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MEDIATED ELECTROCHEMICAL OXIDATION OF MIXED WASTES

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ABSTRACT. The Mediated Electrochemical Oxidation (MEO) process was studied for destroying low-level combustible mixed wastes at Rocky Flats Plant. Tests were performed with non-radioactive surrogate materials: Trimsol for contaminated cutting oils, and reagent-grade cellulose for contaminated cellulosic wastes. Extensive testing was carried out on Trimsol in both small laboratory-scale apparatus and on a large-scale system incorporating an industrial-size 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, and effect of current density. Destruction and coulombic efficiencies were calculated using data obtained from continuous carbon dioxide monitors and total organic carbon (TOC) analysis of electrolyte samples. For Trimsol, the best performance was achieved with the silver-nitrate system at high acid concentrations, temperatures, and current densities. Destruction efficiencies of 99% or greater, and coulombic efficiencies up to 70% were obtained. For the cellulose, high destruction efficiencies and reasonable coulombic efficiencies were obtained for both silver-nitrate and cobalt-sulfate systems.

INTRODUCTION

Mediated Electrochemical Oxidation (MEO) was originally developed for dissolution of difficult-to-dissolve forms of plutonium oxide, but later was 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 (e.g., cobalt in sulfuric acid, and iron and cerium in various acids) have also been investigated.

In the past, work at LLNL has 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).

Recently, the effort has been directed toward 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, an additional recovery step is needed. 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.

EXPERIMENTAL WORK

The experimental work on organic destruction was conducted in two phases. In the first phase, small laboratory-scale experiments that were carried out where it was relatively easy to vary system temperature, acid concentration, and mediator-electrolyte combination. The experiments were conducted with Trimsol as a surrogate for the low-level mixed waste oils at RFP. Preliminary testing of cellulosic wastes was also carried out using reagent-grade cellulose. In all small-scale experiments, a measured amount of organic material was introduced into the anolyte prior to turning on the cell. That is, the test was run in a batch feed mode. In the second phase, organic destruction was demonstrated in a bench-scale system using a commercially available industrial-size cell. Experiments were performed on this system with Trimsol at different acid concentrations and temperatures. In these experiments, the organic was fed and metered continuously to the anolyte during the run. The experiments are described in more detail below.

Small-Scale Experiments with Trimsol

Small-scale experiments were performed in H-shaped cells which could be fitted with an ion-selective membrane separating the two cell compartments. In most of the experiments conducted for organic destruction, the cell was placed in a closed container and the gas within was continuously sampled for carbon dioxide using a Horiba Model 2000 Infrared Gas Analyzer. With this technique, it is possible to determine the instantaneous generation rate of carbon dioxide, which is the desired end-product in the oxidation of organic carbon. A schematic of the setup is shown in Figure 1. Details of the container and the H-cell are shown in Figure 2. One compartment of the cell was fitted with a rotating platinum cylinder for the anode, while the other contained a platinum strip for the cathode. At the end of the experiments, samples of the catholyte and anolyte were removed and sent for TOC analysis.

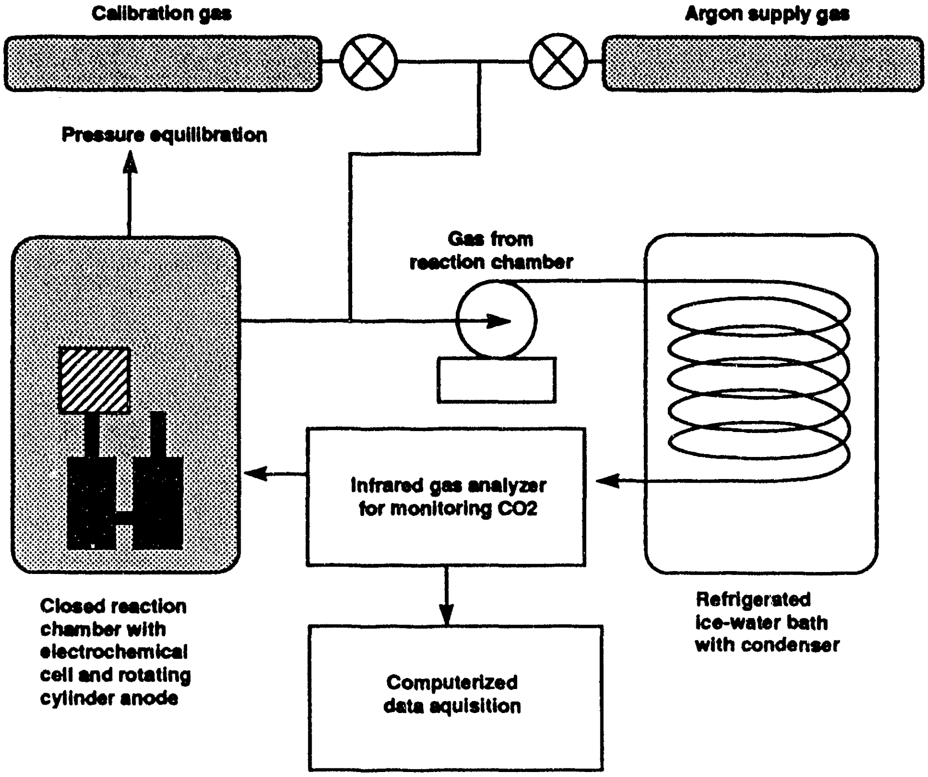

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Figure 1. Schematic of small-scale apparatus in closed container with carbon dioxide monitor.

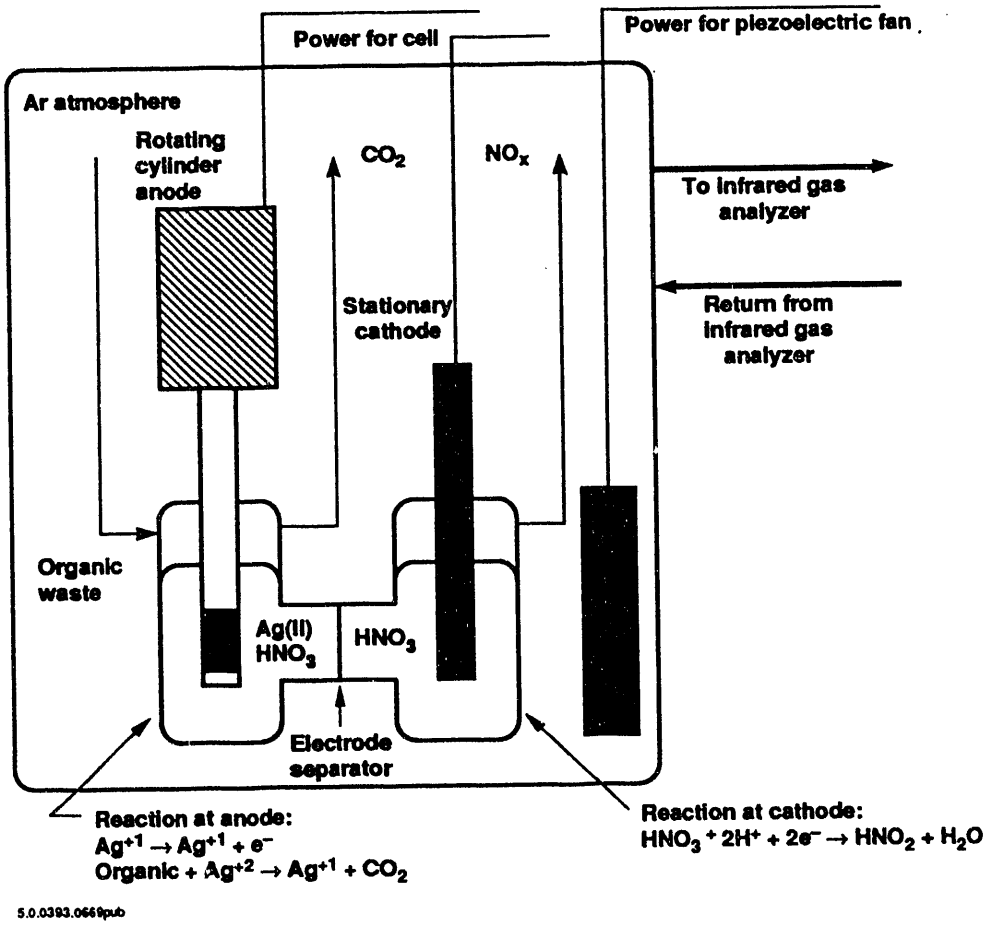

Figure 2. Schematic of closed container and H-cell

Experiments with Trimsol, using the continuous carbon dioxide monitor, were performed at different conditions to determine the effect of various system and operational parameters. The parameters studied and their ranges were as follows:

mediator-acid combination	silver-nitric acid and cobalt-sulfuric acid
acid concentration	4 to 10 M for nitric acid; 1.67 to 6 M for sulfuric acid
cell current	673 to 1020 mA
electrolyte temperature	20 to 70° C

Small-Scale Experiments with Cellulose

Experiments in a small H-cell were conducted with reagent-grade cellulose, using the continuous carbon dioxide monitoring system described above. The parameters studied here were the mediator-acid combination, acid concentration, and electrolyte temperature. The range of parameters was similar to that listed above for Trimsol.

Large-Scale Experiments with Trimsol

The large-scale system was built with a commercially available industrial electrochemical cell, called the FM-21, built by Imperial Chemical Industries (ICI). The cell has a plate-and-frame design, with expanded metal electrodes and turbulence promoters installed on the anodes. The electrodes are made of niobium with the anodes coated with platinum. The cell stack presently has two anodes and three cathodes, with a capacity to expand to accommodate several more electrode pairs. The anode and cathode compartments are divided by cation-selective membranes (Nafion 117). The present system has the capacity of delivering up to 3000 A of limiting current to the mediator.

A schematic of the flow system is shown in Figure 3. Included in the figure are auxiliary carbon dioxide monitoring, gas scrubbing and acid regeneration systems, which have not yet been installed and are part of a future upgrade. In the experiments with Trimsol, the oil was continuously fed to the anolyte just downstream of the reservoir. Samples were taken periodically from the anolyte throughout the runs, and from the catholyte at the end of the runs, for post-test TOC analysis. Experiments were conducted only with the silver-nitric acid system. The experimental parameters studied were acid concentration (4 to 10 M) and electrolyte temperature (25 to 70° C).

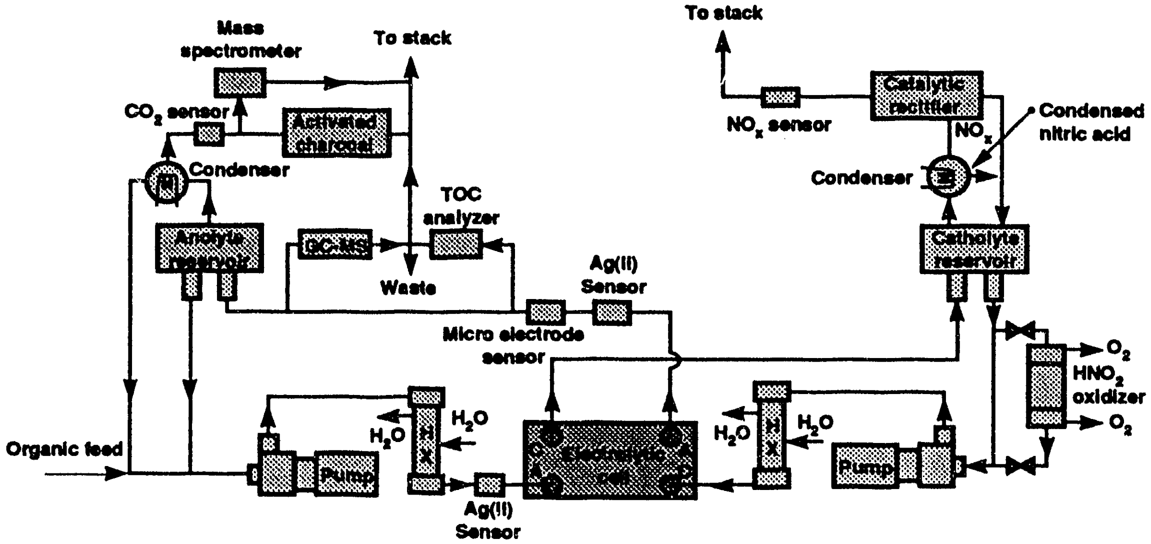

Figure 3. Schematic of the large-scale MEO system.

RESULTS AND DISCUSSION

The results of the Trimsol and cellulose destruction experiments are discussed separately below.

Trimsol Results

Trimsol is a mixture of various heavy oils, chlorinated hydrocarbons and other organics. A pseudo-chemical formula for Trimsol, neglecting the small amounts of sulfur and nitrogen present, is $C_{5.69}H_{10.71}O_{0.47}Cl_{0.31}$, where it is understood that the subscripts refer to moles of each element per 100 g of Trimsol. The number of Ag(II) ions required to completely destroy 100 g of Trimsol is then given by

$$\begin{aligned} &C_{5.69}H_{10.71}O_{0.47}Cl_{0.31} + 10.91H_2O + 32.22Ag^{++} \\ &\quad \longrightarrow 32.22Ag^{+} + 32.53H^{+} + 5.69CO_2 + 0.31Cl^{-} \qquad (1) \end{aligned}$$

Hence, 5.69 moles of carbon dioxide are generated and 32.22 moles of electrons must be removed at the anode when 100 g of Trimsol are completely oxidized. The corresponding water generation occurs in the cathode compartment. Note that the chlorine ions will combine with Ag(I) to precipitate out as insoluble silver chloride from the solution.

In the small-scale experiments with Trimsol, where carbon dioxide evolution is continuously measured, it is possible from Equation (1) to determine the destruction efficiency with time from the percentage of organic carbon converted to carbon dioxide. The coulombic efficiency can also be determined by comparing the amount of charge delivered up to the time of complete destruction with the amount theoretically required from Equation (1). The final destruction efficiency can also be determined from TOC analysis of the post-test samples.

The results from the small-scale tests showed that coulombic and destruction efficiencies increased as the mediator-acid combination was changed from cobalt-sulfuric acid to silver-nitric acid, and as the current increased. The efficiencies increased dramatically when the concentration of nitric acid is increased. For all runs at the higher concentration of nitric acid, irrespective of temperature, the destruction efficiencies were high—in the 98–99+ range. The coulombic efficiency, however, showed a marked dependence on temperature, increasing from about 20% at 20°C up to 70% at 70°C.

The results from the large-scale system, in general, were similar to those from the small scale-system. At low acid concentrations (4 M) and low temperatures (25° C) a build up of waxy material was observed floating at the top of the anolyte reservoir. The various oils in Trimsol are kept emulsified by surfactants, which are immediately attacked by the acid. The oil droplets then begin to coalesce and the reduced available surface area slows down further attack by the mediator. However, the problem of separation did not appear at higher acid concentrations and higher temperatures. A reason for this may be that higher oxidation rates, corresponding to higher temperatures and acid concentrations, result in the destruction of oil droplets before they have a chance to coalesce. At the highest acid concentrations (10 M) and temperatures (70° C) tested, destruction efficiencies of over 99% and coulombic efficiencies of 70% were achieved. Higher coulombic efficiencies are possible but at the expense of a decrease in destruction efficiency.

It should be noted that for both the small rotating anode and the large expanded metal electrodes, the limiting current was calculated, and the cell current in these experiments was always maintained well below the limiting current. Hence, coulombic inefficiencies are due to slow reaction kinetics (especially slow surface kinetics for insoluble organic components) and parasitic parallel bulk reactions, rather than inefficiencies resulting from oxidation of water at the anode.

Cellulose Results

Cellulose is a straight-chain carbohydrate with a chemical formula $(C_6H_{10}O_5)_x$. The repeating unit, $C_6H_{10}O_5$, has a molecular weight of 162 g/mole, and the amount of Ag(II) required to completely oxidize it is given by

$$C_6H_{10}O_5 + 7H_2O + 24Ag^{++} \longrightarrow 24Ag^+ + 24H^+ + 6CO_2 \qquad (2)$$

Hence, the complete destruction of 162 g of cellulose will require 24 moles of Ag(II), which will be generated by 24 moles of electrons removed from the anode. During this process, six moles of carbon dioxide will be released.

In the small-scale experiments with cellulose, the carbon dioxide evolution was continuously measured. From Equation (2), the instantaneous destruction efficiency can be calculated from the percentage of organic carbon converted to carbon dioxide. The coulombic efficiency can be calculated by comparing the theoretical charge required, to produce the carbon dioxide generated, to the actual charge delivered. The results showed that coulombic efficiencies up to 80% and destruction efficiencies close to 100% can be obtained with both cobalt-sulfuric acid and silver-nitric acid systems at higher acid concentrations and electrolyte temperatures of 50° C and above.

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. Since Trimsol is composed of many insoluble oils kept in emulsion by surfactants, which break down in acids, the oil has a strong tendency to coagulate and separate out from the electrolyte. Hence, it is important to have a highly oxidizing 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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