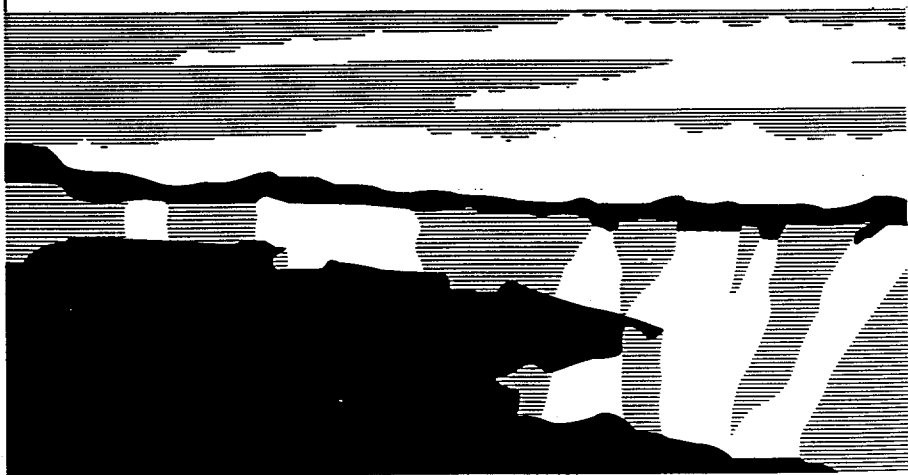


Title: PARAMETRIC OPTIMIZATION OF THE MEO PROCESS FOR TREATMENT
OF MIXED WASTE RESIDUES

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Parametric Optimization of the MEO Process for Treatment of Mixed Waste Residues

by

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ABSTRACT

A series of bench-scale experiments were conducted to determine the optimum reaction conditions for destruction of styrene-divinyl benzene based cation resin and methylene chloride by the mediated electrochemical oxidation (MEO) process. Reaction parameters examined include choice of electron transfer mediator, reaction temperature and solvent system. For the cation exchange resins, maximum destruction efficiencies were obtained using cerium(IV) as mediator in nitric acid at a temperature of 70°C. Reasonable efficiencies were also realized with silver(II) and cobalt(III) at ambient temperature in the same solvent. Use of sulfuric acid as the solvent yielded much lower efficiencies under equivalent conditions. Methylene chloride was found to react only with silver(II) at ambient temperature in nitric acid media, cobalt(III) and cerium(IV) were totally ineffective. These results demonstrate a need to perform bench-scale experiments to determine optimum operating conditions for each organic substrate targeted for treatment by the MEO process.

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INTRODUCTION

Mediated Electrochemical Oxidation (MEO) is an electrochemical-based process used to treat mixed wastes. For our purposes the mixed waste consists of hazardous or non-hazardous organic compounds combined with radioactive materials such as uranium or plutonium. The process consists of the chemical oxidation of the organic component of the mixture by a powerful oxidizing agent generated at the anode of a divided electrochemical cell. The organic compounds present are converted to carbon dioxide, which is then vented from the cell. The inorganic radioactive component dissolves in the anolyte solution and is subsequently reclaimed by standard recovery processes already in place. The MEO process is carried out at ambient pressure and at temperatures between ambient and the boiling point of the solvent, approximately 100 °C.

An MEO process unit is currently being installed at Los Alamos National Lab (LANL) for the treatment of mixed waste residues. The sources of this waste are residues resulting mainly from analytical chemical operations and consist of a wide range of materials. The list of materials includes: solvent extraction solvents and extractants, organic chemical standards used for gas chromatographic analysis, contaminated common solvents, spent ion exchange resin, vacuum pump oil, extraction thimbles, plastic bottles and labware, glovebox gloves, glass vials, and miscellaneous glovebox trash.

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The MEO equipment to be used at LANL was sized to treat the quantity of legacy waste that had accumulated over a period of several years, then to treat new waste on an as-generated basis. A critical component of the calculation used to determine the equipment size was the current efficiency expected for treating a given residue. Some current efficiency data was available from the literature¹⁻⁷ while other data could only be estimated. A summary of calculated throughputs for a given quantity of a particular waste is presented in Table I.

Table I. Estimated Processing Time for Combustible Residues

Waste Form	Quantity	Current, Amperes	Current Efficiency	Electrolysis Time	Total Process Time
Combustible Liquids					
Aqueous Waste < 2% methanol	3 gal	3000	100 %	1 hour	1 day
Pump oil	1.5 gal	3000	20 %	85 hours	13 days
Methylene chloride	2 gal	3000	50 %	45 hours	7 days
Sample extracts	2 gal	3000	50 %	45 hours	7 day
Organic standards	0.25 gal	3000	50 %	6 hours	1 day
Misc. organic waste	12 gal	3000	50 %	272 hours	40 days
Combustible Solids					
Combustible trash	12 gal	3000	20 %	680 hours	85 days
Glovebox combustible trash	10 gal	3000	20 %	567 hours	71 days
Non-Combustible Solids					
Glovebox non-combustible trash	10 gal	3000	leach	1 gal/day	10 days
Extraction thimbles	6 gal	3000	leach	1 gal/day	6 days
Glassware, metals	2 gal	3000	leach	1 gal/day	2 days
Gloves	28 pairs	3000	leach	2 pairs/day	14 days
Vials	1000 count	3000	leach	100 /day	10 days

As implied by the data in Table 1, MEO is a relatively slow process compared to other combustion methods. Some combustible materials such as hard plastics react so slowly as to be considered inert. So, for example, to treat a contaminated polypropylene bottle by MEO would require leaching the contamination from the surface followed by compaction and disposal of the solid polypropylene residue rather than destruction of the polymer matrix. Chemical reaction rates tend to increase exponentially with increasing temperature. A compound that would take several hours to destroy in the ambient temperature MEO process might take just a matter of minutes or even seconds in a high temperature incinerator. Unfortunately, due primarily to negative public sentiment, incineration is not a viable mixed waste treatment option. Other high temperature liquid or supercritical fluid processes are of necessity operated at high pressures. High pressures introduce additional safety considerations, especially if the process is installed in a controlled pressure glovebox that is common in the nuclear industry. Thus there can be an inherent greater risk associated with increasing throughputs by using alternative processes.

Because treatment of mixed wastes by MEO can be slow, it is important to operate the process at the highest possible efficiency. But, each organic substrate will have its own unique set of optimized operating parameters. These parameters can be established on a

small lab scale, using non-radioactively contaminated materials, prior to treatment of real waste on a production scale. This report summarizes the results obtained in a lab scale study for the treatment of two of the more common mixed waste residue components found in the nuclear industry, spent ion exchange resin and methylene chloride solvent.

There are many operational parameters associated with the MEO process. Among them are current density, solution flow rate, choice and concentration of redox mediator, choice and concentration of acid solvent system, temperature, choice of electrode material, electrochemical cell design, and type of electrochemical cell divider. Of these parameters the ones exhibiting the greatest impact on the oxidation chemistry are choice of mediator and solvent system and reaction temperature. These three parameters are the focus of this study. Three mediators, silver(II), cobalt(III) and cerium(IV), two solvents, 6.0 M nitric and 5.8 M sulfuric acids, and a range of temperatures from 20 °C to 90 °C have been investigated.

EXPERIMENTAL

All electrochemical measurements were carried out in a standard glass H-cell fitted with a medium porosity glass frit to separate the anolyte and catholyte compartments. Each compartment held approximately 70 mL total volume. A 31 cm² platinum foil electrode was used as the anode and a platinum wire served as the cathode. A constant current was applied to the electrodes using a Sorensen HPD 15-20 power supply.

Ion exchange resin (Dowex 50W-8X) was dried in a vacuum oven at 110 °C prior to use to obtain an accurate dry weight. Before and after weight comparisons gave as-received water content of approximately 41%. Titration of the resin with standardized base solution yielded 5.33 milli-equivalents per gram of dry resin. Assuming sulfonated vinyl benzene, with a molecular weight of 185 grams, as the standard polymer unit in the resin results in a calculation of a maximum capacity of 5.41 milli-equivalents per gram. Thus for all practical purposes the resin can be considered as consisting exclusively of sulfonated vinyl benzene groups.

The electrochemical cell was placed in a water bath on a Whatman Dataplate 430 stirrer/hot plate, using thermocouple feedback to maintain the temperature to within ± 1 °C of the preset value. Both compartments of the cell were filled with 6 M acid, the reduced form of the mediator was added to the anolyte compartment and the system was allowed to come to thermal equilibrium. A measured quantity of previously dried cation exchange resin was added and a current of 1 ampere was passed through the cell for a period of three hours. At the completion of the electrolysis, placing the cell in a chilled water bath immediately quenched the reaction. The anolyte solution was then filtered through a fine porosity glass filter crucible. The residue was washed twice with 30-mL portions of 6 M acid to remove any residual mediator from the resin, and with three 30-mL portions of deionized water to remove the excess acid. The crucible and its contents were then vacuum dried in an oven at 110 °C.

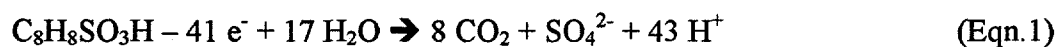
The mediators were added to the solution as nitrate or sulfate salts, AgNO₃ (J. T. Baker), Co(NO₃)₂·6H₂O (Fisher), CoSO₄(NH₄)₂SO₄·6H₂O (EM Science), H₄Ce(SO₄)₄ (J. T. Baker), and Ce(NH₄)₂(NO₃)₆ (Fisher). Cerium(IV) was pre-reduced to Ce(III) at an applied potential of 0.75 volts prior to addition of the ion exchange resin. All experiments were run using a mediator concentration of 0.1 M.

Kinetic studies were performed using a flow-through system. A standard H-cell was placed in a water bath on the thermostatted hot plate. The temperature was maintained to within ± 1 °C of the preset value. Solution from the cell was pumped by means of a peristaltic pump through the sample well of a Perkin-Elmer model 8452 A UV-visible spectrometer fitted with either a 1.0 mm or 0.1 mm path length flow cell. A measured quantity of ion exchange resin or methylene chloride was added to the cell and the mediator concentration was continuously monitored at 370 nm wavelength for cerium(IV), 604 nm for cobalt(III) and 392 nm for silver(II).

RESULTS

Ion Exchange Resin

The complete oxidation of a sulfonated styrene unit of a standard cation exchange resin proceeds according to reaction 1:



Using this reaction stoichiometry and a unit molecular weight of 185 yields a theoretical value of 21,084 coulombs or 5.86 amp-hours of current required for complete oxidation of one gram of dry resin. Each of the resin destruction experiments was run at a current of 1 ampere for 3 hours, a quantity of electricity sufficient to destroy approximately 0.51 grams of resin at 100 percent current efficiency. Results of the resin destruction experiments conducted in 6 M nitric acid are shown in Figure 1.

The blank experiment consisted of adding the resin to a solution containing approximately 6M acid with no mediator present and passing a current of 1 ampere for three hours. The average loss in weight of the resin was approximately 2-3 percent, verifying the chemically inert nature of this material even at elevated temperatures in strongly oxidizing nitric acid solution.

The oxidizing power of the three mediators chosen increases in the order Ce(IV) < Ag(II) < Co(III) ⁸. At room temperature, 20 °C, the disappearance of resin from the solution follows this same trend. With cerium(IV), the weakest of the oxidants, there is essentially no reaction. Using silver(II) or cobalt(III) as mediator at 0.1 M concentration, the reaction proceeds smoothly, with the amount of resin destroyed exceeding the theoretical amount possible based solely on the number of coulombs of electricity passed. Two possible explanations exist for this behavior. First, the resin may not react completely to produce carbon dioxide, but instead form a water soluble

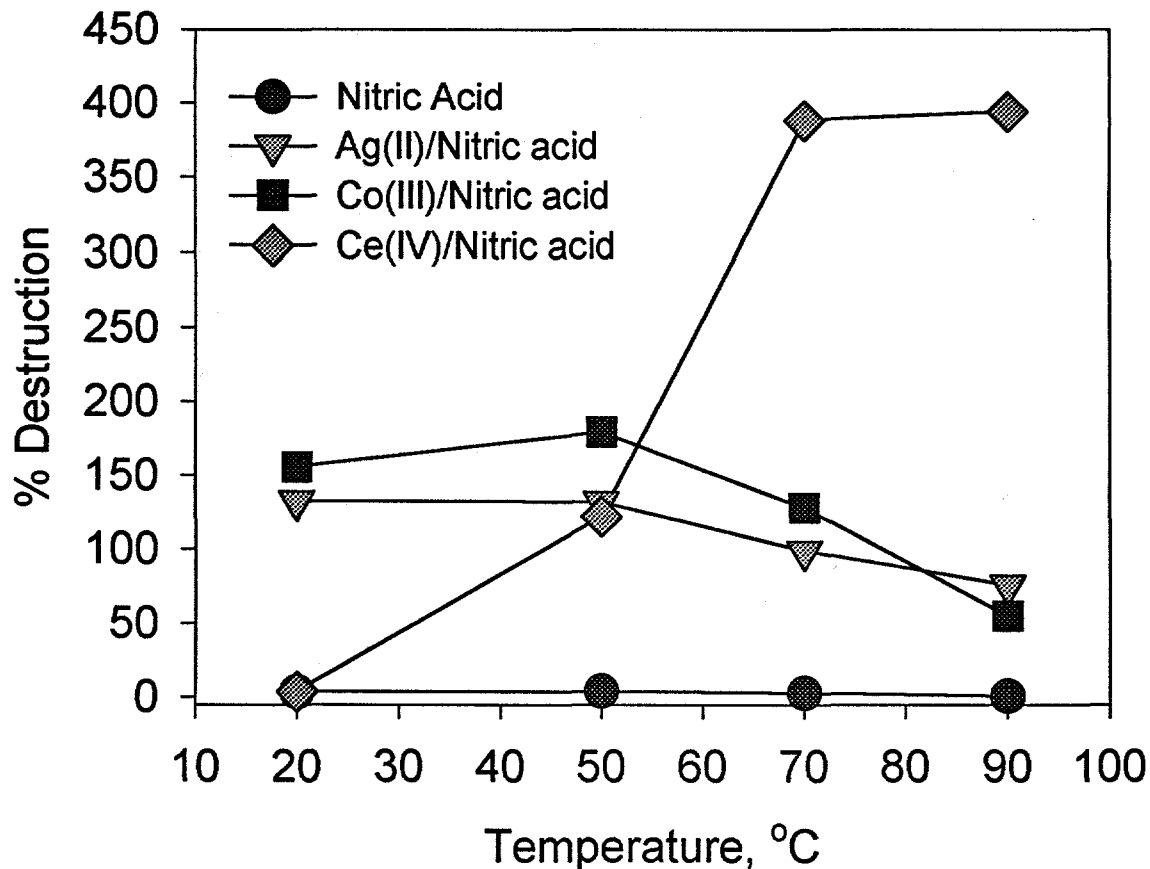
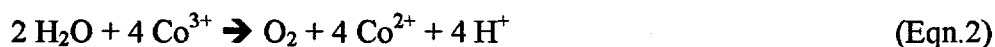


Figure 1. Percent destruction efficiency of cation exchange resin in 6.0 M nitric acid.

intermediate. This incomplete reaction would give an erroneously low weight of solid residue and thus higher calculated destruction efficiency. However, when a deficiency of resin is used instead of an excess, analysis of the resulting solution typically gives results in the order of 100 ppm total organic carbon. Thus the reaction will proceed to completion. A second possible explanation is that while the resin itself is resistant to chemical attack by the strongly oxidizing nitric acid media, the intermediate products generated are not. Once the benzene ring has been opened by attack from the mediator, it may then be possible for the solvent to participate in subsequent oxidation reactions of the intermediates.

When the temperature is raised to 50 °C, the resin destruction efficiency using silver(II) and cobalt(III) as mediators is slightly greater than at room temperature, but the solution never develops the characteristic colors associated with the ions in their higher oxidation states. Two reactions are occurring simultaneously, reaction of the mediator with the resin and reaction of the mediator with solvent, as given in equation 2.



The former reaction is expected to proceed at a faster rate at elevated temperatures, but the latter reaction, which also proceeds at a faster rate, lowers the effective mediator concentration. Thus raising the temperature appears to have little effect on the resin destruction rate. If the temperature is raised still further, to 70 °C and 90 °C, the resin destruction efficiencies with silver and cobalt gradually decrease. The deleterious solvent/mediator reaction rate begins to exceed that of the mediator/resin reaction.

An indication of the reaction of mediator with solvent is given by generating the higher oxidation state of the mediator in the absence of organic material. At room temperature during the electrolysis the characteristic green color of cobalt(III) or brown color of silver(II) is always present indicating a build up of mediator concentration in its higher oxidation state. At elevated temperatures these color changes can only be seen at the electrode surface, dissipating rapidly as the surface solution is swept into the bulk of solution.

The efficiency of resin destruction using cerium(IV) as mediator increases dramatically as the temperature is raised. From essentially an immeasurably low reaction at room temperature it increases to greater than 100% destruction efficiency at 50 °C, comparable to the efficiency observed with silver(II). At 70 °C, the efficiency approaches a phenomenal 400%, far exceeding either cobalt(III) or silver(II). At 90 °C, the efficiency ceases to increase signaling the onset of the solvent reaction with cerium(IV).

Results of the resin destruction experiments in sulfuric acid are shown in Figure 2. Silver was not used in these studies due to limited solubility in sulfuric acid media. Trends observed in this media mimic those seen in nitric acid but in less dramatic fashion. With cobalt(III) as mediator there is a slight gradual decrease in destruction efficiency as the temperature is raised. With cerium(IV) there is essentially no reaction at room temperature but a steady increase in reaction efficiency with increasing temperature. With neither mediator does the destruction efficiency exceed 100 percent of theoretical. This observation lends further validity to the assumption that nitric acid contributes to the oxidation process while the non-oxidizing sulfuric acid does not.

Experiments to measure the reaction kinetics and stoichiometry were carried out using cerium(IV) in nitric acid. Cerium(IV) was chosen due to its stability in aqueous solution at moderate temperatures while both cobalt(III) and silver(II) are not. In these experiments the cerium(IV) concentration was monitored spectrophotometrically with time following addition of resin.

When a deficiency of resin was used the change in absorbance was used to calculate the quantity of cerium(IV) necessary to completely oxidize a given weight of resin. The average value obtained for three runs at 52 °C was 18.5 equivalents of cerium(IV) per equivalent of resin. The value is considerably lower than the theoretical value of 41 equivalents. Yet analysis for total organic carbon demonstrated essentially no soluble organic material remaining in solution.

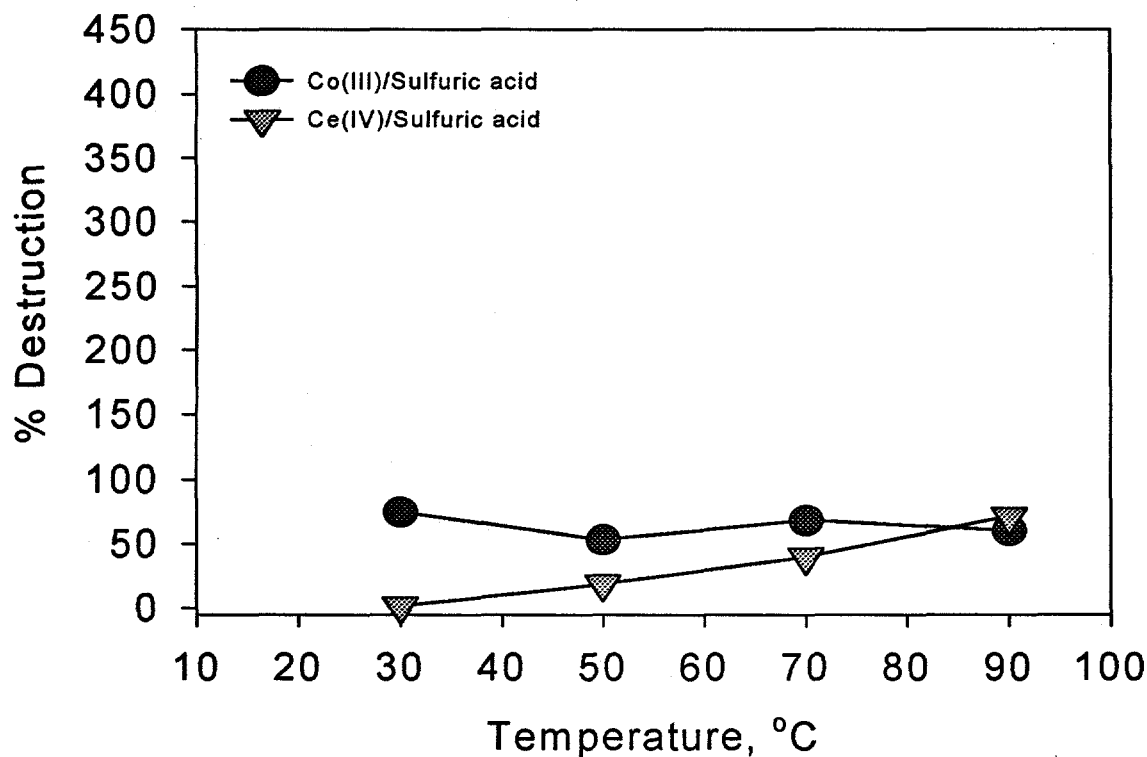


Figure 2. Percent destruction efficiency of cation exchange resin in 5.8 M sulfuric acid.

When an excess of resin was used, the change in absorbance was used to calculate the reaction kinetics. Application of the data to a number of reaction schemes gave a good fit only to a reaction $\frac{1}{2}$ order in cerium(IV). This reaction order is consistent with the shrinking sphere model of a diffusion controlled heterogeneous reaction between a soluble solution species and a solid spherical particle.⁹

In summary, oxidation of sulfonated cation ion exchange resin proceeds via a rate limiting attack of the resin bead by the electrochemically generated mediator. In nitric acid at moderate temperatures, the oxidation efficiency follows the oxidation potential of the mediator with $\text{Co(III)} > \text{Ag(II)} > \text{Ce(IV)}$. At elevated temperature oxidation by cerium(IV) proceeds at a much higher efficiency than either cobalt(III) or silver(III) due to the enhanced stability of cerium in aqueous media. Current efficiencies in sulfuric acid never reach 100 percent under any set of operating conditions whereas in nitric acid efficiencies greater than this number are routinely observed due to a contribution by the solvent. Highest throughputs can be obtained with cerium(IV) at an operating temperature of approximately 70 °C. However, reasonable throughputs can also be obtained with silver(II) or cobalt(III) in the 20-50 degree temperature range.

Methylene Chloride

Methylene chloride is a volatile liquid with a boiling point of 40°C at atmospheric pressure. Treatment by MEO could not be carried out at elevated temperatures due to flash volatilization of the material before any chemical reaction could occur. Therefore the methylene chloride studies were conducted at ambient temperatures, 20-23°C.

In this set of experiments, the mediator was generated electrochemically up to a maximum concentration. The current was then turned off and a baseline was established by allowing the solution to stir while continuously monitoring the mediator concentration spectrophotometrically to determine its stability with no oxidizable organic present. The experiment was then repeated with methylene chloride added immediately following current cessation.

At ambient temperature the concentration of electrogenerated cerium(IV) did not change over a period of approximately six hours, both in the presence and absence of methylene chloride. Cerium(IV) appears to be stable indefinitely in 6 M nitric acid and furthermore is totally unreactive with the chlorinated hydrocarbon under these conditions.

Results for cobalt(III) are shown in Figure 3. A one ampere current was applied to a 0.1

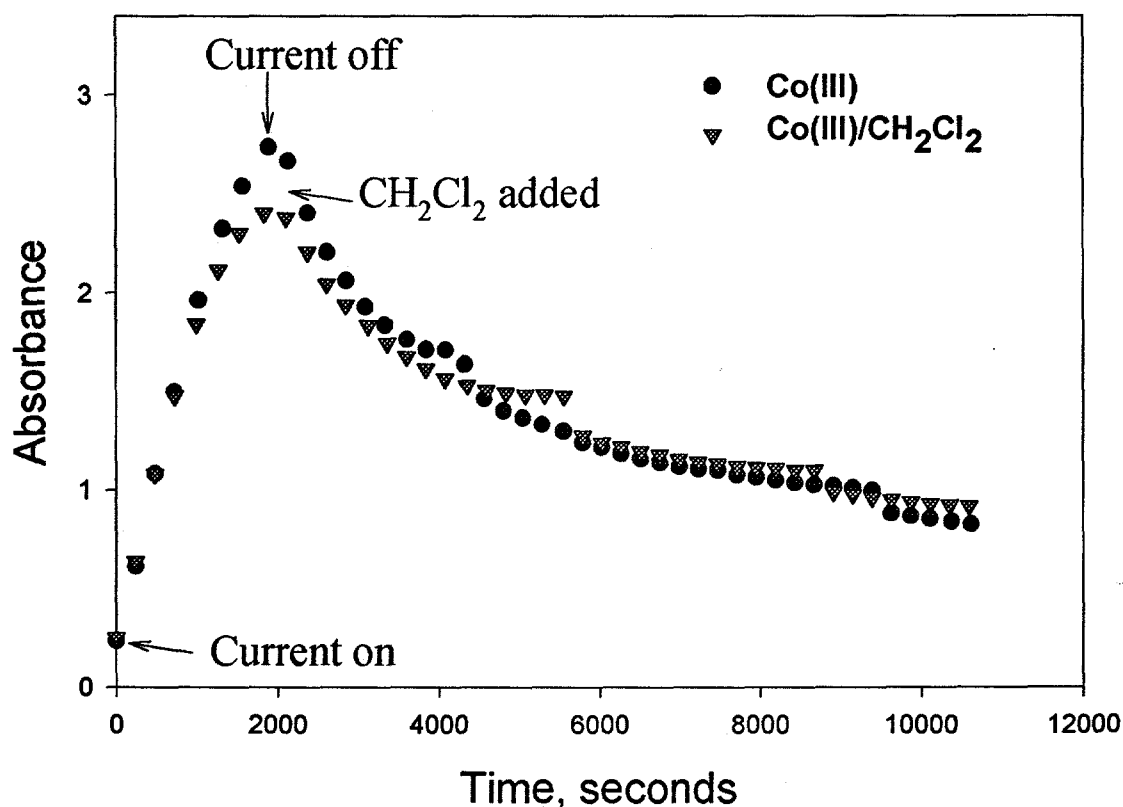
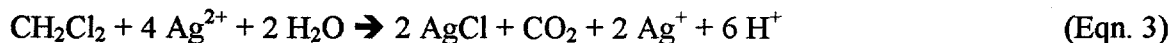


Figure 3. Reaction of methylene chloride with cobalt(III).

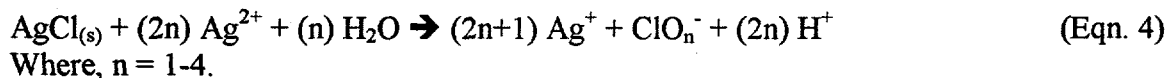
M solution of cobalt(II) in 6 M nitric acid. At approximately 2000 seconds a maximum concentration is obtained and the current terminated at that time. The absorbance measurement for cobalt(III) begins to decrease immediately, indicating a reaction between cobalt(III) and the solvent system even at ambient temperature. When the experiment is repeated, but with methylene chloride added as soon as the application of current is terminated, there is no perceptible increase in the rate of decay of cobalt(III) with time. The reaction between cobalt(III) and methylene chloride is immeasurably slow at ambient temperature.

Silver(II) behaves very similarly to cobalt(III) in the absence of the chlorinated hydrocarbon, as shown in Figure 4. There is a slow reaction with solvent to regenerate the lower oxidation state. However, very different results occur when methylene chloride is added. There is an immediate decrease in measured absorbance of silver(II) indicating a very rapid reaction. This reaction proceeds with the formation of a white precipitate, presumably silver(I) chloride. The change in absorbance can also be used to estimate the initial reaction stoichiometry. In this case the reaction appears to require approximately 4 equivalents of silver(II) per equivalent of methylene chloride. These results suggest the following reaction:



However the reaction does not stop at that point. Silver(II) continues to disappear from solution, and at a faster rate than if there were no methylene chloride present. This secondary reaction eventually consumes all of the remaining silver(II). If the current is once again turned on to oxidize silver(I) back to silver(II), the behavior is different than in its initial formation. Referring to figure 4, application of current at the same level as initially applied produces a low steady state concentration of silver(II) that only over a much longer period of time approaches the same initial concentration level. Newly generated silver(II) is apparently reacting with a reaction product at nearly the rate at which it is being generated. As that product is consumed, the silver(II) is eventually restored to its starting value.

These results suggest that there is a slow oxidation of chloride, in the form of solid silver chloride, to a more soluble oxy-chloro anionic species, as per equation 4.



In summary, of the three mediators studied, only silver(II) reacts to destroy methylene chloride at a measurable rate at ambient temperature. Even though cobalt(III) is a stronger oxidant than silver(II) there appears to be no reaction between the organic material and cobalt. This suggests a reaction pathway that is not initiated by an oxidation

process, but rather by silver's affinity to react with chloride ion to form insoluble silver chloride.

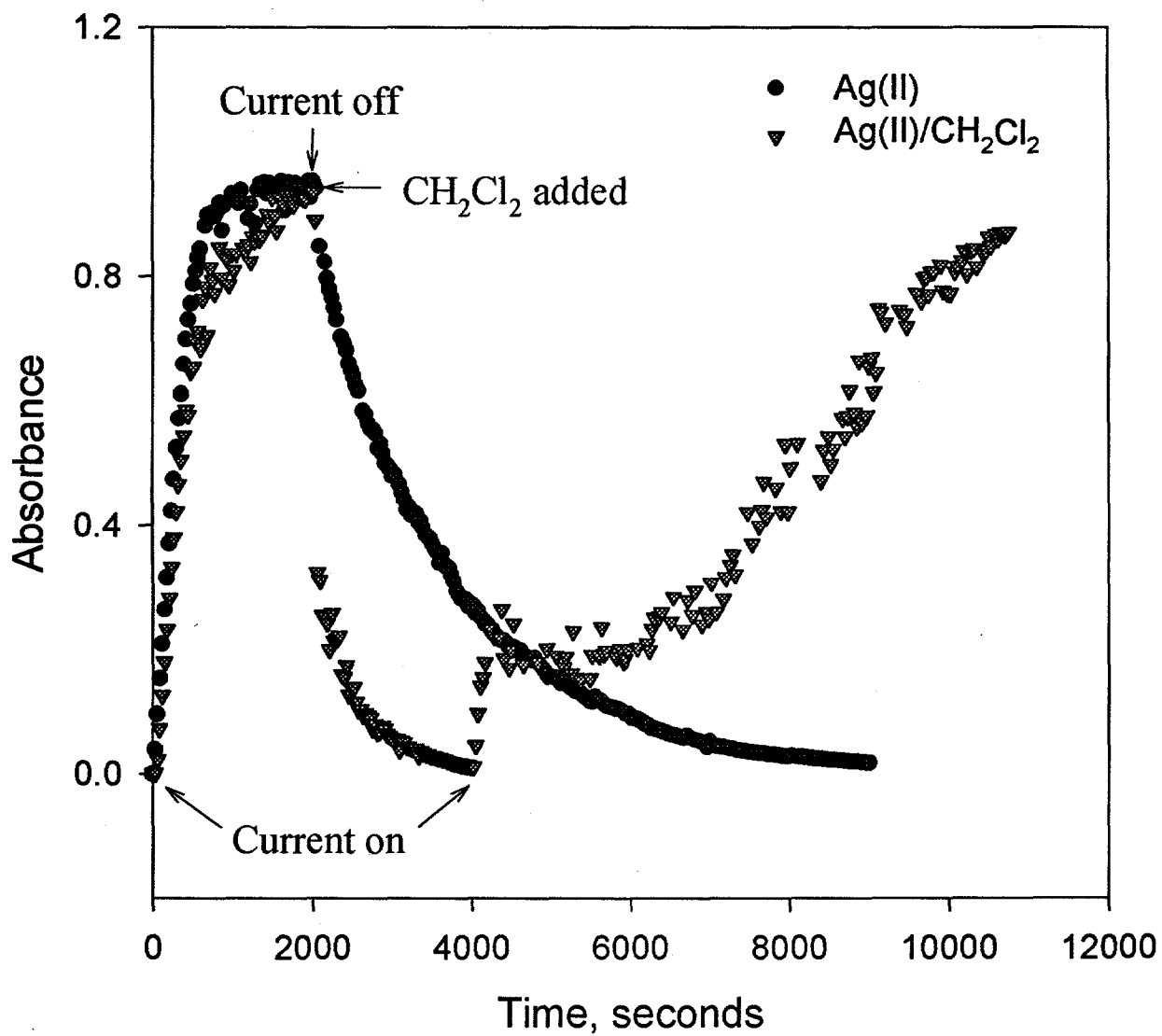


Figure 4. Reaction of methylene chloride with silver(II).

CONCLUSIONS

As predicted, there exists a unique set of operating parameters for each of the two organic substrates examined in this study. For the styrene-divinyl benzene based cation exchange resins maximum destruction efficiency and throughputs are obtained by using cerium(IV) as the electron transfer mediator, in nitric acid media, and at elevated temperatures. However, reasonable throughputs and efficiencies can also be obtained at ambient temperatures using either silver(II) or cobalt(III) as mediator. By comparison, there is essentially no reaction between methylene chloride and either cobalt(III) or cerium(IV) at ambient temperature. Silver(II) does effectively destroy the chlorinated hydrocarbon under these conditions but appears to proceed by a non-oxidative reaction initiation pathway.

The results of this study demonstrate that a set of reaction conditions that are effective for the treatment of one type of combustible residue by MEO will not work at all for another. It is strongly recommended that bench scale studies be performed on each residue type targeted for treatment by this process in order to determine the optimum operating conditions.

FUTURE WORK

A pilot scale MEO unit has been designed with a capacity necessary to treat the legacy combustible residues currently in storage at LANL, and to treat newly created waste on an as-generated basis. This unit will be installed and tested in mid FY 99. It is expected to be treating actual combustible residues before the end of this calendar year. Meanwhile, bench scale studies, similar to those contained in this work, will continue to be carried out on components contained in those residues.

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