¹ A limited number of commercial in situ steam extraction systems are in operation.¹ Soil vapor extraction using steam has been considered to treat one Superfund site in the San Fernando Valley (Area 1), Burbank, California. Steam stripping has been used by petroleum industries for more than 30 years to recover hydrocarbons from coal beds, tar sands, and asphalt deposits.² It has been used in the environmental field to recover VOCs ex situ from aqueous streams and in situ for treating soils contaminated with VOCs.³⁻⁵ The Annex Terminal, San Pedro, California, site demonstration was successful in removing 85% of VOCs and 55% of SVOCs.⁶ At present, applications of this technology are limited to sites with less than 1% grade. Costs for steam extraction generally run a little higher than costs for the similar process, vacuum extraction, principally because of the energy required to produce the steam. The steam injection, however, can raise the extraction rate and lower the costs for the less volatile VOCs because shorter operating times are required. Costs between \$50 and \$150/ton have been reported.

As an accepted technology, no development costs are required, but better methods for assessing soil properties would be helpful.

Science/Technology Needs: If steam extraction systems can be adapted to sites with greater slopes, this technology may prove useful to remediating K-25 sites. Laboratory- and bench-scale tests should be conducted using actual K-25 Site soils to determine VOC removal rates. Experimentation with mixed waste contaminated soils should be conducted to determine if the extracted emissions can be adequately handled with current technologies and regulations. Better methods for assessing soil properties and underground structures would help assess the performance and limitations of this method. The water content of the contaminated vadose zone can be an important parameter.

Large-scale testing and demonstrations. Many waste area groups at K-25 can be quickly eliminated from consideration if steam extraction remains viable for only those sites with $\leq 1\%$ slope. Any demonstration of this technology must include a fairly complex emissions treatment system to handle the heat load as well as concentrate the contaminant.

Implementation Needs: Currently, steam extraction equipment requires a water supply of at least 8–10 gpm at 30 psig and diesel generators for electrical power. Demonstration sites must be capable of supporting a steam injection rig, and adjacent areas must have space for support equipment and trailers. The costs can be moderate (approximately \$50 per ton) or high ($> \$100/\text{ton}$).¹ Waste volume will be low if the off-gas treatment system can separate the contaminant from the condensed water and either discharge the water or recycle it to steam.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Soils, buried waste

Problem Area/Constituent: Volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Characterization:

- Field analyses, laboratory analyses

Retrieval:

- Drilling, wells

Alternatives: Physical separation

Technology: Vapor extraction with radio frequency heating. Remediation of soils contaminated with VOCs using radio frequency enhanced soil vapor extraction.

Status: Predemonstration. The extraction of VOCs from soil can be improved with the use of radio waves to heat the soil in situ. This is an enhancement to vapor extraction. Using a grid of drilled holes into which radio transmitters are placed, soil can be heated using radio waves in the same frequencies as those approved for hospitals. The VOCs, which volatilize as a result of the warmer soil, can then be collected and treated or recycled. A pilot test was performed at Volk Field ANGB, Camp Douglas, Wisconsin^{1,2}. This test was effective in removing VOCs and some SVOCs. Hardware for this method already exists commercially. There are limitations to radio frequency heating in high-clay soils because the waves do not penetrate deeply into the soil. This means the radio frequency heat is difficult to apply to deep formations (deeper than 1-2 meters) without using "down hole" transmitters. Even then, the heating will not occur far from the transmitting hole. Costs at this time are only conjectural, but they could be low (<\$100/ton). Development and demonstration costs could be several million dollars. Wastes will result principally from the off-gas treatment system and could consist of spent carbon beds.

Science/Technology Needs: Substantially more testing is required, particularly with K-25 sites. Currently, only one research team appears to be working on this approach. Characterization of the soils at K-25 must determine the needed frequency for optimum recovery. The testing needs to include recovery of the toxic materials from the off-gas. Vapor flow paths in complex soils like those at K-25 can be difficult to predict or even measure.

Large-scale testing and demonstrations. Additional large-scale testing and demonstrations are needed to substantiate the results of the Volk Field pilot study. It is likely that this technology can be assimilated into other in situ soil treatment technologies, especially where radiation and/or worker exposure are acute problems.

Implementation Needs: Acceptable treatment levels are needed. The soil and underground structure should be determined to be suitable for release and transport of volatile contaminants from the soil. Extensive testing of existing hardware in this application needs to be demonstrated. Low costs have been reported (\$45 per ton), but the costs probably depend upon the degree of organic contamination, the moisture content, and the off-gas cleanup required.

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2. H. Dev, et al., *Radio Frequency Enhanced Decontamination of Soils Contaminated with Halogenated Hydrocarbons*, Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, EPA/600/2-89/008, February 1989.

EM Problem: Remedial action

K-25 Site Problem: Soils, buried waste

Problem Area/Constituent: Volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Treatment

Characterization:

- Field analyses, laboratory analyses

Retrieval:

- Not applicable

Alternatives: Physical separation

Technology: Ground freezing or soil cooling. Removal of soils contaminated with chlorinated VOCs using ground freezing or soil cooling.

Status: Conceptual. This technology involves freezing soils contaminated with VOCs at uncontrolled hazardous waste sites. In theory, freezing helps immobilize VOCs and other hazardous wastes until the contamination can be removed.^{1,2} This is a temporary treatment approach that does nothing to remediate soil contamination. The literature search did not yield documentation of actual ground freezing tests with respect to VOCs.² Currently, this method can only be considered interim and very short-term in application. The costs include installation of cooling coils, freezing the soil, and maintaining the cooling required to keep the soil frozen. Although no costs are given for freezing, the costs are believed to be high (perhaps >\$100/ton). Since freezing does not remediate the site, additional expenses can be expected when the site is finally remediated.

Science/Technology Needs: More experimentation is needed at all levels to substantiate ground freezing as a viable interim treatment for VOC contamination in soils. Actual immobilization of VOCs must be quantified using naturally occurring and synthetic soils. Impacts on soil properties should also be evaluated to determine if soil conditions after freezing remain conducive to future remediation efforts or long-term site use.

Large-scale testing and demonstrations. No large-scale tests nor demonstrations have been performed dealing specifically with VOCs. Large-scale demonstrations are probably not practical unless site-specific conditions require an interim treatment for an uncontrolled contamination source. A treatment system for final treatment will be needed.

Implementation Needs: Because freezing is only a temporary treatment to prevent the spread of contamination, a suitable "final" treatment method for the site should be identified, and development efforts for the treatment method should be initiated. Equipment and materials for ground freezing currently exist, but use of the equipment has not been demonstrated. Costs will probably be high (>\$100 per ton), perhaps very high.³ The cost will obviously depend upon the time the soil must be maintained frozen, but heat losses from deep frozen soil regions may be relatively low. No obvious wastes are created by the freezing operation, but subsequent final treatment could generate wastes. Waste volume is not meaningful this technology doesn't actually treat the soil.

Author: G. Mackin, W. Harwood, J. Watson

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2. U.S. Environmental Protection Agency, *Handbook On In Situ Treatment of Hazardous Waste—Contaminated Soils*, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, EPA/540/2-90/001, January 1990.
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EM Problem: Soils contamination

K-25 Site Problem: Contaminated soils, buried waste

Problem Area/Constituent: Volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Destruction

Technology: In situ bioremediation for removal of VOCs

Status: Predemonstration. Bioremediation of contaminated soil has been attempted under variable conditions with several volatile compounds.¹⁻⁶ The activity of naturally occurring microorganisms is greatly affected by soil conditions such as moisture content, pH, redox potential, temperature, oxygen content, porosity, and most importantly, availability of nutrients. These soil properties can be manipulated to achieve optimal conditions for microbial activity, driving the breakdown of VOC contaminants. At this time, bioremediation enhanced by manipulation of local conditions of soil contaminated with VOCs appears very cost effective. Laboratory-, bench-, and pilot-scale testing is being done on various properties, but no testing is being performed on all parameters at the same time. In situ remediation of highly chlorinated compounds like the TCE found in K-25 soils are not so easily degraded and in situ remediation of soils with these contaminants must be considered only in the laboratory stage. Because of the high volatility of these compounds, it is not always easy to be sure that all (or any) decrease in VOC concentrations are due to biodegradation rather than vaporization. Costs for remediating soils contaminated with highly chlorinated compounds is only conjectural since processes are not developed. However, in situ bioremediation for other less refractive compounds can be relatively inexpensive, perhaps much less than \$100 per ton. Development and demonstration costs could be as little as a few million dollars, perhaps <\$5M. Biodegradation of highly chlorinated compounds is usually slow and difficult.

Science/Technology Needs: Identification of and experimentation with naturally occurring microbes is needed for K-25 soils. Soil characteristics should be explored to determine optimal conditions for degrading VOCs in local microbiological populations. Field-scale tests should be considered if laboratory results indicate significant VOC reduction with this approach. Control and test plots at K-25 sites should be designed so that adequate comparative analysis can be done to establish VOC decay rates. Particular care should be devoted to the more difficult highly chlorinated compounds like TCE.

Large-scale testing and demonstrations. Large-scale tests and demonstrations should be part of an integrated approach that combines two or more treatment technologies that will accommodate the mixed waste problems that are likely to exist at K-25.

Implementation Needs: The acceptable treatment level needs to be established. Then the capabilities of in situ bioremediation for chlorinated contaminants at K-25 must be assessed and demonstrated. Bioremediation usually requires relatively few facilities and low costs. However, it does require time and suitable procedures to verify that the treatment was successful. Costs are generally lower than ex situ methods but vary considerably. Waste volumes should be low.

Author: G. Mackin, W. Harwood, J. Watson

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2. L.E. Sommers, et al., "The Effect of Water Potential On Decomposition Processes in Soils," *Water Potential Relations in Soil Microbiology*, SSA Special Pub. No.9, Soil Sci. Soc. of America. Madison, Wisconsin, 1981.
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EM Problem: Remedial action

K-25 Site Problem: Soils contamination

Problem Area/Constituent: Volatile organic compounds (VOCs) in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Destruction

Technology: Ex situ bioremediation

Status: Demonstrated. This technology has been demonstrated for many compounds; less success has been shown with the compounds most common at K-25. Excavated soils can be biologically treated using naturally occurring or genetically engineered bacteria to remove contaminants, including VOCs, SVOCs, and PAHs. Currently, there appear to be three variations of the ex situ process are apparent: slurry-phase, contained solid phase, and land treatment. Of the three methods, slurry-phase seems the most effective.¹ Demonstration of slurry-phase has been carried out by BioTrol as a pilot study for the U.S. Environmental Protection Agency (EPA).^{2,3} An EPA Site Demonstration for BioTrol was set for the fall of 1991. No literature was found on the results. Besides using microbes that already exist at the contaminated site, one can introduce and adapt organisms normally found elsewhere to degrade the contaminant.^{3,4}

Another approach involves genetically engineering bacteria that thrive in contaminated soils and adapting these populations to degrade VOCs. This approach is a recombinant DNA approach that involves gene manipulation. Microbial inoculants are now commercially available that can degrade a variety of compounds, some of which can degrade chlorinated compounds.⁵⁻⁷ At this time, 34 bacterial and 5 fungal organisms have been identified which degrade PCBs.⁸ A white rot fungus has been discovered that degrades halogenated compounds.⁹ This technology has been demonstrated in the laboratory and used in several full-scale decontamination operations.^{1,2} Augmentation of biological systems with exogenous microbes may be most effective against one compound or a closely related class of compounds. Combining microbes may actually speed up degradation.⁶

Costs for bioremediation are likely to be moderate; one estimate suggested a cost of \$165/ton. The waste produced will be minimal if the treated soil can be returned to the ground. However, as with any ex situ treatment, if the treated soil is not permitted to be returned, the waste volume will be large. Development and demonstration costs are uncertain

because both the probability of success and the difficulties to be encountered are more uncertain than for most technologies. These costs could be a few million dollars.

Science/Technology Needs: Further detailed testing is necessary to show the effectiveness of this technique on VOCs and other contaminants in K-25 soils. Because ex situ bioremediation involves soil extraction, this technology may lend itself as an ancillary treatment to other technologies such as physical separation and soil washing (see Uranium in Soils). Ex situ techniques should be thoroughly evaluated for process flexibility and cost effectiveness when other, possibly less expensive, in situ applications are available. Particular attention should be given to improving the reliability of the treatment. This usually requires an understanding of the parameters that affect biodegradation. Great care must also be given to handling the soils to prevent uncontrolled evaporation that could be confused with bioremediation. Treatment methods that handle the soil in "open" bioreactors probably will not be acceptable at K-25 because the chlorinated volatile compounds most likely to be found at K-25 generally cannot be released to the atmosphere.

Large-scale testing and demonstrations. Testing on K-25 soils would be necessary to establish this approach as a viable full-term soil remediation method. Again, ex situ bioremediation may prove to be an effective treatment method when applied in conjunction with extractive technologies. This point should be fully considered when developing large-scale demonstrations. Attention should focus on the more refractive compounds such as those that are highly chlorinated.

Implementation Needs: Suitable treatment levels must be established. Depending on the advancement of this technology, K-25 will need a large water source and adequate sites for equipment and/or mobile equipment. Further development and demonstration will be needed. Moderate costs may be achieved, but costs up to \$165 per ton have been estimated.² Waste volume should be small.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Chlorinated volatile organic compounds (VOCs)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Destruction

Technology: Microbial degradation with methane. Microbial removal of halogenated hydrocarbons in methane enriched soils.

Status: Predemonstration. Halogenated hydrocarbons threaten the sources of potable drinking water. To study microorganisms that may remove these compounds, soil was exposed to 4% methane atmosphere. The enriched soil was then tested to determine the extent of removal of hydrocarbons by the microorganisms.

Soil samples were taken near the Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma. The soil samples were divided among six tubes, four were in the presence of the methane atmosphere and two were control samples. The samples were allowed to incubate for 6 weeks in the dark at 22°C. Approximately every 10 days, the four experimental vials required methane replenishment. At the end of the test period, the vials were sampled and the methane-enriched vials had a higher success rate of removal. Tetrachloroethylene was the only compound in the group tested that was not removed. It was determined that methane was not required for the removal of some compounds but was required for total removal of others. This process could be a viable remediation process in situ and ex situ. This technology may prove to be useful for in situ operations as well as ex situ operations. Waste volumes should be minimal if the soil can be returned to the ground. However, if the potential for residual radioactivity or toxic metals prevents return of the soil to the ground, the waste volume would be large. Costs could be low to moderate, perhaps <\$100/ton. Development and demonstration costs could be several million dollars.

Science/Technology Needs: The capabilities of this technology need to be confirmed. Tests are needed for a variety of soils and conditions. The development efforts need to show that high removal efficiencies can be achieved. Tests of all technologies with volatile contaminants are difficult because vaporization can be confused with degradation. This technology is interesting, but more development work appears to be needed before large-scale tests are made. K-25 soil composition will need testing to find the correct operating parameters. This technology needs further testing and verification.

Large-scale testing and demonstrations. Large-Scale testing must be conducted to obtain more information concerning this process. The technology is not tested sufficiently for large-scale demonstration.

Implementation Needs (Facility Needs): Treatment levels need to be established. High removal efficiencies must be demonstrated. This technology is not understood well enough to estimate costs, but they have the potential for being moderate or even low. Waste volume could be low to minimal.

Author: G. Mackin, W. Harwood, J. Watson

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1. J.M. Henson et al., "Microbial removal of halogenated methanes, ethanes, and ethylenes in an aerobic soil exposed to methane," *FEMS Microbiology Ecology*, **53**, 1988, pp. 193-201

EM Problem: Remedial action

K-25 Site Problem: Soil contamination

Problem Area/Constituents: Chlorinated VOCs in soils

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Destruction

Technology: Corona discharge/high-energy destruction

Status: Evolving/conceptual technology. This is one of several high-energy techniques for introducing radicals and ions into soils, water, or air which will destroy toxic organic compounds. Corona discharge has developed a significant following and is being developed in the DOE programs.¹ The technology is believed to produce ions and radicals that can penetrate the more open arid soils and reach organic contaminants such as the chlorinated VOCs. However, the mechanism for destruction of organic compounds does not appear to be understood. This leaves important uncertainties in the range of soil and contaminant conditions for which the technology is likely to be effective. For the tight clays at K-25 which contain considerable natural organic matter and have very low conductances to some region, this technology appears to be rather speculative at this time. Although other reactive approaches such as those using oxidants and reductants may involve some of the same degradation reactions, they are viewed as better understood at this time and thus sometimes less speculative.

Here, the technology is described as an in situ process working through the soil. This may be practical for arid sites, but the high moisture content and high electrical conductivity of soils at K-25 may make this approach less attractive. However, the same general approach can be applied to destruction of VOCs after they are vaporized via vacuum extraction or other method. This use of the technology could be applied at any site, but for such uses, the technology would have to compete with more other options such as condensation with backup carbon beds which can produce a more concentrated stream for subsequent use or destruction.

With the limited information available at this time, the cost of Corona discharge treatment of soils can only be speculative. Future work with the VOCs in Arid Soils Integrated Demonstration may bring this technology forward and raise its evaluation. Until the technology is better understood, it will be viewed as speculative. The cost of corona discharge and other high electrical potential approaches will depend upon the time required for

treatment. Corona discharge requires relatively low rates of energy input, but some other high energy approaches may require significantly more energy. The problem with cost is likely to be with the time required for adequate treatment and the reliability of the treatment, at least for in situ approaches. (For ex situ approaches treating groundwater or vapor from vacuum extraction, the reliability should be much better.) One could guess that the costs for in situ treatment would be moderate (perhaps a one hundred to a few hundred dollars per ton). The waste production should be minimal. The cost for fully evaluating and demonstrating these approaches is likely to be several million dollars.

Science/Technology Needs: The major need for this technology (or group of technologies) is to develop an understanding of the mechanisms of degradation. This is necessary to provide confidence in the range of pollutants and conditions for which the technology can be applied. Tests to be considered for evaluating its applications to the K-25 Site include verification of the degradation by observing degradation products (possibly with radiotracer compounds), identification of reactive groups and parameters that affect the lifetime of the groups in K-25-type soils, and the transport of these reactive groups into the soils. Great care must be devoted to the common problem with studies of VOC degradation, correcting the results for losses of VOCs to evaporation.

Implementation Needs: There are no known unusual implementation problems. The required treatment level needs to be established. The presence of residual partially degraded compounds needed to be checked. The effects of the treatment on mobilization of toxic and radioactive metals needs to be evaluated.

Author: Watson

References:

1. R.J. Lenhard, M.A. Gerber, and J.E. Amonette, "Preliminary Evaluation of Selected In Situ Remediation Technologies for Volatile Organic Compounds in Arid Sites," PNL-8333, Pacific Northwest Laboratory, 1992.

EM Problem: Remedial action

K-25 Problem: Groundwater contamination

Problem Area/Constituents: Volatile organic compounds (VOCs) in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Physical separation

Technology: In situ air stripping

Status: Accepted. Air stripping technologies are proven treatment techniques for VOC removal and are used extensively in pilot- and large-scale groundwater remediation systems.¹⁻³ Air stripping is considered by EPA to be a best available technology.^{4,5} Several variations of air stripping currently exist including bubble columns, cooling towers, packed columns, and spray columns. In situ and ex situ demonstrations using a number of aeration and emissions capture configurations are well documented in the literature.^{2,6-8} Air stripping essentially converts the VOC contamination from a liquid to a gaseous phase. Air stripping techniques generally require ancillary treatment of contaminated emissions.

Costs for air stripping are usually low, perhaps even less than \$1/1000 gal. Off-gas treatment is a significant issue and could be a significant portion of the costs. Waste volumes can be low, depending upon the off-gas treatment system. Carbon beds used in off-gas polishing may be the principal wastes.

Air stripping can also be carried out in situ, but care must be taken to contact all of the contaminated water with air and to recover all of the air in collection wells.

Science/Technology Needs: Laboratory- and bench-scale experimentation is necessary to establish operational parameters for treating K-25 groundwater contaminated with VOCs. Scaling up to a pilot plant unit can be done relatively easily by using existing designs. Thorough characterization of VOCs is imperative for designing a suitable air stripping unit. Pretreatment processes should be explored to improve VOC removal efficiencies and to prevent fouling of air stripping equipment.

Any K-25 groundwater air stripping demonstration should have a well-defined sampling/monitoring regime, flexible process controls for variable groundwater conditions and specific treatment objectives for finished effluent quality. Adequate emission controls

must be designed into a K-25 air stripping demonstration with consideration for proper disposal of any contaminated residuals that may be generated.

Implementation Needs: Commercial equipment and private firms are available for stripping most VOCs. The VOCs are usually recovered on granular activated carbon (GAC). Suitable treatment and/or disposal of the spent GAC is needed. Costs for air stripping depend upon the type of column used and the presence of materials in the water that can be corrosive, precipitate, or otherwise plug the column. These costs are usually low. Treatment of the off-gas can be the major cost.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Chemical separation

Technology: Adsorption on activated carbon. Removal of volatile organic compounds (VOCs) from groundwater using granular activated carbon (GAC) as an absorbent.

Status: Accepted. Several pilot- and small-scale systems have been tested upon surface and groundwater sources contaminated with trihalomethanes using various treatment configurations which include coagulation, aeration, and/or chemical oxidation in conjunction with GAC.¹ At least two large-scale operations have been attempted, Rockaway Township, New Jersey^{2,3} and Wurtsmith AFB, Oscoda, Michigan,⁴ both systems were designed to remove high concentrations of TCE. Concentration and molecular weight of organic contaminants as well as pretreatment stages and contact in reaction beds are probably the most influential factors in removing VOCs with GAC.⁵ Costs for acquisition of GAC and disposal or regeneration of spent carbon remains a significant factor and may prove prohibitive in operating large-scale systems. The effectiveness of carbon adsorption is established, but the costs can be high if the concentration of adsorbed materials is high. This requires that the beds be regenerated or replaced often. Capital costs should be low or moderate. Operating costs depend upon the waste generation rate, that is, on the regeneration or replacement for the beds. The costs for diluted streams could be as low as a few dollars per 1000 gal. Costs for more concentrated streams could be higher.

Science/Technology Needs: Laboratory-, bench-, and pilot-scale tests and treatability studies need to be conducted with K-25 groundwater samples to establish design parameters. The principal question will involve interference from other materials in the local groundwater. Pretreatment configurations should be evaluated to support these tests if GAC alone is not able to meet specific VOC removal objectives. Comparative analysis of cost and VOC removal efficiency should be considered for GAC and other potential K-25 groundwater remediation technologies.

Large-scale testing and demonstrations. If GAC technology proves feasible in large-scale tests at K-25, several issues must be addressed, including disposal or regeneration of spent

carbon, long-term operations/maintenance plans and accurate cost accounting for project duration.

Implementation Needs: Once the particular contaminants and their concentrations are identified, suitable GAC columns can be designed. Costs for treatment depend greatly on the regeneration/disposal of the spent carbon. Costs depend upon the volume of VOCs and other adsorbed materials in the water. Non-volatile organic compounds that are not easily desorbed and highly toxic compounds such as PCBs can increase regeneration/disposal costs. The presence of these materials and their accumulation on the beds could prevent off-site regeneration by vendors. Costs probably can be moderate (\$1 to \$10/100 gal) if regeneration and reuse of the carbon is not difficult. Disposing of the carbon without regeneration could result in a mixed waste of uranium and/or Tc accumulates on the carbon.

Author: G. Mackin, W. Harwood, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Sampling, characterization

Alternatives: Air stripping, biodegradation, adsorption, chemical dechlorination

Technology: Ultraviolet-enhanced chemical oxidation. Removal of volatile organic compounds (VOCs) from groundwater using advanced oxidation processes (AOPs) with ultraviolet radiation.

Status: Demonstration/accepted. Advanced oxidation using a combination of ozone, hydrogen peroxide, and ultraviolet radiation has been successfully demonstrated in a full-scale plant at the U.S. DOE Kansas City Plant^{1,2} for treating groundwater contaminated with TCE and other chlorinated VOCs. The efficiency of VOC destruction using this approach appears to be affected by initial VOC concentration, demand upon oxidizing agents (O_3 and H_2O_2) by other inorganic contaminants and residence time of contaminated groundwater within the reaction chambers.^{3,4} AOPs appear to be potential alternatives to other available technologies for remediating groundwater contaminated with VOCs because they destroy VOCs in the liquid phase and eliminate the need for disposing of waste adsorbents. This technology is essentially accepted, and commercial firms offer units for oxidizing many compounds. Costs are reported to be low, less than \$1.00 per 1000 gal, but this cost could increase with higher concentrations of organic compounds and/or quenching agents which destroy hydroxyl radicals (like carbonate ions). Waste volume should be minimal.

Science/Technology Needs: Laboratory-, bench-, and pilot-scale tests (treatability studies and small-scale demonstrations) should be attempted using AOP configuration(s) that will remediate K-25 groundwater samples. A pretreatment system for removing dissolved inorganics should be implemented along with the AOP to avoid sedimentation and/or scaling within the reaction chambers. From this level of tests, an operational model should be developed for evaluating large- and full-scale systems.

Large-scale testing and demonstrations. Large-scale testing of an AOP system will probably require some surveying/characterization of K-25 groundwater conditions, particularly in establishing a suitable site or plume for the demonstration. The total concentration of organic compounds and the presence of significant concentrations of materials such as carbonate

ions which quench the hydroxal radicals responsible for the degradation should be determined. In evaluating a large-scale test, several treatment objectives must be established before attempting a demonstration. These objectives should include operational capacity and flow rate designs; target VOC removal efficiencies and final effluent quality limits; systematic cost analysis and expense accounting; and operation/maintenance schedules and review. Because groundwater remediation is generally a lengthy undertaking, considerable planning and operational "feedback" mechanisms are paramount for successful large-scale demonstration projects.

Implementation Needs: Commercial equipment can be readily installed, but treatability studies should be used to identify potential problems. The technology works well with simple, known contaminants, but some caution should be exercised for complex mixtures. Costs will vary with total oxidizable organic content. Cost estimates range from a few cents to over \$1.00/1000 gal.^{1,4} The system will have to operate with solids in suspension and protect or clean the UV lamp surfaces. (Iron oxide is a likely problem with K-25 waters.) Waste volume should be minimal.

Author: G. Mackin, W. Harwood, J. Watson, Carpenter

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Membrane separations. Removal of volatile organic compounds (VOCs) from groundwater using membrane separation technologies.

Status: Demonstration. Membrane separation technologies have been utilized for removing organics in a number of applications including municipal and industrial wastewater, chemical manufacturing, food processing, and drinking water supply.¹ Applications specifically oriented for VOC removal in groundwater have only recently been demonstrated²⁻⁵ while the potential use of many new membrane separation technologies for groundwater treatment are very likely.⁶⁻⁸ Membrane separation technologies include reverse osmosis, ultrafiltration, electrodialysis, pervaporation, and liquid emulsions membranes. All of these technologies with the exception of liquid membrane emulsions involve permeation across a synthetic porous membrane. Organic compound rejection (or permeation in the case of pervaporation) at the membrane surface are dependent upon a number of factors, including temperature; pH and osmotic pressure of the solution; molecular weight, size, and relative volatility of organic contaminate; and membrane composition.¹ An array of commercial membrane systems is currently available for broad and specific filtration applications.

Removal efficiencies need to be established for K-25 groundwater costs, for the membrane process itself could be low. Quoted values range from a few cents to more than \$1/1000 gal. However, these processes do not usually produce a solid product suitable for disposal; so additional treatment costs could be significant. Waste volume will depend upon the method used to treat the concentrate but should be only a small multiple of the volume of the materials removed from the water. Further development and testing for K-25 waters could cost as much as \$1M for some membrane processes.

Science/Technology Needs: Further analysis of available membrane systems should be conducted to determine which systems are most applicable for treating K-25 groundwater contamination problems. Broad spectrum filters or two-stage systems may be needed, assuming mixed waste contamination with high concentrations of dissolved inorganics exists at K-25. Membrane systems incorporated into pump-and-treat designs should be evaluated

for use in the field. Techniques for reuse and/or disposal of membrane concentrate need to be fully explored using K-25 groundwater samples. A suitable system for handling the VIC concentrate will be needed.

Large-scale testing and demonstrations. Large-scale testing will require design and configuration of field equipment, which may be borrowed from existing groundwater remediation systems. Membrane separation may require pretreatment to prevent fouling. Pretreatment techniques may include one or more of the groundwater remediation techniques already discussed in this document. Adequate planning for concentrate reuse and/or disposal is also required.

Implementation Needs: The overall costs of reverse osmosis and ultrafiltration systems often include the cost of pretreatment and concentrate disposal in addition to the costs for the membrane itself. Costs for pretreatment depend upon the quality and quantity of the waste stream. Values range from \$0.15/1000 gal to in excess of \$1.0/1000 gal. Some systems use ultrafiltration as a pretreatment to reverse osmosis, in which case costs are accordingly higher. Costs for concentrate disposal are site specific and must be determined for each application. Capital costs vary as well, depending upon design flow and filtration rate. Major capital items include membranes, pressure vessels, and pumps. Membrane replacement costs range between \$40 and \$120/m² depending on the design application.

Author: D.E. Beck, Carpenter

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds (VOCs)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Coagulation and lime-softening. Removal of volatile organic compounds (VOCs) from groundwater using conventional water treatment techniques such as coagulation and lime-softening.

Status: Demonstration. A significant amount of research has been conducted to substantiate that conventional treatment techniques for water supplies can remove or reduce VOCs.^{1,2} Most of the analysis performed for this experimentation has focused on total organic carbon (TOC) concentrations rather than specific VOCs such as TCE, making it difficult to evaluate process performance. The literature suggests that conventional methods may be adequate for removing low VOC concentrations from water sources or function as pretreatment steps in handling high VOC contamination problems. However, conventional techniques alone are probably not sufficient for high VOC concentration removal, and they produce large volumes of waste. VOC behavior in coagulation systems will be important if coagulation is applied to remove other contaminants.

Adsorption on precipitates may be difficult to distinguish from evaporation. The removal efficiency is needed for K-25 waters. This is a low-cost treatment. The technology is used in conventional water treatment and usually costs less than \$1/1000 gal. However, the waste volume (the precipitate) could be large. Because of the waste volume, this technology may be unlikely to be used for VOC removal only, but it could be used for other purposes, and VOC removal could be a benefit. Development and testing could cost a few million dollars.

Science/Technology Needs: Coagulation, lime-softening, and other conventional water treatment techniques should be tested as pretreatment steps to other groundwater remediation technologies. Conventional treatment methods appear to remove a broad spectrum of water contaminants, organic and inorganic; this feature may prove advantageous in treating mixed waste contamination in K-25 groundwater and should be exploited fully (see Uranium in Groundwater). The fate of VOCs removed by coagulation/lime softening need to be determined. Are the VOCs permanently contained in the precipitate? Are they decomposed or evaporated?

Large-scale testing and demonstrations. Large-scale demonstrations will most likely include conventional water treatment techniques as an element of several other groundwater remediation technologies for K-25. Because conventional treatment methods are so well understood, there should be only simple modifications required to existing treatment designs and little resistance to their application. Any waste residuals generated through the demonstration of such techniques should be adequately planned for and disposed of.

Implementation Needs: The large waste sludge volume produced makes the use of these techniques solely for removal of VOCs questionable. Costs vary significantly depending upon coagulant demand, flow rates, and disposal/regeneration costs. Suitable waste treatment methods would be needed. Costs for the coagulation operations should be low (like conventional water treatment), but the costs for waste handling may be large.

Author: G. Mackin, W. Harwood, J. Watson, D.E. Beck

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds (VOCs)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Ex situ biodegradation. Removal of volatile organic compounds (VOCs) from ground-water using biological treatment.

Status: Demonstration. A full-scale bioremediation project for TCE-contaminated ground-water is currently being demonstrated at K-25,¹ but no conclusive results have been published to date. A similar cometabolic bioremediation project has been conducted at the DOE Kansas City Plant.² Another bioremediation project is planned for treating groundwater at the DOE Savannah River Integrated Demonstration Program.¹ A considerable amount of research has been conducted to evaluate and identify cometabolic processes using methanotrophic bacteria for degrading PCE, TCE, and DCE into non-toxic final products.³⁻⁷ In situ and aboveground treatment designs have been developed. Operating conditions such as water flow, flow rates for air and methane, and required nutrient concentrations are dependent upon the bioreactor supporting media and the geochemistry of the groundwater source. Present methods still need to demonstrate high removal efficiencies with high reliability for all compounds of interest. Costs are likely to be low, but will depend upon the degradation rates which determine the size of the bioreactor. Waste volumes should be low, probably consisting principally of excess biomass. Additional development and demonstration costs could be a few million dollars.

Science/Technology Needs: More research should be conducted to determine the threshold concentration of PCE and TCE above which bioremediation is inhibited. Variations in bioreactor configurations should be explored to achieve increased VOC removal. New materials should be examined as support media for fixed film systems. Rigorous examination of the bacterial species involved in cometabolism of VOCs should be performed to further understand their ecology and genetics.

Large-scale testing and demonstrations. A thorough evaluation of the current K-25 groundwater bioremediation demonstration needs to be performed when the project is complete. A comparative analysis of the K-25 and Kansas City Plant demonstrations should

be performed to determine significant operating parameters, relative operating costs, and long-term applicability to other full-scale remediation efforts.

Implementation Needs: Only normal implementation needs should be expected. Power consumption will be low. Instrumentation and analytical chemistry services will need to measure all parameters relevant to bioreactor operations. Although no reliable biodegradation system is available for the more refractory (highly chlorinated) contaminants at K-25, one can guess that workable systems, when they are developed, will involve no more than moderate costs (a few dollars per 1000 gal) because most available biodegradation processes work within this range. The volume of waste produced should be low.

Author: G. Mackin, W. Harwood, J. Watson, Carpenter

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CHEMICAL OXIDATION FOR REMOVAL OF VOCs FROM GROUNDWATER

REMA-48-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Chlorinated volatile organic compounds (VOCs)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Chemical oxidation for removal of volatile organic compounds (VOCs) from groundwater.

Status: Demonstration/accepted; commercially available. Chemical oxidation of VOCs has been practiced in the water and wastewater industries for a number of years. This technique usually involves converting the target VOCs into less objectionable compounds by exposing them to strong oxidizing agents such as oxygen or air, ozone, hydrogen peroxide, potassium permanganate, hypochlorite, and/or chlorine dioxide.¹⁻³ More recently, ozone and hydrogen peroxide have become very popular oxidizing agents for groundwater applications because they do not introduce additional salts or chlorine compounds to the treatment stream. Peroxide is most effective when a catalyst such as ferrous iron is available (Fenton's reagent). Small concentrations of iron are often present in K-25 waters. Applications of ozone and hydrogen peroxide in concert with ultraviolet radiation are mentioned in the diagram elsewhere (see REMA-43, "Ultraviolet-Enhanced Chemical Oxidation"). A catalyst such as ferrous iron is often used (Fenton's reagent). Costs could be low, perhaps a few dollars per 1000 gal or less.

Science/Technology Needs: Chemical oxidation of VOCs may also serve to remediate other contaminants that may be encountered in K-25 groundwater. Characterization of K-25 groundwater should include analysis of other non-hazardous dissolved compounds which may consume chemical oxidizing agents. Treatability studies should be conducted to determine if various chemical oxidizing agents are applicable to K-25 groundwater contamination and to what degree these agents can degrade the pollutants. Chemical oxidation may produce secondary contaminants that require additional treatment; if so, this attribute needs to be evaluated for its impact upon effluent quality levels. Cost analysis of various oxidizing techniques should be conducted for comparison to other treatment options.

Large-scale testing and demonstrations. Large-scale demonstrations for treating K-25 groundwater will most likely involve an integrated approach where chemical oxidizing agents

CHEMICAL OXIDATION FOR REMOVAL OF VOCs FROM GROUNDWATER

REMA-48-OG

are used in conjunction with other technologies. Such demonstrations will require that target remediation levels are established and used as a parameter for evaluating the effectiveness of this treatment method. Health and safety issues for handling bulk chemicals must be addressed prior to initiating demonstrations.

Implementation Needs: Capital equipment and system design work is needed to develop full-scale treatment units though many designs and most of the equipment are commercially available. Bulk chemical supplies can be obtained without much difficulty, though transport and handling issues would need to be resolved on a site-specific basis. Costs could vary considerably depending on local conditions. Costs per unit volume of groundwater are likely to be low to moderate, contingent principally upon the total concentration of oxidizable organic compounds.

Author: G. Mackin, W. Harwood, J. Watson, Carpenter, D.E. Beck

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February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: PCBs

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Incineration. Incineration of PCB contamination in soils

Status: Demonstration. Testing was performed at the EPA's Incineration Research Facility to establish the feasibility of incinerating wastes contaminated with hazardous materials. The contaminants were PCBs, cadmium, chromium, copper, and lead.¹ The PCB concentration was greater than 200,000 mg/kg and the rest were several hundred mg/kg. Tests were run at a kiln exit temperature from 824°C to 984°C. Greater than 99.9999% destruction and removal efficiency was achieved, but the treated wastes still contained PCBs. A major portion of the toxic metals were found in the kiln ash. A few commercial firms now offer PCB incineration services.^{2,3} The existing incinerator at K-25 should be able to meet the conditions, but the incinerator is currently committed to burning liquids. The capacity available for treating soils in the future is not known.

The costs for incineration can be high. Reported costs range from \$100 to \$800/ton. With potential traces of radioactivity in the soil (and ash), the costs could be higher. The potential wastes are the treated soil and solids collected in the off-gas system. If these have no residual toxic or radioactive materials, the hazardous waste volume could be small. Several million dollars will be needed for development and testing of any new incinerator prior to approval.

Science/Technology Needs: These results need to be considered with respect to the soil chemistry at the K-25 Site. These test incinerations were performed on marine sediment in New Bedford Harbor. The test results suggest the incineration could be an effective form of PCB remediation. Sediment dewatering prior to incineration and increased kiln residence time may be required. Separations of soil fractions (such as removal of larger particles) may reduce the volume of soil to be processed.

Large-scale testing and demonstrations. There have been a few large-scale tests, and more need to be completed to calculate the optimum operation parameters with respect to K-25 soil. Reliability of operations to maintain temperature, residence time, and exhaust cleanup must be proven.

Implementation Needs: An incineration facility with TSCA and RCRA licensing is needed. Removal efficiencies reported for incinerators and achieved in tests must be approved by regulators. Costs have been reported from \$100 to \$800 per ton.² Agreement should also be reached on disposition of the residual soils which may contain traces of toxic metals. After incineration, the soil is not expected to be agriculturally useful.

Author: G. Mackin, W. Harwood, J. Watson, D.E. Beck

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EM Problem: Remedial action

K-25 Site Problem: Contaminated soils, buried waste

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Destruction

Technology: Bioremediation. Bioremediation of PCB-contaminated soils.

Status: Predemonstration. This technology has been demonstrated in lab-, bench-, and pilot-scale tests, as well as several full-scale decontaminations.^{1,2} The main thrust of this technology is to enhance soil properties so that naturally occurring bacterial species can degrade PCBs.^{3,4} PCB degradation appears to occur under anaerobic conditions. Apparently, the redox potential (Eh) of the environment must be below 0.35V for significant reductive dechlorination to take place, but exact requirements depend on the individual compound being reduced.⁵ Thirty-four bacteria and five fungi have been found to degrade PCBs.⁶ Development of mixed cultures to effectively biodegrade PCBs has been proposed while commercially produced microbial inoculants are available that can degrade a variety of compounds. Microbes can be acclimated to site conditions or genetically engineered species can be tailored for specific applications.⁷ Ex situ applications have been demonstrated upon chlorinated organic compounds in combination with soil washing techniques.^{3,8} Costs could be moderate to low but will depend upon the degradation rates (the required reactor size). The waste volumes could be low if the treated soil does not contain sufficient other toxic or radioactive components to prevent returning the soil to the ground. Considerable additional development and testing will be required to make biodegradation of PCB-containing soils reliable; this could cost several million dollars.

Studies in river sediments have shown that anaerobic bacteria can remove chlorine atoms from the more highly chlorinated compounds, and the resulting lightly chlorinated compounds can be degraded by aerobic organisms.^{9,10}

Science/Technology Needs: A better understanding of the conditions needed by bacteria to biodegrade PCBs is a must. Identification and characterization of site-specific bacteria that can biodegrade PCBs is important for K-25 applications. It is important to explore more fully the idea of using combinations of microbes to further enhance degradation rates. There is a need to better understand the parameters controlling biodegradation of PCBs. Better analytical methods and/or technologies are needed for monitoring PCB degradation.¹¹

February 26, 1993

Large-scale testing and demonstrations. In situ demonstrations using modification of soil properties should be attempted with K-25 soils to establish if this approach is feasible for large-scale applications.

Implementation Needs: It is too early to assess implementation needs. Costs for in situ treatment have the potential for being low. Facility needs could be normal.

Author: D.E. Beck, J. Watson, Carpenter

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EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Alkali metal polyethylene glycolate (APEG). Treating PCB contamination in soil.

Status: Accepted. Several stages of test demonstrations from bench tests to field-scale remediations have been successfully performed in varying degrees of removal efficiency. APEG was used in the Omaha and Buffalo facilities, processes were proven to be capable of degrading not only PCBs but other toxic compounds such as herbicides containing dioxins and furans that may be present with PCBs or may result in partial degradation of PCBs. Reductions in PCB concentrations of 75% to 99+% were achieved. The process is developed for ex situ treatments, but there are possible extensions to in situ treatment in soils above the water table. The pilot-scale demonstration at Moreau, New York, indicates that a scale-up of the laboratory designs is feasible. The achievement at Moreau prompted the EPA to authorize a full-scale remediation demonstration on Guam. This demonstration proved the ruggedness and portability of the designed equipment. The overall performance of the designed system was exceptional with a few minor complications that should be expected in a new design. Costs were reported to be \$200 to \$500/ton. Wastes will be the treated soil which can be returned to the ground if there are no significant concentrations of other toxic materials in the soil. The soil will be enriched in alkali. Development costs have been funded by the EPA, and further testing is expected.

Science/Technology Needs: Exact soil chemistry (acidity and basicity), distribution and concentration of contaminants, and textural classes and structure of K-25 soils must be determined to establish the maximum separation possible. Additional field-scale demonstrations should be performed to optimize the operating parameters and provide more background information on this process. Disposal of end products from the APEG process must be determined, achievement of high removal efficiencies must be ensured, and minor design problems must be resolved.

Large-scale testing and demonstrations. Few large-scale demonstrations have been completed, and more needs to be done with respect to the soil chemistry and PCB type in K-25 soil. Treatability tests will be needed also.

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Implementation Needs (Facility Needs): The required treatment levels need to be determined. The results from EPA tests do not always show extremely high removal efficiencies. These must be considered to be adequate before implementation can begin. Treatment standards need to be established. Portable APEG reactors and processors may be used. A portable analytical laboratory or access to a laboratory is a necessity. The laboratory must be stocked with the appropriate reagents and equipment for this project. There will be a need for electricity, steam, and compressed air for the APEG systems to operate. Other implementation needs are normal. Cost is reported to be \$200 to \$500 per ton.^{4,6}

Author: D.E. Beck, Carpenter

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6. L.J. Amend and P.B. Lenderman, "Critical Evaluation of PCB Remediation Technologies" *Environmental Progress*, 11, 1992, pp. 173-177.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Physical separation

Technology: Low-temperature thermal treatment.

Status: Predemonstration. PCBs are not normally viewed as volatile compounds. However, when they are heated 300 to 600°F, their vapor pressure will be sufficient for effective removal. One system demonstrated by Roy F. Weston, Inc.,¹ used semivolatile organic compounds (SVOCs) as well as other compounds, but it is not clear if any of the SVOCs were PCBs. The concentration of SVOCs was decreased, but it was not clear if the removal levels were as low as needed for PCBs. Dioxins were formed in the process but were not formed in the treated sludge. Stack emissions were controlled with filters, condensers, and carbon beds. Costs are likely to be moderately high, a few hundred dollars per ton. The waste will consist of the treated soil (if it cannot be returned to the ground because of other contaminants) and the materials recovered in the off-gas. If a condenser is used, much of the PCBs may be recovered as liquid in oils. In any case, carbon heads (later wastes) are likely to be used for the final off-gas cleanup. Development is under way in industry. Additional costs may be a few million dollars, perhaps even <\$1M.

Science/Technology Needs: The ability of the technology to handle large concentrations of PCBs need to be determined. The requirements of residence time and temperature for different levels of removal need to be determined. Soils which adsorb PCBs significantly could also affect removal rates.

Large-scale testing and demonstrations. Much better understanding of the science and technology will be needed. There has been little large-scale testing to evaluate this process.

Implementation Needs: Treatment levels need to be evaluated. Will low-temperature treatment have to meet the same removal levels as incineration? The degree of PCB degradation and the toxicity of the degradation products needs to be determined. The role of K-25 soil properties on PCB removal will have to be determined. Off-gas treatment will have to be demonstrated. Costs are likely to be high, near those of incineration. One advantage will be the conduction of the residual soil after low-temperature (below combustion temperature)

treatment; the soil would not be sintered and could sustain organisms. Deposition of the treated soil will be an important consideration. If this remains a waste, the waste volume will be large.

Author: J. Watson, Carpenter

References:

1. U.S. Environmental Protection Agency, *Low Temperature Thermal Treatment (LT3) System*, Demonstration Bulletin, EPA/590/Mr-92/019, Cincinnati, Ohio, 1992.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Solvent extraction. Removal of PCBs soils by solvent extraction.

Status: Demonstrated. One process demonstrated at Y-12 used dimethyl formamide (DMF) to remove PCBs from oils and soil.¹ For the removal of PCBs from oils, water is added to the extractant (DMF) and contaminated substance, and the PCBs are phase separated. Another step is required to remove and destroy the PCBs such as incineration. The water and DMF can be separated by distillation and recycled into the process. For the removal of PCBs from soil—a water-kerosene solvent is used for phase separation of the PCBs. The kerosene containing the concentrated PCBs is distilled for further concentration. The PCB concentrate can be disposed by incineration also. The water and kerosene is collected and reused. PCB concentrations in oil and soil must be reduced from 300 mg/L to 10–15 mg/L. An industrial group has treated an oil soil with approximately 20 mg/L of PCBs and removed 98% of the PCBs,² and another firm has at oily sludges.³ Supercritical carbon dioxide has been considered as a solvent.

Science/Technology Needs: Large-scale studies must be done in regard to the soil chemistry and contamination concentrations at the K-25 Site. Studies will need to be completed on the design and operation parameters of the extraction equipment to be used. A preliminary cost estimate of the entire solvent extraction and PCB removal from soil process has been completed which compares the cost of the solvent extraction process to direct incineration of the PCB-contaminated soil. The solvent extraction process cost was about half of the direct incineration.

Large-Scale Testing and Demonstrations: A need exists for large-scale testing to be completed, confirming the pilot-scale data that was compiled.

Implementation Needs (Facility Needs): The solvent extraction process consists of the following stages: extraction, transfer, and solvent recovery (distillation). The soil extraction process tested consisted of three mixing stages which work countercurrently. The contaminated soil is added to Stage 1 and clean kerosene is added to Stage 3. The system needs to prevent any unnecessary loss of kerosene. Costs are likely to be moderate to high

(a few hundred dollars per ton). Waste volume will be moderate if the soil can be returned to the ground and high if the soil itself remains a waste.

Author: D.E. Beck, Carpenter

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2. H.D. Sonnen, W. Groschel, M. Nels, "Experience with the HARBAUER PB3 Soil Cleaning System," paper presented at *U.S. Environmental Protection Agency Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International*, 1989.
3. G.W. Sudell, "Project Summary Evolution of the B.E.S.T. Solvent Extraction Sludge Treatment Technology Twenty-Four Hour Test," *EPA/600/S2-88/051* 1985.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: Grouting of PCBs in soils (stabilization of PCBs in soil)

Status: Demonstration. PCB stabilization is a process which immobilizes the hazardous waste components in a solid matrix composed of contaminated soil and concrete. The process normally involves excavation of the contaminated soil converted to solid mass which immobilizes all leachable wastes. The stabilized PCBs can be sent to a properly permitted landfill for disposal. This process may be applied in situ through deep soil mixing which reduces the mobility of contaminants but does not destroy them. This process leaves the risk of exposure resulting from leaching wastes over long periods. The cost is likely to be a few hundred dollars per ton. Two vendors suggest costs of \$200 to \$250/ton. The treated soil will have a high volume (original soil plus additives), but this material should be nonleachable. Further development costs for K-25 soils could be less than a million dollars.

Science/Technology Needs: The K-25 soil chemistry must be considered. The organic constituents in the soil inhibit the effectiveness of the curing process and the quality of the stabilized wastes.

Large-scale testing and demonstrations. HAZCON, Inc., has successfully completed field tests of immobilizing low PCB soil levels. The soil contained 25% by weight of oils and grease. HAZCON used their additive Chloran that produced a waste mass in which analysis of laced could not detect PCBs and the limit of 1 µg/L.

Implementation Needs: The proper excavation or deep mixing equipment will be needed, depending on the best type of stabilization according to the K-25 soil type. This process costs \$250 per ton. International Waste Technologies (IWT) developed their own additive, HWT-20. This demonstration was conducted as part of an EPA program, but absolute confirmation of the laced data could not be proven. Unsatisfactory water loss was observed during weathering tests. The IWT process costs \$194 per ton, but because of the uncertainty of the quality of the product, more studies should be performed. Wastewater will be the expanded volume of

grout that cannot remain in the soil. This could be approximately equal to the volume of additives used.

Author: D.E. Beck

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1. S. Sawyer, and M.K. Stinson, *In-Situ Stabilization/Solidification of PCB-Contaminated Soil*, EPA/600/D-89/119, Cincinnati, Ohio, 1989.
2. M. K. Stinson, "EPA SITE Demonstration of the International Waste Technologies/Geo-Con In Situ Stabilization/Solidification Process," *Journal Air Waste Management Association*, **40**, 1990, 1569-1576.

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EM Problem: Remedial action

K-25 Site Problem: Contaminated soil, buried waste

Problem Area/Constituents: PCBs in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: In situ vitrification of PCBs

Status: Predemonstration. Technology has been used at the Hanford Facility as a field demonstration to stabilize radioactive wastes.^{1,4} It has been used by Battelle, Pacific Northwest Laboratories to stabilize or destroy PCB-contaminated soil.² A pilot-scale experiment was completed in 1987 at ORNL on soils spiked with radioactive contaminants.¹ The GeoSafe Corporation is scheduled to perform ISV at a Superfund Site, as is, Re-Tech, Inc.³ The ISV has been tested at the bench-, pilot-, and full-scale levels.^{4,5} ISV has been selected as the preferred remediation technology for several Superfund Sites, with a 99.9% efficiency for PCB destruction;^{4,5} however, the main purpose of the vitrification may be to stabilize other contaminants such as metals or radioactivity. Costs are likely to be high (hundreds of dollars per ton). Waste volumes will consist of materials caught in the off-gas treatment systems, mostly carbon beds. Additional demonstrations could cost a few million dollars.

Science/Technology Needs: Fate of PCBs need to be established more formally, including PCBs in adjacent soils. Further testing on effective electrode feeding systems is needed. The effectiveness of metals to extend melt depth needs to be explored fully.⁶

Large-scale testing and demonstrations. Few large-scale tests or major demonstrations have been done and certainly more need to be done with respect to PCBs and to the soils of K-25.

Implementation Needs (Facility Needs): If chosen, then portable generators will be needed or to install power lines to the sites to be remediated. Costs will be high. Technology is more likely to be needed for other contaminants, but fate of PCBs could be important. Waste volume will depend upon off-gas treatment required.

Author: D.E. Beck

References:

1. U.S. Environmental Protection Agency, *Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils*. Risk Reduction Engineering Laboratory. Cincinnati, OH. EPA/540/2-90/001, January 1990.
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EM Problem: Remedial Action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Fuel-based hydrocarbons

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: In situ biodegradation—hydrocarbons in soils

Status: Biodegradation is an established technology for removing many hydrocarbons from soils. The most extensive experience has been with degradation of petroleum fuels because of the numerous fuel tanks that have failed or leaked at gasoline service stations and other facilities. Significant demonstrations have also shown that biodegradation can handle more refractive materials such as chemicals used in preserving wood. In situ treatment is usually preferred over ex situ methods when it is effective because the costs are likely to be lower, and there is usually less interference with other activities at the site.

Science/Technology Needs: This is an established technology for the most common hydrocarbons such as most fuels. Additional development may be required if unusually refractory compounds are involved. These are more likely to be large polynuclear aromatic hydrocarbons which have been shown to be more difficult to degrade. A major difficulty in all biodegradation processes is delivery of oxygen (for aerobic processes) and nutrients to the organisms. Better delivery systems and better understanding of transport to underground locations should be sought. Most organisms to be used in situ degradation are found either within the contaminated soil or at another site with similar contamination. Such organisms have become acclimated to the contaminant, and colonies have developed the ability to degrade and use the pollutant. Although this approach has usually proven to be adequate, there may be merits in developing as well as seeking organisms with unique capabilities for degrading refractory pollutants. For in situ treatment, such organisms must be robust and able to survive and compete with other organisms in the soils.

Implementation Needs: Numerous characteristics of particular soils, underground structure, and distribution of the pollutant must be determined. Organism must be found which degrade the hydrocarbons of interest and then are tested with the soils and conditions at the K-25 site (treatability studies).

Author: J. Watson

References: A.M. Chakrabarty, *Biodegradation and Detoxification of Environmental Pollutants*, CRC Press, Inc., Boca Raton, Florida, 1982.

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EM Problem: Remedial action

K-25 Site Problem: Contaminated soils, buried waste

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: Incorporation in asphalt

Status: Demonstrated and accepted. Soils are added to asphalt mixes, and the soils becomes an additive to the asphalt.¹⁻⁴ When the contaminated soil is added to the rotary dryers which usually operate between 269°C and 427°C, most of the hydrocarbons are likely to be volatilized. This process is then much like thermal treatments, except the remaining soil becomes incorporated in the asphalt product. On the other hand, the soil can be added to the asphalt mix as an aggregate after the asphalt is prepared. This mixture will vaporize less of the hydrocarbon contamination and incorporate most of the contamination in the asphalt. This latter approach is not likely to be used when the hydrocarbon contamination contains more toxic materials. The use of this technology is limited by the rate of asphalt production because the amount of soils that can be incorporated in asphalt is limited to a few percent. The soils would probably have to be transported to an asphalt facility. The demand for asphalt is seasonal; therefore, the capacity to treat soils will also be seasonable. Costs can be relatively low, perhaps \$50 to \$100/ton. If the asphalt is used in roadways or other applications, there will be little waste left.

Science/Technology Needs: As a commercial technology, the needs are limited to improvements in the off-gas systems and gaining sufficient confidence to expand the use of the technology. The limited capacity of asphalt production makes this only a partial solution to hydrocarbon-contaminated soils; extensive development is not likely to expand the applications beyond the capacity of existing asphalt plants.

Implementation Needs: The nature of the contamination should be examined to ensure that there will be no problems with incorporating it into asphalt. The nature of the contamination also affects the off-gas treatment required. The major limitation may be the location of a suitable asphalt facility that will accept the soil. The presence of radioactivity or other contaminants that would restrict the use of the asphalt would certainly limit the use of this technology, perhaps prevent its use. Cost can be relatively low (\$50 to \$100/ton), but additional transportation costs may be significant.

Author: J. Watson

References:

1. U.S. Environmental Protection Agency, *Technologies and Options for UST Corrective Actions: Overview of Current Practice*. EPA/542/R-92/010, 1992.
2. U.S. Environmental Protection Agency, *Cleanup of Releases from Petroleum USTs: Selected Technologies*. EPA/530/UST-88/001, 1988.
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EX SITU BIOREMEDIATION (OF FUEL-BASED HYDROCARBONS IN SOILS)

REMA-64-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Ex situ bioremediation

Status: Demonstrated. Ex situ bioremediation has become a common technology for removing many hydrocarbons from soils. The use of ex situ bioreactors offers better control over temperature, chemical, and biological conditions than in situ operations. This technology is more likely to be used with difficult contaminants. The bioreactor can be incorporated into a soil washing system. The difficulty of biodegradation depends upon the contaminants of interest, but recent demonstrations have worked with compounds that are normally resistant to degradation such as wood-preserving chemicals. Costs are likely to be moderate (perhaps little more than \$100/ton). If the treated soil doesn't have to be handled as a waste, the waste volume should be small. Demonstrations with K-25 soil may cost less than a million dollars.

Science/Technology Needs: The technology of biodegradation and bioreactor design are developing rapidly, and improvements in cost and performance appear to be resulting from current activities. Most organisms used in bioreactors have been developed from organisms found at similarly contaminated sites, but future modifications of the organisms may provide significant improvements in the future. Innovative bioreactors that can handle solids, retain organisms, and optimize reactor conditions should be encouraged.

Implementation Needs: Biodegradation still is not understood well enough to avoid careful treatability studies. The interaction of soils and the mixture of pollutants present at any site need to be assessed. The cost of ex situ biotreatment is usually moderate; costs of \$100 to \$200 per ton have been quoted. However, costs certainly will vary with the contamination present.

Author: J. Watson

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EX SITU BIOREMEDIATION (OF FUEL-BASED HYDROCARBONS IN SOILS)

REMA-64-OG

References:

1. *Bioremediation in the Field*. (An information update on applying bioremediation to site cleanup), EPA/540/2-92/027, December 1991.
2. *BioTrol Soil Washing System for Treatment of a Wood Preserving Site*. EPA/540/S5-91/003.
3. G.V. Pickwell et al., "Cascade Biodegradation of Fuels in Contaminated, Slurried Soils," *Emerging Technologies for the Special Symposium, Atlanta, Georgia, September 21-23, 1992, Vol. II*, D. William Tedder, ed., American Chemical Society, Washington, D.C., 1992, pp. 432-435.

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LOW-TEMPERATURE THERMAL TREATMENT (OF FUEL-BASED HYDROCARBONS IN SOILS)

REMA-65-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Fuel-based hydrocarbons

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Physical separation

Technology: Low-temperature thermal treatment

Status: Accepted. Developed commercial technology that has been used in treating soils around leaking fuel storage tanks.^{1,2} Soils are heated to between 250°C to 400°C, and the removal efficiency is usually greater than 95%. However, a range of hydrocarbons certainly exists with different vapor pressures. The method is less effective on very heavy oils such as No. 6 fuel oil. With high-moisture-content soils, the time and energy required to vaporize water limits the effectiveness of any thermal treatment. Soils with a large fraction of very fine particles, usually defined as clays or silt, are not as easily treated at these moderately low temperatures. Costs for low-temperature treatment have been reported between \$74 and \$184/ton. The wastes will consist of oils collected in the off-gas system and the treated soil. If there are no PCBs or other similar materials in the collected oils, it may be practical to burn the oils, perhaps even taking advantage of the energy content in the oils. If the soil does not contain significant concentrations of radioactivity or other toxic materials, it may be possible to return the soil to the ground and not handle it as a waste.

Science/Technology Needs: The process is well understood, and reliable equipment is available. The principal need is for sufficient understanding of the soils of interest to ensure that the technique will work adequately. The moisture content of the soil, the clay and silt fraction, and the presence of very high molecular weight contaminants such as asphalt or very heavy oils needs to be determined. In many cases, treatability studies may be the most cost effective way to determine the applicability of this technology to a given contaminated soil.

Implementation Needs: Establishment of treatment levels and either treatability studies or good characterization of the contaminated soil. Cost estimates for the method range from approximately \$74 to \$184/ton. Waste streams (other than the treated soil) include off-gas

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**LOW-TEMPERATURE THERMAL TREATMENT
(OF FUEL-BASED HYDROCARBONS IN SOILS)**

REMA-65-OG

equipment and the "recovered" hydrocarbons. If scrubbers are used, there will be contaminated water. Afterburners can be used and should minimize the volume of waste produced.

Author: J. Watson

References:

1. U.S. Environmental Protection Agency, *Technologies and Options for UST Corrective Actions: Overview of Current Practice*, EPA/542/R-92/010, 1992.
2. U.S. Environmental Protection Agency, *Cleanup of Releases from Petroleum USTs: Selected Technologies*. EPA/530/UST-88/001, 1988.

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EM Problem: Remedial action

K-25 Site Problem: Contaminated soils, buried waste

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Chemical oxidation of polycyclic aromatic hydrocarbon compounds

Status: Predemonstration. This process used the chemical degradation of naphthol and naphthalene in the presence of mangnesenoxide as a basis of study. The compounds used were reagent grade chemicals added to soil samples which were sifted to increase surface area. Samples consisted of mineral medium, Polycyclic Aromatic Hydrocarbon (PAH) stock, and 1.0000 gram of dry soil. Once the samples were measured and placed in centrifuge tubes, they were shaken for four hours. A manganese oxide solution was prepared from the oxygenation of manganese ions and the deoxygenated for ninety minute by purging the sample with nitrogen. Tests were completed on the samples which returned promising data. Degradation of the naphthol began immediately without any lag time and the concentration decreased from 9 mg/L to nondetectable in 9 days. However Naphthalene exhibited no significant degradation over a period of 9 weeks.

Science/Technology Needs: There is much to be learned about this technology before this concept can be utilized at K-25. Experiments and testing need to be completed in regards to the soil chemistry at K-25.

Large-scale testing and demonstrations. Large-scale testing must be done to show how this technology can handle K-25 soils.

Implementation Needs: It is too early to assess all implementation needs with confidence.

Author: D.E. Beck, Carpenter

References:

1. R.G. Luthy, and J.R. Michellic, *Degradation of Polycyclic Aromatic Hydrocarbons Under Various Redox Conditions in Soil-Water Systems*, Carnegie Mellon University, 1987.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils, buried waste

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Physical separation

Technology: Soil venting/vapor extraction (see REMA-31)

Status: Accepted. Soil venting is common practice for light hydrocarbon spills, such as leaking gasoline tanks. The major difference between fuel-based hydrocarbons and the chlorinated VOCs discussed earlier is the lower toxicity of the vapor and the probable presence of lower volatility compounds. Heavy fuels still present a problem. Soil venting introduces oxygen to the soil and usually speeds biodegradation; the term "bioventing"¹ is sometimes used to reflect the benefits of both processes. The performance of soil venting obviously depends upon the volatility of the hydrocarbon contaminant and the permeability of the soil. Costs for soil venting are usually low, perhaps only several dollars per ton. The only wastes produced are the oils recovered in the off-gas system and carbon beds or other materials that may be used to "polish" the off-gas prior to release. (See Remediation of solids contaminated with chlorinated VOCs using vacuum extraction.)

Science/Technology Needs: Although this is a relatively common technique, improvements in predictability of performance and optimization of performance could be achieved with better methods for assessing air flow in complex soils like those at K-25.

Implementation Needs: This is usually a low-cost operation. The wastes produced are minimal, and condensed fuel is sometimes reclaimed. The effectiveness or rate of remediation obviously depends upon the volatility of the contaminants and the porosity of the soil. The complex structure of K-25 soils makes design of venting systems and prediction of performance difficult.

Author: J. Watson

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 3. U.S. Environmental Protection Agency, *The Superfund Innovative Technology Evaluation Program: Progress and Accomplishments. A Report to Congress*, Office of Research and Development, EPA/540/5-90/001, 1988.
 4. U.S. Environmental Protection Agency, *Technology Evaluation Report: Site Program Demonstration Test, Terra Vac In Situ Vacuum Extraction System*, Groveland, Massachusetts, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, EPA/5-89/003a, 1989.
 5. D. W. DePaoli, S.E. Herbes, and M.G. Elliott, Capt., USAF, BSC, "Performance of In Situ Soil Venting System at Jet Fuel Spill Site," 44th Purdue Industrial Waste Conference, May 10, 1983, West Lafayette, Indiana.
 6. J.M. Phelan, "Thermal Entranced Vapor Extraction System for VOCs in Soil," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Ga., September 21-23, 1992, Vol. II*, D. William Tedder, ed., American Chemical Society, Washington, D.C. 1992, pp. 544-546.
 7. D.C. Downey, J.F. Hall, "Results of a Bioventing Test in Clay Soils," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23, 1992, Vol. II*, D. William Tedder, ed., American Chemical Society, Washington, D.C., 1992, pp. 467-469.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Incineration, cement kiln (destruction in cement kiln)

Status: Demonstrated technology for liquids. This technology is much like incineration except that here, the incineration occurs in an existing cement kiln. Soil throughput is limited by the capacity of existing cement kiln. Cement kilns have been used more often for incineration of liquids which can be introduced with the fuel. It is more difficult to introduce solid soils to these units.¹ The costs for adding soils to cement kiln is low. The principal costs are likely to be excavation and transportation, probably only several dollars per ton.

Science/Technology Needs: Handling methods for introducing solids into a kiln and reliable estimates of the amounts of solids from soils that can be incorporated into the cement product. (Incineration of liquids in cement kiln may introduce little solids to the cement product, but introducing soils probably would introduce significant solids.)

Implementation Needs: There is likely to be little capacity for treating solid wastes such as soils in a cement kiln.² The location of the kiln and the limited capacity for handling solids will limit the application of this technology to no more than a few specific cases. The potential for introducing radioactivity into the cement (although there will be some natural uranium present in all cement) is likely to eliminate treatment of many DOE wastes in this manner.

Author: J. Watson

References:

1. U.S. Environmental Protection Agency, *Technologies and Options for UST Corrective Actions: Overview of Current Practices*. EPA/542/R-92/010, 1992.
2. E.R. Hansen "New Way to burn Hazardous Waste." *Rock Products*, April 1990.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Fuel-based hydrocarbons in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Land farming

Status: Accepted. Commercial practice for some hydrocarbon wastes. Land farming is one version of ex situ biodegradation that has been used in numerous applications because it is relatively inexpensive and was once viewed as a simple technology. Care is needed to avoid the buildup of toxic materials in the soil. For instance, lead from gasoline can be a problem. Many DOE wastes may contain traces of radioactivity. Other hydrocarbon wastes may contain materials that are not easily degraded by microorganisms (such as chlorinated compounds) and accumulate in the soils. Some land farms at DOE sites have become contaminated sites because of accumulation of toxic materials. Thus, serious questions remain about many applications of this technology, although it has been used in several applications in the past. The costs for land farming depend upon the rate at which the target compounds degrade. Costs have been reported to be as low as \$10 to \$50/ton. If the treated soil can be left with the land farm, there will be essentially no waste to handle.

Science/Technology Needs: Perhaps the accumulation of toxic materials has become the most serious question for this technology. Proper tilling and dust prevention should be considered. Removal efficiencies can vary up to 99% depending upon the conditions and the time allowed for treatment. Treatment is not rapid, and 1 to 3 years may be required for many pollutants. Nutrients are fed to the soil periodically, and the soil is tilled regularly. Accumulation of non-reactive materials in the soil must be assessed; are all toxic organic contaminants degraded? Toxic metals, including radioactivity, which may be present in K-25 soils is a serious consideration.

Implementation Needs: Land farming has been misused at DOE facilities because of lack of understanding of accumulated contaminants and resulted in spreading of contamination as well as degradation of organic pollutants. Thus there must be good confidence both that radioactive contamination will not be added to the landfarm area and that the natural radioactivity in the landfarm will not become listed as "contamination." Similar questions must be asked about toxic metals. Demonstration that the particular contaminants present

are all degraded is essential; large areas of landfarm must not have to be treated in more expensive ways to remediate them. Large areas are required. If working properly, there will be essentially no waste produced. Costs are likely to be as low as \$10 to \$50/ton.¹

Author: J. Watson

References:

1. U.S. Environmental Protection Agency, *Technologies and Options for UST Corrective Actions: Overview of Current Practices*. EPA/542/R-92/010, 1992.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Heavy metals

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ vitrification of heavy metals in soils

Status: Demonstration. Simulated test of heavy metals such as Hg, Pb, Cd, and Cr buried in soils. The engineering-scale test was performed at the Idaho National Engineering Laboratory (but data were not reported) using electrodes buried in the soil. Transport of volatile metals to nearby soil was minimal; only one sample showed Cd leachability above TCLP limits. Pb and Hg were placed in the test bed as metals; the others, as oxides. (The Hg was in glass bottles.) Toxicity characteristic leaching procedure tests and the extraction procedure toxicity leach test were conducted and met all EPA standards except for Pb. Off-gas treatment was reported to retain all contaminants. The experiment was designed to simulate soil chemistry at the site. A commercial firm also is working with in situ vitrification.³ This is a relatively costly procedure that leaves the soil solidified and not useful for many applications. Good cost estimates have not been prepared, but costs greater than \$500 per ton can be expected. The wastes produced will come from the off-gas treatment system and, thus, be dependent upon the volatile components in the soil. Development and demonstration costs could be high, perhaps greater than \$10M.

Science/Technology Needs: There is much to be learned about this technology before this concept can be used at the K-25 Site. Experiments and testing need to be completed regarding soil chemistry at the K-25 Site. Other questions must be answered, such as what materials can be used as the electrodes, how far apart the electrodes must be for optimum removal, how the contaminants can be removed after isolation. The most serious questions involve the effects of buried metals and other materials on ISV performance and off-gas products to the melt (or disposal). The ability to apply ISV to continuous trenches or regions also needs to be investigated. Other problems that arise are the destruction and removal efficiency of hazardous volatile organics, determining the distribution of contaminants in the soil, designing an ISV off-gas system for volatiles, and determining the leachability of contaminants.

Large-scale testing and demonstrations. Large-scale testing must be done to show how this technology can handle K-25 Site soils and to test other problems such as the ISV off-gas system and electrodes. Integrated systems operating sequentially over large areas need to be tested.

Implementation Needs (Facility Needs): It is too early to assess all implementation needs with confidence. Costs are likely to be more than \$500 per ton but could vary with conditions. It will be important to understand the behavior of all components in the soil during vitrification, especially the volatilities. Because of the high costs, ISV is likely to be used only for the most serious contamination problems. Because it can handle a number of different contaminants, it may be considered when many contaminants are important to avoid multiple treatment steps. Waste volume depends upon the off-gas treatment system and the ability to "recycle" contaminants recovered in the off-gas to the "next melt."

Author: D.E. Beck

References:

1. U.S. Department of Energy, *In Situ Vitrification of Toxic Metals and Volatile Organics Buried in INEL Soils*, Pacific Northwest Laboratory, Richland, Washington, 1991.
2. L.V. Amend and P.B. Lederman, "Critical Evolution of PCB Remediation Technologies," *Environmental Progress*, **11**, 1992, pp. 173-177.
3. Geosafe Corporation, *Application and Evolution Considerations for In-Situ Vitrification Technology: A Treatment Process for Destruction and/or Permanent Immobilization of Hazardous Materials*, Company Publications, GSC, 1902, 1989.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Heavy metals (Hg, Cr)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ cement grouting of heavy metal and radiologically contaminated soils

Status: Accepted. In situ grouting with cement-based materials has been used at Oak Ridge National Laboratory (ORNL) Solid Waste Storage Area (SWSA) 6 as a field demonstration for long term remediation.¹⁻⁴ Suitably prepared grout will pass TCLP tests. Reported costs are moderate, \$30-\$70/ton. Waste volume is equivalent to the volume of additives required to create the grout, typically about 30% of the soil volume. If this can be left with the soil, little additional waste should be produced.

Science/Technology Needs: Detailed characterization of the waste matrix is required to determine the suitability of cement-based grout as a solidifying agent for specific sites. Long-term assessment of grouting technology's ability to maintain the pH necessary for retention and containment of uranium contamination is needed. Continued research might explore grout formulations that limit or reduce the volume of the final solidified product.

Large-scale testing and demonstrations. High confidence in grouting is not universal. More careful demonstrations and operations are needed to create a higher level of confidence in the long-term performance of cement based grouting.

Implementation Needs (Facility Needs): Future uses of soils will be severely affected by significant grouting; therefore, solidification has to be an acceptable final condition for the site. Costs are likely to be moderate, perhaps \$30-\$70/m³.² Because grouting can handle a number of contaminants, this approach can be considered for soils with multiple problem contaminants. Waste volumes are large; the grout consists of the original soil plus the additives.

Author: D.E. Beck

References:

1. R.D. Spence, and T.T. Godsey, E.W. McDaniel, *In Situ Grouting of a Low-Level Radioactive Waste Trench*, ORNL/TM-10462, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1987.
2. T. Tamura and W.J. Boegly, Jr., *In Situ Grouting of Uranium Mill Tailings Piles: An Assessment*, ORNL/TM-8539, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983.
3. E.C. Davis and B.P. Spalding, *Field Evaluation of a Cement-Bentonite Grout and a Chlorosulfonated Polyethylene Fabric Liner in Hydrologically Isolating Low-Level Radioactive Solid Waste*, ORNL/TM-9742, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1986.
4. C.W. Francis, R.D. Spence, T. Tamura, and B.P. Spalding, *In-Situ Grouting of Low-Level Burial Trenches with a Cement-Based Grout at Oak Ridge National Laboratory*, ORNL/TM-11838, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1992.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Heavy metals (Hg, Cr)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Electrokinetic removal of toxic metal contaminants from soils

Status: Conceptual. Simulation studies have been done at the Sandia National Laboratory, New Mexico which addressed chromate ions through a sandy matrix by three different types of transport phenomena—electroosmosis (movement of water in response to an electrical gradient), electrophoresis (movement of charged particles or colloidal suspension in an electrical gradient, and electromigration (movement of solute ions in the electrical field). A dye was used to simulate chromate ions. Contaminants migrating to the electrodes can be potentially removed from the ground by electroplating at the electrode, precipitation at the electrode, or complexing with ion-exchange resins. The concept may be useful for other metals. Costs are uncertain at this time, but they are not expected to be low. The moderately high to high costs are expected to result from the need for moderately close electrode spacing, the slow removal time, and the need for additional treatment once the contaminants reach the electrode regions. The additional development and demonstration costs could be several million dollars.

Science/Technology Needs: This study was performed in arid, sandy, unsaturated soil which requires that more studies be completed with respect to the soil type, soil chemistry, and percentage of soil/water content to understand the feasibility of this process. Other questions arise about the hardware in the process, such as what types of metal are to be used for the electrodes? How far apart should the electrodes be? How strong of a voltage should be applied? Recovery and removal processes will need to be designed to remove chromate ions from the electrodes

Large-scale testing and demonstrations. Large-scale testing will be needed to show that the technology can handle K-25 Site soil. These test also must prove that the chromate ions move strictly along electric field lines and do not allow contaminants to be dispersed more.

Implementation Needs (Facility Needs): More information must be obtained before all implementation needs can be properly assessed. If removal rates are poor, this technology

will have excessive costs. Acceptable treatment levels need to be established, and the performance of the technology needs to be based upon those limits.

Author: D.E. Beck

References:

1. E.R. Lindergren, et al., *Electrokinetic Remediation of Contaminated Soils*, 1991.
2. J. Hamed, Y. Acar, and R. Gale, *Journal of the Geotechnical Engineering Division*, ASCE, 1989.
3. R. Lageman, *Chemistry and Industry*, September 18, 1989.
4. S. Pamukcu, J.K. Wittle, "Electrokinetics and its Enhancement in *in situ* Soil Decontamination," *Emerging Technologies of Hazardous Waste Management*, Vol. II, D. William Tedder, ed., American Chemical Society, Washington, D.C., 1992, pp. 419-420.
5. E.R. Lindgren, et al., "Electrokinetic Remediation of Unsaturated Soils," *Emerging Technologies of Hazardous Waste Management*, Vol. II, D. William Tedder, ed., American Chemical Society, Washington, D.C., 1992, pp. 539-543.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Heavy metals in soil (Hg, Cr)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Ex situ soil washing/leaching

Status: Predemonstration. Little information was found on leaching methods for removing toxic metals from soils by leaching, so this appears to be an area with limited current activity. Some trade literature does indicate activity. This approach appears to be of interest principally for the most seriously contaminated sites, because of the significant costs involved. Similar work on leaching of radioactive contamination was listed under U and Tc in soils. Costs for soil leaching can be high, perhaps \$100/ton or more. The costs will depend upon the leachable components in the soil (limestone, etc.) and must include recovery of the metal(s) from the leach liquor. Waste volume depends upon the method used for recovering the metals from the leach liquor and the ability to recycle the leach solution; waste volumes are likely to be moderate, but could be high in a few cases. The development and demonstration costs for bringing this technology to successful implementation could be several million dollars.

Science/Technology Needs: Much needs to be done in this area if it is to become a viable option for removing toxic metals from soils. The studies will have to include assessment of the metal compound present in the soil as well as its reaction to selected leaching agent. Major consideration should be given to recovery of the toxic metals from the leachate and concentration of the metals into a minimum volume for disposal (or reuse). The final state of the soil also should be considered, especially if large volumes of soil are to be treated. Less aggressive and more specific leaching agents such as chelating agents may be best, available. High selectivity also is desired to permit dissolution of as little material as possible to remove the toxic metals.

Implementation Needs: Soil leaching is likely to be a relatively expensive operation, especially if the further processing of leachate is necessary. The waste volume will depend on the selectivity of the leach liquor and the metal recovery method. This very aggressive approach is likely to be of most interest for radioactive materials. Required treatment levels need to be established for K-25 soils.

Author: D.E. Beck

References:

1. C.A. Ortiz, B. Wilson, "Removal of Arsenic and Hexavalent Chromium from Leachates of an Industrial Landfill," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23, 1992, Vol. I*. D. William Tedder, ed., American Chemical Society, Washington, D.C., 1992, pp. 200-207.
2. K.W. Tsang et al., "Extraction of Bismuth, Cadmium, Lead, and Uranyl Ions from Contaminated Soils and the Influence of Bacteria on the Process," *Emerging Technologies for Hazardous Waste Management: 1992 Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23, 1992, Vol. II*, pp. 597-600.

(For related references, see REMA-840OG and REMA-12-OG.)

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Heavy metals (Hg, Cr)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ polymer grouting. In situ solidification of radiologically contaminated soils using chemical/polymer based grouting.

Status: Demonstration. In situ grouting with polyacrylamide (polymer) has been used Oak Ridge National Laboratory (ORNL) Solid Waste Storage Area (SWSA) 6 in the absence of radioactive contaminants.¹ Additional field demonstrations using polyacrylamide to assure hydrological isolation of mixed waste materials in an inundated trench are currently proposed at the same ORNL site.² Costs could be high, perhaps greater than \$100/ton. The wastes produced will be largely the grouted soil. Further development and demonstration costs could be a few million dollars.

Science/Technology Needs: Detailed comparative analysis of SWSA 6 and K-25 Site disposal site characteristics is required to determine suitability of the grout materials as a solidifying agent for K-25 Site soil contamination problems. Preliminary lab experimentation is needed to determine if K-25 Site leachates inhibit grout composition and solidification. Long-term assessment of grouting technology's ability to contain migration of contamination is necessary.

Large-scale testing and demonstrations. Large-scale test data are not available. Such tests with long-term evaluation of the results are needed for K-25 Site soils before this approach can be seriously considered.

Implementation Needs (Facility Needs): Needs are uncertain at this time. Cost and performance need to be compared with alternate soil treatment methods. Costs for implementing this technology could be high ($> \$100/\text{m}^3$).³ No unusual needs for implementing the technology are anticipated. Waste volume will be that of the soils and polymer (large volume).

Author: D.E. Beck, Carpenter

References:

1. B.P. Spadling, and G.K. Jacobs, E.C. Davis, *Demonstrations of Technology for Remediation and Closure of Oak Ridge National Laboratory Waste Disposal Sites*, ORNL/TM-11286, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.
2. B.P. Spadling, *Task Plan for TARA—II Compaction and Grouting Demonstration*, ORNL/ER-25, Environmental Sciences Division Publication 3808, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1991.
3. From Tamura and Boegly, ORNL/TM-8539, May 1983.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soils

Problem Area/Constituents: Heavy metals (Hg, Cr)

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: Ex-situ vitrification

Status: Demonstrated. One vitrifier was tested under the U.S. Environmental Protection Agency Site Program.¹ Cadmium, lead, chromium, and zinc were added to soils to be tested. Between 76% and 97% of nonvolatile metals were retained in the slag, and the slag produced passed the toxic characteristic leaching procedure (TCLP) for cadmium, chromium, and lead. All other metals were reported to be trapped in the off-gas treatment system. Generally, less than 0.1% was believed to reach the stack gas. Concentrations were often below detection limits. Costs are likely to be high; costs between \$400 and \$600 per ton have been reported. The wastes will be the vitrified soil and wastes from the off-gas treatment system. Future development and demonstration costs could be several million dollars.

Science/Technology Needs: Although the basic furnace appears to have been tested, a better understanding of off-gas treatment and handling of the material collected in off-gas needs to be evaluated. Approximately 10% of the solids were removed in the off-gas filters. It would be desirable to reduce the off-gas emissions. Perhaps small additions of fluxing agents could significantly reduce off-gas emissions. It would also be desirable to recycle as much of the toxic metals as possible to the vitrifier to minimize waste production. The effects of recycling should be evaluated. (Will that increase the volume of metal emissions? Can fluxing agents be added to the recycled solids to assist the recycled material in entering the melt?) Eventual emissions to the stack gas should be minimized. Would additions of HEPA filters after the baghouse reduce the fraction of toxic metals going to the stack gas?

Implementation Needs: A complete system needs to be designed and tested for specific K-25 Site soils that may need to be treated by this method. The "complete system" refers to the off-gas system and solids recycling discussed under Science/Technology Needs. Cost estimates need to be prepared which include all treatment costs, including secondary waste handling. Costs for the Babcock and Wilcox system were estimated to be between \$400 and \$600/ton. A high cost may not be easily justified for large quantities of soils lightly contaminated with toxic metals; other options may be effective for soils with these lower concentration, of

contaminants. The unit's lack of mobility may hinder its use for smaller quantities of more highly contaminated soils.

Author: D.E. Beck

References:

1. U.S. Environmental Protection Agency, *Babcock and Wilcox Cyclone Furnace Vitrification Technology: Applications Analysis Report*, EPA/540/AR-92/017, 1992.

February 26, 1993

EM Problem: Contaminated soil

Problem Area/constituents: Heavy metals in soil

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Fixation

Technology: Ex situ sulfur polymer grouting. Use of sulfur polymer cement (SPC) as a waste solidification and stabilization agent for dry soils contaminated with heavy metals, lead, cadmium, and other toxic metals listed by the EPA.

Status: Predemonstration. SPC has been used at BNL to stabilize mixed waste incinerator fly ash containing 7% lead, and has passed the U.S. EPA and NRC required laboratory tests. Last August it was tested with the eight EPA-listed toxic metals.

SPC is a thermoplastic that is free-flowing at 135°C, hardens upon cooling, does not require an activation agent to initiate solidification, has approximately double the mechanical strength of most hydraulic cements, and is not affected by acids and salts that destroy hydraulic cements. Because of its superior strength, it will accommodate large amounts of wastes and changes in formulation without losing compliance with EPA compressive strength requirements.^{1,2}

Costs for sulfur grouting will depend greatly upon the availability of low-cost sulfur. If sulfur must be purchased at market prices, the costs could be very high, probably several \$100 per ton. However, new flue gas treatment systems on coal-fired power plants could make more sulfur available than the market could handle, and very low costs (perhaps low-grade) sulfur could be available for this application. The waste volume would be largely the grouted soil itself. However, some wastes will result from the off-gas treatment systems when the soils contain components volatile at these temperatures.

Science/Technology Needs: Laboratory and bench-scale studies to achieve optimum grout performance and to understand sensitivity of grout performance to variations in soil properties, grout formulation, and treatment parameters. Work using actual Tc-bearing K-25 soils, to optimize grout performance. Scaled-up demonstration.

Implementation Needs: Costs will be high. Waste volume will be large. This technology will be practical only for the most severely contaminated soils. Cheap supplies of massive quantities of sulfur could be a problem. Future power plant sulfur emission control systems could supply considerable sulfur.

Author: D.E. Beck, J. Watson

References:

1. G.R. Darnell, "Sulfur polymer cement, a solidification and stabilization agent for hazardous and radioactive wastes," *Emerging Technologies for Hazardous Waste Management: Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23, 1992*, D. W. Tedder, ed., American Chemical Society, Washington D.C., Vol. II., p. 711.
2. P.D. Kalb, J.H. Heiser III, P. Colombo, "Comparison of Modified Sulfur Cement and Hydraulic Cement for Encapsulation of Radioactive and Mixed Wastes," *Twelfth Annual U.S. DOE Low-Level Waste Management Conference, summary and proceedings*, Chicago, Illinois, 28-29 CONF-9008119, August 1990, pp. 113-125.

IN SITU REDUCTION AND FIXATION OF HEAVY METALS IN SOILS

REMA-78-OG

EM Problem: Remedial action

K-25 Site Problem: Soils, groundwater, surface water

Problem Area/Constituents: Heavy metals in soils

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ reduction and fixation of heavy metals in soils

Status: Predevelopment—The in situ reduction of a metallic contaminant in soil using Fe(II) is a novel approach to remedial action.^{1,2} Reactions between the metallic contaminant and the ferrous salt can take place at soil pH (7.7 to 8.5 in certain high-limestone soils in aqueous slurry).¹ After addition of ferrous salts to reduce chromate, in a recent study, a destabilized aqueous sodium silicate solution was mixed into create a gel, which acted to lower metal solubility and soil permeability.¹

Long-term behavior of the silica gel has not yet been determined. In the short term, however, silica treatment resulted in a decrease in hydraulic conductivity corresponding to a metal protection, by flow reduction only, of 99.8% and greater. The in situ reduction of Cr(VI) was successful. The combined process of reduction and fixation shows promise for field application for soils containing up to 400 ppm Cr(VI). Gel fixation greatly reduced leaching of metals in DI water and in TCLP solutions, with up to 99% protection against leaching for Cr, Pb, Zn, and Cd. Metal fixation was successful using 6000 ppm Fe addition and zeolite gel fixation, when concentrations of each metal were 100 ppm.

Other studies have concentrated on construction of in situ reducing "curtains" of ferrous iron, through which a plume of groundwater might travel.² As the water passes through the curtain, it is cleansed when reducible metals sorb to the iron and precipitate out.

This could be a low-cost treatment if little Iron II addition is required, perhaps costing only a few dollars per ton. The wastes would be left in the soil. Development costs to provide confidence in the long-term acceptability of the technology could cost several million dollars.

Science/Technology Needs: The mechanisms take place under anoxic conditions. It is important to determine whether soil disturbance would reoxidize and release toxic or hazardous metals.

February 26, 1993

IN SITU REDUCTION AND FIXATION OF HEAVY METALS IN SOILS

REMA-78-OG

Regulatory issues must be addressed. This process may not be viewed as an acceptable permanent closure method.

Long-term gel behavior in the fixation process and its integrity over time, must be understood. Good sources of long-term gel behavior data may be available; construction sites have used silica gels to reduce soil permeability since the late 1880s.

More work in gel refinement is recommended for optimum fixation capabilities.

Implementation Needs: The costs should be moderate, and there will be a minimal volume of secondary wastes. Regulatory acceptance is needed.

Author: D.E. Beck, J. Watson

References:

1. K. Schwitzgebel, M.D. Erickson, "In situ chromate reduction and metal fixation in soil," *Emerging Technologies for Hazardous Waste Management: Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23 1992*. D.W. Tedder, ed. American Chemical Society, Washington, D.C., 1992. pp. 644-647.
2. J.D. Marsh, Jr., G.K. Jacobs, D.K. Solomon, *Treatability of a TCE and Tc Plume in Groundwater by In Situ Metal-Catalyzed Abiotic Degradation and Reduction/Sorption*, proposal submitted to the Environmental Restoration Group, Paducah Gaseous Diffusion Plant, November, 1992.

February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Technetium in soils

Reference Requirements: TCLP. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ cement grouting

Status: Predemonstration.¹

Jet grouting: Jet grouting occasions very little intimate contact with waste already in the ground. Thus, it is not very effective even for relatively immobile species. In addition, jet grouting produces a volume of soil displaced with every volume of grout. For construction work, that is no problem but is not appropriate for radwaste-contaminated soil. This is essentially a construction technology.

Mixing: Mixing in situ is being developed by several firms. NUS-Haliburton and Chem-Nuclear are developing a sort of paddle that will mix soils and concrete together, in ground. It is seen as a remediation method, but the Tc issue isn't being specifically addressed. A barrier is probably still a necessity, to prevent leaching into groundwaters.

Advantages: Grouting has an advantage over vitrification in that there is a **chemical** basis for its fixation of radionuclides. However, the grout mixture must be optimized for each waste (mixture experiments may require only 3 months of time).

Disadvantages: Mobility of Tc may be a problem in in situ grouting unless a barrier can be made to effectively surround the contaminated area.

Because of the inherent physical difficulties of mixing and the mobility of Tc-99, in situ fixation of Tc-99 in soil does not look promising. Costs are likely to be moderate, perhaps on the order of \$50/ton. Wastes will be minimal if expanded soil-grout mixture (usually about 30% expansion) can all remain in the soil. Further development and demonstration will be needed if successful retention of Tc is to be obtained. As noted, there are serious questions about the probability of success. Development costs could be several million dollars.

Science/Technology Needs: Laboratory studies of leach index (LI) optimization for Tc-contaminated soil in concrete. Development of in situ barrier to technetium, beginning with laboratory studies. Vertical barrier walls have been constructed for confining hazardous wastes, not radioactives. There are strong disadvantages, including possible vertical migration, barrier aging and disintegration, and lack of data with Tc.²

Implementation Needs: The most important need is for a reliable method to hold Tc in the grout for long times. Scaled-up demonstration of effective in situ mixing technique is needed along with optimization of grout mix for each batch of contaminated soil.

Author: D.E. Beck

References:

1. R.D. Spence, Oak Ridge National Laboratory, personal communication. December 14, 1992.
2. R. Raghavan, G. Wolfe, and D. Williams; "Technologies applicable for the remediation of contaminated soil at Superfund radiation sites," *Third International Conference New Frontier Hazardous Waste Management*, EPA/600/9-89/072, 1989, pp. 59-66.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Technetium in soils

Reference Requirements: TCLP. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Fixation

Technology: In situ vitrification using resistance heating

Status: Predemonstration.¹ Although technetium is not volatile in the environment, where it is in the reduced state, the heat of vitrification will tend to volatilize Tc. For that reason, vitrification is not a good method for technetium remediation.² If it is considered, a gas collection system will be required for volatilized substances.² Other researchers state that if Tc is to be homogeneously distributed in borosilicate glass, care must be taken to control the valence state of the Tc during processing.³ "Mildly reducing" conditions will produce the 4-valent state which will dissolve uniformly in the molten glass. (This appears to have been achieved only in the laboratory.) In the 7-valent state, Tc enters the glass in molecular form, which then separates into a vapor phase.

Disadvantages: The volatility of Tc would present a problem, with glass encapsulation (vitrification). Because of the heat, inherent physical difficulties of mixing, and the mobility of Tc-99, in situ vitrification of Tc-99 in soil does not look promising. This would be an expensive operation, costing probably hundred dollars per ton, but volatility of Tc is likely to make it unusable.

Science/Technology Needs: Not recommended

Implementation Needs: Not recommended

Author: D.E. Beck

References:

1. R.D. Spence, Oak Ridge National Laboratory, personal communication. December 14, 1992.
2. L. Dole, Ogden Environmental and Energy Services, Oak Ridge, Tennessee. Personal communication to D.E. Beck, December 15, 1992.

3. M.Y. Khalil and W.B. White, "Dissolution of Technetium from Nuclear Waste Forms," *Mat. Res. Soc. Symp. Proc.*, **26**, 1984, Elsevier Science Publishing Co., Inc., 1984, pp. 655-662.

February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Technetium in soils or sludges

Reference Requirements: TCLP. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Element: Treatment

Alternative: Fixation

Technology: Ex situ grouting—fixation of Tc-99 in concrete

Status: Predemonstration. Grouting of sludges has been demonstrated in laboratory work at several DOE facilities. This method immobilizes radionuclides by chemically and physically trapping them in a cementitious matrix. Work at ORNL and K-25 has optimized grout formulas for specific Tc-containing sludges (from Hanford and Portsmouth)^{1,2} and concrete fixation of technetium sludges and other wastes has also been evaluated at Paducah GDP.^{3,4} At the K-25 Site, a pilot plant pond sludge stabilization project has been undertaken. Contaminated soils can be excavated, mixed, and returned to the site; however, this soil fixation technique has been used for hazardous wastes and not for radioactively contaminated wastes.⁵

The two most important parameters for fixation of LLW in concrete are compressive strength and leachability. O.K. Tallent et al. (August 1989) determined the leachabilities of Tc and nitrate wastes from cement-based materials to depend on a number of factors, fine adjustments in any one of which can have a significant impact on leach index (LI). The factors include grout/mix ratio, grout fluid density, dry/solid blends, and waste concentration. Cement to water ratios varying from 1.5 to 2.25 are necessary for adequate compressive strength, according to Bailey (May 1985). Concentrations of Tc in 14 waste drums at Paducah ranged from 0.09 to 25.55 Ci/m³, in Bailey's experiments. In one example, a Tc sludge with 40% moisture required no additional water to obtain a cement/water ratio of 2.0, for fixing Tc. Compressive strength of the resultant "monolith" exceeded the PGDP target of 600 psi. Tc leaching was reduced to 64 ppm from original 1100+ ppm. In this experiment, chrome was also reduced sufficiently to make the waste form non-hazardous (from 99 to 0.5 ppm).⁴

Laboratory work has shown that blast furnace slag (BFS) added to cement will raise the technetium LI (reduce its mobility).⁶ Chemical properties of the slag reduce pertechnetate (TcO₄⁻) to the dioxide (TcO₂), a species that is less soluble and leaches more slowly. For best reducing effects on Tc, the slag-cement blend should contain at least 80% BFS.⁷

Advantages. Grout reacts chemically with radionuclides, enhancing fixation. Fixation in concrete is the EPA's method of choice for metal-bearing wastes.⁷ The material is inexpensive. If BFS or other reductant is added, the concrete mixture will immobilize Tc very effectively as shown by laboratory data.

The mechanism for making and testing grout mixtures exists at DOE sites. A pilot plant for solidifying pond sludges has been built at the K-25 Site.

Disadvantages. Grout mixtures can be strongly affected by other constituents of the sludge. For example, acidic solution, as in nitrate sludges, is extremely deleterious to concrete quality, and the solution must be neutralized before fixation. An excessive amount of chloride ions, also, negatively impacts concrete quality. For each waste, grout mixture experiments must be performed to optimize the composition for compressive strength and LI. Volume requirements are relatively large; about 1.5 ft³/100 lbs water are used in grout.

The cost for ex situ grouting can be relatively expensive, perhaps a few hundred dollars per ton. These costs depend upon the cost of additives required to hold Tc in the grout and the disposal of grouted soil. The waste volume can be large (soil plus additives). Additional development and demonstration costs are likely to be several million dollars.

Science/Technology Needs: Laboratory studies are needed both to optimize grout formulation to achieve the best (least) leaching performance and to understand the sensitivity of grout performance to variations in soil properties and grout formulation and treatment parameters.

Implementation Needs: Scaled up demonstration of sludge solidification is needed along with optimization of grout mix for each different Tc-bearing waste identified as candidate for remediation.

Author: D.E. Beck

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1. W.D. Bostick, B.S. Evans-Brown, *Sorptive removal of technetium from heavy metals sludge filtrate containing nitrate ion*, K/QT-203, Oak Ridge Gaseous Diffusion Plant, Oak Ridge Tennessee, November 1988.
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5. R. Raghavan, G. Wolfe, and D. Williams; "Technologies applicable for the remediation of contaminated soil at Superfund radiation sites," EPA/600/9-89/072, *Third International Conference New Frontier Hazardous Waste Management*, 1989, pp. 59-66.
6. W.D. Bostick et al, K/QT-203, November 1988.
7. R.D. Spence, MMES/K-25 Site, personal communication, December 14, 1992.

EM Problem: Remedial action

K-25 Site Problem: Contaminated soil

Problem Area/Constituents: Technetium in soils

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Soil washing/leaching

Status: Demonstration. Soil washing uses a combination of physical separation and chemical extraction technologies. Contaminated soil is mixed with water and/or extraction reagents. Extraction with inorganic salts, mineral acids, and complexing agents may be part of the treatment. The clean, coarse particle sizes are separated from the liquid containing the fines and radioactive material by a combination of physical separation methods, and could be returned to the site. The radioactive material would then be removed from the liquid by processes such as carbon adsorption, filtration, ion exchange, chemical treatment and membrane separation. The processes and reagents must be customized for each site. Application of this process depends on the reagents used.¹ Soil washing technology used to recover radioactive contaminants (and other metallic and organic contaminants) "must be tailored to the differing chemical properties of each radionuclide."² At this time, aqueous soil washing is the "best bet" for Tc-contaminated soils.³ Soil washing may be applied in situ or ex situ.

The method is reportedly used commercially in Europe. In the U.S., some pilot-scale work is operated under the U.S. Environmental Protection Agency Emerging Technologies Program.^{4,5} A high percentage of contaminant removal is possible. Soil washing is an appropriate technology for removing heavy metals, various organics including PCBs, and radionuclides, and can be simultaneously applied to all pollutants of a complex mixture of contaminants. An extraction process called the GHEA process⁵ (used at the above-mentioned pilot plant) has been used to treat samples of contaminated soil, sludge, and water from contaminated sites and plant operations, including PCB, steel mill, and chromium smelter residues were extracted in the laboratory by stirring with water solutions containing surfactants and other additives. The contaminant-laden wash liquors were purified by ultrafiltration, followed by air flotation. The developers state that the process is suitable for on-site installation. The GHEA process reportedly produces far less secondary waste than conventional extraction techniques, due to a process for separating the surfactant-contaminant complex from the wash water (producing very pure water) and subsequently separating the contaminants into

a very small waste volume for recovery or disposal and recycling the surfactant portion indefinitely.

The cost appears comparable with grouting. Both soil washing and grouting are far less expensive than off-site disposal. The GHEA Process cost of treatment is estimated to be in the \$50-\$80 per ton of treated soil, which include the extraction and the wash liquor purification steps in a full-scale, integrated process.⁵ This is in line with the EPA's estimate of \$45-\$100 per ton.⁶ The volume of waste produced will depend upon the method used to recover the Tc from leach liquor and upon disposition of the treated soil, normally expected to be returned to the ground. Additional development and demonstration costs for K-25 soils could cost from one million to a few million dollars.

Science/Technology Needs: Basic research is needed to determine the chemistry of technetium with surfactants. A DOE finding is that soil washing has limited application to fission product contamination, because they are strongly sorbed on clay fractions (ion-exchange sites) of soils.² Soil washing and physical separation has been used on plutonium contaminated soil and to extract radium from uranium mill tailings.⁶ The GHEA process, attractive because of its waste minimization possibilities, has apparently not been tested with technetium or other radionuclides. Its inventors say it is adaptable to most contaminants.⁷ Complexity of soil and contaminants at the site must be characterized and understood, along with the distribution of contaminants on the soil particles. Development of on-line monitoring capabilities might be advisable. Laboratory testing on actual K-25 contaminated soils is necessary.

Implementation Needs: If washing of mixed-waste-contaminated soils is feasible, scale-up to pilot plant and then full size will be necessary, with concomitant engineering and technician needs, for design, construction, radiological analyses, etc.

Author: D.E. Beck

References:

1. R. Raghavan, G. Wolfe, and D. Williams, "Technologies Applicable for the Remediation of Contaminated Soil at Superfund Radiation Sites," *Proceedings of the Third International Conference on New Frontiers for Hazardous Waste Management*, EPA/600/9-89/072, 1989.
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3. L. Dole, Ogden Environmental and Energy Services, Oak Ridge. Personal communication to D.E. Beck, December 15, 1992.
4. A. Cachette, U.S. Environmental Protection Agency, Cincinnati, personal communication to D.E. Beck, January 4, 1993.
5. I. Gotlieb and J.W. Bozzelli, "Soil and Water Decontamination by Extraction with Surfactants," available from Dr. Gotlieb at GHEA Associates, Chemical and Environmental Engineering, 5 Balsam Court, Roseland, New Jersey.

6. *Technological Approaches to the Cleanup of Radiologically Contaminated Superfund Sites*, EPA/540/2-88/002. U.S. Environmental Protection Agency, Washington D.C., August 1988.
7. I. Gotlieb, GHEA Associates, personal communication to D.E. Beck, January 5, 1993.

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Fuel-based hydrocarbons in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Adsorption, biodegradation, oxidation

Technology: Gas stripping

Status: Accepted. The solubility of most fuel hydrocarbons in water is low, and the toxicity is usually not as great as those of chlorinated VOCs and PCBs discussed in other sections of this report. However, the aromatic components of fuels is notably toxic; benzene can be significant in water around spills. The gas stripping methods described for chlorinated VOCs in groundwater apply to the more volatile fractions of fuels. This is a relatively inexpensive process, but the cost depends upon the volatility of the hydrocarbons (air requirements). Cost probably should be nearly or even less than (\$1.00/1000 gal.) Wastes may be minimal if the recovered fuel is recovered or destroyed. Iron oxide precipitate and carbon beds which may be used for "polishing" the water may be the major wastes.

Science/Technology Needs: Gas stripping equipment is available, but treatability studies will be needed to determine the volatility of any hydrocarbons found in K-25 groundwaters and the fraction that can be removed practically by gas stripping. Improvements can be made in off-gas treatment to recover or destroy the toxic materials to minimize waste. Equipment to handle the ferric iron precipitates that are likely to form at K-25 would be desirable.

Implementation Needs: This is standard technology with only normal implementation needs. An off-gas treatment system is needed. The presence of environmentally significant non-volatile components needs to be established to ensure that the treated water can be discharged. Otherwise, further treatment may be required.

Author: J. Watson

References:

1. S.P. Singh and R.M. Counce, *Removal of Volatile Organic Compounds from Groundwater: A Survey of the Technologies*, ORNL/TM-10724, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1989.

2. P.C. McCarty, "Removal of Organic Substances from Water by Air Stripping", in *Control of Organic Substances Water and Wastewater*, B.B. Berger, ed., EPA/600/8-83/011, 1983.
3. J.W. Mercer et al., *Basics of Pump-and-Treat Ground-Water Remediation Technology*, EPA/600/8-90/003, U.S. Environmental Protection Agency, Robert Kerr Environmental Research Laboratory, Ada, Oklahoma, 1990.
4. "National Primary Drinking Water Regulations; Synthetic Organic Chemicals, Monitoring from Unregulated Contaminants," *Federal Register*, **52**(130), 2590 (1987).
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6. H. Schade and A. Sapulak, "Application of Air Stripping and Adsorption Processes to Volatile Chlorinated Hydrocarbons Removal and Removal from Water and Wastewaters," *Water Science and Technology* (ES & T), **24**(7) 1991, pp. 157-163.
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8. R.E. Speece et al., "Evaluation of Cascade Air Stripping—Pilot-Scale and Prototype Studies," *Journal of Environmental Engineering—ASCE*, **117**(6) 1991, 788-798.
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ADSORPTION ON CARBON (OF FUEL-BASED HYDROCARBONS) REMA-92-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Fuel-based hydrocarbons

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Stripping, oxidation, biodegradation

Technology: Adsorption on carbon

Status: Accepted. This is a standard treatment method, especially for "polishing" to remove the last traces of contaminant. Carbon can be regenerated by heating, but regeneration rate and temperature depends upon the vapor pressure of the contaminants. Other hydrophobic adsorbents can also be used as adsorbents. Regeneration can be done on-site, or carbon beds can be returned to the vendor for regeneration. The presence of PCBs and other especially toxic compounds on the beds may prevent their acceptance by vendor for regeneration. Since uranium and/of Tc could also collect on carbon beds, return of beds to the vendor should not be considered assured. Carbon beds can be relatively inexpensive if the concentration of adsorbable components is low. The costs are strongly affected by the concentration of adsorbed materials. If little besides low concentrations of hydrocarbons is present, the costs should be moderate, perhaps to a few dollars per 1000 gal. The total costs also depend upon the regeneration/disposal plan. If the contaminated carbon must be treated as solid waste and sent for disposal, the cost for carbon and volume (also cost) of waste could become high.

Science/Technology Needs: With the exact composition of hydrocarbon contaminants unknown or uncertain, treatability studies will be needed to assess the adsorption capacity and proper regeneration conditions. Because most organic compounds in the soil will adsorb, they will all affect the capacity of the carbon for the hydrocarbons of interest. A variety of carbons are available, and a selection will be needed. It will be necessary to determine whether other contaminants such as PCBs, uranium, or Tc will accumulate (even slowly) in the beds and, if so, how they behave during regeneration.

Implementation Needs: Because there are less expensive alternatives, adsorption is likely to be used only on lightly contaminated groundwater and as a "polishing" step to back up other treatment methods. The cost of carbon beds and the regeneration of the beds will be largely related to the total material adsorbed, not to the amount of water treated. The beds can be regenerated on site or shipped to the vendor (if no radioactivity or PCBs exist on the

ADSORPTION ON CARBON (OF FUEL-BASED HYDROCARBONS) REMA-92-OG

bed) for regeneration and recovery of the more volatile and semi-volatile portion of the hydrocarbons.

Author: J. Watson

References:

(See the section on adsorption of PCBs and VOCs.)

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Fuel-based hydrocarbons

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Stripping, adsorption, oxidation

Technology: Biodegradation

Status: Demonstrated. Several bioreactors have been developed for degrading organic compounds. Light hydrocarbons degrade relatively rapidly in any of several aerobic reactors; heavier and more aromatic compounds may degrade somewhat more slowly. Organisms are usually chosen from those found around old oil spills; especially prepared organisms are not always essential. Biodegradation can be relatively inexpensive (perhaps little more than \$1.00/1000 gal), but the cost will be affected by the rates at which the contaminants can be degraded. If the excess biomass can be easily handled as a non-toxic waste, the waste volume should be small. However, possible accumulation of uranium, Tc, other metals, and PCBs should be considered if they are also present in the groundwater. Further development costs should be small, at least for ex situ processes.

Science/Technology Needs: Tests with the actual groundwater is needed to establish degradation rates. Other contaminants will affect degradation rates, including some metal ions that inhibit microorganisms. Many metals may also "adsorb" on the biomass and could affect the treatment of excess biomass. This needs to be assessed.

Implementation Needs: Biodegradation in ex situ reactors involves only normal implementation needs. If in situ biodegradation is to be used, good knowledge of groundwater flow and methods for getting nutrients and oxygen to the contamination is needed.

Author: J. Watson

References:

(See references for VOCs in Groundwater.)

CHEMICAL OXIDATION WITH HYDROGEN PEROXIDE AND OZONE

REMA-94-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Fuel-based hydrocarbons

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Adsorption, stripping, biodegradation

Technology: Chemical oxidation

Status: Accepted. Chemical oxidation with hydrogen peroxide and ozone (often catalyzed) is commercial technology used in the food industry and in other waste problems. Ultraviolet radiation is helpful with more refractive compounds, and that form of oxidation has been demonstrated at DOE sites. Supercritical water oxidation has been demonstrated and is offered commercially. Supercritical water oxidation will oxidize even most of the more refractive organic compounds. Supercritical water oxidation appears to be the most expensive of these options principally because of the need to compress the oxygen to the high pressures required. If sufficient organic compounds are available, the heat of oxidation will be sufficient to supply the thermal energy required; cooling may even be needed. Costs can range from very low (for peroxide oxidation of waters with low organic content) to high (for supercritical water oxidation). Waste volume should be minimal.

Science/Technology Needs: Treatability tests to confirm the total oxygen demand and the ability of the less aggressive oxidation processes to suitably degrade the contaminants. None of the fuel based hydrocarbons that are most likely to be present at K-25 are believed to be particularly refractory to oxidation.

Implementation Needs: Although commercial equipment for some forms oxidation are available, a suitable form of oxidation needs to be selected.

The costs and reliability of ultraviolet catalyzed oxidation is likely to make this an increasingly attractive approach. Its ability to handle chlorinated compounds as well as hydrocarbons adds to its attraction. Unusually severe problems with solids formation (such as insoluble iron oxides) could limit its used with some groundwaters.

Author: J. Watson

February 26, 1993

CHEMICAL OXIDATION WITH HYDROGEN PEROXIDE AND OZONE

REMA-94-OG

References:

(See oxidation of VOCs in Groundwater)

February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater and surface water

Problem Area/Constituents: PCBs in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Adsorption of PCBs on carbon

Status: Accepted. Adsorption techniques for removing hazardous organics including PCBs from aqueous streams has been practiced widely for municipal and industrial water and wastewater treatment systems on medium to large scales.¹ Activated carbon, coal chars, some naturally occurring soils and clays as well as biomass have been demonstrated to act as adsorptive surfaces for PCB removal for aqueous solutions.² The adsorptive capacity of any material is largely a function of the total organic carbon (TOC) content. The unique adsorption constant for a given material can be calculated using a linear relation between the quantity of PCB adsorbed per unit weight and the equilibrium concentration of PCB in solution. Adsorption of high molecular weight, low solubility PCB compounds is more easily accomplished, yet several others factors including temperature, flow rate, retention time and adsorbent particle surface area greatly influence adsorption rates.

Regeneration of carbon beds is an important aspect of the waste management and cost for removing PCBs from K-25 by adsorption. In many cases, vendors will exchange carbon beds and take "spent" beds for regeneration in their facilities. However, few, if any companies will accept carbon beds loaded with PCBs for regeneration at their site. If the possibility exists for accumulation of radioactivity on the carbon, probably little chance exists that a vendor would accept a carbon bed for regeneration that contained both PCBs and radioactivity. Thus, if the beds are to be regenerated to concentrate the PCBs and reuse the beds, the regeneration is expected to be done "on-site."

The cost of adsorption is expected to be high if the beds cannot be regenerated, but the costs will depend upon the concentration of the PCBs and the maximum loading of the beds. Waste volumes will be large if the beds are not regenerated.

Development efforts should include a study of newer regeneration methods such as the use of supercritical fluids and could cost a few million dollars.

Science/Technology Needs: Site-specific information would be required to implement adsorption techniques upon K-25 groundwater. Thorough characterization of PCB contaminants would be necessary to determine their concentration and solubilities in the groundwater source. Additional consideration must be given to the disposal or regeneration of the proposed adsorbent. A critical factor in implementing adsorption technologies will involve the method used to regenerate spent beds, this area must be focused upon before attempting large-scale treatment. Bench-scale testing or treatability studies of candidate adsorbents could be conducted fairly inexpensively. Large-scale reactor designs should not be difficult to develop, given that a variety of systems currently exist and are easily modelled.

Large-scale testing and demonstrations. Large- or full-scale adsorption systems at K-25 would require a thorough understanding of the subsurface environment and the extent of the PCB contamination. Significant well development and groundwater sampling would be involved. Target treatment objectives must be established, however, current drinking water standards may be employed. Long-term operation of pump-and-treat systems can be costly, particularly if regeneration costs are factored in. Mixed waste contamination would present a significant problem, especially in the regeneration of beds. Pretreatment may also be a consideration depending upon existing groundwater quality.

Implementation Needs (Facility Needs): Costs for supplying adsorbents can be high depending upon local demand and availability. Granular activated carbon can be very expensive particularly when regeneration costs are considered. Locally available sources of adsorbents such as earth materials should be explored as alternatives to GAC. Integrated treatment and disposal techniques should be investigated for handling the spent adsorbent. For instance, it might be possible to biologically degrade the PCBs and regenerate the spent beds or spent adsorbent and PCB-laden soils might be mixed and treated before disposal.

Author: J. Watson

References:

1. D.G. Ackerman et al., *Destruction and Disposal of PCBs by Thermal and Nonthermal Methods*, Noyes Data Corporation, Park Ridge, New Jersey, 1983.
2. R.A. Griffin and E.S.K. Chian, "Attenuation of Water Soluble Polychlorinated Biphenyls by Earth Materials," EPA/600/2-80/027, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1980.

EM Problem: Remedial action

K-25 Site Problem: Contaminated water

Problem Area/Constituents: PCBs in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Biodegradation of PCBs in groundwater

Status: Predemonstration. Water-soluble PCB isomers have been shown to be biodegradable by mixed microbial cultures in laboratory experimentation.^{1,2} Mixed microbial cultures isolated from soils and sediments exposed to PCBs before testing. Experimental results suggested that cometabolic degradation of PCBs was faster and more complete, and lower chlorinated isomers were more easily attacked by bacterial populations. Wastewater activated sludge treatment also poses a possible method for degrading PCBs though it has been shown that PCBs tend to accumulate in the sludge as the less degradable, more highly chlorinated isomers adsorb to bacterial cell walls and settle out in thickened floc.

- The potential for developing a successful bioreactor to remove PCBs from groundwater is uncertain, especially for the more refractive highly chlorinated compounds.

Although it is too early to estimate costs for biodegradation with much accuracy, there is hope that the costs can be low. The costs will depend upon the degradation rates that can be achieved; these determine the reactor size. The waste production rate will be low, principally excess biomass. Several million dollars are likely to be needed to develop and demonstrate bioreactors for PCBs.

Status/Technology Needs: The degree of solubility of PCB compounds influences their transport in groundwater as well as their availability to biodegradation.³ Solubility of PCBs is related to the degree of chlorination of the biphenyl structure. It is, therefore, important to determine these characteristics before initiating biodegradation studies. Biodegradation is greatly influenced by the concentration of PCBs and the presence of other organic materials and dissolved salts in the aqueous solution. Carbon sources also must be available as growth substrate for bacterial populations. Thorough characterization of K-25 groundwater would be essential to developing laboratory- and field-scale bioremediation systems. PCBs are relatively insoluble in water and readily adsorbed to soil particles yet very soluble in the presence of organic solvents. An abundance of soluble PCBs in a groundwater source would

suggest the possibility of additional organic contaminants. A practical method for developing a biomediation system would be to culture local bacterial populations in the presence of the contamination source(s). It will be desirable to confirm the presence of degradation products, possibly by using PCBs with isotopic tracers. The toxicity of any products of incomplete degradation will need to be checked.

Large-scale testing and demonstrations. This level of testing would require significant site-specific treatability tests with demonstrated bacterial populations. Pump-and-treat methods would most likely be employed because of the degree of control that can be applied in such systems. Biodegradation of PCBs can be a rapid phenomenon, yet because PCB mobility in subsurface environments is very slow, large-scale applications may require long-term operation to achieve complete site remediation.

Implementation Needs: Costs for this type of treatment are not well defined; however, because much of the monitoring/sampling, analytical, pump-and-treat, and similar equipment is currently available in the market, this method should be very cost effective.

Author: J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: PCBs in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Chemical oxidation/reduction—PCBs in groundwater

Status: Predemonstration. Oxidation reactions have been examined using hydroxyl radicals, generated with Fenton's reagent, to degrade soluble PCBs in aqueous solutions.¹ This type of oxidation reaction appears to be pH dependent requiring acidic buffers to maintain the pH range within 2.3–4.3. Highly chlorinated PCB compounds are more resistant to the reaction and exhibit lower reaction rates. Reduction reactions or dehalogenation have been examined for PCBs though the efforts have concentrated largely upon soil rather than water contamination. A surfactant based electrocatalytic system using carbon felt cathodes has been demonstrated in laboratory-scale applications.² This reaction involved an aqueous PCB solution contacted with a lamellar surfactant during electrolysis. Again, pH was a critical factor in the reaction, pHs above nine significantly decreased reaction rates. Alkaline metal hydroxide/polyethylene glycol (APEG) has been demonstrated in full-scale applications for dehalogenating PCBs (not oxidation) in soil,^{3,4} but the literature does not offer an example of this reagent's use upon groundwater. Ultraviolet catalyzed oxidation is nearing acceptance, even for most chlorinated compounds. However, backup carbon beds may be recommended for PCBs. Costs are likely to be moderate, perhaps a few dollars per 1000 gal. The waste will consist largely of backup adsorption beds and any solids that may precipitate in the reactor. Several participants in the Environmental Protection Agency SITE program have developed chemical oxidation technologies that may be capable of complete destruction of PCBs in aqueous solutions.⁵

Science/Technology Needs: Further laboratory- and bench-scale tests should be conducted to determine feasibility of full-scale applications of these chemical oxidation/reduction reagents. Emphasis might be placed on establishing reagent-to-PCB ratios required to achieve a specific percentage of contaminate reduction, say 90% or 95%. The hydroxyl radical and/or surfactant-based electrolysis systems should be scaled up and attempted with K-25 groundwater samples with known quantities of PCB contamination. The precipitation of iron oxides in the reactor and coating of these and other solids on the ultraviolet lamp surfaces could limit the use of this technology.

Large-scale testing and demonstrations. Demonstrations of chemical oxidation/reduction technologies are probably contingent upon results of the experimental work suggested above. Large-scale testing would require target PCB remediation levels and a significant amount of analytical work to demonstrate that PCB species and reaction by-products in the treated effluent were within acceptable levels. Applications of these technologies could take in situ or pump-and-treat configurations via adaption and modification of existing well designs. Of course, a comparative analysis of these and other PCB remediation technologies would be required to establish the most cost-effective treatment scenario.

Implementation Needs (Facility Needs): Assuming full-scale implementation of any of the above chemical treatments for PCB contaminated groundwater proves feasible, several issues will need to be addressed. Operating costs are not mentioned in the cited references pertaining to water based applications, these expenses may be significant depending upon costs and availability of chemicals. Equipment costs for pumping groundwater and delivering chemicals are not likely to be different from other remediation technologies and may prove to be a one-time capital investment.

Authors: D.E. Beck, J. Watson

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: PCBs in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Dechlorination with iron

Status: Predemonstration. Recent results from the University of Waterloo (Canada) have indicated that many chlorinated organic compounds, including common pollutants such as TCE and PCBs, can be dechlorinated by slowly passing them over beds of metals; iron can be particularly effective.¹ Different sources of iron and iron alloys gave different dechlorination rates. These results are not known to have been reproduced by other workers, and for that reason, the results should be considered speculative. However, the consequence of a relatively inexpensive and low temperature process which would convert toxic chlorinated compounds into non-toxic or much less toxic and easily biodegradable compounds certainly should be investigated. Costs could be low, and waste volume would be minimal. A few million dollars will probably be needed for development and demonstration.

Science/Technology Needs: First the practical dechlorination rates reported by the Waterloo group should be verified elsewhere and tested over a range of water compositions. The mechanisms and rate controlling steps in the dechlorination should be determined, and parameters such as iron or solution properties that affect dechlorination rates should be explored. Then practical testing should be undertaken using real waters and engineering scale equipment.

Large-scale testing and demonstrations. If successful this technique may offer the potential for in situ dechlorination in groundwater plumes using trenches or other underground structures as well as in more conventional packed beds operating ex situ. The amount of treatability testing and demonstrations with K-25 groundwater will depend upon the importance found for parameters of different waters.

Implementation Needs: No costs estimates would be meaningful for a process which may be just starting serious testing and evaluation. However, the simple materials used suggest that costs should be low unless the rates are slow enough that unreasonably large beds are required. If the technique can be used in situ, the costs of large beds may not be great. If the

DECHLORINATION WITH IRON PARTICLES

REMA-104-OG

iron does not become contaminated with other pollutants, the waste volume should be small. Adsorption of Tc on the iron particles could be a positive result since it would remove Tc as well as dechlorinate the organic pollutants, but this would also contaminate the iron and may make it a solid waste.

Author: J. Watson

References:

(Contact author for reference details.)

February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Heavy metals and chromium in water (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Adsorption on activated carbon

Status: Accepted. Sorption on fixed media such as activated carbon and ion-exchange beds is an excellent polishing technique.¹ Several other heavy metals should also be removed.

Activated carbon adsorption effectively removes chromium from water.² In a bench-scale system using two different chemically treated carbon-based materials in columns, chromium was very effectively removed. One carbon column had a very high capacity to remove chromium: equal to "1100 column volumes."³ Activated carbon is available in many sizes, densities, source materials (coal, wood, peat, lignite), and with various "enhancements."

Costs for process system will be moderate (a few dollars/1,000 gal.). Costs for waste disposal may be significant, especially if the chromium is not removed from the carbon.

Wastes. The spent carbon or concentrated chromium, if regeneration is practical.

Science/Technology Needs: Tests with K-25 groundwater will be needed. Effects of principal contaminants need to be evaluated. Selection of specific carbon for given treatment is necessary. Regeneration and recovery or concentration of Cr should be considered.

Implementation Needs: For groundwater remediation, portable systems may be available commercially. The fate of radioactivity needs to be determined, principally to determine whether spent sorbent is a mixed waste. Regeneration to minimize waste volume should be considered.

Author: D.E. Beck

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ADSORPTION/COPRECIPITATION WITH SULFIDES AND/OR IRON

REMA-112-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Heavy metals and chromium in water (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Adsorption, biosorption, iron exchange

Technology: Adsorption/coprecipitation with sulfides and/or iron. Adsorption/coprecipitation of chromium using sulfides and/or iron or commercial preparations.

Status: Demonstrated. This method involves reduction of Cr(VI) to Cr(III) followed by precipitation of hydrated Cr_2O_3 which is removed by filtration. In water-treatment plants, precipitation or coprecipitation is generally followed by sludge removal and filtration, supernatant treatment with anionic polymers to flocculate and suspend solids that are too fine to filter, and ion-exchange beds for polishing.¹

The hexavalent form of chromium is more difficult to remove from water (also more toxic) than the trivalent; thus, Cr(VI) (hexavalent) must be reduced to Cr(III) (trivalent) before being precipitated. Lime precipitation is the classic method for Cr(III) removal, but it is not discussed here because it is more appropriate for wastewaters than for groundwaters. Iron metal and ferrous iron are reductants, but other chemical precipitants will require pretreatment of the chromium-bearing waters with a reducing agent. Some common reducing agents are ferrous sulfate, sodium metabisulfite, and sulfur dioxide.²

Iron coprecipitation. Using iron metal or iron oxyhydroxides (magnetite, hematite) as coprecipitants/sorbers, Cr(VI) is reduced to form hydrolyzable Cr(III), which is then removed by coprecipitation with (and sorption to) iron oxyhydroxides upon solution neutralization.³ The Cr is precipitated as $\text{Cr}(\text{OH})_3$.⁴ The use of iron metal or ferrous iron can cause other free and complexed soluble metals to coprecipitate also. The iron coprecipitation process can be effective for all the trace metals at a single neutral pH. The iron must be ferrous or iron metal, for chromium reduction, and the pH may be acidic to neutral. Ferric iron will cause Cr(VI) to sorb to its surface and remain in solution.⁵ Ferric chloride is, however, an effective coprecipitation agent for priority trace elements, including trivalent Cr.⁶ Ferrous chloride or ferrous sulfate are used in a single-step coprecipitation process, in which the soluble metals

(among them may be chromium and copper) oxidize the ferrous ions into the ferric state and precipitate out.¹

Other researchers, in attempting to remove chromium from groundwater to less than 50 ppb, found that a 97.9 to 99.5% removal was effected using iron coprecipitation, if sodium metabisulfite was added first, to reduce hexavalent Cr to the trivalent form.⁷ In this experimental work, final concentration was 1-4 ppb, and secondary waste volume was "extremely low" (0.4 gal/1000 gal feed). Efficiency of trace element removal by iron coprecipitation depends on the oxidation state and initial concentration of the trace element, iron dosage, and composition and pH of the general solution.⁸ More than 95% Cr(III) but only 40% Cr(VI) was removed as trace elements in pond water when Fe was added at 14 mg/l, in one laboratory study.⁶ A large amount of sludge is generated, although less than when FeSO₄ is the precipitating agent.⁵

In a process used at Wright-Patterson Air Force Base, chromium reduction is not required before precipitation with ferrous sulfate, sodium sulfide, and a polymeric coagulant.¹

Sodium sulfide is mentioned elsewhere in the literature.⁹ The low solubility and reduced leaching of metal sulfides compared with the hydroxide process (neutralization or iron coprecipitation), improves metal removal efficiency and makes disposal easier and safer.¹⁰ However, in this process Cr(VI) must first be reduced using sodium metabisulfite.

Among the commercial/proprietary sorbants or "precipitants" claimed effective: Thio-Red, a patented polythiocarbonate formula, is used in polishing to remove chelated heavy metals¹¹ Cr(VI) must be reduced before treating with Thio-Red.

Disadvantages. Precipitation with iron oxides may result in significant remobilization of some toxic metals due to microbial iron reduction, particularly under anaerobic conditions. Bacteria use iron as an alternate electron acceptor; this may release the metals associated with iron. Chromium was one of the metals investigated in a study.¹² Cr is less strongly affected than Ni, Cd, or Zn, but a small amount of Cr was solubilized by direct action due to enzymatic reduction of ferric iron.

Diminishing availability of landfill space may contraindicate precipitation methods; these methods generate large volumes of sludges. Every effort should be taken to minimize secondary waste generation.

Advantages. Precipitation with iron metal or other inorganic sorbents produces less waste than sorbing onto organic ion-exchange resins. In addition, the inorganic precipitant is easily incorporated in cement grout for disposal; grouting is an effective stabilization method for mobile species such as technetium.¹³ Materials cost for the metallic sorbents, which may be metallic filings or scrap iron, is very low.

Costs: Process costs are low. One estimate of the process cost for iron co-precipitation is \$353 per million gallons.⁶ That is for a water treatment facility that is sized to treat a peak

flow of 1.5 m³/sec (35 mgd), with an average flow of 26 mgd, with an iron dose of 14 mg/L as Fe. However, if the precipitates are found to contain radioactive contaminants, disposal costs could be significantly higher. The waste volume will be large. Little further development is suggested.

Science/Technology Needs: Basic research to determine extent of chromium remobilization from iron coprecipitation under specific disposal conditions, over time.

If sorption and/or precipitation are the preferred method, the media should be evaluated to optimize efficiency and cost, and minimize secondary waste generation.

Implementation Needs: Removal of pollutants by coprecipitation generates considerable waste. The volume of waste produced will be approximately proportional to the volume of water treated, not proportional to the amount of Cr removed. The large volume of waste that could be produced by this technology could limit its use. However, the existing iron content in K-25 waters could precipitate in some treatment processes, and any coprecipitation/sorption on those solids could be important.

Author: D.E. Beck, Carpenter

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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Heavy metals in groundwater (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Reverse osmosis (RO) will be used to remove dissolved mercury, copper, or chromium from groundwater.

Status: Commercial. An appropriate treatment technology for removal of some inorganics, including mercury, chromium, and copper.¹ To avoid membrane fouling, feed precipitation and filtration pretreatment is generally required (ultrafiltration is an option for pretreatment).² The possibility of metals precipitation in the concentrate should be considered; one authority says RO is not for precipitable metals.³ RO produces a concentrated liquid stream that often must be treated further. Both commercial membranes and commercial RO systems are available. Costs are likely to be relatively high, perhaps several dollars per 1000 gal. RO produces a concentrated liquid stream, not a solid suitable for disposal. Thus, the costs required for further treatment of the concentrate will need to be added to the costs attributed to the RO. The waste volume will depend upon the technique used to remove the metals from the concentrate.

Science/Technology Needs: Treatability studies are needed for any specific groundwater to determine the degree of metal removal, the allowable degree of concentration, and any cause of membrane degradation. a suitable method for handling the concentrated stream of rejected electrolyte will be needed. The materials could be incorporated into a waste form and/or recycled for other uses.

Implementation Needs: RO is usually effective for removal of most metals, but it still leaves a liquid concentrate that must be handled. Waste treatment and disposal is an important question and could add significantly to the overall costs. The volume of waste produced will be determined by the way this concentrated stream is treated. Generally, RO is not selective, so all electrolytes from the original groundwater will be in the concentrate. Thus the volume of waste is determined by the electrolyte in the groundwater, not by the amount of a contaminant in the groundwater. The cost of RO can be moderate to high because of the high pressure and the capital cost of the membrane system. The lifetime of the membrane with the particular groundwater in question can be an important factor in determining the cost.

Waste volume and waste handling costs will depend upon the treatment process used on the concentrate.

Author: D.E. Beck

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1. B.R. Willey, "Finding Treatment Options for Inorganics," *Water/Engineering & Management*, October 1987. pp. 28-31.
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EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Toxic or hazardous metals in groundwater (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Biosorption—Innovative or emerging technologies. Biological materials will be incorporated into treatment processes for removing copper (and other metals) from groundwater. Synergistic combinations of microorganisms (or biochemicals) and polymers will be used in particulate form to act as sorbers for dissolved metal ions.

Status: Predemonstration. Some innovative work is reported in the literature, but work appears to be purely bench scale, at this time. Among the work reported are the following scenarios.

Calcium or sodium alginate (a biopolymer from kelp and some bacterial strains) is used to absorb copper in aqueous media.¹ This method appears to be most successful when copper concentrations are relatively high (~140 ppm) and alginate spheres are formed in situ by dispensing sodium alginate solution directly into reactor. At lower concentrations (10-100 ppm), calcium alginate spheres must be used (because they can be made ex situ); however, the calcium does reduce effective copper binding density. Addition of EDTA seems to enhance copper sorption. The authors state that "absorption of copper by either calcium alginate spheres or semi-rigid algin spheres (formed in situ) should belong to Type IV of ion exchange."

In other work, *Micrococcus luteus* is incorporated into gel beads for the incorporation of strontium from dilute aqueous solutions passing through the packed adsorption column.² No other applications are specifically addressed by the authors, but the implication is that the cell-biopolymer system (with components chosen for desired selectivity) is very promising for selective removal of certain other metal ions. The study suggests that "the combined biosorbent has significant ion-exchange capabilities." It could prove to be much less expensive than commercial IX resins. High adsorption/exchange rates were obtained in this study, indicating good sorbent utilization and high removal efficiency.

The less costly biosorbents are likely to leave regeneration or destruction of the sorbent to concentrate the toxic metals as the most costly part of the technology. There is reason to hope that these costs can be no more than a few dollars per 1000 gal, perhaps less. The

waste volume will depend upon the sorbent regeneration or treatment, but could be moderate to low. A few million dollars may be adequate for further development and demonstration.

Science/Technology Needs: This is an emerging technology with concomitant basic research needs.³ Many biomaterials will adsorb most heavy metals. The major questions concern the maximum loading that can be achieved and fabrication of the biomaterials into beads or other forms for efficient mass transfer. Development efforts should focus on those issues. The adsorption (or ion exchange) capacity of the biological materials needs to be explored and maximized. Selectivity for the toxic materials should also be maximized. Adsorption/exchange rates need to be evaluated, and the biological material needs to be incorporated into a form (such as gel beds) that will give provide good rates and low liquid mixing (dispersion) in the columns. Degradation of biological materials (useful lifetime of beads) should be evaluated.

Implementation Needs: Once a suitable biosorbent is developed, the implementation needs should be normal. One should note that more than a simple biosorbent is needed. There must also be a suitable regeneration or spent sorbent handling system. This technology is not developed sufficiently for meaningful cost estimates. However, a major goal for the use of biological materials is to have low cost (as well as effective) adsorbents. These materials are made of low cost ingredients. Waste volume depends upon the regeneration/concentration method used. With low cost biological materials, there is the potential for degrading or burning the adsorbent and concentrating the toxic materials.

Author: D.E. Beck, J. Watson

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ION EXCHANGE (REMOVAL OF HEAVY METALS FROM GROUNDWATER)

REMA-115-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Heavy metals in water (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Ion exchange. Removal of dissolved metals from groundwater by IX. Organic ion-exchange resins are used to remove Cr, Cu, Hg, and other metals from groundwater.

Status: Accepted. Ion exchange is appropriate for tertiary treatment (such as remediation of groundwater). Hexavalent chromium can be removed by anion exchange. Both anion and cation exchange resins are commercially available. Trivalent chromium and copper are also removable by anion exchange resins. Removal efficiencies are <90% and <95%, respectively, for Cr and Cu.¹ Some resins not only exchange but chelate the heavy metals.²

Removing chromate: The anion-exchange resin used for removal of chromate is originally in chloride, sulfate, or hydroxide form. Generally (for cooling tower blowdown water), a polishing column would be used in series with the primary load column, to meet environmental regulations and minimize the possibility of breakthrough. Waste treatment, in this application, is resin regeneration and regeneration effluent recycle to the makeup water.³ A disadvantage is that capital and operating costs of an ion-exchange unit are relatively high. When concentration is low (that in cooling tower blowdown never exceeds 100 mg/L) so that recovered chromate value is small, the IX method is not economically attractive.³

Removing mercury: In tests to remove soluble mercury from a heavy metals sludge filtrate, Type I strong base anion-exchange resin (Dowex SRB-OH) removed 91.3% and cross-linked PVP resin (Reillex 402) removed 90.2% of the mercury.⁴

The cost of ion exchange systems depend upon the selectivity of the resins for the target contaminants. With poor selectivity, the maximum loading on the resin will be lower. This will result in more frequent regeneration and more extraneous electrolyte in the elute solution. The costs also depend on the total electrolyte concentration in the groundwater. If highly selective resins are found, costs for treating groundwater with normal concentrations of ions should be moderate, perhaps a few dollars per 1000 gal.

ION EXCHANGE (REMOVAL OF HEAVY METALS FROM GROUNDWATER)

REMA-115-OG

The wastes will be formed when the resin is regenerated. The volume of wastes will depend upon the additional electrolyte on the resin and upon the regeneration/treatment procedure. One would expect the waste volume to be moderately more than the mass of electrolyte removed.

Development and demonstration costs (largely to test promising resins, evaluate the ion exchange equilibria and kinetics, and to demonstrate with a small portion of a K-25 stream) should be low, less than a million dollars.

Science/Technology Needs: Laboratory- and bench-scale testing of K-25 groundwaters is needed to determine the efficiency and effectiveness of various ion-exchange systems, and optimal pretreatment. Thorough characterization of samples should be developed. Basic research on secondary waste treatments and/or regeneration is necessary. Ion exchange resins are difficult to dispose of. Selectivity for specific contaminants will affect the amount of secondary waste generated.

Implementation Needs: Mobile ion-exchange systems can be built. One estimate of capital cost for a complete ion-exchange treatment system for groundwater, including all equipment (pumps, tanks, filtration assembly, IX units, monitoring devices, data acquisition system and process controller, and 2.5 miles of pipeline for treated water) is estimated at \$786,800.⁵ Waste disposal or regeneration costs may be significant.

Author: D.E. Beck, J. Watson

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February 26, 1993

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Toxic/hazardous metals in groundwater (Hg, Cr)

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Oxidation/precipitation using ozone

Status: Development or predevelopment. In treating wastewaters, although lime treatment alone will precipitate most metals, the same or better removal at a lower pH can be effected by lime treatment followed by ozonation.¹ This produces less sludge.

Heavy metals which exist in more than one oxidation state can be oxidized to their highest state by ozone, in the pH range of 7 to 9. If the oxidized metal cations form insoluble hydroxides, they can be removed from solution by simple filtration.²

According to the data in cited report,² both chromium and copper are >99.5% removed from solution by lime at a pH of 9.00 and by lime + ozonation at a pH of 7.0.

Note that this approach would be applicable to only some toxic metals that could be problems at K-25. It could even have some harmful effects if significant Cr (III) is oxidized and left as Cr (VI). The cost would be low to moderate, perhaps not much more than a few dollars per 1000 gal, but the treatment level may not be adequate for the metals of most interest. The waste is likely to result largely from precipitated iron oxides; the toxic precipitate is likely to be a minor component.

Science/Technology Needs: Basic research to determine chemistry of the reaction with metals, especially with Cr.

Not cost effective for trace elements.³ Possibly basic research to improve "stamina" of the process is necessary.

A good deal more information is available in the literature on ozonation of organics and such inorganics as sulfides, etc., than on ozonation of metals probably because ozone seems an unlikely candidate for remediation of groundwater from metal ions.

Implementation Needs: This technology probably has limited potential use at the K-25 Site, but implementation needs are expected to be normal. Not likely to be useful for trace concentration of metals.

Author: Beck/Watson

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1. A. Netzer, A. Bowers, "Removal of trace metals from wastewater by lime and ozonation," *Proceedings of the First International Symposium on Ozone for Water and Wastewater Treatment*, R.G. Rice and M.E. Browning, eds., International Ozone Association, Vienna, Virginia, 1975, pp. 731-747.
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3. E.R. Alley, P.E., Alley, Young, and Baumgartner, Inc., Nashville, Tennessee, personal communication to D.E. Beck, July 27, 1990.

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Technetium in groundwater

Reference Requirements: Adsorption/coprecipitation of technetium from water using inorganic materials. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Reductive adsorption of Technetium from groundwater

Status: Predemonstration. Inorganic sorbents and reducing agents show great potential as effective means of removing technetium from contaminated ground water or other aqueous solutions. Among them are the following examples.

Iron metal. Either as iron filings, or as scrap iron, iron metal is a very inexpensive and efficient means to reduce and sorb Tc from ground- or wastewater. The pertechnetate ion is reduced to TcO_2 .¹ The kinetics are relatively slow; however, heating to 50°C effectively speeds the reaction.² Recent experimental use of packed bed columns has successfully removed Tc from aqueous raffinate solutions. The volume of wastewater treated in the cited experiments for a given volume of iron sorbant was significantly higher than for organic polymers, including ion-exchange resins.³ An added advantage is that technetium-iron compounds are very stable. It has been found that high-iron groundwater may reduce Tc and prevent its mobility under anoxic conditions; deep groundwater systems are often reducing and Tc is likely to be present in the reduced form).⁴ If both iron and sulfide-bearing minerals are present, the effects appear to be additive.⁵ Work has been done only at the bench-scale level. Development work and scale-up is needed.

Iron sulfide. Fe_3O_4 was the most effective of several iron sulfide compounds tested for technetium removal.⁶ Sulfide treatment is also effective for the removal of many toxic/priority metals from aqueous solutions.³ Again, bench-scale work is reported in the literature, but development and scale-up work is needed.

Zinc metal. Zinc metal has been demonstrated to reduce and sorb technetium from simulated groundwater.⁷ Sorption is independent of Tc oxidation state and is effective at pHs between 2 and 9 (Del Cul says that because of the amphoteric characteristics of zinc, the effective pH range is limited to between 4 and 8). The kinetics on zinc dust are very rapid; within 5 minutes, 95% of the Tc in a 10^{-10}M solution was sorbed. Desorption is achieved with NaOH.

This is likely to be a low to moderate cost treatment, perhaps a few dollars per 1000 gal. The cost will depend upon the maximum Tc loading that can be achieved on the solids (when in equilibrium with the K-25 water); this hasn't been determined. The waste volume will be the adsorption/precipitate bed itself and, of course, also depends upon the maximum loading as well as the Tc concentration. The waste volume probably will be moderate when compared with wastes from alternative treatment methods. One proposal suggested that \$1.25 M would be needed to develop the technology.

Science/Technology Needs: In principle, customized sorbers could be synthesized for recovering technetium from groundwater with inorganic sorbers. Development is necessary to prepare materials with high surface area and appropriate particle size for their use in continuous applications.⁸ Development to pilot plant scale will be needed. Waste treatment focus may be on microwave sintering for spent inorganic sorbers.

Implementation Needs: Development costs are estimated at \$1.25M for a three year development plan and technology transfer to private industry of advanced inorganic sorbents for the selective removal of technetium and other contaminants.⁹

Author: D.E. Beck

References:

1. G.D. Del Cul, P.E. Osborne, and D.E. Beck, *Evaluation of Alternatives for Best Available Technology Treatment and Retreatment of Uranium-Contaminated Wastewater at the Paducah Gaseous Diffusion Plant C-400 Facility*, K/QT-394, Part 1, Martin Marietta Energy Systems, Inc., Oak Ridge, Tennessee. January 1991.
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3. G.D. Del Cul, W.D. Bostick, D.R. Trotter, and P.E. Osborne, "Technetium-99 removal from process solutions and contaminated groundwater," *Separation Science and Technology*, 28(1-3), published by Marcel Dekker, Inc., 1993, pp. 551-564.
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8. G.D. Del Cul, "Technetium removal from contaminated groundwater, recycling of cleaning-, decontamination-, and process-solutions, and soil washing solutions," OR-4DAH-93, Office of Technology Development, 1992.
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ION EXCHANGE FOR REMOVAL OF Tc FROM GROUNDWATER REMA-122-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Technetium in water

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternatives: Sorption, precipitation

Technology: Organic ion-exchange resins for removal of technetium from groundwater

Status: Demonstration. Strong-base anion exchange resins are often chosen for the pertechnetate anion.^{1,2,3} This media has a very high affinity for the pertechnetate ion, although high concentration of other anions such as nitrates and sulfates can compete for ion sites. At Portsmouth, one strong base anion exchange resin (Dowex SRB-OH) is used as a standard unit operation to remove Tc. These resins shouldn't be used with acidic solution but could be effective with groundwater. One disadvantage is that they are not selective, and many other ions can be sorbed which will produce a mixed waste. Incorporation of waste Dowex SRB-OH resins in grout has been demonstrated, with about 40% by volume waste loading.⁴ For relatively dilute solutions such as groundwater, without many competing anions, Dowex SRB-OH resin is more efficient for Tc-99 removal than PVP resins (below).¹ The anion exchange resin is commercially available.

Costs will depend upon the maximum resin loading in equilibrium with K-25 soil and the regeneration or spent resin treatment. Costs will probably be moderately high. Waste volume will depend upon the regeneration procedure or the handling of spent resin; the volume could be low. Development costs to evaluate resins and demonstrate on a small scale could be less than a million dollars.

Polyvinylpyridine polymer based resins are selective for technetium in very concentrated solutions or sludges.^{1,5,6} It is estimated that far more than 100 bed volumes of Tc-contaminated groundwater could be treated before breakthrough occurs.⁶ It is very difficult to remove Tc from the resin, although removal with very strong acids might be possible. In either case, the secondary waste presents a problem. The PVP resins are commercially available.

Science/Technology Needs: Laboratory and bench-scale testing of K-25 groundwater samples will be necessary, to determine actual efficiency. Thorough characterization of samples should be developed.

ION EXCHANGE FOR REMOVAL OF Tc FROM GROUNDWATER REMA-122-OG

Some filtration will probably be necessary upline of the IX process, and reverse osmosis is recommended prior to IX also.⁶

Basic research on secondary waste treatment or regeneration is important to minimize disposal costs. A proposal exists to develop an innovative method(s) to treat spent ion exchange resins by catalyzed molten salt combustion, at a cost of \$1.4 M over a 3-year period.⁷

Implementation Needs: Capital cost for a complete ion-exchange treatment system for groundwater, including all equipment (pumps, tanks, filtration assembly, IX unit(s), monitoring devices, data acquisition system and process controller, and 2.5 mi. pipeline for treated water is estimated at \$786,800.⁶ Operating costs were reported at \$6.70 per 1000 gal in 1988.⁸ Waste disposal or regeneration costs may be significant.

Author: D.E. Beck

References:

1. G.D. Del Cul, W.D. Bostick, D.R. Trotter, and P.E. Osborne, "Technetium-99 removal from process solutions and contaminated groundwater," to be published in *Separation Science and Technology: 7th Symposium on Separation Science and Technology for Energy Applications*, Knoxville, Tennessee, October 20-25, 1992.
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REVERSE OSMOSIS (RO) TO REMOVE Tc FROM GROUNDWATER

REMA-123-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Technetium in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Reverse osmosis (RO) to remove Tc-99 from water

Status: Predemonstration for RO with Tc¹ operates by ionic salt rejection. The solvent moves through the membrane from a concentrated solution to a more dilute one using pressure exceeding that of the osmotic pressure. Because this method rejects all ions present in the solution, the secondary waste volumes can be large. In one series of tests, for example, the secondary waste volume was 114 gal/1000 gal groundwater for RO (vs, for example, 0.1 gal/1,000 gal groundwater using a SLM).¹ However, Tc was reduced to below minimum contaminant levels in the tests.

There are three basic types of membrane configuration: tubular, spiral-wound, and hollow fiber. Tubular membranes process dirty feed with minimal pretreatment and are easy to clean, but they have a high holdup per unit area, are very expensive, and require a great deal of floor space. Advantages of spiral-wound and hollow-fiber membranes are their low cost, compactness, and low holdup per unit area, but they are very difficult to clean.

Although RO has a good record concerning rejection of uranium,² there isn't much data on RO with technetium. One proposal for removing Tc from groundwater does call for an RO pretreatment, to remove nitrates so that they will not compete with technetium for ion-exchange sites.³ Another series of tests treated Tc-contaminated water (786 pCi/L) with RO and reported that Tc and U were both reduced to well below the maximum contaminant level (MCL). The percent rejection for Tc was 95.3 after nine passes.¹ The concentrate amounted to about 12% of the original groundwater volume. That amount could be prohibitively large, since it requires further treatment for disposal if a great amount of water is treated.

Reverse osmosis is relatively expensive if the concentrate treatment taken into account, probably several dollars per 1000 gal, perhaps more if several stages are required to reach the required degree of rejection. Waste volumes could be relatively high, but they depend

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REVERSE OSMOSIS (RO) TO REMOVE Tc FROM GROUNDWATER

REMA-123-OG

upon the treatment of the concentrate. Significant development, perhaps a few million dollars, may be needed to make RO an accepted technology for Tc removal.

Science/Technology Needs: Basic research is needed to determine whether RO can be applied efficiently and effectively to Tc removal from groundwater.

Cost investigation is also necessary, particularly of membrane system capital costs and membrane delicacy (frequency of replacement). One estimate for an RO unit and replacement membranes for one year is \$160,000 (130K for the unit, 30K for the membranes), not including installation or operating costs.³

Scale-up to pilot plant will be required if RO appears feasible, along with optimization of parameters.

Implementation Needs: RO is a relatively expensive process. There are insufficient data on RO for Tc. The disadvantages of RO seem to preclude its use in groundwater remediation except possibly in unusual cases, where a diverse set of ionic contaminants must be removed. (RO might work equally effectively for all but the secondary waste stream is apt to be prohibitively large.)

Author: D.E. Beck

References:

1. K.M. Hodgson and L. Garrett, "Demonstration of Technologies to Remove Contamination from Groundwater," *Proceedings of the Third International Conference on New Frontier for Hazardous Waste Management*, Pittsburgh, Pennsylvania. (Westinghouse Hanford Company, Report WHC-SA-0367). September 10-13, 1989.
2. G.D. Del Cul, P.E. Osborne, and D.E. Beck, *Evaluation of Alternatives for Best Available Technology Treatment and Retreatment of Uranium-Contaminated Wastewater at the Paducah Gaseous Diffusion Plant C-400 Facility*, K/QT-394, Part 1, January 1991.
3. J. Fancher, Westinghouse Hanford Company, personal communication to W.D. Bostick, Martin Marietta Energy Systems, Inc., (class paper, "Remediation of Groundwater Contaminated with Uranium and Technetium").

SUPPORTED LIQUID MEMBRANE (SLM) TO REMOVE Tc-99 FROM WATER

REMA-124-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Technetium in water

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: Support liquid membrane (SLM) to remove Tc-99 from water

Status: Predemonstration, for SLM.¹ Supported liquid membranes operate on a molecular level, removing metal ions into an organic phase as the aqueous solution passes through the cell. It is "a combination of extraction and stripping under nonequilibrium conditions."¹ The process can achieve large concentration factors and show good selectivity when the appropriate extractant is used. The extractant (carrier) volume requirements are low, and the process is simple. In one series of tests, the Tc from 100 gal of groundwater was concentrated into 4 gal. Its concentration in the 96 remaining gallons had been reduced from 786 to 2 pCi/L in 48 hours.² SLM was one of several membrane processes recommended for U and Tc removal from groundwater prior to biologically treating for nitrate and CCl_4 .³ Pilot-scale experience with the SLM process is limited.

This technology is not sufficiently well developed for reliable cost estimates. If costs were based upon the low degree of concentration and the slow rates reported in the current preliminary experiments, the costs probably would be unreasonably high, but further development may be able to reduce those costs greatly. The waste volume would depend upon the concentration and composition of the concentrated stream. With initial data, this volume seems large, but significant improvements may be achievable. Development costs will probably be a few million dollars.

Science/Technology Needs: Basic research is needed to determine the most effective carriers in SLMs. This technology is in an early stage of development.

Scale-up to pilot plant, and optimization of parameters.

Membrane cell configurations will need to improve rates and, possibly, handle solids. Methods must be developed for handling the concentrate stream. The behavior of other components in K-25 waters in this technology must also be understood.

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SUPPORTED LIQUID MEMBRANE (SLM) TO REMOVE Tc-99 FROM WATER

REMA-124-OG

Implementation Needs: SLM is a process still being developed; therefore, implementation needs will probably be high. Design, construction, and testing are necessary at every level from bench scale upward. There is insufficient information or process description available to assess either costs or waste volume.

Author: D.E. Beck

References:

1. G.D. Del Cul, P.E. Osborne, and D.E. Beck, *Evaluation of Alternatives for Best Available Technology Treatment and Retreatment of Uranium-Contaminated Wastewater at the Paducah Gaseous Diffusion Plant C-400 Facility*, K/QT-394, Part 1, January 1991.
2. K.M. Hodgson and LaPriel Garrett, "Demonstration of technologies to remove contamination from groundwater," *Proc. Third International Conference on New Frontiers for Hazardous Waste Management*, Pittsburgh, Pennsylvania, September 10-13, 1989. (Westinghouse Hanford Report WHC-SA-0367).
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IN SITU REDUCTION AND FIXATION OF Tc IN GROUNDWATER

REMA-125-OG

EM Problem: Remedial action

K-25 Site Problem: Contaminated groundwater

Problem Area/Constituents: Technetium in groundwater

Reference Requirements: CWA. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Chemical separation

Technology: In situ reduction and fixation of Tc in groundwater

Status: Conceptual/evolving technology. The in situ reduction of a metallic, radioactive, or organic groundwater contaminants in a soil reaction zone is a novel approach to remedial action.^{1,2} Construction of an in situ reaction curtain of ferrous iron is proposed, through which a plume of groundwater might travel.¹ As the water passes through the curtain, it is cleansed when Tc-99 and other reducible metals are reduced and sorbed to the iron surfaces. A proposed study would determine the applicability of such treatment to a plume of groundwater at the PGDP.

The costs should be low, and there will be a minimal volume of secondary wastes.

Science/Technology Needs: The Paducah study is still in the proposal stage. An estimate of development costs is \$380,000 over a three-year period.¹ This may not complete the development and demonstration.

The mechanisms described take place under anoxic conditions. However, "based on existing groundwater data for Paducah, it appears the RGA is neutral to slightly oxidizing."³ If the method does succeed in removing Tc, it is important to determine whether soil disturbance would reoxidize and release the technetium. Not only bench scale, but also field tests will have to be done. Technetium mechanisms and behavior are not well understood.

Regulatory issues must be addressed. This process may not be viewed as an acceptable permanent closure method.

Implementation Needs: This can be viewed as an in situ version of reductive adsorption, and the potential low cost for placing inexpensive material in situ and operating with little maintenance cost is most attractive. However, the ability to leave the iron barrier in place indefinitely needs to be evaluated and approved by regulators. If iron must be excavated, the

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IN SITU REDUCTION AND FIXATION OF Tc IN GROUNDWATER

REMA-125-OG

waste volume could exceed that from ex situ beds because there can be less control of flow rates and flow distributions needed for efficient loading of the iron beds. This could cause a similar rise in overall costs. One serious question will concern the long-term stability of the immobilized Tc. Can oxidation and remobilization be prevented long enough for sufficient Tc decay; the Tc would remain in the soil.

Author: D.E. Beck

References:

1. J.D. Marsh, Jr., G.K. Jacobs, and D.K. Solomon, "Treatability of a TCE and Tc plume in groundwater by in-situ metal-catalyzed abiotic degradation and reduction/sorption," proposal submitted to the Environmental Restoration Group, Paducah Gaseous Diffusion Plant, November 1992.
2. K. Schwitzgebel and M.D. Erickson, "In situ chromate reduction and metal fixation in soil," *Emerging Technologies for Hazardous Waste Management: Book of Abstracts for the Special Symposium, Atlanta, Georgia, September 21-23, 1992*. D.W. Tedder, ed., American Chemical Society, Washington D.C., 1992. pp. 644-647.
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EM Problem: Remedial action

K-25 Problem: Groundwater contamination

Problem Area/Constituents: VOCs in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Corona discharge

Status: Evolving. This is one of several high-energy techniques for introducing radicals and ions into soils, water, or air which will destroy toxic organic compounds. Corona discharge has developed a significant following and is being developed in the DOE program.¹ The technology is believed to produce ions and radicals that can penetrate the more open arid soils and reach organic contaminants such as the chlorinated VOCs. However, the technology should work for groundwater as well as soils, perhaps even better. The mechanism for destruction of organic compounds does not appear to be understood. This leaves important uncertainties in the range of contaminant and water conditions for which the technology is likely to be effective. Although other reactive approaches such as those using oxidants and reductants may involve some of the same degradation reactions, they are viewed as better understood at this time and thus sometimes less speculative.

The same general approach can be applied to destruction of VOCs after they are vaporized via vacuum extraction or other method. This use of the technology could be applied at any site, but for such uses, the technology would have to compete with more other options such as condensation with backup carbon beds which can produce a more concentrated stream for subsequent use or destruction.

With the limited information available at this time, the cost of corona discharge treatment of soils can only be speculative. Future work with the VOCs in Arid Soils Integrated Demonstration may bring this technology forward and raise its evaluation. Until the technology is better understood, it will be viewed as speculative. The cost of corona discharge and other high electrical potential approaches will depend upon the time required for treatment. Corona discharge requires relatively low rates of energy input, but other high-energy approaches may require significantly more energy. The reliability should be much better for treatment of water than for treatment of soils. One could guess that the costs would be moderate (perhaps a few dollars per 1000 gal). The waste production should be minimal.

The cost for fully evaluating and demonstrating these approaches is likely to be a few million dollars.

Science/Technology Needs: The major need for this technology (or group of technologies) is to develop an understanding of the mechanisms of degradation. This is necessary to provide confidence in the range of pollutants and conditions for which the technology can be applied. Tests to be considered for evaluating its applications to K-25 include verification of the degradation by observing degradation products (possibly with radiotracer compounds) and identifying of reactive groups and parameters that affect the lifetime of the groups in K-25 waters. Great care must be devoted to the common problem with studies of VOC degradation, correcting the results for losses of VOCs to evaporation.

Implementation Needs: There are no known unusual implementation problems. The required treatment level needs to be established. The presence of residual partially degraded compounds needs to be checked.

Author: J. Watson

References:

1. R.J. Lenhard, M.A. Gerber, and J.E. Amonette. "Preliminary Evaluation of Selected In Situ Remediation Technologies for Volatile Organic Compounds in Arid Sites," *PNL-8333*, 1992.

EM Problem: Remedial action

K-25 Problem: Groundwater contamination

Problem Area/Constituents: Chlorinated VOCs in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Ultrasonic destruction of organics

Status: Preconceptual/evolving technology. Ultrasound is believed to degrade organic compounds by producing very small micro-bubbles that generate very high temperatures locally as the bubbles disappear. Thus this is essentially a thermal degradation technique, but the temperature is created in a novel way. Little experience and few publications are available on the method, but proposals have been submitted based upon favorable tests with carbon tetrachloride.¹ It is likely that the technique could also be used with PCBs and hydrocarbons. It is suggested to be potentially useful for soils and sludges as well as water. Not nearly enough data exist to determine the energy input and the costs required. If very high temperatures are always obtained, it may be possible to have moderately high destruction overall without producing significant quantities of immediate products which can be especially toxic. Prices are likely to be moderately high, perhaps a few dollars per 1000 gal, but there is little basis for any estimate at this time. Development costs could be a few million dollars. There should be no significant waste production.

Science/Technology Needs: Better understanding is needed of bubble behavior and the effect of sonic energy and frequency on degradation rates. Experiments and mathematical models should investigate the temperatures reached, the temperature distributions, and the temperature history (time at temperature) around bubbles and correlate these to degradation rates and efficiencies. Mass balance of VOCs is needed to confirm destruction vs possible evaporation.

Implementation Needs: It will be necessary to compare this method of thermal destruction with alternatives to ensure that this is the most cost-effective way to supply energy to degrade the pollutants of interest. The production of toxic intermediate compounds should also be checked.

Author: J. Watson

References:

1. DOE/EM/OTD TTP CH201202, *Ultrasonic Process for Detoxifying Groundwater and Soil*, 1992.

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EM Problem: Remedial action

K-25 Problem: Groundwater contamination

Problem Area/Constituents: Chlorinated VOCs in groundwater

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Treatment

Alternative: Destruction

Technology: Electron beams, high energy

Status: Predemonstration. This technology uses high-energy electron or ion beams to generate active radicals in water which will destroy various organic compounds. Little published results were found, but the idea has been proposed by at least two DOE laboratories.¹² Both proposals refer to preliminary experiments with positive results. This is an innovative approach, and the results should be compared with results from more conventional approaches such as ultraviolet and catalyzed oxidation. Numerous compounds can be produced by electron beams and ion beams that could degrade organic compounds, but little information was found on the mechanism of degradation.

Cost for high-energy degradation would appear to be high, especially if extremely large and expensive equipment is required. Until the requirements of the accelerator are known, the costs for this technology can only be guessed. However, this does not appear likely to be a low-cost approach, especially if the accelerators have to be large. Development costs could also be relatively large, especially if large test equipment is required, but tests can be made on low groundwater rates. There should be little waste produced.

Science/Technology Needs: The first need is to determine the requirements on the accelerator. Therefore, the sensitivity of the phenomenon to acceleration voltage or beam current must be determined. This will eventually require an understanding of the active radicals and the mechanism of degradation. Degradation will be a function of the groundwater composition, and these effects must be understood and factored in the assessment of this technology. Will ions such as carbonate quench the effects of the electron beams by reacting with some of the active groups formed by irradiation?

A detailed assessment of the costs for electron beams should be made and compared on the same bases with costs for other competing approaches.

Implementation Needs: Perhaps the only implementation problem would be with siting of the accelerator and associated equipment. If the accelerator is relatively compact, there should be no unusual difficulty in locating it near the desired treatment site. However, large accelerators would be more difficult to site. The electrical power required for the accelerator could be another siting limitation if the power requirements are higher than those for most competing approaches. As with any degradation process, care must be taken to ensure that either the contaminant is completely degraded or that the remaining immediate degradation products are not excessively toxic.

Author: J. Watson

References:

1. DOE/ERSM/OTE TTP SF 221103, *Destruction of TCE by Electron Beam Processing at the Savannah River Site*, 1992.
2. DOE/ERWM/OTD TTP ID101301, *High Energy Decomposition of Halogenated Hydrocarbons*, 1992.

ROBOTICS/ AUTOMATION

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents:

Characterization

- Provides methods of deploying sensors and instruments required under *Alternatives*: "Sampling," "In Situ Chemical," and "In Situ Physical."
- Provides methods for the automation of analytical laboratory operations including *Alternatives*: "Sample Preparation," "Data Collection/Data Management," and "Ex Situ Chemical."

Decontamination

- Provides methods of deploying tools or performing operations necessary for decontamination of equipment or facilities. Would be useful for those decontamination technologies requiring deployment in a glove box/room on previously disassembled equipment where programmed motions of a manipulator arm would increase the efficiency of operations, as in *Alternatives*: "Mechanical Substrate Surface Removal."
- Good, useful, and perhaps necessary for in situ decontamination technologies that generate secondary environmental hazards, for example, Grinding (DCON-43 and -44), Plasmas Torch (DCON-72), Carbon Dioxide Blasting (DCON-39), etc.

Dismantlement

- Provides methods of deploying the tools or performing the operations necessary for the dismantlement of facilities or equipment. The dismantlement technologies identified below, for example, may require robotics or automated motions to increase their cost-effectiveness or protect cleanup personnel.

Abrasive Jet (high-pressure water)	DISM-11, -35, -52, and -59
Diamond Wire Cutting	DISM-12
Microwave Scabbing	DISM-31
Laser Cutting	DISM-34, -42, -49, -51, -53, and -63
Conventional Disassembly	DISM-33
Advanced Automatic Fixtures	DISM-57
Plasma Arc Cutting	DISM-36
Grabbler for Remotely Cutting Metals	DISM-43 and -58
Vacuum Systems	DISM-46 and -47
Positioning or Equipment Using Laser/Bar Codes	DISM-54

Reference Requirements: Characterization will require light-duty vehicles. Dismantlement and decontamination will normally require medium- or heavy-duty vehicles. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Robotic wheeled/tracked vehicles. (1) Heavy duty (>10,000 lb), (2) medium duty (>1,000 lb), and (3) light duty (>100 lb).

Status: Accepted

Efficacy. High probability of being useful for K-25 decommissioning. Indeed, if robotics are used at K-25, this is the primary method of deployment.

Waste. Possible emissions for internal combustion power sources. Decontamination of system after use.

Additional Comments. Examples of both wheeled and tracked vehicles exist, ranging from small, light-duty machines of the type used for internal pipe and conduit inspection to large, heavy-duty earthmoving machines such as backhoes and bulldozers. An example of a medium-duty machine is a wheeled, high lift device that can be steered from a manned bucket.

All of these three classes of devices are proven for single machine/single operator remote operation. None of them have been significantly demonstrated for either autonomous or multiple machine/single operator control.

Science/Technology Needs: Improved controls to allow more autonomy of operation.

Implementation Needs: Development costs will range between \$100K and \$300K per application. Capital costs will range from \$75K for light-duty robotic vehicles to \$300K for large systems. Operating costs depend on the mode of operation, but they will range from \$250K to \$400K/machine/year.

Author: B. Huston Singletary

References: MMES staff members' personal experiences/opinions and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Areas/Constituents: Support of characterization and decontamination. Pipe/duct crawlers for characterization and, perhaps, decontamination of the inside surfaces of pipes and ducts

Reference Requirements: Size varies from small (2- to 4-in.) pipe up to approx 2 x 4-ft ducts. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Pipe/duct crawler, internal. A remote deployment system is required for deployment of sensors for characterization and the deployment of process methods for decontamination within pipes and ductwork. Technology exists to deploy remote devices within pipes and ductwork; however, the capability of those devices to do useful work is limited. Work to date has been limited to primarily video and simple sensing.

Status: Predemonstration.

Efficacy. The ability for internal pipe and duct crawlers to provide adequate mobility has been demonstrated in the absence of obstacles.

Waste. Secondary waste may be generated during decontamination of the system after use.

Additional Comments. A major driver for pursuing internal pipe or ductwork systems is to help establish the exact extent of contamination within these areas. Without internal characterization, all of these extensive systems must be considered contaminated and treated as such in dismantlement and waste handling. Internal characterization and possibly decontamination could potentially limit the extent of work required and waste generated from the D&D of these systems.

Science/Technology Needs:

Technology development is required in the following areas:

- Miniaturization of sensors and tooling. Considerable effort is required to develop the small scale sensors, manipulation and/or decontamination process systems needed within this highly constrained environment.
- Obstruction removal or bypass. A major impediment to extensive deployment of internal pipe and ductwork systems is the frequent existence of obstructions such

- as valves, flow vanes, etc., which must be considered.
- Development of control and data collection autonomy for these systems is required to allow multiple systems to traverse longer runs with little or no direct operator supervision.

Implementation Needs: No development or demonstration program in this area is currently underway. A viable demonstration project would require hardware and software development, integration, and testing. A ROM estimate for such a feasibility demonstration program specifically looking at the characterization of the ventilation ductwork in Bldg. K-33 would be 1 to 1.5 years and a total of \$1.0M to \$2.0M.

Current technology exists to deploy remote video within pipes and ductwork. Current internal pipe and ductwork systems are primarily deployed with tethers for communications, power, and retrieval. An area of concern is cable management for tethered systems. Engineering modifications of development systems as well as integration and test for specific applications will be required for implementation. Emphasis should be placed on the autonomy of these systems to allow multiple systems under the control of a single operator to reduce operating costs. Mobility systems with simple manipulation, but excluding decon or sensing system are estimated to cost under \$1M/vehicle.

Author: D. Haley

References: Personal communication and vendor literature

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination. Requires robotic device capable of negotiating the external surface of a pipe or duct. Asbestos removal and packaging is one particularly large application.

Reference Requirements: The ability to detect and remove or bypass obstructions. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Pipe/duct crawler, external. A remote deployment system is required for deployment of sensors for characterization and the deployment of process methods for decontamination on external pipes and ductwork. Similar crawler/climber systems are required for other complex access or complex geometry areas. Technology exists to deploy remote devices on external pipes and ductwork; however, the capability is primarily in laboratory development stages.

Status: Predemonstration. Current commercial costs for asbestos removal from linear pipe runs is approximately \$35 per foot and is expected to more than double when low-level radiation contamination is present. The amount of pipe insulation removal required will be on the order of 100,000 linear feet with costs in the multimillion dollar range for manual removal. An effective remote system would provide cost benefits, particularly considering applications at other sites and possible commercial potential. Primary considerations for robotic deployment include reduced secondary waste generation from protective clothing and barriers, current low worker productivity, and reduced worker exposure to asbestos.

Efficacy. The ability of an external crawler to provide mobility for sensors or tooling is high in the absence of obstacles in the path.

Waste. Secondary waste may be generated during decontamination of the system after use.

Additional Comments. Several areas consisting of complex geometry or complex access pose problems for both manual and remote characterization, decontamination and/or dismantlement. A prime candidate for this type of remote deployment is the removal of asbestos insulation from pipe runs.

Science/Technology Needs: Technology development is required in the following areas:

- Robotic compatibility of tooling. Current manual methods for removing asbestos must be modified for robotic deployment or new robotic methods developed.
- Obstruction bypass. A major impediment to extensive deployment of external pipe crawling systems is the frequent encounter with obstructions such as valves and pipe hangers.

Implementation Needs: OTD RTDP demonstration project—A development project for a robotic demonstration system for asbestos removal and bagging from straight pipe runs is underway with the Office of Technology Development (OTD) Robotics Technology Development Program (RTDP). Demonstration on straight runs with no obstacles is expected in early FY 1994. Development will continue into FY 1995 in the area of obstacle bypass. This project is funded at approximately \$1M for FY 1993. Development for other applications would require similar funding levels.

Engineering modifications of development systems as well as integration and test for specific applications will be required for implementation. Depending on the complexity of the crawler and tooling, system cost of as much as \$1M could be expected.

Author: D. Haley

References: MMES staff members' personal experiences/opinions and vendor literature

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of dismantlement and decontamination

Reference Requirements: Adaptability to existing bridges. Virtually any device that is to be mounted on existing bridges must have the mechanical and electrical interfaces custom-designed and fabricated. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Bridge-mounted robotic platform. Robotic devices that can be mounted on and deployed from existing bridge cranes in the building being decommissioned. Such devices are now relatively common. Examples are master-slave servomanipulators, metal cutting devices, video inspection equipment, and radiation detection and measurement systems.

Status: Accepted

Efficacy. High; it will be particularly useful for dismantlement and transport of heavy equipment items.

Waste. Little, if any, waste will result from the use of bridge-mounted robotic platforms.

Additional Comments. Single robot bridge-mounted robotic platforms are thoroughly demonstrated. They include both rigid mast cranes and telescoping tubes mounted on trolleys. A wide variety of sizes and weight capacity devices have been built and successfully operated.

Science/Technology Needs: None

Implementation Needs: (1) Improved standardization and (2) Improved remote maintenance methods. These needs will add little to the development cost of the system. Capital costs will range from \$100K to \$200K per application.

Author: B. Huston Singletary

References: MMES staff members' personal experiences/opinions and personal communication

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Methods of providing power/energy to mobile platform, manipulator arms, sensors, and tools in the remote environment must be developed. Generic methods identified include batteries, fuel cells, internal combustion engines, and umbilical cords.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Power sources for mobile platforms. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. All mobile platforms require power sources for platform mobility, manipulation, sensors, and/or controls. Batteries, internal combustion engines, and umbilical cords are accepted technologies and have been widely used on mobile robotic platforms. Each has limiting features for the K-25 application requiring science/technology investments or implementation investments. Fuel Cells are at the demonstration level for this application and require science/technology investment.

Status: Accepted. Batteries, internal combustion engines, umbilicals; Demonstration—fuel cells.

Efficacy. High for internal combustion engines and umbilicals, medium for batteries and fuel cells.

Waste. Potential chemical waste from batteries and fuel cells, emissions for IC engines, and decon wastes for umbilicals.

Additional Comments. None

Science/Technology Needs: Battery power for mobile robotic platforms is severely limited by the energy storage capacity on a weight basis. Lead acid batteries and other newer designs remain much too heavy for practical use in operations other than characterization. In addition, the charge/discharge characteristics limit system availability. Fuel cells are limited in current capacity and discharge rate and are not demonstrated for this application to date. Internal combustion engines for power generation require emission control development to be suitable for K-25 applications. In order to successfully implement hard-wired umbilical

power supplies in remote robotic applications, clear and unobstructed movement passageways must be allowed to minimize the likelihood of snagging or cutting the trailing cable. The link must use either a retrievable or sacrificial approach. Costs will be prohibitive for sacrificial power cables, and the safety issues would likely preclude this use. Impediments to maintaining continuity (i.e., closing doors, multitraverse operation, etc.) must be eliminated. These requirements can make trailing cable applications undesirable and/or uneconomical for many applications where task area is complex and movement restrictions are undesired. The other approach would be for the design to allow the mobile platform to maintain the ability to plug its power cord into available power supplies. This solution would require the demonstration of a hybrid battery/hard-wire power system.

Implementation Needs: Normal deployment needs. Costs for deployments are generally included in the costs identified for the robotic vehicle or platform and include:

- Batteries. Improved capacity and duty cycles (\$1M to 2M)
- Fuel Cells. Improved capacity and discharge work (\$2M to 4M)
- Internal Combustion Engines. Improved emission controls (\$1M to 2M)

Author: J.N. Herndon

References: MMES staff members' personal experiences/opinions.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: There is a wide variety of remote recovery systems in use today. Examples include redundant drives, continuously connected tethers, additional overhead or mobile crane systems, special rigging for remote lifting, etc. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; mobility

Technology: Failure recovery. Redundant drives and tethers, methods to retrieve robotic devices from the hazardous environment in the event they fail while performing a remote task.

Status: Accepted

Additional Comments. Both redundant drives and tethers have been frequently demonstrated for the remote recovery of bridges, trolleys, and wheeled/tracked vehicles in the event of their failure. The need for totally remote vehicles or other device recovery methods during K-25 D&D is not strong because of the lack of a high radiation environment.

Science/Technology Needs: None

Implementation Needs: Capital costs to include either tethers or redundant drives will be less than \$50K per application.

Author: J.N. Herndon

References: MMES staff members' personal experiences/opinions and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Long-reach arms with a reasonable level of dexterity are required to deploy tools and sensors. These are categorized as light-duty, medium-duty, and heavy-duty.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; manipulation

Technology: Long-reach arms (2-30 m), light-duty (<50 lb payload). A light-duty, long-reach, manipulator system is required to deploy sensor systems throughout large-volume areas during characterization. Payload capacity up to 50 lb will be required.

Status: Predemonstration

Efficacy. Long-reach manipulators exhibit structural and joint flexibility which may limit positioning accuracy. Control system development or accurate positioning mechanisms at the end of the manipulators may solve this concern.

Waste. Possible hydraulic fluid during operation and secondary waste may be generated during decontamination after use.

Additional Comments.

Science/Technology Needs: Technology development is required in the following areas:

- Flexible body control. Flexibility characteristics of long manipulators is a major control issue and must be addressed.
- End-point sensing. With flexible members, external sensing is required to correctly determine the end-point position of the manipulator for proper position control.
- Collision avoidance. The size of the manipulator and the large volumes swept during motion make collision avoidance capabilities essential.
- Lightweight, small cross-section design. Light weight, long reach, systems are required which can be deployed on mobile systems for large area characterization.

Implementation Needs: OTD RTDP demonstration project. A development project for a light-duty, long-reach, manipulator system is underway within the OTD Robotics Technology Development Program (RTDP). Demonstration of the system is expected in FY 1994. This

multimillion dollar development effort is targeted at underground storage tank remediation. Engineering modifications of development systems as well as integration and test for specific applications will be required for implementation. Low-volume production or unique hardware requirements would dictate system cost of \$1M to \$5M.

Author: D. Haley

References: MMES staff members' personal experiences/opinions, personal communications, and vendor literature.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination. Long-reach arms with a reasonable level of dexterity are required to deploy tools and sensors. These arms are categorized as light-duty, medium-duty, and heavy-duty.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; manipulation

Technology: Long-reach arms (2-30 m), medium-duty (<50- to 200-lb payload). A medium-duty, long-reach manipulator system is required to deploy tooling systems throughout large volume areas during decontamination. Payload capacity between 50 and 200 lb will be required.

Status: Predemonstration

Efficacy. Long-reach manipulators exhibit structural and joint flexibility which may limit positioning accuracy. Control system development or accurate positioning mechanisms at the end of the manipulators may solve this concern.

Waste. Possibly hydraulic fluid during operation and secondary waste may be generated during decontamination after use.

Additional Comments. All data are identical to heavy-duty, long-reach manipulator system data sheet (ROBA-7).

Science/Technology Needs: Technology development is required in the following areas:

- Flexible body control. As weight-to-payload ratios are reduced, flexibility characteristics of long manipulators becomes a major control issue and must be addressed.
- End-point sensing. With flexible members, external sensing is required to correctly determine the end-point position of the manipulator for proper position control.
- Collision avoidance. The size of the manipulator and the large volumes swept during motion make collision avoidance capabilities essential.

Implementation Needs: OTD RTDP demonstration project. A development project for a heavy-duty, long-reach manipulator system is underway within the OTD Robotics Technology

Development Program (RTDP). Demonstration of the system expected in FY 1994. This development activity is applicable to medium-duty systems as well. Engineering modifications of development systems as well as integration and test for specific applications will be required for implementation.

Author: D. Haley

References: MMES staff members' personal experiences/opinions and vendor literature.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Long-reach arms with a reasonable level of dexterity are required to deploy tools and sensors. These are categorized as light-duty, medium-duty, and heavy-duty.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; manipulation

Technology: Long-reach arms (2–30 m), heavy-duty (>200-lb payload). A heavy-duty, long-reach manipulator system is required to deploy tooling systems throughout large-volume areas during decontamination. Payload capacity in excess of 200 lb will be required.

Status: Predemonstration

Efficacy. Long-reach manipulators exhibit structural and joint flexibility which may limit positioning accuracy. Control system development or accurate positioning mechanisms at the end of the manipulators may solve this concern.

Waste. Possibly hydraulic fluid during operation and secondary waste may be generated during decontamination after use.

Science/Technology Needs: Technology development is required in the following areas:

- Flexible body control. As weight-to-payload ratios are reduced, flexibility characteristics of long manipulators becomes a major control issue and must be addressed.
- End-point sensing. With flexible members, external sensing is required to correctly determine the end-point position of the manipulator for proper position control.
- Collision avoidance. The size of the manipulator and the large volumes swept during motion make collision avoidance capabilities essential.
- Weight-to-payload ratio reduction. Currently available commercial systems are extremely heavy, limiting deployment (mobility) options.

Implementation Needs: OTD RTDP demonstration project. A development project for a heavy-duty, long-reach manipulator system is underway within the OTD Robotics Technology Development Program (RTDP). Demonstration of the system is expected in FY 1994. This

project is a multimillion dollar development effort. Engineering modifications of development systems as well as integration and test for specific applications will be required for implementation. Low volume production or unique hardware requirements could drive system cost from \$1M to \$5M or higher.

Author: D. Haley

References: Personal communication and vendor literature.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination. For some of the facilities at K-25, robotic arms with a high level of dexterity and redundant kinematics will be required.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; manipulation

Technology: Arms with >6 degrees of freedom (DOF). To provide manipulation for the variety of characterization, decontamination, and dismantlement tasks, dexterous manipulators with a minimum of 6 DOF are required. Kinematically redundant manipulators (>6 DOF) may be required for access in cluttered environments.

Status: Demonstration

Efficacy. Kinematically redundant manipulations have been shown to greatly increase dexterity.

Waste. Possibly hydraulic fluid during operation and secondary waste may be generated during decontamination of the system after use.

Additional Comments. In general, currently available 6-DOF manipulators are adequate for many D&D tasks. The areas of concern relative to technology are >6-DOF systems and modular systems. Modular systems are desirable both for reconfiguration to more directly address unique tasks and for ease of maintenance.

Science/Technology Needs: Technology development is required in the following areas:

- Redundant manipulator planning and control. For >6 DOF arms, reliable kinematically redundant manipulator control algorithms are required.
- Modular manipulator design. Modular manipulator designs must be developed and verified as providing high payback due to standardization and ease of maintenance.
- Nonreplica master/slave operation. Teleoperation of redundant manipulators with a replica master controller requires excessive operator mental and physical agility to control the physical redundancy of the mechanical manipulator. Use of nonreplica masters requires the redundant manipulator planning and control capability stated earlier.

Implementation Needs: Development of redundant control technologies is an active area of university research. This activity is predominantly a software development in algorithm design, implementation, and verification. This area generally requires advanced degree level personnel in servo-control systems (generally an Electrical Engineering discipline). Fairly robust capability should be available for demonstration and evaluation within 2 to 5 years. Modular robotic systems are also under study within the university community as well as within the OTD Robotics Technology Development Program. Modular mechanical and actuator design, fabrication, integration, and test are required to evaluate these concepts. This area generally requires personnel with advanced degrees in mechanical design (mechanical engineering). Engineering development units at the component level exist today. Total system implementations for demonstration and evaluation should be available in 2 to 5 years.

Currently available 6 DOF manipulators are adequate for many decontamination and decommissioning (D&D) tasks. A basic commercially available hydraulic, force reflecting, master/slave 6-DOF manipulator system can be purchased for approximately \$300K. Deployment of redundant manipulators will increase the applicability of robotics to more complex access and geometry areas. Robotic systems for D&D applications are under development within the OTD Robotics Technology Development Program and will be available within the 2- to 5-year time frame for feasibility demonstrations and benefit evaluations. Efficient teleoperation of redundant systems requires the implementation of compact nonreplica Cartesian master controllers with redundancy control provided via software.

Author: D. Haley

References: MMES staff members' personal experiences/opinions and CMU modular system research.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of dismantlement and decontamination. In constrained areas for dismantlement and decontamination tasks, robotic arms which are both compact and "strong" will be required.

Reference Requirements: Approximately the size of an average human arm (lengths and cross-sections) with lifting capabilities in any orientation of approximately 100 lb/arm. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; manipulation

Technology: Compact, high-capacity arms

Status: Evolving technology; conceptual

Efficacy. Medium—The use of hydraulic arms would probably be acceptable for most K-25 needs.

Waste. Decontamination of equipment after use would generate some waste materials (<5 gal).

Additional Comments. For constrained areas, small robotic arms, with lifting capabilities sufficient to carry decontamination or dismantlement tools, will be required. Small hydraulic arms with high capacity presently exist. However, there are no equivalent, electrically driven arms.

Science/Technology Needs: Compact, high-output, electrical motors. Two potential approaches are AC induction motors or superconducting motors. Neither of these possibilities, however, has been demonstrated for this type of application, and researchers are only beginning to consider how to approach the problem.

Implementation Needs: Survey of existing commercial motors, followed by an analysis and conceptual design of a compact robotic arm based on these motors. Survey may indicate that motors with the necessary characteristics do not presently exist and that new motors may have to be developed.

No unusual implementation needs. Development costs are estimated at \$1.0M to \$2.0M. Capital and operating costs are included in other technologies. Incremental capital and operating costs associated with this technology would be minimal.

Author: J.N. Herndon

References: MMES staff members' personal experiences/opinions.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—There are numerous potential applications for a multifingered (>2) end effector including the handling of sensors, tools, and glassware (in an automated laboratory).

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; end-of-arm tooling

Technology: Multifingered Effector. A need exists for more dexterous, general-purpose, end effectors to allow the use of robotic or automated systems for more complex manipulation tasks. Current technology relies heavily on special purpose tooling, increasing hardware complexity (multiple end effectors, tool exchange systems) and cost. General purpose two-fingered or parallel jaw grippers are inadequate for most dexterous manipulation tasks because of the inability of such devices to provide a stable grip in the presence of disturbance forces.

Status: Predemonstration

Efficacy. Hardware demonstrations in laboratory bench tests have proven the capability of these systems. Packaging and robust control algorithms will allow operational use.

Waste. Secondary waste may be generated during decontamination after use.

Additional Comments. Three-fingered end effector hardware is becoming available, but these systems lack the advanced control and planning functions to allow proper utilization of the manipulation capabilities of such devices.

Science/Technology Needs: Technology development is required in the following areas:

- Compact distributed control sensors and electronics.
- Dexterous, multifingered, end effectors require complex control algorithms relying heavily on real-time sensor input and reaction. Such control requires highly capable yet compact computational and sensor systems preferably located at the end-effector device.
- Multifinger planning and control algorithms. Stable grasp and manipulation control algorithms must be developed as well as more autonomous grasp and manipulation planning algorithms.

Implementation Needs: Development of multifingered end-effector control technologies is an active area of university research. This activity is predominantly a software development in algorithm design, implementation, and verification. This area generally requires advanced degree level personnel in servo-control systems (generally an Electrical Engineering discipline). Fairly robust capability should be available for demonstration and evaluation within 5 years. Deployment of multifingered end effectors will increase the applicability of robotics to more complex manipulation tasks. Engineering modifications of development systems as well as integration and test with specific robotic systems will be required for implementation. Low quantity production of hardware will probably maintain system costs at fairly high levels (\$100K to \$500K per end effector).

Author: D. Haley

References: MMES staff members' personal experiences/opinions.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of dismantlement and decontamination. Automated interchangeability of tools on a universal end-effector that also provides services to the tool would find many applications and would improve the efficiency of dismantlement and decontamination tasks.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; end-of-arm tooling

Technology: Remote/automated interchangeability. To allow a single robotic system to use a number of different sensors/tools, a remote automated end-effector changeout mechanism is required. Such a system should provide mechanical, electrical, data, and hydraulic interfaces between the manipulator and the sensors/tools.

Status: Demonstration

Efficacy. Quick change devices are commercially available and have been used for a variety of tool-to-manipulator interfaces. Modification may be required for the special purpose sensors and tooling used for D&D.

Waste. Secondary waste may be generated during decontamination after use.

Science/Technology Needs: None. No science or technology needs exist for the end-effector remote changeout technology area.

Implementation Needs: Engineering modifications of existing commercial systems as well as integration and test with specific robotic systems will be required for implementation. Additional costs are associated with tool holders compatible with automated tool exchange.

Author: D. Haley

References: MMES staff members personal experience/opinion.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of dismantlement and decontamination. The application is secure gripping of tools and, perhaps, sensors using a standard interface.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical end effectors

Technology: Tool-arm interface. As an alternative to using a quick change interface as described in Auto- 10, standard interfaces between tools/sensors and the manipulator gripper can be established and used. Such interfaces as "T" handles and "H" handles are candidate interfaces.

Status: Demonstration

Efficacy. This option provides a reliable, simple, passive hardware interface that has been proven in many applications.

Waste. Secondary waste may be generated during decontamination after use.

Additional Comments. The advantage of such an interface is that the manipulator uses a single gripper continuously and uses that gripper to pick up and maneuver sensors/tools. Each sensor/tool must be fitted with the interface "handle" which in general is a simple, low cost passive hardware device. The disadvantage of this approach is that resources (power, data, etc.) for the sensor/tool must be supplied via an umbilical, which poses problems of cable management during manipulation.

Science/Technology Needs: None. No science or technology needs exist for the tool-arm interface technology area.

Implementation Needs: The design of these interfaces should be such that forces and torque at the interface do not tend to drive the gripper open and cause the sensor/tool to be dropped. Engineering modifications of existing systems as well as integration and test with specific robotic systems will be required for implementation. Costs associated with an appropriate gripper and the required hardware interface will be minimal.

Author: D. Haley

References: MMES staff members personal experience/opinion.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization. For both characterization in situ, as well as in an analytical laboratory, methods of limiting the force applied to a sensor or a piece of glassware will be required.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical; end-of-arm tooling

Technology: Force limiter. Because many of the manipulation tasks associated with D&D require contact between sensors/tools and the environment, some means is required to limit the forces that are applied. Mechanical compliance devices can be used to provide passive compliance during contact.

Status: Demonstration

Efficacy. Both passive and active force limitings have been demonstrated and incorporated into production systems.

Waste. Secondary waste may be generated during decontamination after use.

Additional Comments. Some form of active force sensing should also be present for control feedback for active compliance or for safety limit shutdown. A less desirable mechanical solution is the design of an interface structure to break at predetermined load limits to avoid damage to the overall robotic system.

Science/Technology Needs: None. No science or technology needs exist for the force limiting technology area. This data sheet covers only the mechanical (passive) approach to force limiting. Active force control is covered in the Control Algorithm area.

Implementation Needs: None. Engineering modifications of existing systems, as well as integration and test with specific robotic systems, will be required for implementation. Minimal costs are associated with active force/torque sensor systems and passive hardware compliance mechanisms.

Author: D. Haley

References: MMES staff members personal experience/opinion

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of material disposition

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Mechanical. Other—automated separation technology. Separation of weakly magnetic materials.

Technology: Automated separation technology. Automated methods of separating materials with similar physical properties will be required to recovery valuable metals/alloys. Magnetic separators offer one method of performing this separation.

Status: Accepted for magnetic vs nonmagnetic materials. Evolving tech-conceptual for other material combinations.

Efficacy. Very high for separation of ferromagnetic and nonmagnetic materials. Unknown for other material combinations.

Waste. Decontamination of hardware after use would generate minimal volumes of waste.

Additional Comments. The separation of highly magnetic materials from nonmagnetic or weakly magnetic materials is an accepted and proven technology. Separation technology for nonmagnetic or weakly magnetic materials is not an established technology at this time.

Science/Technology Needs: The initial step in the development of magnetic separators will be a theoretical analysis, perhaps working with an industrial partner, to assess feasibility. If successful, components would be selected and bench scale tests conducted. Again, if successful, a system would then be designed for high throughput capacity.

Implementation Needs: Development costs could range from \$0.5M to \$1.0M. Estimated capital costs for an eventual developed system are \$75K to \$150K per system. Operating costs would be about \$200K/system/year.

Author: S. Schrock

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization and decontamination

Reference Requirements: Transportability. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, algorithms

Technology: Multiple, concurrent mobile platform control. The control of multiple, robotic, mobile platforms operating either semiautonomously or preprogrammed by a single operator.

Status: Predemonstration

Efficacy. High, with potentials for significant increases in operator efficiency.

Waste. No secondary waste stream generated; however, a potential exists for minimizing current technology waste streams.

Additional Comments. Control of multiple, concurrent mobile platforms requires emphasis on the coordination of activities, as well as allocation of functions between platforms in real time. How control is distributed between platforms is a key issue (i.e., should much of the processing be done locally or should it be done centrally and allocated?). For the latter, baud rates may be a concern, especially if high data rate transmission is required. It can be expected that one human could effectively control three semiautonomous platforms, each of which is replacing two or three suited humans. A manual system vs multiple-controlled robotic system cost ratio of 3 : 5 is estimated.

Science/Technology Needs: (1) Algorithms for semiautonomous, decentralized control, (2) improved on-board computational capabilities, and (3) centralized vs decentralized control. Software development is a significant factor for implementation and greater computation throughput must be achieved for effective deployment.

Implementation Needs: Control is significantly different from traditional approaches to warrant significant new training in simulations. Development costs: \$1.0M to \$4.0M; Capital Costs: \$500K to \$1000K; Operational Costs: \$300K to 500K per year.

Author: H.E. Knee

References: MMES staff member personal experience/opinion and personal communication

February 26, 1993

COMBINED MOBILITY/MANIPULATION/ END-EFFECTOR CONTROL

ROBA-28-OG

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, algorithms

Technology: Combined mobility/manipulation/end-effector control. This technology would permit parallel motion/mobility functions to approach or perform a work task and would improve the speed of operations.

Status: Demonstration

Efficacy. High, with potentials for simultaneous execution of activities that are currently done in series.

Waste. No secondary waste streams generated.

Additional Comments. Real-time task planning to simultaneously support mobility, manipulation and end-effector control is necessary to facilitate effective and continuous robotic system performance. Single-channel robotic functions tend to be ineffective. Functions conducted in parallel could reduce operational time by 50% over nonparallel robotic functions (i.e., single channel functionality).

Science/Technology Needs: Real-time task planning. Activities to facilitate deployment include (1) real-time task planning and (2) software development.

Implementation Needs: Development costs: \$500K to \$2000K; capital costs: \$200K to \$1000K. Some special training may be required to facilitate parallel rather than series execution.

Author: H.E. Knee

Reference: MMES staff members' personal experiences/opinions and personal communication.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization and decontamination

Reference Requirements: Accurate definition of work space. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Other, controls, algorithms

Technology: Preprogrammed obstacle avoidance. Preprogrammed obstacle avoidance will permit the automated characterization and decontamination of large area work spaces.

Status: Accepted

Efficacy: High, if a good model of work space exists.

Waste: No secondary waste stream.

Additional Comments: A relatively mature area. No real scientific or technological needs exist in this area. Fielded systems could be made more effective by emphasizing technological assimilation into the area. Upgrading of the technology currently employed in the obstacle avoidance area could lead to a reduction of computer-based processing time and an increased availability of the robotic system for nonobstacle avoidance functions. An increase of robotic system efficiency of about 30% is expected.

Science/Technology Needs: Real-time on-board processing is a necessity for development of this technology. For deployment, the following are required: accurate definition of work space, effective application outside of laboratory environments, effective man-machine interfaces, and improved reliability of hardware/software.

Implementation Needs: Development costs: \$500K to 1000K; capital costs: \$100K to \$400K.

Author: H.E. Knee

References: MMES staff members' personal experiences/opinions and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization

Reference Requirements: EPA acceptance of automations. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, algorithms

Technology: Programmed motions (per EPA protocols). Programmed motions of robotic devices in an analytical laboratory per EPA analytical protocols.

Status: Accepted

Efficacy: High, with potential benefits minimizing staffing and enhancement of reliability.

Waste: Waste streams will be minimized as compared to current technologies.

Additional Comments: This technology is primarily related to analytical laboratories. It will facilitate automation of redundant and simple (but labor-intensive) activities. Utilization of programmed motions to facilitate an automated laboratory could replace the equivalent of three laboratory technicians.

Science/Technology Needs: Real-time, on-board processing is necessary for development and for deployment. EPA approvals of automated protocols and effective man-machine interfaces are required. Note this is an area being funded by the OTD Robotics program at a level of ~\$1.0M/year.

Implementation Needs: Development costs: \$0.5M to 1.0M/protocol; capital costs: \$200 to \$400K/protocol.

Author: S. Schrock

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, algorithms

Technology: Sample management. Management and handling of numerous analytical samples and characterization data in a secure, reliable, and auditable manner.

Status: Demonstration

Efficacy. Medium, although the technology is demonstrated, it must be customized for each application, which may be a bottleneck.

Waste. Need for decontamination of support hardware after use.

Additional Comments. Effective sample management may be one of the bottlenecks for effective characterization. Although the technology has been demonstrated, there is a need to increase effectiveness and to embrace new and emerging technologies within the process. Emphasis on increased reliability, fault recovery, and utilization of emerging technologies could increase the effectiveness of such systems by 100%.

Science/Technology Needs: Deployment requires increased reliability, fault recovery, and acceptance of emerging technologies for management of physical data (e.g., bar coding).

Implementation Needs: Development costs: \$0.5M to \$1.0M; capital costs: \$0.5M to \$1.0M.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Areas/Constituents: Support of characterization and decontamination

Reference Requirements: Transportability. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Single-human, multiple-vehicle control station. Man-machine interface controls that will permit a single operator to monitor and control multiple robotic platforms.

Status: Predemonstration

Efficacy. High. Staffing can be minimized and reliability increased.

Waste. No secondary waste streams generated.

Additional Comments. One of the principal ways of capitalizing on robotics technologies is by providing the ability of one operator to "run" multiple vehicles. To facilitate such activities, an effective man-machine interface must be developed that utilizes multiple human I/O modes, utilizes high levels of embedded intelligence and can support varying levels of autonomy. Poorly designed interface stations may be only half as efficient as a properly designed human-system interface.

Science/Technology Needs: (1) Multimodal interface capabilities, (2) embedded intelligence for operator support, and (3) advanced information visualization. For development to take place, effective supervisory control must be realized.

Implementation Needs: Development costs: \$1M to \$3M; capital costs: \$0.5M to \$1.0M.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Areas/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Data integration/fusion. Presentation of understandable and usable data to the robotic device operator via data fusion.

Status: Demonstration

Efficacy. High. Data fusion provides a greater ability for human operators to assimilate and act on data, making them more efficient.

Waste. No secondary waste streams generated.

Additional Comments. The plethora of new data and information that is potentially available to a human operator as a result of an increased usage of digital technologies provides a challenge for the system designer to provide integrated data and information. This emphasis on data fusion is required to minimize the cognitive work load of humans involved in the control of complex systems. Although effective methods of data fusion seem to be emerging (and are being demonstrated), no clear data fusion methodologies or concepts stand out above the rest. New metaphors for information display are necessary in order for information technologies to remain effective.

The benefits of good data integration or fusion are difficult to quantify. Appropriately integrated displays could minimize search times of operators and enhance the efficiency of other activities. For decision making, uncertainty and risk could be reduced leading to more efficient operation. It is estimated that appropriate data fusion for high data environments could enhance operator efficiency by 100%.

Science/Technology Needs: (1) Techniques for verification of data, (2) techniques for functioning with missing data, and (3) techniques for navigation within complex interface displays. For development, the following are required: (1) appropriate methods for modeling a process in order to facilitate data fusion and (2) effective visualization metaphors.

Implementation Needs: Development costs: \$500K to \$2000K; capital costs: \$100K to \$500K.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Teach/playback. The use of teach/playback to enhance the efficiency of robotic operations. Particularly useful for repetitive tasks.

Status: Accepted

Efficacy: High. Will lead to the automation of many redundant labor intensive activities.

Waste: No secondary waste streams generated.

Additional Comments: Current teach/playback methods are based on limited lists of performance measures for teaching. Emerging technologies may be able to facilitate newer measures that would enhance the efficiency of these relatively rudimentary systems. Teach/playback is most effective for redundant, labor-intensive activities. These types of tasks comprise about 70% of what human operators are expected to do and, for the most part, can be taught to be accomplished by robotic systems. After being taught, the system can do such tasks more error free and more quickly. They also free up human operators for other activities. It is estimated that such systems could enhance human operator effectiveness by 100%.

Science/Technology Needs: Expansion of performance measure list for teaching. For development, increased precision and accuracy are required. For deployment, increased speed capabilities are required.

Implementation Needs: Development costs: \$500K to \$1000K; capital costs: \$200K/system.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Voice control. Voice control enhances the efficiency of remote operations.

Status: Accepted

Efficacy. High, if language expansion and robustness to phonetic variability are activated.

Waste. No secondary waste streams generated.

Additional Comments. Voice control is a means of capitalizing on a different human I/O channel. Although the technology is accepted, significant inefficiencies still remain. These inefficiencies pertain primarily to the flexibility of and robustness of the voice control capability. Effective utilization of voice control could enhance human operator effectiveness by 50%.

Science/Technology Needs: (1) Language expansion and (2) Robustness to phonetic variability. For development, integration with other modes of I/O are necessitated. For deployment, some training using a voice I/O might be required.

Implementation Needs: Development costs: \$500K to \$1000K; capital costs: \$100K to \$300K. Some special training may be required for effective control.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Man-robot symbiosis. The ability of a control system to learn repetitive tasks, to perform these tasks, and to allocate tasks to a human operator or to automated performance.

Status: Predemonstration

Efficacy. Medium to low. A fair amount of science and technology needs exist for resolution prior to gaining high-efficacy potential.

Waste. No more than current technologies.

Additional Comments. Man-robot symbiosis involves two principal areas of research that are necessary for appropriate functionality. They are machine learning and dynamic task allocation. Machine learning in its broadest sense can encompass a number of methodologies, including teach/playback. For other than the most rudimentary applications, machine learning is an area that still remains in its infancy. Neural networks, hybrid artificial intelligence architectures, and genetic algorithms are being utilized as a basis for enhancement of intelligent machines to learn from experience.

Dynamic allocation of functions will allow humans and intelligent control systems to assume or delegate responsibilities for control based on various performance criteria such as the work load of the human operator or the number of errors committed by a human operator. Dynamic allocation based on such measures will enhance efficiency and minimize system costs.

It is estimated that appropriately implemented symbiotic systems could enhance human operator effectiveness by 100%.

Science/Technology Needs: (1) Definition of an appropriate machine learning concept

adaptable to intelligent machines. (2) appropriate architecture for dynamic allocation of functions, (3) effective integration of various classification methods, and (4) effective conflict resolution algorithms/methods.

Implementation Needs: Development costs: \$2M to \$5M; capital costs: to be determined. Operator training may be significant activity.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communications.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Fuzzy control. Fuzzy control or fuzzy logic for implementation of qualitative reasoning in the operator's control system.

Status: Demonstration

Efficacy. Medium, efficiency gain is marginal and applications may be limited.

Waste. No secondary waste streams.

Additional Comments. Fuzzy control offers opportunities to implement qualitative reasoning into the control environment (i.e., to be able to make decisions without high precision quantification). Fuzzy control is extremely fast and requires minimal programming. Much emphasis is currently placed on calibrating such systems for particular applications.

Navigational speeds of mobile platforms with fuzzy control are estimated to be five times faster than conventional robotic navigation systems. However, for certain D&D activities such as characterization, the required mobile platform speed is minimized by the requirements of the characterization or the decontamination processes. From evidence of fuzzy control systems in Japan, there is a 10% to 30% increase in efficiency that may be achieved for control activities other than mobility.

Science/Technology Needs: (1) Formalism for calibrating fuzzy rule sets and (2) more appropriate emulation of human logic/reasoning. For development, integration with traditional control concepts is required.

Implementation Needs: Development costs: \$1M to \$3M; capital costs: \$1.0M/station.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, man-machine interface

Technology: Transportable control systems. The ability to design and build high performance, transportable control systems that can be moved to the work site.

Status: Accepted

Efficacy: High. Portable control systems require minimum setup time and are field hardened for durability.

Waste: None

Additional Comments: Issues associated with the physical transport of hardware and software are well understood. Increased reliability, durability, and generally field hardening will result in less down time and are estimated to increase availability by about 30%. This improvement is necessary to achieve an availability goal for robotic devices of 90%.

Science/Technology Needs: For deployment, the following are required: (1) increased reliability, (2) increased durability, and (3) field hardening.

Implementation Needs: Development costs: \$200K to 400K; capital costs: Included in control station costs.

Author: B. Huston Singletary

References: MMES staff members' personal experiences/opinions and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination. The use of umbilical cords to transmit signals between the control system and the robotic device.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Technology: Hardwire (umbilical). Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. All mobile platforms require communication links to a central location for monitoring, control, and data archival purposes. The degree of autonomy installed on the mobile platform will drive the communication needs. Nevertheless, all mobile platforms will require a degree of communication. Hard-wired communication through trailing cable umbilicals is an accepted technology in remote applications.

Status: Accepted

Efficacy: High, with some limitations in cluttered environments or multitraverse operations.

Waste: Decontamination fluid for retrievable design, contaminated waste for sacrificial designs.

Additional Comments: None

Science/Technology Needs: For successful implementation of hard-wired umbilical communication in remote robotic applications, clear and unobstructed-movement passageways must be allowed to minimize the likelihood of snagging or cutting the trailing cable. The communication link must use either a retrievable or a sacrificial approach. Impediments to maintaining communication (e.g., closing doors, multitraverse operation, etc.) must be eliminated in the facility design. These requirements can make trailing cable applications undesirable and/or uneconomical for many applications where the task area is complex and movement restrictions are undesired.

Implementation Needs: None. Costs are negligible.

Author: J.N. Herndon

References:

1. MMES staff members personal experience/opinion.
2. *Military Robotics Sourcebook*, 1991-1992 Edition, L&B Limited.

EM Problem: Decommissioning

K-25 Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—The use of high-frequency microwaves to transmit signals between the control system and the robotic device.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, signal transmission

Technology: Microwave. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. All mobile platforms require communication links to a central location for monitoring, control, and data archival purposes. The degree of autonomy installed on the mobile platform will drive the communication needs. Nevertheless, all mobile platforms will require a degree of communication. Wireless microwave-based communication is an accepted and widely used technology for free space communication in a nonreflective environment. In addition, significant technology has been demonstrated for focused transmission in reflective environments in the United States, with proposed spread-spectrum solutions in reflective environments in the French CEA program. Early undemonstrated systems using spread-spectrum techniques are now available from at least one commercial vendor in the United States.

Status: Demonstration

Efficacy: High.

Waste: None

Additional Comments: None

Science/Technology Needs: Numerous wireless microwave systems for remote mobile platform applications have been demonstrated at ORNL in "line-of-sight" applications. In addition, free space outdoor applications are numerous, and commercially available hardware is more than adequate for the needs. To be useful in K-25 characterization, dismantlement, and decontamination activities, systems that can deal with highly reflective, non-line-of-sight applications must be developed. Although proposals for these systems have been discussed (particularly in the French CEA program), a full demonstration has not been performed on

remote mobility platforms. At least one commercially available system advertises a degree of operability in enclosed buildings through the use of spread-spectrum operational techniques, but no test data are available to verify operability in the K-25 environment.

Implementation Needs: Normal implementation needs. Technology presently limited to free space and near line-of-sight applications indoors. Some commercial hardware is available but must be tested. Development costs estimated at \$0.6M to \$0.8M. Capital costs would be approximately \$200K/system. Operating costs are included in the cost of the control station.

Author: J.N. Herndon

References:

1. MMES staff members personal experience/opinion.
2. *Microwave Signal Transmission System Design and Testing*, ORNL/TM-1192, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., September 1991.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—The use of radio frequency (RF) communications to transmit signals from the control system to the robotic device.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, signal transmission

Technology: Radio frequency. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. All mobile platforms require communication links to a central location for monitoring, control, and data archival purposes. The degree of autonomy installed on the mobile platform will drive the communication needs. Nevertheless, all mobile platforms will require a degree of communication. Wireless RF-based communication is an accepted and widely used technology for free space communication in a nonreflective environment. Early undemonstrated systems using spread-spectrum techniques are now available from at least one commercial vendor in the United States. At RF frequencies, available channel allocations in the Oak Ridge area are always a difficult problem. In addition, commercially available RF transmitters have bandwidth limitations that may make television transmission capability very limited.

Status: Demonstration

Efficacy: Medium

Waste: None

Additional Comments: None

Science/Technology Needs: Free space outdoor applications are numerous, and commercially available hardware is more than adequate for the needs if the number of required video channels is limited. To be useful in K-25 characterization, dismantlement, and decontamination activities, systems must be developed to deal with highly reflective, non-line-of-sight applications. At least one commercially available system advertises a degree of operability in enclosed buildings through the use of spread-spectrum operational techniques,

but no test data are available to verify operability in the K-25 environment. It is likely that the bandwidth limitations for this system may limit its applicability.

Implementation Needs: Technology presently limited to free space outdoor and near line-of-sight applications indoors. Some commercial hardware is available, but it must be tested. Development costs of \$0.5M to \$0.7M.

Normal deployment needs. Multiple units likely needed for bandwidth requirements. This limitation is severe because of the frequency allocation problems. Capital costs would be approximately \$50K/unit, and operating costs would be included in control station costs.

Author: J.N. Herndon

References: MMES staff members personal experience/opinion.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—The use of lasers to transmit signals between the control system and the robotic device.

Reference Requirements: Line-of-sight between transmitter and receiver. Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Controls, signal transmission

Technology: Laser. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. All mobile platforms require communication links to a central location for monitoring, control, and data archival purposes. The degree of autonomy installed on the mobile platform will drive the communication needs. Nevertheless, all mobile platforms will require a degree of communication. Wireless laser-based communication is a demonstrated, commercially available technology. The applications are limited to tasks where line-of-sight operation is possible.

Status: Demonstration

Efficacy. Low

Waste. None

Additional Comments. None

Science/Technology Needs: Technology is presently limited to line-of-sight applications indoors and fair weather line-of-sight applications outdoors. Laser-based systems for remote mobile platform applications have been demonstrated at ORNL and other locations. To be useful in K-25 Site characterization, dismantlement, and decontamination activities, systems must be developed to deal with indoor non-line-of-sight applications. Laser-based communication systems will not likely be practical for most of the applications encountered at the K-25 Site.

Implementation Needs: None. This is a commercially available component; hence development costs are negligible. However, it is unlikely to be useful at K-25.

Capital costs would be <\$50K/system, and operating costs would be included in the cost of the control station.

Author: J.N. Herndon

References: MMES staff members' personal experiences/opinions.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: None

Subelements: Robotics/automation

Alternatives: Sensors, perception

Technology: Three-dimensional (3-D) vision. The use of 3-D vision systems to improve the efficiency and accuracy of remote operations.

Status: Demonstration

Efficacy. Medium. Effective 3-D vision capabilities will increase speed of operations. Good for inspection tasks.

Waste. No secondary waste streams generated.

Additional Comments. Three dimensional vision capabilities are required by a robotic system for effective mobility, manipulation, planning, decision-making, etc. There are two elements to this area. The first involves robotic capabilities to sense three dimensions in order to carry out autonomous or semiautonomous functions. The second involves appropriately displaying three-dimensional data and information to a human operator in a fashion that is sensitive to all other data and information to be managed by the human operator. Effective human maneuverability within computer-based environments is a significant research issue.

Cost benefit estimates for utilization of 3-D vision sensors are difficult to make. An efficiency of less than 50% can be expected.

Science/Technology Needs: (1) Sensor fusion and (2) advanced visualization capabilities. For development, the technology must be environmentally hardened.

Implementation Needs: Development costs: \$800K to \$1000K; capital costs: \$300K/unit. Some special training for the human operator may be required for effective deployment of 3-D vision.

Author: J.N. Herndon

Reference: MMES staff members personal experience/opinion and personal communications.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, perception

Technology: High-definition television (HDTV) vision. The use of high-definition television viewing systems to improve the efficiency and accuracy of remote operations.

Status: Demonstration

Efficacy. Medium. In general, the quality of data/information presented by such systems has less uncertainty and allows more sophisticated graphical processing. May also be useful for inspection tasks.

Waste. No secondary waste streams generated.

Additional Comments. The quality of data and information resulting from a high-definition television (HDTV) will facilitate enhanced visual recognition capabilities and will minimize uncertainties associated with autonomous processing of visual data. Furthermore, when such systems are employed as operator interface devices, they provide an interface medium that allows for more efficient data/information management (e.g., enhanced multiple windowing capabilities). Such systems also provide the capability to function as high-resolution big-board or overview displays.

Less than a 50% improvement in system efficiency is expected to be obtained through utilization of HDTV.

Science/Technology Needs: (1) Sensor fusion and (2) advanced visualization capabilities. For development, the technology must be environmentally hardened.

Implementation Needs: Development costs: \$300K to \$500K; capital costs: \$200K/unit.

Author: J.N. Herndon

References: MMES staff members personal experience/opinion and personal communication.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, perception

Technology: Directional audio. The use of directional audio to improve the efficiency of remote operations.

Status: Predemonstration

Efficacy: Medium. Although not a critical technology, it could significantly enhance self-location/navigation.

Waste: No secondary waste streams generated.

Additional Comments: Directional audio is a technology that can enhance the self-location and navigation/obstacle avoidance capabilities of robotic systems. Currently, directionality in conjunction with audio input is not well utilized, and movement toward such capabilities can aid in removing the load currently put on the robotic vision systems.

It is expected that use of directional audio could enhance system effectiveness by less than 30% for various locational functions.

Science/Technology Needs: (1) Sensor fusion and (2) appropriate representation to the operator. For development, the technology must achieve increased processing speed.

Implementation Needs: Development costs: \$500K to \$1000K; capital costs: \$200K/unit.

Author: J.N. Herndon

References:

1. MMES staff members personal experience/opinion and personal communication.
2. T. J. Doll, T. E. Hanna, and J. S. Russotti, "Masking in Three-Dimensional Auditory Displays," *Human Factors*, 34(3), June 1992, 255-265.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, perception

Technology: Force feedback. The use of force feedback to enhance remote operations with teleoperated robotic devices.

Status: Accepted

Efficacy. High; advanced force feedback allows for enhanced human-in-the-loop performance.

Waste. No secondary waste streams generated.

Additional Comments. Force feedback continues to be one of the primary control feedback loops that exist within telerobotics. This technology is well accepted and could be improved by greater sensitivities of the direct interface or an enhanced representation/ metaphor that may be used by the human operator.

A 30% improvement can be expected in system performance by using advanced force feedback for selected decommissioning tasks, particularly characterization and decontamination activities.

Science/Technology Needs: Improved tactile sensitivity (e.g., via "smart skins"). For development, the technology requires enhanced representation to operators.

Implementation Needs: Development costs: \$200K to \$400K; capital costs: \$200K/unit.

Author: H.E. Knee

References: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: In support of material disposition

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, perception

Technology: Imaging and image processing. The use of image processing to assist in the segregation of metals/materials for eventual recovery of valuable materials and for inspection/comparison tasks.

Status: Predemonstration

Efficacy. Medium. Allows for application of robotics to more sophisticated activities.

Waste. No secondary waste streams generated.

Additional Comments. Advanced image processing capabilities that use sensor data directly to facilitate object recognition (and an associated display to the human operator if necessary) will be crucial toward application of robotics to more sophisticated and autonomous activities. Such systems will minimize the burden on human operators and will enhance their supervisory control nature.

This is a very difficult area to quantify with respect to cost benefits. Very roughly, a less than 30% improvement in system efficiency could be expected.

Science/Technology Needs: (1) Data sensor fusion and (2) appropriate representation to operators. For development, the technology requires improved processing speed.

Implementation Needs: Development waste: \$0.5M to \$2.0M; capital costs: \$300K to \$500K/unit.

Author: H.E. Knee

Reference: MMES staff members personal experience/opinion and personal communication.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization

Reference Requirements: Surfaces that come in contact with sensors may be roughened by corrosion/oxidation, making it difficult to get a good coupling between sensor and wall.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Wall thickness measurements. Sensors that can be robotically deployed to determine wall thickness (e.g., of UF₆ cylinders) are required.

Status: Still being assessed.

Efficacy. High for inspection tasks, such as, UF cylinder inspection, where a knowledge of wall thickness may be required on selected surfaces.

Waste. Negligible

Additional Comments. None

Science/Technology Needs: To be determined

Implementation Needs: To be determined

Author: S. Schrock

References:

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Proximity probes to alert a supervisory operator of impending obstacles.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Proximity probes. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning applications. For the implementation of telerobotic and autonomous operations, proximity probes are needed for control of operations to prevent collisions with obstacles in the environment.

Status: Predemonstration

Efficacy. High for small volume coverage; low for large volume coverage.

Waste. None

Additional Comments. None

Science/Technology Needs: Present proximity sensors used for robotic operation are limited in both range and signal quality. This limitation results in artificially large "boundaries" being drawn around potential collision areas in the work space. Significantly improved operational efficiency could be realized by improved sensors.

Implementation Needs: Development costs for probes that are useful for large area coverage and are estimated at \$1.0M to \$2.0M.

Normal deployment needs. Capital costs are estimated at \$200K to \$300K/unit after development. There would be no separate operating costs associated with this sensor.

Author: J.N. Herndon

References: MMES staff members personal experience/opinion.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Positioning sensors to track a robotic device and feed this information to the operator and the control system.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Positioning. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. For the implementation of telerobotic and autonomous operations, accurate position information is required for the robotic system within the work space. Various systems have been used for this application to date. Outdoor applications are gravitating to use of the satellite-based Global Positioning System, in addition to local triangulation methods. Indoor applications have used ultrasonic, optic, and other triangulation systems. In addition, dead reckoning systems have been applied. Present approaches do not yield sufficient accuracies to provide for the elimination of dead-reckoning inaccuracies.

Status: Predemonstration

Efficacy. Medium for high-accuracy, real-time navigation.

Waste. None

Additional Comments. None

Science/Technology Needs: Present positioning approaches are not sufficient to provide highly accurate position information for mobile robotic platforms within the K-25 Site. Significantly improved operational efficiency could be realized by improved approaches and eliminating the need for dead reckoning. Dead reckoning combined with presurveyed way-point recalibration is probably the best approach for K-25 applications.

Implementation Needs: Development costs of \$0.5 to \$1.0M. Normal deployment costs. Capital costs are estimated to be \$200K to \$300K/unit. There are no "separate" operating costs for this sensor.

Author: J.N. Herndon

References: MMES staff members personal experience/opinion.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Laser range finders to provide a means of accurately ascertaining the position of a robotic device relative to the work site.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Laser range finders. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. For the implementation of telerobotic and autonomous operations, accurate position information is required for the work space, relative to the robotic platform. Laser range cameras presently have insufficient reliability and accuracy for the long-range needs of the K-25 efforts.

Status: Predemonstration

Efficacy. Medium.

Waste. None

Additional Comments. None

Science/Technology Needs: Present methods for generating three-dimensional sensory information of the local task site have insufficient reliability and accuracy to allow widespread robust automation of local tasks. Significant benefits could be realized through improvement of laser range finder hardware. Limitations exist in both hardware reliability and data interpretation.

Implementation Needs: Development costs of \$0.5 to \$1.0M. Normal deployment costs. Capital costs after development would be approximately \$250K/unit. Increased operating costs would be negligible.

Author: H.E. Knee

References:

1. MMES staff members personal experience/opinion.

2. F. J. Sweeney, *Random and Systematic Errors in Laser Range Camera Data.*

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization. Primarily for characterization activities, the ability to control the force (e.g., for swipes or sensor sweeps) is a necessary feature of the robotic manipulator.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Force controls. Mobile robotic platforms are required for deployment of characterization, dismantlement, and decommissioning sensors and tooling. For the implementation of telerobotic and autonomous operations, accurate force control information is required to control the forces exerted in the remote environment. Presently, adequate end-of-arm force-torque sensing capability has been demonstrated for control of the tasks. Significant improvement in accuracy and sensor robustness is needed for tactile sensing.

Status: Predemonstration

Efficacy. High for cartesian and joint space sensing; Medium for tactile sensing.

Waste. None

Additional Comments. None

Science/Technology Needs: Present accuracy and robustness of tactile sensors preclude strong reliance on these sensors for many applications, including laboratory sample handling operations.

Implementation Needs: Development costs estimated to be from \$0.2M to \$0.5M. Normal deployment needs. Capital costs estimated at \$100K/unit. No separate operating costs.

Author: H.E. Knee

References: MMES staff members personal experience/opinion.

February 26, 1993

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Liquid-liquid interface detection. The automated/robotic detection of liquid-liquid interfaces in an analytical laboratory.

Status: The status of this technology for application in an automated analytical laboratory is still being assessed.

Efficacy.

Waste.

Additional Comments.

Science/Technology Needs:

Implementation Needs:

Author: S. Schrock

References:

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization. Automated control of physical parameters (flow, mass, volume, etc.).

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements: Robotics/automation

Alternatives: Sensors, control

Technology: Flow, mass, volume. Present industrial-grade sensors are sufficient for expected applications of these sensors in the K-25 characterization tasks.

Status: Accepted

Efficacy. High for applications in automated analytical laboratories.

Waste. No additional waste generated by this technology.

Additional Comments. None

Science/Technology Needs: None

Implementation Needs: Normal deployment needs. Capital costs are estimated at \$20K/unit.

Author: S. Schrock

References: MMES staff members personal experience/opinion.

EM Problem: Decommissioning

K-25 Site Problem: Enrichment process buildings

Problem Area/Constituents: Support of characterization, dismantlement, and decontamination—Sensors are required on the manipulator arm/end-effector to accurately determine its position.

Reference Requirements: Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelements:

Alternatives: Sensors, control

Technology: Position sensors. Present industrial-grade position sensors are sufficient for expected applications of these sensors in the K-25 characterization, dismantlement, and decontamination tasks. The available technologies are expected to be sufficient for any applications related to manipulator arm and end-effector position sensor requirements.

Status: Accepted

Efficacy: High for application in analytical laboratory or for sensor sweeps.

Waste: None

Additional Comments: None

Science/Technology Needs: None

Implementation Needs: Development costs are negligible. Normal deployment needs. Capital costs are estimated as <\$10K/sensor. There are no separate operating costs.

Author: H.E. Knee

References: MMES staff members personal experience/opinion.

WASTE MANAGEMENT

EM Problem: Waste management

K-25 Site Problem: Disposal of final residues from decontamination and decommissioning, environmental restoration, and waste management operations

Problem Area/Constituents: Permanent disposal of uranium, low-level, mixed, and special case wastes in a matrix of boreholes in clay-rich rocks.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Technology: Borehole disposal—The concept of disposal in a matrix of boreholes in clay-rich rocks is a relatively inexpensive method for the permanent disposition of uranium, low-level, mixed, and special case wastes. Its unique features are its complete flexibility and modular nature in operational conditions. A limited area is used at a time, and a complete borehole site can be rapidly returned to normal land use. Disposal depths may vary from a few hundred meters to 1000 m. For the purpose of preliminary demonstration design, the borehole would be assumed to be 0.52 m in diameter and extending vertically to a depth of about 250 m. The depth from the surface to the disposal zone would be about 80 m. Because the lateral homogeneity of host material cannot be assumed for more than a few thousand meters, the general repository design practice would be to minimize lateral extent to not more than 1000 m in any direction. The bore holes would be laid out in hexagonal configuration.

Status: Predemonstration.

Science/Technology Needs: The concept is practicable by efficient use of existing experience from civil and mining engineering technology. However, the satisfactory application of the technology for mixed wastes disposal needs to be demonstrated.

Although the complete evaluation of clay-rich rocks for disposal of radioactive and hazardous wastes includes consideration of the hydrologic, geologic, rock mechanical, geochemical, and thermal factors that would affect the construction, operation, and performance of these rocks, the findings related to their hydrologic elements are believed to be of overriding importance in this work. Because excessive groundwater inflow into the borehole workings is probably going to be the most important consideration that would lead to the need for nonroutine engineering measures, this groundwater inflow would likely be selected as the principal criterion for the hydrologic evaluation of prospective borehole disposal sites.

Implementation Needs: Development and demonstration of the use of the technology to dispose of radioactive mixed-wastes are estimated to require \$2M-\$3M (1992 dollars). However, the payback could be significant when compared to the cost of alternate permanent disposal options.

Author: T. F. Lomenick

References:

1. T. F. Lomenick, "The Development of Technologies for the Long-Term Containment of Low-Level Radioactive and Hazardous Wastes Into Geologic Formations," Chapter 15 in *Effective and Safe Waste Management*, R. L. Jolley and R. G. M. Wang, eds., Lewis Publishers, Boca Raton, Florida, 1993.

EM Problem: Waste management

K-25 Site Problem: Disposal of final residues from decontamination and decommissioning, environmental restoration, and waste management operations

Problem Area/Target Constituents/Media: Permanent disposal of noncontaminated debris from decontamination and decommissioning, remedial action, and current waste management operations

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: Landfill

Technology: Y-12 Plant industrial landfill—This landfill will accept clean debris (including demolition waste) for permanent disposal. The landfill is expected to be operational in July 1993. The landfill has a design capacity of 1.5 million cubic feet and a design life of 43 years.¹ The wastes disposed in this landfill must meet the waste acceptance criteria (WAC) for the landfill and obtain approval from the facility manager for the disposal of the wastes. The wastes likely to be disposed at this landfill include noncontaminated construction debris and sanitary wastes.

Status: Accepted—The application for the use of the landfill is currently pending with the Tennessee Department of Environment and Conservation (TDEC). Additional details such as the WAC for the landfill could be provided at a later date when the permit is granted.

Science/Technology Needs: None

Implementation Needs: Implementation needs for disposing the wastes include obtaining regulatory approval for the disposal of the wastes and funding.

Funding would be required for performing waste analyses (to ensure compliance with the landfill WAC) and waste packaging, handling, and transportation (WPH&T) to the landfill. Estimated funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, tipping fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

1. Y-12 Plant Staff, *Y-12 Construction/Demolition Landfill VII*, Y/TS-854, April 1992.

EM Problem: Waste management

K-25 Site Problem: Disposal of final residues from decontamination and decommissioning, remedial action, and waste management operations

Problem Area/Target Constituents: Permanent disposal of low-level radioactive waste from decontamination and decommissioning, remedial action, and current waste management operations that meets the waste disposal site's waste acceptance criteria (WAC)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: Trench disposal

Technology: Nevada Test Site—This site has been earmarked for the disposal of DOE low-level radioactive wastes provided the waste meets the site's WAC.

Status: Accepted—Additional details such as the site's WAC could be provided at a later date, if required.

Science/Technology Needs: None

Implementation Needs: Implementation needs for disposing the wastes include obtaining regulatory approval for the disposal of the specific low-level radioactive wastes at the site and funding.

Funding would be required for performing waste analyses (to ensure compliance with the site WAC) and waste packaging, handling, and transportation (WPH&T) to the site. Estimated

funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, tipping fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Disposal of solid wastes meeting Resource Conservation and Recovery Act of 1976, as amended (RCRA) requirements. These wastes are also known as RCRA wastes.

Problem Area/Target Constituents/Media: Permanent disposal of solid RCRA wastes from decontamination and decommissioning, remedial action, and current waste management operations that meet the waste disposal site's waste acceptance criteria (WAC)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: In-ground disposal

Technology: Commercial RCRA landfill sites—There are several commercial landfill sites that have been approved by the regulators for the disposal of RCRA wastes. Some of these sites are Chemical Waste Management site at Emelle, Alabama, Rollins site near Baton Rouge, Louisiana, and U. S. Ecology site near Beatty, Nevada. These sites have been approved to accept strictly RCRA wastes for disposal provided the waste meets the site's WAC. RCRA wastes meeting the disposal site's WAC are proposed to be disposed at these sites.

Status: Accepted—Additional details such as the WAC for any of the commercial landfills could be provided at a later date, if required.

Science/Technology Needs: None

Implementation Needs: Implementation needs for disposing the wastes include obtaining regulatory approval for the disposal of the specific RCRA wastes at the site, meeting the site's WAC, and funding.

Funding would be required for performing waste analyses (to ensure compliance with the site WAC) and waste packaging, handling, and transportation (WPH&T) to the site. Estimated funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, disposal fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

EM Problem: Waste management

K-25 Site Problem: Disposal of wastes that are contaminated with both low-level radioactive and hazardous components. These wastes are also known as mixed wastes.

Problem Area/Target Constituents: Permanent disposal of low-level mixed wastes from decontamination and decommissioning, remedial action, and current waste management operations that meet the waste disposal site's waste acceptance criteria (WAC)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: Landfill

Technology: Envirocare, Utah Landfill—The low-level mixed waste residues are proposed to be permanently disposed at Envirocare's landfill near Clive, Utah. This landfill accepts low-level wastes for disposal that meet its waste acceptance criteria.

Status: Accepted—Additional details such as the WAC for the landfill could be provided at a later date, if required.

Science/Technology Needs: None

Implementation Needs: Implementation needs for disposing the wastes include obtaining regulatory approval for the disposal of the specific wastes at the site, meeting the site's WAC, and funding.

Funding would be required for performing waste analyses (to ensure compliance with the site WAC) and waste packaging, handling, and transportation (WPH&T) to the site. Estimated funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, disposal fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Disposal of transuranic (TRU) wastes. These are wastes that contain transuranic elements above certain concentration limits.

Problem Area/Target Constituents: Permanent disposal of TRU wastes from decontamination and decommissioning, remedial action, and current waste management operations that meet the waste disposal site's waste acceptance criteria (WAC)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: Underground waste retrievable facilities

Technology: Waste Isolation Pilot Plant (WIPP) Facility, New Mexico—The TRU waste residues are proposed to be permanently disposed at the WIPP facility in New Mexico, provided they meet the facility's WAC. This facility is being developed specifically for disposing of TRU wastes from DOE facilities.

Status: Accepted. Additional details such as the WAC for the facility could be provided at a later date when it is finalized.

Science/Technology Needs: None

Implementation Needs: Implementation needs for disposing the TRU wastes include obtaining regulatory approval for the disposal of the specific wastes at the site, meeting the site's WAC, and funding.

Funding would be required for performing waste analyses (to ensure compliance with the site WAC) and waste packaging, handling, and transportation (WPH&T) to the site. Estimated funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, disposal fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Disposal of low-level radioactive waste

Problem Area/Target Constituents: Permanent disposal of low-level radioactive waste from decontamination and decommissioning, remedial action, and current waste management operations that meets the waste disposal site's waste acceptance criteria (WAC)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste disposal

Alternative: Landfill

Technology: Oak Ridge Reservation (ORR) class L-I low-level-waste landfill (disposal facility)^{1,2}—This is a trench-type disposal facility being developed for the disposal of ORR Class L-I solid low-level wastes containing long half-life radionuclides such as uranium and technetium. The facility will have a proposed waste disposal capacity of 1.6 million cubic feet and an expected useful life of 30 to 40 years. The facility is currently undergoing engineering development. This facility is being developed in case the ORR low-level wastes cannot be disposed at an acceptable out-of-state facility.

Status: Predemonstration—This facility is currently being developed and designed. Additional details such as the site's WAC could be provided at a later date after they are finalized.

Science/Technology Needs: Additional research, development, and demonstration (RD&D) still needs to be conducted to determine the environmental acceptability of this disposal option for the low-level radioactive wastes.

Implementation Needs: The ORR Class L-I disposal facility is projected to be ready in early 1999. The capital cost for the facility is estimated to be \$90M (1992 dollars) and the annual operating costs are estimated to be around \$8M (1992 dollars).

Implementation needs for disposing the wastes (after the facility is ready to accept wastes) include obtaining regulatory approval for the disposal of the specific low-level radioactive wastes at the site and funding.

Funding would be required for performing waste analyses (to ensure compliance with the site WAC) and waste packaging, handling, and transportation (WPH&T) to the site. Estimated funding requirements cannot be forecast because they are dependent upon several factors such as waste volumes, tipping fees, analytical requirements, and WPH&T costs.

Author: Singh

References:

1. *Systems Requirements Document for Low-Level Waste Disposal Facilities*, X-OE-612, July 1992.
2. *Conceptual Design Report for Low-Level Waste Disposal Facilities*, K/D-5832-R1, July 1992.

EXCEPTED PACKAGES— STRONG, TIGHT CONTAINERS

WPHT-100-OG

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation for radioactive materials whose activity per package does not exceed the limits for limited quantities as specified in the regulations

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171–179
- Atomic Energy Act
- DOE Orders 1540.1, 1540.2, 1540.3, 5700.6C
- IAEA Safety Series No. 6, 7, 37 (1990)
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Packaging

Technology: Excepted packages—strong, tight containers—Limited quantities of radioactive materials, as defined in the regulations, are authorized to be packaged and shipped in strong, tight containers if the provisions made in the regulations are met. These strong, tight packages will not leak any of the radioactive materials during conditions normally incident to transport. Adequate technology currently exists for strong, tight packages.

Status: Accepted—Strong, tight packages are currently used throughout DOE to ship limited quantities of radioactive materials.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

February 26, 1993

**EXCEPTED PACKAGES—
STRONG, TIGHT CONTAINERS**

WPHT-100-OG

Implementation Needs: Because the technology for strong, tight packages is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation of nonfissile concentrated wastes having total activities less than Type-A package limits, as specified in the regulations

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- Atomic Energy Act
- Nuclear Regulatory Commission regulations under 10 CFR 71
- DOE Orders 1540.1, 1540.2, 1540.3, 5610.1, 5700.6C
- IAEA Safety Series No. 6,7,37 (1990)
- NRC Regulatory Guides—Series 7
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Multiuse containers

Technology: Multiuse, standardized, Type-A packaging—Multiuse packagings are needed to improve compliance in Type-A shipments in general. Improved, standardized Type-A packaging is needed for shipping radioactive materials during the K-25 site cleanup. Design emphasis will be placed on incorporating human factors design features to minimize the potential for human error. A standardized multiuse Type-A package will help ensure safe, effective, and efficient transportation of Type-A quantities of radioactive materials during decommissioning and decontamination of the K-25 site. Safe transport, in turn, will support environmental restoration efforts and aid in the prevention of environmental damage as a

result of transportation-related releases of radioactive materials. An acceptable multiuse Type-A packaging should be low cost, light weight, widely applicable, and user friendly, and should be reusable and/or recyclable. It must meet DOT and international regulations for transport by all modes.

Status: Evolving Technology/Conceptual. The basis for the packaging technology exists. However, multiuse, standardized Type-A packaging designs need to be developed.

Science/Technology Needs: An operationally efficient multiuse Type-A package, or packages, for radioactive materials needs to be developed to support decommissioning and decontamination efforts. This technology will provide better, standardized packaging for small quantities of radioactive liquids, solids, and gases. This design should be as widely applicable as possible and made available, where appropriate, for cleanup of the K-25 site.

Implementation Needs: Development Costs. For development, testing, and qualification of multiuse Type-A packaging designs an estimate of funding requirements is \$1M (1992 dollars).

Author: K. S. Boes

References: Not applicable

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation for nonfissile hazardous and/or radioactive materials having total activities greater than Type-A package limits, as specified in the regulations

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- Atomic Energy Act
- Nuclear Regulatory Commission regulations under 10 CFR 71
- DOE Orders 1540.1, 1540.2, 1540.3, 5610.1, 5700.6C
- IAEA Safety Series No. 6, 7, 37 (1990)
- NRC Regulatory Guides—Series 7
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Light-weight containers

Technology: Type-B packaging—Used to package nonfissile concentrated wastes having total activities greater than Type-A package limits. Adequate technology currently exists for Type-B packaging. Certified package designs can be identified from the Radioactive Material Packaging (RAMPAC) and the Packaging Management Transportation System (PMTS) data base, which will identify numbers and status of packagings available or under development by EM-561.

Status: Accepted. Type-B packages are currently used throughout DOE to ship radioactive materials.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

Implementation Needs: Because the technology for Type-B packages is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation, using Type A fissile certified and Type-B fissile certified packages, for fissile radioactive materials having total activities less than or greater than Type-A package limits, respectively, as specified in the regulations

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- Atomic Energy Act
- Nuclear Regulatory Commission regulations under 10 CFR 71
- DOE Orders 1540.1, 1540.2, 1540.3, 5610.1, 5700.6C
- IAEA Safety Series No. 6, 7, 37 (1990)
- NRC Regulatory Guides—Series 7
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Light-weight containers

Technology: Type-A and Type-B fissile certified packaging—Type-A fissile certified packaging is used to package concentrated wastes containing fissile material with total activities less than Type-A package limits. Type B fissile certified packaging is used to package concentrated wastes containing fissile material with total activities greater than Type-A package limits. Adequate technology currently exists for both Type-A fissile certified packaging and Type-B fissile certified packaging. Certified package designs can be identified from the Radioactive Material Packaging (RAMPAC) and Packaging Management Transportation System (PMTS)

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data base, which will identify numbers and status of packagings available or under development by EM-561.

Status: Accepted—Both Type-A fissile certified packages and Type-B fissile certified packages are currently used throughout DOE to ship fissile radioactive materials.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

Implementation Needs: Because the technology for Type-A fissile certified and Type-B fissile certified packages is adequate, there are currently no implementation needs.

Author: E. S. Boes

References: Not applicable

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**PERFORMANCE-ORIENTED PACKAGING
GROUPS II AND III, FOR POLYCHLORINATED BIPHENYLS**

WPHT-104-OG

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation for polychlorinated biphenyl (PCB)-contaminated materials and wastes

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- DOE Orders 1540.1, 1540.2, 5700.6C
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Performance-oriented packaging

Technology: Performance-oriented packaging (POP), groups II and III, for PCBs—This technology includes packing group II and III containers and bulk strong, tight containers. PCBs are normally regulated by air and water only and are authorized to be shipped in POP packing group II containers except if there is a reportable quantity (RQ). If there is a reportable quantity of PCBs (the reportable quantity is 1 pound), then all modes are regulated. When rail and highway shipments are regulated, POP packing group III containers are authorized. Bulk shipments are authorized to be made in strong tight containers, per the regulations. Adequate technology currently exists for packaging and shipping PCBs.

Status: Accepted—Performance-oriented packaging and strong tight packages are currently used throughout the DOE to ship PCBs.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

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**PERFORMANCE-ORIENTED PACKAGING
GROUPS II AND III, FOR POLYCHLORINATED BIPHENYLS**

WPHT-104-OG

Implementation Needs: Because the technology for performance-oriented packaging and strong tight packages is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

February 26, 1993

**PERFORMANCE-ORIENTED PACKAGING,
GROUPS II AND III, FOR ASBESTOS**

WPHT-105-OG

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation for asbestos materials and wastes

Reference requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- DOE Orders 1540.1, 1540.2, 5700.6C
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.
- National Emission Standards for Hazardous Air Pollutants (NESHAP)

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Performance-oriented packaging

Technology: Performance-oriented packaging (POP), groups II and III, for asbestos-- This technology includes packing group II and III containers used for shipping asbestos. Friable, white asbestos is authorized to be shipped in POP packing group III containers. Friable, blue or brown asbestos is authorized to be shipped in POP packing group II containers. Asbestos immersed or fixed in a natural or artificial binder material (such as cement, plastic, asphalt, resins or mineral ore) and manufactured products containing asbestos are not subject to the requirements of the packaging regulations. Adequate technology currently exists for packaging and shipping all types of asbestos.

Status: Accepted--Performance-oriented packaging is currently used throughout the DOE to ship asbestos.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

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**PERFORMANCE-ORIENTED PACKAGING,
GROUPS II AND III, FOR ASBESTOS**

WPHT-105-OG

Implementation Needs: Because the technology for performance-oriented packaging is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

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**PERFORMANCE-ORIENTED PACKAGING, GROUPS I-III,
FOR RCRA NONRADIOACTIVE HAZARDOUS WASTE**

WPHT-106-OG

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: Packaging, handling, and transportation for nonradioactive hazardous waste

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- DOE Orders 1540.1, 1540.2, 5700.6C
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Performance-oriented packaging

Technology: Performance-oriented packaging (POP), groups I-III, for RCRA nonradioactive hazardous waste—This technology includes packing group I, II, and III containers, specification packaging, and strong, tight containers for handling RCRA nonradioactive hazardous wastes. These wastes or materials are authorized to be shipped in POP packing group I, II, and III packages for nonbulk shipments, per the regulations. For bulk shipments, specification packaging and strong, tight containers are authorized, per the regulations. Adequate technology currently exists for packaging and shipping RCRA nonradioactive hazardous waste.

Status: Accepted. Performance-oriented packaging, specification packaging, and strong tight containers are currently used throughout DOE to ship nonradioactive hazardous waste.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

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**PERFORMANCE-ORIENTED PACKAGING, GROUPS I-III,
FOR RCRA NONRADIOACTIVE HAZARDOUS WASTE**

WPHT-106-OG

Implementation Needs: Because the technology for performance-oriented packaging, specification packaging, and strong, tight containers is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: On-site packaging, handling, and transportation of hazardous and/or radioactive materials and wastes

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- Atomic Energy Act
- Nuclear Regulatory Commission regulations under 10 CFR 71
- DOE Orders 1540.1, 1540.2, 1540.3, 5610.1, 5700.6C, 5480.X (draft)
- IAEA Safety Series No. 6, 7, 37 (1990)
- NRC Regulatory Guides—Series 7
- International Maritime Dangerous Goods Code
- Transportation and Traffic Management regulations under 41 CFR 109
- 49 U.S.C. 1803 et. seq.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging

Alternatives: Packaging

Technology: On-site packaging—This includes Type-A; Type-B; fissile; strong, tight; industrial packaging (IP); performance-oriented packaging (POP); and bulk packaging or packaging equivalent in safety. Full adherence to federal regulations applicable to off-site packaging and transportation of hazardous materials is an acceptable approach to meeting the requirements. Packaging that has the equivalent safety of off-site packaging is also acceptable. Assuring equivalent safety can be achieved by relying on package performance or incorporating specific hazardous communications and enroute control measures along with package performance. Adequate technology currently exists for on-site packaging and transportation.

Status: Accepted. On-site shipments of hazardous and radioactive materials and wastes are currently made throughout the DOE.

Science/Technology Needs: New package designs may be required if current designs are not suitable; however, current technology will be used for the new designs.

Implementation Needs: Because the technology for on-site packaging and transportation is adequate, there are currently no implementation needs.

Author: K. S. Boes

References: Not applicable

EM Problem: Waste management

K-25 Site Problem: Waste packaging, handling, and transportation

Problem Area/Constituents: PHT user information; interface definition. The specific needs for packaging, handling, and transportation of wastes (radioactive, other hazardous, mixed waste, etc.) have not been clearly defined for the K-25 site. The waste/material forms, quantities, locations of origination and destination, and time-period when packaging, handling, and transportation must occur need to be clearly specified. Then the availability of acceptable packagings, the need for package design, development, testing and certification, and the physical interfacing of the package/transportation system with the physical plant and materials can be defined.

Reference Requirements:

- Hazardous Materials Transportation Act regulations under 49 CFR 171-179
- Atomic Energy Act
- Nuclear Regulatory Commission regulations under 10 CFR 71
- DOE Orders 1540, 4700.1, and 5480
- IAEA Safety Series No. 6 (1990)
- ICAO, IATA, IMO codes and regulations
- Transportation and Traffic Management regulations under 41 CFR 109-40
- ANSI, ASME, ASTM standards

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste packaging, handling, and transportation

Alternative: Physical interface between the waste generators and the transportation system

Technology: Administrative and physical interfaces with users—DOE 4700.1 defines the systems engineering requirements which must be satisfied in defining the administrative and physical interfaces. These interfaces need to be defined early in the K-25 remediation program, and continually tracked, to ensure adequate development of the packaging and

transportation system and any ancillary equipment which will be needed to facilitate the on- and off-site movements of the waste materials.

Status: Technology is generally available, efforts are needed to adequately, safely and economically apply the technologies. Interface working groups, involving waste generators and developers/operators of packaging/transportation systems, are needed.

Science/Technology Needs: None

Implementation Needs: Because interface working groups involving waste generators and developers/operators of packaging/transportation systems are needed, implementation costs associated with this problem are estimated at \$400K over a two to three year period, with follow-on funding of approximately \$100K per year to assure interfaces remain properly defined as the remediation effort proceeds. Thus a total implementation funding over the lifetime of the program on the order \$1M is anticipated.

Author: R. B. Pope

References:

1. *Shippers - General Requirements for Shipments and Packagings*, 49 CFR 173.
2. *Packaging and Transportation of Radioactive Material*, 10 CFR 71.
3. *Regulations for the Safe Transport of Radioactive Material*, 1985 Edition (As Amended 1990), Safety Series No. 6, International Atomic Energy Agency, Vienna, Austria, 1990.
4. *Transportation Regulations; Compatibility With the International Atomic Energy Agency (IAEA)*, *Federal Register*, Vol. 53, No. 110, June 8, 1988, Proposed Rule (Nuclear Regulatory Commission).
5. *Transportation Regulations; Compatibility with Regulations of the International Atomic Energy Agency; Notice of Proposed Rule, HM-169A*, *Federal Register*, Vol. 54, No. 218, November 14, 1989 (Department of Transportation).

EM Problem: Waste management

K-25 Site Problem: Minimize the generation of hazardous and mixed wastes

Problem Area/Constituents: Plantwide wastes from decontamination and decommissioning (D%D), remedial action, and waste management operations at the site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste minimization

Alternatives:

Technology: Waste Minimization Evaluation System (WMES)—An ORNL-developed computerized process simulation model, WMES can be used as an effective waste minimization evaluation tool. Effective waste minimization and pollution prevention techniques should be used to minimize the toxicity and quantity of wastes and pollutants resulting from normal operations as well as D&D activities at the K-25 Site.¹ Previous applications of the WMES model have yielded significant reduction of wastes and pollutants because of application of waste minimization techniques. This has, in turn, resulted in substantial savings in both operating and clean-up costs.^{2,3} The WMES can be customized to model any specific waste management operation. Briefly, the WMES integrates the following essential elements to develop waste minimization strategy for a given application:

- systems analysis,
- process modeling,
- waste minimization experiences,
- knowledge of available treatment options,
- regulatory requirements, and
- alternative evaluation and selection processes.

Status: Demonstration

Science/Technology Needs: The generic methodology for the evaluation system has been developed along with a computerized prototype. The evaluation system is implemented using a modular approach. Several modules must be further developed to provide a full-scale application, including the waste minimization experience data base, the regulations data base, basic process models, the treatment selection process, and the data exchange mechanism. Customization for the particular application at the K-25 Site will require additional treatment and other process models, waste characterization data bases, and specific reporting features. When customized, the evaluation system will be used to perform waste minimization studies for specific problems associated with normal operations and/or D&D activities at the K-25 Site to demonstrate the efficacy of the system.

Implementation Needs: Development of the evaluation system is expected to require a team effort over 2 years and funding of about \$3M-\$5M (1992 dollars). Previous waste minimization experiences have shown that an appreciable reduction in waste production^{4,5}—ranging from 15% to 50% of volume generation—can be achieved. The cost of D&D for the K-25 Site has been estimated at about \$7 billion.⁶ Hence, the impact of an effective waste minimization effort could be expected to produce savings of about \$1 billion or more.

Author: Ferrada

References:

1. Martin Marietta Energy Systems, Inc., *Pollution Prevention*, Draft Standard No. ESS-EP-137, Rev. 0, October 1992.
2. U. S. EPA, *Experience with the EPA Manual for Waste Minimization Opportunity Assessments*, PB91-137133.
3. J. M. Hoegler, "Magnetic Separation of Uranium from Waste Materials," *Waste Minimization Practice*.
4. T. C. Keener, "The Application of a Mobile Solvent Recovery Process to Minimize Hazardous Waste," *Waste Minimization Practice*.
5. P. F. Mahoney and J. F. Muller, "Utilization of Ash Products from Combustion of Shredded Solid Waste," *Waste Minimization Practice*.
6. Ebasco Services, Inc., *Environmental Restoration of the Gaseous Diffusion Plants*, report prepared for the U. S. DOE under Contract No.: DE-AC05-91OR21928, October 1991.

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EM Problem: Waste Management

K-25 Site Problem: Contaminated wastewater, contaminated oil, contaminated solvents, contaminated concrete rubble, scrap transite, scrap asbestos, pipe and insulation, other scrap building materials, scrap metal, other scrap materials, contaminated clothing and rags, contaminated soil

Problem Area/Constituents: Polychlorinated biphenyls (PCBs) and other halogenated organics in water, PCBs in solvents, PCBs in oil, contaminated concrete rubble, scrap transite, metals, soil, etc., contaminated with PCBs or other halogenated or aromatic solvents.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992.
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation.
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992.
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders.

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing**Alternative:** Chemical treatment

Technology: Gamma radiolysis—In-situ/in-drum gamma radiolysis of PCBs, TCE, and other halogenated contaminants can be useful for destroying the halogenated species by direct removal of halogens by solvated electrons, as reported,¹⁻³ or by attack of hydroxyl free radicals (and perhaps other free radicals) on the unhalogenated portion of the PCB ring structure.⁴⁻⁶ The generation of free radicals is enhanced by irradiation of water-containing materials (wet) or by addition of such chemicals as hydrogen peroxide, alcohol, etc.^{7,8} The irradiation could proceed until the complete destruction of the contaminants into innocuous

species or could be complemented by subsequent bioremediation of the biodegradable fragments.

Status: Evolving technology

Science/Technology Needs: The radiolytic destruction of halogenated and aromatic compounds is well documented. Issues to be addressed are the complete characterization of the fragments under different conditions and different materials and their relative toxicities.⁹ Another important issue is the possibility of combining radiolysis with enhanced biodegradation of the radiolytic byproducts.¹⁰

Implementation Needs: Development costs are estimated to be \$1.25M (1992 dollars). These are the costs for development and technology transfer to the private industry of "In-situ/in-drum radiolytic destruction of PCBs and other halogenated substances from mixed wastes, TSCA wastes, contaminated soil, concrete, gaskets, pipes, etc." These costs are based on TTP No. OR-4TAK-93 by G. D. Del Cul, et al., submitted to DOE-OTD. A similar proposal (OR-PCBS-UT, G. D. Del Cul and D. C. White) would utilize gamma radiolysis followed by bioremediation with an estimated funding requirement of \$2.5M.

Author: Del Cul

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1. R. E. Arbon et al., "Gamma radiolysis of chlorinated hydrocarbons," *Spectrum '92, International Topical Meeting, Nuclear and Hazardous Waste Management*, 1266-1268, Boise, Idaho, August 23-27, 1992.
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5. R. F. Cichy et al., "Polychlorinated biphenyl reduction in lake trout by irradiation and broiling," *Bull. Environ. Contam. Toxicol.*, **22**, 807-812, 1979.
6. A. Singh et al., "Radiolytic dechlorination of polychlorinated biphenyl," *Radiat. Physics. Chem.*, **25**, 11, 1985.
7. Evans et al., "Mechanism of the radiation induced dechlorination of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane in alcoholic solutions," *J. Phys. Chem.*, **75**, 2762, 1971.
8. T. Sawai et al., "The radiolytic-chain dechlorination of polychlorinated biphenyls in alkaline 2-propanol solutions," *Bull. Chem. Soc. Japan*, **47**, 1989, 1974.
9. G. D. Del Cul et al., *In-situ/in-drum radiolytic destruction of PCBs and other halogenated substances from mixed wastes, TSCA wastes, contaminated soil, concrete, gaskets, pipes, etc.*, OTD-TTP No. OR-4TAK-93.
10. G. D. Del Cul, D. C. White et al., *In-situ/in drum PCB destruction: utilization of gamma irradiation for acceleration of bioremediation technologies for PCB destruction*, OTD-TTP OR-PCBS-UT.

EM Problem: Waste management

K-25 Site Problem: Radioactive and hazardous metals in waste; uranium tails;

Problem Area/Constituents: Chemistry of fullerenes (bucky balls)/encapsulation of radioactive and hazardous metals in fullerenes

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Chemical treatment

Technology: Bucky ball chemistry—Involves the innovative use of fullerenes (also known as bucky balls) to treat and encapsulate radioactive and hazardous species in high-molecular-weight carbon cages. The process is envisaged to consist of laser and/or electrical arc or plasma treatment for trapping transuranium materials (and hazardous metals) within closed graphitic spheres (i.e., fullerene with transuranium metals inside). This is expected to result in the trapping of radionuclides (and toxic metals) inside a graphite or carbon moderator for indefinite storage.

Status: During the past 2 years, major advances in the new materials area have occurred following the discovery of facile synthetic routes to the production of macroscopic quantities of fullerene materials. Fullerenes are edgeless, hollow, all-carbon molecules that contain hexagonal and pentagonal arrangements of sp^2 carbon atoms around the surface. The word fullerene is derived from the word buckminsterfullerene, which is the name given to the most symmetrical fullerene (C_{60}), in honor of the late R. Buckminster Fuller, to recognize the similarity of the C_{60} 's geometry to his geodesic architectural style. Fullerenes can range in size from 20 carbon atoms to many thousands of carbon atoms. Those fullerenes that have

been well characterized have approximately spherical shapes; however, tubular shapes of varying lengths and diameters are proposed to exist as well as fullerenes with negative curvature. Oak Ridge National Laboratory (ORNL) has instituted a major research activity in this area through the laboratory Directors Research Program. Scientists in many divisions throughout the laboratory are using their well-developed and powerful techniques to fully characterize this new class of molecules. Potential applications resulting from this new technological advance are many. Applied research also is devoted to tribology (frictional properties), nuclear medicine, batteries, catalysis, and other areas.

When fullerenes are produced using the electrical arc vaporization method, a build-up of material occurs on the negatively charged electrode. When this material is observed using electron microscopy, the structure revealed is that of concentric tubules of graphite. These materials, which are amicably called "bucky tubes," are shown to possess lengths which are centered at about one micron. Bucky tubes and the observation of the encapsulation of many atoms into coalesced fullerenes⁴ leads to a remarkable synthesis of observations: bucky tubes with numerous metal atoms inside. Current thinking within the fullerene research community is that metal atoms so trapped will never be released, except when exposed to extraordinarily harsh treatment. Because only metal atoms with low ionization potentials are encapsulated into the bucky tubes and spheres, this method may also represent a new way to reduce waste volume.

Recent observations by Ugarte using electron microscopy show that, when bucky tubes are exposed to a high flux of MeV electrons, they will anneal into structures that can be thought of as onions or "Russian dolls" of graphite: spheres within spheres. Ugarte, has recently shown that these species can trap small crystallites of metal species, specifically lanthanum. These crystallites are forever protected from the rest of the world by many layers of closed, edgeless graphitic spheres. These exciting new results suggest that it may be possible to mix radioactive waste together with "soot" from the carbon arc reactors. Irradiation of this mixture with high-energy electrons would allow encapsulation of these wastes into the spheres-within-spheres fullerene structures (bucky onions).

Fullerene technology is an evolving technology that could be applied to encapsulating radioactive and hazardous metals before their safe disposal in the environment. The technology is in an early phase of development and shows considerable promise. At present, development is at the bench-scale level. Considerable research, development, and demonstration will need to be undertaken before the technology reaches the implementation phase.

Science/Technology Needs: To fully evaluate the proposed encapsulation of radioactive and toxic metals in the all-carbon fullerene spheres, the following technical items must be acquired:

- A high-power, pulsed, multi-wavelength laser, such as a high-power, Nd:YAG laser with doubling crystals for development and use of the laser vaporization technique and qualification of recipes. A neodymium:yttrium-aluminum-garnet (Nd:YAG) laser is widely available commercially. This solid-state laser easily produces radiation at wavelengths

of 1065nm, 532nm, 355nm, and 266nm and has been proven to be effective in producing endohedral fullerene species. This laser would be used along with an existing 15 kW CO₂ laser, which is currently available at ORNL.

- An advanced, elevated-temperature target zone for tuning the annealing zone for the growing metallofullerenes. Such an apparatus would require oven and high-temperature vacuum and pressure materials for controlling the environment and position of the composite graphite target and for recovery of the products. This apparatus would constitute an improvement over our existing experimental designs. The desired temperatures would range from 1000°C to 2000°C. Desired pressures: 1 microns to 2 atmospheres.
- Laser desorption mass spectrometry, notably fourier-transform mass spectrometry or time-of-flight mass spectrometry using a supersonic molecular beam source, has proven to be the most sensitive approach for initial analysis of the materials produced. One such device would be required to effectively study these materials.
- A new fullerene/metallofullerene generator based on the idea of the three-zone fullerene generator, where the atomic carbon and metal are generated using a novel approach currently being studied elsewhere. Power generators for such a device would be in the 20-30kW range. Insulation, heaters, and/or cooling devices for tuning the annealing zone to the optimal temperature would be required. Also, provisions would be allowed for rapid removal of the products from the damaging temperatures required for annealing. Miscellaneous supplies for plumbing such a generator to various gas supplies, water cooling, and exhaust provisions would be required. Such a generator would be a (large) laboratory-scale test plant for the scaling-up of this process.
- Sufficient wet-chemistry supplies and equipment, such as a UV/VIS spectrophotometer, an IR spectrometer, a RAMAN spectrometer, fume hoods, balances, glassware, a glove box for air sensitive samples, and miscellaneous wet chemistry supplies.

The Health and Safety Research Division (HASRD) at ORNL possesses many of the necessary techniques required to examine the encapsulation of toxic or radioactive metals and actinides within the fullerenes. The High Flux Isotope Reactor (HFIR) neutron facility along with the High Temperature Materials Laboratory (HTML) possesses unique techniques which can be used to characterize these types of encapsulated species.

Implementation Needs: To scale up to include the encapsulation of large-scale wastes, new methodologies for encapsulation should be developed. To this end, a surplus 15 kW CO₂ laser from the Space Defense Initiative (SDI) program at ORNL is available to test the possible large-scale encapsulation of metal atoms in carbon clusters using the laser-based approach. We propose that this possibility be examined. The CO₂ laser represents a \$1M facility which could be devoted to this project. To implement this facility, the laser must first be put into operation. Trained operators continue to attend to this laser facility; therefore, putting the laser into operation will not be a problem. Also, it will be necessary to design and construct the actual radiation reactor and the separations technology for recovering the encapsulated waste material.

An estimated investment of \$10M (1992 dollars) will be required to scale this process to a level where significant quantities of radioactive or hazardous materials can be safely fixed in

graphitic spheres. The potential payback on this investment is expected to be in the range of \$150M, considering the waste treatment and disposal aspects of this technology and the potential spinoffs in other fields such as nuclear medicine and new materials development.

Authors: Armstrong, Haufler, Compton

References:

1. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, "Solid C_{60} : a New Form of Carbon," *Nature*, **347**, 354, 1990.
2. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, " C_{60} : Buckminsterfullerene," *Nature*, **318**, 162, 1985.
3. Sumio Iijima, "Helical Microtubules of Graphitic Carbon," *Nature*, **354**, 56, 1991.
4. Sumio Iijima, Toshinari Ichihashi, and Yoshinori Ando, "Pentagons, Heptagons, and Negative Curvature in Graphite Microtubule Growth," *Nature*, **356**, 767, 1992.
5. D. Ugarte, "Curling and Closure of Graphitic Networks Under Electron-Beam Irradiation," *Nature*, **359**, 707, 1992.

EM Problem: Waste management

K-25 Site Problem: Uranium tails; depleted uranium cylinders

Problem Area/Constituents: Treatment and handling of the depleted uranium ("tails") in 14-ton gas cylinders stored on site. The target constituent is the depleted uranium which exists as UF_6 . This can be considered a "source material" but may have to be disposed from the site under the decontamination and decommissioning (D&D) scenario.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Enhanced storage—Implies continued storage of the depleted UF_6 in cylinders under improved conditions. These improved conditions could include, for example, transferring the UF_6 to improved storage cylinders, developing improved paints and coatings for the depleted uranium cylinders (such as use of zinc-rich paints to enhance galvanic protection of the cylinders¹), and relocation of the UF_6 cylinders to sites (presumably under DOE control) located in drier climates, such as Arizona.²

Status: Predemonstration

Science/Technology Needs: These could consist of developing the strategy and technology (if needed) for providing enhanced storage for depleted uranium cylinders.

Implementation Needs: Development and implementation of the enhanced storage strategy is estimated to require \$1M-\$2M (1992 dollars). This estimate is for developing the strategy

and evaluating the options. This cost does not include the cost for implementing the selected strategy, such as fabricating the new cylinders, painting and refurbishing the existing cylinders, or acquiring title to the new storage site. These costs cannot be estimated because they depend on several factors which are presently unknown.

Authors: Singh, Little

References:

1. T. R. Lemons et al., *The Ultimate Disposition of Depleted Uranium*, K/ETO-44, December 1990.
2. J. M. Googin, personal communication with S. P. N. Singh, ORNL, December 16, 1992.

EM Problem: Waste management

K-25 Site Problem: Spent ion exchange media

Problem Area/Constituents: Ion exchange media are used extensively in liquid effluent treatment. While the media can be regenerated and recycled, they eventually lose their effectiveness and are called "spent ion exchange media." This spent media has to be disposed. To minimize hazardous waste volume, this media is treated to remove the undesirable components to permit disposal of the media as a nonhazardous waste. Before disposal, the spent media will be treated to remove, for example, inorganic, organic, or radioactive species.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Supplement: Waste Processing

Alternative: Chemical treatment

Technology: Elution—The removal of the adsorbed hazardous and/or radioactive compounds from spent ion exchange media using chemical agents such as acids, bases, and solvents. Elution is like the stripping operations that occur during the regeneration step.

Status: The status is labelled "demonstration," even though most elution operations are commercial technologies, because application of a particular elution operation to treat a given spent ion exchange medium may need to be demonstrated before it is used.

Science/Technology Needs: Because elution is closely linked to ion exchange operations, science/technology needs also are closely related. However, the efficacy of a given elution

operation may need to be demonstrated for a given application before the operation is used full-scale.

Implementation Needs: None, for the elution operations. However, treatment of the spent ion exchange medium before its disposal could significantly reduce waste disposal costs for spent media.

Author: Singh

References: None

EM Problem: Waste management

K-25 Site Problem: Scrap aluminum, copper, and other nonferrous metals (except nickel)

Problem Area/Constituents: Scrap aluminum generated during D&D operations at the gaseous diffusion plants, such as the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Chemical treatment

Technology: NAC process—According to Mattus et al.,¹ the NAC process can use contaminated scrap aluminum for denitration and disposal of nitrate wastes at several DOE facilities, such as those at Hanford, Idaho Falls, Oak Ridge, and Savannah River. The process causes aluminum to react with nitrate wastes to produce ammonia (which can be burned) and a ceramic-like alumina waste form (which can be disposed in land). Presently, this is a developmental technology. Mattus, et al.,¹ estimated that the process would require approximately 2.3 kg of aluminum per kg of nitrate waste. If aluminum is obtained at \$0.88/kg, the process is estimated to cost \$2.01-\$2.66/kg of nitrate destroyed.

Status: Predemonstration.

Science/Technology Needs: The feasibility of the NAC process has been proven on a bench-scale. However, further research and development needs to be conducted to establish the capabilities of the technology. For example, research needs to be conducted to determine if the final process waste form will encapsulate residual radioactive and hazardous components present in the contaminated aluminum and nitrate wastes. From a technology viewpoint,

process capabilities need to be demonstrated on, for example, the 1-2 ton/hour pilot-plant scale. In addition, technology assessments need to be conducted to establish the viability and economics of the process.

Implementation Needs: Further development of the process is expected to require \$2M-\$5M. However, because the process will dispose of two major, large volume, DOE waste streams (contaminated scrap aluminum and nitrates), its payback potential is expected to be at least one order of magnitude higher than the above-mentioned development costs. This is based on current disposal costs for these two streams.

Author: Singh

References:

1. A. J. Mattus et al., *A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process*, ORNL/TM-12245 (draft report), October 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated concrete rubble

Problem Area/Constituents: Volatile organic compounds (VOCs) in soil, contaminated concrete rubble, and PCBs in soil

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Thermal treatment

Technology: Thermal desorption—Thermal treatment of wastes contaminated with organic compounds can be performed with many different treatment systems. However, the four main types of treatment systems are rotary dryer systems, indirect-fired systems, heated screw-type systems, and asphalt plant aggregate dryers. Each treatment system uses the same basic principal of operation. Each system consists of a furnace in which the organic compounds are desorbed from the waste feed. Desorbed organics are removed from the furnace by a purge gas and are destroyed in an afterburner or are collected by a physical/chemical treatment system. The systems are operated between 300 and 800°F and are fed with 5-100 tons of contaminated waste per hour. The desorbed organic compounds are removed from the furnace by a purge gas stream, which may flow co-current or counter-current to the waste feed. A typical system consists of a feed pretreatment system, feed hoppers and conveyors, a co-current or counter-current furnace (directly or indirectly fired),

a treated soil cooling system, cyclones, an afterburner, a bag house, an induced draft (ID) fan, and a stack.

Status: Accepted by industry. Greater than 99% efficient in removing VOCs from soil. Costs range from \$35/ton (for low contamination-low moisture content soils) to \$120/ton. Thermal desorption of contaminated solids is in use at various remediation sites around the U.S. (some clean-ups have been completed).

Science/Technology Needs: The following concerns may cause problems during operation:

- Limitations exist on the types of waste and contaminants that can be treated.
- The presence of some contaminants may cause permitting problems.

Implementation Needs:

- Process equipment (e.g., indirect- or direct-fired rotary kiln, heated screw kiln, etc.)
- Minimum 2000 ft² equipment battery limit
- All utilities, including reliable electricity, cooling water, natural gas, steam, air, nitrogen, etc.
- Drum and material handling equipment
- Trained chemical operators
- U.S. Environmental Protection Agency (EPA)-certified laboratory support

Author: Dukes

References:

1. J. J. Cudahy et al., "Petroleum Contaminated Soils and Sludges-Markets, Permitting and Thermal Desorption Technologies," *Proceedings of the 1992 Incineration Conference*, Albuquerque, NM, May 1992.
2. R. K. Nielson and M. G. Cosmos, *Low Temperature Thermal Treatment (LT³) of Volatile Organic Compounds from Soil: A Technology Demonstration*, paper presented at the 1988 Summer National Meeting of the AIChE, Denver, CO, August 1988.

EM Problem: Waste management

K-25 Site Problems: Contaminated concrete rubble

Problem Area/Constituents: Treatment of mixed-waste contaminated solids such as TSCA Incinerator wet ash and secondary solid effluents containing PCBs, organics, inorganics, radionuclides, and metals

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Plasma Arc Furnace (PAF)—This technology builds on plasma hearth melting developments.¹ The plasma arc furnace is a new and promising technology that uses an electrically heated plasma gas to destroy organic contaminants and bind radionuclides and heavy metals in a glassy slag. The PAF represents an alternative to cementation and incineration that may be more acceptable to the public.

The plasma technology typically includes a continuous plasma torch operated in transfer mode (one end of the torch arc impinges on the material being heated) or non-transferred mode. The system includes an enclosed feeder, an afterburner, a slag removal system, a waste-gas chiller, a waste-gas scrubber, a continuous emissions monitoring system, stack samplers, and various controls and diagnostic equipment. The PAF can be operated under reducing or oxidizing conditions.

The term "plasma" refers to a highly ionized gas. Plasmas can be generated by a variety of techniques and occur over a wide range of pressures and energy levels. Typically, a torch uses a flowing gas to stabilize an electrical discharge (arc) between two electrodes. One or both of these electrodes is contained within the torch. For treatment of solid materials, the second electrode is usually the material being processed (using arc welding terminology, this is called the "work piece"). Energy is dissipated as heat and light as the electrical current flows through the gas. Through resistance heating (Joule heating), this process creates a high-temperature gas as well as directly heats the work piece.² Plasma torches have high energy densities with local temperatures up to 15,000°K.¹ Qualitative benefits of this technology are high-integrity final waste form, portability, and low off-gas and contamination control. Potential disadvantages are that plasma processes are very energy intensive, and power costs could limit applications to small-scale.⁶

Status: Demonstration; the following pilot-scale systems are installed:

- Centrifugal Retech Furnace—Switzerland
- Centrifugal Retech Furnace, DOE/EPA Site Program—Butte, Montana⁵
- Fixed Hearth Retech Furnace—Ukiah, CA
- Plasma Facility—Charleston, S.C.³
- Westinghouse Pilot Facility—Pittsburgh, PA³

Some operating and emissions data exist for these facilities, but additional data are needed for process design and scale-up to meet DOE mixed waste management objectives for treatment of K-25 Site waste streams.

Science/Technology Needs: Research and development (R&D) is required to assess metals carry-over from the primary chamber (hot zone) and optimize slag chemistry regarding metals stabilization, variations in waste input streams, reintroduction of condensed volatile metals into the slag phase, and radionuclide partitioning⁴ in the effluent streams, including metal specification studies in the entrained particulates in the off-gas as a function of particle size. Additional development is required to determine and improve electrode life, materials of construction in general, destruction and removal efficiency of hazardous/toxic organics, power efficiency, mass/energy balances to effect minimum secondary waste generation, and optimal safe operating methods as a function of heterogeneous waste processing.

Implementation Needs: The cost of demonstrating this technology to treat a wide range of low-to-high ash inorganic/organic waste feed streams to produce a low leachable slag is estimated to be \$10M. Estimated time to complete full-scale demonstration to treat specific K-25 Site waste streams at 1–2 tons/hour capacity is 3 years (Funding requests: FY 1993: \$0.5M; FY 1994: \$1.5M; and FY 1995: \$1.0M).

Author: Hermes

References:

1. W. Hoffelner et al., "Plasma Technology for Rapid Oxidation, Melting and Vitrification of Low/Medium Radioactive Waste," *Nuclear Engineering International*, October 1992.
2. M. I. Morris, *The Plasma Hearth Process: The Fixed Hearth Arc Plasma Treatment Process for Mixed Waste Treatment Applications*, draft TTP, December 10, 1992.
3. W. H. McCulla, personal communication with M. I. Morris, December 1, 1992.
4. J. B. Berry et al., *Mixed Waste Treatment Research, Development, Demonstration, Testing and Evaluation*, draft report, DOE Office of Technology Development, December 1992.
5. Retech, Inc., *Plasma Centrifugal Furnace Applications Analysis Report*, EPA/540/A5-91/007, June 1992.
6. L. C. Borduin et al., *Thermal and Photochemical Processes Applicable to Environmental Restoration and Waste Management Operations*, 1989.
7. C. G. Whitworth et al., *Slag Chemistry and Metals Volatilization in the Plasma Arc Furnace Experiment*, background file.
8. W. H. Hermes, background file containing personal notes of discussions with SAIC regarding emissions from centrifugal furnace in Switzerland, Retech Lab-Scale System, and Fixed Hearth Plasma System at Ukiah, CA.

EM Problem: Waste management

K-25 Site Problem:

Problem Area/Constituents: K-25 solid waste stream requiring new thermal treatment due to radioactive contamination:

- Composite roofing (tar, tar paper, rock) with no contamination¹
- Composite roofing (tar, tar paper, rock) with U contamination²
- Composite roofing (tar, tar paper, rock) with U and Tc contamination¹

General waste characterization that meets existing TSCA Incinerator Waste Acceptance Criteria:

- Combustible low-level RCRA hazardous organic compounds and metals
- Low-level PCBs, including solids, liquids and sludges, low to high ash, contaminated aqueous streams

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated 20 February 1992.
- Resource Conservation and Recovery Act and the Hazardous and Solid Waste Amendments of 1984, 40 CFR 260-270
- NEPA, 40 CFR 1500-1508
- National Emissions Standards for Hazardous Air Pollutants, 40 CFR 61, Subpart H
- DOE Order 5480.11, "Radiation Protection for Occupational Workers" (draft)
- DOE Order 5480.12, "Prevention, Control, and Abatement of Environmental Pollution"
- 40 CFR 270.32 ("omnibus" authority)
- 40 CFR 264-342(b) (POHC selection)
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- Toxic Substances Control Act
- RCRA Part 64 Subpart O

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Subelement: Waste processing

Alternative: Decontamination and thermal treatment

Technology: Incineration, including liquid injection, rotary kiln, fixed hearth, and fluidized bed. Second-stage destruction of gas phase organics is included in each technology

Incineration Practice:

Incineration is an engineered process that employs decomposition via thermal oxidation at high temperature (usually 900 C or greater) to destroy the organic fraction of the waste and reduce volume.³ Generally, combustible wastes or wastes with significant organic content are considered most appropriate for incineration. Technically, however, any waste with a hazardous organic fraction, no matter how small, is at least a functional candidate for incineration. For instance, significant amounts of contaminated water were being incinerated in the United States during the early 1980s.⁴ Contaminated soils are also being incinerated with increasing frequency. EPA, for example, has employed a mobile incinerator to decontaminate 40 tons of Missouri soil which had been contaminated with 4 lb of chlorinated dioxin compounds.⁵⁻⁸

The key element of any incineration system is the combustion reactor, or combustor. The combustor is supported by several subsystems that together with the combustion reactor make up a total incineration system. These subsystems include feed preparation and delivery system, ash removal and packaging systems, off-gas cleaning systems, system controls, and auxiliary utility supply systems. The state of technology of incineration systems could be made sufficient to provide safe and effective treatment of low-level radioactive, hazardous and toxic wastes. Not all proven incineration systems are designed to handle all these waste feed types.⁹ The incinerator design is based on specific waste profiles to establish basis flows, temperatures, residence times, and mixing requirements to meet waste treatment processing objectives and pollutant destruction and removal efficiencies. The design of the incinerator is done hand-in-hand with off-gas cleaning trains. In several instances, DOE incinerators appear to represent the most advanced application of incineration technology available anywhere. As examples, the Idaho National Engineering Laboratory PREPP system designers appear to have solved several difficult and chronic problems with rotary-kiln combustors, including positive sealing of the rotating combustor and reliable mechanisms for injection of solid feed and removal of ash from the combustor. The Los Alamos National Laboratory CAI system designers have developed an advanced controlled-air incinerator with positive sealing of the waste feed mechanism, safe liquid waste injection, vastly improved secondary air injection, and supplementary steam injection to prevent the formation of soot. The Savannah River Site CIF system will include a steam-atomized free-jet scrubber that has been proven effective in radioactive service during extensive semi-scale testing at SRS. The TSCA Incinerator (rotary kiln/SCC/4-stage wet scrubber) located at the K-25 Site in Oak Ridge, TN is the only TSCA, RCRA low-level mixed waste permitted and operating in the USA. Over 2×10^6 lb/year of liquid low-level mixed waste were processed in FY 1991 and FY 1992.

Status: Accepted—The incineration of roofing materials is accepted by the Environmental Protection Agency.¹⁰ The incineration of contaminated combustible building materials is common in the nuclear industry.¹¹

Waste generated: This will depend on the design of the incineration system, which is dependent on waste phase, the rad component(s), halogen, ash, and heating value content. Minimizing secondary waste generation and maximizing volume reduction are design and operating objectives.¹²

Cost summary: For example purposes, the existing TSCA Incinerator capital cost \$26M (1987 dollars); operating cost \$10/lb (1992 dollars)¹³ which can be lowered by additional process improvements focused on achieving higher waste throughput and tighter emission controls.

Science/Technology Needs:

New incinerator: Not applicable for the K-25 roofing materials mixed waste streams, but the proof of design assumptions related to mass/energy balance could be done using the existing TSCA Incinerator.

TSCA Incinerator: Regarding overall mixed waste thermal treatment using conventional incineration, the thermal technologies are proven. Off-gas particulate emission regulations, overall stack metals release, and final ash waste form leachability characteristics are general areas where applying research is cost effective. This is driven by both regulation and public perception. Understanding steady-state and upset trace emissions from incinerators, and thereby instituting mitigative feed and operational controls to reduce emissions, is justifiable. Such specific areas associated with K-25 Site are

1. Specification definition of sludge additive (clays, alumina-silicates entrapment matrix) that can be added to solid waste feed into primary chamber to reduce volatility of hazardous/toxic metals and rad isotopes.
2. Gas sampling/analysis definition and application to determine particulate carry-over (size, mass, metal specification) from hot zone to scrubber system as a function of waste feed/operating conditions.
3. Sampling/analysis of effluents to understand uranium and other rad isotope partitioning mechanisms.
4. Develop "corrosive environment" durable, high-temperature-rated inorganic porous membranes to demonstration phase for applications to remove fine particulate upstream of scrubbers to minimize mixed secondary waste effluents (such as liquids from wet scrubbers and process HEPA filters). Microfiltration technology can also be applied to liquid mixed waste to remove insoluble metals of regulatory concern upstream of the thermal treatment process step.
5. Quantify ash stabilization technologies to meet necessary physical/chemical requirements for economical handling/monitoring/disposal.
6. Support national continuous stack monitoring program by testing various technologies (e.g., metals, radionuclides, organics) using the TSCA Incinerator wet stack (already fitted

with two sampling platforms with isokinetic ports and trained certified sampling team on-site).

Implementation Needs:**Roofing Materials Mixed Waste Streams:**

A new incinerator would be needed because the existing TSCA incinerator cannot accept waste with more than 5 ppm total uranium and enrichments higher than 1% ^{235}U .¹⁴ The present incinerator requires the services of about 30 maintenance workers (maintenance mechanics, electricians, pipe fitters, welders, and instrument mechanics), their supervisors, 34 chemical operators, their supervisors, and 7 engineers.¹⁵ About 8–10 years is required for writing an environmental impact statement, holding public hearings, and obtaining the necessary permits TSCA permit, RCRA permit, NESHAP permit, and Clean Air Act permits.¹⁶

Note: Due to the large investment required, a new mixed waste solids incineration unit would likely be designed for a significant degree of versatility in waste acceptance.

Generic R&D Applied to Existing TSCA Incinerator:

The estimated costs for research needs cited is \$5M based on a three-year plan and the author's judgement. These needs are technically driven and apply to all the DOE facilities. The operating TSCA unit and trained K-25 technical staff, across all disciplines, allow for effective use of resources, considering thermal treatment technologies are likely to be the mainstay for the overall DOE waste treatment programs.

Author: W. H. Hermes

References:

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2. R. L. Farrar, Jr., "K-27 Roof Rocks" (letter to J. L. Gamble), (U) Union Carbide Corp., Nuclear Div., January 20, 1979, K-ET-124 (RPT:C-RD).
3. Clyde R. Dempsey et al., "Incineration of Hazardous Waste: A Critical Review Update," *Air and Waste Management*, **43**, January 1993.
4. G. Vogel et al., *Composition of Hazardous Waste Streams Currently Incinerated*, Mitre Corp., U.S. Environmental Protection Agency, April 1983.
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7. H. Mortensen et al, *Destruction of Dioxin Contaminated Solids and Liquids by Mobile Incineration*, EPA Final Report, EPA/600/R2-87/033, NTIS PB 87-188512/AS, June 1987.
8. F. Freestone et al., "Evaluation of On-site Incineration for Cleanup of Dioxin-Contaminated Materials," *Nuclear and Chemical Waste Management*, 7, 3-20, 1987.
9. *Summary of Radioactive and Mixed Waste Incineration Technologies within DOE Nuclear Weapons Complex*, prepared by the Congress of the United States, Office of Technology Assessment, Ralph A. Koernig, Merlin CO/Boulder, Inc., February 1991.
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11. R. Kohout, "Incineration." *Radioactive Waste Technology*, edited by A. Alan Moghissi, Herschel W. Godbee, and Sue A Hobart, American Society of Mechanical Engineers and American Nuclear Society, 1986.
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LM Problem: Waste management

K-25 Site Problem: Spent ion exchange media

Problem Area/Constituents: Destruction of organics (including halogenated organics) in gas or liquid effluents and radioactively-contaminated, spent ion exchange resins

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Catalytic destruction¹⁻⁴—Recently, much R&D has been performed internationally on pulse combustors. Maximum VOC destruction efficiency greater than 99% has been achieved in some experiments. The concept involves the unique characteristics of pulse combustors which effect a two-stage (thermal and catalytic) destruction process by exploiting both the high-combustion intensity in the pulse combustor chamber and the acoustic resonances in the combustor tailpipe. High combustion intensity results from rapid fluid-dynamic mixing and will lead to compact, transportable designs; acoustic resonances result in significantly increased mass transport to the catalyst, leading to high destruction efficiencies.

A pilot plant system using catalytic destruction (via incineration) has successfully destroyed radioactively-contaminated, spent, ion-exchange resins. This system was evaluated by the Japan Atomic Energy Research Institute.⁴

Status: Predemonstration

Science/Technology Needs: A complete investigative study of all experimental work done on the subject process must be conducted. Development work at the bench scale then will be performed for VOCs of interest, and their combustion chemistry will be established. If technical viability and economics justify further work, scale-up to pilot- or full-scale processes subsequently will follow.

Implementation Needs: The above-mentioned development study is expected to cost \$0.75M-\$1.5M (1992 dollars). As development work progresses and technical promise is clearly demonstrated, collaborative research efforts with the private sector can be established. As a result, lower implementation costs may be possible, particularly for the latter part of the development activities.

Author: Chiang

References:

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3. R.H. Perry and D.W. Green, eds., *Chemical Engineers' Handbook*, 6th Edition, McGraw-Hill Book Co., New York, 1984.
4. T. Yahata, S. Kihara, M. Hirata, and M. Abe, *Incineration of Spent Ion Exchange Resins in Combination with Fluidized Bed and Catalyst*, Japan Atomic Energy Research Institute, Japan, 1992.

EM Problem: Waste management

K25 Site Problem: Other scrap building materials (e.g., wood, tile, roofing, fixtures, gaskets)

Problem Area/Constituents: Treatment of other scrap building materials (e.g., wood, tile, roofing, fixtures, gaskets, etc.). Pyrolysis is most applicable for the following types of waste:

- Waste stored in containers or drums that cannot be easily drained
- Sludges or liquids that contain (1) high ash content; (2) volatile inorganics (e.g., NaCl, FeCl₂, Zn, and Pb); and (3) high levels of chlorine, sulfur, and/or nitrogen

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Pyrolysis combustion—Pyrolysis is defined as the chemical decomposition or change brought about by heating in the absence of oxygen. Application of pyrolysis to hazardous-waste treatment leads to a two-step process for disposal. In the first step, wastes are heated, separating the volatile components (combustible gases, water vapor, etc.) from nonvolatile char and ash. In the second step, volatile components are destroyed under proper conditions to assure incineration of all hazardous components.

The first step in pyrolysis treatment of hazardous waste is endothermic and generally is done at 425-760°C (800-1400°F). Normal feed rate is 0.25-5 tons of contaminated waste per hour.

The heating chamber is called the pyrolyzer. The endothermic property makes the process much easier to control. Hazardous organic compounds can be volatilized at this low temperature, leaving a clean residue. The volatiles are burned (second step) in a fume incinerator at conditions that make it possible to achieve destruction efficiency of more than 99.9999%. Separating the process into two very controllable steps allows precise temperature control and makes possible the construction of smaller equipment.

Status: Accepted by industry, and units are in use. Removal efficiencies of much greater than 99% are expected. Cost is unknown, but it is expected to be like thermal desorption (\$35-\$120/ton).

Science/Technology Needs: The following may cause problems during operation:

- Energy content in a waste feed may be retained by the char.
- Products of incomplete combustion (PICs), principal organic hazardous constituents (POHCs), and carcinogens present in the waste require fume incineration.
- Solids may prematurely enter the second stage resulting in shutdown.
- High water content in the waste may quench, or high plastic content may overwhelm the combustion process.

Implementation Needs:

- Process equipment (e.g., indirect- or direct-fired rotary kiln, heated screw kiln, etc.)
- Minimum 2,000 ft² equipment battery limit
- All utilities, including reliable electricity, cooling water, natural gas, steam, air, nitrogen, etc.
- Drum and material handling equipment
- Trained chemical operators
- EPA-certified laboratory support

Author: Dukes

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, p. 8.91-8.104, 1989.

EM Problem: Waste management

K-25 Site Problem: Other scrap building materials (e.g., wood, tile, roofing, fixtures, gaskets)

Problem Area/Constituents: Removal of inorganic, organic, and radioactive compounds from scrap aluminum, copper, and other ferrous and nonferrous metals

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Smelting^{1,2} —A pyrometallurgical process for decontaminating and treating scrap metals such as aluminum, copper, and other ferrous and non-ferrous metals generated during decontamination of the site. Basically, smelting consists of heating contaminated scrap metal in a furnace with various fluxes (such as limestone and coke) to high temperatures (generally, 700-2000°C) in the presence of reducing gases to yield molten metal and a slag or dross. Organic contaminants are destroyed during the smelting operation, and nonvolatile inorganic and radioactive species are (hopefully) removed with the slag. The slag can be further processed (if necessary) and disposed while the metal is cooled, cast in molds, and recycled (provided that radioactive contamination is within regulatory limits).

Status: Accepted by industry. However, satisfactory application of the technology to treat radioactively-contaminated metals at the site needs to be demonstrated.

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Science/Technology Needs: The major science/technology needs for using smelting to treat mixed-waste-contaminated metals consists of demonstrating that the radioactive species are removed preferentially with the slag or dross resulting from the smelting operations and that the slag can be disposed in compliance with environmental regulations. This may require bench-scale studies and demonstrations to prove its applicability.

Implementation Needs: Development and demonstration of the technology to treat mixed-waste contaminated metals are estimated to cost \$3M-\$5M (1992 dollars). However, the payback could be significant when compared to the cost of alternative treatment options. Also, the process could result in significant waste minimization because the metals could be recovered and recycled.

Author: Singh

References:

1. D. M. Considine, ed., *Chemical and Process Technology Encyclopedia*, McGraw-Hill Book Company, New York, 1974.
2. R. N. Shreve, *Chemical Process Industries*, McGraw-Hill Book Company, New York, 1967.

EM Problem: Waste management

K-25 Site Problem: Scrap porous nickel

Problem Area/Constituents: Scrap porous nickel generated during D&D operations at the gaseous diffusion plants, such as the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60–65
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Mond process—Also known as the carbonyl process. In this process, contaminated nickel reacts with carbon monoxide (CO) at around 100°C to form nickel carbonyl $[\text{Ni}(\text{CO})_4]$. The nickel carbonyl is taken to another reactor containing uncontaminated nickel pellets and heated to around 200–300°C. The nickel carbonyl decomposes at these temperatures to yield nickel metal and CO. The nickel is deposited on the pellets, and the CO is recycled to the first reactor. This process is highly selective for the recovery of nickel, because carbonyls of the other elements present in the contaminated nickel are not likely to be formed under the above process's operating conditions.¹

Status: Demonstration

Science/Technology Needs: Although the Mond process is commercial technology, its applicability to satisfactory treatment of the porous nickel recovered from D&D operations at the K-25 Site needs to be demonstrated.

Implementation Needs: Technology demonstration is estimated to cost \$1M–\$2M (1992 dollars). However, if the process can satisfactorily decontaminate the nickel to the desired

level, the payback for the process is expected to be greater than \$20M-\$30M, based on estimates of current disposal costs.

Author: Singh

References:

1. "Nickel and Nickel Alloys," *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 15, John Wiley and Sons, New York, New York, 1982.

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Scrap plastics, paper, and cloth (except PPC and rags)

Problem Area/Constituents: Organic ion-exchange media, radionuclides and technetium in oil, heavy metals in oil, PCB in oil, nonhalogenated organics in oil, mercury in oil, radionuclides in solvents, heavy metals in solvents, PCB in solvents, plastics, paper, cloth, organics, wood, combustible residues, organics.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Molten salt oxidation—The basic concept is to (1) introduce waste and air into a ceramic-lined vessel containing a bed of molten salt, (2) oxidize organic wastes in the molten salt, (3) use the heat of oxidation to keep the salt molten, and (4) remove spent salt for processing and recycling or for disposal.¹

Molten salt oxidation is a combination of chemical and thermal treatment and is perceived as having several advantages: the molten salt (1) acts as a dispersing medium for both waste and air, (2) enhances oxidation reactions, (3) enhances completeness by providing a better contact over a relatively long period, (4) neutralizes and retains acid gases and is self-scrubbing, (5) retains soot, chars, and ashes, and (6) can be designed as a mobile unit. A potential problem is generation of a spent salt that has to be processed (and recycled) or

disposed. For particular waste streams, the waste volume reduction can be significant or, for others, minimal or negative.

Status: Demonstration

Science/Technology Needs: Molten salt oxidation is not a new process. Small prototype units were operated and tested during the 1970s,² and R&D efforts continue today.³⁻⁶ A technology evaluation of molten salt process technology recently was conducted,⁷ and a 5-year implementation plan is under way.¹ Sodium carbonate-based molten salt beds are the most developed, but nitrate salts⁴ or other species are being tested.⁵ The molten salt oxidation process also may be suitable as an off-gas treatment operation for other thermal processes.¹

Implementation Needs: The 5-year implementation plan,¹ which includes bench-scale testing, prototype construction and demonstrations, and basic and applied research, is expected to cost \$35.6M. The estimated cost is \$1.4M for a 3-year development plan and technology transfer for the destruction of ion-exchange resins using molten salts, recovery of special materials, and salt recycling based on DOE-OTD-TTP No. OR-4TAH-93 by G. D. Del Cul and C. E. Bamberger.⁸

Author: Del Cul

References:

1. Task Force Report, *Molten Salt Oxidation Technology Five-Year Implementation Plan*, P-GJPO-650, May 1992.
2. D. E. McKenzie et al., *Disposal of Transuranic Solid waste Using Molten Salt Combustion Process*, AI-ERDA-13151, 1975.
3. O. H. Krikorian, *A Preliminary Assessment of Salt and Radionuclide Volatilities in the Molten Salt Reactor*, UCRL-ID-105173, 1990.
4. R. W. Bradshaw, "Hazardous Waste Treatment Using Oxidizing Molten Salts," *Emerging Technologies Meeting*, Atlanta, Georgia, October 1991.
5. G. D. Del Cul and C. E. Bamberger, "Catalyzed Molten Salt Oxidation of Spent Ion-Exchange Resins," *Gaseous Diffusion Process and Long Range Technical Support*, Milestone report, 1993.
6. R. S. Upadhye and J. F. Cooper, "Molten-Salt Destruction Process for Mixed Wastes," *Chemistry & Material Science 1990-1991*, UCRL-53943-91, 1991.
7. *Evaluation of the Molten Salt Oxidation Process Technology*, DOE/ID/12584-97, GJPO-105, January 1992.
8. G. D. Del Cul and C. E. Bamberger, *Catalyzed Resin Destruction: Catalyzed Low-Temperature Combustion of Spent Organic Ion-Exchange Resins*, DOE-OTD TTP-OR-4TAH-93, 1993.

EM Problem: Waste management

K25 Site Problem: Spent ion exchange media

Problem Area/Constituents: Treatment of refractory organohalides; wastes containing heavy metals along with refractory organic materials; mixed wastes containing organic sludges with radionuclides; spent, radioactive, ion-exchange resins and contaminated soils

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Chem char process—Destroys hazardous wastes by reverse-burn (where flame and oxidant move in opposite direction) gasification. The wastes to be treated are mixed with char, and the mixture is mechanically pushed upward through a gasifier. The char, prepared by reverse-burn gasification of subbituminous coal, has a macroporous structure and a surface area of approximately 200 m²/g, which can effectively sorb and immobilize waste liquids and sludges and provide an ideal physical matrix for treatment. Limited oxygen is supplied from the bottom of the gasifier so that a thin layer of flame travelling upward is created in the middle of the gasifier. Flame zone temperature is about 1500°C. The flame supplies the energy needed to gasify the wastes. The gaseous products then flow upward to pass through a heated char bed, which is claimed to provide a strong reducing atmosphere that will effectively destroy the refractory organic compounds without producing undesirable by-products.

This gasification process is claimed to be a significant breakthrough for thermal treatment of environmental wastes. No inorganic particulates are present in the gas effluent, and metal emissions are minimal, probably because of capture of the volatilized metal vapors by the char bed, either through condensation or chemisorption. Char residue is a dry, inert, carbonaceous solid which is either nonhazardous or can be mixed readily with cement to prevent leaching of radioactive, toxic, or heavy metal constituents which are retained in the char residue or ash. Char residue can be gasified further in a forward-burn mode to produce a highly stable, low volume, glassy slag.

Status: Predemonstration

Science/Technology Needs: Development work will be initiated with a thorough review of the chem char process in collaboration with researchers of Chem Char Research, Inc. (CRI), holder of a patent on this process. Experimental studies on treating various liquid and solid wastes then will be conducted. Work will occur in conjunction with CRI (or independently at the K-25 Site) and will involve design and installation of a pilot gasifier system. Experiments will be planned to collect data, such as gasifier temperature profile, product gas composition, particle size, mixture flow rate and residence time, and treatment quality. Potential operational problems also will be investigated (e.g., channeling of oxygen and product gases, controllability of a stable and uniform flame front in a gasifier, incomplete combustion, and non-uniformity of treatment quality). Subsequently, an assessment of this process will be made regarding its technical and economic viability, and the result of this assessment will determine whether a larger facility (and its capacity) can be justified.

Implementation Needs: Development work is estimated to cost \$0.75M-\$1.5M.

Author: Chiang

References:

1. *The Chem Char Process for Hazardous Waste Treatment*, technical bulletin, Chem Char Research, Inc.
2. C. D. Reach, personal communication with W. D. Altman, Martin Marietta Energy Systems, Inc., March 2, 1992.
3. T. C. Ho, "Comments on the Chem Char Process," personal notes, July 8, 1992.

EM Problem: Waste management

K25 Site Problem: Waste processing sludges

Problem Area/Constituents: Mixed-waste-contaminated ashes, sludges, and other waste processing solid residues

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
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Subelement: Waste processing/waste stabilization

Alternative: Thermal treatment

Technology: Microwave heating—Microwaves are electromagnetic energy waves having frequencies between 300 megahertz (MHz) and 300 gigahertz (GHz). When microwaves interact with matter, energy is transferred into vibrational modes. This vibrational energy is dissipated in the form of heat. This heating can take place inside the bulk of the material or near the surface, depending on how much the microwaves are absorbed. Several groups in Japan, Europe, and the U.S. currently are developing processes that use microwave energy to thermally treat radioactive wastes.^{1,5} A pilot plant-scale operation in Japan is using microwaves to melt plutonium-contaminated ash from conventional radioactive waste incinerators. In this process, microwaves are fed directly to the ash, causing the ash particles to fuse together to form a monolithic solid that, upon cooling, forms a leach-resistant waste form suitable for long-term storage in a geologic repository.³

Status: Demonstration

Science/Technology Needs: Development is necessary to establish the feasibility of scaling up the microwave heating process from laboratory scale to pilot-plant scale. At the same time, development is required to treat off-gas effluents in particular, when the wastes to be treated contain, for example, technetium, beryllium, PCBs, and organics.

Implementation Needs: Development costs are expected to be \$2.5M (1992 dollars). These are the costs for developing bench-scale units, designing an industrial-scale prototype, and transferring microwave solidification/sintering technology to private industry. These costs are based on TTP OR-4WAA-93, by T. L. White and G. D. Del Cul, entitled *Microwave Sludge Stabilization: Dewatering of Contaminated Mixed-Waste Sludges and Ashes using Microwave Heating*, submitted to DOE-OTD.

Author: Del Cul

References:

1. T. L. White et al., "Microwave Processing of Radioactive Materials," *Emerging Technologies for Hazardous Waste Treatment*, American Chemical Society, Atlanta, Georgia, May 1989.
2. M. S. Morrell et al., "A Pilot Plant Demonstration of the Vitrification of Radioactive Solutions Using Microwave Power," *Nuclear and Chemical Waste Management*, **6**, p. 193-195, 1986.
3. Y. Ogata et al., *Processing at the Plutonium-Contaminated Waste Treatment Facility*, IAEA-SM-303/68, 1989.
4. R. D. Petersen, *Microwave Vitrification of Rocky Flats TRU Sludge*, RFP-4414, 1990.
5. E. P. Bescher et al., *Microwave Sintering of Ashes*, Air & Waste Management Association, 84th Annual Meeting & Exhibition, Vancouver, Canada, June 1991.

EM Problem: Waste management

K-25 Site Problem: Waste processing sludges

Problem Area/Constituents: Solid and liquid organics, nitrate-bearing chemicals, PCB-contaminated liquids and solids

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE Orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Molten glass combustor^{1,2}—This device adds glass-forming constituents to waste feed to produce a pool of molten glass at the bottom of a reactor in which solid wastes react. Gases produced during combustion are released from the surface of the glass pool. Ash remains in the pool and is periodically removed with the carrier glass matrix. The removed glass is collected in storage containers and solidifies upon cooling.

The glass pool is melted and brought to operating temperature by passing a current between electrodes immersed in the glass at the sides of the combustor. The resistance of the glass to the flow of electrical current creates the needed rise in temperature in the molten-glass pool. Typical materials used to form a base glass are oxides of silicon, boron, and phosphorus. Sodium and potassium oxides are added to adjust glass melting temperature and viscosity. Aluminum oxide is added as required to decrease leachability of the glass.

Volatile constituents of solid and liquid waste feed streams are combusted in the volume of the combustor above the molten-glass pool. Combustion air typically is supplied through ports in the sides of this section of the combustor. Auxiliary fuel burners are used to ensure that the volume above the molten-glass pool is maintained at proper temperature for combustion of the volatiles.

The thermal vitrification process involves heating the materials by electricity or fossil fuels to temperatures beyond 1000 °C. At these temperatures, any free liquid or organic material is evaporated, pyrolyzed, or oxidized, and residual inorganics are vitrified to form a molten glass. Thermally formed glasses are produced by fusing or melting crystalline materials and/or amorphous materials at elevated temperatures to produce liquids. Subsequently, these liquids are cooled to a rigid condition without crystallization.

Normally, glass waste forms are obtained by mixing one or more waste streams containing radioactive and hazardous inorganic chemical compounds with other glass-forming materials and melting these materials during a vitrification process. The glass-forming materials may be commercially melted glass frit, select chemicals, or in some cases, materials that are present in the waste streams. Generally, silicon oxide (SiO_2) is the major component and provides the three-dimensional network which strongly influences the glass-waste-form character and properties.

The glass waste form discussed in the vast majority of references is borosilicate glass ($\text{B}_2\text{O}_3\text{-SiO}_2$), as employed in the high-level radioactive waste program. The waste form usually contains less than 30 wt% of waste solids; however, the vitrification process generally reduces the volume significantly. Specific waste streams can be added at higher levels and, under conditions where the waste contains sufficient glass formers, a glass containing only waste can be produced. A wide variety of glass compositions may be suitable as glass waste forms and may provide advantages for the vitrification of a particular waste stream.

Because glass can accept a wide variety and amount of radioactive or hazardous materials and because its physical properties normally are consistent with time, glass has been selected to stabilize a variety of waste streams. It should be noted that the EPA has determined that vitrification is the "best-demonstrated available technology" for chemically hazardous constituents in high-level nuclear waste.

Status: Molten glass combustors are accepted by industry, and units are in use. Removal efficiencies of greater than 99% can be obtained for most waste types. Cost is not well established, but is expected to exceed \$200 per ton. The vitrification process has proven effective, but the costs of operation are not well known.

Science/Technology Needs: The following may cause problems during operation:

- Monitoring the need for changes in additives can be difficult.
- The presence of certain organics and/or metals can result in problems caused by changes in the valence of the glass. This may result in precipitates forming in the glass matrix.

- Certain elements (eg., chromium, ruthenium, and noble metals) have limited solubilities in specific glass structures.

Implementation Needs:

- Process equipment (e.g., indirect or direct-fired rotary kiln, heated screw kiln, etc.)
- Minimum 2,000 ft² equipment battery limit
- All utilities, including electricity, cooling water, natural gas, steam, air, nitrogen, etc.
- Drum and material handling equipment
- Trained chemical operators
- EPA-certified laboratory support

Author: Dukes

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill, New York, p. 8.91-8.104, 1989.
2. J. B. Berry, P. W. Lurk, and G. J. Coyle, Jr., *Mixed-Waste Treatment Research, Development, Demonstration, Testing, and Evaluation*, pp. 13-16, U. S. Department of Energy, Office of Technology Development, 1992.

EM Problem: Waste management

K25 Site Problem: Waste processing sludges

Problem Area/Constituents: Sludges generated as a result of other waste treatment operations. These sludges could contain organics, heavy metals, inorganic salts, and radionuclides such as uranium and technetium.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternatives: Biotreatment

Technology: Biodegradation^{1,2}—Consists of the molecular decomposition of organics and/or the assimilation of inorganic elements by the complex reactions of living organisms, such as naturally occurring or genetically engineered microbes. Given the proper environment, these microbes often can destroy complex hazardous molecules. Often, the process is slow, but destruction efficiency is impressive. Aerobic and anaerobic digestion historically have been used for treatment of wastewaters and resulting sludges. Much research is being conducted to genetically engineer microbes (e.g., white rot fungus) to treat specific, recalcitrant, hazardous pollutants such as chlorinated organics.

Status: Demonstration/evolving technology. The status is partially labeled "demonstration," even though aerobic/anaerobic digestion is commercially available, because the microbes' suitability for treatment of a particular K-25 Site waste stream may need to be demonstrated.

The evolving technology status is for the biodegradation processes that would use genetically-engineered microbes.

Science/Technology Needs: Certain variations of biodegradation, such as aerobic/anaerobic treatment, are commercial technologies; therefore, their additional science/technology needs will be minimal. However, development of engineered microorganisms to treat specific pollutants is still in its infancy and has significant science/technology needs. These needs range from fundamental research to pilot-plant-scale demonstrations of the treatment process(es).

Implementation Needs: Costs for developing the technology for treating the waste sludges likely to be generated at the site are estimated to be around \$1M-\$10M (1992 dollars). If a successful technology can be demonstrated, the payback could be at least one order of magnitude higher than development costs, when compared to the costs of treatment and waste disposal alternative.

Author: Singh

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, 1989.
2. J. B. Berkowitz et al., *Unit Operations for Treatment of Hazardous Industrial Wastes*, Noyes Data Corporation, Park Ridge, New Jersey, 1978.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Volatile organic compounds (VOCs) in groundwater, soil, and wastewater

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Physical treatment

Technology: Air sparging¹—The in situ or extracted removal/bioremediation of volatile organics from saturated soils and/or groundwater by exposing the contaminants to increased volumes of nutrient-containing air. It allows for effective removal of VOCs from groundwater in situ or using recovery or treatment systems. It is effective in treating petroleum hydrocarbons and chlorinated/nonchlorinated solvents. Treatment is accomplished by both volatilization and by enhanced bioremediation.

Air sparging is gaining rapid use for treating VOC contamination caused by solvent (chlorinated or nonchlorinated) and petroleum products in a variety of geological settings. Systems have been operated successfully without groundwater treatment, reducing both soil and groundwater contamination. Full-scale operation has been demonstrated for removal of halogenated volatiles/semivolatiles, solvents and BTEX at capacities of 10-100 lb/h and at costs of \$40-\$70/ft³.

Air sparging technology allows for rapid treatment of soil and groundwater contaminated with volatile organics. By stripping groundwater, treatment can occur without groundwater

recovery (pumping) and treatment. The in situ processes are much more rapid than conventional pump-and-treat or soil vapor extraction systems. This technology is applied to remediation of subsurface groundwater or vadose zones contaminated with VOCs resulting from leaking underground storage tanks or similar releases/spills or to use in wastewater treatment systems.

Status: The process is accepted; however, satisfactory application of the process to treat specific site problems need to be demonstrated.

Science/Technology Needs: The technology is commercially available. The main limitation to the technology is the lack of (or blocking of) air dispersion in the subsurface. If soil permeability is too low or the soils are highly layered, air sparging may not be effective because of the hindering of vertical (escape) air travel. Additional development of techniques for dispersion or injection of air for in situ remediation is required to reduce remediation expense and expedite the process.

Implementation Needs: These will be determined by the site-specific application.

Author: Schaefferkoetter

References:

1. U. S. EPA, *Vendor Information System for Innovative Treatment Technologies (VISITT)*, Version 2.0, EPA/540/2-91/011, No. 2, June 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Removal of inorganic, organic, and radioactive compounds and particulates from various liquids and gaseous streams at the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Physical treatment

Technology: Filtration—Generic treatment technology for the physical removal of solid particulates from liquid or gaseous streams, often using a porous medium.¹ This waste management operation includes various forms of solids separation such as decantation, centrifugation, gravity separation, sedimentation, cake filtration, bag house and HEPA filtration, and electrostatic precipitation. At the K-25 Site, filtration may be used for removal of inorganics, organics, and particulates from the various liquid and gaseous effluent streams generated, for example, in D&D, remedial action, and other site waste processing operations.

Status: Demonstration, even though most filtration processes are commercial technologies, because application of a particular filtration process to treat a K-25 Site stream may need to be demonstrated before it is used.

Science/Technology Needs: Because filtration is a commercial technology, science/technology needs generally are minimal. However, the efficacy of a given filtration process may need to be demonstrated for a given application before its full-scale use.

Implementation Needs: Because of the wide range of processes covered under filtration and because its cost depends on numerous factors, it is impractical to provide a meaningful cost for this technology. In general, implementation costs for technology demonstration of a filtration process may range up to \$1M. However, because filtration often enables the discharge of large volume waste streams (by removing the contaminants), the payback for use of the technology often is quite significant compared with the cost of alternatives.

Author: Singh

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, New York, 1989.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Technetium in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE Order 5400.5

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Subelement: Waste processing

Alternative: Physical treatment

Technology: Adsorption—When some species migrate (adsorbate) from the bulk or a surface and concentrate at the interface of another (adsorbent), they are said to be adsorbed. Absorption is a similar process but involves the entire bulk of the absorbent. In some cases, the actual transfer process is unknown, and the term "sorption" is used to avoid controversies. In our particular case, we are interested in the migration of technetium from an aqueous solution into (or onto) a solid sorbent.

Several organic and inorganic sorbers have been evaluated in the literature including:

- Polyvinylpyridine polymer-based resins^{1,3}—Reillex Poly-4-vinylpyridine polymer-based resins are good sorbers of technetium in the presence of competing anions, including nitrates at high concentrations. The resin is more effective at pH values greater than 4.
- Iron sulfides— Fe_3O_4 was the most effective of several iron sulfide compounds tested for technetium removal. Sulfide treatment also is effective in removing many priority metals from wastewaters (e.g. Cd, Ni, Cr^{+6} , Hg, Pb, Cu, etc.).^{1,3-7}
- Iron metal—It is a very inexpensive and efficient means to reduce and sorb technetium from wastewater. In batch experiments, the kinetics may be relatively slow, but recent

packed bed column flow experiments have been successful in removing technetium. (The volume of wastewater treated for a given volume of sorbent was significantly higher than for organic polymers, including ion-exchange resins.)^{1,3,6,8,9}

- Zinc metal—It has been demonstrated to reduce and sorb technetium from simulated wastewater. Because of the amphoteric characteristics of zinc metal the effective pH range is limited to between 4 and 8.^{8,10}
- Natural minerals—Various minerals were demonstrated to sorb technetium under anoxic conditions, but they were less effective under toxic conditions.^{6,11,12}

Status: Predemonstration

Science/Technology Needs: Development is necessary to establish the feasibility of scaling up use of the most promising sorbers from the laboratory scale to the pilot-plant scale. Development also is necessary to prepare materials with high surface area and appropriate particle size to allow their use in continuous applications. Spent inorganic sorbers should be amenable to microwave sintering, while organic resins could be destroyed using thermal or oxidation techniques. In principle, customized sorbers could be synthesized for recovering technetium from wastewater.⁸

Implementation Needs: Development costs are expected to be \$1.25M (1992 dollars). These are the costs for developing advanced inorganic sorbents for the selective removal of technetium and other contaminants and transferring the technology to private industry. These costs are based on TTP No. OR-4DAH-93, G. D. Del Cul, C. E. Bamberger, and J. L. Collins, submitted to DOE-OTD for Technetium Removal.

Author: Bostick

References:

1. W. D. Bostick and B. S. Evans-Brown, *Sorptive Removal of Technetium from Heavy Metals Sludge Filtrate Containing Nitrate Ion*, K/QT-160, 1988.
2. W. D. Bostick et al., "Treatment and disposal options for a heavy metals waste containing soluble technetium," *Emerging Technologies in Hazardous Waste Management*, D. W. Tedder and F. G. Pohland Eds., American Chemical Society, 345-367, 1990.
3. G. D. Del Cul et al., "Technetium-99 removal from process solutions and contaminated groundwater," *Separation Science and Technology*, in press, 1992.
4. A. V. Metzner, "Removing soluble metals from wastewater," *Water Sewage Works*, 124(4), 98-101, 1977.
5. J. S. Whang et al., "Soluble-sulfide precipitation for heavy metals removal from wastewaters," *Environmental Progress*, 1(2), 110-113, 1982.
6. R. Strickert, A. M. Friedman, and S. Fried, "The Sorption of Technetium and Iodine Isotopes by Various Minerals," *Nuclear Technology*, 49, 283, 1980.
7. S. Y. Lee and E. A. Bondietti, "Technetium behavior in sulfide and ferrous iron solutions," *Material Research Society Symposium Proceedings*, 15, 315, 1981.

8. G. D. Del Cul, *Technetium removal from contaminated groundwater, recycling of cleaning-, decontamination-, and process-, solutions, and soil washing solutions*, TTP No OR-4DAH-93, OTD, 1992.
9. T. T. Vandergraaf et al., "Reactions between technetium in solution and iron-containing minerals under oxic and anoxic conditions," Chap. 2 in G. S. Barney et al., eds., *Geochemical Behavior of Disposed Radioactive Waste*, ACS Symposium No. 246, American Chemical Society, Washington, DC, 1984.
10. A. Mushtaq, "Sorption Behavior of Carrier-Free Tc-99m on Zinc Dust," *Separation Science and Technology*, In press, 1992.
11. D. A. Palmer and R. E. Meyer, "Adsorption of technetium on selected inorganic ion-exchange materials and on a range of naturally occurring minerals under oxic conditions," *Journal of Inorganic Nuclear Chemistry*, **43(11)**, 2979-2984, 1981.
12. F. B. Walton et al., "Tc(IV) and Tc(VII) interactions with iron oxyhydroxides," *Nuclear Chemical Waste Management*, **6**, 121 1986.

ADSORPTION (USING ACTIVATED CARBON OR MOLECULAR SIEVES)

WPRO-203-OG

EM Problem: Waste management

K-Site Problem: Contaminated wastewater

Problem Area/Constituents: Volatile and nonvolatile organics, PCBs, benzene, toluene, ethylbenzene, and xylene (BTEX), other halogenated and nonhalogenated solvents in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternatives: Physical treatment

Technology: Activated carbon—Removes organic contaminants from water by adsorption or the attraction and accumulation of one substance on the surface of another. In general, high surface area and pore structure are the prime considerations in adsorption of organics from water; whereas, the chemical nature of the carbon surface is of relatively minor significance. Granular activated carbons typically have surface areas of 500-1,400 m²/g. Activated carbon has a preference for organic compounds and, because of this selectivity, is particularly effective in removing organic compounds from aqueous solutions.

Status: Accepted

February 26, 1993

Science/Technology Needs: Adsorption properties of activated carbon are influenced by the material from which the carbon is manufactured. Additional investigation is necessary to isolate the carbon type applicable to the specific contaminant.

Implementation Needs: Some bench-scale studies are needed to identify the specific activated carbon required to remove the contaminant in question. Activated carbon is commonly used as a polishing unit in removal of organics from waste streams.

Author: Schaefferkoetter

References:

1. United States EPA, *Process Design Manual for Carbon Adsorption*, Technology Transfer, October 1983.
2. K. J. Deeny, J. A. Heldman, and A. J. Condren, *Project Summary, Performance of Activated Sludge - Powdered Activated Carbon - Wet Air Regeneration Systems*, EPA/600/52-90/012, August 1990.

EM Problem: Waste management

K-25 Site Problems: Contaminated wastewater

Problem Area/Constituents: Wastewater, waste oils, spent solvents, and waste gases generated at the K-25 Site which are contaminated with radioactive species such as uranium, technetium, and magnetic particulates (e.g., iron, nickel, chromium, and manganese)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
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Subelement: Waste processing

Alternative: Physical treatment

Technology: High gradient magnetic separation (HGMS)—A process that uses a high-intensity magnetic field (up to 20,000 gauss) to remove and recover radioactive and weakly paramagnetic materials from contaminated wastewater, waste oils, spent solvents, and gas streams before their disposal. Use of the process can help reduce (minimize) the volume of hazardous or mixed wastes for disposal, thereby lowering disposal costs. HGMS can be used to recover nonmagnetic waste species (by seeding the waste stream with a magnetic floc, such as Fe_3O_4 ; however, using the other conventional filtration techniques for this purpose may be more cost effective). HGMS is best suited to treating large volume or high flow-rate waste streams or streams contaminated with paramagnetic materials. Where applicable, the process can recover particulates as small as one micron in diameter; however, it is most effective for recovering 30-100-micron particulates.¹ HGMS cost estimates (in 1978 dollars) for treating various industrial wastewaters range from \$0.10-\$0.50/1000 gal (for removing highly magnetic materials) to \$1-\$4/1000 gal (for removing weakly magnetic contaminants).¹

Status: Demonstration

Science/Technology Needs: Application of the technology to treat the appropriate liquid and gaseous waste streams at the K-25 Site needs to be demonstrated.

Implementation Needs: The above-mentioned technology demonstration of the HGMS process could cost from \$500K to \$1M (in 1992 dollars). If the process could be demonstrated to apply to treatment of certain K-25 Site waste streams, the technology could prove to be cost-effective, because its major advantage is that it can readily process large volumes of lightly contaminated waste streams.

Author: Singh

References:

1. J. B. Berkowitz et al., *Unit Operations for Treatment of Hazardous Industrial Wastes*, Noyes Data Corporation, Park Ridge, New Jersey, pp. 590-609, 1978.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides, heavy metals, and mercury in wastewater.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders

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Subelement: Waste processing

Technology: Electrolysis—The term electrolysis or electrolyte reaction are applied to those reactions of oxidation or reduction that take place at the surface of conductive electrodes immersed in a chemical medium under the influence of an applied potential. Reductive reactions take place at the cathode while oxidation reactions take place at the anode. The voltage range for the treatment of aqueous wastes is limited to conditions below the voltage that decomposes water into oxygen and hydrogen (i.e., slightly above 1.23 volts). Electroflotation is a process that utilizes electro-generated bubbles for the separation of oil-water mixtures.

For conventional electrolysis, the transport toward and from the electrodes is limited by standard concentration-gradient diffusion and stirring. On the other hand, for electrophoresis and electromigration processes, the transport takes place as a result of a high voltage electric field applied on charged species.

Successful uses of electrolysis in waste treatment may be divided in three broad categories namely, reduction of a dissolved species at the cathode, oxidation of a dissolved species at the anode, or the useful electrolysis of a solvent, as in electroflotation.¹ Electrolytic processes may be envisioned for the removal of heavy metals and radionuclides (including uranium and technetium) from contaminated wastewater and for the decontamination of metallic surfaces.

Status: Demonstration

Science/Technology Needs: Many electrochemical waste treatment processes can be envisioned for the removal of heavy metals and radionuclides. The efficiency, applicability, and the process economics for a specific application need to be evaluated.

Implementation Needs: Development Costs: The development costs are estimated to be \$1.25M (1992 dollars) for the use of electrolysis to treat wastewaters at the K-25 site. These costs are for a three-year development plan and technology transfer to private industry of advanced electrolysis treatment processes. Electrical energy costs range from 10% to 35% of the total direct operating costs.

Author: G. D. Del Cul, 574-5743

References:

1. J. B. Berkowitz et al., *Unit Operations for Treatment of Hazardous Industrial Wastes*, Noyes Data Corp., New Jersey, 1978.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides and technetium in water, heavy metals in water, PCBs in water, other nonvolatile organics in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
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Subelement: Waste processing

Alternative: Physical treatment

Technology: Membranes—This data sheet includes a discussion of reverse osmosis (RO), ultrafiltration (UF), advanced membrane filtration (AMF), supported liquid membranes, and electrodialysis systems.

Membrane systems are replacing several older, costly separation technologies because of the lower cost and greater flexibility of these systems.¹ Breakthroughs in developing membrane materials have led to commercialization of membrane separation systems for waste treatment, desalinization, gas-mixture separations, and other high-volume applications.²

Reverse osmosis (RO) is a separation technology based on the preferential transport of water through a membrane, from a concentrated solution to a more diluted solution, using a pressure exceeding the osmotic pressure. The process can produce highly purified water (permeate); however, rejection of salts is a function of salt concentration in the feed. The

combined advantage and disadvantage of RO is that it removes all of the ions present. This is a disadvantage, because the volume of the secondary waste (consisting of the concentrate or reject stream) is increased by the presence of ions, such as sodium and calcium, that need not be removed. The concentrate may have to be treated using other technologies, such as evaporation, to remove or recover the water and produce a saltcake for disposal.

Ultrafiltration (UF) is very similar to RO, but UF will not remove solutes of low-to-intermediate molecular weight.

Advanced membrane filtration (AMF)³ is a technology that uses membranes with pore sizes larger than those typical of UF and RO. AMF has been used as a final step in the treatment of industrial laundry wastewater for removing suspended solids of low-level radioactive wastes containing uranium and heavy metals.

A supported liquid membrane consists of an organic phase which is held by capillary forces within the pores of a microporous polymeric membrane.⁴

Electrodialysis is a membrane separation process by which aqueous solutions are deionized by the electromigration of cations and anions through semipermeable membranes.⁵

Physical parameters of membranes for RO, UF and AMF³

	Reverse Osmosis (RO)	Ultrafiltration (UF)	Advanced Membrane Filtration
Pore size (µm)	0.001	0.05–0.1	>0.1
Pressure (psi)	300–400	50–100	40–50
Flow rate (gal/ft ² of membrane/day)	10–25	30–75	200–400

Several reverse osmosis and ultrafiltration systems have been evaluated in the literature, including the following.

- Full-scale treatment system have been developed for removing Ra-226 and several heavy metals,⁶ uranyl nitrate solution,⁷ and actinides.^{8–10}
- Advanced membrane filtration units have been used for treating industrial laundry wastewater and for removing uranium and heavy metals from low-level radioactive wastewater.³
- Supported liquid membranes were used for removing uranium from contaminated groundwater.¹¹
- Electrodialysis has been used for removing several radionuclides including cesium-137, strontium-90, cobalt-60, ruthenium-106, and heavy metals such as mercury and chromium.^{12,13}

Status: Demonstration

Science/Technology Needs: Development is necessary to establish the feasibility of scaling up from a pilot-plant scale to an industrial scale. Development also is needed to prevent or minimize membrane fouling caused by bacteria and colloidal materials.¹⁴ Laboratory-scale development is proposed for novel inorganic membranes¹⁵ that may be readily cleanable, and this development could alleviate the fouling problem.

Implementation Needs: RO was identified as the baseline treatment technology for total dissolved solids removal at the K-25 Central Neutralization Facility.¹⁶ The estimated installed cost for this 100,000-gal/day unit is about \$10M (1992 dollars). Estimated cost to develop the novel inorganic membranes is about \$750K (1992 dollars). This cost is based on the Technical Task Plan submitted by D. E. Fain (DOE-OTD TTP OR-1211-08, *Development of Inorganic Membranes for Mixed Waste Landfill Cleanup*).

Author: Del Cul

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EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Surface cleaning of contaminated surfaces by high pressure liquids or dry blasting processes, during D&D operations at the gaseous diffusion plants, such as the K-25 Site, generates enormous quantities of contaminated liquids or gases which must be reduced in volume for cost-effective waste management.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Physical treatment

Technology: Inorganic microporous filters—These can be optimized to filter contaminated particulates from surface cleaning liquids and gases. Development is progressing well on an inorganic HEPA filter that can be used in strong detergents and solvents and can be cleaned and reused indefinitely. The filter will prove valuable in solving these problems.

Status: Predemonstration. Laboratory testing of a HEPA filter that approaches target criteria is under way. Tests indicate that target permeabilities with design pore sizes are close, and this has instilled confidence in the efficacy of the technology.

Science/Technology Needs: Ongoing development efforts for the HEPA filter will prove enormously helpful in optimizing inorganic filters to remove and concentrate contaminated

particulates from waste fluids. The main goal of these development efforts will be to develop the criteria necessary for achieving separations, designing the filters, and then fabricating the filters with high permeabilities to achieve effective separation with minimum pressure drops. The technology needs to be demonstrated on a pilot-plant scale with a filter for liquids and for gases. Also, technology assessments need to be conducted to establish the viability and the economics of the process.

Implementation Needs: Development of the process through the demonstration phase is expected to cost \$0.75M-\$1M (1992 dollars). Cost reductions provided by the process are expected to be \$20M-\$25M, based on simplified waste management operations and significantly reduced waste disposal costs.¹

Author: Vance

References:

1. S. P. N. Singh, personal communication with J. M. Vance, K-25 Site, November 30, 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Oils, solvents, soils, and (perhaps) debris contaminated with PCBs and/or other halogenated organics

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement—Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60–65
- Clean Water Act regulations under 40 CFR 110–146 and 400–471
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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Chemical dechlorination¹—PCBs and other chlorinated organics are easily and rapidly dechlorinated by "solvated electrons" generated by dissolution of elemental metallic calcium in liquid ammonia. The products of the reaction are calcium chloride, calcium hydroxide, and the organic backbone of the chlorinated waste (e.g., biphenyl). This chemistry has been well known for some time; however, its application to the treatment of hazardous wastes is novel. Furthermore, liquid ammonia is a good solvent for many metals and radionuclides; thus, this process may be able to separate these constituents as well as degrade the chlorinated organics. Liquid ammonia also is an effective dispersant for clayey soils. The concept for a hazardous waste treatment process is a batch reactor. Reaction times are on the order of several minutes or less. It may be possible to treat contaminated solid debris, depending on the presence of other chemicals that may quench the solvated electrons.

Status: Predemonstration. A. L. Sandpiper Corporation, a small R&D company in Columbus, Ohio, has a patent on the process and has done many treatability studies for various clients using a bench-scale apparatus. The company is planning to scale up soon to a capacity of 50–100 kg of soil per batch.

Science/Technology Needs: The ability of the process to destroy PCBs is proven. The primary need for DOE applications is determination of the fate of heavy metals and radionuclides and characterization of the waste streams for ultimate disposal. These data can be obtained easily from laboratory-scale treatability tests.

Implementation Needs: Implementation needs for further development of the process are minimal. The cost for lab verification studies and process scale-up and design are expected to be \$200K–\$500K. Cost for a pilot-scale demonstration of the process on DOE wastes at a DOE site is expected to be \$1M–\$2M (1992 dollars). However, should the technology prove successful, the payback on the process could be about \$1 billion, based on disposal costs for the applicable waste streams.

Author: Donaldson

References:

1. *Technical Report on Agent 313™ Remediation Technology*, A. L. Sandpiper Corporation, P. O. Box 16423, Columbus, Ohio, 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides (RAD) and technetium in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Chemical precipitation—Precipitation refers to the process of removing some chemical species in solution by formation and segregation of a solid (either crystalline or amorphous) which can be considered a primarily pure phase. Other species may be incorporated into the crystal or polymeric structure during the growing process of the solid phase. Some constituents also may be adsorbed or physically entrapped in the evolving matrix. Coprecipitation is the name used to identify these kinds of phenomena. To thoroughly remove the generated particles (by filtering, by settling, or by other means), induction of optimal conditions is essential for small particles to coalesce into larger ones.

For crystalline particles, the usual procedure is to precipitate under conditions of low supersaturation. Under these circumstances, few nucleation sites are generated, leading to the growth of fewer and larger crystals. Good agitation, use of complexing agents, and appropriate choice of parameters, such as pH and temperature, are some of the techniques commonly used to improve removal. Aging of the precipitate also will induce larger particles by dissolution of small crystals and growth of bigger, more stable ones.

For gelatinous products, coalescence of the precipitate is accomplished by using two mechanisms: flocculation and coagulation. The process of agglomeration that occurs when particles collide and stick together is known as flocculation. This mechanism is enhanced by slow mixing and/or heating. If the particles are very small, their agglomeration usually is hindered by mutual electrical repulsion. Coagulation is the process that occurs upon suppression of the repelling forces preventing small particle coalescence. Several coagulation mechanisms that reduce the interparticle repulsion have been described in the literature. Among these are adsorption, enmeshment, and bridging.

A charged surface tends to surround itself with an atmosphere of oppositely charged ions. Small charged particles cannot coalesce into larger ones because of the mutual electrical repulsion between them and their charged surroundings. Neutralization of the surface charge by adsorption of oppositely charged species will eliminate the repulsion. These neutral particles, which no longer repel each other, will tend to flocculate by collision. Adsorption-coagulation is the predominant mechanism of removal when, for example, ferric-iron is used at low concentrations to form soluble iron-hydroxy complexes. Bulky particles can trap or enmesh small particles. The enmeshment process is the primary mechanism of removal when insoluble, bulky coagulant is added, as when ferric iron is added at doses exceeding the solubility of iron oxyhydroxide. (Such enmeshment is the predominant process used in iron treatments.) Bridging is typical of polymeric coagulants. In this process, a charged, long-chain polymer (anionic or cationic) bridges several smaller particles to form a larger conglomerate.

- Several iron compounds were evaluated in the literature for the adsorption-coprecipitation of radionuclides from wastewaters.
 - Addition of ferrous salts (usually sulfate) will remove metal ions by chemical reduction and adsorption-coprecipitation. Fe (II) can, under certain conditions, reduce uranyl ions to highly insoluble U (IV) species, chromium (VI) will be reduced to chromium (III), and Tc (VII), to Tc (IV). The presence of carbonate complexes will interfere and keep the uranium in solution.¹ To minimize this problem, the solution to be treated usually is acidified (pH 2-4) and sparged to remove the carbon dioxide.² Because the precipitated solids from ferric ions are more effective for radionuclides removal, ferrous iron addition usually is followed by air oxidation to ferric iron under alkaline conditions (pH 8.5-12) using sodium hydroxide or lime. Insoluble chromium (III) will change into soluble chromate (VI) at high pH.³ It was found that 12 mg of FeSO_4 were needed to remove each milligram of technetium.⁴
 - The addition of Fe (III) at pHs of 4-12 is a very common practice for coprecipitating/adsorbing several heavy metals and radionuclides. Removal efficiency is about the same whether the iron was precipitated before being added to the waste (adsorption) or afterwards (coprecipitation). Removal of anions is enhanced at low pH and is higher at high pH for cations.⁵
 - Potassium ferrate (a strong oxidant) can be used as a coagulant for removing uranium, transuranic elements, and several heavy metals from aqueous waste

streams. Advantages claimed for this technique are homogeneous dispersion of reagent and reduced sludge volume.^{6,7} Limited testing at the K-25 Site did not show satisfactory uranium and technetium removal from incinerator liquid effluent (further development work to show applicability may be required).

- Uranium can be precipitated from solutions of uranyl salts by hydrogen peroxide as $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ at pH values of 0.5–3.5.^{8–10} Any uranium present in the lower oxidation states will be oxidized by hydrogen peroxide. The global reaction can be written as

An excess of H_2O_2 is necessary, but adding more than twice the stoichiometric quantity is counterproductive. The peroxide precipitation is rather selective, and the final product is predominantly pure. Complexing ions, such as fluoride, will interfere mildly with the precipitation. The complexing effect can be greatly reduced by keeping the pH low (0.5–1.0). However, at a pH < 0.5, precipitation of uranyl ions will be incomplete. After treatment at optimal conditions, residual uranium concentration will be in the ppm range. The H_2O_2 excess will tend to self-decompose; however, complete removal can be achieved by contacting the H_2O_2 with activated charcoal in a vented system.

- Lime softening: This process consists of adding lime to create a final pH between 9 and 12. This technique is particularly useful when fluoride ions are present, because it will remove them as calcium fluoride. Uranium (IV) or (VI) will precipitate as oxyhydroxides that include calcium and will coprecipitate with the calcium fluoride. The presence of carbonate complexes will interfere and keep uranium in the solution. To minimize this interference, the solution to be treated must be previously acidified and agitated or sparged to remove the dissolved carbon dioxide. Lime softening can be complemented with iron coprecipitation.
- Sulfide precipitation: Several metallic ions [particularly technetium (VII)] form rather insoluble sulfides (pertechnetate).

Status: Accepted

Science/Technology Needs: Precipitation technologies are fairly mature and iron coprecipitation presently is being used at the K-25-CNF (Central Neutralization Facility at the K-25 Site). However, significant development still is necessary to resolve the new challenges originated by increasingly lower regulatory limits. Potassium ferrate is not a demonstrated alternative, and further development work is needed to show its applicability and relative performance.

Implementation Needs: Iron coprecipitation is the baseline treatment at the K-25-CNF for heavy metals and radionuclides removal. According to a proposed treatability study to upgrade the K-25-CNF treatment facility, the estimated cost to develop, test, and document the different upgraded treatment options is about \$400K.¹¹

Author: Del Cul

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1. L. Maya, "Dioxo Uranium(VI) Carbonate Complexation in Uranium Recovery by Reactive Ion-Exchange," *Journal of Inorganic Nuclear Chemistry*, **43**, 2133, 1981.
2. G. D. Del Cul et al., *Evaluation of Alternatives for Best Available Technology Treatment and Retreatment of Uranium-Contaminated Solutions at the Paducah Gaseous Diffusion Plant C-400 Facility*, Final Report , K/QT-394 Part 3, 1991.
3. M. Pourbaix, *Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, New York, 1966.
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5. M. A. Manzione and D. T. Merrill, *Trace Metal Removal by Iron Coprecipitation: Field Evaluation*, EPRI GS-6438, 1989.
6. M. E. Potts et al., "Removal of uranium, transuranic elements and priority pollutant metals from wastewaters utilizing potassium ferrate (VI)," *Emerging Technologies for Hazardous Waste Management*, 294, Atlanta, Georgia, October 1-3, 1991.
7. M. E. Potts et al., *Treatment of Uranium Containing Wastewaters*, 92-38.07, 85th Annual Meeting & Exhibition, AWMA, Kansas City, Missouri, June 21-26, 1992.
8. P. N. Palei, *Analytical Chemistry of Uranium*, London-Ann Arbor, Michigan, 1970.
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11. W. D. Bostick, *Proposed Treatability Study in Support of the Central Neutralization Facility Upgrade/Replacement Line Item*, Interoffice Memorandum, October 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Halogenated and nonhalogenated volatiles and semivolatiles, organics, pesticides, dioxins, PCBs, solvents, BTEX, cyanides/corrosives in solids, soils, sludges, sewage, and oil; radionuclides in solids, soils, sludges, sewage, and oil

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Solvent extraction, general¹⁻⁷—Various forms of solvent extraction technology are available or under development. These include:

- Continuous solvent extraction technology using common organic solvents to extract pollutants from soils, sediments and sludges and a second solvent to concentrate them. The second solvent, containing all of the contaminants, is removed from the process for final destruction. Decontaminated solids and water are returned to the environment. Contaminants are separated from the solids in a multistage countercurrent, solid-liquid contactor. The contaminant-rich leaching solvent subsequently is contacted with a second solvent in a liquid-liquid counter-current extractor. Residual leaching solvent in the decontaminated soil is recovered in a screw dryer and recycled back to the leaching

step. The contaminant-free leaching solvent mixture from the liquid-liquid extraction step is sent to a solvent recovery unit and then returned to the leaching step.

- Solvent extraction technology using triethylamine as the solvent. Triethylamine is a biodegradable solvent formed by reacting ammonia and ethyl alcohol. The key to success of the process is triethylamine's property of inverse miscibility; below 65°F, triethylamine is soluble in water (hydrophilic) and, above 65°F, triethylamine is insoluble in water (hydrophobic). Therefore, cold triethylamine can extract water and water-soluble compounds, and warm triethylamine can extract organic contaminants such as PCBs, pesticides, semi-volatile organics, and VOCs. When treating nonpumpable wastes (soils), the process is configured as a batch extraction system. Extraction is continuous when treating pumpable wastes (sludges and sediments). Solvent recovery and recycling is continuous.
- Solvent extraction is an effective process to treat wet sludges containing volatile/semi-volatile organics, oils, grease, and coal-tar compounds. The key components of this process are the solvent system and a multistage, counter-current extractor. The special solvent system is a mixture of polar and nonpolar components which help in breaking the emulsion of oil, water, and inorganic constituents. The process consists of three unit operations. The process extracts organics from a concentration as high as 40% by weight and discharges a relatively nonhazardous stream of inorganics with less than 0.1% organics. The water stream (in the case of wet sludges) containing organics dissolved in the lower ppm range can be biotreated. The organic phase containing solvent and contaminants from the extractor is distilled. The solvent is recovered and recycled back to the process. Contaminants are collected for further disposal.
- Heteroatom extraction technology can treat multiple wastes including crude oils, oil fractions, heavy oils, shale oils, and coal liquids which are present in soil, waste streams, etc. The process requires only CO₂ and water at low temperatures and pressures. Extractive components can be recycled, which reduces costs and waste discharges. Treated and extracted oil remain unchanged. This nondestructive extraction procedure selectively separates the most toxic fractions of wastes, such as the nitrogen and sulfur containing compounds.

Status: Predemonstration or demonstration, depending on the particular application

Science/Technology Needs: Technical application depends on the contaminant(s) and the base matrix. Much of the development is on a pilot scale. R&D (ranging from bench-scale to demonstration) may be required to develop (identify) the appropriate solvent and removal technology.

Implementation Needs: Solvent extraction applies to removal of multiple contaminants from D&D and RA-derived solid wastes. Estimated cost could range from \$75 to \$400/ton for plants treating 5-30 tons/day of solid wastes. Payback for the technology is difficult to evaluate without information on the specific application.

Author: Schaefferkoetter

References:

1. W. Steiner, "New Technologies Offer Site Cleanup Alternatives," *Civil Engineering News*, p. 24, September 1991.
2. D. Hall, "An Overview of Solvent Extraction Treatment Technologies," *Environmental Progress*, **9**, No. 2, May 1990.
3. *Extraction and Drying of Superfund Wastes with the Carver-Greenfield Process*, U.S. EPA Forum, June 11-13, 1991.
4. T. C. Halcombe, *Process for Recovering Dry Solids from Aqueous Solids Mixtures*, U.S. Patent No. 4,702,798, October 27, 1987.
5. U.S. EPA, *Engineering Bulletin—Solvent Extraction Treatment*, EPA/540/2-90/013.
6. R. L. Fellows, W. D. Bostick, and J. L. Shoemaker, *Extraction of Organics From Sludge: CPCF Sludge Extraction Evaluation Bench-Scale Chemistry Tests*, K-25 Site, Oak Ridge, TN, April 1991.
7. S. I. Saferman and S. K. Bhattacharya, *Treatability of RCRA Compounds in BOD/Nitrification Wastewater Treatment System with Dual Media Filtration*, EPA/600/S2/90/013, August 1990

SOLVENT EXTRACTION/CENTRIFUGAL CONTACTOR TECHNOLOGY

WPRO-212-OG

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides, technetium, heavy metals, PCBs, solvents, and oils in various media such as solid wastes, wastewater, and spent oils and solvents

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Solvent extraction/centrifugal contactor technology¹⁻³—This process uses solvent extraction and centrifugal contactor technology for separation of radioactive and hazardous waste components from the various waste media generated in the course of performing D&D and remedial action operations.

Status: Demonstration/predemonstration. The separation of heavy metals, uranium, actinides, and other radionuclides using centrifugal contactor-based solvent extraction technology has been an accepted process at DOE nuclear sites for over 25 years. However, other possible applications of this technology may require considerable R&D.

Science/Technology Needs:

- Configuration of a chemical process flow sheet for dilute concentrations of contaminants (e.g., heavy metals, uranium, other radionuclides, etc.) relative to the potentially higher concentrations of other contaminants in the waste stream

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SOLVENT EXTRACTION/CENTRIFUGAL CONTACTOR TECHNOLOGY

WPRO-212-OG

- Determination of extraction stages required to reduce waste content of the liquid phase to below regulatory limits for release
- Demonstration of closed-loop operation, in which extractant is recovered for reuse with surrogate waste stream
- Determination of materials of construction (if required) due to composition of the waste stream

Implementation Needs: R&D costs for developing the technology for a specific application are estimated to range between \$1M and \$2.5M (1992 dollars). Payback for the technology is application-specific but could be significant considering alternate treatment technologies and waste disposal costs.

Authors: Jubin, Plummer

References:

1. U.S. EPA, *Test Methods for Evaluating Solid Waste, Volume 1B: Laboratory Manual for Physical/Chemical Methods*, PB88-239223, Part 2 of 4, November 1986.
2. M. Germain and P. Pluot, "Diluent Washing of Aqueous Phase Using Centrifugal Contactors," 80-219, *Proceedings of International Solvent Extraction Conference*, 1980.
3. M. E. Whatley, *The Removal of Residual Tributyl Phosphate from Aqueous Solvent Extraction Effluent Streams by Organic Diluent Washing*, ORNL/CFRP-88/24, September 1988.

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Waste processing solid residuals

Problem Area/Constituents: Solids and liquids contaminated with RAD, technetium, heavy metals, and hazardous organics and inorganics

Reference Requirements:

- Resource Conservation and Recovery Act of 1976, as amended (RCRA) Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated 12 June 1992.
- Federal Facilities Agreement (FFA) for Oak Ridge Reservation.
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (abbreviated as FFCA-TSCA) dated 20 February 1992.
- Clean Air Act regulations under 40 CFR 60-65.
- Clean Water Act regulations under 40 CFR 110-146 and 400-471.
- DOE orders.

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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Leaching/stripping—Leaching and stripping are processes that consist of the contacting of a fluid (usually an aqueous solution) containing one or more active species (i.e., the leaching solvent or leachant) with the contaminated material. This operation results in a partial or total transfer of the contaminants to the leachant.

There are various ways of performing leaching/stripping operations¹ namely: (1) batch leaching. This involves contacting the contaminated material and the leaching solvent in a batch until leaching is complete and then separating the phases; (2) cocurrent continuous leaching. This process involves the continuous addition of leachant and contaminated material to a stirred mixer and co-current discharge of the reaction products; (3) counter-current continuous leaching. This involves counter-current flow of the leachant and the contaminated material; and, (4) percolating leaching. This is a process in which the leachant

passes down through a column or pile of the contaminated material and the leachate is collected at the bottom of the column or pile.

A wide variety of reagents can be used. For example, acids (e.g., sulfuric, hydrochloric, nitric, phosphoric and carbonic), bases (e.g., sodium hydroxide, lime-sodium sulfate, and ammonia), complexants (e.g., EDTA, ammonium salts, and sodium cyanide), and oxidants (e.g., air, oxygen, chlorine, hydrogen peroxide, and steam).

Substantial experience exists on the recovery of relatively high-value metals from relatively low-value ores and scrap materials. The experience of selective leaching or removal of small or trace amounts of contaminants from diverse waste materials however, is scarce. Development of specific technologies to achieve this objective is required. For stripping and leaching to be successful, a thorough knowledge of the waste to be treated is essential. The choice of a particular leachant and the operating conditions will depend on the specific waste or range of wastes to be treated.

Status: Demonstration. Use of leaching/stripping technologies for the removal of contaminants can be used as a generic technique. However, each application or range of applications needs development to determine the optimum leachant composition and treatment conditions.

Science/Technology Needs: Specific waste streams to be treated will need development work to verify the applicability of the technologies and determine the treatment characteristics and conditions.

Implementation Needs: Different types of processing equipment are already commercially available. The experience of selective leaching or removal of small amounts of contaminants from diverse waste materials is scant and development of specific technologies is required. For these technologies to be successful, a thorough knowledge of the waste to be treated is essential.

The choice of a particular leachant and the operating conditions will depend on the specific waste or range of wastes to be treated. The cost of researching and developing specific applications is estimated to be about \$1M-\$2M (1992 dollars). The potential payback for the use of the technology could be significant for certain applications.

Author: G. D. Del Cul

References:

1. J. B. Berkowitz et al., *Unit Operations for Treatment of Hazardous Industrial Wastes*, Noyes Data Corporation, New Jersey, 1978

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Organics in water, PCBs in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Ozonation-photolysis—Chemical treatment (also known as advanced oxidation)—ozonation, photolysis, ultraviolet (UV)/H₂O₂, Fe^{+2/+3}/H₂O₂ (Fenton Reagent), etc. Advanced oxidation technologies can be very useful for destroying organic contaminants in soil and water. Several processes can be found in the literature,¹ such as ozonation at acidic pH, ozonation at near neutral pH, UV/H₂O₂, Fe^{+2/+3}/H₂O₂ (Fenton Reagent), photocatalysis, etc. Except for ozone under acidic conditions (pH<3), where the primary oxidant is molecular ozone itself,² oxidation of organic compounds occurs mainly through hydroxyl-free radicals OH.³ Hydroxyl-free radicals are produced during decomposition of ozone under neutral or basic pH, ultraviolet (UV)-light photocatalysis using titanium dioxide,⁴ UV-light photocatalysis of H₂O₂,¹ oxidation of Fe⁺² with H₂O₂ (Fenton Reagent),⁵ etc. Hydroxyl-free radicals have been shown to be powerful oxidants that react nonspecifically with organic compounds.⁵ Although some organic species are easily destroyed by oxidation agents, they are rarely converted completely to carbon dioxide and water, and some rather hazardous

compounds can be produced as "end products of oxidation." For these technologies to be successful, a thorough knowledge of the waste to be treated is essential.

The choice of a particular oxidation system over others will depend on the specific waste or range of wastes to be treated.

Status: Demonstration. Use of oxidation technologies for destroying organics cannot be used as a generic technique, and each application or range of applications needs R&D.

Science/Technology Needs: As previously mentioned, although some organic species are easily destroyed by oxidation agents, they are rarely completely converted to carbon dioxide and water, and some rather hazardous compounds can be produced as "end products of oxidation." The equipment needed to implement these technologies is relatively simple and can be coupled easily to other chemical treatments, such as coprecipitation (e.g., Fenton reagent, $\text{Fe}^{+2/+3}/\text{H}_2\text{O}_2$, could be used to destroy organic matter and could be followed by pH adjustment for iron-coprecipitation of radionuclides and heavy metals). Specific waste streams to be treated will need some development work to verify the applicability of oxidation technologies.

Implementation Needs: The cost of demonstrating applicability of the technology to treat a given waste stream is estimated to be \$1M-\$2M (1992 dollars). If use of the process proves successful, payback for the technology is likely to be significant (on the order of tens to hundreds of millions of dollars), especially when considering the cost of waste disposal alternatives for some waste streams containing relatively refractory compounds.

Author: Del Cul

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1. C. C. D. Yao et al., *Kinetic Features of Advanced Oxidation Processes for Treating Aqueous Chemical Mixtures*, Second International Symposium: Chemical Oxidation, Technology for the Nineties, Nashville, Tennessee, 1992.
2. R. G. Rice, *Ozone Chemistry Applied to Cooling Tower Water Treatment*, Second International Symposium: Chemical Oxidation, Technology for the Nineties, Nashville, Tennessee, 1992.
3. C. Munz et al., *Oxidative treatment of Process Water in a Soil Decontamination Plant: I. Laboratory Studies*, Second International Symposium: Chemical Oxidation, Technology for the Nineties, Nashville, Tennessee, 1992.
4. C. S. Turchi and M. S. Mehos, *Solar Photocatalytic Detoxification of Groundwater: Developments in Reactor Design*, Second International Symposium: Chemical Oxidation, Technology for the Nineties, Nashville, Tennessee, 1992.
5. K. A. Flaherty and C. P. Huang, *Continuous Flow Applications of Fenton's Reagent for the Treatment of Refractory Wastewaters*, Second International Symposium: Chemical Oxidation, Technology for the Nineties, Nashville, Tennessee, 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Organics in water, PCBs in water, organic residues, and organics in sludges

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Waste processing

Alternative: Chemical treatment

Technology: Wet air oxidation (WAO)—Wet air oxidation is the process of oxidizing dissolved or suspended contaminants in aqueous wastes streams at elevated temperatures and pressures.¹ It is generally considered applicable for treating certain organic-containing media that are too toxic to treat biologically and yet too dilute to incinerate economically.^{2,3} A leading manufacturer of commercially available WAO equipment reports that WAO occurs at temperatures of 175-320° C and at pressures of 300-3000 psig. The reaction proceeds, without need for auxiliary fuel, at feed chemical oxygen demand (COD) concentrations of 20-30 g/L.⁴ The extent of contaminant destruction depends on the wastes to be oxidized and reaction conditions. Typically, 80% of the organics will be oxidized to CO₂ and water.⁵ Although some organic species are easily destroyed by WAO, they are rarely completely converted to carbon dioxide and water. Residual organics generally will be low-molecular-weight, biodegradable compounds such as acetic and formic acids. Nevertheless, with some waste streams, hazardous compounds can be produced as "end

products of oxidation." For this technology to be successful, thorough knowledge of the waste to be treated is essential. For the destruction of halogenated aromatics such as PCBs, more energetic conditions and catalysts are necessary, and the destruction is likely to be incomplete.

Status: Demonstration. The technology is commercially available; however, satisfactory destruction of highly refractory organics requires treatability studies and development. Also, use of the technology to treat a specific site waste stream will need to be demonstrated.

Science/Technology Needs: As previously mentioned, although some organic species are easily and completely destroyed by WAO, they are rarely completely converted to carbon dioxide and water, and some rather hazardous compounds can be produced as "end products of oxidation." Specific waste streams to be treated will need development work to verify applicability of the process to treat the problem waste stream.

Implementation Needs: A comparison between a 20-gal/min WAO system and a comparable incinerator for wastewater containing 7% COD showed an installation cost 50% higher than that of an incinerator. However, the operating costs for WAO were only one fourth that of an incinerator [\$163,000 for WAO vs \$463,500 for incineration (1979 dollars)].⁵ Cost estimates of \$0.1-\$0.5/gal of waste have been proposed. Development costs to determine the treatability of K-25 Site wastes by WAO are estimated to be \$1M (1992 dollars).

Author: Del Cul

References:

1. M. Breton et al., *Treatment Technologies for Solvent Containing Wastes*, Pollution Technology Review No. 149, Noyes Data Corporation, New Jersey, 1988.
2. M. J. Dioptric et al., "Wet Air Oxidation of Hazardous Organics in Wastewater," *Environmental Progress*, 4(3), 1985.
3. H. Freeman, *Innovative Thermal Hazardous Treatment Processes*, U.S. EPA, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio, 1985.
4. California Air Resources Board, *Air Pollution Impacts of Hazardous Waste Incineration: A California Prospective*, December 1983.
5. A. R. Wilhelm and D. G. Datums, "Wet Air Oxidation, An Alternative to Incineration," *Chemical Engineering Progress*, August 1989.

EM Problem: Waste management

K-25 Site Problem: Contaminated oil

Problem Area/Constituents: Organic ion-exchange media, radionuclides and technetium in oil, heavy metals in oil, PCB in oil, nonhalogenated organics in oil, radionuclides in solvents, heavy metals in solvents, PCB in solvents, organics

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Supercritical water oxidation—The basic concept of supercritical oxidation technology is based on the complete miscibility of oxygen, carbon dioxide, and many organics with dense supercritical water (the critical point for pure water is 374° C and 221 Bar). Under supercritical conditions, both flameless oxidation and flaming combustion can occur.¹⁻⁴ Work conducted in the mid-1980s by Modell⁴ and his colleagues showed that many organic compounds can be almost completely destroyed in a supercritical homogeneous phase and that the heat of reaction can substantially reduce, and sometimes completely eliminate, the need for additional fuel to sustain the process.⁵ The perceived advantages of a supercritical water reactor follow. (1) The reactor is a closed system, and there are no emissions to the atmosphere. (2) If it malfunctions, it can be shut down relatively easily. (3) The prototypes to treat wastes run at 500-600° C, considerably lower than conventional thermal methods. (4) If carbon content of the waste is at least 10%, the supercritical process can be energy-

sufficient. The potential problems are: (1) corrosion of the reactor parts, (2) plugging and caking, and (3) separation of solids under high-pressure, high-temperature conditions.

Status: Demonstration

Science/Technology Needs: Small laboratory demonstration units (a few gallons of waste per day) were operated and tested, and R&D efforts continue today.⁶ Significant development is needed to solve the corrosion, plugging, and caking of the reactors. Overall experience is needed in the specific problems related to particular types of wastes to generate a data base to support the applicability and relative merits of this promising technology.

Implementation Needs: The estimated cost for a 3-year development plan and technology transfer for destruction of spent organic ion-exchange resins using supercritical water oxidation, recovery of special materials, and recycling, based on DOE-OTD-TTP No. OR-4TAJ-93 by G. D. Del Cul and C. E. Bamberger, is \$1.6M.⁸ A full-scale implementation program for designing, testing, and developing bench-scale and industrial-scale prototypes would cost approximately \$40M (based on molten salt 5-year implementation plan costs).

Author: Del Cul

References:

1. R. K. Helling and J. W. Tester, "Oxidation of Simple Compounds and Mixtures in Supercritical Water: Carbon Monoxide, Ammonia and Ethanol," *Environ. Sci. Technol.*, **22**, 1319, 1988.
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3. C. F. Mellus et al., *Effects of Water on Combustion Kinetics at High Pressure*, 23rd Symposium (International) on Combustion, The Combustion Institute, 1991.
4. T. B. Thomason and M. Modell, "Supercritical Water Destruction of Aqueous Wastes," *Hazardous Waste*, **1**, 453, 1984.
5. R. W. Shaw et al., "Supercritical Water a Medium for Chemistry," *C&EN*, December 1991.
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7. S. J. Buelow, "Destruction of Hazardous Wastes by Supercritical Water Oxidation," *Second International Symposium: Chemical Oxidation, Technology for the Nineties*, Nashville, Tennessee, 1992.
8. G. D. Del Cul and C. E. Bamberger, *Supercritical Water Oxidation: Low Temperature Destruction of Organic Polymeric Resins Using a Supercritical Water Reactor*, OTD-DOE OR-4TAJ-93, 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste Processing

Alternative:

Technology: Ion-exchange—A process involving the mass transfer of ions between a polar solvent and an inert liquid or solid matrix containing highly polar groups which can be ionized.

Several different ion-exchange media have been evaluated in the literature including:

- Strong-base anion exchange resins. Dowex 2 X-8 resin has been reported as having a very high affinity for the uranyl ion complexed with carbonate as a tricarbonat complex in the presence of competing anions. This carbonate complex is the predominant uranium species in groundwater.¹
- Inorganic ion-exchange media. Inorganic hydrous oxides and phosphates can be used to remove uranium and cesium from contaminated groundwater and brines.² Titanium monohydrogen phosphate microspheres can be used to remove uranium from nitrate solutions.³ Glass-based materials (e.g. Durasil media) were used to remove radionuclides from contaminated wastewaters.⁴
- Polyvinylpyridine polymer-based resins. Reillex 1-methyl-4-vinylpyridine polymer-based resins are good sorbers of plutonium (iv) from nitric acid with high capacity and rapid

sorption kinetics. This resin has a greater stability to chemical and radiolytic degradation than conventional anion exchange resins.⁵

- Cation exchange resins. Cesium-137 and strontium-90 can be removed from aqueous solutions using cation-exchange resins such as Duolite CS-100 (a bifunctional phenolic-carboxylate resin in the sodium form) or Dowex HGR-W2 sodium-form.^{6,7}

Status: Demonstration

Science/Technology Needs: Use of organic ion-exchange resins is a standard unit operation for radionuclides removal from contaminated wastewater. Inorganic ion-exchangers-sorbers are in the development/predemonstration stage, and their applicability and process economics will need to be evaluated.

Implementation Needs: Development costs are estimated to be \$1.25M (1992 dollars). These are costs for development and technology transfer to private industry of advanced inorganic sorbents for selective removal of technetium and other contaminants. These costs are based on TTP No. OR-4DAH-93, by G. D. Del Cul, C. E. Bamberger, and J. L. Collins, submitted to DOE-OTD for Technetium Removal.

Author: Bostick

References:

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2. J. L. Collins et al., "Sorption of metal ions from groundwaters using hydrous titanium oxide microspheres," *Emerging Technologies for Hazardous Waste Management*, Atlanta, Georgia, October 1-3, 1991.
3. T. J. Takacs, "Removal of Uranium from Nitrate Wastes," *Y-12 Development Division, Technical Progress Report*, Part. 6, Period Ending June 15, 1992, Y-2455-6, 1992.
4. S. P. N. Singh and T. F. Lomenick, *Summary Report on the Demonstration of the Duratek Process for Treatment of Mixed-Waste Contaminated Groundwater*, ORNL/TM-11927, April 1992.
5. S. F. Marsh, *Evaluation of a New, Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange*, LA-11490, 1989.
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7. R. Hall, *Treatment of Low-Activity-Level Process Wastewaters by Continuous Countercurrent Ion Exchange*, CONF-900210, 2, 429 (1990).

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Technetium in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Ion-exchange resins—Ion exchange is a process involving the mass transfer of ions between a polar solvent and an inert liquid or solid matrix containing highly polar groups which can be ionized. Under toxic conditions, the predominant form of technetium is the pertechnetate anion and, for this reason, anionic ion-exchange resins are the usual choice.

Several organic ion-exchange resins have been evaluated in the literature, including:¹⁻⁸

- Strong-base anion exchange resins. This medium has a very high affinity for the pertechnetate ion, although high concentrations of other anions, such as nitrates and sulfates, can compete for ion sites. Dowex SRB-OH has been used for removing technetium-99 at the Portsmouth Gaseous Diffusion Plant (GDP) as a standard unit operation. Use of amine-based resins, such as the SRB-OH, is not advised for acidic nitrate solutions because of the possibility of exothermic degradation. Strongly basic anion-exchange media are not inherently selective and many other ions (including complex anions of chromium and mercury) also can be sorbed, giving the potential to form a mixed waste.

- Polyvinylpyridine polymer-based resins.⁶⁻⁸ Reillex Poly-4-vinylpyridine polymer-based resins are good sorbers of technetium in the presence of competing anions, including nitrates at high concentrations. This resin behaves as an anion-exchange medium at pH values <4; however, under this condition, it is less effective for the removal of technetium.
- Weakly-basic anion exchange resins. Palmer and Meyer report that pertechnetate is bound by Amberlite IR-45 (sorption is greatest at acidic pH values and ions such as nitrate interfere).⁹ At a large molar ratio of nitrate vs technetium, no selective sorption was observed.^{6,7}

Status: Demonstration. Use of SRB-OH resins is a standard unit operation at the Portsmouth GDP. Laboratory-scale investigations have indicated that this medium is more effective for contaminated groundwater but less effective for decontamination of brines containing competing anions. Reillex resins have been demonstrated only at the lab scale, where they were more effective and selective for technetium removal from brines.

Inorganic ion-exchangers/sorbers are in the development/predemonstration stage, and their applicability and economics have to be evaluated.

Science/Technology Needs: Use of the technology to meet the site requirements needs to be demonstrated.

Implementation Needs: Development costs are estimated to be \$1.25M (1992 dollars). These are the costs for development and technology transfer to private industry of advanced inorganic sorbents for selective removal of technetium and other contaminants. These costs are based on TTP No. OR-4DAH-93, by G. D. Del Cor, C. E. Bamberger, and J. L. Collins, submitted to DOE-OTD for technetium removal.

Author: Bostick

References:

1. E. H. Huffman et al., "Anion-Exchange Separations of Molybdenum and Technetium and of Tungsten and Rhenium," *Inorganic Nuclear Chemistry*, **3**, 49, 1956.
2. D. I. Ryabchikov and Pozdnyakov, "Investigation of the Adsorption of Technetium from Aqueous Solutions on Domestic Anion-Exchange Resins," *Dokl. Akad. Nauk SSSR*, **161**, 896, 1965.
3. F. B. BeCraft and M. E. Holland, *Ion Exchange Removal of Technetium-99 from Nitrate-Containing Wastes at the Portsmouth GDP: Safety Aspects*, Report GAT-T-2962, Goodyear Atomic Corporation, Piketon, OH, Aug. 1979.
4. A. J. Saraceno, *The Control of Technetium at the Portsmouth GDP*, Report GAT-2010, Goodyear Atomic Corporation, Piketon, OH, Nov. 1981.
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7. W. D. Bostick et al., "Treatment and disposal options for a heavy metals waste containing soluble technetium," *Emerging Technologies in Hazardous Waste Management*, D. W. Tedder and F. G. Pohland, Eds., American Chemical Society, 345-367, 1990.
8. G. D. Del Cul et al., "Technetium-99 Removal from Process Solutions and Contaminated Groundwater," *Separation Science and Technology*, **28**, 189, 1992.
9. D. A. Palmer and R. E Meyer, "Adsorption of Technetium on Selected Inorganic Ion-Exchange Materials and on a Range of Naturally Occurring Minerals Under Oxidic Conditions," *Journal of Nuclear Chemistry*, **43**(11), 2979-2984, 1981.

EM Problem: Waste management

K-25 Site Problem: Waste processing, solid residuals

Problem Area/Constituents: Technetium in water

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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Subelement: Waste processing

Alternative: Chemical treatment

Technology: Transmutation—This technology, as envisioned, would irradiate concentrated nuclear waste with a high-intensity thermal flux of accelerator-produced neutrons (in the range of 10^{16} n/cm².s). As a result of this irradiation, the initial radionuclides will transmute. Some of the radionuclides will transmute into stable or more stable nuclides, while some will transmute into shorter-lived radioisotopes that will then decay into stable nuclides. To produce the high intensity neutron flux needed for this technology to be practical (100 times larger than in large-scale thermal reactors), a proton linear accelerator with 1.5-GeV energy and a 250 mA CW current is proposed.¹ The accelerated proton beam would collide with a lead or lead-bismuth spallation target and generate a high flux of neutrons.

Technetium-99 ($T = 2.1 \times 10^5$ years) is a very good candidate for the transmutation concept. It has a relatively high cross section for the capture of thermal neutrons (19 Barns, 1 Barn = 10^{-24} cm²) and all of the higher technetium isotopes that could be generated by single or multiple neutron capture will rapidly decay into stable ruthenium, rhodium, or palladium.²

Status: Conceptual

Science/Technology Needs: Several national laboratories, including Los Alamos, Brookhaven, Hanford-PNL, etc.,^{1,3-6} have conceptual plans for constructing "transmutation" reactors based on the hybrid proton accelerator subcritical lattice reactor. A detailed neutronic analysis of the proposed schemes also has been conducted.³ The next step should be design and construction of a prototype unit.

Implementation Needs: The future of an industrial-scale transmutation facility depends on availability of a permanent, high-level waste repository. Development and construction costs for a "national transmutation facility" would be in the billion dollar range and would take many years to complete and become operational. This waste treatment option has been suggested for treatment and disposal of the long half-life radionuclides (such as technetium-99) in a "national" facility.

Author: Del Cul

References:

1. G. P. Lawrence, "High Power Linear Accelerators for Tritium Production and Transmutation," *Nucl. Instrum. Methods Phys. Res., Sect. B*, B56-B57 (Pt. 2), 1000-471-1, 1992.
2. W. Seelmann-Eggbert et al., *Chart of the Nuclides*, Kernforschungszentrum Karlsruhe, 1981.
3. M. A. Lone et al., *An Overview of the ATW Reactor for Transmutation of Neptunium-237*, AECL-10953, 1992.
4. C. D. Bowman et al., "Nuclear Energy Generation and Waste Transmutation Using an Accelerator-Driven Intense Thermal Neutron Source," *Nucl. Instrum. Methods Phys. Res., Sect. A*, A320(1-2), 336-67, 1992.
5. G. J. Van Tuyle et al., *The Phoenix Concept: Proposed Transmutation of Long-Lived Radioactive Wastes to Produce Electric Power*, BNL-52279, 1991.
6. *CURE: Clean Use of Reactor Energy*, WHC-EP-0268, 1990.

EM Problem: Waste management

K-25 Site Problem: Waste off-gases from D&D, RA, and WM operations

Problem Area/Constituents: Removal of inorganic, organic, and radioactive compounds and particulates from various gaseous streams at the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Low-temperature separation¹—This process can be used for removing hazardous volatile contaminants [e.g., volatile organic compounds (VOCs)] from waste-gas streams. Briefly, low-temperature separation consists of cooling the waste gas (by refrigeration, if necessary) to temperatures where the volatile contaminants can condense out of the gas stream. The condensed liquids then can either be distilled to recover and recycle the individual VOCs or be disposed, for example, by incineration. The process can be used for separating, for example, freons, acetone, benzene, etc., from the waste-gas stream.

Status: Predemonstration

Science/Technology Needs: These are likely to be minimal, because the fundamentals of the process can be obtained from, for example, the petroleum industry. However, use of the process to treat waste-gas streams at the site may require bench-scale studies and demonstrations to prove its applicability.

Implementation Needs: Development and demonstration of use of the technology to treat waste-gas streams are estimated to cost \$1M-\$2M (1992 dollars). However, payback could be significant when compared to the cost of treatment alternatives. Also, the process could

result in significant waste minimization because of recovery and recycling of the hazardous compounds.

Author: Singh

References:

1. R. H. Perry and D. W. Green, eds., *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw-Hill Book Company, New York, 1984.

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EM Problem: Waste management

K-25 Site Problem: Waste off-gases from decontamination and decommissioning, remedial action, and waste management operations

Problem Area/Constituents: Waste streams containing volatile organic compounds (VOCs) such as methylene chloride, chloroform, carbon tetrachloride, etc., and gaseous wastes containing water-soluble gas contaminants

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Steam stripping—An industrially accepted process for removing low-boiling, organic compounds from aqueous wastes. The process also can be used in gas treatment to remove water-soluble contaminants. It is a continuous fractional distillation process in which live steam is injected directly into the bottom of a packed or tray tower to separate VOCs from wastewater in multiple equilibrium stages. It is most effective in treating liquid wastes containing organic solvents with low boiling points and which are relatively immiscible in water.

Status: Demonstration

Science/Technology Needs: Specific waste treatment applications for this technology will be identified. A pilot facility then could be designed and installed or purchased as a skid-mounted package. This package likely will consist of a fractionation column, heat exchanger(s), reboilers, tanks, instrumentation controls, and other accessory equipment. Optimum operating conditions will be established during pilot runs, and scale-up to a larger facility will follow, if required. The pilot unit can be a mobile unit for ease of transport to the waste sites.

Implementation Needs: The above-stated work is estimated to cost \$1M-\$2M (1992 dollars) to implement.

Author: Chiang

References:

1. R. J. Turner, "Waste Treatability Tests of Spent Solvent and Other Organic Wastewaters," *Environmental Progress*, May 1989.
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4. *Handbook of Industrial Water Conditioning*, Betz Laboratories, Inc., 1980.
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EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radionuclides in water, heavy metals in water, PCBs in water, other volatile organics in water, PCBs in oil, nonhalogenated organics in oil, radionuclides in solvents, radionuclides (including technetium) in mercury, and contaminated specialty freons

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Distillation^{1,2}—Basic distillation involves application of heat to a liquid mixture, vaporization of part of the mixture, and removal of heat from the vaporized portion. The resulting condensed vapor, called distillate, is richer in the more volatile components, and the residual, unvaporized bottoms are richer in less volatile components.

In simple distillation, a single equilibrium stage is used to obtain a desired separation, and the operation may be either batch or continuous. Simple continuous distillation (also called flash distillation) has a continuous feed to an equilibrium stage; the liquid and vapor leaving the stage are in equilibrium. Flash distillation is used in applications where crude separation is adequate. The component separation in simple distillation is limited by thermodynamic

partitioning constraints, and multiple staging must therefore be used to increase separation efficiency.

Multiple staging in column design is achieved by returning part of the condensed overhead vapors to the top of the column, thereby bringing this reflux liquid into intimate contact with the rising vapors. Either a tray or a packed column normally is used to provide the necessary gas-liquid interfacial area for mass transfer. The degree of component separation for a given system configuration depends on operating conditions, the number of stages, and the amount of reflux.

Status: Accepted by industry; many units are in use (solvent recovery and chemical purification for example). Capital costs are high.

Science/Technology Needs: The following may cause problems during operation:

- Feed to a column must be free-flowing with negligible solids content. Solids generally plug and foul the internals of a distillation column.
- Other compounds that can cause problems during distillation include organic peroxides, pyrophoric organics, most inorganic wastes, and feeds that tend to polymerize.
- Feeds should not exhibit large and/or frequent variations in composition.

Implementation Needs:

- Process equipment
- All utilities, including reliable electricity, air, water, etc.
- Drum and material handling equipment
- Trained chemical operators
- EPA-certified laboratory support

Author: Dukes

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, p. 6.23-6.38, 1989.
2. R. H. Perry and D. W. Green, eds., *Chemical Engineers' Handbook*, 6th edition, McGraw-Hill Book Company, New York, 1984.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Radioactive species (including technetium), organics, and inorganic salts in water or other organic solvents

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Evaporation^{1,2}—A process of bringing the contaminated liquids or slurries to their boiling point and vaporizing either pure water (for aqueous wastes) or the organic solvent (for wastes in an organic medium). The vapor either can be used for power production or condensed and either reused or disposed separately. The solids concentrate in the residue to the point where the residue either can be reused in the process (e.g. the use of sulfate liquors in paper processing) or can be packaged for disposal. Evaporation often is used as a waste reduction method in the disposal of radioactive wastes.

Status: Accepted by industry; many units are in use. Application of the technology may need to be demonstrated for the specific site problem.

Science/Technology Needs: The following may cause problems during operation:

- Scale formation on heating tubes can result in a decrease in the overall heat transfer coefficient.
- When evaporating organic-laden wastes, thermal degradation or coking of organics also may pose a problem.
- Initial solute concentrations in the waste stream must be high enough to warrant use of evaporation (generally >10,000 ppm).

Implementation Needs:

- Process equipment
- All utilities, including reliable electricity, natural gas, steam, air, water, etc.
- Drum and material handling equipment
- Trained chemical operators
- EPA-certified laboratory support

Author: Dukes

References:

1. N. L. Nemerow and A. Dasgupta, *Industrial and Hazardous Waste Treatment*, Van Nostrand Reinhold, New York, p. 151-152, 1991.
2. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, Sec. 7.7, 1989.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents: Volatile organics and nonvolatile organics in water and soils; nonhalogenated organics in oil (if oil can be codegraded with organics)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Clean Air Act regulations under 40 CFR 60-65
- Clean Water Act regulations under 40 CFR 110-146 and 400-471
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Subelement: Waste processing

Alternative: Biological treatment

Technology: Aerobic Digestion¹—Many naturally occurring microorganisms can oxidize a wide variety of organic chemicals to carbon dioxide and water at ambient temperature, pressure, and neutral pH. This is the basis for traditional biological treatment of municipal and industrial wastewaters. Approximately half of the carbon typically is incorporated into new biological cell mass; thus, significant biosludge may be generated for subsequent disposal. Various types of suspended-growth and fixed-film bioreactors are used. The rate of biooxidation, and thus the residence time required, depends highly on the individual organic species to be degraded.

Status: Demonstration. The status is labeled "demonstration," although aerobic digestion is commercially available (and used widely for treating various municipal and industrial wastewaters), because its suitability for treating a particular K-25 Site waste stream may need to be demonstrated before its use.

Science/Technology Needs: Because aerobic digestion is a commercial technology, science/technology needs generally are minimal. However, the efficacy of the process to treat a particular K-25 Site waste stream may need to be evaluated/demonstrated before its full-scale use at the site.

Implementation Needs: Because of the wide spectrum of applying aerobic digestion, it is impractical to list a meaningful cost for the technology, because this depends on numerous factors. In general, implementation costs for bench-scale treatability studies and a technology demonstration may cost \$1M-\$2M. However, use of the process could enable the discharge of large volume waste streams (by removing the contaminants). Payback for the technology is quite significant compared to the cost of alternatives.

Author: Donaldson

References:

1. C. P. L. Grady and H. C. Lim, *Biological Wastewater Treatment, Theory, and Application*, Marcel Dekker, New York, 1980.

EM Problem: Waste management

K-25 Site Problem: Contaminated wastewater

Problem Area/Constituents/media: PCBs in water; volatile and nonvolatile organics in water and soils; PCBs and nonhalogenated organics in oils (if the oil can be codegraded)

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
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Subelement: Waste processing

Alternative: Biological treatment

Technology:

Specific. Anaerobic digestion¹

Generic. Biological treatment. Many organic chemicals can be degraded anaerobically (reduced) by naturally occurring microorganisms. The rates are usually slower than aerobic (biooxidation) degradation, but only about 10% of the carbon typically is converted to biological cell mass, compared with 50% for biooxidation. Thus, much less biosludge is produced. Major products of anaerobic digestion are carbon dioxide and methane; the latter can be recovered economically from treatment of high-strength wastes. Suspended-growth and biofilm reactors are used. Anaerobic digestion also can affect reductive dehalogenation of organics; thus, it may be suitable for treatment of PCBs.

Status: Demonstration. The status is labeled "demonstration," although anaerobic digestion is commercially available for stabilizing (degrading) biosludge from aerobic wastewater treatment and for treating high-strength organic wastes from food processing and agricultural operations. This is so because the suitability of the technology for treating particular K-25 Site waste streams may need to be developed/demonstrated. For example, treatment of halogenated organics (e.g., PCBs) is still in the developmental phase, though treatment of chlorinated solvents has been demonstrated in bench- and pilot-scale studies.

Science/Technology Needs: Opportunities exist for improving methane recovery/use and for improving degradation rates via clever bioreactor and process designs. However, although the technology is practiced commercially, its application to K-25 Site waste streams may need to be evaluated/demonstrated. More development work is needed on halogenated compounds (e.g., PCBs and solvents).

Implementation Needs: Treatability studies are always a good idea to evaluate the suitability of the technology to treat a particular waste stream. For chlorinated compounds, a pilot-scale demonstration should be conducted before commitment to a full-scale facility. Cost of the pilot-scale demonstration is likely to be \$1.5M-\$2M at a DOE site. Biotreatment of PCBs is still at the predemonstration stage, and technical breakthroughs are needed to move confidently to the demonstration stage. As before, payback for the technology could be quite significant compared to the cost of alternatives.

Author: Donaldson

References:

1. C. P. L. Grady and H. C. Lim, *Biological Wastewater Treatment, Theory, and Application*, Marcel Dekker, New York, 1980.

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Contaminated solvents (halogenated and nonhalogenated)

Problem Area/constituents: Radionuclides, technetium, mercury, and heavy metals in water, oils, and solvents

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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Subelement: Waste processing

Alternative:

Technology: Biosorption¹—Many naturally occurring microorganisms sorb radionuclides (including technetium) and heavy metals (including mercury). This sorption may be extracellular (adsorption) or intracellular (absorption). Resting cells may be used; active metabolism does not seem to be necessary. Usually, some means may be found to recover radionuclides and heavy metals from the cells, if desirable (although significant loss of cells may accompany the treatment). Biosorption is analogous in many ways to removal using ion-exchange materials and other sorbents. Kinetic and equilibrium behaviors are widely variable and must be determined experimentally for each system of interest. In some cases, biosorption appears to exhibit better selectivity and higher extents of removal than nonbiological sorbents and, thus, may be preferable.

Status: Predemonstration. Much information is available in the scientific literature. However, little pilot-scale work has been done yet.

Science/Technology Needs: More basic information is needed on mechanisms, rates, and equilibria for systems of practical interest under realistic process conditions, including mixtures of contaminants.

Implementation Needs: Treatability studies are critical to characterize performance of the particular system of interest. Biosorption may or may not perform comparably to nonbiological sorption processes. Development of the technology is estimated to cost \$1M-\$3M (1992 dollars); however, payback of the technology is estimated to be hundreds of millions of dollars, based on avoided waste disposal costs for the waste streams in question.

Author: Donaldson

References:

1. H. Eccles and S. Hunt, *Immobilization of Ions by Bio-Sorption*, Ellis Horwood, Ltd, Chichester, England, 1986.

EM Problem: Waste management

K-25 Site Problem: Contaminated solvents (halogenated and nonhalogenated)

Problem Area/Constituents: PCBs in water, solvents, oils (if the oils can be codegraded), and soils; other halogenated organics in the above-mentioned media.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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Subelement: Waste processing

Alternative: Biological treatment

Technology: Microbial Dechlorination^{1,2}—Reductive (anaerobic) dechlorination of a variety of chlorinated organics has been demonstrated in laboratory experiments. Also, strong evidence exists for microbial dechlorination in natural environments. Compared to manufactured PCB Aroclors, weathered PCB-contaminated sediments show lower relative amounts of the higher-chlorinated congeners and higher amounts of the lower-chlorinated congeners, which is consistent with dechlorination. Weathered spills of trichloroethylene and perchloroethylene often show dichloroethylenes and vinyl chloride, which are believed to be products of dechlorination. Presently, the mechanisms and pathways for microbial dechlorination are poorly characterized and understood. However, much work is under way at numerous institutions. The leading conceptual process configuration is now probably a slurry bioreactor or a composting/landfarming system for contaminated soils and water. A system capable of treating oils is not obvious, although oils could be applied to a slurry bioreactor or a landfarming system.

Status: Conceptual to development, depending on application. Phenomena are demonstrable at bench-scale, but process development work is only beginning. A few field tests have been attempted.

Science/Technology Needs: More basic understanding is needed to improve ability to manipulate and control the process and to ensure adequate performance. Then, pilot-scale demonstrations will be needed.

Implementation Needs: Development costs for the technology are estimated to be \$5M to \$10M (1992 dollars). However, should the technology prove successful, payback for the process could be as much as \$100-200 M, based on disposal costs for the waste streams in question.

Author: Donaldson

References:

1. M. L. Rochkind-Dubinsky, G. S. Sayler, and J. W. Blackburn, *Microbial Decomposition of Chlorinated Aromatic Compounds*, Marcel Dekker, Inc., New York, 1986.
2. D. A. Abramowicz, "Aerobic and Anaerobic Biodegradation of PCBs: A Review," *Critical Reviews in Biotechnology*, **10**, 241-251 (1990).

EM Problem: Waste management

K-25 Site Problem: Waste off-gases from decontamination and decommissioning (D&D), remedial action, and waste management operations

Problem Area/Constituents: Gases generated during D&D operations at the gaseous diffusion plants, such as the K-25 Site, using ClF_3

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste treatment

Alternative: Physical treatment

Technology: Inorganic membrane separations—Inorganic membranes can be optimized to separate gases. Specifically, ClF_3 can be separated from the contaminated gas stream for recycling to the decontamination process. UF_6 gas can be removed in a subsequent separation stage for uncomplicated cold trapping and can be reclaimed in a pure state for useful purposes. Presently, this is a development technology. Development of an inorganic membrane to separate hydrogen from gas streams is progressing well and will prove very valuable to this development.

Status: Predemonstration. Technology development is at the bench-scale level, and testing of gas membranes is approaching target criteria. Tests show that theoretical analysis is on-target and that this has instilled confidence in the efficacy of the technology.

Science/Technology Needs: Ongoing development efforts for the hydrogen membrane will prove a giant step forward in developing a membrane for these gas separations. The main goal of these efforts will be to develop the criteria necessary for the separations, to design the membranes, and then to fabricate gas membranes with pore sizes sufficiently small to achieve effective separation by molecular sieving. A pore radius of 5–10 Å is expected to be required. Pore radii of 7 Å have been achieved in ceramics membranes, but these membranes will have to be fabricated from materials that can survive in corrosive gases. The technology should be demonstrated with two membrane modules in series and should be at the pilot-plant scale. In addition, technology assessments need to be conducted to establish the viability and economics of the process.

Implementation Needs: Development of the process through the demonstration phase is estimated to cost \$1.5M–\$2M (1992 dollars). However, the process will not generate any additional wastes (NaF, alumina, etc.), will reduce ClF_3 usage, and will facilitate the uncomplicated recovery of UF_6 for useful purposes. This membrane stage can be followed by a slurry system to scrub out the contaminated gases, with the slurry directed to another membrane stage to separate and concentrate the mixed waste. The cost benefits of this process are expected to exceed \$20M.¹

Author: Vance

References:

1. S. P. N. Singh, personal communication with J. M. Vance, K-25 Site, November 30, 1992.

EM Problem: Waste management

K-25 Site Problem: Waste off-gases from D&D, RA, and WM operations

Problem Area/Constituents: Removal of inorganic, organic, and radioactive compounds and particulates from various gaseous streams at the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternative: Physical treatment

Technology: Scrubbers^{1,2}—Mechanical devices used to remove solid and/or gaseous contaminants from gas streams using a solvent (usually water). Briefly, the solvent is intimately mixed with the contaminated gas stream in a countercurrent, cocurrent, or cross-flow configuration. The contaminants dissolve or are collected in the solvent stream. Rich or loaded solvent solution then is treated separately to recover contaminants from the solvent for recycling or disposal. Conventional scrubbers include packed-bed, tray-type, venturi, liquid-film, or cyclone scrubbers. When properly designed and operated, scrubbers are very efficient in removing contaminants from the waste-gas stream.

Status: Demonstration. The status is labeled "demonstration," although most scrubbers are commercially available, because application of a particular scrubber to treat a K-25 Site stream may need to be demonstrated before its full-scale use.

Science/Technology Needs: Because scrubbers are commercial technology, generally, science/technology needs are minimal. However, the efficacy of a particular scrubber may need to be demonstrated for a given application before its full-scale use.

Implementation Needs: Because of the wide range of applications where scrubbers can be used, it is impractical to list a meaningful cost for the technology, because it depends on numerous factors. In general, implementation of a technology demonstration of a scrubber application may cost up to \$1M. However, because scrubbers enable the discharge of (often) large volume waste streams (by removing the contaminants), payback for use of the technology can be quite significant compared to the cost of alternatives.

Author: Singh

References:

1. H. M. Freeman, ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York, 1989.
2. R. H. Perry and D. W. Green, eds., *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw-Hill Book Company, New York, 1984.

EM Problem: Waste management

K-25 Site Problem: Waste off-gases from decontamination and decommissioning, remedial action, and waste management operations

Problem Area/Constituents: Removal of inorganic, organic, and radioactive compounds and particulates from various gaseous streams at the K-25 Site

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
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Subelement: Waste processing

Alternative: Physical treatment

Technology: Cyclone separators¹—Like scrubbers, cyclone separators are used to separate solids and entrained liquids from gas streams. Cyclone separators use centrifugal action to separate particulates and entrained liquids from the waste-gas stream. When properly designed and operated, cyclone separators are very efficient at removing contaminants from the waste-gas stream.

Status: Demonstration. The status is labeled "demonstration," although most cyclone separators are commercially available, because application of a particular separator to treat a K-25 Site stream may need to be demonstrated before its full-scale use.

Science/Technology Needs: Because cyclone separators are commercial technology, generally, science/technology needs are minimal. However, the efficacy of a particular separator may need to be demonstrated for a given application before its full-scale use.

Implementation Needs: Because of the wide range of applications where cyclone separators can be used, it is impractical to determine a meaningful cost for the technology, because it depends on numerous factors. In general, implementation of a technology demonstration may cost up to \$1M. However, because cyclone separators enable the discharge of (often) large volume waste streams (by removing the contaminants), payback for use of the technology is quite significant compared to the cost of alternatives.

Author: Singh

References:

1. R. H. Perry and D. W. Green, eds., *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw-Hill Book Company, New York, 1984.

EM Problem: Waste management

K-25 Site Problem: Waste gases of unknown characteristics from decontamination and decommissioning (D&D) and remedial action operations (some possibly in cylinders of uncertain integrity)

Problem Area/Constituents: Orphan gas cylinders lacking information of their contents

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
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Subelement: Waste processing

Alternative: Physical treatment

Technology: Recharacterize and repackage—Environmental restoration and D&D operations at the site likely will uncover orphan gas cylinders of unknown content. Safe disposal of these gas cylinders in compliance with regulations is likely to require recharacterization of the contents of the cylinders and (depending on the physical condition of the cylinders) repackaging in approved cylinders for treatment, use, or disposal. This is likely to be an operation that can be managed with current technology.

Status: Accepted

Science/Technology Needs: Minimal to none

Implementation Needs: These are likely to be minimal. The estimated costs for conducting the operations will depend on the number of such cylinders found, their physical state, and the nature of their contents. Payback for this operation is expected to be high, considering the alternatives.

RECHARACTERIZE AND REPACKAGE

WPRO-303-OG

Author: Singh

References: None

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Waste off-gasses from decontamination and decommissioning, remedial action, and waste management operations

Problem Area/Constituents: Treatment of pollutants such as vinyl chloride, benzene, H_2S , and methyl mercaptan and aqueous effluents containing hazardous organics such as benzene, carbon tetrachloride and trichloroethylene.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternatives: Thermal treatment

Technology: Electron-beam (E-beam) destruction^{1,2}—The process is claimed to be a simple, energy-efficient method for reducing small concentrations of pollutants in air (or other carrier gases) to less than the 1 ppm level using a high-energy electron beam.

E-beam irradiation ionizes the carrier gas; these ions then can react with the pollutant to destroy it while leaving the carrier gas relatively unreacted. This reaction is accomplished primarily by rapid-charge transfer from the carrier gas to the pollutants, which normally have lower ionization potential. Pollutant ions subsequently are destroyed.

For wastewater treatment, E-beam destruction of organic molecules is a very effective mechanism, because irradiation of water with high-energy electrons results in production of

oxidizing and reducing species, such as hydroxyl (OH) and aqueous electron (e_{aq}^-) radicals. These reactive species then react with and destroy the organic molecules. Essentially, the E-beam process is insensitive to effluent quality, with effective removal of organic chemicals observed in both lightly contaminated-water effluent streams and raw sewage.

Status: Predemonstration

Science/Technology Needs: A study must be conducted of all experimental work done involving E-beam destruction technology. Development work at the bench scale with the pollutants of interest then will begin. If technical viability and economics justify it, scale-up and testing on a larger scale unit will follow.

Implementation Needs: Implementing the development needs outlined above is estimated to cost \$0.75M–\$1.5M (1992 dollars). As development work progresses and the application appears promising, collaborative research efforts with the private sector or with academia can be established. As a result, the potential may exist for lower implementation cost, particularly during the latter part of the development cycle.

Author: Chiang

References:

1. R. C. Slater and D. H. Douglas-Hamilton, *Electron-Beam-Initiated Destruction of Low Concentrations of Vinyl Chloride in Carrier Gases*, AVCO Everett Research Laboratory, Everett, Mass., 1981.
2. T. D. Walte, C. N. Kurucz, and W. J. Cooper, *Utilizing High Energy Electrons for Treatment of Industrial Wastes Containing Non-Biodegradable Organic Compounds*, proceedings of the 22nd mid-Atlantic Industrial Waste Conference, 1990.

EM Problem: Waste management

K-25 Site Problem: Waste off-gases from decontamination and decommissioning (D&D), remedial action, and waste management operations

Problem Area/Constituents: All environmental restoration and D&D processes that emit volatile organic compounds (VOCs) exceeding the regulatory limits

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
- Federal Facilities Agreement (FFA) for the Oak Ridge Reservation
- Federal Facilities Compliance Agreement-Toxic Substances Control Act (FFCA-TSCA) dated February 20, 1992
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Subelement: Waste processing

Alternative: Thermal treatment

Technology: Flameless thermal oxidizer¹—This oxidizer can achieve greater than 99.99% removal of VOCs from the waste streams with negligible innocuous by-product formation. The principal feature of the oxidizer is the inert ceramic bed or "matrix," which provides thorough mixing of oxygen with the waste gases. Designed for optimal mixing and residence time, the matrix is preheated and controlled at a desirable temperature to achieve complete oxidation of the hydrocarbons, producing carbon dioxide and water. The large thermal mass of the matrix absorbs heat released during oxidation, preventing flames or flashback. If the inlet fume is laden with chlorinated or sulfur-containing organics, a system to remove the HCl or SO₂ generated is incorporated, when necessary for regulatory compliance. Versatile in handling widely fluctuating flow rates and organic concentrations, the process provides advantages over other VOC control technologies, such as incineration, carbon adsorption, etc. It eliminates the drawbacks inherent in other alternate processes (i.e., process instability, by-

product of waste formation, flame safety issues, and poor treatment of chlorinated hydrocarbons).

Status: Demonstration

Science/Technology Needs: The flameless thermal oxidation process will be thoroughly reviewed. A pilot-scale oxidizer will be designed, and experimental runs will be performed to optimize operating conditions. Optimal design of the ceramic matrix is crucial to achieving the desirable mixing of air and hydrocarbons and to provide proper residence time for complete oxidation. Instrumentation and control are to be incorporated into the system adequately to maintain desired bed temperature and to control air flow in response to varying hydrocarbon flow rates and concentrations.

Implementation Needs: R&D work is estimated to cost \$1M-\$1.5M. As this is a process covered by a patent, an additional user fee may be incurred for its full-scale application. The development cost estimated may be offset somewhat by contributions from the private sector or academia if collaborative research efforts are established. This process is envisioned to have the potential for being a viable option to eliminate toxic emissions from the oil and gas, chemical, and pharmaceutical industries.

Author: Chiang

References:

1. J. T. Schofield, *Flameless Thermal Oxidizers for VOC Control*, bulletin, Thermatrix, Inc., 1992.
2. J. T. Schofield, Thermatrix, Inc., personal communication to Jim Pelmer, MMES Office of Technology Transfer, 1992.

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues that result from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes have to be prepared for final disposal in compliance with regulations.

Reference Requirements:

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- Clean Water Act regulations under 40 CFR 110-146 and 400-471
- DOE orders

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: Cementitious solidification/stabilization (CS/S)—One of the most widely used techniques for treating and ultimately disposing of hazardous wastes and low-level radioactive wastes. Cementitious materials are the predominant materials of choice because of their low associated processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. Cementitious materials include cement; granulated blast furnace slag; fly ash; lime; and fumed silica. Various clays and additives are used to help immobilize contaminants or otherwise enhance waste form properties. Soluble constituents in the waste chemically interact with the cementitious materials to form low-solubility products at the low pH and Eh prevailing in the waste form. These interactions usually affect cementitious hardening and properties to some degree. Testing with a specific waste or waste stream is required to tailor

formulation to the desired properties. Sufficient attention must be given to characterizing the waste, developing the formulation to treat the waste, and implementing this formulation in the field to assure correct mixing of the formulation. Adding these dry ingredients inevitably increases the volume of the waste treated, which can add significantly to lifetime disposal costs. The volume decrease claimed by techniques such as thermoplastic encapsulation come from evaporation of water and encapsulation of the solids. The same evaporation pretreatment could be used with CS/S to obtain a net volume decrease, but some of the simplicity of CS/S would be lost. Cementitious waste forms are porous, making them more leachable than polymeric or glass waste forms. The key to success has been controlling this leachability (by pH, Eh, and/or absorbents) within satisfactory limits for a simpler and cheaper treatment.

For relatively inert materials, such as rubble or scrap metal, cementitious materials are ideal for macroencapsulation. Encapsulated ion-exchange resins can lead to breakdown of the solid matrix because of the volume changes that result from wetting and drying of the resin. Proper formulation and pretreatment has succeeded in overcoming this problem for encapsulated resins.

Status: Accepted

Science/Technology Needs: Better understanding of immobilization mechanisms and chemistry of these waste forms can lead to improved performance and better predictions about their durability. This technique is currently in wide-scale use.

Implementation Needs: These are relatively minimal, because it is accepted technology. However, formulations need to be developed, or at least tested, for the specific wastes intended for treatment. Proper implementation is necessary to ensure that waste forms tested in the laboratory represent what will be produced in the field. This means having the necessary equipment and expertise to properly blend and mix these solid constituents and manage the operation properly, so that the right formulation is mixed.

Author: Spence

References:

1. J. R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.
2. I. L. Morgan and W. D. Bostick, *Performance Testing of Grout-Based Waste Forms for the Solidification of Anion Exchange Resins*, K/QT-382, October 1990.
3. A. van Dalen and J. E. Rijpkema, *Modified Sulphur Cement: A Low Porosity Encapsulation Material for Low, Medium and Alpha Waste*, paper published by the Commission of the European Communities, EUR 12303 EN, 1989

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues that result from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance with regulations.

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: Polymer impregnated concrete (PIC)—Basically, this technique is an extra step to achieve waterproofing after cementitious solidification/stabilization. Polymer impregnation has been studied for many years, and usually it is restricted to treatment within a few millimeters of the surface. It has been used as a means of waterproofing and environmental protection for structural concrete. A technique was invented at ORNL¹ to achieve essentially complete monomer permeation throughout a waste form by adding polystyrene foam during mixing of the cementitious waste form. This introduces porosity into the waste form, potentially making a weaker product (not a great concern for waste forms). The monomer is polymerized, giving a waterproofing component throughout the waste form. This treatment has protected cementitious waste form samples from attack by concentrated hydrochloric acid. Laboratory development is still needed to optimize treatment and test the properties of

the resulting waste form. The product has the advantages of a cementitious waste form with the added protection of a waterproofing layer throughout the waste form. Leaching will still occur across the polymeric barrier from the porous cementitious waste form. Brookhaven National Laboratory (BNL)² acquired a patent using polymer impregnation of cement as a means of disposing of tritiated water.

Status: Evolving technology/conceptual. Some laboratory work has been conducted on the technology.

Science/Technology Needs: These include further development of the technology to where it can be used to successfully stabilize some of the residues likely to be generated at the site.

Implementation Needs: Development and demonstration of the efficacy of this stabilization method are expected to cost \$5M-\$10M (1992 dollars). However, payback for the process could be significant, if it is demonstrated that the technique can successfully stabilize radioactive and/or hazardous residues generated at the site.

Author: Spence

References:

1. A. J. Mattus and R. D. Spence, ORNL, *Process for Impregnating a Concrete or Cement Body with a Polymeric Material*, U.S. patent 4,828,761, May 9, 1989.
2. Peter Colombo, Robert M. Neilson, Jr., and Walter W. Becker, BNL, *Process for Disposal of Aqueous Solutions Containing Radioactive Isotopes*, U.S. patent 4,174,293, November 13, 1979.

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues that result from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance with regulations.

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: Thermoplastic encapsulation—Two thermoplastics, bitumen and polyethylene, have been developed as encapsulation waste forms. Ostensibly, thermoplastics do not interact with the waste, so extensive testing to tailor the waste form is not needed, and net volume reductions can result for liquid wastes. The waste must be dried and the dried solids encapsulated in the thermoplastic. The waste is exposed to higher temperatures during drying and mixing with the molten thermoplastic, so volatile species such as mercury may not be amenable to such treatment. The processing is more complex than cementitious solidification/stabilization (CS/S). The waste is not chemically immobilized or stabilized, but the thermoplastic is nonporous and, hence, less leachable. It is questionable whether such physical encapsulation waste forms will pass the required TCLP leachability test. Also, current EPA guidance states that chemical fixation, rather than just physical encapsulation,

is required. For this reason, CS/S is the best demonstrated, available technology (BDAT) for hazardous RCRA metals.

Bitumen has been used extensively in Europe, and a couple of commercial vendors have offered bitumen encapsulation in the U.S. However, bitumen creeps and requires a container (e.g., 55-gal drum or concrete vault) for structural integrity. Bitumen absorbs water, swelling as it does so. Encapsulated soluble salts will set up large osmotic pressures within thermoplastic waste forms upon contact with water, causing further expansion for bitumen waste forms. Concern also exists about encapsulating nitrate salts (known oxidizers) in thermoplastics and the biodegradability of these waste forms. Once ignited, such a mixture may burn without air. The combination of these problems has made bitumen less popular than cementitious waste forms, despite its superior leach resistance. Polyethylene may overcome most, if not all, of these problems, but presently it is only a laboratory development. Polyethylene offers the structural integrity that bitumen lacks. Also, BNL has studied polyethylene as a waste form for DOE and claims that nitrate salts encapsulated in polyethylene will pass fire and self-ignition tests. BNL has not developed the technology for drying the waste before encapsulation in polyethylene, nor has BNL encapsulated actual wastes. BNL has mainly studied the properties of dry salts encapsulated in polyethylene. So, the technology is mainly a laboratory development. It has yet to be demonstrated that the process can pass the required TCLP leaching test and that the process has production-scale capabilities with actual wastes.

Status: The bitumen stabilization process is at the demonstration-scale level, while the process using polyethylene is adjudged to be at the predemonstration scale of development.

Science/Technology Needs: These include developing the particular technology to where it can be used to stabilize residues generated at the site in compliance with regulations. These could include, for example, developing the waste form that will pass the TCLP test; techniques to dry the waste before encapsulation for the polyethylene process; developing the waste forms' resistance to biological degradation; and developing methods for handling volatile hazardous compounds that may be present in residues. Materials susceptibility to corrosion at the elevated temperatures for the processing equipment also needs to be explored, especially if chloride or fluoride species are present in the waste.

Implementation Needs: Developing and demonstrating the efficacy of this stabilization method are estimated to cost \$2M-\$5M (1992 dollars). However, payback for the process could be significant, if it is demonstrated that the technique can successfully encapsulate or isolate radioactive and/or hazardous compounds from the environment for the required period.

Author: Spence

References:

1. J. R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.

THERMOPLASTIC ENCAPSULATION [SULFUR POLYMER CEMENT (SPC)]

WSTA-103-OG

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of the final contaminated residues that result from the decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance with regulations.

Reference Requirements:

- Resource Conservation and Recovery Act of 1976 (RCRA), as amended, Land Disposal Restriction (LDR) Federal Facilities Compliance Agreement (FFCA) dated June 12, 1992
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- DOE orders

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: Thermoplastic encapsulation—Sulfur polymer cement (SPC) encapsulation is like thermoplastic encapsulation in that the dried waste solids are encapsulated in the molten sulfur. The advantages are similar in that little interaction is anticipated, a nonporous waste form results in less leaching, and drying the liquids results in a net volume decrease. Sulfur is resistant to acid attack, so that SPC has been used as a construction material in aggressive acid environments. On the other hand, sulfur cannot be used in other environments, such as high alkalinity. These deleterious environments have been identified and must be avoided. SPC has been studied as a waste form by BNL and in Europe. These studies have been on a laboratory scale, so pilot-scale testing and demonstrations still are needed. As with thermoplastics, it is questionable whether SPC will meet EPA's guidance

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THERMOPLASTIC ENCAPSULATION [SULFUR POLYMER CEMENT (SPC)]

WSTA-103-OG

regarding the use of chemical fixation, because it is a purely physical encapsulation technique. SPC is being touted as an acceptable waste form for disposing of radioactive wastes. The Europeans succeeded in pretreating ion-exchange resins, so that resins encapsulated in SPC could be immersed in water without resin swelling, causing a breakdown of the SPC matrix.

Status: Predemonstration

Science/Technology Needs: These include performance testing of the SPC waste form in the TCLP test; developing the technology for drying the waste before encapsulation; and demonstrating the technique on an industrial scale.

Implementation Needs: Those needed to develop this process to where it can be used to treat residues at the K-25 Site are given above. Development is estimated to cost \$2M-\$5M (1992 dollars).

Author: Spence

References:

1. P. D. Kalb, J. H. Helser III, and P. Colombo, *Encapsulation of Mixed Radioactive and Hazardous Waste Contaminated Incinerator Ash in Modified Sulfur Cement*, BNL-43691, undated (approximately 1991).
2. A. van Dalen and J. E. Rijpkema, *Modified Sulphur Cement: A Low Porosity Encapsulation Material for Low, Medium and Alpha Waste*, paper published by the Commission of the European Communities, EUR 12303 EN, 1989.
3. G. R. Darnell, *Sulfur Polymer Cement, A New Final Waste Form for Radioactive and Hazardous Wastes*, paper published by Idaho National Engineering Laboratory, November 19, 1992.

February 26, 1993

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues resulting from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance with regulations.

Reference Requirements:

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: Thermosetting plastics encapsulation—Vinyl Ester Styrene (VES) encapsulation is a form of thermosetting plastics encapsulation. This thermosetting encapsulation is accomplished by infiltration of, or mixing with, the monomer followed by polymerization, encapsulating the waste. Thermoplastic (polyethylene and bitumen) encapsulations require melting the polymer and mechanically mixing it with waste, requiring elevated temperatures and dried wastes. Thermoset encapsulation does not require elevated temperatures or dried wastes. VES encapsulation originally was developed by Dow Chemical, but it is now being developed and marketed by Diversified Technologies of Chestertown, Md. Primarily, it has been developed as a means of encapsulating ion-exchange resin without the matrix failure experienced by cementitious solidification/stabilization methods when the resin shrinks and swells with wetting and drying. The process developed is quite simple and does not require

resin drying or mechanical mixing. The resin bed is drained of aqueous solution, the VES monomer mix is infiltrated into the bed of wet resin (displacing residual water clinging to the resin beads), and finally, the monomer is polymerized, forming a monolith of VES, with the wet resin encapsulated inside. VES encapsulation of a resin bed does not result in a net increase in bulk volume, an important economic advantage for ultimate disposal. Likewise, it is also possible to encapsulate beds of other large solids. Fine solids, such as ashes from incineration, may be encapsulated, but mechanical mixing likely will be required to get a homogenous mix. Ostensibly, no interaction occurs between the waste and VES, but some materials may interfere with polymerization of the monomers, especially organic materials. Liquid wastes cannot be handled presently, except by evaporation to solids. But conceptually, an emulsion could be formed, leading to liquid waste dispersed throughout the solid VES. Technically, this does not meet some definitions of "no liquid" for disposal purposes. Also, this is a physical encapsulation technique with no chemical immobilization of the waste species. It is questionable whether VES encapsulation would pass the required TCLP test.

Status: VES is an accepted technology for encapsulating spent ion-exchange resins; it is adjudged to be at the predemonstration scale for disposal of ashes and other fine solids and is considered conceptual for disposal of liquid wastes.

Science/Technology Needs: These include developing this technology to where it can be used to stabilize (in compliance with regulations) more of the expected residues likely to be generated at the site than just the spent ion-exchange resins. These needs include, for example, conducting development studies to determine the following: whether the VES waste form will meet the TCLP leachability test for RCRA metals; the need to develop means to incorporate ashes into the monomer mix and test the performance of the resulting product, the need to determine what materials will interfere with polymerization of VES or weaken the resulting waste form, and the need to quantify residual monomer content after polymerization and determine the potential release rate of this monomer to the environment.

Implementation Needs: Developing and demonstrating the efficacy of this stabilization technique are estimated to cost \$2M-\$5M (1992 dollars). However, payback for the process could be significant, if it is demonstrated that the technique can successfully encapsulate and isolate residues other than the spent ion-exchange resins for the required period.

Author: Spence

References:

1. J. R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues that result from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance regulations.

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: High-temperature crystalline materials (ceramic)—Ideally, mineral phases can be identified and generated for each waste specie, but this may not prove feasible, and some species may be encapsulated or limited to grain boundaries. One advantage of this waste form is its thermodynamic stability. The amorphous calcium-silicate-hydrate matrix of cementitious waste forms is thermodynamically unstable, although it may last for millennium in dry environments. Glass is a supercooled liquid. Ceramics are dense mineral phases, thermodynamically stable. As with glass, ceramics can be made with low porosity, making them less leachable than cementitious waste forms. As with cementitious waste forms, the chemical phases have low solubility, potentially making them less extractable than glass waste forms. Species relegated to grain boundaries, or physically encapsulated, may be just as extractable as before treatment. TCLP testing of specific waste forms is needed to verify

this chemical stability. This technique is in its infancy. Some wastes are ready-made for conversion into ceramics, whereas others may require significant chemical conversion. The waste must not only be characterized as to elemental species, but also as to chemical species. This is a high-temperature technique with thermal destruction of organics, but may not be amenable to some volatile and semivolatile species, such as mercury, tritium, iodine, cesium, and technetium.

Status: Evolving technology/conceptual. Some laboratory work has been conducted on the technology.

Science/Technology Needs: These include, for example, the following: laboratory development to prove the concept for encapsulating certain wastes; development of the required ceramic wasteform; identification of the hazardous species that are incorporated into ceramic phases and those that are not; and demonstration of the required destruction and disposal of hazardous organics and nondestructible volatilized species that may be present in the waste. Also, the technology will need to be successfully demonstrated on a large pilot-plant scale after laboratory development has been completed.

Implementation Needs: Development and demonstration of the efficacy of this stabilization method are estimated to cost \$5M-\$10M (1992 dollars). However, payback for the process could be significant, if it is demonstrated that the technique can successfully encapsulate or isolate radioactive and/or hazardous compounds from the environment for the required period.

Author: Spence

References: None

HIGH-TEMPERATURE NONCRYSTALLINE MATERIALS (VITRIFICATION)

WSTA-106-OG

EM Problem: Waste management

K-25 Site Problem: Contaminated solid wastes

Problem Area/Constituents: Stabilization of final contaminated residues that result from decontamination and decommissioning, environmental restoration, and waste management operations performed at the site. These radioactive and/or hazardous wastes must be prepared for final disposal in compliance with regulations.

Reference Requirements:

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Subelement: Waste stabilization

Alternatives: Solidification, macroencapsulation, microencapsulation, chemical fixation

Technology: High-temperature noncrystalline materials (vitrification)—Vitrification is a physical encapsulation technique that has been accepted for high-level waste. Vitrification results in a net volume reduction, even starting with a bed of solids and no liquids. This results in significant economic savings for ultimate disposal to compensate for the higher capital and production costs required to generate this waste form compared to cementitious waste forms. Ostensibly, no interaction occurs with the waste, but it is questionable whether vitrified waste will pass the required TCLP test. The waste form is nonporous and less leachable than cementitious waste forms, but the RCRA metal may be just as extractable after treatment as before, if truly allowed to come to equilibrium, as intended in the TCLP test. Laboratory testing would be required to identify compatible melt compositions. This

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technique is performed at temperatures higher than those for thermoplastic encapsulation. Thus, water is driven off, but the method is inappropriate for volatiles and may not be suitable for semivolatiles. Organics likely are destroyed, but other volatiles and semivolatiles that cannot be destroyed (such as mercury, tritium, cesium, and technetium) may not be encapsulated by vitrification. Such contaminants are likely to be found in residues to be processed at the K-25 Site.

Status: Vitrification is adjudged to be at the predemonstration scale of development for treatment of low-level and/or hazardous wastes. However, a large data base exists for treating high-level nuclear wastes but not for low-level and hazardous wastes.

Science/Technology Needs: These include, for example, the following: the need to demonstrate the effectiveness of the technology for those semivolatile species commonly found in low-level waste and, for hazardous wastes, incinerator efficiencies must be demonstrated for organics as well as for the ability to handle volatile and semivolatile metals. Typically, mercury must be removed before vitrification, and Cs-137 has been found in off-gas from vitrification units. Claims are made that the vitrified waste form will pass the TCLP test, but this must be verified and the RCRA metal limits in the vitrified waste, quantified. Also, laboratory testing of a specific waste or waste stream is necessary to establish the required glass composition. Some laboratory testing of certain wastes has been done, but would need repeating for the K-25 Site residues, and pilot-scale testing and demonstrations would have to be done. The development likely would have to be repeated on a case-by-case basis, just as with development of the cementitious waste forms.

Implementation Needs: Development and demonstration of the efficacy of this stabilization technique are estimated to cost \$5M-\$10M (1992 dollars). This is expected to cover the costs of meeting the above-mentioned science/technology needs.

Author: Spence

References: None

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4 / 7 / 93