

# Electrochemical Treatment of Liquid Wastes

Presenter: Dave Hobbs, Westinghouse Savannah River Company

EM Focus Areas: mixed-waste characterization, treatment, and disposal; high-level waste tank remediation

radionuclides (e.g.,  $^{99}\text{Tc}$  and  $^{106}\text{Ru}$ ); and Resource Conservation and Recovery Act (RCRA) metals (e.g., chromium, cadmium, and mercury).

## Task Description

Electrochemical treatment processes are being evaluated and developed for the destruction of organic compounds and nitrates/nitrites and the removal of other hazardous species from liquid wastes stored throughout the DOE complex. This activity consists of five major tasks: 1) evaluation of different electrochemical reactors for the destruction and removal of hazardous waste components, 2) development and validation of engineering process models, 3) radioactive laboratory-scale tests, 4) demonstration of the technology in an engineering-scale size reactor, and 5) analysis and evaluation of testing data. The development program team is comprised of individuals from federal, academic, and private industry. Work is being carried out in DOE, academic, and private industrial laboratories.

Possible benefits of this technology include 1) improved radionuclide separation as a result of the removal of organic complexants; 2) reducing the concentrations of hazardous and radioactive species in the waste; 3) reducing the size of the offgas handling equipment for vitrifying low-level wastes by reducing the source of  $\text{NO}_x$  emissions; 4) recovering chemicals of value; and 5) reducing the volume of waste requiring disposal.

## Technology Needs

This technology is being developed to destroy and/or remove the following species present in Hanford and Savannah River high-level, low-level, and mixed wastes: nitrates, nitrites, and organic compounds;

## Technology Description

In an electrochemical reaction, charge is transferred at the interface between an electrode and reactive species in a conductive liquid. An electrochemical reactor consists of an anode, a cathode, a conducting electrolyte, and power supply. At the cathode, charge is passed into the reacting species resulting in a reduction in the oxidation state. At the anode, charge is passed from the reactive species into the electrode resulting in an increase in the oxidation state. The change in oxidation state changes the chemical properties and form of the reacting species. The reduced or oxidized species can form a deposit on the electrode or desorb from the electrode surface and dissolve in the electrolyte.

Depending on the characteristics, the modified species may no longer be a hazardous substance or may be easily separated from the liquid phase (e.g., gas or solid). For example, previous work has shown that nitrate and nitrite are reduced to a mixture of molecular nitrogen, ammonia, and nitrous oxide at the cathode of electrochemical cell. These product gases can be easily separated from the waste solution. Testing has also shown that organic compounds (e.g., ethylenediaminetetraacetic acid, citrate, acetate, formate; and oxalate) can be oxidized to carbon dioxide and water at the anode.

## Benefits

A significant quantity of waste at Hanford contains complexing agents that prevent the efficient separation of radionuclides. Electrochemical destruction of

these organic compounds would enable efficient radiochemical separation processes to be carried out in subsequent processing operations. The destruction of organic compounds in both Hanford and Savannah River waste also reduces risks associated with waste storage and evaporation.

Nitrate and nitrite are two of the major hazardous species present in Hanford and Savannah River HLW. After removing the bulk of radioactivity, the decontaminated salt solution will be disposed of in a cement waste form referred to as Saltstone at the Savannah River site and in a borosilicate glass waste form at Hanford. Destruction of the nitrate and nitrite before disposing of the decontaminated salt solution in Saltstone eliminates the possible groundwater contamination from leaching of nitrate and nitrite from the waste form. Destruction of nitrate and nitrite before vitrification at Hanford would significantly reduce the size of the offgas system by eliminating the formation of  $\text{NO}_x$  gases in the melter.

In the electrochemical destruction of sodium nitrate and nitrite, sodium hydroxide is the major liquid phase product of the process. If the sodium hydroxide could be recovered and recycled significant reduction in the quantity of waste requiring disposal would be realized. Onsite use of the recovered sodium hydroxide would include neutralization of fresh waste and as a corrosion inhibitor in the waste storage and evaporation facilities. Thus, the quantity of sodium hydroxide that would be available for recovery and recycle would be increased by converting the sodium nitrate and nitrite into sodium hydroxide.

Modern electrochemical reactor designs make it relatively simple to scale the treatment facility to the size of the waste stream by the addition of modular reactor units. Aqueous electrochemical processes operate at low temperature ( $<90^\circ\text{C}$ ) and near atmospheric pressure in contrast to high temperature and pressure processes also being evaluated for the destruction of

organic compounds and nitrates. The electrochemical reactions can be shut down instantaneously by shutting off the power to the electrochemical reactor. No additional chemicals are added in the process; therefore, minimal or no secondary wastes are generated.

Electrochemical removal of radionuclides and RCRA metals from the wastes would also be beneficial. For example, removal of  $^{99}\text{Tc}$  from the Savannah River decontaminated salt solution would eliminate the possible release of this mobile, long-lived radionuclide from Saltstone. Removal of RCRA metals from a waste stream would allow a mixed waste to be delisted or eliminate the possible leaching of these species from low-level wastes forms into groundwater.

## Technology Transfer

Electrochemical processes are used to produce a variety of industrial chemicals and treat waste streams and waters before disposal and release to the environment. Thus, there is an extensive database for the design and scale-up of electrochemical processes. Electrochemical reactors developed by private industry are currently being evaluated in this testing activity.

Alternate reactor designs are also being evaluated. Development of these alternate reactor designs will be carried out in collaboration with private industry through Cooperative Research and Development Agreements or licensing agreements. In addition to the specific waste components that are being evaluated, the technology developed in this program should also be of value in the development of electrochemical treatment processes for nonradioactive, hazardous wastes such as those from the chemical, plating, pulp and paper, and electronics industries.

## Accomplishments and FY 1996 Activities

The following items have been accomplished in this technology development effort:

- demonstrated the destruction of nitrate and nitrite in actual Savannah River waste in a laboratory-scale flow reactor
- demonstrated the destruction of organic compounds and nitrates/nitrites in Hanford and Savannah River waste simulants in a full-scale electrochemical reactor
- conducted tests in laboratory-scale flow reactors to determine the effects of key operating parameters on the destruction of organic compounds and nitrates/nitrites in Hanford and Savannah River waste simulants
- developed and validated engineering models for the electrochemical destruction of nitrate, nitrite and organic compounds in a parallel-plate reactor
- conducted evaluations of alternate reactor designs including: porous metal, packed-bed, fluidized-bed, and gas-diffusion electrodes for the destruction of nitrates, nitrites, and RCRA metals.

During FY 1996, the following activities will be carried out: 1) conduct preliminary engineering

design and cost evaluations for treating the Hanford complexant waste and the Savannah River decontaminated salt solution waste, 2) demonstrate nitrate/nitrite and organic compound destruction with radioactive Hanford waste, 3) conduct an independent review of nitrate and organic destruction technologies, and 4) complete installation of a pilot-scale testing facility at the Savannah River Technology Center.

## Keywords

Hanford, Savannah River, nitrate, nitrite, organics, radionuclides, RCRA metals, alkaline, destruction, removal

## For further information, please contact:

David Hobbs  
Principal Investigator  
Savannah River Technology Center  
P.O. Box 616  
Aiken, SC 29802  
(803) 725-2838, fax (803) 725-4704  
E-mail: david.hobbs@srs.gov  
TTP Number: SR16C341