**FY 1994
Final Report**

**Mediated Electrochemical Oxidation
Treatment for Rocky Flats Combustible
Low-Level Mixed Waste**

**Final Report to Rocky Flats Plant
FY 93 and 94 Tasks under TTP SF 221207**

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September 1994

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FY 94 Final Report

Mediated Electrochemical Oxidation Treatment of Rocky Flats Combustible Low Level Mixed Waste

Summary

Mediated Electrochemical Oxidation (MEO) is a low-temperature, low-pressure aqueous process which destroys organics by electrochemical means. It can be used to treat mixed waste containing hazardous organics by destroying the organic component of the waste. The MEO process has been investigated at LLNL for about two years as an alternative to incineration for Rocky Flats Plant (RFP) combustible low-level mixed wastes. Tests were performed with non-radioactive organic components of RFP mixed wastes. Trimsol was tested as a surrogate for contaminated cutting oils. Reagent grade cellulose, and clean wipes and cloth were tested for contaminated wipes, rags and overalls. Rubber and plastics such as latex, Tyvek, polyethylene and clear polyvinyl chloride were tested for contaminated gloves, laboratory coats and bags. Biomass was also destroyed as a surrogate of spent radioactive waste left over from biodegradation treatment. Extensive testing was carried out on the oils and cellulosic materials in both small laboratory-scale apparatus and on a bench-scale system incorporating an industrial-size electrochemical cell. Only small-scale system tests were carried out with rubber, plastics and biomass.

The following operating and system parameters were studied: use of a silver-nitric acid versus a cobalt-sulfuric acid system, effect of electrolyte temperature and effect of acid concentration. Some tests were carried out under strong mechanical mixing and shear conditions. For Trimsol, high oxidation conditions and high shear environments were important in realizing best system performance. For cellulosic materials, those conditions had less influence on performance. Total destruction efficiencies of around 99 % were obtained for both Trimsol and cellulose at coulombic efficiencies of 70 %. Higher total destruction efficiencies – up to 99.97 % – were achieved at coulombic efficiencies of 45 %. For biomass, latex, Tyvek and polyethylene, destruction efficiencies in the range of 95 to 99 % were readily attained at reasonable coulombic efficiencies. Polyvinyl chloride was the only material tested that was not easily destroyed. Only 20 % of polyvinyl chloride was destroyed at coulombic efficiencies of less than 10 %.

In addition to the organics destruction tests, a contactor to minimize NO_x formation at the catholyte was designed, fabricated and tested. The results indicated that the contactor is capable of preventing about 95 % or more of the NO_x that can be generated in this process. Finally a conceptual design was completed for the whole system which comprises the electrochemical process and secondary processes, including NO_x prevention, acid regeneration and silver recovery.

1. 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 plutonium oxide. 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 plutonium oxide, 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 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

Work on this project at LLNL for Fiscal Year 1993 and part of 1994 was a continuation of the work initiated in 1992, namely, the destruction of the organic components of major low-level mixed wastes streams at the Rocky Flats Plant.¹² The work so far comprises 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 has been 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 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 much 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. The calculation of limiting current has been discussed in earlier LLNL reports.¹⁰

The experiments performed for this project were of two types. A large number of small-scale experiments were performed on laboratory-sized apparatus where the process parameters could be easily varied. These experiments gave a preliminary assessment of the important process parameters and their influence on coulombic and destruction efficiencies. A smaller number of experiments were then carried out in a bench-scale facility containing an industrial-sized

commercial electrochemical cell. These experiments were for demonstrating destruction on large industrial-scale equipment so results could be confidently extrapolated to plant-sized operations. As mentioned above, the limiting current depends upon the fluid mechanics in the cell; therefore it is important that the fluid flow in each compartment of the electrochemical cell stack is close to that in a full-scale operation.

While the organics are being oxidized in the anode compartment, the nitric acid is reduced to nitrous acid at the cathode. Eventually the nitrous acid will decompose into NO_x unless it is converted back into nitric acid by contacting it with oxygen. A compact contactor based on a turbo-aerator design¹³ was fabricated and successfully tested. Also a conceptual design for the complete MEO process, including secondary processes, was developed. The conceptual design is presented in Appendix A of this report.

2. Objectives

The primary objective of this work was to evaluate the Mediated Electrochemical Oxidation (MEO) process as an alternative to incineration of Rocky Flats Plant (RFP) low-level mixed wastes. Experiments were conducted to determine the important process parameters influencing destruction of the organic component of the RFP mixed wastes. The effect of the important process parameters was quantified, and the rates of destruction, and corresponding coulombic and destruction efficiencies were measured. In addition to numerous small-scale experiments, enough demonstration experiments were carried out on an industrial-sized electrochemical cell so that the results could be extended to a plant-scale system.

3. Experimental Work

The experimental work on organic destruction was conducted in two stages. In the first stage, small laboratory-scale experiments were carried out with each organic component to test the influence of the process parameters. 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 stage, organic destruction was demonstrated in a bench-scale system using a commercially available industrial-size cell. Experiments were performed on this system only on the organics of most interest, i.e., Trimsol and cellulosic materials, and the tests were conducted with fewer parameters over a limited range of conditions. Only those parameters and conditions that had been shown to have a significant effect on performance in the small-scale experiments were carried forward to the bench-scale experiments. In most of the latter experiments, the organic was fed and metered continuously to the anolyte during the run.

However, a few experiments were also carried out in a batch feed mode in this system. The full set of experiments are described in the following subsections.

3.1 Small-Scale Experiments

Small-scale experiments were performed in H-shaped cells which were fitted with an ion-selective membrane (cationic, Nafion 117) separating the two cell compartments. 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. In these experiments the gas generated in the anolyte chamber was drawn through a Horiba Model 2000 Infrared Gas Analyzer and continuously sampled for carbon dioxide. In order to ensure that carbon dioxide did not escape out from the anode compartment, the chamber was kept at a slight negative pressure by the action of a peristaltic pump. Ambient air was allowed to enter the anode chamber and was drawn in with the carbon dioxide into the infrared analyzer. A flow meter placed in the line measured the total flow rate of the gas. This measurement along with the fraction of carbon dioxide in the mixture gave 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. At the end of most of the experiments, samples of the catholyte and anolyte were removed and sent for TOC analysis. To control the system temperature, the whole cell was placed in a bath equipped with an automatic temperature controller, which was able to maintain the temperature in the cell to within ± 1 °C.

The organics tested in the small-scale experiments were components of low-level mixed wastes streams at the Rocky Flats Plant. The experiments on Trimsol, a cutting oil, are a continuation of the experiments conducted in Fiscal Year 1992. The process parameters studied were: mediator-acid combination, acid concentration and system temperature. The mediator-acid combinations tested were silver in nitric acid and cobalt in sulfuric acid. Other mediator-acid combinations, such as cerium and iron in nitric and sulfuric acids, had been tested earlier at LLNL, but were found to be less powerful than the two selected. Hence, the other mediators were not tested further.

The mediator concentration in the solution was always maintained at 0.5 M. The reason for this is that the limiting current is proportional to the mediator concentration. At concentrations below 0.5 M the limiting current and current densities are too low for a practical electrochemical system. The acid concentration was varied from 4 M to the highest concentration at which 0.5 M of the mediator could be dissolved in the acid. For cobalt in sulfuric acid the maximum acid concentration was 6 M. For silver in nitric acid the maximum acid concentration was 10 M at

Figure 1. Schematic of small-scale experiment

room temperature, and 12 *M* at 70 °C. Although some tests were conducted at 70 °C with 12 *M* nitric acid, it was later decided that it would be best to limit the concentration to 10 *M* to prevent possible problems with re-crystallization of silver nitrate. The temperature in the system was varied from 50 to 70 °C. There were only a few experiments at room temperature, since those tests had been carried out during the previous year. There were no runs conducted at temperatures much above 70 °C because of the possibility of materials-related problems.

Finally, one process variable, the electrode current density, was not tested this year since it was evaluated in the tests performed in the previous year. The results were essentially that the best performance was obtained at the highest possible current density as long as it was below the limiting current density. Hence, the experiments conducted this year were conducted under those conditions, and that variable was not tested further. The complete test matrix for the small-scale system tests on Trimsol in Fiscal Years 1993-94 is given in Table 1.

Table 1. Test Matrix for Small-Scale Experiments on Trimsol

Exp No.	Mediator-Acid	Acid Conc. (M)	Temp (C)	Mass (g)	Current (A)	Anolyte & Cath Vols (ml)
156	Co-H ₂ SO ₄	4	23	0.5186	1.02	170
157	Co-H ₂ SO ₄	4	50	0.4858	1.02	170
158	Co-H ₂ SO ₄	4	70	0.5236	1.02	170
159	Co-H ₂ SO ₄	6	23	0.5061	1.02	170
160	Co-H ₂ SO ₄	6	50	0.5212	1.02	170
161	Co-H ₂ SO ₄	6	70	0.5473	1.00	170
162	Co-H ₂ SO ₄	6	70	0.5108	1.00	170
163	Ag-HNO ₃	8	50	0.5373	1.00	170
150	Ag-HNO ₃	8	70	0.4880	1.02	165
153	Ag-HNO ₃	12	50	0.4942	1.02	165
151	Ag-HNO ₃	12	70	0.5123	1.02	165

Anode: Rotating Pt cylinder 1.2 cm dia x 1.78 cm long
 Anode rotational speed: 1500 rpm
 Separator membrane: Nafion 117

Experiments were also performed on various cellulosic substances. Experiments with reagent grade cellulose had been initiated during the previous year and continued in Fiscal Years 1993-94. The destruction of reagent grade cellulose was tested as a function of the parameters listed below. The ranges over which the parameters were varied in the experiments are also listed.

Mediator-acid: silver with nitric acid and cobalt with sulfuric acid.

Acid concentration: 4 to 10 M for nitric acid
 4 to 6 M for sulfuric acid

Temperature: 21 to 70 °C

In addition to the reagent grade cellulose, other forms of cellulose were tested. Rocky Flats sent LLNL cloth overalls and two kinds of wipes which are typical of the cellulosic material in their mixed wastes inventory. The wipes and cloth were shredded and destroyed under various conditions. For these materials only a partial matrix of tests was conducted. The mediator-acid combination used in all tests was silver-nitric acid, and only tests at higher acid concentrations (8 to 10 M nitric acid) and higher temperatures (50 to 70 °C) were performed. The complete set of tests carried out on all cellulosic materials in Fiscal Years 1993-94 is given in Table 2.

Table 2. Test Matrix for Small-Scale Experiments on Cellulosic Materials

Exp No	Material	Mediator-Acid	Acid Conc. (M)	Temp (C)	Mass (g)
173	Reag. grade	Co-H ₂ SO ₄	4	22	0.5042
174	Reag. grade	Co-H ₂ SO ₄	4	50	0.5067
177	Reag. grade	Co-H ₂ SO ₄	4	70	0.5019
175	Reag. grade	Co-H ₂ SO ₄	6	22	0.5030
176	Reag. grade	Co-H ₂ SO ₄	6	50	0.5006
178	Reag. grade	Co-H ₂ SO ₄	6	70	0.5030
164	Reag. grade	Ag-HNO ₃	4	21	0.5042
165	Reag. grade	Ag-HNO ₃	4	50	0.5018
166	Reag. grade	Ag-HNO ₃	4	70	0.5075
167	Reag. grade	Ag-HNO ₃	8	22	0.5027
168	Reag. grade	Ag-HNO ₃	8	50	0.5064
169	Reag. grade	Ag-HNO ₃	8	70	0.5055
170	Reag. grade	Ag-HNO ₃	10	22	0.5011
171	Reag. grade	Ag-HNO ₃	10	50	0.5019
172	Reag. grade	Ag-HNO ₃	10	70	0.5045
179	Wipe 1	Ag-HNO ₃	8	50	0.3011
197	Wipe 2	Ag-HNO ₃	8	50	0.4907
180	Wipe 1	Ag-HNO ₃	8	70	0.3168
198	Wipe 2	Ag-HNO ₃	8	70	0.4884
181	Wipe 1	Ag-HNO ₃	10	50	0.3141
196	Wipe 2	Ag-HNO ₃	10	50	0.4853
182	Wipe 1	Ag-HNO ₃	10	70	0.3041
195	Wipe 2	Ag-HNO ₃	10	70	0.4916
186	Cloth	Ag-HNO ₃	8	50	0.5031
187	Cloth	Ag-HNO ₃	8	70	0.5054
184	Cloth	Ag-HNO ₃	10	50	0.5010
185	Cloth	Ag-HNO ₃	10	70	0.5144

Anolyte volume: 170 mL
 Catholyte volume: 170 mL
 Anode: Rotating Pt cylinder 1.2 cm dia x 1.78 cm long
 Anode rotational speed: 1500 rpm
 Cell current: 1.00 A
 Separator membrane: Nafion 117

Rocky Flats also sent latex gloves, Tyvek laboratory coats, and polyethylene and polyvinyl chloride bags to LLNL for evaluating their destruction with the MEO process. These materials were shredded and tested under limited conditions on a few process parameters similar to those used in the testing of wipes and cloth. RFP also asked that biomass be tested for destruction. Freeze dried bacteria were used for those tests which were carried out under similar process conditions. The test matrix for the biomass, rubber and plastics experiments carried out in the small-scale facility is given in Table 3.

Table 3. Test Matrix for Small-Scale Experiments on Biomass, Rubber and Plastics

Exp No	Material	Mediator-Acid	Acid Conc. (M)	Temp (C)	Mass (g)
199	Biomass	Ag-HNO ₃	8	50	0.3690
200	Biomass	Ag-HNO ₃	8	70	0.3330
201	Biomass	Ag-HNO ₃	10	50	0.3300
202	Biomass	Ag-HNO ₃	10	70	0.3291
191	Latex	Ag-HNO ₃	8	50	0.3030
192	Latex	Ag-HNO ₃	8	70	0.3113
193	Latex	Ag-HNO ₃	10	50	0.3073
194	Latex	Ag-HNO ₃	10	70	0.3043
183	Tyvek	Ag-HNO ₃	8	50	0.4985
188	Tyvek	Ag-HNO ₃	8	70	0.3375
189	Tyvek	Ag-HNO ₃	10	50	0.3530
190	Tyvek	Ag-HNO ₃	10	70	0.3505
203	Polyethylene	Ag-HNO ₃	8	50	0.3360
204	Polyethylene	Ag-HNO ₃	8	70	0.3262
205	Polyethylene	Ag-HNO ₃	10	50	0.3039
207	Polyethylene	Ag-HNO ₃	10	70	0.3118
208	PVC	Ag-HNO ₃	8	50	0.3548

Anolyte volume: 170 mL
 Catholyte volume: 170 mL
 Anode: Rotating Pt cylinder 1.2 cm dia x 1.78 cm long
 Anode rotational speed: 1500 rpm
 Cell current: 1.00 A
 Separator membrane: Nafion 117

3.2 Bench-Scale Experiments

The bench-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 more electrode pairs. The active surface area of each electrode is 0.85 m^2 . The anode and cathode compartments are separated by Nafion 117 cation-selective membranes. The present system has the capacity of delivering up to 3000 A of limiting current at a mediator concentration of 0.5 M with a flow of 4 gpm per cell compartment. At these flow rates, the flow in the anode compartment of the cell is fully turbulent and so is the fluid in the rest of the system. The voltage drop across the cell is low as long as it is operated at or below the limiting current. Even at the maximum rated limiting current (3000 A), the cell voltage was below 2 V. When the cell was run at 2000 A the cell voltage was usually between 1.65 and 1.85 V. A schematic of the main flow loops in the bench-scale facility is shown in Figure 2.

So far only Trimsol and cellulosic materials have been destroyed using this equipment. Experiments on Trimsol are a continuation of the tests carried out in the previous year. In most

Figure 2. Schematic of bench-scale experiment

of the experiments conducted on this system, the organic was fed continuously into the anolyte. For Trimsol, the oil was metered to the anolyte piping just downstream of the reservoir. For cellulose, the material was fed directly into the anolyte reservoir. In the case of reagent grade cellulose, it was fed from a hopper to a chute leading to the reservoir. The feed rate was controlled by means of a vibrator attached to the hopper. For wipes and cloth, the material was first shredded, compacted, and loaded in a feed tube. The compacted cellulose was advanced pneumatically or with a stepper motor controlled screw drive to a set of blades where the material was sheared and fed to the chute.

Samples of the electrolyte were taken for post-test TOC analysis. Anolyte samples were taken periodically during most of the runs, and anolyte and catholyte samples were obtained at the beginning and end of all runs. All experiments were conducted with silver in nitric acid for the mediator-electrolyte combination. The experimental parameters varied were acid concentration (8 to 10 M) and electrolyte temperature (50 to 70 °C). For Trimsol, the experiments carried out in the prior year indicated that the high concentrations and temperatures resulted in optimal destruction conditions. Hence, most of the experiments with Trimsol were at an acid concentration of 10 M and a temperature of 70 °C.

In almost all of the continuous feed experiments conducted on the bench-scale system, the current to the cell and the organic feed to the anolyte were turned on at the same time and also stopped simultaneously. This results in a very conservative measure of destruction efficiency, since all but the very simplest of organics require time to be converted completely to carbon dioxide. Generally, there is not sufficient time for the organic material introduced just prior to shutting down to be destroyed. However, in some of the later continuous feed experiments, the current was kept on for a while after the feed was stopped. Samples were taken immediately after the feed was terminated and periodically thereafter until the current was switched off.

A few runs were also carried out in a batch feed mode. With reagent grade cellulose, the entire batch was introduced into the reservoir while the pumps were running. This ensured that the cellulose was dispersed throughout the anolyte when the current was switched on later. However, when Trimsol is fed *en masse* into a strong acid, the emulsifier is attacked immediately by the acid causing some of the oils to separate out and float to the surface. These oils then become difficult to destroy because of their limited contact with the mediator. Hence, for the Trimsol batch run, a mechanical mixer was placed in the anolyte reservoir to entrain the floating oils back into the bulk of the fluid. The batch of Trimsol was introduced while the pumps and the mixer were running. The test matrices for the bench-scale experiments carried out in Fiscal Years 1993-94 are shown in Tables 4 and 5 for Trimsol and cellulosic materials respectively.

Table 4. Test Matrix for Bench-Scale Experiments on Trimsol

Exp No.	Acid Conc (M)	Temp (C)	Current (A)	Mass (g)	Run Time (h:min)	Feed Rate (g/h)
ORGM	10	72	2030	354	3:14	109.5
ORGN	10	74	2035	670	4:00	167.5
ORGO	10	74	2100	595	2:40	223.1
ORG(O+P)	10	62	1754	595	3:55	151.9
ORGQ	10	75	3050	290	1:00	290.0
ORGR	12	73	2010	655	3:45	174.7
ORGAB	10	69	2135	200	1:45	Batch

Mediator: 0.5 M AgNO₃
 Anolyte volume: 15.5 L
 Catholyte volume: 17.8 L
 Anodes: Two Pt-coated Nb-expanded metal electrodes
 Anode area: 0.85 m² each
 Separator membranes: Nafion 117

Table 5. Test Matrix for Bench-Scale Experiments on Cellulosic Materials

Exp No.	Material	Acid Conc (M)	Temp (C)	Current (A)	Mass (g)	Run Time (h:min)	Feed Rate (g/h)
ORGS	Reag. Gr.	10	72	2045	771	2:00	385.5
ORGT	Reag. Gr.	10	54	2015	746	2:00	373.0
ORGU	Reag. Gr.	Pump	Failure				
ORGV	Reag. Gr.	8	54	2070	760	2:00	380.0
ORGW	Wipes 2	10	67	1315	33	0:35	56.6
ORGX	Wipes 2	10	71	2105	307	2:00	153.5
ORGY	Wipes 2	10	72	2115	761	1:50	415.1
ORGZ	Wipes 2	10	70	2125	780	2:00	390.0
ORGAA	Reag. Gr.	10	69	2135	400	1:35	Batch
ORGAC	Cloth	10	72	2130	366	2:00	183.0
ORGAD	Cloth	10	73	2135	395	1:40	237.0

Mediator: 0.5 M AgNO₃
 Anolyte volume: 15.5 L for runs ORGS-ORGU, 17.5 L for others
 Catholyte volume: 17.8 L for runs ORGS-ORGU, 40 L for run ORGAD, 19.8 L for others
 Anodes: Two Pt-coated Nb-expanded metal electrodes
 Anode area: 0.85 m² each
 Separator membranes: Nafion 117

4. Results and Discussion

The results of the destruction experiments on Trimsol, cellulose and other materials are discussed separately below.

4.1 Trimsol Results

Trimsol is a cutting oil composed of a mixture of various oils and other organics. The elemental composition of Trimsol is given in Table 6. Also shown in the table is the number of moles of each element per 100 g of Trimsol. Hence, 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

Therefore, 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 chloride ions will combine with Ag(I) to precipitate as insoluble silver chloride from the solution.

Table 6. Elemental Composition of Trimsol

Element	Percent by Weight	Atomic Weight	Moles per 100g of Trimsol
C	68.37	12.011	5.69
H	10.79	1.0079	10.71
O	7.50	15.9994	0.47
Cl	11.1	35.453	0.31
S	1.0	32.06	0.03
N	0.86	14.0067	0.06

4.1.1 Small-Scale Experiments with Trimsol

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. In general, the TOC results are more accurate and are therefore used whenever possible. However, errors with TOC measurements can arise if organic components separate and float to the top of the chamber when samples are taken. In contrast, carbon dioxide measurements are susceptible to interference from NO_x generated in the anolyte.

Examples of the experimental data obtained with the carbon dioxide monitor in conjunction with the flow rate meter is shown in Figures 3 and 4. These figures show the rate of carbon dioxide generation as a function of time for two small-scale experiments in which Trimsol was destroyed using silver in nitric acid at 70 °C. Figures 3 and 4 pertain to Experiment Nos. 150 and 151 which were conducted with 8 and 12 M acid concentration respectively. From these data, the data in Table 1, and Equation (1), the instantaneous values of coulombic and destruction efficiencies can be calculated as a function of time. Plots of these efficiencies are shown in Figures 5 and 6 for Experiment Nos. 150 and 151 respectively. In these figures, the plots for destruction and coulombic efficiencies show a typical rapid initial rise consistent with the rapid initial evolution of carbon dioxide from the anolyte. As the carbon dioxide evolution slows down and gradually goes to zero, the rise in destruction efficiency also declines and finally levels off. The coulombic efficiency meanwhile reaches a maximum and then starts to decline gradually. As expected from the results of last year's experiments, the destruction rate increases with higher acid concentration.

As shown above, destruction and coulombic efficiencies can be calculated from the carbon dioxide data for each run. The time required for destruction can also be determined. However, as is clear from Figures 5 and 6, the destruction curves tend to become asymptotic towards the end of the run, making it difficult to pinpoint the exact time at which the curves level off. A more reproducible measure is obtained by determining when 99 % of the maximum destruction occurs. The 99th percentile time, the time at which the maximum coulombic efficiency occurs, the values of coulombic efficiency at those times, and the final destruction efficiency are shown in Table 7 for all small-scale experiments conducted on Trimsol this year. TOC data are also listed in the table. TOC analysis was performed only for cases where the organic material had

Figure 3. Carbon dioxide generation rate vs. time for Trimisol: Exp. No. 150

Figure 4. Carbon dioxide generation rate vs. time for Trimisol: Exp. No. 151

Figure 5. Destruction and coulombic efficiencies vs. time for Trimsol: Exp. No. 150

Figure 6. Destruction and coulombic efficiencies vs. time for Trimsol: Exp. No. 151

Table 7. Results of Small-Scale Experiments on Trimsol: Efficiencies

Exp No.	Mediator-Acid	Acid Conc (M)	Temp (C)	Anolyte TOC (ppm)	Cathol TOC (ppm)	Max Dest Eff (%)	Max Coul Eff (%)	CE at .99 MDE (%)	Time at .99 MDE (h)	Time at MCE (h)
156	Co-H ₂ SO ₄	4	23	No TOC	No TOC	8.40	8.20	3.90	9.40	2.30
157	Co-H ₂ SO ₄	4	50	No TOC	No TOC	7.90	17.80	5.60	5.80	0.80
158	Co-H ₂ SO ₄	4	70	No TOC	No TOC	8.80	31.00	6.50	5.90	0.50
159	Co-H ₂ SO ₄	6	23	No TOC	No TOC	10.06	9.40	3.50	12.10	2.00
160	Co-H ₂ SO ₄	6	50	No TOC	No TOC	16.57	27.20	4.96	14.60	0.85
161	Co-H ₂ SO ₄	6	70	No TOC	No TOC	13.66	41.00	15.00	4.20	0.70
162	Co-H ₂ SO ₄	6	70	No TOC	No TOC	13.70	36.80	10.30	5.80	0.80
163	Ag-HNO ₃	8	50	15	36	99.29	85.27	23.27	19.50	1.70
150	Ag-HNO ₃	8	70	No TOC	No TOC	90.60	79.60	23.30	15.90	1.20
153	Ag-HNO ₃	12	50	55	116	97.15	45.78	22.40	13.60	2.20
151	Ag-HNO ₃	12	70	89	185	95.41	80.12	37.55	10.90	2.00

not separated out at the end of the run. When TOC data was available, the final destruction efficiency was calculated on the basis of those results rather than carbon dioxide data. The data in the table show that some of the organic migrates to the catholyte during the run. This does not represent a loss in destruction efficiency, since the flow sheet for the final system (see Appendix A) calls for a continuous transfer of the catholyte fluid to the anode side. Hence, the organic migrated over to the cathode side will again be subject to oxidation by the mediator.

The results given in the table and figures confirm the general trends observed in the previous year, that is, stronger oxidizing conditions result in higher efficiencies in destroying Trimsol. The silver-nitric acid combination is clearly superior to cobalt-sulfuric acid. The influence of temperature and concentration, above 50 °C and 8 M respectively, are less clear-cut since there is some scatter in the data. However, it also indicates that as long as temperatures and concentrations are above 50 °C and 8 M, respectively, these conditions do not have a strong effect on process performance.

Table 7 summarizes the Trimsol destruction data; however, it would be useful to cast the results in the form of parameters which could be used to rank the process conditions or to scale up the process. A common procedure to characterize the rate of destruction of organics is to calculate a pseudo-first order reaction rate constant for the overall reaction. This is, of course, a gross

Table 8. Results of Small-Scale Experiments on Trimsol: Rate Constants

Exp No.	Med-Acid	Acid Conc (M)	Temp (C)	k_I (1/s)	k_0' (g/s)	f_0' (%)	k_I' (1/s)
156	Co-H ₂ SO ₄	4	23	2.57E-06	1.58E-05	4.30	1.68E-06
157	Co-H ₂ SO ₄	4	50	3.90E-06	3.44E-05	3.46	2.57E-06
158	Co-H ₂ SO ₄	4	70	4.29E-06	1.02E-05	3.50	2.86E-06
159	Co-H ₂ SO ₄	6	23	2.41E-06	3.08E-06	4.39	1.65E-06
160	Co-H ₂ SO ₄	6	50	3.41E-06	8.92E-06	5.24	2.53E-06
161	Co-H ₂ SO ₄	6	70	9.61E-06	1.32E-05	6.08	6.55E-06
162	Co-H ₂ SO ₄	6	70	6.98E-06	1.18E-05	6.68	4.26E-06
163	Ag-HNO ₃	8	50	5.81E-05	2.75E-05	31.80	5.76E-05
150	Ag-HNO ₃	8	70	3.97E-05	2.61E-05	23.12	3.80E-05
153	Ag-HNO ₃	12	50	6.67E-05	1.50E-05	25.51	7.24E-05
151	Ag-HNO ₃	12	70	7.37E-05	2.63E-05	40.47	7.41E-05

approximation of the very complex reactions occurring among the many chemical species participating in the overall reaction. Nevertheless it can serve as a useful figure of merit for the process conditions. The overall first order reactions (k_I) calculated from time zero to 99 % maximum destruction are given in Table 8 for the experiments with Trimsol. Although there is a fair amount of scatter in the data, the overall trend of destruction rate as a function of process conditions is similar to the discussion above.

It should be emphasized that this rate constant cannot be used directly to scale up reaction rates since it does not represent the actual rate-limited steps in the process. During the initial part of each run, the limiting rate is governed by the useful current at the anode. That is, initially the destruction rate is proportional to the rate of oxidation of the mediator. In that case, the initial destruction should be represented by a zeroth order reaction. The zeroth order reaction rate constant should scale directly with the current, as long as it is less than or equal to the limiting current. Eventually, only the more-difficult-to-destroy organics are left in the solution and the reaction proceeds more slowly. The later destruction rates may be approximated by a simple first order reaction. As before, the first order reaction rate cannot be used directly for scale-up. The question of when the reaction changes from zeroth to first order is not clear from the data. The time at which the coulombic efficiency reaches a maximum is a convenient point, and fits intuitively with the simplified zeroth-first order model, since the coulombic efficiency should

decrease when the easy-to-destroy organics are depleted. This model then requires three parameters: the zeroth order initial rate constant (k_0), the first order rate constant (k_1), and the fraction of organic destroyed (f_0) when the rate constant changes from zeroth to first order. These parameters are included in Table 8. The fraction of organic destroyed by the zeroth order reaction is also not directly scalable. It may depend upon the rate of mixing between the mediator and organic and the likelihood of oils and other organics separating out from the bulk of the anolyte. For an efficient and rapid destruction process f_0 should be as high as possible.

It is now possible to speculate on why the performance levels off at high temperatures and acid concentrations in the small-scale experiments with silver in nitric acid. These conditions may result in faster destruction of the surfactant which keeps the Trimsol emulsified. Hence, there may be a higher tendency under these conditions to separate out the oil from the anolyte. This tendency is reflected by the values of k_0 which remain constant for most of the runs, while the values of f_0 fluctuate and in some cases even decline slightly with temperature. As was indicated by the results of last year's experiments, mixing is very important in the destruction of insoluble organics. If the oil droplets in Trimsol have an opportunity to coalesce into larger drops or an oil film, the reaction rate slows down dramatically due to the limited surface area available and the slow surface kinetics. It appears that at these conditions of higher temperature and acid concentrations, the weak mixing in the small-scale facility is about in balance with the coalescing tendency of the oils. This may also explain the fluctuations in the destruction data. It should be noted that this effect may not be very significant in a larger well-mixed system. This issue will be revisited when the bench-scale system results are discussed.

4.1.2 Bench-Scale Experiments with Trimsol

The results of the bench-scale experiments conducted this year with Trimsol are shown in Table 9. In these experiments, the total destruction efficiency was calculated from the amount of organic added and the pre- and post-test TOC levels in the electrolyte. As explained earlier, this results in conservative values of the destruction efficiency. In some cases, when insoluble organics remained in the electrolyte after the run they were removed and weighed, and assessed against the destruction efficiency. Also, in the runs with continuous organic feed (which comprise most of the tests on the bench-scale system), the cell current was synchronous with the organic feed. This also tends to give lower values of destruction efficiency, especially for short runs.

The best conditions for destruction of continuously-fed Trimsol in the bench-scale experiments were established in tests conducted last year. It was found that high oxidation conditions, that is,

Table 9. Results of Bench-Scale Experiments on Trimsol

Exp No.	Pre Anol TOC (ppm)	Pre Cath TOC (ppm)	Post Anol TOC (ppm)	Post Cath TOC (ppm)	Rem Mat'l (g)	Coul Eff (%)	Dest Eff (%)	k_0' (g/s)	k_0'/I (g/s-A)
ORGM	27	0	60	37		46.35	99.79	3.03E-02	1.49E-05
ORGN	19	20	177	31		70.67	99.47	4.63E-02	2.27E-05
ORGO	3	30	535	39	10	88.32	96.29	5.97E-02	2.84E-05
ORG(O+P)	3	30	64	64	10	73.26	98.08	4.14E-02	2.36E-05
ORGQ	56	31	546	50		78.83	96.16	7.75E-02	2.54E-05
ORGR	38	29	601	44		73.54	98.05	4.76E-02	2.37E-05
ORGAB	0	10	19	20		80.58	99.76	5.54E-02	2.60E-05
ORGAB	0	10	2	20		46.15	99.97		

high silver(II) generation rates, acid concentrations and temperatures, resulted in highest destruction efficiencies. Consequently, most of this year's experiments were performed at these conditions with only a few exceptions. The focus of this year's effort was to determine how the coulombic efficiency could be improved without significantly degrading the destruction efficiency. Within certain limits, the coulombic efficiency in a continuous feed system can be increased by merely increasing the organic feed rate for a given current. In the first three experiments of this year (runs ORGM through ORGO), the feed rate was gradually increased in each run, while the current and other conditions were kept approximately invariant. It is seen from Table 9 that it was possible to increase the coulombic efficiency from about 45 to 70 % and still maintain destruction efficiencies well above 99 %. However, the attempt to increase the coulombic efficiency to 88 % resulted in the destruction efficiency dropping to about 96 %.

In the last run of that series (ORGO), some material floated to the top of the anolyte reservoir and formed a scum on the surface. The experiment was continued the next day (as run ORGP) without adding any additional organic material, to see if the residual material could be destroyed and to determine the overall coulombic and destruction efficiencies for the combined runs. As seen from Table 9, the overall coulombic efficiency dropped to 73 % and the destruction efficiency increased to 98 %. Generally, it is undesirable to allow the formation of scum on the surface of the anolyte, because once formed it is difficult to destroy. Two methods, or combinations thereof, can be used to prevent this. The first is to operate the system at conditions of high destruction efficiency, such as in ORGM and ORGN, so that the organics are destroyed

before they have a chance to coalesce. The second is to use a mechanical mixer in the reservoir which entrains the floating material back into the anolyte and re-emulsifies it. The second approach was tried in an experiment conducted in the batch-feed mode which will be discussed later.

Two other experiments were performed in the continuous-feed mode. Run ORGQ was conducted at higher cell current and higher Trimsol feed rates. Run ORGR was conducted at higher acid concentration. In both of these run problems were experienced with the power conditioner for the power supply. There were fluctuations in power during the runs and the power supply abruptly turned off at the end of one of the runs. The results of these two runs are presented in Table 9 but should not be considered to be definitive.

As with the results of the small-scale experiments, the destruction rates on the bench-scale experiment can be cast in the form of rate constants. For the continuous-feed experiments, a zeroth order rate constant (k_0) makes sense and can be easily computed from the data. The rate constant is given in Table 9. Since it was surmised earlier that this rate constant would be proportional to the current, the rate constant divided by the current (k_0/I) is given in the table and can be compared directly with the values of k_0' in Table 8, since those experiments were conducted at approximately 1 A of current. It is interesting that the values of k_0/I are around 2.5×10^{-5} g/(s-A) for most of the experiments, although the tests were conducted on apparatus which differ in their current capacity by over three orders of magnitude.

One batch-fed experiment (run ORGAB) was carried out with 200 g of Trimsol. A mechanical mixer was installed in the anolyte reservoir to keep the mixture emulsified and prevent separation of the oils. The anolyte remained milky during the initial phase of the run since the dark colored silver(II) was consumed immediately by the excess Trimsol. After one hour the fluid had turned completely black indicating an excess of silver(II). At that point the anolyte contained 19 mg/l (ppm) of organic carbon. The run continued for another 45 minutes by which time the organic carbon content dropped to 2 ppm. In Table 9, the results of this run are listed in two entries: the first pertains to the first hour of the run, and the second accounts for the entire run. Coulombic and destruction efficiencies are calculated for each entry. Comparing these results to those of runs ORGM and ORGN, it is seen that destruction and coulombic efficiencies show small but significant improvements over the earlier runs. The mechanical mixer, which also served as a homogenizer, could be responsible for these increases since it may have reduced the size of the oil particles. Moreover the mixer prevents oil from floating and staying at the top of the

reservoir. It would be prudent to incorporate such a device into the system for destruction of insoluble organics.

In terms of rate constants, this run can be divided into zeroth-order and first-order phases, as was done in the small-scale experiments. Taking the first hour as the initial phase, the zeroth order rate (k_0) constant is calculated to be $5.54\text{E-}02$ g/s. This yields a rate constant per unit current (k_0/I) of $2.6\text{E-}05$ g/(s-A), which is very close to the earlier small-scale and bench-scale results. The first order rate constant (k_1) for the later phase is $8.73\text{E-}04$ 1/s, which is over an order of magnitude higher than the values from the small-scale experiments. However, as explained earlier, it is difficult to scale this rate constant. Another factor which is difficult to scale is the fraction destroyed by the zeroth order reaction (f_0). In this case, f_0 is synonymous with the destruction efficiency at 1 hour, which is 99.76 %. This is far above the values of 25 to 40 % obtained in the small-scale experiments. Obviously, better mixing in the bench-scale equipment, coupled with the mixing by the homogenizer, results in a very large fraction of the organics being destroyed by the efficient zeroth-order current-limited reactions. Finally, it should be noted that this batch process yielded a final total destruction efficiency of 99.97 %, that is all but 0.03 % of the original carbon in Trimsol was completely mineralized.

4.2 Cellulose Results

Cellulose consists of a carbohydrate molecule with a chemical formula $(\text{C}_6\text{H}_{10}\text{O}_5)_x$. The basic unit, $\text{C}_6\text{H}_{10}\text{O}_5$, has a molecular weight of 162 g/mole, and the amount of Ag(II) required to completely oxidize it is given by

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

Elemental analysis was carried out for the cellulosic materials sent by Rocky Flats Plant, that is, two kinds of wipes and cloth from overalls. It was found that they all had the same basic chemical composition as pure cellulose. However, due to possible differences in the size of fibers and the carbohydrate chain, the different materials are listed separately in the results tables. The two types of wipes are lumped together, but the type of wipe used in the tests is identified.

4.2.1 Small-Scale Experiments with Cellulose

In the small-scale experiments with cellulose, the material was fed in a batch mode, and the carbon dioxide evolution was measured continuously. The rate of carbon dioxide generation as a function of time is shown as examples in Figures 7, 8 and 9, for Experiment Nos. 166, 169 and 172, respectively. These refer to experiments in which reagent grade cellulose was destroyed with silver in nitric acid at 70 °C, at acid concentrations of 4, 8 and 10 M. The corresponding destruction and coulombic efficiencies are shown in Figures 10, 11 and 12. These data can be summarized by noting the maximum coulombic and destruction efficiencies, the times at which they occur, and the coulombic efficiency at maximum destruction efficiency. As with the Trimsol data, it is difficult to describe exactly when the destruction efficiency curve has reached a maximum. Hence, the point at which 99 % of the maximum destruction efficiency occurs was selected to obtain reproducible results. The data for all cellulosic material summarized in this manner are shown in Table 10. The TOC data are also shown. In general, for cellulose the TOC data were considered more reliable than the carbon dioxide data, and hence were used to calibrate the carbon dioxide data.

The data in Table 10 show the effect of mediator-acid combination, acid concentration and temperature on destruction of reagent grade cellulose. For this material, these parameters do not appear to have a major effect on destruction efficiency. However, in general the coulombic efficiency is much better with the silver-nitric acid combination, and increases somewhat with acid concentration and temperature, although the trend is a little irregular because of the scatter in the data. The wipes and cloth were tested only with the silver-nitric acid combination at high acid concentration and temperatures. Compared to reagent grade cellulose, both the coulombic and destruction efficiencies decreased for wipes, and decreased further for cloth. The effect of acid concentration and temperature was marginal in the limited range tested. The lower efficiencies can be attributed to the longer fibers in wipes as compared to reagent grade cellulose, and even longer fibers in cloth.

The cellulose data can be compiled in the form of rate constants as was the Trimsol data. As before, a simple pseudo-first order reaction rate constant can be calculated from the initial conditions and those at the 99 % maximum destruction point. The value of this rate constant is tabulated in the column titled k_1 in Table 11. The destruction of cellulose can also be broken down into an initial zeroth order reaction, which would be directly dependent on the useful current, followed by a slower first order reaction. The breakpoint for the change in reaction rates was selected to be the time at which the coulombic efficiency reached a maximum. (See Section 4.1.1 for a detailed discussion). The zeroth order reaction rate constant (k_0), the subsequent first

Figure 7. Carbon dioxide generation rate vs. time for cellulose: Exp. No. 166

Figure 8. Carbon dioxide generation rate vs. time for cellulose: Exp. No. 169

Figure 9. Carbon dioxide generation rate vs. time for cellulose: Exp. No. 172

Figure 10. Destruction and coulombic efficiencies vs. time for cellulose: Exp. No. 166

Figure 11. Destruction and coulombic efficiencies vs. time for cellulose: Exp. No. 169

Figure 12. Destruction and coulombic efficiencies vs. time for cellulose: Exp. No. 172

Table 10. Results of Small-Scale Experiments on Cellulose: Efficiencies

Exp No.	Material	Mediator	Acid Conc (M)	Temp (C)	Anol TOC (ppm)	Cathol TOC (ppm)	Max Dest Eff (%)	Max Coul Eff (%)	CE at .99 MDE (%)	Time at .99 MDE (h)	Time at MCE (h)
173	Reag. gr.	Co	4	22	42	1	96.81	34.37	10.66	18.10	2.80
174	Reag. gr.	Co	4	50	13	4	99.02	51.25	11.12	17.70	1.40
177	Reag. gr.	Co	4	70	1	3	99.92	72.29	13.96	14.10	1.10
175	Reag. gr.	Co	6	22	1	10	99.92	30.32	18.38	10.70	4.40
176	Reag. gr.	Co	6	50	7	10	99.46	57.38	31.54	6.20	1.30
178	Reag. gr.	Co	6	70	3	13	99.77	75.78	38.63	5.10	1.65
164	Reag. gr.	Ag	4	21	0.1	25.8	99.99	58.82	43.04	4.60	2.00
165	Reag. gr.	Ag	4	50	13	20.7	98.99	64.37	26.85	7.30	1.10
166	Reag. gr.	Ag	4	70	8.3	26.3	99.36	79.72	20.81	9.60	0.90
167	Reag. gr.	Ag	8	22	5.2	51.6	99.59	87.34	45.51	4.30	1.40
168	Reag. gr.	Ag	8	50	6.3	42.7	99.51	69.15	15.84	12.50	1.35
169	Reag. gr.	Ag	8	70	19.8	31.6	98.47	84.67	35.80	5.50	1.50
170	Reag. gr.	Ag	10	22	7	50	99.44	55.73	41.86	4.70	2.90
171	Reag. gr.	Ag	10	50	15	106	98.76	81.66	39.19	5.00	1.50
172	Reag. gr.	Ag	10	70	193	58	84.69	75.73	60.16	2.80	1.90
179	Wipe 1	Ag	8	50	10	92	98.56	66.61	31.17	3.70	1.40
197	Wipe 2	Ag	8	50	60	29	95.21	71.56	45.46	4.00	2.30
180	Wipe 1	Ag	8	70	15	53	98.07	82.24	62.62	1.95	1.30
198	Wipe 2	Ag	8	70	29	42	97.65	84.34	50.97	3.70	2.00
181	Wipe 1	Ag	10	50	18	31	97.72	65.85	42.19	2.90	1.50
196	Wipe 2	Ag	10	50	29	23	97.67	74.83	67.18	2.80	2.40
182	Wipe 1	Ag	10	70	44	59	94.02	56.27	30.84	3.60	1.80
195	Wipe 2	Ag	10	70	40	60	96.74	81.28	51.41	3.60	2.10
186	Cloth	Ag	8	50	36	119	96.99	80.68	39.41	4.90	1.80
187	Cloth	Ag	8	70	73	33	94.33	83.03	26.29	7.10	1.50
184	Cloth	Ag	10	50	39	59	96.88	76.94	23.74	8.00	1.80
185	Cloth	Ag	10	70	51	86	95.95	82.72	24.45	7.90	1.80

Table 11. Results of Small-Scale Experiments on Cellulose: Rate Constants

Exp No.	Material	Media- tor	Acid Conc (M)	Temp (C)	kI (1/s)	k _o ' (g/s)	f _o ' (%)	kI' (1/s)
173	Reag. gr.	Co	4	22	4.88E-05	2.41E-05	48.16	4.58E-05
174	Reag. gr.	Co	4	50	6.16E-05	3.59E-05	35.81	5.93E-05
177	Reag. gr.	Co	4	70	8.93E-05	5.06E-05	40.03	8.59E-05
175	Reag. gr.	Co	6	22	1.18E-04	2.12E-05	67.37	1.50E-04
176	Reag. gr.	Co	6	50	1.87E-04	4.02E-05	37.85	2.10E-04
178	Reag. gr.	Co	6	70	2.40E-04	5.31E-05	63.29	2.74E-04
164	Reag. gr.	Ag	4	21	2.78E-04	4.12E-05	59.99	3.93E-04
165	Reag. gr.	Ag	4	50	1.49E-04	4.51E-05	36.14	1.55E-04
166	Reag. gr.	Ag	4	70	1.19E-04	5.58E-05	36.36	1.17E-04
167	Reag. gr.	Ag	8	22	2.75E-04	6.12E-05	63.82	3.11E-04
168	Reag. gr.	Ag	8	50	9.35E-05	4.84E-05	48.02	8.85E-05
169	Reag. gr.	Ag	8	70	1.86E-04	5.93E-05	64.89	1.83E-04
170	Reag. gr.	Ag	10	22	2.46E-04	3.90E-05	84.53	3.55E-04
171	Reag. gr.	Ag	10	50	2.11E-04	5.72E-05	66.93	2.14E-04
172	Reag. gr.	Ag	10	70	1.81E-04	5.30E-05	75.20	1.32E-04
179	Wipe 1	Ag	8	50	2.79E-04	4.66E-05	88.41	1.89E-04
197	Wipe 2	Ag	8	50	1.98E-04	5.01E-05	86.52	1.40E-04
180	Wipe 1	Ag	8	70	5.04E-04	5.76E-05	90.89	4.87E-04
198	Wipe 2	Ag	8	70	2.56E-04	5.91E-05	90.03	1.79E-04
181	Wipe 1	Ag	10	50	3.28E-04	4.61E-05	82.38	3.35E-04
196	Wipe 2	Ag	10	50	3.38E-04	5.24E-05	95.01	2.87E-04
182	Wipe 1	Ag	10	70	2.06E-04	3.94E-05	90.69	4.58E-05
195	Wipe 2	Ag	10	70	2.44E-04	5.69E-05	91.81	1.22E-04
186	Cloth	Ag	8	50	1.83E-04	5.65E-05	80.01	1.45E-04
187	Cloth	Ag	8	70	1.06E-04	5.81E-05	63.72	8.45E-05
184	Cloth	Ag	10	50	1.11E-04	5.39E-05	72.97	8.46E-05
185	Cloth	Ag	10	70	1.05E-04	5.79E-05	77.95	6.75E-05

order reaction rate constant (k_I), and the fraction of organic destroyed by the zeroth order reaction (f_o), are given in Table 11. Note that the high values of k_o' are around $5.0E-05$ g/s, which are roughly double the corresponding values for Trimsol.

4.2.2 Bench-Scale Experiments with Cellulose

The results of the bench-scale experiments conducted in Fiscal Years 1993-94 are summarized in Table 12. In the continuous-feed runs with reagent grade cellulose, the purpose of the tests (runs ORGS, ORGT and ORGV) was to see the effect of changes in temperature and acid concentration on performance. From the table it is seen that a drop in temperature from about 70 to 50 °C results in a small decrease in coulombic efficiency and a slight decrease in destruction efficiency. Keeping the temperature at around 50 °C and dropping the acid concentration from 10 to 8 M results in very small further decreases in the efficiencies.

Run ORGU is not listed in the table since a pump failure occurred during this run causing a shut down of the system. New pumps were installed and changes were made to the inlet piping to increase the net positive suction head. Also, going from continuously fed reagent grade cellulose to shredded wipes proved to be problematic initially since feed was pneumatically controlled.

Table 12. Results of Bench-Scale Experiments on Cellulose

Exp No.	Pre Anol TOC (ppm)	Pre Cath TOC (ppm)	Post Anol TOC (ppm)	Post Cath TOC (ppm)	Rem Mat (g)	Coul Eff (%)	Dest Eff (%)	k_o' (g/s)	k_o'/I (g/s-A)
ORGS	31	7	137	29	1.9	74.22	99.27	1.06E-01	5.20E-05
ORTG	31	60	0.4	6.5	7.4	72.77	99.01	1.03E-01	5.09E-05
ORGV	1	5	36	5	6.3	72.16	98.99	1.04E-01	5.05E-05
ORGW	1	12	1	12	3.8	15.12	88.48	1.39E-02	1.06E-05
ORGX	1	11	36	12	2.4	28.60	98.77	4.21E-02	2.00E-05
ORGY	6	55	240	55	8.9	76.08	97.62	1.13E-01	5.32E-05
ORGZ	0	8	130	12		72.38	99.34	1.08E-01	5.06E-05
ORGZ	0	8	5	12		48.56	99.97		
ORGAA	0	1	25	7		88.99	99.75	1.33E-01	6.23E-05
ORGAA	0	1	20	7		46.86	99.80		
ORGAC	2	2	15	8		34.04	99.79	5.08E-02	2.38E-05
ORGAD			3	0.1		44.06	99.97	6.58E-02	3.08E-05

Changing over to a stepper motor-controlled feed system provided a much more uniform feed rate. Runs ORGW and ORGX were conducted with the pneumatic feed and are listed in Table 12 for completeness, but the data from those runs are not very useful since the feed rate was erratic. All tests from run ORGW onwards were conducted with 10 M nitric acid and at 70 °C.

The last two tests with wipes, runs ORGY and ORGZ, were conducted with the new feed system. In run ORGZ, the feed was terminated after 2 hours, but the current was kept on for an additional hour. The two entries in Table 12 for this run refer to results at the end of 2 and 3 hours of testing. Then in run ORGAA, 400 g of reagent grade cellulose was fed in a batch mode. Samples were taken 50 minutes after the start of the run and also when the run was terminated after 1 hour and 35 minutes of current delivery to the cell. The two entries for run ORGAA in the table refer to the results at these times.

Finally, two tests with cloth, runs ORGAC and ORGAD, were conducted with continuous feed. Since the cloth was shredded very finely – almost to the consistency of cotton wool – it compacted to a much greater degree than the wipes in the feeder tube. Hence, the feed rates for those runs were lower than planned.

The results of the continuous (and uniform) feed runs with wipes are similar to comparable runs with reagent grade cellulose. The destruction efficiency increases in the batch-feed runs, especially for longer run times. However, this is accompanied by a substantial decrease in coulombic efficiency. The results of the runs with cloth are similar to the batch tests with reagent grade cellulose and wipes at longer run times, since the average feed rate in all of those cases are comparable. The small differences in destruction efficiencies in the small-scale tests between different kinds of cellulose, attributed to fiber length, are not apparent here. This is probably due to better mixing and shear in the bench-scale system. The overall result is that total destruction efficiency of higher than 99 % can be readily attained with a coulombic efficiency of about 70 % or higher, but to approach 99.99 % total destruction efficiency will require a drop in coulombic efficiency to around 45 %.

The results of the bench-scale tests with cellulose can also be formulated in terms of rate constants. The zeroth order rate constants (k_0) for both batch and continuous feed tests are included in Table 12. To compare these with the results of the small-scale experiments, the value of the rate constant divided by the current (k_0/I) is given, since k_0 is presumably directly proportional to the current (if the current is less than or equal to the limiting current). The values of k_0/I can be compared directly with the values of k_0' in Table 11, since the current in the small-

scale runs is close to 1 A. It is seen that in both cases the values of k_0/I under optimal destruction conditions ranges between 5. E-05 and 6. E-05 g/(s-A). This correspondence between the small-scale and bench-scale experiments is remarkable considering the vastly different setups and scale-up factor of 2000 in current. The fraction of organic at the end of the zeroth order reaction (f_0) is given by the destruction efficiency at the end of the run or initial phase of a batch run. This value is usually in the high 90's percent for the bench-scale system, but the discrepancy between the values of f_0 for the small and bench scale systems is not as high as it was for Trimsol. This is probably due to the fact that mixing and shearing of the organics is very important in the case of Trimsol and less so for cellulose.

4.2 Biomass, Rubber and Plastics Results

These materials were tested only in the small-scale system. Prior to testing, samples of the materials were sent out for elemental analysis. Their elemental composition, along with the number of moles of each major element per 100 g of organic, is given in Table 13. With this information, the number of moles of electrons to completely destroy 100 g of the organic and the amount of carbon dioxide produced can be determined, and is given in Table 14. The procedure

Table 13. Elemental Composition of Biomass, Rubber and Plastics

	C	H	O	N	Cl	P	S
<u>Bacteria</u>							
Percent by Weight	48.07	6.79	29.00	10.35		1.21	
Moles per 100 g	4.00	6.74	1.81	0.74		0.04	
<u>Latex</u>							
Percent by Weight	79.06	10.08	1.85	0.30			1.70
Moles per 100 g	6.58	10.00	0.12	0.02			0.05
<u>Tyvek</u>							
Percent by Weight	83.39	14.18	1.14	0.21			
Moles per 100 g	6.94	14.07	0.07	0.02			
<u>Polyethylene</u>							
Percent by Weight	83.85	14.04	1.87	0.24			
Moles per 100 g	6.98	13.93	0.12	0.02			
<u>Polyvinyl Chloride</u>							
Percent by Weight	50.26	6.53	5.45	0.10	37.52		
Moles per 100 g	4.18	6.48	0.34	0.01	1.06		

Table 14. Current Requirements for Biomass, Rubber and Plastics

Organic	Moles of Electrons per 100g	Moles of CO ₂ per 100g
Bacteria	23.02	4.00
Latex	36.41	6.58
Tyvek	41.69	6.94
Polyethylene	41.61	6.98
Polyvinyl Chloride	21.46	4.18

consists of writing a balanced reaction showing complete oxidation of the material by the mediator, similar to that described earlier for Trimsol and cellulose. Comparisons of the actual current used and carbon dioxide produced versus the theoretical values yield the coulombic and destruction efficiencies for the process. Results from TOC analyses were also used when available to calibrate the destruction efficiencies based on the carbon dioxide data.

4.2.1 Small-Scale Experiments with Biomass, Rubber and Plastics

A limited number of experiments were carried out with these materials. Specifically, the silver-nitric acid combination was the only one tested. Also, the tests were conducted only at 8 and 10 M nitric acid concentration and at temperatures of 50 and 70 °C. The results of the small-scale experiments on bacteria, latex, Tyvek, polyethylene and polyvinyl chloride are shown in Tables 15 and 16. Table 15 gives the maximum destruction and coulombic efficiencies and the times at which they occur. Table 16 gives the rate constants including a simple overall first order rate constant (k_1); and the more complex model: the zeroth order rate constant (k_0) up to the time of maximum coulombic efficiency, the percentage of organic destroyed (f_0) up to that time, and the first order rate constant (k_1') beyond that time. (See Section 4.1.1 for a detailed discussion).

From Table 15 it can be seen that with the exception of polyvinyl chloride, the other materials are readily destroyed with maximum destruction efficiencies of 95 % and above. It is also seen that with bacteria, and to a lesser degree with latex, the maximum coulombic efficiencies are very high, approaching and at times even exceeding 100 %. Coulombic efficiencies higher than the theoretical maximum are due to oxidation of organics by reagents other than the mediator. Since nitric acid is also an oxidizer, some of the breakdown and destruction of organics takes

Table 15. Results of Small-Scale Experiments on Biomass, Rubber and Plastics: Efficiencies

Exp No.	Material	Mediator	Acid Conc (M)	Temp (C)	Anol TOC (ppm)	Cathol TOC (ppm)	Max Dest Eff (%)	Max Coul Eff (%)	CE at .99 MDE (%)	Time at .99 MDE (h)	Time at MCE (h)
199	Biomass	Ag	8	50	30	12	97.09	98.89	50.69	4.30	1.80
200	Biomass	Ag	8	70	29	53	96.74	105.4	67.01	2.90	1.60
201	Biomass	Ag	10	50	42	44	95.28	85.63	43.76	4.40	1.70
202	Biomass	Ag	10	70	31	76	96.37	102.3	52.53	3.70	1.60
191	Latex	Ag	8	50	39	120	96.97	27.44	14.91	19.00	5.90
192	Latex	Ag	8	70	22	34	98.44	99.00	61.52	4.80	1.90
193	Latex	Ag	10	50	85	26	93.94	38.58	24.66	11.30	4.30
194	Latex	Ag	10	70	68	98	94.84	92.05	45.35	6.10	2.20
183	Tyvek	Ag	8	50	44.5	23	98.16	51.34	32.13	16.90	5.80
188	Tyvek	Ag	8	70	33	23	97.98	51.06	25.69	14.20	4.30
189	Tyvek	Ag	10	50	59	109	96.36	56.96	32.27	11.70	3.70
190	Tyvek	Ag	10	70	37	81	97.74	61.40	30.82	12.30	4.20
203	Polyeth	Ag	8	50	0.6	1.4	99.96	17.15	13.88	26.70	19.90
204	Polyeth	Ag	8	70	0.6	1.2	99.96	37.02	30.02	14.60	9.70
205	Polyeth	Ag	10	50	35.28	40.48	97.58	25.77	19.87	16.50	10.70
207	Polyeth	Ag	10	70	28.23	49.03	98.10	45.70	34.41	9.90	6.10
208	PVC	Ag	8	50	No TOC	No TOC	20.80	8.80	3.76	11.20	1.76

place due to reactions with the acid, which elevates the efficiency calculated on the basis of mediator reactions alone. By the end of the test (that is, when destruction efficiency has reached 99 % of its maximum) the overall coulombic efficiencies are in the range of 45 to 50 %. These are comparable to the values obtained in the small-scale tests with cellulose.

With Tyvek and polyethylene (which incidentally have similar elemental compositions), the maximum coulombic efficiencies are in the range of 45 to 60 %. The overall coulombic efficiencies (at 99 % maximum destruction efficiency) were in the range of 30 to 35 %. These values are close to the Trimsol small-scale test results.

The only material tested that performed very poorly, both in terms of destruction and coulombic efficiencies, was polyvinyl chloride. The maximum destruction efficiency was 20 % and the

**Table 16. Results of Small-Scale Experiments on Biomass, Rubber and Plastics:
Rate Constants**

Exp No.	Material	Mediator	Acid Conc (M)	Temp (C)	k_I (1/s)	k_0' (g/s)	f_0' (%)	k_I' (1/s)
199	Biomass	Ag	8	50	2.10E-04	4.46E-05	79.17	1.87E-04
200	Biomass	Ag	8	70	3.03E-04	4.75E-05	87.06	2.39E-04
201	Biomass	Ag	10	50	1.81E-04	3.86E-05	75.11	1.52E-04
202	Biomass	Ag	10	70	2.31E-04	4.61E-05	87.92	1.28E-04
191	Latex	Ag	8	50	4.71E-05	7.82E-06	59.91	4.89E-05
192	Latex	Ag	8	70	2.13E-04	2.82E-05	63.47	2.55E-04
193	Latex	Ag	10	50	6.54E-05	1.10E-05	56.39	7.26E-05
194	Latex	Ag	10	70	1.27E-04	2.62E-05	73.34	1.05E-04
183	Tyvek	Ag	8	50	5.87E-05	1.28E-05	54.01	6.99E-05
188	Tyvek	Ag	8	70	6.86E-05	1.27E-05	59.10	7.33E-05
189	Tyvek	Ag	10	50	7.31E-05	1.42E-05	57.08	7.75E-05
190	Tyvek	Ag	10	70	7.75E-05	1.53E-05	69.17	7.73E-05
203	Polyethylene	Ag	8	50	4.75E-05	4.28E-06	91.27	8.71E-05
204	Polyethylene	Ag	8	70	8.69E-05	9.23E-06	98.89	3.97E-06
205	Polyethylene	Ag	10	50	5.70E-05	6.43E-06	83.70	7.51E-05
207	Polyethylene	Ag	10	70	9.96E-05	1.14E-05	82.90	1.30E-04
208	PVC	Ag	8	50	5.72E-06	4.25E-06	7.60	1.40E-04

maximum coulombic efficiency was about 8 %. However, there was only one test performed on this material, and it was conducted at with 8 M nitric acid at 50 °C. It is not clear whether more aggressive electrolyte conditions, and greater mixing and shear would significantly improve the effectiveness of this process for destroying PVC.

The rate constants follow the general trends of destruction and coulombic efficiencies. The zeroth order rate constant (which scales with the current) is highest for bacteria, followed by latex, then by Tyvek and finally by polyethylene and polyvinyl chloride. It should be noted that although k_0' is about the same for polyethylene and polyvinyl chloride at the same test conditions, f_0' is an order of magnitude lower for PVC. Hence, although the initial destruction rates for both plastics are similar, the point at which PVC switches to the slower first order reaction is much sooner than it is for polyethylene.

Although these materials were not tested in the bench-scale system, an indication of their behavior in a larger system may be obtained by their values of the zeroth order rate constant, k_0' . From the results of the tests with Trimsol and cellulose, k_0' scaled with cell current from the small-scale to the bench-scale system. Also, in the bench-scale system, with its high levels of shear, mixing and turbulence, the destruction rate is almost completely governed by k_0' . Comparing the optimal values of k_0' of these materials with those for Trimsol and cellulose, it is seen that the rates for biomass and cellulose are very close, while the rate for Tyvek is close to Trimsol. Hence, it may be expected that in a larger scale system, the rates of destruction of biomass will be similar to cellulose, and Tyvek to Trimsol. Latex will fall in between biomass and Tyvek, and polyethylene should be destroyed at a slightly slower rate than Trimsol.

5. Conclusions

The Mediated Electrochemical Oxidation (MEO) process is capable of achieving very high total destruction efficiencies and reasonably high coulombic efficiencies for both Trimsol and cellulose. Destruction of these organics was demonstrated in a large industrial-sized cell equipped with full-scale electrodes. For both materials, total destruction efficiencies above 99 % can be obtained with coulombic efficiencies of 70 %. Total destruction efficiencies as high as 99.97 % have been achieved for both, with coulombic efficiencies of 45 %. The total destruction efficiency referred to here is the complete conversion of organic carbon to carbon dioxide.

For Trimsol, the best results were obtained when chemically, high oxidation conditions prevailed, and mechanically, high mixing and shear conditions were present. The high oxidation conditions require a silver-nitric acid combination for the mediator and electrolyte, 8 to 10 M nitric acid concentration, and 50 to 70 °C system temperature. The high mixing and shear conditions require fully turbulent flow throughout the system and a homogenizer/mixer in the reservoir or anywhere the oil can separate out and float to the surface.

For cellulose, the best results were again obtained at high oxidation conditions, but these conditions did not have a very strong influence on performance as with Trimsol. Hence, weaker mediator-acid combinations, such as cobalt in sulfuric acid, and lower temperatures and acid concentrations can be used with only a small effect on the efficiencies. Since cellulose does not coalesce, shear is not as important, but the cellulose must be kept slurried to prevent settling. This will require turbulent flow in the system. Also the flow must be turbulent in the cell so it can deliver its rated limiting current.

It is important that the cell is operated at the limiting current so that electrical current will not be wasted in generating oxygen at the anode. Cells operated at higher than limiting current will not only result in poor coulombic efficiency, but will increase the cell voltage, resulting in high power consumption. The cell voltage drop should not be much greater than 2 V.

Other organics of interest to RFP were destroyed at LLNL in the small-scale system. These include material from latex gloves, Tyvek laboratory coats, plastic bags of polyethylene and polyvinyl chloride, and biomass (bacteria). The tests indicated that all of these materials, with the exception of polyvinyl chloride, can be destroyed with destruction efficiencies above 95 % and reasonable coulombic efficiencies.

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Appendix A

Conceptual Design for MEO System

This section presents a conceptual flowsheet for an integrated MEO system based on silver as mediator and nitric acid as electrolyte. It includes secondary processes to regenerate the reagents and remove secondary wastes. Prior to presenting the flowsheet, the electrochemical and mediated reactions that occur in the process are reviewed. These reactions indicate the requirements for the secondary processes.

At the anode, silver in the form of Ag(I) is oxidized to Ag(II) at a redox potential of 1.98 V with respect to a standard hydrogen electrode:

The high redox potential allows the Ag(II) to attack organics converting the organic carbon to carbon dioxide. For example, for benzene:

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, plutonium dioxide is notoriously difficult to dissolve completely even in strong solutions of nitric and hydrofluoric acids. However, Ag(II) very efficiently dissolves plutonium dioxide by converting it to a plutonyl ion:

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 which achieves very high efficiencies in a small volume. 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 (A-5) shows that water is generated on the cathode side. Although water is broken down on the anode side as shown in reactions (A-2) and (A-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 a thin film 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 is 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 polymerization.

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.

Figure A-1. Functional flowsheet for integrated MEO system

From the above discussion, it is apparent that the MEO primary (electrochemical) process must have 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 A-1. This flowsheet also shows the secondary waste generated and suggests further treatments that may be required before they are discharged or disposed.

A more detailed conceptual process flowsheet indicating the major equipment required for the integrated MEO system is shown in Figure A-2. The major subsystems (primary, acid recovery and silver recovery) are labeled. Note that the nitrous acid converter is included in the primary system in the catholyte flow loop. Some preliminary flow and sizing calculations have been performed for this system. They are discussed below.

Primary System

The electrochemical reactor is a 65 kW unit consisting of 16 divided cells with 1 m² electrodes running at a current density of 2000 A/m² and a voltage drop of 2 V per cell. At a coulombic efficiency of 70 %, this cell would destroy approximately 2.5 kg/h of cutting oil or 5.5 kg/h of cellulosic wastes. The anolyte consists of 10 M nitric acid with 0.5 M silver nitrate. The catholyte is 6 M nitric acid. Both electrolytes are maintained at 70 C by means of heat exchangers (not shown). The pumps for the anolyte and catholyte loops are capable of delivering 75 gpm each. The volumes of anolyte and catholyte in the system are approximately 200 and

300 liters respectively. The turbo-aerator to convert nitrous acid has a 7 inch diameter rotor turning at 1140 rpm. At that rate it will convert 98 % of the nitrous acid generated back into nitric acid.

Acid Recovery System

In order to maintain acid concentrations in the primary system, the water generated by the oxidation of organics must be removed. Although there is a net gain, from reactions (A-2), (A-3) and (A-5) shown above, it is seen that water is consumed in the anolyte and generated in the catholyte. Since some of the organics in the anolyte pass through the divider (even if the divider is a cationic membrane), these organics need to be destroyed. One way to accomplish this is to continuously bleed the catholyte (at approximately 1 L/min) into the anolyte. The catholyte can be pumped directly into the anolyte reservoir, but as discussed below, it is preferable to pump it into the thin film evaporator bottoms tank and from there to the anolyte reservoir.

The water in the primary system is removed by feeding a small portion of the anolyte (approximately 0.6 L/min) to the thin film evaporator. The anolyte is first passed through a centrifuge to remove silver chloride and other insoluble material from the stream. On reaching the 80,000 Btu/h (23 kW) thin film evaporator, most of the fluid is evaporated and the vapor is separated into water and concentrated nitric acid by means of a fractionator. A 10 stage fractionator would be capable of separating the vapor into nitric acid at 13 M and water at a pH of 4. The water is sent to the water treatment facility for eventual discharge into the sewer. The 13 M nitric acid is fed back into the catholyte reservoir to maintain the acid concentration in catholyte loop. The bottoms stream from the thin film evaporator is concentrated in dissolved solids. To facilitate pumping of the slurry, the catholyte bleed is fed into the bottoms tank and the resulting liquid mixture is fed back into the anolyte reservoir.

Silver Recovery System

The silver recovery system consists of two tanks and a centrifuge. One of the tanks is used to dissolve the silver chloride in hot sodium hydroxide and hydrogen peroxide. The silver precipitated out of solution is centrifuged and dissolved in nitric acid in the second tank. Note that in contrast with the semi-continuous processes discussed above, silver recovery is a batch process. The frequency of batch operations depends upon the amount of chlorine in the organics and also the amount of inorganics in the waste. For example, if the waste consists mostly of cutting oils such as Trimsol, approximately 1.1 kg/h of silver chloride will be removed from the anolyte stream in the acid recovery system centrifuge. This amount could be processed in 8 h batches. Now if the inorganics constitute 1 % of the feed, they will accumulate in the anolyte and will have to be removed from the system approximately every 200 h. Before the inorganics are concentrated by drying in the evaporator, the silver in the system must be removed first by precipitating it as silver chloride. The 17 kg of silver chloride thus produced could be processed within two 8 h batches. Hence, every 200 h the continuous organics destruction process will have to be interrupted for 16 h by the batch process to removing inorganics (including radionuclides) from the system.