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Destruction of Hazardous and Mixed Wastes using Mediated Electrochemical Oxidation in a Ag(II)/HNO₃ Bench Scale System

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ABSTRACT

Mediated Electrochemical Oxidation (MEO) is a promising technology for the destruction of organic containing wastes and the remediation of mixed wastes containing transuranic components. The combination of a powerful oxidant and an acid solution allows the conversion of nearly all organics, whether present in hazardous or in mixed waste, to carbon dioxide. Insoluble transuranics are dissolved in this process and may be recovered by separation and precipitation. The oxidant, or mediator, is a multivalent transition metal ion which is cleanly recycled in a number of charge transfer steps in an electrochemical cell.

The MEO technique offers several advantages which are inherent in the system. First, the oxidation/dissolution processes are accomplished at near ambient pressures and temperatures (30-70 °C). Second, all waste stream components and oxidation products (with the exception of evolved gases) are contained in an aqueous environment. This electrolyte acts as an accumulator for inorganics which were present in the original waste stream, and the large volume of electrolyte provides a thermal buffer for the energy released during oxidation of the organics. Third, the generation of secondary waste is minimal, as the process needs no additional reagents. Finally, the entire process can be shut down by simply turning off the power, affording a level of control unavailable in some other techniques.

Although the oxidation of organics and the dissolution of transuranics by higher valency metal ions has been known for some time, applying the MEO technology to waste treatment is a relatively recent development. Numerous groups, both in the United States and Europe, have made substantial progress in the last decade towards understanding the mechanistic pathways, kinetics, and engineering aspects of the process. At Lawrence Livermore National Laboratory, substantial contributions have been made to this knowledge base in these areas and others. Conceptual design and engineering development have been completed for a pilot plant-scale MEO system, and numerous data have been gathered on the efficacy of the process for a wide variety of anticipated waste components.

This presentation will review the data collected at LLNL for a bench scale system based primarily on the use of a Ag(II) mediator in a nitric acid electrolyte; results from several other mediator/acid combinations will be included. Data obtained on the chemical, electrochemical, and engineering aspects will be presented. The topics of organics destruction, transuranic recovery, and some of the ancillary systems will be addressed, and areas requiring further study will be mentioned.

INTRODUCTION

Due to the political and regulatory difficulties encountered in the remediation of mixed wastes, few traditional techniques have demonstrated sufficient acceptability. Even if the waste is classified as simply "hazardous", problems still exist if there is the possibility of the formation of harmful species such as dioxins or furans. Typically, these problems arise due to the volatility of radionuclide species or to the reactivity of certain organics when treating waste at elevated temperatures and attention has therefore been focused on low temperature alternatives. One of these alternatives, Mediated Electrochemical Oxidation (MEO), mineralizes organics species to carbon dioxide and water while operating at near ambient pressure and temperature(1-11) in an aqueous system. In addition, insoluble transuranic oxides may be dissolved and separated out in a specialized MEO system known as Catalyzed Electrolytic Plutonium Oxide Dissolution, or CEPOD (12-16).

MEO is based upon the oxidation of organics to carbon dioxide, and the oxidation of transuranics to a soluble species, through a series of charge transfer steps involving a mediator. This mediator, typically a

transition metal in its highest valency state, is generated at the anode of an electrochemical cell and is dispersed throughout the anolyte solution. Upon oxidation of the organic or transuranic by the mediator, the reduced mediator species is reoxidized at the anode and the cycle repeats until all oxidizable material in the cell is depleted. Equations (1) and (2) are listed as representative stoichiometric reactions for ethylene glycol and plutonium oxide, respectively.

The electrochemical current loop is completed by the cathode reaction, which is typically the reduction of the electrolyte itself.

The MEO technique offers several advantages which are inherent in the system. First, the oxidative processes are accomplished at near ambient pressures and temperatures (30-70 °C). Second, all waste stream components and oxidation products (with the exception of evolved gases) are contained in an aqueous environment. This aqueous electrolyte acts as an accumulator for inorganics which were present in the original waste stream and also provides a thermal buffer for the energy released during exothermic oxidation of the organics. Third, the generation of secondary waste is minimal as the process needs no additional reagents. Finally, the entire process can be shut down by simply turning off the power, avoiding problems such as thermal runaway.

Over the past 20 years, several high-valency metal ions have been investigated as mediators, including Ag(II) (1-7), Ce(IV) (6,12-16), Co(III) (6,8-10) and Fe(III) (10,11). Each of these shows different kinetics with respect to oxidative chemistry and optimal waste streams differ slightly for each system. We report here studies done with the systems Ag(II)/HNO₃ and Co(III)/H₂SO₄, with both laboratory and bench scale systems.

EXPERIMENTAL METHODS

For the laboratory scale experiments, an H cell thermostated in a water bath to within ± 1 °C was used. This cell contained a rotating platinum cylinder anode in one arm and a platinum strip cathode in the other arm; the two compartments were separated by a Nafion 117 membrane. The mediator concentration was 0.5 M, a value which allowed reasonable current densities without exceeding solubility limits, while the acid concentrations were varied from 4-6 M for the Co/H₂SO₄ system and from 4-12 M for the Ag/HNO₃ system. The organic substrate was introduced into the cell in a batch mode, and the offgas was analyzed for carbon dioxide by passage through an infrared analyzer by means of a peristaltic pump. By integrating the volume of carbon dioxide produced over the period of a run, an estimate of the destruction efficiency could be obtained. For the destruction efficiencies listed in the results, either this method was used, or Total Organic Carbon analyses were done before and after a run and the D.E.'s were calculated using the equation: $\text{D.E.} = ((\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}}) / \text{TOC}_{\text{initial}}) \times 100\%$.

The bench scale organics destruction experiments (17,18) were performed on a commercial plate and frame cell (Imperial Chemical Industries Model FM-21). This two channel cell contained three niobium cathodes and two platinum-coated niobium anodes, each with an active surface area of 0.85 m²; the anode and cathode compartments were separated by a Nafion 117 membrane. This system has a capability of up to 3000 amps, with a flow rate of 4 gpm per cell channel and anolyte and catholyte fluid volumes of 20 and 40 liters, respectively. The electrolyte used in this system was 0.5 M AgNO₃ in 8-10 M HNO₃, at operating temperatures of 50-70 °C. Organic substrates were introduced into the cell in a continuous feed mode, and destruction efficiencies were calculated solely by the method of TOC analysis described above.

The plutonium dissolution cell (CEPOD) is similar to the MEO system described above, with a dissolver loop added in the anolyte flow stream. The electrolyte is Ag(II)/HNO₃, and the cell is of an annular configuration with a gold anode, allowing current efficiencies of 100% for production of Ag(II) at

high current densities. Dissolution of transuranic oxides was modeled with cupric oxalate, as this material is insoluble in nitric acid in the presence of Ag(I), but dissolves in the presence of Ag(II) due to the facile oxidation of oxalate anions by the higher valent silver ion.

RESULTS AND DISCUSSION

Process Chemistry for Organics Destruction

Although the organic oxidation process chemistry for the systems Ag/HNO_3 and $\text{Co}/\text{H}_2\text{SO}_4$ is similar, significant differences exist between the two systems. For instance, in the Ag/HNO_3 system, the cathodic reaction is the reduction of nitrate ions, which can result in the formation of NO_x . To prevent this, the nitrous acid can be converted back to nitric acid by reacting it with oxygen; this method is described in more detail below. Also, this cathodic reaction is electrochemically reversible and a cationic exchange membrane must be employed to prevent the reoxidation of nitrite ion at the anode and consequent loss of current efficiency. In the system $\text{Co}/\text{H}_2\text{SO}_4$, the cathodic reaction is the reduction of protons (Eq. 3), resulting in the release of hydrogen gas from the catholyte. As this reaction is irreversible, no membrane is required in this system.

Another difference between the cobalt and silver systems is in the relative rates of the reaction of the oxidized form of the mediator with water. This reaction is parasitic as it leads to a sterilization of the mediator, although there may be some benefits due to the production of radical species (19). The rate of reaction of Ag(II) with water is relatively rapid (19), whereas Co(III) is somewhat more stable in water, especially at low pH (20-23).

Organics Destruction-Laboratory Scale Experiments

The destruction efficiencies for a variety of organic substrates are given in Table I. In general, the Ag/HNO_3 system performed more effectively than did the $\text{Co}/\text{H}_2\text{SO}_4$ system. This is due to three factors: 1) the oxidation potential of Ag(II) is higher than Co(III) , 2) the Ag/HNO_3 system is believed to involve OH radical species due to the oxidation of water by Ag(II) (19), and 3) nitric acid is in itself a more powerful oxidant than sulfuric. A limited number of experiments were done on systems using Fe(III) (10) and Ce(IV) as mediators, but the effectiveness of these for organics destruction was judged to be less than either Ag(II) or Co(III) .

Although an all-encompassing maxim for the destruction efficacies of organic functional groups is not possible, a general rule of thumb is that the ease of oxidation of a particular species follows the general order:

$\text{Alcohols} > \text{Chloro/Amino/Nitro/Phospho} > \text{Aromatic} > \text{Ketones/Aldehydes} > \text{Aliphatic}$.

Also, the more oxidizable functional groups that an organic substrate has, the more facile the oxidation by MEO. Thus, a diol would result in faster oxidation than a single alcohol group. The current efficiency of the MEO process is related to the oxidation rates but a discussion of this is deferred to the results given below for the bench scale system. The only functional group that exhibited no detectable oxidation was the C-F bond such as contained in polytetrafluoroethylene (Teflon) and polyvinylidene fluoride (Kynar). In fact, both of these polymers make excellent materials of construction for MEO systems due to their inertness.

In many of the cases, the amount of evolved carbon dioxide was insufficient to account for complete destruction even though a TOC analysis indicated no remaining organic material in either the anolyte or catholyte solutions. Thus, it appeared that either the original organic substrate, or its oxidation products, volatilized before complete oxidation could occur. This effect was especially pronounced with extremely volatile organics such as acetone and benzene. In Table I, a note is made of those organics in which volatilization appeared to be a significant factor in non-quantitative conversion to carbon dioxide.

Even if thermodynamic predictions would indicate that a given organic might be oxidizable by Co(III) or Ag(II) , little oxidation will occur if few collisions between mediator and organic occur. That is, the surface area of contact should be maximized if one wants to achieve maximum rates of destruction. For soluble organics, this is not a problem as the organic is dispersed homogeneously throughout the

electrolyte. However, with insoluble or immiscible compounds, this contact issue can be a significant factor. In tests with these types of substrates, the organic simply floated on the top of the electrolyte solution (or sank to the bottom) and conversion to carbon dioxide was exceedingly slow. This was the case with organics such as benzene, dodecane, and trimsol. It is believed that the formation of an emulsion with a surfactant might be one way of attacking this problem.

Organics Destruction-Bench Scale Experiments

A diagram of the bench scale MEO system at LLNL is shown in Figure 1. The heart of the system is of course the electrochemical cell, but the system also contains several ancillary units for offgas treatment and electrolyte recycling which are described in more detail below (see also Figure 4). Destruction data for several organics obtained with this Ag/HNO₃ MEO unit are given in Table II.

Figures 2 and 3 illustrate the relationship between destruction efficiency and current efficiency observed with this bench scale system for trimsol and cellulosic materials, respectively. This current efficiency is defined as the ratio of the amount of current *theoretically* required to oxidize a given quantity of organic completely to carbon dioxide to that amount of current required *in an actual test*. As can be seen, gains in destruction efficiencies are obtained only at the expense of current, or coulombic, efficiency. In batch mode tests, as the concentration of readily available organic substrate decreases at the completion of a particular run, inordinately long time periods are required to oxidize the few organic fragments that remain. Hence, current is "lost" due to parasitic reactions such as the oxidation of water by the mediator and thus the observed current efficiency drops.

Ancillary Systems

Several associated systems have been designed and tested in associating with this bench-scale MEO system, including the recycling of the electrolyte, offgas treatment, and final electrolyte disposal. A schematic of these systems are shown in Figure 4, and each is described in more detail below.

Silver Chloride recovery: In the destruction of chloride-containing organics in the Ag/HNO₃ system, the chlorine released upon oxidation of the organic is immediately precipitated as insoluble silver chloride. In order to prevent loss of the mediator when treating chloro-organics, a method has been developed to recover this mediator (24). This method is based upon the reduction of silver chloride to silver (Eq. 4),

and subsequent separation and redissolving of silver in nitric acid (Eq. 5) for reuse.

The advantages of this method are: 1. the chemicals are inexpensive, 2. the only waste generated will be sodium chloride which may be dried and disposed of via polymer encapsulation, and the quantity is minimal if a low stoichiometry of sodium hydroxide is used. Despite these advantages, there is no quantitative information available in the literature and therefore a lab scale experiment was initiated to study this process.

Optimal results were obtained when using an excess of hydroxide and hydrogen peroxide, with 98% conversion of silver chloride obtained for stoichiometries of 1.25X NaOH and 10.32X H₂O₂ at 80 °C. The excess H₂O₂ is unstable and breaks down into water and oxygen, which are not undesirable additions to the waste stream. Since this decomposition occurs quickly in alkaline solutions at high temperatures, the conversion efficiency decreases as the reaction time increases and a careful control of reaction time is required.

Silver removal: A system has been designed and tested to recover the silver mediator from the anolyte before final disposal/treatment of the used electrolyte in the Ag/HNO₃ system (25). This process is based

upon the reaction of Ag(I) with hydrochloric acid to form insoluble silver chloride, which is then separated by centrifuging. Tests with this system at a bench-scale yielded silver removal efficiencies of 99.999% with HCl in 5% excess, 99.990% with HCl in 0.5% excess, and >99.5% with HCl added in stoichiometric quantities. After removal of the silver the electrolyte is boiled off until almost dry by passing it through a thin film evaporator. The evaporator bottoms are carried out and if desired, any radionuclides present can be recovered by ion exchange. If recovery is not desired or feasible, the radioactive material is disposed of via grouting or ceramicization.

Nitrite oxidation/NO_x reduction: In nitric acid based systems, the reduction of nitrate is the dominant cathodic reaction when the concentration of nitrate is greater than 2 M (Eq. 6).

The nitrous acid generated must be converted back to nitric acid, otherwise the nitrous acid will eventually decompose to form NO_x (Eq. 7):

Contacting the nitrous acid with oxygen regenerates the nitric acid and prevents the formation of NO_x (Eq. 8):

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 (26). 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. This device is installed in the catholyte flow loop, and the advantages of intimate mixing and the high surface area contribute to measured efficiencies of 95 to 99%.

CEPOD Bench-Scale System

A flow diagram of the CEPOD system for transuranic recovery is shown in Figure 5. Although modeling studies (27), engineering design, and construction of this system are complete, insufficient testing has been done to report any conclusive data. However, the chemistry of this system is very similar to the bench-scale MEO system above, and many of the ancillary systems are also applicable.

CONCLUSIONS

In general, the Ag(II)/HNO₃ and Co(III)/H₂SO₄ MEO systems were able to oxidize completely the vast majority of organics, although the functionalities present played a significant role in the ease of oxidation. At one extreme, alcohol, double bond and carboxylic acid groups greatly facilitated the process, while at the other extreme, aliphatic hydrocarbons exhibited little or no evidence of oxidation. In practice, no oxidation occurred if no favorable functionalities were present. Most organics fell somewhere in between, with more -OH groups and fewer C-H or C-C bonds accelerating the oxidation.

Mediated Electrochemical Oxidation is a viable alternative for the low temperature destruction of the organic components of waste streams and for the dissolution/separation of transuranic oxides. Because of the system operating parameters, several advantages are offered in the area of offgas composition, secondary waste generation, and volatile species containment. For most organics, the Ag(II)/HNO₃ system provided a more powerful combination; however, each combination of mediator and electrolyte offers a unique mix of treatable waste streams. The decision as to the proper system to use will likely be determined by the actual composition of the target waste stream.

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FIGURE 1. Diagram of Bench-Scale MEO System at LLNL.

FIGURE 2. Relationship Between Current and Destruction Efficiencies for Bench-Scale Tests of Trimsol.

FIGURE 3. Relationship Between Current and Destruction Efficiencies for Bench-Scale Tests of Cellulosic Materials.

FIGURE 4. Flow Diagram for MEO System including Ancillary Components.

FIGURE 5. Flow Diagram for CEPD System.

TABLE I. Summary of Organics Destruction Data for Laboratory-Scale MEO System.

Organic Substrate	Mediators Tested	Acid Concentrations	Destruction Efficiency, %
Alcohols			
ethylene glycol	Ag/Co	4-12M/2-6M	100
2-propanol	Co	2-4M	65*
1-chloro-2-propanol	Co	2-4M	>99*
1,3-dichloro-2-propanol	Co	2-4M	>99*
Aromatics			
benzene	Ag	3M	88*
2,4-diaminotoluene	Ag	4-12M	100
CH ₃ -X			
nitromethane	Ag	4M	0
Aliphatic			
dodecane	Ag	6M	99
Organic materials			
trimsol (cutting oil)	Ag/Co	8-12M/4-6M	>99/60
cellulose	Ag/Co	4-12M/2-6M	>99.9/>99.9
biomass	Ag	8,10M	97
latex	Ag	8,10M	98
tyvek	Ag	8,10M	98
polyethylene	Ag	8,10M	>99.9
polyvinylchloride	Ag/Co	8M/4M	21/0

* organic volatilization judged to account for efficiencies of <100%.

TABLE II. Summary of Organics Destruction Data for Bench-Scale MEO System.

Organic Substrate	Mediator	Acid Concentration	Destruction Efficiency, %
trimsol	Ag	10-12M	>99.9
cellulosic materials	Ag	8-10M	>99.9