EMSP
Environmental Management Science Program
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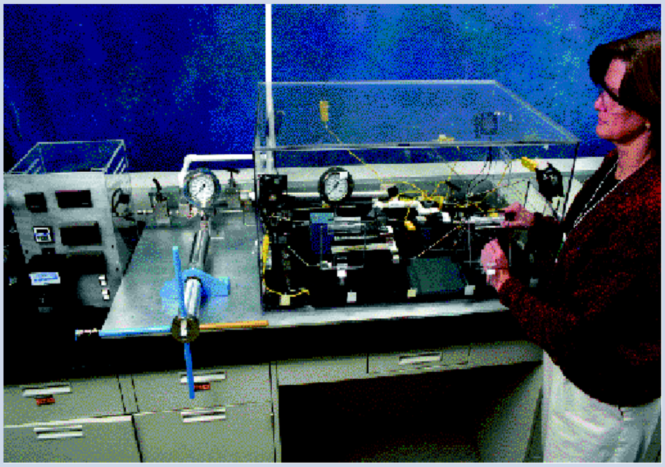
MIXED WASTE – ALTERNATIVES TO INCINERATION

ALTERNATIVE OXIDATION METHODS ARE NEEDED FOR ORGANIC MATERIALS THAT MAY PRODUCE HAZARDOUS EMISSIONS DURING INCINERATION

The Mixed Waste Focus Area has identified needs for alternate oxidation methods for treating organically contaminated wastes such as chlorinated solvents, radionuclide-contaminated filters, debris with volatile metals or radionuclides, and internal surfaces of pumps and other equipment. Perhaps as much as 5,400 cubic meters of oxidizable mixed waste materials could be considered as unsuited for incineration. Several alternatives, including peroxydisulfate oxidations, have already been investigated, so EMSP projects have focused on the basic science of several less well-developed alternatives:

- Above the critical temperature a gas cannot be liquefied by increasing the pressure, and supercritical fluids at high pressures can act as powerful solvents or separating agents. The solvent power can be adjusted by changing the temperature and pressure or by adding co-solvents. Three projects have investigated properties of supercritical water as a medium for oxidations. One has focused on acid-base behavior and transport phenomena, another on some basic thermodynamic properties of water-carbon dioxide-nitrogen systems, and a third has worked on development of electrochemical monitoring devices that are usable in supercritical water.
- The mechanism by which ultrasonic irradiation causes decomposition of organic compounds has been explored by one project in order to optimize this technique for liquid waste remediation.
- Reactions of metal oxides with chlorinated hydrocarbons have been shown to produce inorganic chlorides and carbon dioxide, which are the ideal decomposition products for those materials. Detailed studies of the mechanisms of these reactions may lead to improved practical applications.
- Another EMSP project has used some recently discovered properties of tiny semiconductor crystals to design potential catalysts for oxidative photochemistry.



Oxidations in Supercritical Fluids
A National Renewable Energy Laboratory project (54847) uses an experimental system to study photocatalytic oxidation of organic substances in supercritical carbon dioxide. Organic compounds are monitored by an online gas chromatograph or by UV-visible spectroscopy.

PROBLEMS/SOLUTIONS

- Supercritical carbon dioxide is an attractive solvent for removal of organic materials from metal surfaces, for example; however, the subsequent separation of the organics from carbon dioxide may prove to be difficult or expensive. An EMSP project has investigated a photochemical procedure to oxidize organics in supercritical carbon dioxide.
- The ideal products from the decomposition of chlorinated hydrocarbons, such as carbon tetrachloride, are carbon dioxide and inorganic chloride salts. An EMSP project has shown that these are the products of reactions on certain basic metal oxides, and a cyclic process for these reactions has been studied.
- Semiconductors such as molybdenum disulfide have many ideal properties for use as photocatalysts for oxidation of organic materials, but they absorb light in the near infrared region of the spectrum. An EMSP project has demonstrated that by making tiny crystals or nanoclusters of these materials they are usable with visible light.

ANTICIPATED IMPACT

- A technology to treat mixed waste containing chlorinated hydrocarbon solvents used in machining and degreasing operations is listed as a high-priority need at several U.S. Department of Energy (DOE) sites. Several EMSP projects are exploring methods to meet this need.
- Electrical equipment debris is frequently contaminated with polychlorinated biphenyl (PCB) compounds. Oxidations in supercritical fluids may prove to be useful for difficult remediation problems such as cleaning of equipment debris.
- According to Hanford needs statements, there is no available technology to destroy organic materials in certain remote-handled wastes. The Savannah River Site has cited needs to destroy organic constituents in high activity transuranic waste. Several of the EMSP investigations of alternative oxidation methods may lead to solutions for these needs.

Oxidations in Supercritical Fluids

Supercritical water oxidation is being explored as a method for treating mixed and high-level wastes. The University of Texas project (54506) has focused on acid-base behavior and transport phenomena in hydrothermal solutions above 350°C in order to understand corrosion, metal-ion complexation, and salt precipitation and recovery. They have completed a simulation study of ion transport in water under extreme conditions and have investigated hydrolysis reactions in supercritical water.

As mentioned, supercritical water has been explored as an oxidizing agent for organic compounds, resulting in needs for monitors that can operate in this harsh environment. The Pennsylvania State University/INEEL project (55171) is developing a flow-through electrochemical cell for use in supercritical water, with the goal of being able to make reliable pH measurements and to monitor corrosion processes on metals exposed to supercritical water.

The ORNL/University of Tennessee group (55276) has also investigated fundamental chemistry and thermodynamics of hydrothermal oxidation processes. They have measured some basic thermodynamic properties of water-carbon dioxide-nitrogen systems, and they have used molecular-level simulations to develop a predictive level of understanding of the chemical and physical properties of hydrothermal oxidation processes. They have also measured the solubility and speciation of uranium oxide and related carbonates in aqueous solutions at elevated temperatures, finding that the solubility of UO_3 in a carbonate buffer decreased with increasing temperature due to the conversion of UO_3 to a polymeric species under these conditions.

PROJECT TEAMS

LEAD PRINCIPAL INVESTIGATOR (AWARD NUMBER)

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Supercritical carbon dioxide, $scCO_2$, has been widely studied as a solvent for extractions such as the removal of hazardous organic solvents from metal parts. The National Renewable Energy Laboratory group (54847) has investigated a method to oxidize the organic compounds while they are in $scCO_2$. The only reagents are oxygen in $scCO_2$, photocatalyst titanium dioxide supported on glass spheres, and ultraviolet light. The group's work showed that the concentration of several organic compounds could be reduced from 2,000 parts per million to below detection limits while maintaining CO_2 as a supercritical fluid. Thus, they have shown that it is possible to purify this benign solvent using photochemical oxidation with no chemical additives other than oxygen.

Other Methods for Remediation of Organic Compounds in Mixed Waste

When a liquid is subjected to ultrasonic irradiation, very high temperatures and pressures are achieved inside of small bubbles formed in the liquid. Thus, ultrasonic irradiation can be used to decompose organic compounds in mixed waste liquids without the dangers associated with bulk heating. The University of Washington project (54897) has focused on a study of the fundamentals of acoustic cavitation and bubble dynamics. They have used the emission of near infrared light from the microscopic bubbles to probe the environments inside the bubbles as well as to excite emission that is useful for analytical purposes. They have found that sudden jumps in the pressure above an irradiated liquid results in a temporary large increase in luminescence, so they explored this result as a possible means to optimize acoustical parameters for liquid-waste-contaminant remediation.

Alternatives to incineration are particularly of interest for chlorinated hydrocarbons because of the possibility of forming hazardous products during combustion. A Texas A&M group (55115) has investigated the reactivity of chlorinated hydrocarbons on metal oxides to form inorganic chlorides and carbon dioxide. They have identified some of the reaction intermediates, and they have studied the reactions of various metal oxides. They found that barium oxide could be used in a cyclic process for carbon tetrachloride decomposition and that alkali metal oxides, such as sodium oxide, also have superior reactivities. The chemistry on the surfaces of these compounds has also been explored.

Many potential semiconductor catalysts that are stable when photoexcited in aqueous solutions are not chemically stable, while stable materials like molybdenum sulfide, MoS_2, have absorption at energies that are too low. However, the SNL/Colorado State project (55387) has shown that if tiny crystallites or nanoclusters are prepared, then the absorption edge can be shifted into the visible, so the electron-hole pair induced in the semiconductor may have sufficient energy for redox reactions. They found that it was possible to oxidize phenol in water with visible light using MoS_2 nanocrystals supported on titania. Although the species reduced in these studies would probably not be satisfactory for use in a practical application, several alternatives have been suggested.

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