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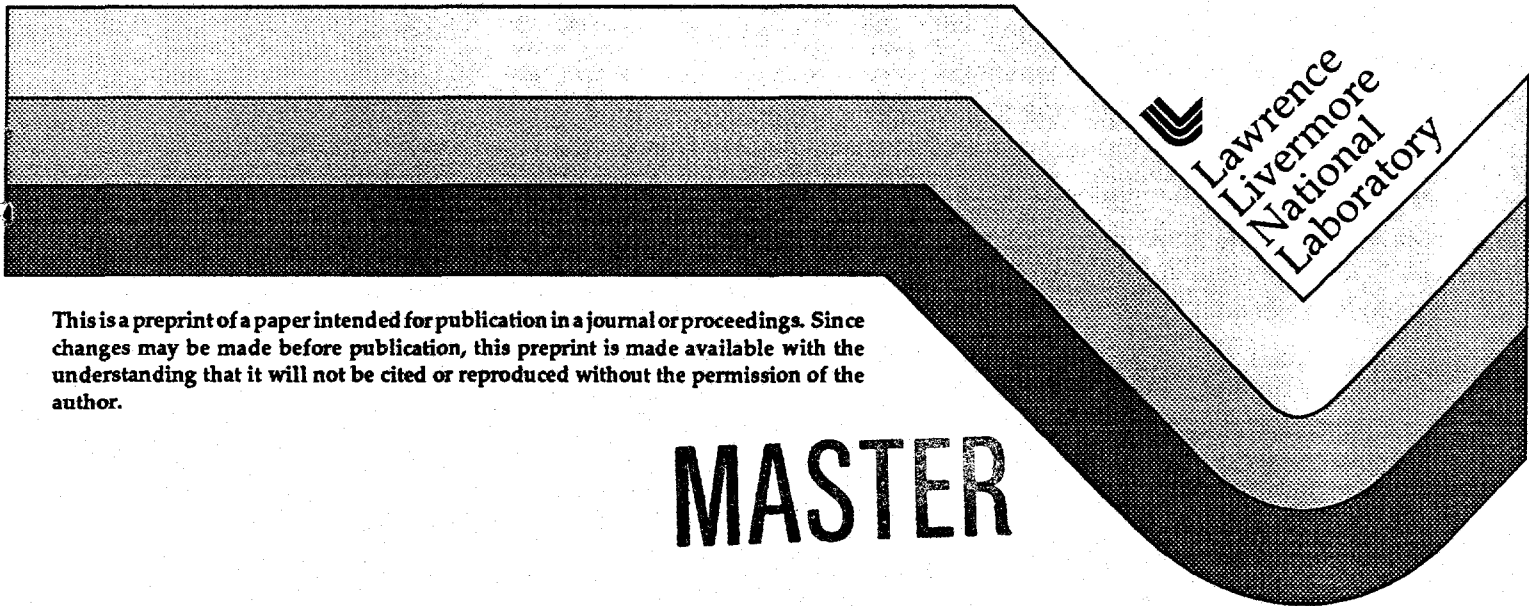
UCRL-JC-119133
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This paper was prepared for presentation to the
WM95 Symposia
Tucson, AZ, March 1, 1995

February 1995



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Mediated Electrochemical Oxidation as an Alternative to Incineration for Mixed Wastes

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Abstract

Mediated Electrochemical Oxidation (MEO) is an aqueous process which oxidizes organics electrochemically at low temperatures and ambient pressures. The process can be used to treat mixed wastes containing hazardous organics by destroying the organic components of the wastes. The radioactive components of the wastes are dissolved in the electrolyte where they can be recovered if desired, or immobilized for disposal.

The process of destroying organics is accomplished via a mediator, which is in the form of metallic ions in solution. The ions, initially at their lower valence state, are oxidized to a higher valence state at the anode surface. The oxidized ions in turn destroy organics throughout the bulk of the fluid. This results in a very efficient process, since the system can be optimized to oxidize the mediator at the anode, while the organics are dispersed at low concentrations throughout the anolyte. At Lawrence Livermore National Laboratory (LLNL) we have worked with several mediators, including silver, cobalt and cerium. We have tested mediators in nitric as well as sulfuric acids.

We have recently completed extensive experimental studies on cobalt-sulfuric acid and silver-nitric acid systems for destroying the major organic components of Rocky Flats Plant combustible mixed wastes. The study was conducted on small-scale laboratory equipment and on a bench-scale facility that incorporated an industrial-sized electrochemical reactor. Organics tested were: Trimsol (a cutting oil), cellulose (including paper and cloth), rubber (latex), plastics (Tyvek, polyethylene and polyvinyl chloride) and biomass (bacteria). The process was capable of destroying almost all of the organics tested, attaining high destruction efficiencies at reasonable coulombic efficiencies. The only exception was polyvinyl chloride, which was destroyed very slowly resulting in poor coulombic efficiencies.

Besides the process development work mentioned above, we are working on the design of a pilot-plant scale integrated system to be installed in the Mixed Waste Management Facility (MWMF) at LLNL. In addition to the electrochemical process, this system will comprise the requisite secondary processes to replenish the reagents for continuous operation. These include processes for electrolyte regeneration and mediator recovery. The system will also be completely integrated with upstream and downstream processes (for example, feed preparation, off-gas and water treatment, and final forms encapsulation). The conceptual design for the MEO-MWMF system has been completed and preliminary design work has been initiated. Demonstration of the process with low-level mixed wastes is expected to commence in 1998.

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Introduction

Mediated Electrochemical Oxidation (MEO) is an aqueous process which destroys hazardous organics by oxidizing a mediator at the anode of an electrochemical cell; the mediator in turn oxidizes the organics within the bulk of the electrolyte. With this process organics can be nearly completely destroyed, that is, the carbon and hydrogen present in the hydrocarbon are almost entirely mineralized to carbon dioxide and water. The MEO process is also capable of dissolving radioactive materials, including difficult-to-dissolve compounds such as transuranic oxides. Hence, this process can treat mixed wastes, by destroying the hazardous organic components of the waste, and dissolving the radioactive components. The radioactive material can be recovered if desired, or disposed of as non-mixed radioactive waste. The process is inherently safe, since the hazardous and radioactive materials are completely contained in the aqueous phase, and the system operates at low temperatures (below 80 °C) and at ambient pressures.

Mediated Electrochemical Oxidation was originally developed for dissolution of difficult-to-dissolve forms of transuranic oxides, but later was found to be effective for oxidizing many organic materials. Extensive development work on this technology has been carried out at PNL and at LLNL, in the United Kingdom, and in France.¹⁻⁴ At LLNL, work in the past was concentrated 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 Other mediators studied were cobalt, iron and cerium. Mediators were tested in nitric and sulfuric acids. 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 transuranic oxides was also modeled and system studies were conducted to optimize system operating parameters.^{9,10} Also, a full-scale system was built for transuranic oxides dissolution and tested with surrogate materials.¹¹

More recently work at LLNL has focused on the destruction of the organic components of major low-level mixed wastes streams at the Rocky Flats Plant.^{12,13} The work comprised the destruction of Trimsol, a cutting oil; various cellulosic substances, including wipes and cloth; biomass; and rubber (latex) and plastics (Tyvek, polyethylene and polyvinyl chloride). The emphasis of the work was on process development, that is, the determination of optimal process conditions for destruction of each organic. The parameters which can be controlled in the MEO process are system temperature, strength of the electrolyte, type of mediator and electrolyte, and current density at the electrodes. The destruction rates of various organics and the destruction and coulombic efficiencies were measured as a function of the process parameters which were varied in each experiment.

The destruction efficiency in this work refers to the *total* destruction of the organics, that is, the degree of complete mineralization of the carbon in the organics to carbon dioxide. Hence, it is a more stringent measure of destruction than the commonly used Destruction & Removal Efficiency (DRE). The DRE measures the destruction or removal of the original organics only, regardless of whether they are merely transformed into other organics, or are completely destroyed.

The coulombic efficiency refers to the theoretical amount of electric charge needed to destroy the organics versus the actual amount required. Usually the coulombic efficiency

will be less than 100 percent since the total destruction of the organic requires a number of steps, some of which may be limited by homogeneous or heterogeneous (surface) kinetics. In such cases, so-called parasitic reactions of the mediator with the water in the electrolyte will consume some of the current. However, it should be noted that if the decrease in coulombic efficiency is due to operation of a cell above its limiting current, oxygen will be generated at the anode. This will not only waste current but will also require higher cell voltages. The combined effect of both will result in much higher power consumption. At LLNL great care has been taken to operate the cells at or below their limiting current. The limiting current is the maximum amount of useful current at the anode which is utilized to convert the mediating ions from their lower to their higher valence states. It depends upon the anode area and geometry, the mediator concentration, the mechanics of flow, and electrolyte properties that govern diffusion of the mediator to the electrode surface.

Process Chemistry

The chemical reactions given here are for a process based on silver as mediator and nitric acid as electrolyte. In addition to the electrochemical process, the secondary processes to regenerate the reagents and remove secondary wastes are discussed.

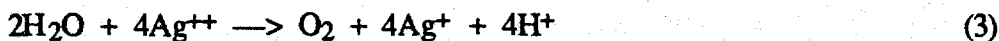
Starting with the reactions in the electrochemical reactor, silver in the form of Ag(I) is oxidized to Ag(II) at the anode:



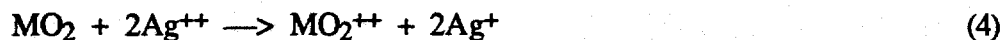
The redox potential for this reaction is 1.98 V with respect to a standard hydrogen electrode. The high potential allows the Ag(II) to attack organics, eventually converting the organic carbon to carbon dioxide. For example, for cellulose:



The Ag(I)/Ag(II) redox potential is high enough to break down water molecules. Although this is a competing reaction which consumes Ag(II) ions, it may not be entirely parasitic since OH radicals may be formed as intermediate products. The complete reaction is written down as:

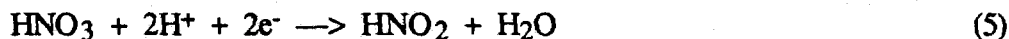


Ag(II) is very reactive and will dissolve many radioactive compounds which are otherwise very hard to dissolve. For example, many transuranic oxides are notoriously difficult to dissolve completely even in strong solutions of nitric and hydrofluoric acids. However, Ag(II) very efficiently dissolves the oxides converting them to ionic form:



For the silver-nitric acid system, the fluids on the anode and cathode sides of the electrochemical cells must be kept separate, since nitrous acid which is produced at the cathode reduces Ag(II). The silver is introduced only at the electrolyte on the anode side (anolyte), and the electrolyte on the cathode side (catholyte) is separated by means of a porous divider or an ion selective membrane. The reactions shown above are those that occur at the anode or in the anolyte.

The hydrogen ions formed in the reactions above migrate through the divider to the cathode. There the nitric acid is reduced to nitrous acid. Hydrogen gas is not formed at the cathode unless the concentration of nitric acid there is low (below 2 M).



This reaction indicates the secondary processes required to support the primary electrochemical process. First, the nitrous acid generated must be converted back to nitric acid. Otherwise the nitrous acid will eventually decompose to form NO_x :



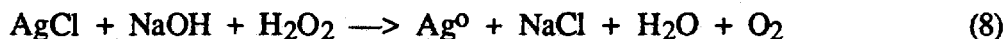
Contacting the nitrous acid with oxygen regenerates the nitric acid, and prevents the formation of NO_x :



However, since oxygen is only very sparingly soluble in the solution, typical contactors in the form of packed bed columns would have to be very tall to attain reasonable conversion efficiencies. A turbo-aerator was developed at LLNL which achieves very high efficiencies in a small volume.¹⁴ The turbo-aerator draws the gas and the fluid together, and passes them through a row of stator blades which disperses the gas into very small bubbles. The intimate mixing and the high surface area contribute to measured efficiencies of 95 to 99 %. The contactor is installed in the catholyte flow loop.

In addition to the nitrous acid, reaction (5) shows that water is generated on the cathode side. Although water is broken down on the anode side as shown in reactions (2) and (3), there is a net accumulation of water in the system when hydrocarbons are destroyed. Essentially, all the hydrogen present in the organic molecule is converted to water, which must be removed from the system. This is done using an evaporator in conjunction with a fractionation column. The electrolyte is passed through the evaporator and a small amount is evaporated off, enough to remove the extraneous water. The concentrated electrolyte is returned to the cells. The vapor from the evaporator contains both water and nitric acid, which are separated in the fractionation column. The column can be designed to produce water which is directly sewerable, while the acid is reused.

Besides the secondary systems to convert the nitrous acid and remove the water, a system is required for silver recovery. When chlorinated organics are destroyed in the anolyte, chloride ions are formed which immediately combine with silver ions to form insoluble silver chloride. The silver chloride precipitate is removed from the electrolyte by settling or centrifuging. It is then introduced into a hot solution of sodium hydroxide and hydrogen peroxide. The silver chloride is reduced to silver:



The silver is filtered or centrifuged and dissolved in nitric acid for reuse. The chloride remaining in solution is in the form of salt (sodium chloride). It is dried and disposed of via polymer encapsulation.

Since silver chloride is almost insoluble, it affords a method for removal of silver from the electrolyte, when desired. For example, when the electrolyte becomes loaded with dissolved radionuclides and metals, they must be removed; but the silver in solution must be removed first for reuse. By adding chlorides into the electrolyte, the silver precipitates

out and is separated. Then the solution is boiled off until almost dry by passing it through the thin film evaporator. The evaporator bottoms are carried out, and if desired, the radionuclides can be recovered by ion exchange. If recovery is not desired or feasible, the radioactive material is disposed of via grouting or ceramicization.

Hence, the MEO primary (electrochemical) process requires secondary processes for the conversion of nitrous acid to nitric acid, recovery of silver, and regeneration of nitric acid by removal of water. A functional flowsheet showing the relation of these processes is shown in Figure 1. The flowsheet also shows the secondary waste generated and suggests further treatments that may be required before they are discharged or disposed. A conceptual design for the integrated MEO system based on this flowsheet has been completed for the Mixed Waste Management Facility (MWMF) at LLNL. Preliminary design for the system is currently underway.

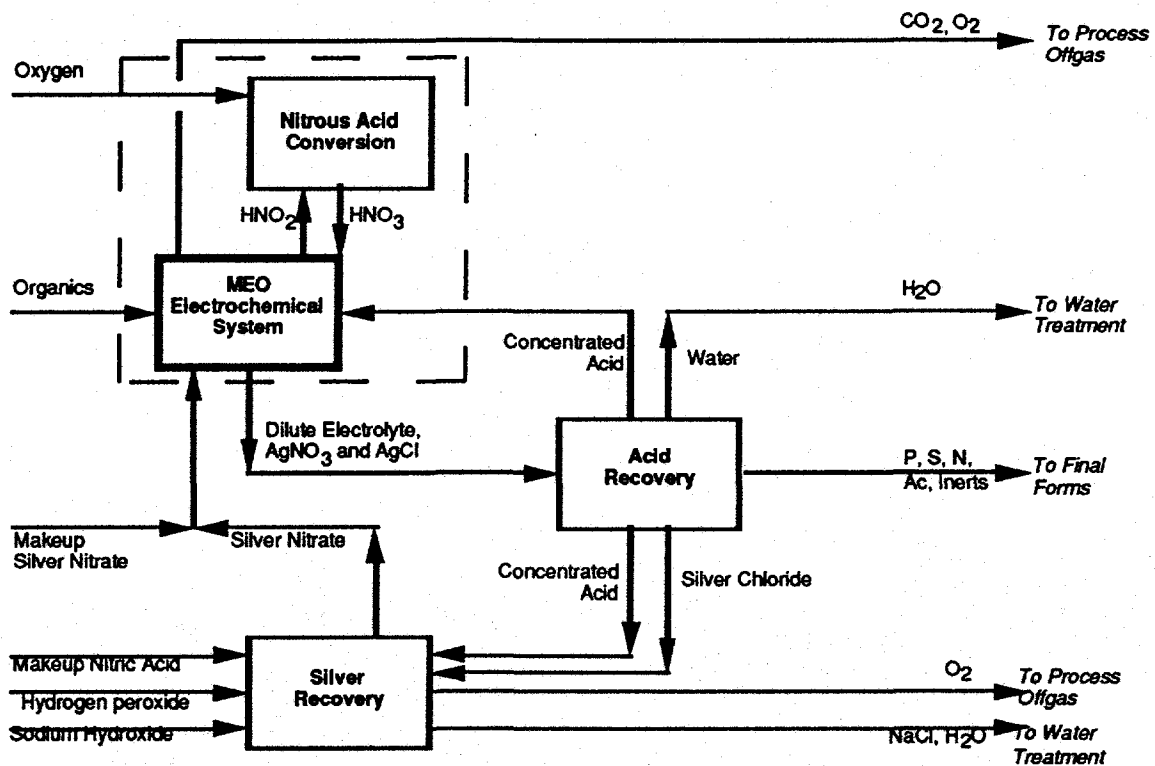


Figure 1. Flowsheet for Integrated Mediated Electrochemical Oxidation System

Experimental Work And Results

The experiments performed for electrochemical destruction of organics were of two types. A large number of small-scale experiments were performed where the process parameters could be easily varied. They were carried out in laboratory-sized H-cells with a capacity of destroying approximately 0.5 g of organics at a time in a batch mode. These experiments gave a preliminary assessment of the important process parameters and their influence on destruction rates. A smaller number of experiments were then carried out in a bench-scale facility containing an industrial-sized commercial electrochemical cell. This system was built with an Imperial Chemical Industries (ICI) FM-21 electrochemical reactor, which is widely employed in chlor-alkali chemical plants. The reactor presently

contains a cell stack composed of two anodes and three cathodes. It has a capacity of 3000 A of limiting current at mediator concentrations of 0.5 M, and can destroy up to 0.5 kg/h of organics in either continuous or batch modes of operation. The cell voltage drop at maximum current is below 2 V. The bench-scale experiments were conducted to demonstrate organics destruction on large industrial-scale equipment so results could be confidently extrapolated to plant-sized operations.

The parameters varied in the small-scale experiments were temperature, acid concentration and acid-mediator combination. Two types of acid-mediator combinations were tested: silver in nitric acid, and cobalt in sulfuric acid. The concentration of the nitric acid was varied from 4 to 10 M, and that of sulfuric from 4 to 6 M. The temperature of the electrolyte was varied between 20 and 70 C. The concentration of the mediator in all tests was 0.5 M. In general, the results indicated that higher temperatures, higher acid concentrations and a more aggressive acid-mediator combination (silver with nitric acid) resulted in higher destruction rates. An example of the influence of these parameters is shown in Figure 2 for destruction of cellulose. Here the initial destruction rate of cellulose is plotted as a function of temperature. Since the destruction rate is directly proportional to the limiting current in the cell it is normalized by the current. It is seen from Figure 2 that the destruction rate rises steeply with temperature, especially for the cobalt-sulfuric acid system. The silver-nitric acid system outperforms the cobalt-sulfuric acid system, although they tend to converge at higher temperatures and acid concentrations. The effect of acid concentration is not very strong for cellulose, but that is not the case with all organics.

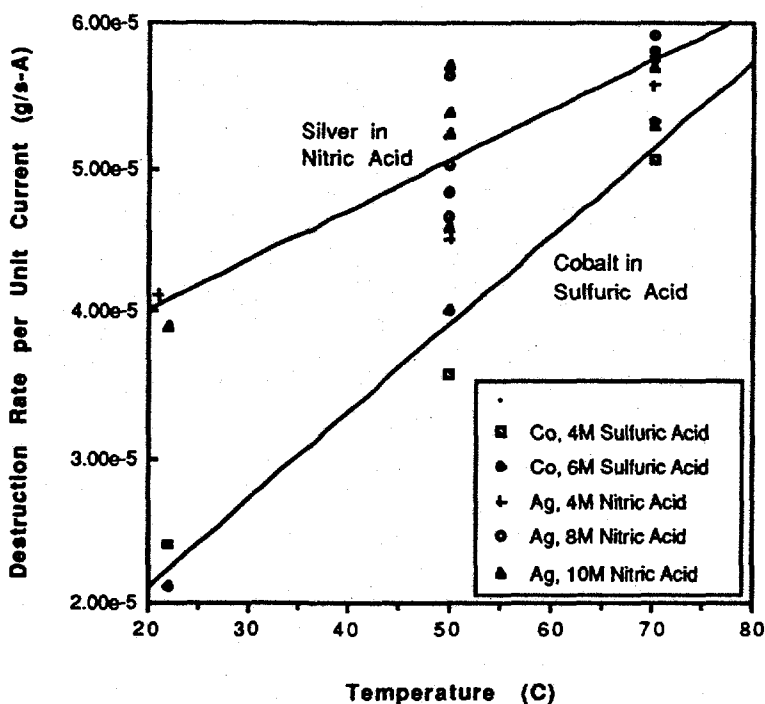


Figure 2. Cellulose Destruction in Small-Scale Experiments

Various organics of interest to Rocky Flats Plant were tested for destruction using the MEO process. These included different types of cellulosic substances (wipes and cloth), Trimsol (a cutting oil), rubber and plastics (latex, polyethylene, polyvinyl chloride and Tyvek), and biomass. A comparison of the destruction rates of the organics tested are shown in Table I. The results in the table are for the silver-nitric acid system at high acid concentrations (8-12 M) and high temperatures (70 C). It is seen that reasonable destruction rates were achieved for most organics tested except for polyvinyl chloride.

Table I. Destruction Rates of Various Organics

ORGANIC	DESTRUCTION RATE PER UNIT CURRENT (g/s-A)
Cellulose	5.5×10^{-5}
Trimsol	2.6×10^{-5}
Latex	2.7×10^{-5}
Tyvek	1.4×10^{-5}
Polyethylene	1.0×10^{-5}
Polyvinyl Chloride	4.2×10^{-6}
Biomass	4.6×10^{-5}

In addition to the destruction rates, the coulombic and destruction efficiencies of the process are of interest. In general, the destruction efficiency increases as more current is passed through the system, that is, with a decrease in coulombic efficiency. The results of the trade-off between destruction and coulombic efficiencies are shown in Figure 3 for Trimsol and Figure 4 for cellulose. These results are from experiments conducted in the bench-scale system with silver and nitric acid at acid concentrations of 8 M and temperatures of 70 C. It is seen in both cases that destruction efficiencies of 99 % or higher can be achieved at coulombic efficiencies of 70 %. To obtain destruction efficiencies of 99.99 % requires coulombic efficiencies in the range of 40 to 50 %.

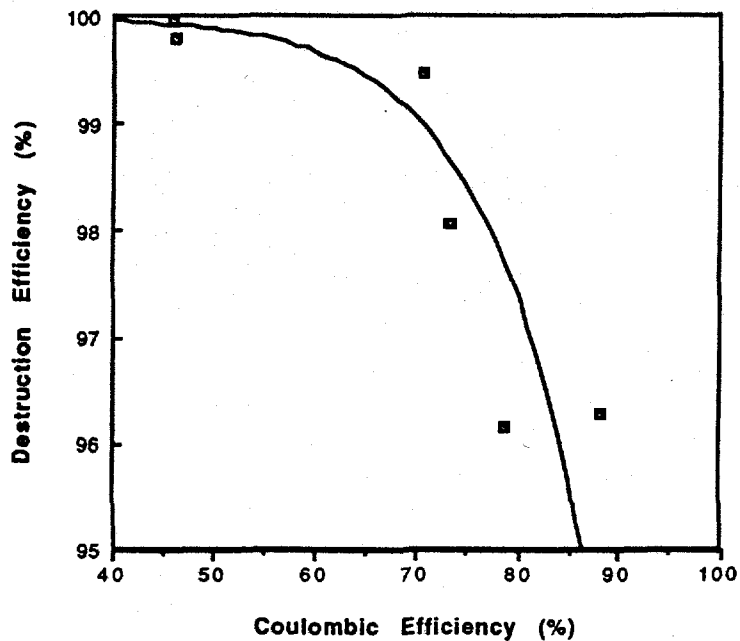


Figure 3. Destruction and Coulombic Efficiencies for Trimsol Destruction in Bench-Scale Experiments

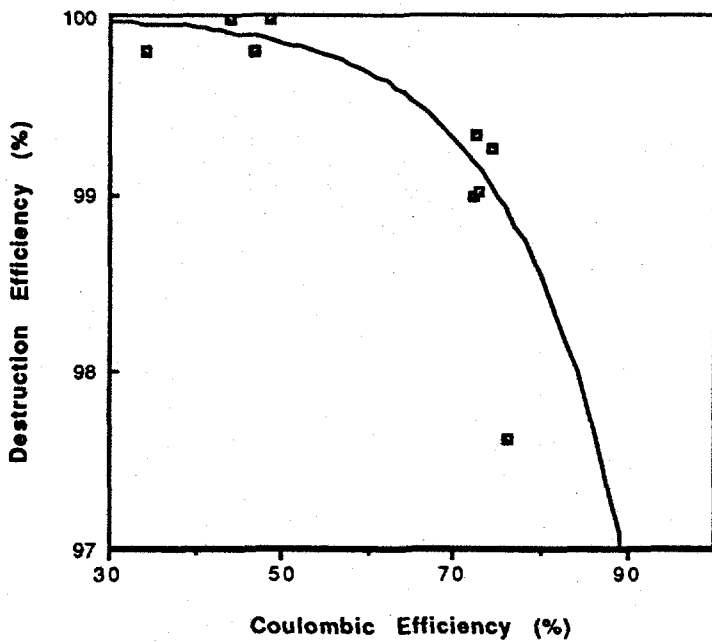


Figure 4. Destruction and Coulombic Efficiencies for Cellulose Destruction in Bench-Scale Experiments

Conclusions

The Mediated Electrochemical Oxidation (MEO) process is capable of destroying a wide variety of organics. Many such organics, contaminated with radioactive and RCRA-listed materials, are currently being stored at sites throughout the DOE Complex awaiting suitable means of disposal. MEO can be used as an alternative to incineration for treating these mixed wastes by destroying the organic components of the wastes. MEO mitigates some of the perceived problems with incineration, since it operates at low temperatures and pressures, and since the radioactive materials are contained in an aqueous media.

The primary electrochemical process requires a number of secondary processes to recycle the reagents. The secondary processes include removal of water and inorganics (including radionuclides) from the electrolyte, regeneration of the acid and mediator recovery. A conceptual design for the integrated process has been completed, and work has been initiated on the preliminary design to be installed in the Mixed Waste Management Facility (MWMF) at LLNL. MWMF is expected to demonstrate the treatment of low-level mixed wastes using the MEO process starting in 1998.

Acknowledgments

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. The work for treatment of Rocky Flats Plant wastes was sponsored by the Office of Technology Development (EM-50). The Mixed Waste Management Facility work is supported by the Office of Waste Management (EM-30).

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