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Electrochemical Organic Destruction in Support of Hanford Tank Waste Pretreatment

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Summary

The development of electrochemical organic destruction technologies for destroying organic compounds, including organic complexants, has been undertaken in support of Hanford tank waste pretreatment needs. Through an experimental evaluation of electrode materials and process operating conditions, information for process design and scale-up was obtained to support ongoing engineering-scale testing and preconceptual design. Electroanalytical and bench-scale flow cell tests were conducted to evaluate the effect of anode materials (platinized titanium, Ebonex, tin oxide, nonstoichiometric titania, and indium oxide) and process operating conditions (temperature and flowrate) on the rate and efficiency of organic destruction.

Cyclic voltammetry was used to examine the oxygen overpotential for various electrode materials and provide insight into the mechanisms of complexant oxidation. Tests were conducted using standard organic/electrolyte solutions as well as a nonradioactive simulant SY1-SIM-93A complexant concentrate Hanford tank waste. Results from the electroanalytical testing with standard solutions show that ethylenediaminetetraacetic acid (EDTA) undergoes a two or more step oxidation at the electrode interface. With the exception of tin oxide, all electrode materials evaluated with the SY1SIM-93A simulant did not show any significant anodic current before water oxidation. This indicates that tin oxide may be more efficient at the initial oxidation of EDTA than the other materials; however, other factors need to be considered, such as the destruction of other organics, intermediates, and electrode fouling. These considerations were addressed through bench-scale electrochemical flow cell testing with SY1-SIM-93A tank waste simulant.

Flow cell test results show that the anode material has a pronounced effect on the destruction of organics. Platinized titanium showed significantly higher destruction rates and current efficiency than the other electrode materials. Tin oxide looked promising as an electrode material based on cyclic voltammetry; however, flow cell test results showed poor organic destruction efficiency. This is, in part, attributed to electrode fouling and the fact that the organic intermediates produced from the step wise oxidation of EDTA may not be as easily oxidized at the tin oxide electrode. Flow cell test results for an Ebonex anode clearly show a decrease in performance with successive runs indicating that the electrode was fouling. Platinized titanium exhibited the best overall electrode performance, and showed no evidence of fouling. Therefore, platinized titanium was selected as the preferred anode material for engineering-scale electrochemical organic destruction studies.

Additional bench-scale flow cell testing with the platinized titanium electrodes was conducted to qualitatively investigate the influence of temperature and flow rate on the rate of total organic carbon (TOC) destruction. For the temperature range tested (30°C to 90°C), and the flow rates tested (130 mL/min to 230 mL/min), a maximum in the destruction rate occurs near 50°C and 230 mL/min. The maximum destruction rate obtained for the bench-scale flow cell operating at a current density of 5000 A/m^2 was 4.8×10^{-6} g TOC/Coulomb. In comparison, a run conducted in an engineering-scale flow cell showed a significant increase in destruction rate (30%) up to 6.1×10^{-6} gTOC/C, with a current efficiency of 22%. The increase in destruction efficiency is attributed to enhanced mass transfer in the larger flow cell. The engineering-scale cell was configured with turbulence promoting mesh spacers to increase the mass transfer rate, while the bench-scale flow cell did not contain turbulence promoters.

In addition, ongoing work includes an engineering-scale flow cell evaluation of cathode materials, cell configuration (divided versus undivided), chloride and solids concentration, organic speciation, and operating parameters (temperature, flow rate, and current density). This testing will provide information for design optimization, process scale-up, modeling, and process operating conditions in support of preconceptual design for electrochemical treatment of Hanford tank waste.

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1.0 Introduction

The U.S. Department of Energy's Hanford Site in Richland, Washington, has 177 underground storage tanks that contain approximately 61 million gallons of radioactive waste. The current cleanup strategy is to retrieve the waste and separate components into high-level and low-level waste. However, many of the tanks contain organic compounds that create concerns associated with tank safety and efficiency of anticipated separation processes. Therefore, a need exists for technologies that can safely and efficiently destroy organic compounds. Laboratory-scale studies conducted during FY 93 have shown proof-of-principle for electrochemical destruction of organics. Electrochemical oxidation is an inherently safe technology and shows promise for treating Hanford complexant concentrate aqueous/slurry waste. Therefore, in support of Hanford tank waste pretreatment needs, the development of electrochemical organic destruction (ECOD) technology has been undertaken.

Electrochemical treatment processes have many attributes that make them attractive for destroying complexants in Hanford type wastes. Electrochemical processes are considered clean, as only electrons are added for treatment. ECOD has minimal or no secondary waste generation, and operates at low temperature and pressure, which eliminates concerns for radionuclide volatilization and extensive off-gas treatment. In addition, the existing theoretical and experimental data base is large and the process is modular in design which facilitates scale-up, increases reliability, and simplifies maintenance.

The primary objective of this work is to develop an electrochemical treatment process for destroying organic compounds, including tank waste complexants. Through an experimental evaluation of electrode materials and process variables, the data obtained will be used to support design and process operating information for engineering-scale studies.

Electroanalytical analyses and bench-scale flow cell testing will be conducted to evaluate the effect of anode material (platinized titanium, Ebonex, tin oxide, non-stoichiometric titania, and indium oxide) and process operating conditions (temperature, flow-rate) on the rate of organic destruction. The electrode materials referred to above were chosen for this study because they have been reported in the literature to be promising for the treatment of organic contaminated wastes (Almon and Buchanan 1992; Kotz et al. 1991; Koziol 1984; Stucki et al. 1991). Cyclic voltammetry will be used to identify oxygen overpotentials for the anode materials and provide insight into reaction steps for the electrochemical oxidation of complexants. In addition, a bench-scale flow cell evaluation will be conducted to evaluate the influence of process operating conditions and anode materials on the rate and efficiency of organic destruction using the nonradioactive SY1-SIM-93A Hanford tank waste simulant (Hohl 1993). Finally, based on the data obtained, an anode material will be selected for engineering-scale flow cell studies.

Electrochemical reactions are heterogenous chemical reactions that occur by transferring charge across the interface between the electrode and electrolyte. A potential is applied across two electrodes (cathode and anode) to provide the driving force for chemical reactions, such as the oxidation of organic species. A schematic of an electrochemical cell with an electrolyte solution containing organic species and nitrate/nitrite is shown in Figure 1.1. At the cathode, electrons are supplied to reduce electroactive species such as nitrate. Conversely, at the anode, electroactive species, such as organics, release electrons and are oxidized. Common electrolysis reactions competing in aqueous solutions are water oxidation and reduction.

For applying ECOD to Hanford complexant concentrate tank wastes, the net oxidation reaction of EDTA to carbon dioxide and water is given as

$$C_{10}H_{16}NO_8 + 12H_2O \rightarrow 40e^- + 40H^+ + 10CO_2 + N_2 \qquad (1)$$

Equation (1) shows that 10 moles of CO_2 and 1 mole of N_2 are produced for the complete oxidation of 1 mole of EDTA. In alkaline wastes, the CO_2 will react to form carbonate. Four electron equivalence are required per mole of carbon destroyed. The organic species undergo a series of oxidation steps via direct and indirect oxidation. In the direct oxidation process, electron transfer occurs at the anode/electrolyte interface, whereas with indirect oxidation, electron transfer is facilitated by a mediator or intermediate. In Hanford tank waste, the chloride/hypochlorite redox couple is expected to be a mediator available for indirect oxidation.

Through an experimental evaluation of electrode materials and process, operating conditions data will be obtained to quantitatively measure the process performance. The performance of electrochemical treatment is based on the organic destruction rate and current efficiency. Comparing destruction efficiencies will enable selection of a preferred electrode material and process operating conditions for ongoing engineering-scale flow cell studies.

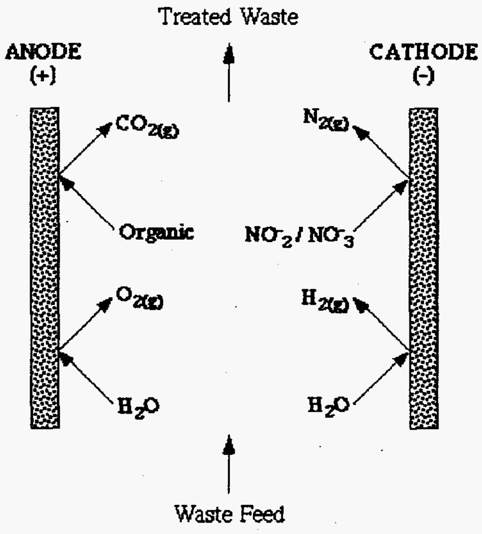

Figure 1.1. Schematic of Simplified Electrochemical Flow Cell

The organic destruction rate will be taken as the slope of the organic concentration versus time curves in 30 minute increments, and averaged over the run duration, taking into consideration the operating current density and the electrode surface area. An additional measure of the process performance will be based on the current efficiency ϕ, given by (6)

$$\phi[\%] = Q/Q_{tot} * 100 \tag{2}$$

where Q, is the charge used for the desired reaction, and Q_{tot}, is the total charge passed from the definition of current efficiency; thus showing that a more efficient process has a higher current efficiency. For example, when $\phi = 0\%$, all of the charge is consumed by undesired or side reactions, whereas when $\phi = 100\%$, all charge is used to produce the desired reaction. A description of the current efficiency relations are included in Appendix A.

A description of the experimental apparatus, procedure, and tests is contained in Section 2. Section 3 contains the results and discussion. Section 4 discusses concerns raised by the IPM Committee. The conclusions and references are contained in Section 5, and Section 6, respectively. Appendix A describes the current efficiency calculations.

2.0 Experimental

2.1 Cyclic Voltammetry Apparatus

Cyclic voltammagrams are obtained by varying the potential applied across the electrodesolution interface and measuring the resulting current. Cyclic voltammetry is capable of rapidly observing redox behavior over the entire potential range available which, for the purpose of this study, provides insight into reaction mechanisms and oxygen overpotentials. All cyclic voltammagrams were obtained using Princeton Applied Research, Model 273A, potentiostat/galvanostat. The instrument was operated in potentiostatic mode and controlled by an IBM compatible computer (Zeos 486) through a general-purpose-interface bus. Two cell configurations were used: a rotating disk electrode (RDE), and a standard corrosion cell. Because of the corrosive nature of the tank waste simulant, all experiments used a platinum wire reference electrode. The voltage was ramped linearly at a scan rate of 20 mV/sec, and all experiments were run at room temperature.

A Princeton Applied Research, Model 636, ring-disk electrode system was used to rotate and control the RDE. Although this system allowed for rotation speed ranging between +/- 9000 rpm, only rotation speeds less than 4000 rpm were used to provide controlled mass-transfer conditions. Two RDE electrode materials were used, platinum and glassy carbon, each with an area of 0.126 cm^2. The RDE cell volume was approximately 100 mL, and a platinum wire was used for the counter electrode.

2.2 Flow Cell Apparatus

A schematic of the electrochemical flow cell experimental apparatus is shown in Figure 2.1. The apparatus consists of the plate-and-frame flow cell, feed tank, pump, flow meter, and power supply. Flow cell operation was conducted in a batch recycle, where the solution from the feed tank was pumped through the flow cell and recycled back to the feed tank.

The flow cells used were a bench-scale and engineering-scale cell commercially available from ElectroCell AB. Figure 2.2 shows an expanded view of the cell stack used for the electrochemical organic destruction experiments. The electrochemical cell stack consists of base plates, electrodes, and gaskets. The bench-scale cell has a planer electrode surface area of approximately 9 cm^2, teflon base plates, teflon spacers, and viton gaskets. Turbulence promoting mesh spacers were not used in the bench-scale flow cell. The engineering-scale cell used has 100 cm^2 of electrode area, stainless steel base plates, PVDF turbulence promoting mesh spacers with flow distributors, and viton gaskets. The flow cell was configured with three compartments. The simulant solution was passed through the center compartment between the two electrodes. The other compartments between the end plates and electrodes were used to pass cooling water to remove the heat generated during operation.

The bench-scale electrochemical flow cell was powered with a Hewlett-Packard Model 6261 B power supply that could provide an output potential up to 20 V and current up to 50 A. A Fasco Ind., Inc., fluid pump was used to provide constant flow through the cell at rates up to 330 mL/min. Engineering-scale flow cell test were controlled with a Model 730 "Boss" Electrochemical Process Control Unit from Electrosynthesis Co., Inc. The Boss control unit provides an output voltage

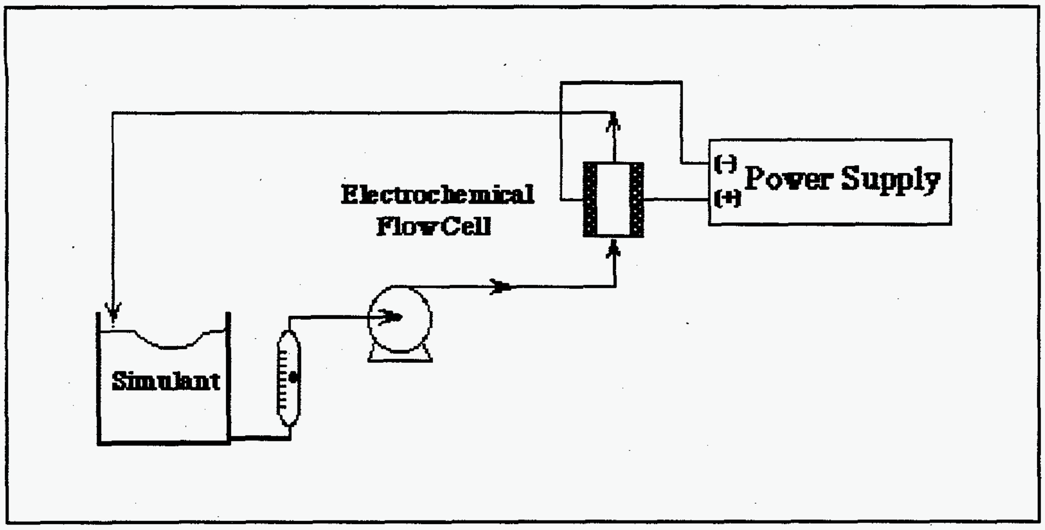

Figure 2.1. Schematic of Experimental Flow Cell Apparatus

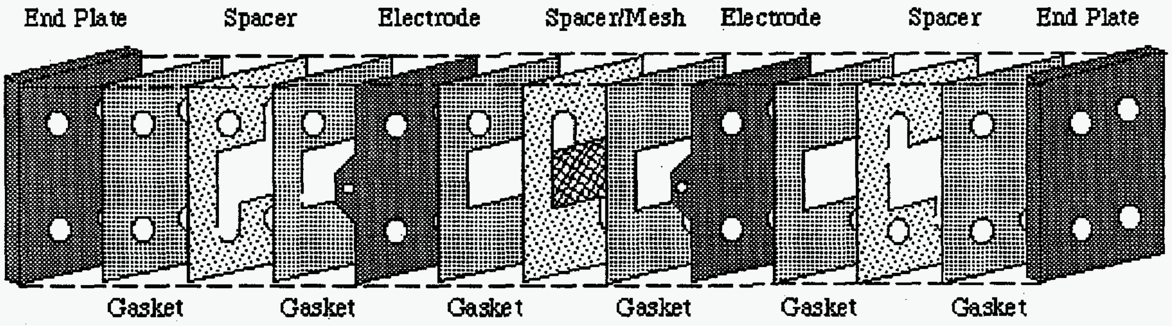

Figure 2.2. Expanded View of the Plate-and-Frame Electrochemical Flow Cell

of 60 V and a current up to 50 A. The Boss also supplies power to a 0.07 hp centrifugal fluid pump for circulating the feed from the storage reservoir. For all tests, the voltage, current, flow rate, and temperature were continuously monitored and recorded. An inert gas purge was connected to the sealed feed reservoir to sweep reactant gases through the off-gas line into the fume hood. Ports in the feed reservoir provided access for waste stream sampling.

2.3 Cyclic Voltammetry Test Procedure

Initially, a standard solution of EDTA and NaOH was prepared and cyclic voltammagrams were obtained using the RDE. A rotation speed of 1000 rpm was used for both electrode materials, platinum and glassy carbon, the voltage ramped linearly at a scan rate of 20 mV/sec, and experiments were run at room temperature. EDTA was used as the surrogate organic compound in the organic/sodium hydroxide solution. The hydroxyl ion concentration was 0.32 M and the organic concentration 0.05 M. In addition, cyclic voltammagrams from SY1-SIM-93A tank waste simulant were measured using the corrosion cell. Cyclic voltammetry scans were obtained with and without solution stirring for the various electrode materials. Also, suspended solids from the simulant waste were separated and removed by centrifugation. The supernate liquid was examined by cyclic voltammetry using the RDE to elucidate the effect of solids on the voltammagram.

2.4 Flow Cell Test Procedure

A test matrix showing the series of flow cell experiments conducted is shown in Table 2.1. First, the five anode materials were screened for their organic destruction efficiency. Additional experiments

Table 2.1. Flow Cell Test Matrix

Anode Material[a]	Temperature (°C)	Flow Rate (mL/min)
Microcell Flow Tests		
Platinized Titanium	50	230
Ebonex	50	230
Tin Oxide	50	230
Indium Oxide	50	230
Nonstoichiometric Titania	50	230
Platinized Titanium	50	230
Ebonex	50	230
Tin Oxide	50	230
Indium Oxide	50	230
Nonstoichiometric Titania	50	230
Platinized Titanium	30	130
Platinized Titanium	30	130
Platinized Titanium	50	130
Platinized Titanium	50	130
Ebonex - New	70	230
Ebonex	70	230
Ebonex	70	230
Platinized Titanium	30	230
Platinized Titanium	30	230
Platinized Titanium	70	230
Platinized Titanium	70	230
Platinized Titanium	90	230
Platinized Titanium	90	230
MP Flow Test		
Platinized Titanium	50	4300

(a) Cathode material for all tests was platinized titanium were conducted using the most promising electrode materials, followed by a parametric study with the preferred anode material for organic destruction. The anode materials evaluated include platinized titanium (Electrosynthesis Co., Inc.), Ebonex (Electrosynthesis Co. Inc.), tin oxide [Pacific Northwest Laboratory (PNL)],(a) nonstoichiometric titania (PNL), and indium oxide (PNL). The parametric study considered temperatures over the range of 30°C to 90°C, and flow rates from 130 mL/min to 230 mL/min. Finally, an engineering-scale flow cell test was completed based on operating conditions determined from the bench-scale flow cell testing.

Before testing, the flow cell was assembled with the desired anode material and platinized titanium cathode. Leak testing was performed by flowing deionized (DI) water through the cell. The DI water was then completely drained from the cell, pump, and connecting tubing. The feed tank was then charged with 100 mL of well mixed SY1-SIM-93A simulant. The solution temperature was controlled by a hot plate and magnetic stirrer, and the flow rate was adjusted with a flow meter. Liquid flow meters were calibrated before testing by flowing simulant solution through the cell and measuring the time required to fill a flask of known volume. The purge gas flow (0.2 mL/min) was started and additional checks of temperature and flow rate were made to ensure the system equilibrated before starting the run. Next, a 2 mL sample of the simulant was taken from the solution reservoir for TOC analysis. The current was set to 4.5 Amps to achieve an operating current density of approximately 5000 A/m^2. Constant current operation was maintained during the duration of the experiment (300 minutes). A 2 mL sample of the simulant solution was taken each hour for TOC analysis. During cell operation, the temperature, flow rate, current, applied cell potential, and time were recorded. In addition, observations of precipitant formation and solution color were noted. After the experiment was completed, the cell was disassembled and visual observations of the electrodes and ancillary equipment were made.

For the engineering-scale flow cell tests, the same procedure was followed, except 1 L of solution was charged to the feed reservoir, 5 to 10 mL samples were taken for TOC analysis, and the volumetric flow rate was set at approximately 4.3 L/min. The temperature, flow rate, current, applied potential, and time were monitored and recorded throughout the duration of the experiment.

2.5 Waste Simulant

For all experiments with SY1-SIM-93A simulant, a 3:1 (water:waste) dilution by volume was used to simulate the anticipated composition of retrieved tank waste. Table 2.2 shows the undiluted and diluted compositions of the SY1-SIM-93A simulant in weight percent (Walsh 1993). The TOC concentration was based on the concentration of EDTA in the simulant. All chemicals for simulant preparation are reagent grade, obtained from Aldrich Chemical Co. Deionized water (DI) was used for all simulant preparations.

(a) PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Table 2.2. Composition of SY1-SIM-93A Simulant

Component	Weight Percent Undiluted	Weight Percent Diluted (As Retrieved)
Na	20.7	7.05
Al	3.2	1.12
Cr	0.41	0.14
Ca	0.023	0.0080
Fe	0.028	0.0097
K	0.326	0.11
Ni	0.015	0.0052
Zn	0.002	0.00071
Cs	0.00145	0.00049
Sr	0.000058	0.000021
NO3	11.7	4.07
NO2	10.5	3.65
OH	2.47	1.02
TIC, C as carbonate	0.63	0.22
PO4	0.64	0.22
SO4	0.4	0.14
Cl	0.79	0.27
F	0.03	0.01
TOC, C as EDTA	1.53	0.53
H2O	35.5	78.46

2.6 Analytical Methods

TOC analysis was used to measure the organic concentration in the simulant waste. A Dohrmann Model DC-80 Carbon Analyzer was used for the measurements. A 2000 ppm TOC calibration standard of potassium acid phthalate ($KHC_8H_40_4$) was prepared according to manufacturer instructions. The TOC analyzer was calibrated before and during sample analysis (approximately every 20 samples) to verify analyzer accuracy. Samples were prepared by mixing 0.5 mL of simulant with 1 mL of a 5% phosphoric acid solution followed by sparging for three to five minutes. For each sample, three 5 mL injections were analyzed.

3.0 Results and Discussion

3.1 Cyclic Voltammetry

Initially, cyclic voltammagrams were obtained from solutions of pure NaOH and a mixture of NaOH and EDTA using the RDE. Figures 3.1 and 3.2 show two current responses from a stationary RDE for platinum and glassy carbon, respectively. In these figures, negative currents correspond to oxidation reactions, while positive currents result from reduction reactions. One curve was obtained from a solution of pure NaOH and the other from the mixture of NaOH and EDTA. Figures 3.1 and 3.2 show two anodic current peaks for the NaOH/EDTA mixture as the voltage is ramped from 0.5 V to 2.25 V. However, these peaks do not appear in the voltammagram from the pure NaOH solution. Therefore, this indicates that the oxidation reactions are a result of a two or more step EDTA oxidation at the electrode interface. As the potential is ramped beyond 2 V, the water oxidation dominates the current response.

The results with the simple organic/electrolyte solution are encouraging as, apparently, cyclic voltammetry can used to identify reaction steps during the oxidation of organic compounds. Therefore, the platinum RDE was examined further, and Figure 3.3 shows the current responses at rotation speeds of 1000, 2000, and 4000 rpm. Similar results were obtained with the glassy carbon electrode. The peaks observed in Figures 3.1 and 3.2 are seen as plateaus in Figure 3.3 because of the reactions at the mass-transfer limited value. The RDE flow characteristics force all products generated at the electrode surface to be swept away, usually eliminating a secondary reaction. Therefore, the two peak currents are contributions from two different and independent reactions of EDTA with the electrode surface.

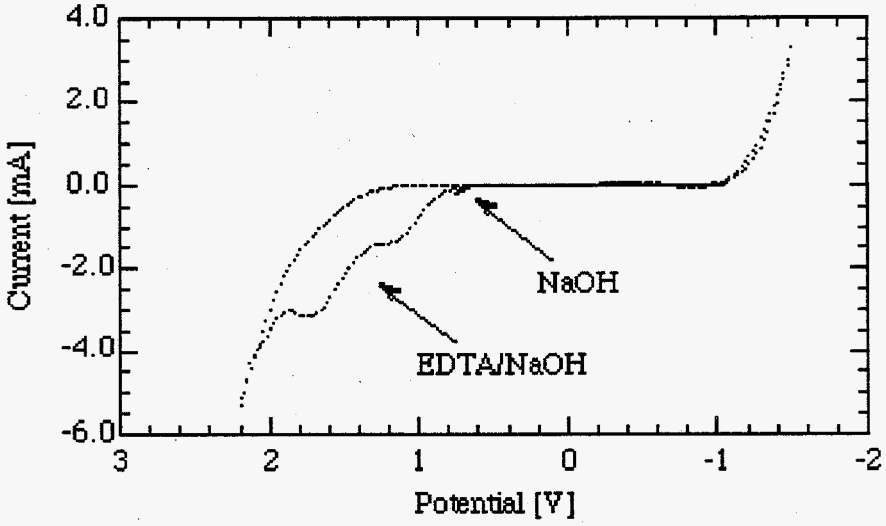

Figure 3.1. Cyclic Voltammograms of 0.32 M NaOH and 0.32 M NaOH/0.05M EDTA Using a Stationary RDE with the Working, Counter, and Reference Electrode All Platinum, and a Sweep Rate of 20 mV/s.

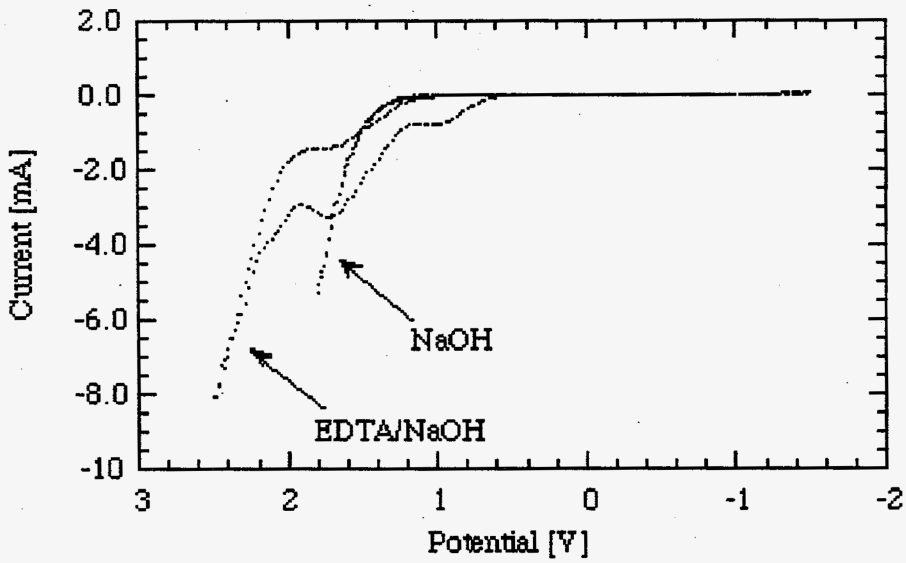

Figure 3.2. Cyclic Voltammograms of 0.32 M NaOH and 0.32 M NaOH/0.05M EDTA Using a Stationary RDE with a Working Electrode of Glassy Carbon, Counter Electrode of Platinum, Reference Electrode of Platinum, and a Sweep Rate of 20 mV/s.

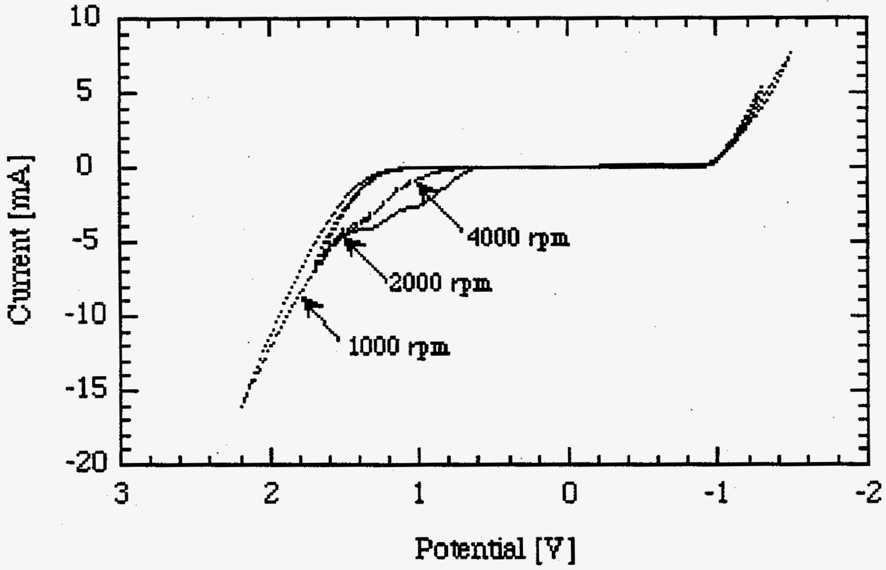

Figure 3.3. Cyclic Voltammograms of 0.32 M NaOH/0.05M EDTA Using a RDE at Rotation Speeds of 1000, 2000, and 4000 rpm. The working, counter, and reference electrode were all platinum. A sweep rate of 20 mV/s was used.

In Figure 3.3, the current response at 4000 rpm also supports this hypothesis. The first peak has disappeared, but the second peak is still visible. This suggests that at high mass-transport conditions, the first reaction is suppressed while the second reaction is still possible. However, the higher rotation speed should provide an associated higher current, though Figure 3.3 does not show this expected behavior. Therefore, caution is advised in assuming the validity of this qualitative interpretation.

The corrosion cell was used to examine the various electrode materials for preferential oxidation of organics in the tank waste simulant. Figures 3.4 through 3.7 show voltammagrams using anode materials of platinum, tin oxide, Ebonex, and platinized titanium, respectively. Similar curves were obtained during scans without solution stirring. The platinum, Ebonex, and platinized titanium materials do not show any significant anodic current before the water oxidation. Therefore, these materials are anticipated to have a relatively low current efficiency for organic oxidation. In comparison, tin oxide shows a broad peak before the water electrolysis. The broad current peak appears to be a composite of smaller reactions, as is seen when the peak is expanded in Figure 3.8. This suggests that tin oxide should provide a higher destruction efficiency than the other materials examined.

The difference in performance observed for the anode materials tested in the SY1-SIM-93A simulant, as compared to the RDE runs with standard EDTA/NaOH solution, suggested that the organic material may be chemi- or physi-sorbed onto the solids in the tank waste simulant as this would decrease the probability of contacting the electrode surface and lead to the lack of anodic current before water oxidation. Thus, 500 mL of simulant was centrifuged and the solid-free supernate examined by

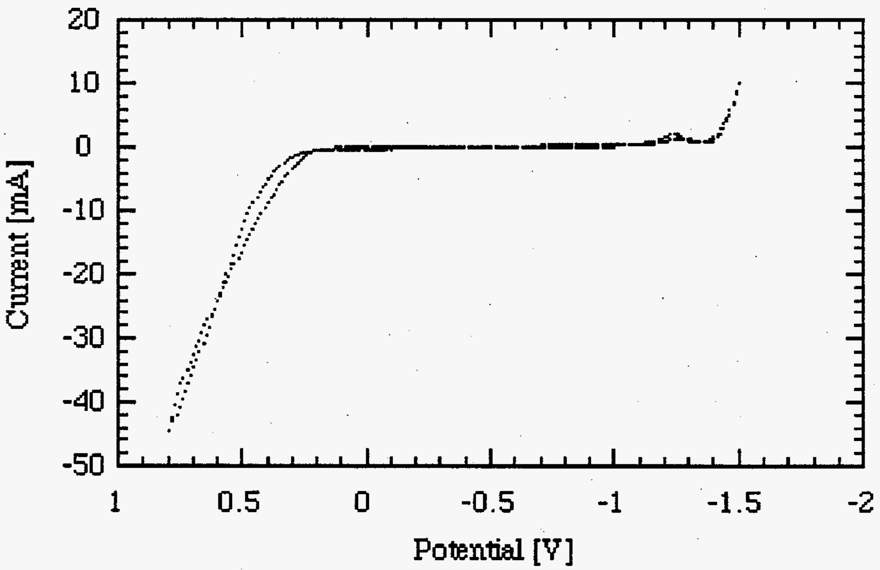

Figure 3.4. Current as a Function of Voltage Using a Corrosion Cell With SY1-SIM-93A Simulant Solution for a Platinum Foil Working Electrode, Carbon Counter Electrode, and a Platinum Wire Reference Electrode. The scan rate was 20mV/s and the solution agitated with a magnetic stirrer.

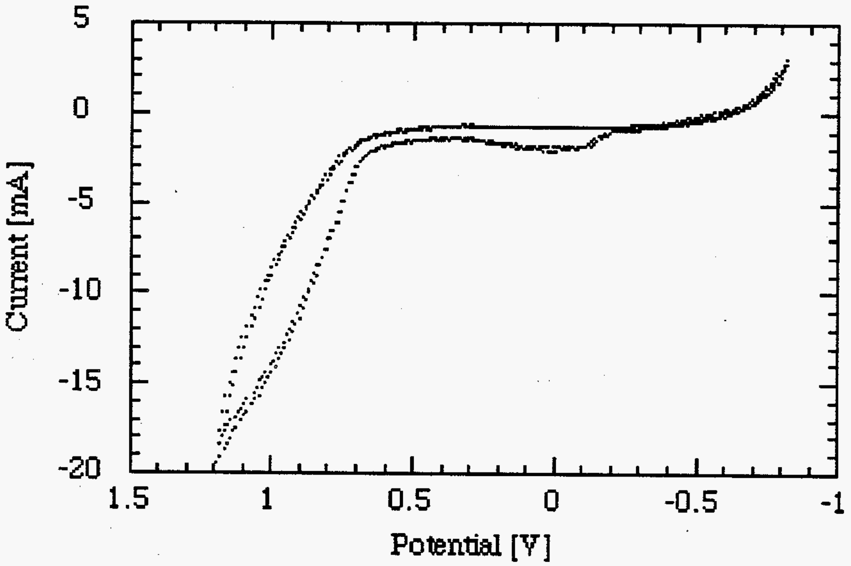

Figure 3.5. Cyclic Voltammogram for a SnO_2 Working Electrode Using a Corrosion Cell with SY1-SIM-93A Simulant Solution. The counter electrode was a carbon rod with a platinum wire reference electrode. The scan rate was 20mV/s and the solution agitated with a magnetic stirrer.

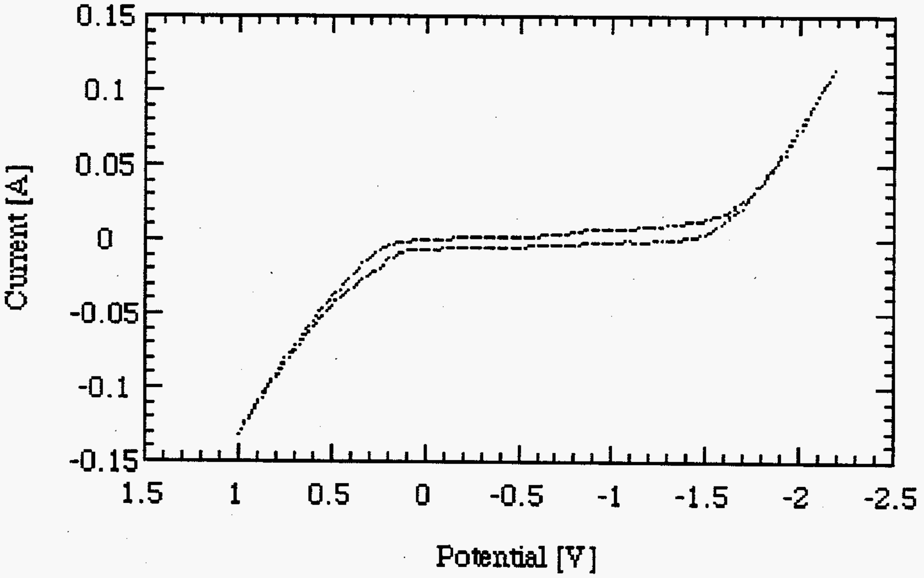

Figure 3.6. Current As a Function of Voltage Using a Corrosion Cell With SY1-SIM-93A Simulant Solution for a Ebonex Working Electrode, Carbon Counter Electrode, and a Platinum Wire Reference Electrode. The scan rate was 20mV/s and the solution agitated with a magnetic stirrer.

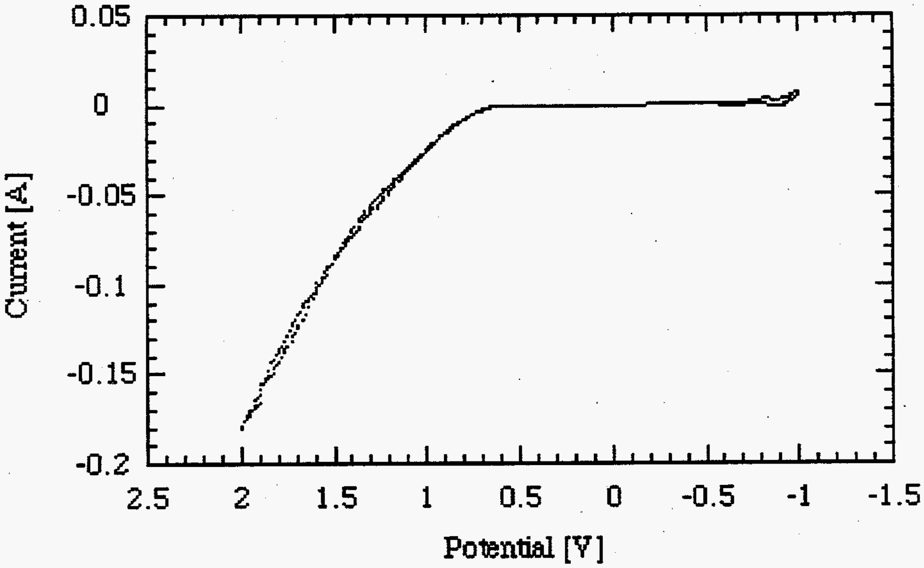

Figure 3.7. Cyclic Voltammogram for a Platinized Titanium Working Electrode Using A Corrosion Cell With SY1-SIM-93A Simulant Solution. The counter electrode was a carbon rod with a platinum wire reference electrode. The scan rate was 20mV/s and the solution agitated with a magnetic stir bar.

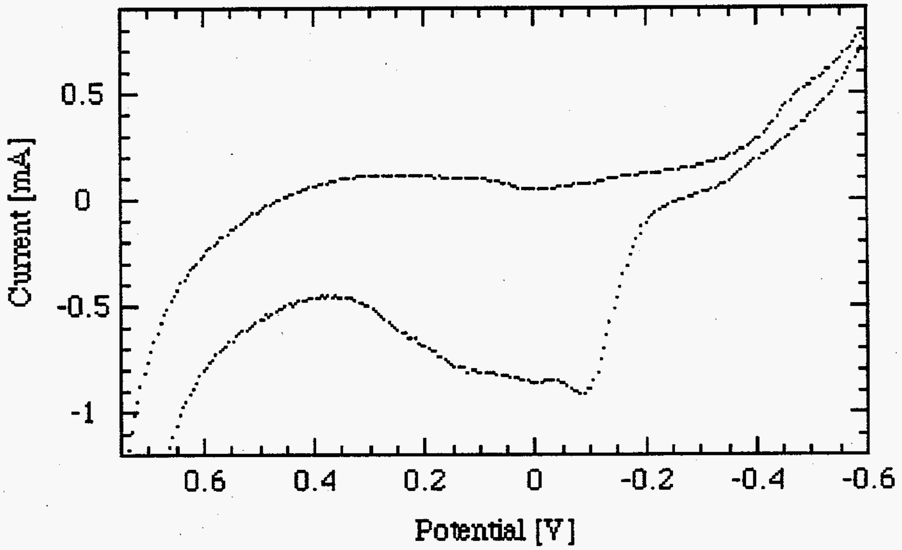

Figure 3.8. An Expanded View of the Tin Oxide Cyclic Voltammagram Showing the Anodic Current Peaks That Are Assumed to be Attributed to Organic Oxidation

TOC analysis and RDE. The TOC analysis showed that the organic species are almost completely partitioned to the aqueous phase, and not attached to the solids. Figure 3.9 shows the current response from the platinum electrode for various rotation speeds. A small anodic current is evident at approximately 1.0 V, and roughly corresponds to the first peak shown in Figure 3.1. The current is assumed to be from an organic oxidation reaction and indicates that some (and possibly all) organic material remains soluble in the liquid phase. Therefore, the difference in performance can not be attributed to chemi- or physi-sorbed organics. It has been suggested that the presence of metals and the chelating properties of EDTA are leading to the differences observed between the organic/electrolyte solution and SY1-SIM-93A simulant.

3.2 Flow Cell

Bench-scale batch electrochemical flow cell tests have been conducted to evaluate the effect of anode material, temperature, and flow rate on the rate and efficiency of organic destruction. Five anode materials were evaluated at several process operating conditions. Results from the bench-scale flow cell ECOD studies are discussed below.

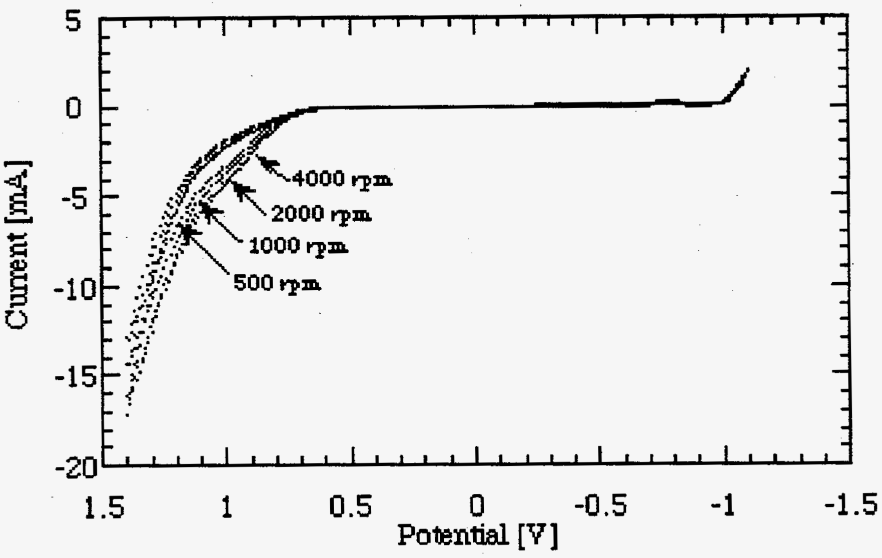

Figure 3.9. Cyclic Voltammograms Using a Supernate From a SY1-SIM-93A Simulant With the Suspended Solids Separated by Centrifugation. An Pt RDE Electrode was used at Rotation Speeds of 500, 1000, 3000, and 4000 rpm. The counter and reference electrodes were a platinum wire and the sweep rate was 20 mV/s.

Figure 3.10 shows the effect of anode material on the organic destruction rate. TOC concentration is plotted versus time for the five anode materials. Comparing the slopes of the TOC versus time curves for each anode material shows that the platinized titanium anode material exhibits a higher organic destruction rate than the other materials. Ebonex shows an intermediate destruction rate, while indium oxide, tin oxide, and nonstoichiometric titania show minimal efficiency for organic destruction. Figures 3.11 through 3.15 show the TOC concentration versus time curves, including replicate runs for each of the anode materials (platinized titanium, Ebonex, tin oxide, indium oxide, and nonstoichiometric titania), respectively. The destruction rate and current efficiency for replicate experiments are summarized in Table 3.1. The three worst performing materials (indium oxide, tin oxide, and nonstoichiometric titania), with current efficiencies less than 4%, were removed from further consideration. The low destruction rate for tin oxide is in part attributed to electrode fouling, while the nonstoichiometric titania and indium oxide require high operating potentials (> 10 V) to achieve the desired operating current density. These factors and economic considerations inhibit implementing these anode materials for organic destruction. Platinized titanium and Ebonex showed the highest destruction efficiencies; therefore, additional experiments to evaluate their destruction performance were conducted.

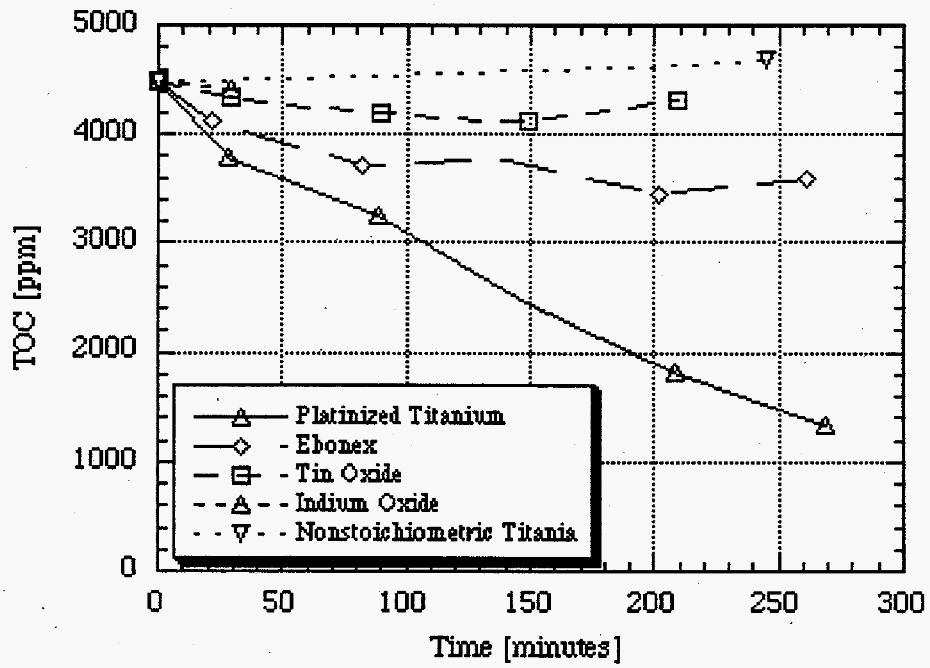

Figure 3.10. Effect of Anode Material On The Destruction of EDTA In SY1-SIM-93A Tank Waste Simulant. Anode materials evaluated include platinized titanium, Ebonex, tin oxide, indium oxide and nonstoichiometric titania. Experiments were performed at a constant current density of 5000 A/m^2, a temperature of 50°C and a flow rate of 230 mL/min.

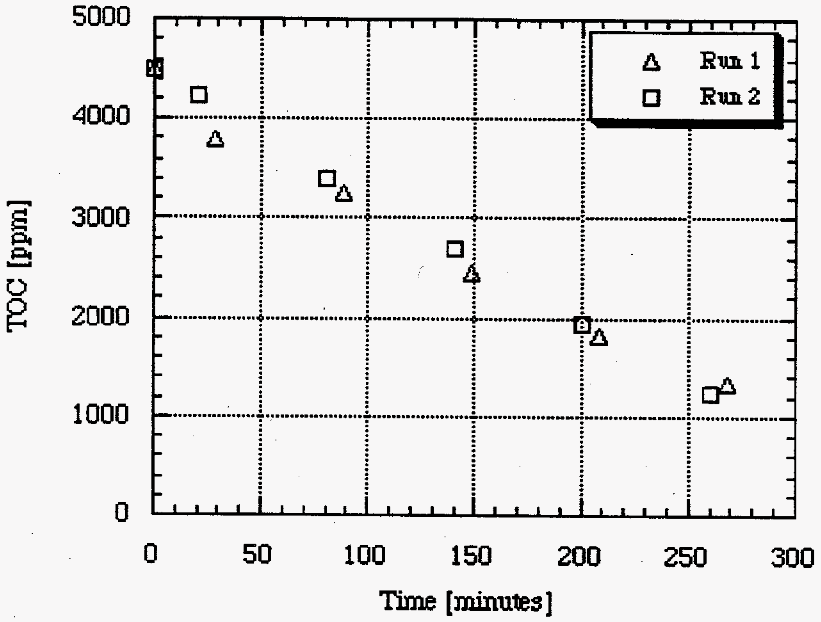

Figure 3.11. TOC Destruction For Replicate Flow Cell Runs With SY1-SIM-93A Tank Waste Simulant for a Platinized Titanium Anode and Cathode at an Operating Current Density of 5000 A/m^2, a Temperature of 50°C, and a Flow Rate of 230 mL/min.

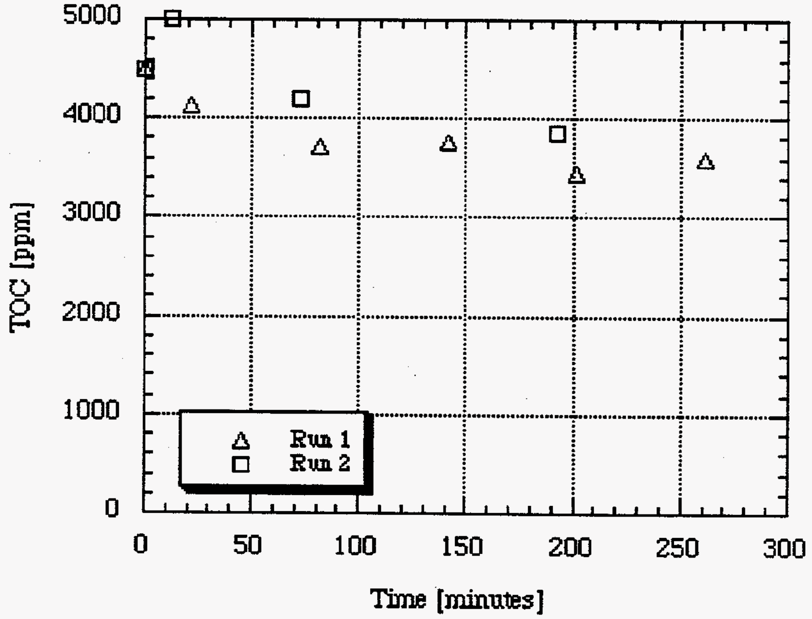

Figure 3.12. TOC Destruction for Replicate Flow Cell Runs With SY1-SIM-93A Tank Waste Simulant for an Ebonex Anode and Platinized Titanium Cathode at an Operating Current Density of 5000 A/m^2, a Temperature of 50°C, and a Flow Rate of 230 mL/min.

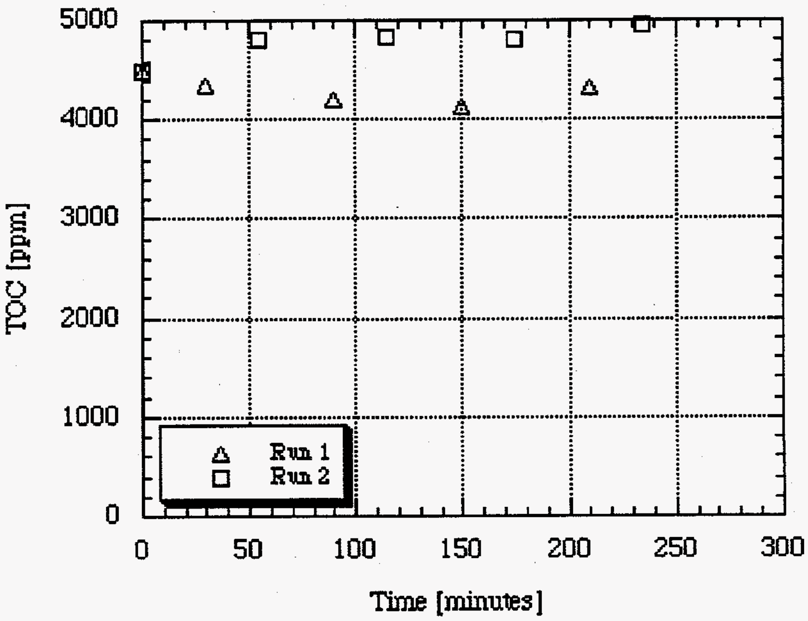

Figure 3.13. TOC Destruction for Replicate Flow Cell Runs With SY1-SIM-93A Tank Waste Simulant for a Tin Oxide Anode and Platinized Titanium Cathode at an Operating Current Density of 5000 A/m^2, a Temperature of 50°C and a Flow Rate of 230 mL/min.

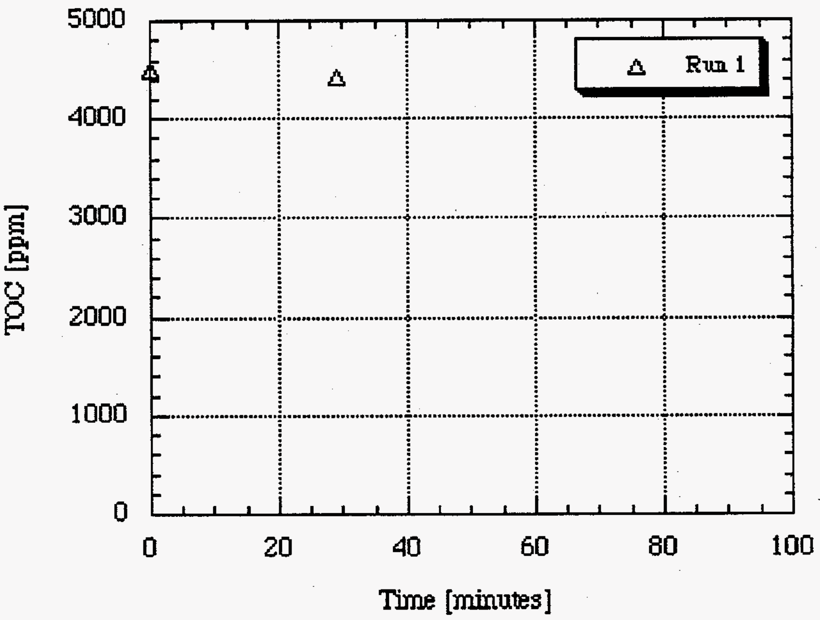

Figure 3.14. Flow Cell Run Showing TOC Destruction In SY1-SIM-93A Simulant Waste for an Indium Oxide Anode and Platinized Titanium Cathode at an Operating Current Density of 5000 A/m^2, a Temperature of 50°C and a Flow Rate of 230 mL/min.

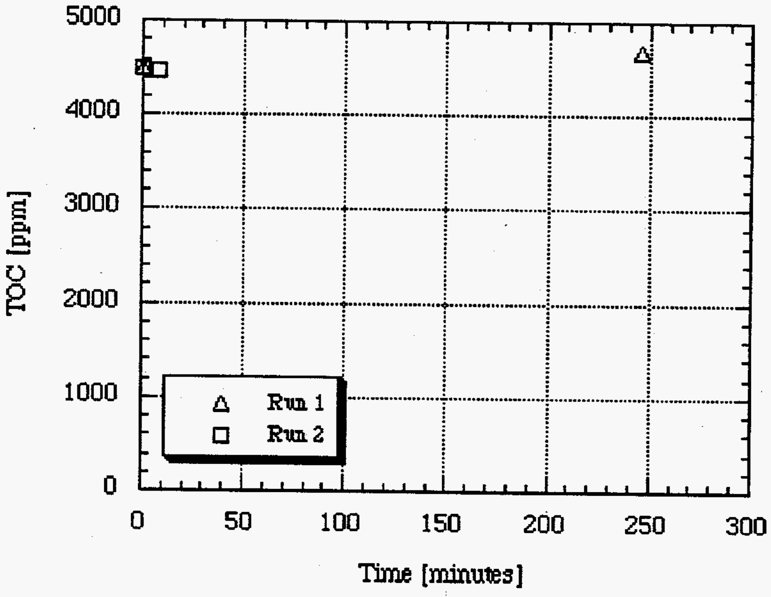

Figure 3.15. TOC Destruction for Replicate Flow Cell Runs With SY1-SIM-93A Tank Waste Simulant for a Nonstoichiometric Titania Anode and Platinized Titanium Cathode at a Current Density of 5000 A/m^2, a Temperature of 50°C and a Flow Rate of 230 mL/min.

Table 3.1. Organic Destruction Summary

Anode Material(a)	Temperature (°C)	Q (mL/min)	Destruction Rate (10^{-6} g TOC/C)	Destruction Extent (%) (@300 min)	Current Efficiency (%)
Microcell Flow Tests					
Platinized Titanium	30	230	4.5±0.2	73	14.2
Platinized Titanium	50	230	4.8±0.3	71	14.3
Platinized Titanium	70	230	3.5±0.3	76	16.1
Platinized Titanium	90	230	4.3±0.5	79	17.1
Platinized Titanium	30	130	4.0±1.1	70	13.8
Platinized Titanium	50	130	4.0±0.6	66	15.2
Ebonex	50	230	1.7±0.3	26	6.0
Ebonex	70	230	1.6	35	5.9
Ebonex	70	230	0.49	11	1.7
Ebonex	70	330	0.30	4	1.1
Tin Oxide	50	230	0.55	7	2.0
Indium Oxide	50	230	1.1	-	4.0
Nonstoichiometric Titania	50	230	1.0±0.7	-	3.5
MP Flow Test					
Platinized Titanium	50	4300	6.1	98	21.9

(a) Cathode material for all tests was platinized titanium

Figure 3.16 shows the performance of Ebonex over three consecutive runs. A significant decrease in the rate of destruction is observed, comparing the first run with each additional run. The destruction rates decrease from 1.6 x 10^{-6} g TOC/C to 3.1 x 10^{-7} g TOC/C in just over three runs, with a decrease in current efficiency from approximately 6% to 1%. These results indicate that fouling of the Ebonex electrode surface is occurring in the SY1-SIM-93A simulant. In comparison, the performance of the platinized titanium electrode over several runs is shown in Figure 3.17. More than 15 runs were conducted with platinized titanium, and no evidence of fouling was observed, as the latter runs do not show a decrease in the destruction rate. Overall, platinized titanium showed more than three times the destruction rate of Ebonex, and after a series of tests totalling over 100 hours of operation, the platinized titanium anode showed no evidence of fouling. These factors and the fact that platinized titanium electrodes are commercially available, led to its selection as the preferred material for the bench-scale parametric study and engineering-scale studies.

Figure 3.18 shows the effect of temperature on the organic destruction rate for a bench-scale flow cell test configured with platinized titanium electrodes at current density of 5000 A/m^2 and volumetric flow rate of 230 mL/min. The average destruction rate for replicate runs are reported with the error bars representing the deviation of the replicate data from the average. Qualitatively, the destruction rate is observed to pass through a maximum near 50°C. An increase in temperature from 30°C to 50°C increases the potential destruction rate through an increase in kinetics; however, as the temperature is raised, a decrease in organic destruction rate is observed and attributed to a decrease in process selectivity as competing reactions become more significant.

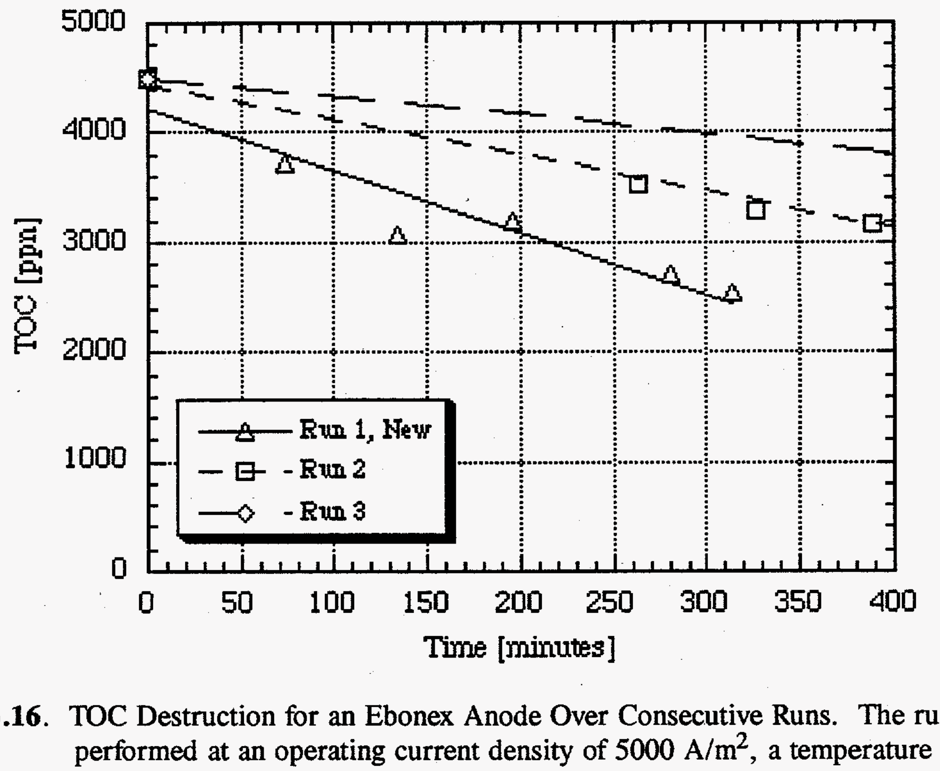

Figure 3.16. TOC Destruction for an Ebonex Anode Over Consecutive Runs. The runs were performed at an operating current density of 5000 A/m^2, a temperature of 70°C and a flow rate of 230 mL/min.

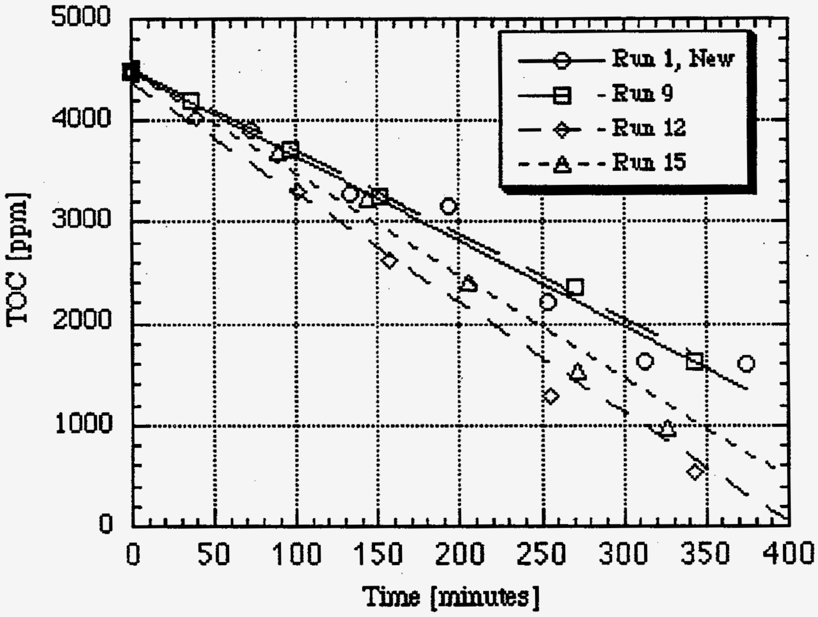

Figure 3.17. Performance of Platinized Titanium Anode Over Several Runs Showing TOC Concentration as a Function of Time. Experiments were performed at an operating current density of 5000 A/m^2, temperatures of 50°C and 70°C, and a flow rate of 230 mL/min.

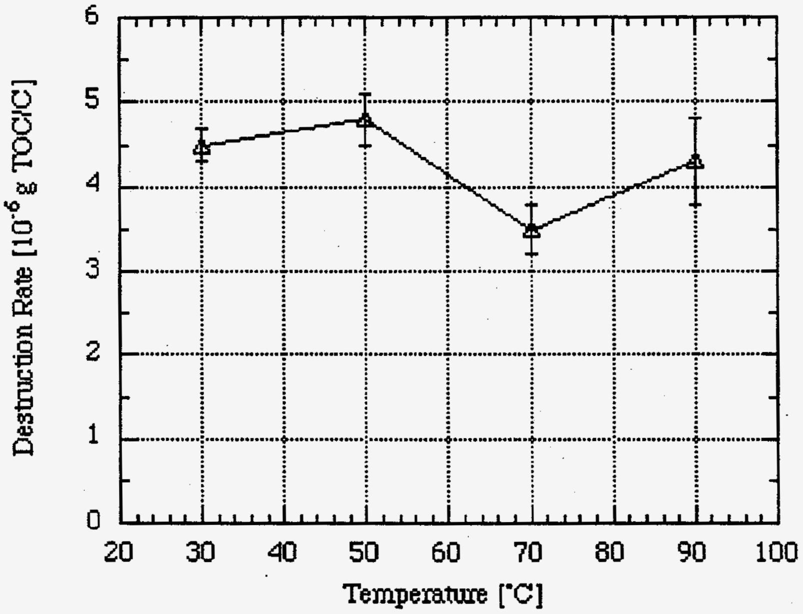

Figure 3.18. Effect of Temperature on the Organic Destruction Rate Based on Bench-Scale Flow Cell Tests Performed at an Operating Current Density of 5000A/m^2, a Flow Rate of 230 mL/min, and Temperatures of 30°C, 50°C, 70°C, and 90°C.

Figure 3.19 shows the effect of flow rate on the organic destruction rate. The destruction rate is slightly higher at the higher volumetric flow rate of 230 mL/min compared to the lower volumetric flow rate of 130 mL/min. This is attributed to enhanced mass transfer through increased turbulence at the higher flow rate. The effect of mass transfer on the destruction rate is even more pronounced when comparing the bench-scale flow cell tests to the engineering-scale flow-cell, where turbulence promoters were used.

Figure 3.20 shows the TOC versus time data for an engineering-scale flow cell run. The run was conducted at a temperature of 50°C, current density of 5000 A/m^2, and a flow rate of 4.3 L/min. A significant increase occurred in the destruction rate (approximately 30% over the bench-scale tests with a similar increase in the current efficiency from 17.1% to 21.9%). The average destruction rate was 6.1 x 10^{-6} g TOC/C, which gave approximately 98% destruction after 300 minutes. The increase in destruction efficiency is attributed, in part, to enhanced mass transfer in the engineering-scale flow cell as a result of turbulence promoting meshes and better flow distribution. The destruction rate is essentially linear until a TOC concentration of 1000 ppm is reached, where the rate begins to rapidly drop off. Thus, the destruction rate and current efficiency above 1000 ppm, where most of the destruction is occurring, is approximately 40% higher than the average rate reported.

In addition, technology development concerns identified early in the course of this work have been, in part, addressed by this study, and are continuing to be addressed in ongoing studies. These concerns include the ability of the electrochemical technology to meet treatment objectives for organics in Hanford complexant concentrate tank waste streams that contain solids, or in streams that contain little or no chloride. Other concerns include fouling and erosion of the electrode materials in Hanford type waste streams. The needs addressed by this study are discussed in more detail below.

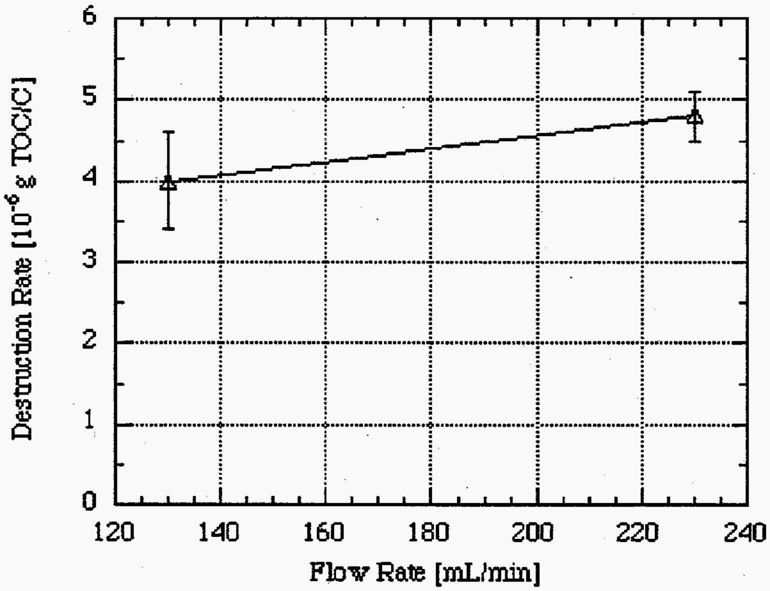

Figure 3.19. Effect of Flow Rate on the Organic Destruction Rate Based on Bench-Scale Flow Cell Tests Performed at an Operating Current Density of 5000A/m^2, a Temperature of 50°C and a Flow Rate of 230 mL/min.

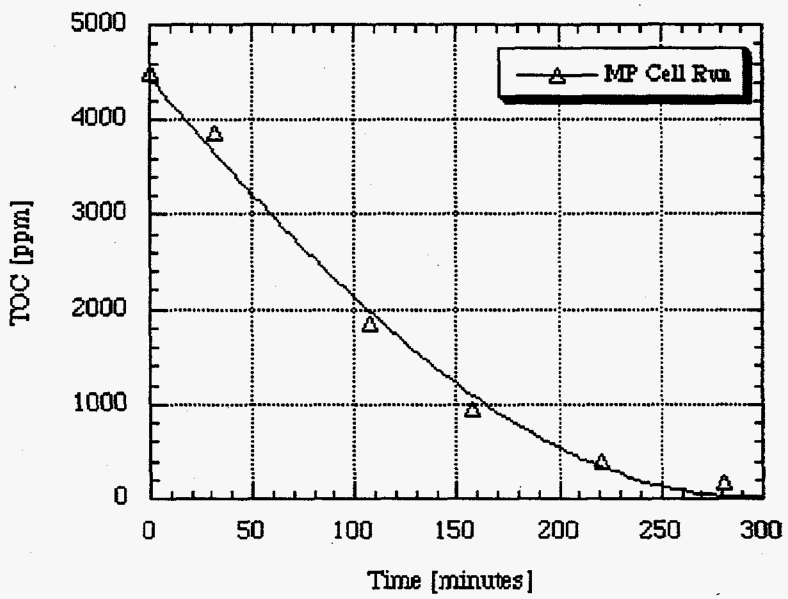

Figure 3.20. TOC Destruction in SY1-SIM-93A Simulant as a Function of Time for the Engineering-Scale (MP) Electrochemical Flow Cell. The cell was configured with a platinizied titanium anode and platinizied titanium cathode. The cell was operated at a current density of 5000 A/m, a simulant feed temperature of 50°C, and a flow rate of 4.3 L/min.

This work has demonstrated that electrochemical treatment is a viable and promising technology for treatment of complexant concentrate Hanford tank waste. This process has also shown the ability to reduce the TOC concentration well below the 1556 ppm specification, previously identified based on limits for a grouted waste form. In addition, electrochemical treatment offers the potential for simultaneous nitrite/nitrate destruction.

One concern is related to the ability of electrochemical treatment to destroy organics in streams that contain solids. Solids could, potentially, lead to cell plugging and blockage. However, during the course of this study, no problems due to the presence of solids were noted. The solids present in the SY1-SIM-93A simulant are representative of those found in actual 241-SY-101 tank waste, and therefore, should provide a measure of the ability of electrochemical treatment to destroy organics in the presence of solids. These observations alleviate, to some extent, this concern, which will be examined in further detail on the engineering-scale level.

Another concern was related to electrochemical treatment of Hanford type waste streams that contain little or no chloride. Without indirect oxidation through the chloride/hypochlorite couple known whether the electrochemical process could meet the treatment objectives is not known. Figure 3.21 shows the destruction of EDTA in an electrolyte solution containing 0.075 M and 0.0 M chloride. The destruction rate with chloride is slightly higher than without chloride, indicating that the chloride/hypochlorite mediator contributes to the organic destruction process. However, electrochemical organic destruction was still able to easily meet treatment objectives, even in the absence of chloride.

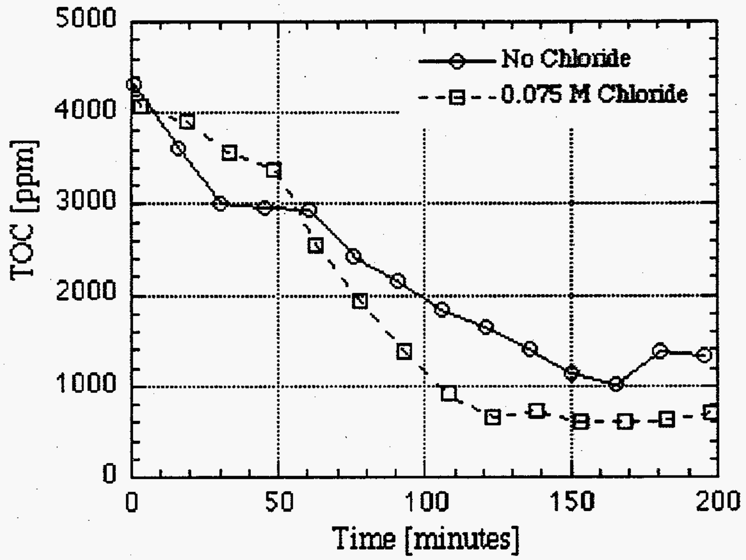

Figure 3.21. TOC Destruction in Electrolyte Solutions Containing 0.075 M and 0.0 M Chloride. The cell was configured with a platinizied titanium anode and platinizied titanium cathode. The cell was operated at a current density of 5000 A/m, a temperature of 50°C, and a flow rate of 110 mL/min.

Finally, the issue of electrode fouling and erosion in Hanford type wastes was investigated. This study has shown the performance of platinized titanium over 100 hours of testing in SY1-SIM-93A simulant. A good destruction efficiency and no deterioration in destruction performance was observed. No fouling or erosion of the electrode was observed during any of the flow cell tests. These results are encouraging, though further validation of material performance will be determined by long term testing.

4.0 Continuing Work

Significant progress has been made in the area of electrochemical organic destruction technology development for treating Hanford complexant concentrate tank waste. However, work is ongoing to further address technology development needs. Ongoing work includes an engineering-scale flow cell evaluation of cathode materials, cell configuration (divided versus undivided), chloride and solids concentration, organic speciation, and operating parameters (temperature, flow rate, and current density). This testing will provide information for design optimization, process scale-up, modeling, and process operating conditions in support of preconceptual design for electrochemical treatment of Hanford tank waste. WSRC and the University of South Carolina are actively involved in addressing technology development needs for application of electrochemical organic destruction to Hanford tank wastes.

Future development needs require long term testing and testing with actual tank waste. A continuous error free test of 1000 hours is a common standard used to judge successful electrochemical treatment process operation. Should funding be available for FY95, radioactive testing with actual Hanford tank waste is proposed, followed by 1000 hour flow cell tests to rigorously evaluate the electrochemical treatment process.

5.0 Conclusions

This work has demonstrated that cyclic voltammetry is a viable tool to examine electrochemical oxidation of organic material before water electrolysis. Pure EDTA appears to oxidized in two independent steps that are controlled by the applied potential. The broad oxidation current associated with tin oxide is probably a composite of multiple reaction or absorption/desorption steps.

The bench-scale flow cell studies support selecting platinized titanium as the preferred electrode material for engineering studies with SY1-SIM-93A type simulants. The Ebonex test results indicate that fouling is a concern significantly influencing its organic destruction ability. Platinized-titanium has shown no decrease in organic destruction efficiency after testing totalling more than 100 hours. Tin oxide, indium oxide, and non-stoichiometric titania were shown to not be as effective for organic destruction in SY1-SIM-93A simulant.

The organic destruction rate was observed to pass through a maximum near 50°C over the temperature range of 30°C to 90°C. This initial increase in destruction rate from 30°C to approximately 50°C was attributed to an increase in kinetics with temperature, while at higher temperatures a decrease in the destruction rate occurred due to a decrease in selectivity/increased competition. In addition, the flow rate was shown to influence the destruction rate through mass transfer. At higher flow rates and conditions of increased turbulence, the rate of organic destruction was observed to increase.

Process operating conditions and a preferred electrode material were selected for engineering-scale flow cell testing. An improvement in the destruction rate and current efficiency was observed for the engineering-scale flow cell due to enhanced mass transfer, through the use of turbulence promoters.

This study has shown that electrochemical organic destruction is a viable and promising technology for treatment of organic tank waste complexants. Ongoing studies will build on this work to address technology development needs, and further optimize the electrochemical organic destruction process and provide a sound basis for a conceptual design.

6.0 References

Almon, A. C., and B. R. Buchanan. 1992. "Electrochemical Oxidation of Organic Waste." Chapter 15 in *Electrochemistry for a Cleaner Environment*, eds. J. D. Genders and N. L. Weinberg. Electrosynthesis Company, Inc., East Amherst, New York.

Hohl, T. M. 1993. SY1-SIM-93A, WHC-SD-WM-TI-549.

Kotz R., S. Stucki, and B. Carcer. 1991. "Electrochemical Waste Water Treatment Using High Overvoltage Anodes. Part I Physical and Electrochemical Properties of SnO_2 Anodes." *J. Appl. Electrochem.*, 21, pp. 14-20.

Koziol, K. R. 1984. "Modern Electrodes Systems for Electrochemical Processes." Proceedings of the Symposium on Advances in the Chlor-Alkali and Chlorate Industry, eds. M. M. Silver and E. M. Spore. The Electrochemical Society, Pennington, New Jersey.

Stucki, S., R. Kotz, B. Carcer, and W. Suter. 1991. "Electrochemical Waste Water Treatment using High Overvoltage Anodes. Part II Anode Performance and Applications." *J. Appl. Electrochem.*, 21, pp. 99-104.

Walsh, F. 1993. "A First Course in Electrochemical Engineering, the Electrochemical Consultancy." Hants, England.

Appendix A

Current Efficiency Calculations

Appendix A

Current Efficiency Calculations

The current efficiency. ϕ, is given by [6]

$$\phi[\%] = Q/Q_{tot} * 100 \tag{1}$$

where Q, is the charge used for the desired reaction, and Q_{tot}, is the total charge passed.

The charge is determined as the integral of cell current, I, with respect to time:

$$Q = \int I \, dt \tag{2}$$

For a process operated at constant current, the charge is the cell current multiplied by t, the total time the current was applied to the cell:

$$Q = I \, t \tag{3}$$

Substituting Equation (3) into Equation (1) gives a simplified relation for current efficiency:

$$\phi = I_p/I_{tot} * 100 \tag{4}$$

where I_p is partial current for desired reaction and I_{tot} is total current. The partial current can be determined as

$$I_p = w \; n \; F/(Mt) \tag{5}$$

where w = mass in grams of desired species destroyed
n = equivalence/mole
F = Faraday's Constant = 96485 Coulombs/equivalence
M = molecular weight of reacting species
t = experiment run time in seconds.

The equivalence/mole of organic or carbon were determined from the overall net organic oxidation reaction for EDTA listed below.

EDTA

$$C_{10}H_{16}N_2O_8 + 12H_2O \rightarrow 40e^- + 40H^+ + 10CO_2 + N_2 \qquad (6)$$

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