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2.1 Development Studies of a Novel Wet Oxidation Process

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Needs

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. Incineration and similar combustive processes do not appear to be viable options for treatment of these waste streams due to various considerations. There is a need for non-combustion processes with a wide application range to treat the large majority of these waste forms. The non-combustion process should also be safe, effective, cost-competitive, permit-able, and preferrably mobile.

Objectives

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-combustion 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.

Approach

Although the DETOX℠ process had been investigated to a limited extent for application to mixed wastes, there was not sufficient data or experience with the process to determine its full range of application to multicomponent waste forms such as DOE site wastes and remediates.

First, the potential applications of the process needed to be better identified. Following identification of potential applications, the process needed to be demonstrated on waste and remediate types on a practical scale in order that data could be obtained on application range, equipment size, capital and operating costs, effectiveness, safety, reliability, permit-ability, and potential commercial applications of the process. The basic approach for the project was, therfore, to identify the potential range of applications of the process, and then to demonstrate the process on mixed wastes. The effort for the Phases of the project is as follows:

Phase I

The approach for the Phase I effort was to determine the possible range of applications for the DETOX℠ process and to develop a conceptual design for a demonstration unit.

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Phase II

The approach for the Phase II effort was 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 approach for the Phase III effort is to prepare a Demonstration Test Plan, fabricate and assemble a demonstration unit, install the demonstration unit at Savannah River Site's TNX facility, and perform shakedown tests to verify that the unit operates properly.

Phase IV

The approach for the Phase IV effort will be to cold test the demonstration unit at Savannah River Site and hot test the demonstration unit at Weldon Spring Site Remedial Action Project.

Project Description

Technology

The DETOX^{SM} 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.

Project Effort

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.

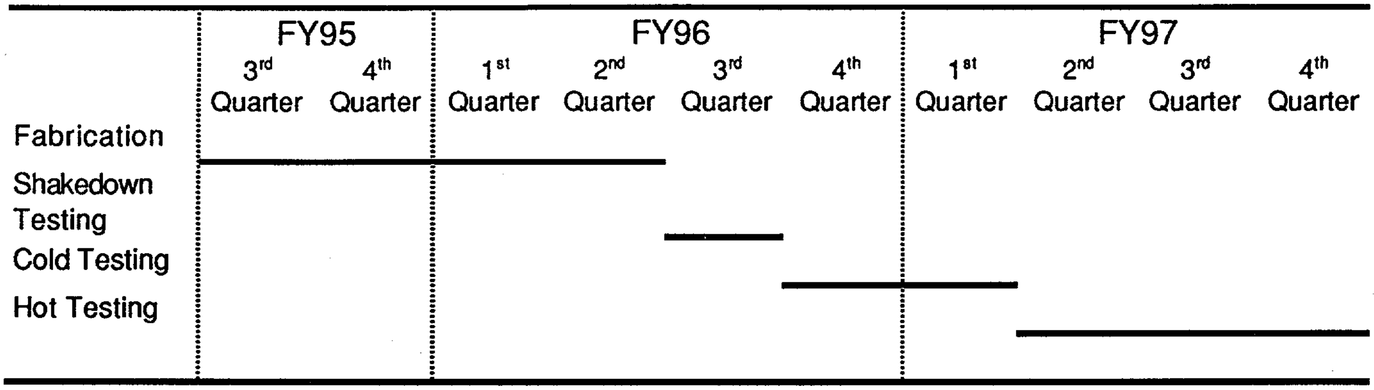

Figure 1: Schedule and Milestone
FY95-FY97 Program Schedule

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.

Phase III. Phase III, now ongoing, is preparation of a Demonstration Test Plan (DTP), and fabrication and shakedown testing of the demonstration unit with mineral oil and tributyl phosphate.

Phase IV. Phase IV will be demonstration of the process on a variety of hazardous materials at SRS and on a variety of low-level mixed wastes at WSSRAP.

Results

Phase I

The DETOX^{SM} process was found to be capable of destroying organic compounds with good efficiency, solvating many toxic metals, and removing organic compounds and toxic metals from soils. The results of Phase I have been presented at the 1994 METC meeting.

Phase II

Sites selected for demonstration were Savannah River Site and Weldon Spring Site Remedial Action Project. A Title II design for the demonstration unit was completed. The results of Phase II have been presented at the1994 METC meeting.

Phase III

Demonstration Test Plan. A DTP has been completed following guidance supplied by METC, and has been approved by the Primary Stakeholders in the demonstration effort.

One of the primary goals of the DTP is to establish lists of stakeholders in the demonstration effort. The stakeholders were divided into three categories.

Primary stakeholders were those parties who are directly involved in the demonstration, and included Delphi, JAT, METC, EM-50, SRS, and WSSRAP. RFETS has been added to the list of Primary Stakeholders due to their great involvement in development and potential use of

DETOX^{SM}. Approval of the DTP by the Primary Stakeholders is required.

Secondary Stakeholders in the demonstration are those parties which have a direct interest in the demonstration, those being representatives for EM-30, EM-40, EM-50, and EM-60, demonstration site representatives, the MIxed Waste Focus Area, as well as the EPA and regulatory agencies in pertainent regions and states. Secondary Stakeholders were asked for input to and comments on the DTP.

Extended Stakeholders are those parties which may represent potential users of the technology. Extended Stakeholders include other DOE sites, members of the Mixed Waste Focus Area, DOD waste offices, the Defense Nuclear Safety Board, the National Institute of Occupational Safety and Health, the Western Governer's Association DOIT Committee, the State of New Mexico, the California Water Resources Control Board, and other EPA Regions. The DTP gives the project plan, schedule, and the organization by which the project plan will be accomplished. The DTP is considered to be a living document, and refinements continue to be added with the Primary Stakeholders' approval.

Permit Process and NEPA Documentation. Permitting for the demonstration unit is being pursued for both the demonstration sites. A viable plan has been formulated for each site. Delphi has received a letter from EPA stating that the DETOX^{SM} process unit is considered to be a miscellaneous unit for the pruposes of permitting under RCRA.

After consultation with SRS environmental personnel and representatives of South Carolina Department of Health and Environmental Control, it was determined that the route to pursue for the demonstration at the TNX facility was to obtain a letter of approval from SCDHEC to operate the demonstration unit as a wastewater treatment unit under the clean water act. This approach required preparation of estimates of water effluent for the demonstration unit during the demonstration. The effluent from the demonstration unit will meet the requirements of NPDES after treatment in the TNX facility's Organics Removal Facility (ORF). Estimates of air emissions have also been submitted. The demonstration unit should not require an air permit. A determination has been made that the demonstration at SRS can be conducted under a NEPA Categorical Exclusion (CX). Delphi has supplied information to SRS and filled SRS's Environmental Evaluation Checklist to support the CX.

As WSSRAP is a CERCLA site, no formal permit is required for operating the demonstration unit. However, the substantive requirements of a RCRA Part B RD&D Permit must be met for the demonstration to proceed. Estimates of air emissions from the demonstration unit have been supplied to WSSRAP, and an air dispersion model performed for WSSRAP by Argonne National Laboratory. The results of the air dispersion model indicated that no air permit was required for the demonstration unit if the emission stack height was 16. feet or greater. Delphi is in the process of preparing information on the demonstration for meeting the substantive requirements of RCRA Part B. A determination has been made that the demonstration at WSSRAP can be conducted under a NEPA Categorical Exclusion (CX). No NEPA information is required from Delphi by WSSRAP.

Engineering Design. Final design engineering is being completed and equipment purchase has begun. Several changes have been made in the unit design to improve operation of the unit.

In order to reduce volatile organic compounds in the vent gases, a secondary reaction vessel has been added to the unit. The secondary reaction vessel contains a bubble tower of DETOX^{SM} solution through which product gases from the primary reaction vessel must pass. The height of the DETOX^{SM} solution in the bubble tower is designed to provide sufficient residence time to give four to five "nines" destruction of volatile organic organic compounds in the gases.

More accurate simulations of the demonstration unit overhead system identified a shortcoming of the Title II design. When non-chlorinated compounds are being oxidized in the system, it is desired to operate the reflux condenser at near 100. C to return the majority of HCl in the product gases to the primary reaction vessel. However, at this temperature not enough water could be carried through the reflux condenser with the anticipated product gas flow to remove product water from the DETOX^{SM} reaction vessel. Thus, more gas flow through the reflux condenser was necessary, which involved adding a gas recycle compressor to the system to return vent gas through the reflux condenser. This arrangement worked well in simulations, and by adjusting recirculated gas flow the amount of water removal can be closely controlled.

Consideration of solids rinsing determined that rinse volumes could be reduced significantly by reusing one of the acid rinses and eliminating the water rinses (since the solids would be treated by some stabilization process in any event). The main objective of rinsing is to return the large majority of the residual DETOX^{SM} solution in the solids to the primary reaction vessel, which the acid washes accomplish. Therefore, it was determined that the primary reaction vessel was sufficient to evaporate the water from the acid rinse, and that the evaporator, evaporator condenser, evaporator overhead receiver, and associated equipment could be eliminated from the design. This design change resulted in simplification of the demonstration unit and lowered capital costs.

Modified PFD, P&IDs, heat and material balances, and equipment data sheets were prepared, and the design changes were re-HAZOPed. Tantalum and titanium equipment pieces have now been ordered and detailed design is under way.

Operations and Safety Analysis. One operational concern which needed to be addressed was the identification of conditions where explosive mixtures could be formed in the headspace of the primary reaction vessel. Computer simulations of organics and oxygen in the DETOX^{SM} headspace gases, conducted by Sandia National Laboratories explosives group, had established that there were compositions which could be explosive. However, experiments on actual mixtures needed to be conducted. SNL's explosives group conducted these experiments in a test fixture supplied by Delphi. Mixtures of organic vapor, oxygen gas, and the steam content of a DETOX^{SM} reaction vessel headspace were sparked with an electrical discharge to ignite any flammable or explosive compositions. Organic compounds used were toluene, acetone, and hexane. Only one explosive event was experienced, and for all organics there was no flammability below oxygen concentrations of approximately 5.% by volume. The design parameter for oxygen in the vent gases from the demonstration is approximately 5.% by volume, which translates to less than 1.% by volume in the primary reaction vessel headspace. This leaves a margin for error or upset without generation of any flammable mixture. In addition, a nitrogen inlet line has been added to the primary reaction vessel so that it may be purged of oxygen if excessive levels start to develop.

The University of New Mexico's Chemical and Nuclear Engineering Department is conducting simulations of the demonstration unit to identify operating conditions for the unit and the response of the demonstration unit to potential upset conditions. These studies are on-going as of this report.

Personnel at Argonne National Laboratory are investigating the use of a chemically bonded phosphate ceramic waste form to stabilize the DETOX^{SM} solution residue. Samples of the ceramic have been prepared using simulants of the solution residue loaded with lead and mercury, and ferric phosphate solids which will be produced from tributyl phosphate treatment. The samples show good physical strength and are non-hazardous for lead by the standard EPA Toxicity Characteristic Leaching Procedure. Phosphate ceramic also has very low leach rates for the radionuclide simulants cesium and cerium.

Personnel at SRS are conducting a Process Hazards Review (PHR) to determine the safety requirements for the demonstration. Delphi and JAT have supplied SRS with documentation on the demonstration unit, the demonstration project, and permitting to support the PHR. The PHR is on-going as of this paper.

Benefits

The DETOX^{SM} process is a viable alternative to incineration and similar high temperature or combustive-type processes for the treatment of organic mixed wastes.

Because the process is conducted at relatively low temperatures and pressures, its emissions are more easily controlled than many other thermal treatment processes. This gives advantage not just in operations, but in permitting.

The DETOX^{SM} process can destroy a wide variety of organic materials, making it versatile in application. The DETOX^{SM} solution's ability to solvate toxic and radioactive metals allows seperation of these metals from inert materials in a waste stream. Although some small amount of radioactive material will almost always remain in the inert portion, it will no longer be a mixed waste, and if the input waste was TRU the inerts will in many instances be sufficiently low in radioactivity to be low-level waste only. Careful monitoring of the DETOX^{SM} solution when processing TRU waste can also assure that the process solution residue is also low-level only.

Estimated costs for waste treatment using the process range from \$2.50/kg to \$25.00/kg, depending on the size of the unit and the amount of waste processed. Estimated cost of waste treatment with the 25. kg (dry weight, organics) demonstration unit is \$9.40/kg (dry weight, organic). Process units can be mobile for on-site treatement of wastes.

Future Activities

The demonstration 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.

Phase IV is the planned demonstration of the unit on hazardous and mixed wastes . Phase IV demonstration at SRS will use hazardous organic wastes only, to evaluate the performance of the demonstration unit in a non-radioactive setting. The unit will treat an assortment of hazardous wastes including oils contaminated with toxic metals, non-halogenated solvents, halogenated solvents, and contaminated solids. After the hazardous waste experimental campaign, the unit will be cleaned, inspected, serviced, and transported to WSSRAP. This will demonstrate transportability of the unit. At WSSRAP, the unit will be installed, checked out, and used to treat a variety of low level mixed wastes 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 performed during the demonstration, 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.

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