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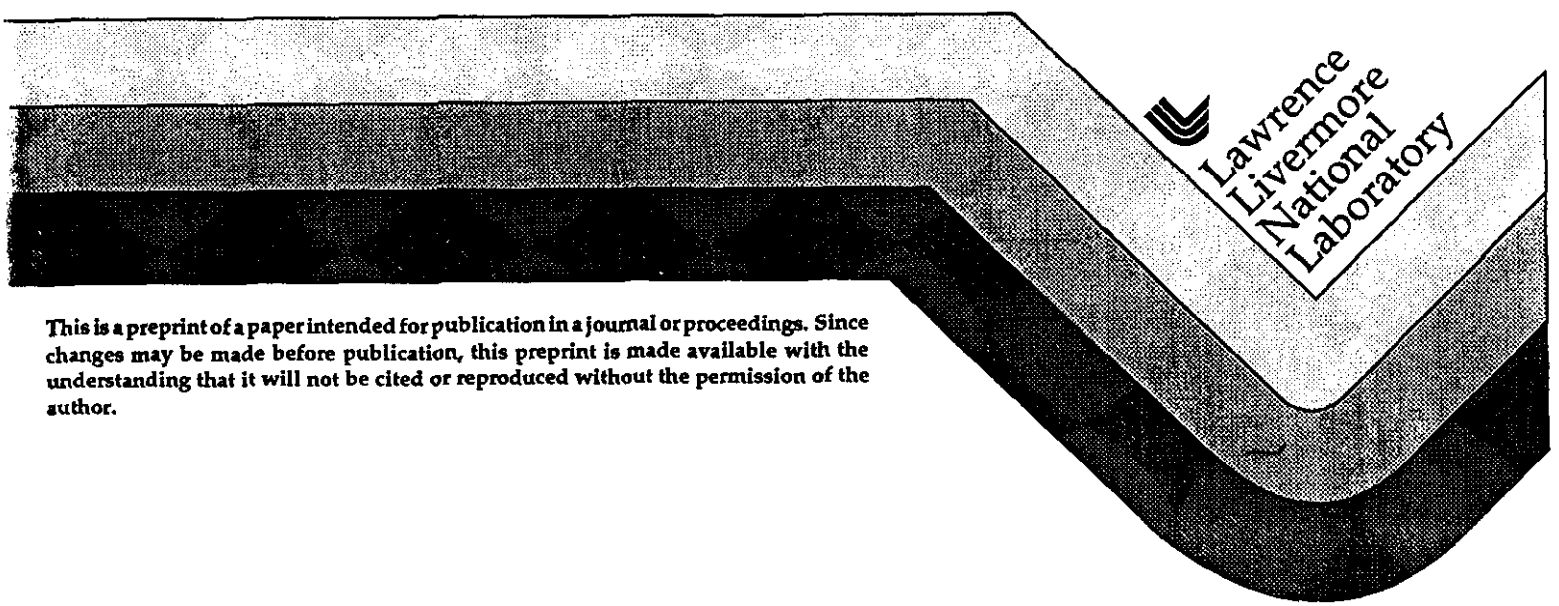

MEDIATED ELECTROCHEMICAL OXIDATION OF ROCKY FLATS COMBUSTIBLE LOW LEVEL MIXED WASTES*

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Introduction

Mediated Electrochemical Oxidation (MEO) was originally developed for dissolution of difficult to dissolve forms of plutonium oxide. It was also found to be effective for oxidizing non-polymerized organic materials. Extensive development work on this technology has been done at PNL and at LLNL, in the United Kingdom, and in France.[1-4] MEO is an inherently safe process since the hazardous and radioactive materials are completely contained in the aqueous phase, and operating temperatures and pressures of the system are low (well below 100 °C and 30 psig).

The most commonly used mediator-electrolyte combination is silver in nitric acid. The process produces divalent silver ion, a strong oxidizing agent, which dissolves the radioactive components of mixed wastes and destroys the organic components. Other mediator-electrolyte combinations, such as cobalt in sulfuric acid, and iron and cerium in various acids have also been investigated.

In the past, work at LLNL has been focused on understanding the basic science and modeling the dissolution and destruction mechanisms. To this end the reaction rates of water with Ag(II) were measured using spectrophotometric methods, and the diffusivity of silver ions in nitric acid was estimated using a rotating disk electrode.[5] The breakdown of organics, such as ethylene glycol, was modeled in detail with the formation and eventual destruction of intermediate compounds.[6-8] Dissolution of plutonium oxide was also modeled and system studies were conducted to optimize system operating parameters.[9,10] Also a full scale system was built for plutonium oxide dissolution and tested with surrogate materials.[11]

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Part of last year's effort was directed towards studying the destruction of combustible Rocky Flats mixed wastes, specifically, wastes containing Trimsol and cellulosic material. Although a major part of the work involved small-scale laboratory apparatus, it was important to demonstrate destruction on large industrial-scale equipment so results could be confidently extrapolated to plant-sized operations. Also, since Trimsol contains chlorinated organics, and silver is precipitated by chlorides, it necessitates an addjtional recovery step. Hence, an alternate mediator, cobalt, was tested. Cobalt also has the advantage that it may be possible to use it in undivided cells, and its removal from sulfuric acid has been demonstrated at UCLA down to 2 ppm levels. Therefore, cobalt was also used for testing the destruction of cellulosic materials.

Objectives

The primary objective of this work was to evaluate the Mediated Electrochemical Oxidation (MEO) process as an alternative to incineration of certain low level waste oils (cutting oils) and cellulose. The experimental work was pursued on small laboratory-scale apparatus and also on a large-scale system equipped with an industrial cell. Enough experimental data was gathered so that destruction and coulombic efficiencies could be determined for the process.

Experimental Work and Results

Tests were performed with non-radioactive surrogate materials: Trimsol for the contaminated oils, and reagent grade cellulose for the cellulosic wastes. Extensive testing was carried out on Trimsol in both small laboratory-scale apparatus and on a large-scale system incorporating an industrial-sized electrochemical cell. Preliminary tests were also carried out in the small-scale system with cellulose. Operating and system parameters that were studied were: use of a silver-nitric acid versus a cobalt-sulfuric acid system, effect of electrolyte temperature, effect of acid concentration, effect of current density, and use of ultrasonic agitation. Destruction and coulombic efficiencies were calculated from data obtained from continuous carbon dioxide monitors and TOC analysis of electrolyte samples.

For Trimsol, it was found that the best performance was achieved with the silver-nitrate system at high acid concentrations, temperatures, and current densities. Destruction

efficiencies of 98 percent or greater, and coulombic efficiencies of 40 to 50 percent were obtained in both small and large scale systems. For the cellulose, high destruction efficiencies (97 percent or greater) and reasonable coulombic efficiencies (45 to 60 percent) were obtained for both silver-nitrate and cobalt-sulfate systems.

Conclusions

The MEO process is capable of achieving high destruction efficiencies and reasonable coulombic efficiencies for both Trimsol and cellulose. For Trimsol, the tests show that high currents, acid concentrations, and temperatures enhance the destruction efficiencies. The silver-nitric acid combination is preferred since it is a more powerful oxidizing system than cobalt in sulfuric acid. Also high shear rates appear to increase destruction rates. Since Trimsol is composed of many insoluble oils kept in emulsion by surfactants which break down in acids, there is a strong tendency for the oil to de-emulsify and separate out from the electrolyte. Hence, it is important to have a highly oxidizing, high-shear environment when Trimsol is fed into the electrolyte so the destruction processes have a chance to attack the large initial surface area available before the droplets start to coalesce. Cellulose on the other hand does not coalesce and appears to break down easily, thus allowing the use of less powerful oxidizing agents.

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