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Electrochemical Treatment of Liquid Wastes

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Electrochemical Treatment of Liquid Wastes

Summary

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. The development program consists of five major tasks: (1) evaluation of 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 test data. The development program team is comprised of individuals from federal laboratories, academic institutions, and private industry. Possible benefits of this technology include: (1) improved radionuclide separation as a result of the removal of organic complexants, (2) reduction in the concentrations of hazardous and radioactive species in the waste (e.g., removal of nitrate, nitrite, mercury, chromium, cadmium, technetium-99, and ruthenium-106), (3) reduction in the size of the off-gas handling equipment for the vitrification of low-level wastes by reducing the source of NO_x emissions, (4) recovery of chemicals of value (e.g., sodium hydroxide), and (5) reduction in the volume of waste requiring disposal.

Target Problem

The following species present in Hanford and Savannah River high-level, low-level, and mixed wastes have been targeted for development of this technology: (1) destruction of nitrates, nitrites and organic compounds, (2) removal of radionuclides (e.g., technetium-99 and ruthenium-106), and (3) removal of RCRA metals (e.g., chromium, cadmium, and mercury).

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 liquid phase. Depending on the characteristics, the modified species may no longer be a hazardous substance or may easily separate from the liquid phase (e.g., gas or solid). For example, previous work showed that nitrate and nitrite 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 also demonstrated that organic compounds (e.g. ethylenediaminetetraacetic acid, citrate, acetate, formate, and oxalate) 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 also reduces flammability risks associated with the storage and evaporation of the waste.

Nitrate and nitrite are two of the major hazardous species present in Hanford and SR HLW. After removal of the bulk of radioactivity, the decontaminated salt solution will be disposed in a cement wasteform referred to as Saltstone at the SR site and in a borosilicate glass wasteform at Hanford. Destruction of the nitrate and nitrite prior to disposing the decontaminated salt solution in Saltstone eliminates the possible groundwater contamination from the leaching of nitrate and nitrite from the wasteform. Destruction of nitrate and nitrite prior to vitrification at Hanford would significantly reduce the size of the off-gas system by eliminating the formation of 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 available for recovery and recycle would increase 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 ($\leq$90 °C) and near atmospheric pressure in contrast to high temperature and pressure processes that are 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, and therefore there is minimal or no secondary wastes generated by the process.

Electrochemical removal of radionuclides and RCRA metals from the wastes would also be beneficial. For example, removal of technetium-99 from the SR 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 groundwaters.

Technology Transfer

Electrochemical processes are used for the production of a variety of industrial chemicals and for the treatment of waste streams and waters prior to disposal and release to the environment. Thus, there is a 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 occur in collaboration with private industry through CRADA's or licensing agreements. In addition to the specific waste components evaluated, the technology developed in this program should also prove of value in the development of electrochemical treatment processes for non-radioactive, hazardous wastes such as those from the chemical, plating, pulp and paper, and electronics industries.

Prior Years Accomplishments

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

(1) demonstrated the destruction of nitrate and nitrite in radioactive SR wastes with a bench-scale flow reactor (see Figures 1 and 2),

(2) demonstrated the destruction of organic compounds and nitrates/nitrites in radioactive Hanford wastes with a bench-scale flow reactor,

(3) demonstrated the destruction of organic compounds and nitrates/nitrites in Hanford and SR waste simulants with a commercial-scale electrochemical flow reactor,

(3) 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 SR waste simulants,

(4) developed and validated engineering models for the electrochemical destruction of nitrate, nitrite and organic compounds in a parallel-plate reactor,

(5) 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

(6) installed a pilot-scale testing facility at SRTC for non-radioactive simulant testing to support scale-up and design activities, and

(7) completed a preliminary conceptual design for an Electrochemical Denitration and Caustic Recovery (EDCR) facility for treating SRS decontaminated salt solution (see Figure 3).

FY97 Activities

During FY97, the following activities will occur: (1) complete cost evaluations for treating the SR Decontaminated Salt Solution waste, (2) determine if SRS High-Level Waste Division wishes to proceed with implementation of the technology , (3) resolve process control strategy and any problems with the evolution of ammonia/hydrogen, (4) review other work performed at LANL and LLNL, (5) conduct an independent review of nitrate destruction technologies, (6) determine feasibility of using porous electrode technology for chromate removal, and (7) determine feasibility of using electrochemical technology for the removal of technetium, other RCRA metals and actinides from waste solutions.

Participants

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Electosynthesis Company, Inc.

Keywords

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

Figure 1. Change in the Total Moles of Nitrate and Nitrite in Radioactive Savannah River Site Waste with Charge Passed
(batch test - undivided bench-scale electrochemical reactor with different cathode/anode combinations)

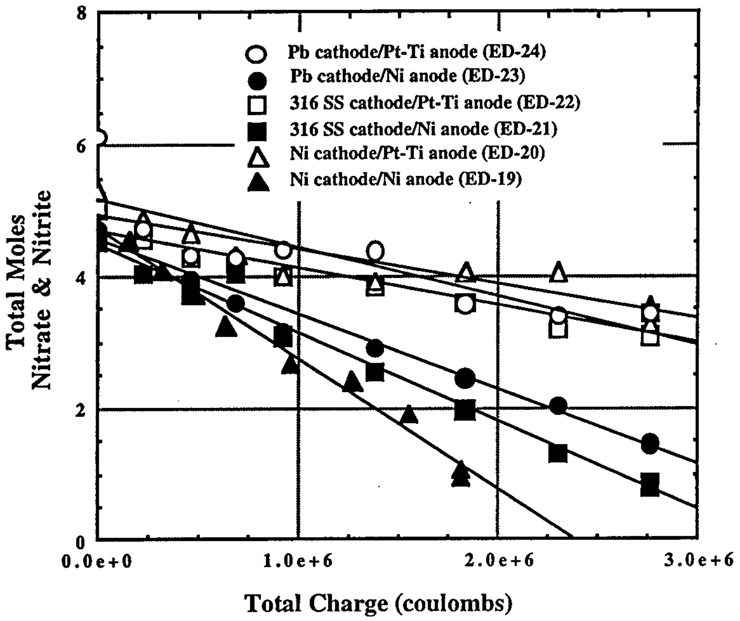


Figure 2. Change in the Total Moles of Nitrate and Nitrite in Radioactive Savannah River Site Waste with Charge Passed (batch test - divided bench-scale electrochemical reactor with different cathode/anode combinations)

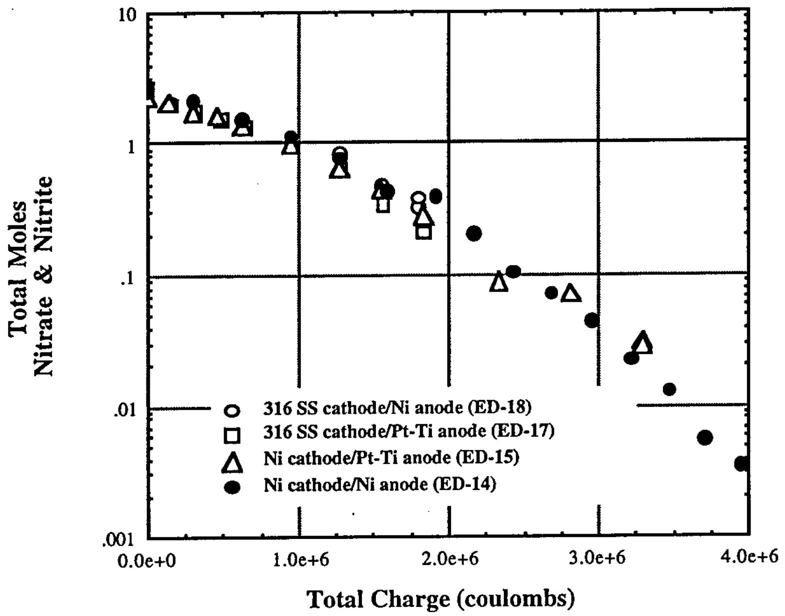
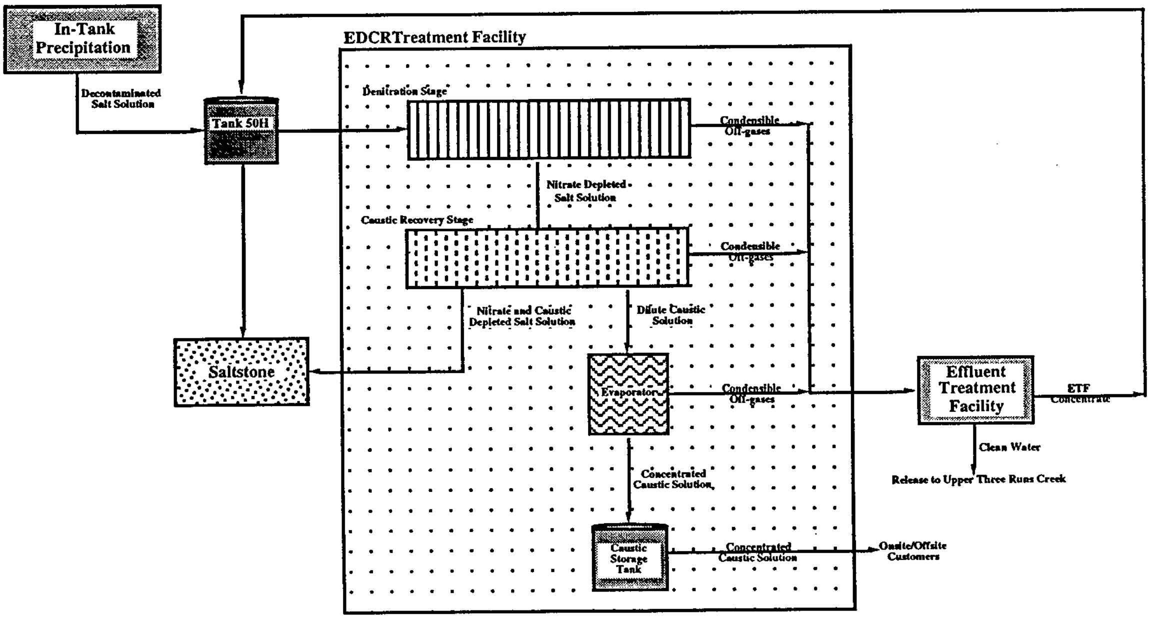


Figure 3. Schematic Flow Diagram for the Electrochemical Denitration and Caustic Recovery Facility at SRS for Treating Decontaminated Salt Solution



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