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DEVELOPMENT OF A NOVEL WET OXIDATION PROCESS FOR HAZARDOUS AND MIXED WASTES

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38

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Development of a Novel Wet Oxidation Process for Hazardous and Mixed Wastes

CONTRACT INFORMATION

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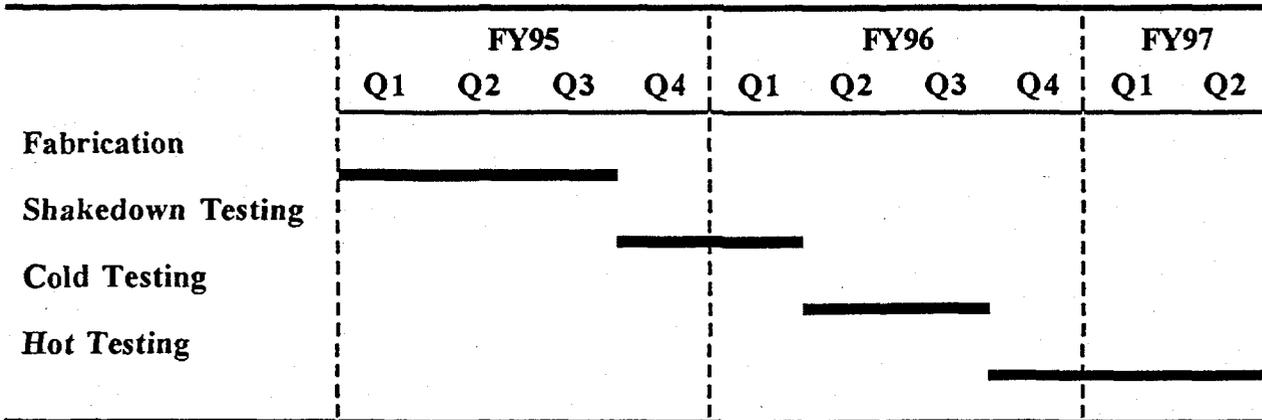
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METC Project Manager Keith Westhusing

Period of Performance September 22, 1992 to April 11, 1997

Schedule and Milestones

FY95-FY97 Program Schedule



OBJECTIVES

Phase I

The objectives for the Phase I effort were to determine the possible range of applications for the DETOXSM process and to develop a conceptual design for a demonstration unit.

Phase II

The objectives for the Phase II effort were to conduct a demonstration site survey to determine best sites for demonstrating the process, and perform Title II design of a demonstration unit.

Phase III

The objectives for the Phase III effort will be to fabricate and assemble the demonstration unit, install it at the chosen site, and perform shakedown tests to verify that the unit operates properly.

Phase IV

The objectives for the Phase IV effort will be to cold test and hot test the demonstration unit.

BACKGROUND INFORMATION

Many DOE waste streams and remediates contain complex and variable mixtures of organic compounds, toxic metals, and radionuclides. These materials are often dispersed in organic or inorganic matrices, such as personal protective equipment, various sludges, soils, and water. The

over all objective of the effort described here is to develop a novel catalytic wet oxidation process for the treatment of these multi-component wastes, with the aim of providing a versatile, non-thermal method which will destroy hazardous organic compounds while simultaneously containing and concentrating toxic and radioactive metals for recovery or disposal in a readily stabilized matrix.

The DETOXSM process uses a unique combination of metal catalysts to increase the rate of oxidation of organic materials. The process has been patented by Delphi Research, Inc. in the U. S. and several foreign countries. The metal catalysts are in the form of salts dissolved in a dilute acid solution. A typical catalyst composition is 60.% ferric chloride, 3.-4.% hydrochloric acid, 0.13% platinum ions, and 0.13% ruthenium ions in a water solution. The catalyst solution is maintained at 423.-473. K. Wastes are introduced into contact with the solution, where their organic portion is oxidized to carbon dioxide and water. If the organic portion is chlorinated, hydrogen chloride will be produced as a product.

The major reaction in the process is oxidation of organic compounds by ferric iron. Ferric iron is reduced to ferrous state during the reaction. Ferrous iron is in turn re-oxidized to ferric iron by oxygen bubbled into the catalyst solution. Although iron participates in the oxidation reaction, it is returned to its original state and is not consumed, therefore it meets the criteria for a catalyst. Platinum and ruthenium aid in oxidation of organic compounds by iron, and have been designated "cocatalysts."

Many metals will dissolve to an extent in the catalyst solution. This property of the solution can be used to remove toxic and radioactive metals

from larger amounts of more inert inorganic material. Since the catalyst solution keeps metals in the ionic state, one does not have to be as concerned with escape of volatile metals such as mercury and cadmium. Many metals can be concentrated in the catalyst solution, if desired, for eventual disposal or recovery. The catalyst solution can be reduced to an iron oxide matrix by boiling off hydrogen chloride and water. The iron oxide matrix is a good form for stabilization by one of a number of methods, preparatory to ultimate disposal of inorganic contaminants.

The process is a viable alternative to incineration for the treatment of organic mixed wastes. Estimated costs for waste treatment using the process are from \$2.50/kg to \$25.00/kg, depending on the size of the unit and the amount of waste processed. Process units can be mobile for on-site treatment of wastes.

PROJECT DESCRIPTION

Phase I

In Phase I, destruction efficiencies were measured for six organic compounds, the fates of representative metals in the catalyst solution were determined, the ability of the catalyst solution to treat contaminated soils was established, and a conceptual design for a field demonstration unit was performed.

The organic compounds tested were poly(vinyl chloride), picric acid, tetrachlorothiophene, pentachloropyridine, Aroclor 1260 (a polychlorinated biphenyl containing approximately 60.% by weight chlorine, and hexachlorobenzene. Measured amounts of the compounds were oxidized in the presence of

catalyst solution and oxygen in sealed, unstirred 125. ml titanium bombs. Post-oxidation measurements of oxygen, carbon dioxide, residual volatile organic compounds, residual semivolatile organic compounds, and residual non-volatile organic carbon and hydrogen were made on the gases and liquids in the bombs. Oxygen and carbon dioxide analyses were done in house by isothermal gas chromatography using a Carbosphere® column with standardization using pure carbon dioxide and oxygen. Volatile and semivolatile organic compounds were analyzed by standard Environmental Protection Agency (EPA) Methods 624 and 8270. Non-volatile organic carbon and hydrogen were determined by elemental analysis.

Solubilities for arsenic, barium, beryllium, cadmium, cerium (a surrogate for plutonium), chromium, lead, mercury, neodymium (a surrogate for uranium), nickel, and vanadium in the catalyst solution at room temperature were determined. The effects of sulfate and phosphate ions on metals solubilities were measured. Chromium(VI) reduction by the catalyst solution was studied. Lead solubility was measured at several catalyst solution temperatures and water contents. All of these studies were conducted in sealed, unstirred 23. ml fluorocarbon-lined stainless steel digestion bombs. Non-soluble residues were weighed using calibrated analytical balances. Metals analysis was conducted by atomic absorption spectrometry (AAS) with standardization using commercial standards and use of the method of standard addition to correct for matrix effects when necessary. Chromium(VI) concentrations were determined by colorimetric analysis using diphenylcarbazide as per standard methods for water analysis.

Six soils contaminated with arsenic, barium, beryllium, chromium, neodymium, lead, mineral oil, benzene, trichloroethene, and Aroclor 1260 were treated with the catalyst solution in unstirred, 125. ml titanium bombs. The soils were characterized as a loam, a silty loam, a clay loam, a clay, a sand, and a sandy clay loam. After treatment with the catalyst solution, the soils were rinsed with dilute hydrochloric acid and water to remove traces of the catalyst solution and tested for contaminant metals and organics. Metals were analyzed by AAS as described for the solubility tests above. Organics were analyzed as described for the organics above.

Conceptual design was performed for two units capable of destroying 5. kg/hr of PCBs and 25. kg/hr of tributyl phosphate, respectively. Approximate component sizes, materials of construction, unit schematics, mass and heat balances, monitors and controls, secondary waste streams, critical engineering issues, and health and safety issues were addressed in the conceptual design.

Phase II

In Phase II, a demonstration site selection survey was conducted and detailed engineering design for a modular, skid-mount demonstration unit was performed.

The site selection survey concentrated on multi-component, low level mixed and hazardous wastes. Sites for survey were selected based on the types of wastes likely to be present as determined by general site information and the Mixed Waste Data Base. Ten sites were chosen for survey, and the field was narrowed to seven based on the fundamental criteria of having wastes suitable for demonstration, permitting Delphi

Research and its engineering subcontractor support personnel access to the site, and providing or facilitating site-specific support. The seven sites were then evaluated using the criteria of the draft *Demonstration Site Identification Criteria for Environmental Restoration and Waste Management Technology Development Projects* provided by DOE's Morgantown Energy Technology Center (METC).

Title II engineering design for the demonstration unit was subcontracted to Jacobs Applied Technology (JAT), a company having great experience in modular chemical process design. The design proceeded through development and review of the process flow diagram (PFD), mass balances for three "typical" waste types (a hydrocarbon oil, tributyl phosphate, and a polychlorinated biphenyl containing 60.% by weight chlorine), development and review of the piping and instrumentation diagrams (P&ID's), a hazards review (HAZOP), and finalization of the Title II design. Representatives from the chosen demonstration sites were included in the review and HAZOP process in order to include their considerable expertise in the design process and to address their site-specific needs and concerns in the design.

Phases III and IV

Planned Phases III and IV are fabrication and shakedown testing of the demonstration unit, then demonstration of the unit in treatment of hazardous and mixed wastes, respectively. Phase III is scheduled for FY 95-96, and Phase IV is scheduled for FY 96-97.

Phase III assembly of the demonstration unit is planned to be conducted by JAT at their facilities in Orangeburg, South Carolina. The unit will then

be transported to the first demonstration site, installed, and subjected to shakedown testing with non-hazardous organic materials. Equipment and controls will be evaluated in this Phase before the unit is used on hazardous or radioactive materials. During Phase III, National Environmental Policy Act (NEPA) information and permit information for the Phase IV demonstration will be prepared, and operations and safety analysis will be conducted for the demonstration unit.

Phase IV demonstration is planned to begin at the same site where the Phase III testing would be conducted. This part of the demonstration will use hazardous organic wastes only, to evaluate the performance of the demonstration unit in a non-radioactive setting. After the hazardous waste experimental campaign, the unit will be cleaned, inspected, serviced, and transported to the second demonstration site. This will demonstrate transportability of the unit. At the second site, the unit will be installed, checked out, and used to treat a variety of low level mixed wastes. A commercialization assessment will be performed during the demonstration, and at the conclusion of the demonstration a determination will be made as to the disposition of the demonstration unit.

RESULTS

Phase I

Table I gives the destruction efficiencies achieved in oxidation of poly(vinyl chloride), picric acid, tetrachlorothiophene, pentachloropyridine, Aroclor 1260 (a polychlorinated biphenyl containing approximately 60.% by weight chlorine), and hexachlorobenzene. We have found from previous experimentation that these destruction efficiency

values in an unstirred reaction vessel correspond to >99.9999% destruction in a stirred reaction vessel. These tests demonstrated essentially complete destruction of representative organic compounds by the catalyst solution.

Table 1. Organics Destruction Efficiencies

Organic	Destr. Efficiencies *	
	Absolute (%)	Specific (%)
Picric Acid	99.7	
Poly(vinyl) Chloride	99.8	
Tetrachlorothiophene	98.1	99.925
Pentachloropyridine	99.5	99.984
Aroclor 1260	98.9	99.52
Hexachlorobenzene	99.97	99.97
* Unmixed reaction bombs at 473°K		

Beryllium, cerium, chromium, mercury, neodymium, nickel, and vanadium were found to be quite soluble in the catalyst solution. Figure 1 shows the metals' solubilities over a range of acid concentration in the catalyst solution. Presence of sulfate anion in the catalyst solution reduced solubility for some metals, in particular neodymium (a surrogate for uranium and plutonium). It may be useful to scavenge sulfate from the catalyst solution with calcium ions.

Excess arsenic precipitated as ferric arsenate, which tested as non-hazardous by the EPA's Toxicity Characteristic Leaching Procedure (TCLP) after being rinsed with dilute citric acid. Barium solids precipitated as barium sulfate also tested non-hazardous by TCLP. Chromium(VI) was shown to be reduced to chromium(III) by the catalyst solution. Figure 2 shows the solubility of

lead in the catalyst solution at various temperatures and water contents. Lead solubility is a maximum at somewhere between 6.0M ferric chloride and 1.5M ferric chloride, particularly at elevated temperatures, which means that this metal, and presumably others as well, can be separated from the catalyst solution by adjustment of temperature and water content of the solution.

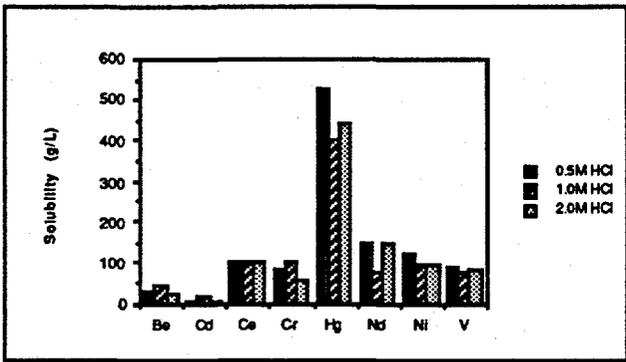


Figure 1. Metal Solubility in DETOXSM Process Solution

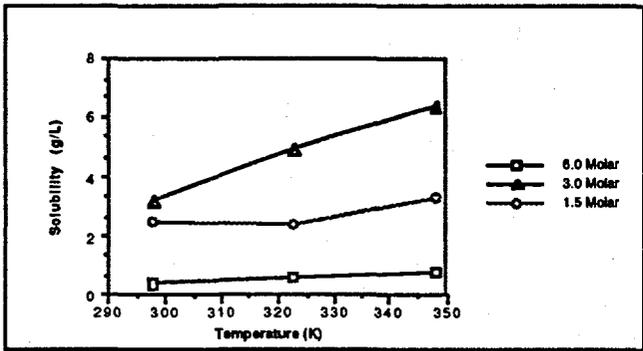


Figure 2. Lead Solubility in Chloride-Based DETOXSM Solutions

Figure 3 shows representative results from extraction of contaminant metals from soils. All contaminant metals used in these tests were extracted such that the soils tested non-hazardous

by the TCLP. Organics analysis results showed that 1.% benzene and 1.% trichloroethene in the soils were also reduced to non-hazardous levels by treatment with the catalyst solution. PCBs and oil were not removed completely, probably due to lack of agitation, but significant reductions were achieved for most soil types.

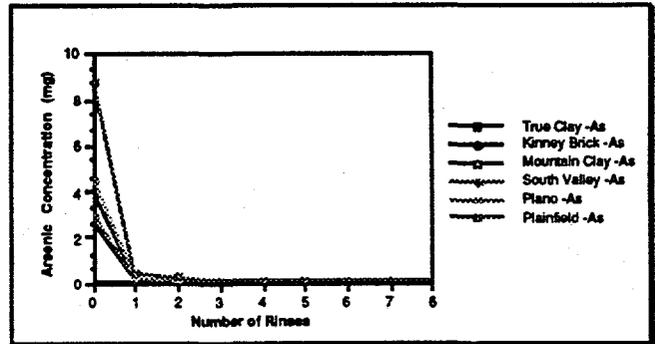


Figure 3. Arsenic Removal from Contaminated Soils

Conceptual design was performed based on two demonstration unit applications. One of these applications was treatment of approximately 5. kg/hr 50.% mineral oil/50.% polychlorinated biphenyl (PCB) waste contaminated with small amounts of solvents and plutonium. The second application was treatment of approximately 25. kg/hr tributyl phosphate (TBP) waste contaminated with small amounts of PCBs, mercury, uranium, and thorium.

Mass and energy balances were performed for the applications, and two conceptual demonstration units designed. Vessels, piping, pumps, condensers, and other major items of equipment were sized. Suitable materials of construction were identified. Sensors and controls were also identified to some extent. A schematic of one of the systems is shown in Figure 4.

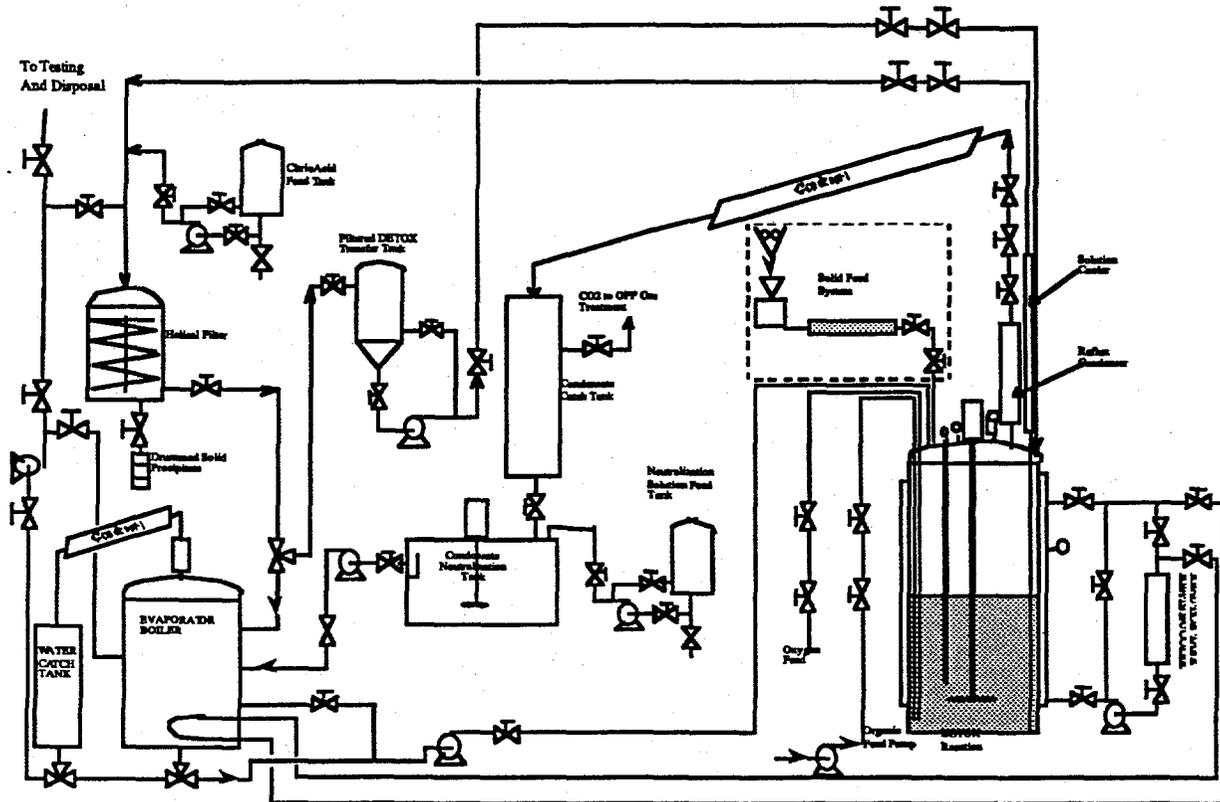


Figure 4. DETOXSM Simplified Equipment Schematic

The compositions and amounts of secondary waste streams from the demonstration units were calculated.

Destruction of 5. kg/hr oil/PCB waste would produce approximately 16.5 kg/hr carbon dioxide, approximately 11.3 kg/hr of a 20.% sodium chloride brine solution, and some amount of the iron oxide residue resulting from the catalyst solution at the conclusion of processing. The amount of iron oxide residue will depend on the level of radioactivity in the waste and the desired level of radioactivity in the residue, e.g., it may be desirable for disposal purposes to limit the amount of plutonium in the residue to <100. nCu/gm, such that the residue is not a TRU waste. There would be approximately 50. kg of iron oxide

produced from every batch of catalyst solution which is converted to oxide form.

Destruction of 25. kg/hr tributyl phosphate waste would produce approximately 49.6 kg/hr carbon dioxide, approximately 21.1 kg/hr water (some of which will be in the wet ferric phosphate solids produced in the process), approximately 14. kg/hr of ferric phosphate solids, and some amount of the iron oxide residue resulting from the catalyst solution at the conclusion of processing. For this unit there would be approximately 250. kg of iron oxide produced from every batch of catalyst solution which is converted to oxide form.

Critical engineering issues for the demonstration unit were determined to be suitable

materials of construction, quality fabrication, highly reliable components and controls, containment, reliability and service-ability, and cost.

Phase II

The site selection survey identified several appropriate sites for demonstration, the best rated of which were Savannah River Site's TNX facility and Weldon Spring Site Remedial Action Project (WSSRAP). A two part demonstration at these sites was proposed, with shakedown testing and cold testing at Savannah River Site, followed by transportation of the unit to WSSRAP and subsequent hot testing on wastes at that site.

Letters of support from both Savannah River Site and WSSRAP have been obtained, and Delphi has

received a preliminary communication from the Missouri Department of Natural Resources indicating that no air permit will be required for the unit. Since WSSRAP is a CERCLA site, no RCRA permit is required to treat wastes there.

Engineering design has been completed for a 25 kg/hr nominal capacity modular demonstration unit capable of feeding liquid and solid wastes. The unit is a modular design having one vertical module of approximately 8' x 8' x 30' dimension, and a horizontal module of approximately 8' x 10' x 25' dimension. The unit has both solids and liquids feeds, and a solid residues removal system which will allow it to be demonstrated on sludges and other materials with solids content or which produce solids when treated. Figure 5 shows an isometric illustration of the demonstration unit.

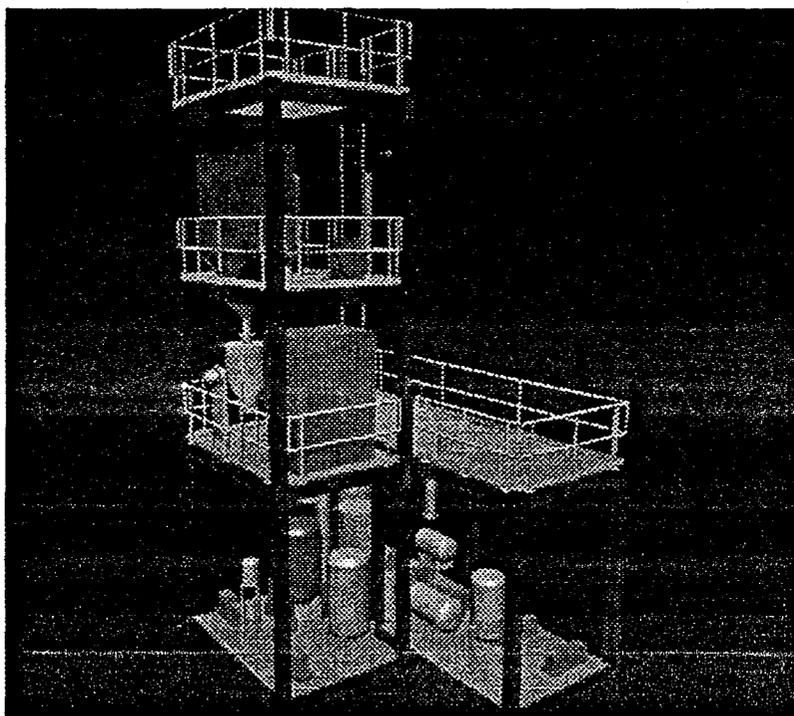


Figure 5. Isometric Illustration of the DETOXSM Demonstration Unit

FUTURE WORK

Phase III is the planned Title III engineering, fabrication, assembly, and shakedown testing of the demonstration unit. The unit will be installed at Savannah River Site's TNX facility, and tested for functionality using mineral oil, tributyl phosphate, and organic solids composed of personal protective equipment (PPE). These tests will establish the suitability of the unit for treatment of hazardous and mixed wastes. This Phase is scheduled to begin 12/94 and be complete 1/95.

Phase IV is the planned demonstration of the unit on hazardous and mixed wastes. The unit will first be used to treat an assortment of hazardous wastes including oils contaminated with toxic metals, non-halogenated solvents, halogenated solvents, and, if available, some contaminated PPE. Following these tests, the unit will be cleaned, inspected, serviced, and moved to WSSRAP, where it will be installed, checked out, and used to treat a variety of mixed waste types including contaminated ethylene glycol, contaminated oils and solvents, paints and paint sludges, PCB wastes, and tributyl phosphate contaminated with PCBs, uranium, thorium, and mercury. A commercialization assessment will be conducted which will include conceptual design of a baseline commercial process unit and sensitivity analysis for factors affecting performance and cost. Following the demonstration, a determination will be made as to the disposition of the unit and its possible future use at WSSRAP or other sites.