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Pacific Northwest National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Electrochemical Destruction of Organics and Nitrates in Simulated and Actual Radioactive Hanford Tank Waste

M. R. Elmore
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Prepared for the U.S. Department of Energy
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Summary

Pacific Northwest National Laboratory has conducted an evaluation of electrochemical processing for use in radioactive tank waste cleanup activities. An electrochemical organic destruction (ECOD) process was evaluated, with the main focus being the destruction of organic compounds (especially organic complexants of radionuclides) in simulated and actual radioactive Hanford tank wastes. A primary reason for destroying the organic species in the complexant concentrate tank waste is to decomplex/defunctionlize species that chelate radionuclides. The separations processes required to remove the radionuclides are much less efficient when chelators are present. A second objective, the destruction of nitrates and nitrites in the wastes, was also assessed. Organic compounds, nitrates, and nitrites may affect waste management and safety considerations, not only at Hanford but at other U. S. Department of Energy sites that maintain high-level waste storage tanks.

A flowthrough electrochemical cell (FM01-LC), manufactured by ICI (Great Britain), was used for the testing. Two cell configurations were tested: "divided cell" with a Nafion 450® membrane separating the anolyte and catholyte solutions, and "undivided cell" with the membrane removed. The cell was operated at a current density of ~3500 A/m^2. Each test was run for 3 to 4 h. The electrolyte was recirculated at a rate of ~1.2 to 1.5 L/min, and the resultant electrolyte temperature ranged from ~50°C to 65°C.

A simulated waste was prepared for this testing based on a previously developed formula, designated SY1-SIM-93A, to match waste in Hanford Tank 101-SY, an organic-bearing high-level tank waste. Furthermore, two radioactive tests were conducted with actual Tank 101-SY waste supernatant. Due to limited availability of tank wastes for this testing, a third radioactive test was conducted using a mixture of 101-SY and 103-SY wastes. (Waste from Tank 103-SY has a composition similar to Tank 101-SY.) The results from simulant testing and actual waste testing were then compared.

The results from this study showed the rate of destruction of total organic carbon (TOC) in the actual waste for the undivided cell configuration to be comparable to that obtained for simulant testing. The undivided cell destruction rate is on the order of 6 E-07 mole TOC/C with an overall current efficiency of 23%. These results indicate that, over this test duration, the simulant adequately reflects the TOC characteristics of the actual waste. However, a longer test duration may show that the simulant does not represent the actual waste, as several organic species are known to be present and some are expected to be refractory to oxidation.

The TOC destruction rate was observed in this study to be lower in the divided configuration by a factor of 3 to 6 times compared with the undivided configuration. This difference in rates was also observed during pilot-scale testing conducted by The Electrosynthesis Company (ESC) with Hanford simulants. ESC attributed this observation to the difference in solubility as a result of the higher sodium/alkalinity in their divided run.

Nitrate and nitrite species reduction was observed to be one to two orders of magnitude slower in the actual waste (2.7 E-08 mole/C) than that obtained with simulant waste and compared with tests conducted by Westinghouse Savannah River Company. This slow destruction rate may be attributable to the "induction" period observed by other researchers during simulant testing. It is postulated that a chromium hydroxide film forms on the cathode that inhibits the rate of nitrate and nitrite reduction. The actual waste contains a three to five times higher concentration of chromium than the simulated waste, which would support the induction period hypothesis. Further support is provided by the fact that inspection of the cathode after testing showed a fine black/dark brown film adhered to the electrode surface. The effects of electrochemical oxidation on the dispositions of ^{90}Sr and ^{99}Tc were also investigated. The results show a decrease in the soluble ^{90}Sr concentration for both the divided and undivided cell oxidations. This decrease provides evidence that the organic chelators for ^{90}Sr in the waste are being defunctionalized.

However for ^{99}Tc, the results do not provide conclusive evidence that nonpertechnetate species were oxidized or that ^{99}Tc was electrodeposited. The short test duration and the induction period described above, which inhibits the electrodeposition of the ^{99}Tc, may explain the inconclusive results, as it has been reported that pertechnetate deposits concomitantly with nitrate and nitrite destruction.

The test results indicate that on a short-term basis the simulant adequately reflects the characteristics of the actual waste with respect to TOC. However, inorganic species such as chromium, which are believed to influence cathode reactions, will require further investigation in future electrochemical testing activities. A longer duration (50 to 100 h) test with actual waste is recommended to investigate the system performance with respect to film formation, complexant defunctionalization, and metal disposition. The complexant defunctionalization and organic destruction results are encouraging, although the longer-term stability must be addressed with respect to the performance issues described above. Performance issues raised in a technology downselection conducted in 1994 related to the ability of the process to handle an actual waste feed were addressed by this study. The downselection in 1994 rated electrochemical processing as one of the top technologies for organic and nitrate destruction in Hanford tank waste, and the results of this latest study further substantiate this technology. Electrochemical processing offers a low-temperature and low-pressure alternative to thermal-based processes.

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1.0 Introduction

Millions of gallons of high-level radioactive wastes are stored in underground tanks at several U.S. Department of Energy sites around the United States. The current cleanup strategy for these sites, including the Hanford Site in southeastern Washington state, is to retrieve the wastes and separate the components into high-level and low-level waste streams. Many of the tanks contain organic compounds, nitrate, and nitrite that may have an impact on waste management and safety considerations, and affect the performance of candidate treatment processes and ultimate waste disposition. Consequently, technologies are needed that can safely and efficiently destroy those organic compounds and/or nitrate in the waste stream to eliminate those safety and disposal issues. Electrochemical oxidation/reduction is a promising technology for the treatment of Hanford liquid wastes (oxidation to destroy organic compounds and reduction to destroy nitrates and nitrites).

During FY 1993 and FY 1994, Pacific Northwest National Laboratory (PNNL)[a]conducted investigations of the destruction of organic compounds by electrochemical processes for the Tank Waste Remediation System (TWRS) program and the Westinghouse Savannah River Company (WSRC). The primary objective of that study was to develop data for the preconceptual design of an electrochemical process for the treatment of Hanford tank wastes. The study investigated several candidate electrode materials and cell configurations, and compared the oxidation of several organic species (e.g., EDTA, HEDTA, citrate, etc.) that are present in many of the tank wastes. Testing was conducted with a simulated nonradioactive tank waste based on Hanford complexant concentrate waste from Tank 101-SY, a high-level waste tank.

Electrochemical organic destruction (ECOD) testing conducted before FY 1996 had involved only simulated tank wastes. Although the inorganic species in most of the organic-bearing tanks have been well characterized, the identification of organic species and determination of their individual concentrations is much less understood. Destruction of certain organic species will help to mitigate safety issues. Additionally, pretreating the supernatant may simplify waste disposal by destroying or defunctionalizing organic compounds that may complex and solubilize strontium and transuranic (TRU) species in the waste. The term "defunctionalize" refers to the breaking up of a complexant through heating or radiolysis into other organic products that can no longer complex the radionuclide, without reducing the observed concentration of total organic carbon (TOC) in the solution. Reducing the radionuclide content, especially TRU components, in the supernatant would enhance separation of the waste into a large volume low-level waste fraction and a small volume high-level waste sludge, which is a major waste disposal goal.

Since the performance of this electrochemical process for organic destruction had not yet been confirmed with samples of actual tank waste, the main purpose for FY 1996 tests was to validate simulant tests by comparison with actual radioactive waste tests. Therefore, in FY 1996, PNNL undertook a study to conduct tests not only with simulated waste but with actual radioactive tank wastes as well, and compare results of the tests. The main focus of the work was the destruction of organic compounds (especially organic complexants of radionuclides) in the wastes. A second objective was to assess the destruction of nitrates in the wastes. This report presents the results of an electrochemical process evaluation using both the simulated and radioactive tank wastes.

(a) Operated for the U. S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

2.0 Conclusions and Recommendations

Electrochemical organic and nitrate destruction in Hanford simulant and actual radioactive tank waste was demonstrated with an ICI FM01-LC bench-scale electrochemical flow cell. The cell was operated in both divided and undivided cell configurations, and the destruction rate and current efficiency determined for TOC and nitrite/nitrate species. The actual waste used for testing were complexant concentrates wastes from Hanford Tanks 101-SY and 103-SY.

The rate of destruction of TOC in the actual waste for the undivided cell configuration was found to be comparable to that obtained for simulant testing, which indicates that, over this test duration, the simulant adequately reflected the TOC characteristics of the actual waste. Over a longer test duration, the simulant may not represent the actual waste, as many other species are known to be present and some are expected to be more refractory to oxidation.

The TOC destruction rate was observed to be lower in the divided configuration than in the undivided configuration. A similar observation was made during pilot-scale testing conducted by The Electrosynthesis Company (ESC) with Hanford simulants. ESC attributed this difference in rate to the difference in solubility as a result of the higher sodium/alkalinity in the divided run.

Nitrate and nitrite species reduction was observed to be slower in the actual waste than that obtained with simulant. This difference may be attributable to the "induction" period observed by ESC during simulant testing. ESC postulated that a chromium hydroxide film may form on the cathode, which inhibits the rate of nitrate and nitrite reduction. The actual waste contains a much higher concentration of chromium than the simulated waste, which would support the induction-period hypothesis. Further support is provided by an inspection of the cathode after testing that showed a fine black/dark brown film adhered to the electrode surface. A smear of the film was taken, although not enough film was available to provide a sample for chemical analysis. Further investigation of the film and effect on reduction reactions is recommended.

A primary reason for destroying the organic species in the complexant concentrate tank waste is to decomplex/defunctionalize species that chelate radionuclides. The separations processes required to remove the radionuclides are much less efficient when chelators are present. Therefore, the effects of electrochemical oxidation on the dispositions of ^{90}Sr and ^{99}Tc were investigated. The results show a decrease in the ^{90}Sr concentration for both the divided and undivided cell oxidations. This decrease provides evidence that the organic chelators present in the waste are being defunctionalized. On the other hand, the results for ^{99}Tc do not provide conclusive evidence that nonpertechnetate species were oxidized or that ^{99}Tc was electrodeposited. This lack of conclusive evidence is attributed to the short test duration and the induction period described above that inhibits the electrodeposition of the ^{99}Tc. It has been reported that pertechnetate deposits concomitantly with nitrate and nitrite destruction.

In all runs, both gas chromotography (GC) and mass spectroscopy (MS) data indicate ammonia is present in the offgas. The actual volume depends on the offgas production rate, which varies from test to test and within each test. The quantity of ammonia detected is of sufficiently small volumes that it can be attributed to one or a combination of the following sources: 1) the reduction of nitrate and nitrite; 2) the oxidation of organic species that fragment to ammonia; and 3) vaporization of dissolved ammonia by the increase in temperature and mixing during electrochemical processing. However, caution must be exercised with respect to the offgas data, as ammonia is a difficult compound to detect and measure accurately.

3.0 Electrochemical Testing

A description of the anticipated reactions and the premise behind electrochemical organic and nitrate destruction can be found in Hobbs (1995) and Chai et al. (1995). The following sections describe the objectives, testing approach, equipment, and procedures used in PNNL's investigation.

3.1 Objectives

In this investigation, tests were conducted using both simulated tank waste and actual radioactive tank waste with the same test conditions in order to identify any differences in system performance as a result of the two different materials. The principal objectives of this study were 1) to evaluate the rate of destruction of organic compounds in the two wastes, and 2) assess the destruction of nitrates and nitrites in the wastes. Other objectives included evaluating changes in concentrations of other inorganic species (especially certain radionuclides such as strontium and technetium) as a function of the charge passed.

3.2 Test Approach

Electrochemical testing was first conducted using a nonradioactive simulated tank waste that has been used extensively for this work and for other testing. The simulant, SY1-SIM-93A, is based on the Tank 101-SY organic complexant waste composition. Two different electrochemical cell arrangements were used: divided cell configuration (using a cation exchange membrane between the cathode and anode) and undivided cell configuration (no membrane). Following the simulant tests, the equipment was relocated to a hood in a radiation zone, and similar tests were conducted using the actual radioactive tank waste. Initial radioactive testing in the divided cell configuration was done with diluted Tank 101-SY waste. However, due to a limited volume of waste available, subsequent testing in the undivided cell configuration was conducted using a mixture of Tank 101-SY and Tank 103-SY wastes. (Tank 103-SY waste is chemically very similar to Tank 101-SY waste.) No significant impact was anticipated from using a mixture of the two different wastes.

Evaluation of the process included analyses of waste solutions and offgas samples collected throughout the tests, and observations of the condition of electrodes and membranes over the course of the testing. Analyses of TOC and nitrate/nitrite concentrations as functions of time, temperature, cell voltage, and current density provided most of the basis for the evaluation. For all tests, the electrochemical cell was configured with a platinized titanium anode and platinized titanium cathode.

3.2.1 Divided Cell Configuration

With the divided cell configuration, a Nafion 450® (E. I. DuPont de Nemours and Company) membrane was placed between the cathode and anode of the electrochemical cell to separate the cell into two compartments and the electrolyte into two streams (catholyte at the cathode and anolyte at the anode). Previous testing has shown increased efficiency for organic destruction. This higher efficiency is attributed to the membrane's ability to block the passage of certain species and thereby inhibit competing reversible reactions, such as the reduction of nitrate to nitrite at the cathode followed by its reoxidation to nitrate at the anode. While higher current efficiency is possible in a divided cell, over time the membrane may become fouled by precipitates that form due to changes in pH, solubility, etc., depending on composition of the electrolyte. The membrane was visually inspected after each test run.

3.2.2 Undivided Cell Configuration

For the undivided cell configuration, the membrane was removed from between the electrodes. In this configuration, electrical resistance across the cell remains lower than in the divided cell, which eliminates the potential for fouling of the membrane. However, current efficiency can be lower than for the divided cell configuration due to competing electron shuttle reactions.

3.3 Test Apparatus/Facility Description

This evaluation of the ECOD process used established electrochemical testing apparatus and support equipment and laboratories. Electrochemical testing was performed with a bench-scale ICI FM01-LC cell that was procured for use as a laboratory plate-and-frame flow cell. Figure 3.1 shows a photograph of the electrochemical treatment apparatus used for this testing. The apparatus consists of an electrochemical flow cell, power supply, pumps, feed reservoirs, and data acquisition equipment. The test apparatus was set up and operated in laboratory fume hoods both for the nonradioactive simulant tests (first) and for the actual waste tests (second). The flow cell, feed reservoirs, and pumps were placed inside the fume hood as shown in Figure 3.2. The data acquisition equipment and power supply and offgas sampling were connected outside the fume hood.

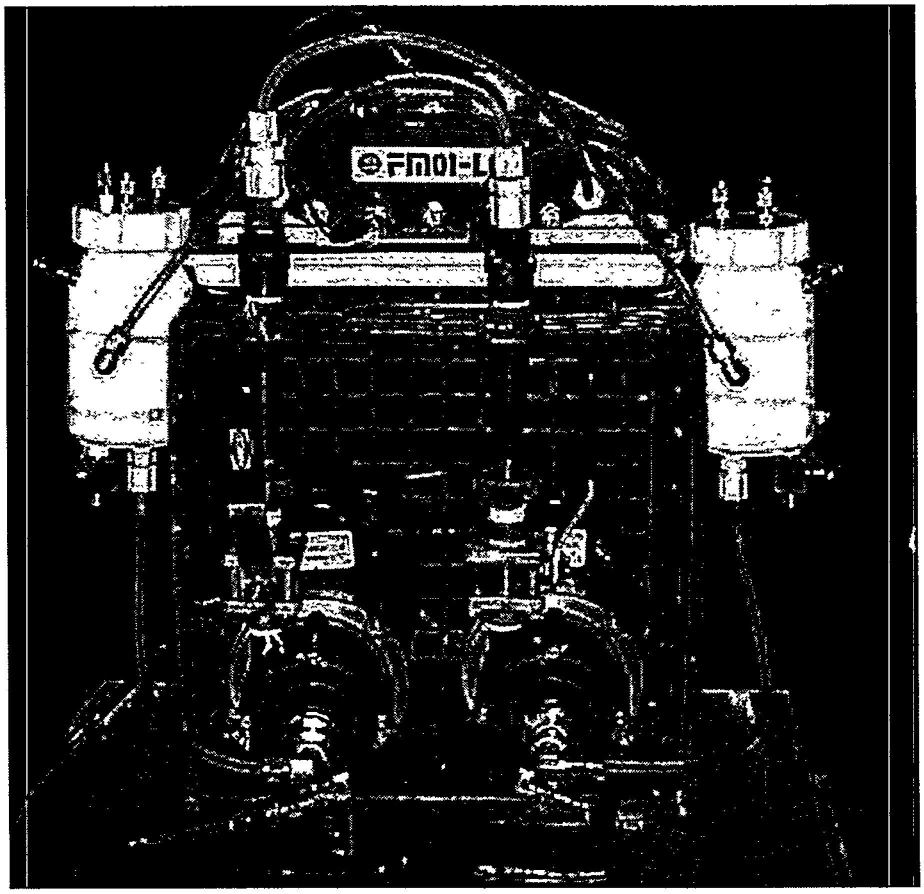

Figure 3.1. Photograph of Electrochemical Test System (FM01-LC Plate-and-Frame Flow Cell, Pumps, Flow Meters and Solution Reservoirs).

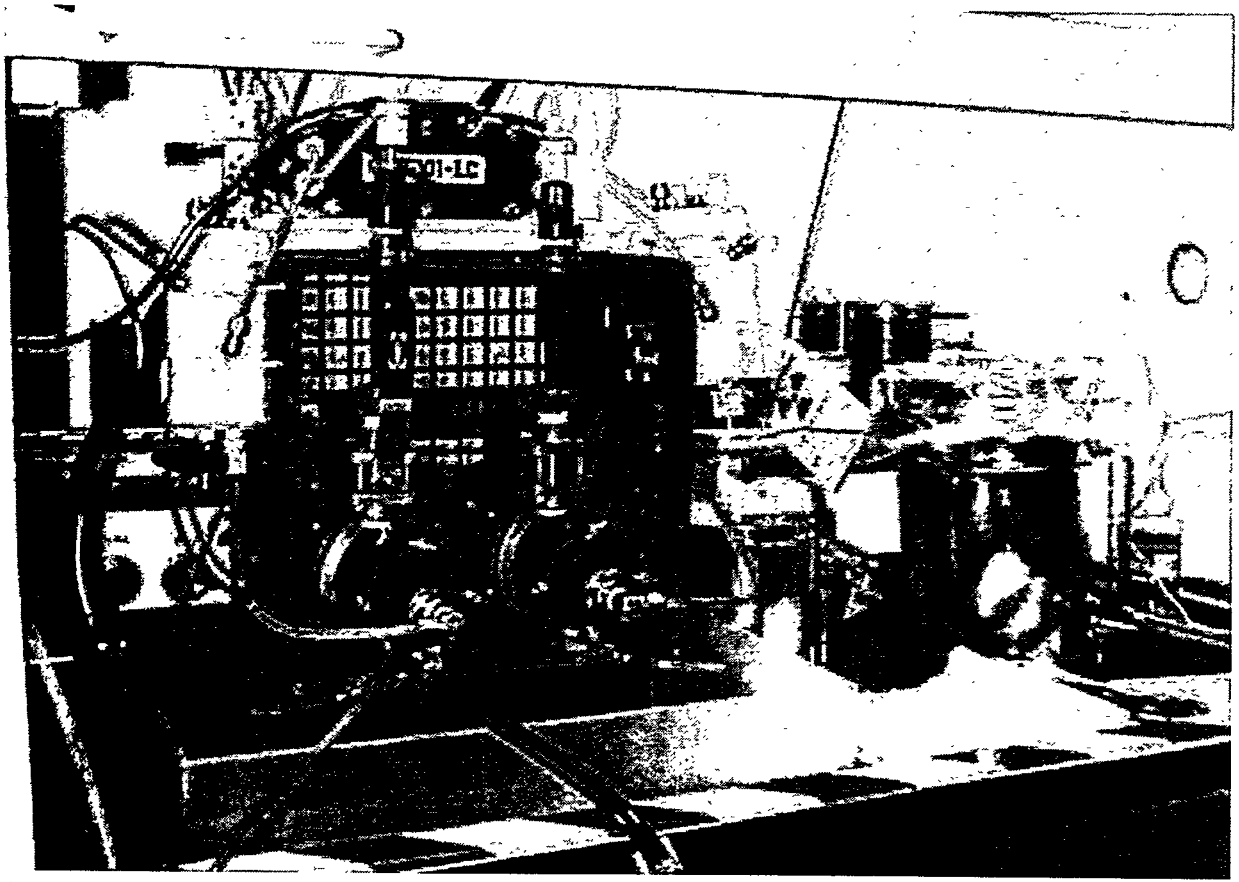

Figure 3.2. Photograph of Electrochemical Test System Installed in Radioactive Contamination Area Fume Hood.

3.4 Testing Procedures/Methods

Before the simulant testing began, leak testing and operability testing of the system were performed using deionized water. Water was then drained from the system, and the feed reservoirs were filled with the simulated waste. The simulant was pumped through the cell and back to the feed reservoir. The system was operated at a constant current density of ~3500 A/m^2. The current, voltage, time, temperature and flow rate were recorded throughout each test. All simulant tests and actual waste tests were run for ~4 h. The cell was operated at ~50°C to 65°C, which was the resultant temperature of the cell with no cooling or heating applied. Liquid samples were collected periodically throughout the test for later analysis. During the actual waste testing the offgas was monitored online using GC and MS.

Simulant testing consisted of three separate tests. In the first test the simulant was placed in the catholyte chamber and tested under conditions described earlier. A solution of 5 M NaOH was used in the anolyte compartment. The liquid was sampled throughout the test, which was run up to 4 h. For the second test, the simulant was taken from the catholyte chamber of the first test and placed in the anolyte chamber. A fresh 5 M NaOH solution was then used for the catholyte. The second test was also run under similar conditions. The third test was conducted in the undivided configuration. All tests were conducted without temperature control and, as such, were allowed to equilibrate at a slightly elevated temperature of ~50 °C to 65 °C . The solution flow rates for each test was operated at ~ 1.25 to 1.5 mL/min.

For the radioactive work, a fume hood was preferred over either a hot cell or glovebox to greatly simplify operation of the equipment. However, the radioactive waste first had to be pretreated to remove ^{137}Cs and thereby lower the dose rate. The ^{137}Cs was removed by contacting the waste supernatant with IE-96 zeolite ion exchange material. The ion exchange was performed successfully in the hot cell; then the treated waste was taken from the hot cell to the laboratory fume hood for ECOD testing.

Radioactive testing also consisted of three separate tests. In the first test the Tank 101-SY waste was placed in the catholyte chamber and tested under conditions described earlier. A solution of 5 M NaOH was used in the anolyte compartment. The test was run for 4 h, and samples of the catholyte were taken each hour. For the second test the waste was taken from the catholyte chamber of the first test and placed in the anolyte chamber. A fresh 5 M NaOH solution was then used for the catholyte. The second test was also run for 4 h and sampled at each hour. The third 4-h test was conducted in the undivided configuration where the Nafion membrane was removed. Dilute combined 101-SY/103-SY waste was used for the electrolyte in the third test. Again, all tests were conducted without temperature control and, as such, allowed to equilibrate at a slightly elevated temperature of ~50°C to 65 C. Once the equilibrium temperature was reached the temperature did not vary by more than ± 3 C. The solution flow rates for each test were ~1.25 to 1.5 mL/min.

3.4.1 Divided Cell Operation

Two divided cell tests were completed: the first test for nitrate and nitrite destruction and the second test for organic destruction. In the first test, 300 mL of waste were added to the catholyte reservoir and 300 mL of 5 M NaOH were added to the anolyte tank. The circulation pumps continuously circulated the simulated waste through both compartments at flow rates from 1.2 L/min to 1.5 L/min. The system was operated under galvanostatic control at a constant current of 22.4 A, which corresponded to a current density for the FM01-LC cell of 3500 A/m^2. Periodically throughout the test, samples of the simulated waste were removed from both the catholyte and anolyte chambers for analysis. Analyses for the simulant waste consisted of TOC, NO_2, and NO_3. The additional analyses performed for the actual waste tests are described in Section 3.6.2. At the end of each test, the simulated waste was drained from the system; the cell was disassembled; and the conditions of the membrane and electrodes were observed.

In the second divided cell test, the waste treated in the catholyte during the first test was placed in the anolyte reservoir and fresh 5 M NaOH was added to the catholyte tank. The same operating conditions and procedures were used during both divided cell tests.

3.4.2 Undivided Cell Operation

The undivided cell testing was similar to the divided cell, except that the dividing membrane was removed so there were no separate catholyte and anolyte solutions. The liquid waste simulant was sampled at 30-min intervals and analyzed. The same chemical analysis used for the divided cell tests was used for samples collected during the undivided cell test.

3.5 Test Material Description

In PNNL work on tank wastes in general, most testing has been done with simulated wastes. Much of that testing has been done with a simulant composition based on analyses of waste from Tank 101-SY. This ECOD testing effort was performed using the same composition for the simulated waste.

The simulated waste was designated SY1-SIM-93A, Hanford Complexant Concentrate Tank Waste Simulant. The composition of the primary components in this waste simulant is described in Section 3.5.1.

Divided cell testing was conducted with Tank 101-SY supernatant. However, there was insufficient Tank 101-SY waste available for all the planned tests. Therefore, subsequent undivided cell testing included the addition of Tank 103-SY supernatant to the remaining Tank 101-SY supernatant to make up the extra volume required for the final test. Supernatant from Tank 103-SY was described as being very similar chemically to Tank 101-SY supernatant, only slightly more dilute. The feed compositions of the Tank 101-SY waste and the combined 101-SY/103-SY waste are shown in Section 3.5.2.

3.5.1 Simulated Tank Waste

For this testing, a target volume dilution of 3:1 (waste:2 M NaOH) was assumed for the simulated and actual wastes to represent the anticipated composition of retrieved tank waste. Table 3.1 shows the initial dilute composition of the SY1-SIM-93A simulated waste.

3.5.2 Actual Radioactive Tank Waste

A limited amount of Tank 101-SY supernatant was available for this testing. The initial target dilution for this testing was ~3:1 as described above. Actual dilution was adjusted to give sufficient waste volume to adequately fill the test cell. In addition, the waste was ion exchanged with IE-96 zeolite prior to testing to remove ^{137}Cs, and thereby lower the dose rate of the waste for safer handling. The ion exchange preparation slightly affected the dilution of the waste. The starting composition for the Tank 101-SY supernatant is shown in Table 3.2. The Tank 103-SY waste was also ion exchanged with IE-96 and diluted before blending it with remaining Tank 101-SY waste for the undivided cell test. The starting composition of the combined 101-SY/103-SY waste is shown in Table 3.3.

3.6 Analytical Procedures/Methods

3.6.1 Offgas Analyses

During the actual waste testing, the offgas was continuously monitored using both GC and MS techniques. The GC (Microsensor Technology, Inc.) had two columns: Column A, PLOT Molecular Sieve 5A; and Column B, Poraplot Q. The GC was interfaced to a Dell 486 laptop computer running MTI EZChrom Software. The GC sampled the process offgas every 2 to 3 min throughout the run duration. The MS system consisted of a Hewlett Packard 5972 Mass Selective Detector and 59822B Ionization Gauge Controller interfaced to a Vectra 486/66 XM computer. The MS sampled at a rate of 0.3 to 6 data points per second scanning up to 100 mass units. For the system, neon gas served as the internal standard/tracer as well as a purge for the solution reservoir head space. The gas was fed at a constant 36 mL/min through an Omega FMA-766-V mass flow controller. The offgas analysis equipment was calibrated with three concentrations of individual and mixtures of gas standards before and after testing. In addition, the total gas volume was monitored using a wet test meter (American Meter Company) connected to the offgas line.

Table 3.1. Composition of Dilute SY1-SIM-93A (Simulated Tank 101-SY Waste)

Component	Wt%	Component	Wt%
Na	7.05	NO_3	4.07
Al	1.12	NO_2	3.65
Cr	0.14	OH	1.02
Ca	0.008	TIC	0.22
Fe	0.0097	PO_4	0.22
K	0.11	SO_4	0.14
Ni	0.0052	Cl	0.27
Zn	0.00071	F	0.01
Cs	0.00049	TOC (EDTA)	0.53
Sr	0.000021	H_2O	78.46

Table 3.2. Composition of Diluted Tank 101-SY Waste Supernatant

Component	mg/L	Component	pCi/L
Al	564.0	Gross Alpha	2.03E+05
Ca	93.8	^{137}Cs	1.82E+11
Cr	84.9	^{60}Co	5.01E+09
Fe	8.73	^{90}Sr	2.58E+06
Ni	16.3	^{99}Tc	8.44E+07
Zn	0.366		
NO2	7560		
NO3	6210		
SO4	885		
PO4	850		
TOC	5160		

Table 3.3. Composition of Combined 101-SY/103-SY Waste Supernatant

Component	mg/L	Component	pCi/L
Al	9540	Gross Alpha	4.09E+04
Ca	79.7	^{137}Cs	1.82E+11
Cr	54.1	^{60}Co	6.13E+06
Fe	23.5	^{90}Sr	7.06E+05
Ni	8.72	^{99}Tc	8.31E+07
Zn	0.085		
NO2	12100		
NO3	10700		
SO4	1850		
PO4	660		
TOC	281		

3.6.2 Liquid Sample Analyses

Samples of the radioactive waste were taken periodically from the test apparatus throughout each test. Small aliquots (5 to 10 mL each) were placed in vials and analyzed by Environmental Physics, Inc. (Charleston, SC) for inorganics, TOC, and radionuclides. In addition to these samples, a selected subset of these samples (2 to 3 mL each) was analyzed onsite for ^{99}Tc. Table 3.4 summarizes the analytical methods used for liquid analyses.

Table 3.4. Methods Used to Analyze Radioactive Liquid Samples

Laboratory	Analysis	Method
Environmental Physics, Inc.	Metals (nonradioactive)	Inductively-Coupled Plasma Spectroscopy (ICP) (EPA 6010.A)
	Nitrate, Nitrite, Sulfate	Dionex DX-300 Ion Chromatography (EPA 300.0)
	Total Organic Carbon	Dohrman TOC Analyzer (EPA 9060 modified)
	Phosphate	TRAACS Total Phosphorous Analyzer (EPA 365.4)
	Gross Alpha	Proportional Counting (EPA 900.0)
	Cesium-137	Gamma Spectroscopy (HASL 300)
	Strontium-90	Proportional Counting (EPI A-004)
	Technetium-99	Liquid Scintillation Counting (EPI A-005)
PNNL	Technetium-99	ICP-Mass Spectroscopy

4.0 Results and Discussion

4.1 Simulated Waste Testing

The simulant and actual waste tests were conducted under similar conditions to directly compare the results. Therefore, the results for the simulant tests are discussed in conjunction with the actual waste test results in Sections 4.2 and 4.3.

4.2 Radioactive Waste Testing

4.2.1 Divided Cell Configuration Tests

The first radioactive test was run in the divided configuration with the waste in the catholyte compartment. Over the course of this test, the catholyte volume steadily increased with time. It is believed that the increased catholyte volume is due to the transport of hydrated water molecules across the membrane from the anolyte into the catholyte. The volume increase was ~40 mL/h with ~8 mL removed each hour for analytical samples. Sample analyses were corrected for the effects of this dilution. In a similar manner, the second test with the waste as the anolyte showed a steady decrease in volume as water passed from the anolyte into the catholyte. Sodium hydroxide solution was added twice to the anolyte to maintain a minimum volume of waste in the anolyte chamber. The first addition was after 2 h of operation when 25 mL were added; the second was at 3 h when an additional 66 mL were added to the anolyte. The following tables summarize the analytical results for waste samples taken during the divided cell tests, as either catholyte (Table 4.1) or anolyte (Table 4.2) tests.

4.2.2 Undivided Cell Configuration Tests

The third test with radioactive tank waste was run in the undivided configuration. Since there were no separate anolyte and catholyte compartments there was no volume change, and therefore no concentration change due to cross-membrane transport of water. Like the divided tests, samples were taken each hour and the test duration was 4 h. Table 4.3 summarizes the analytical results of samples collected over the course of the undivided cell test.

4.3 Comparison of Results

4.3.1 Test 1 - Divided Cell - Catholyte

In the divided cell configuration, catholyte side, organic destruction was minimal in the simulant test and insignificant in the actual waste test (Figure 4.1). This is expected as the cathode provides a reducing environment, and the organic destruction should occur in the oxidizing anolyte compartment. However, results of tests with simulated tank waste differed substantially from tests with actual radioactive tank wastes with respect to nitrate and nitrite destruction at similar conditions.

Table 4.1. Analyses of Radioactive Waste as Catholyte During Divided Cell Tests[a]

Component	Catholyte Concentrations (mg/L) or (pCi/L)[b]				
	Initial	1 h	2 h	3 h	4 h
Total Organic Carbon	5160	5245	5330	5040	5544
Nitrite	7560	7354	7147	7038	6468
Nitrate	6210	6134	6057	6045	5880
SO_4	885	N/A[c]	N/A	N/A	899
PO_4	850	N/A	N/A	N/A	1014
Al	564	N/A	N/A	N/A	505
Ca	92.8	N/A	N/A	N/A	61.0
Cr	84.9	N/A	N/A	N/A	42.6
Fe	8.7	N/A	N/A	N/A	6.2
Ni	16.3	N/A	N/A	N/A	15.0
Zn	0.366	N/A	N/A	N/A	0.367
^{90}Sr[b]	2.58E+06	9.11E+06	8.13E+06	8.71E+06	7.69E+06
^{137}Cs [b]	1.82E+11	N/A	N/A	N/A	1.76E+11
^{99}Tc (PHA) [b,d]	8.84E+07	N/A	N/A	N/A	7.64E+07
^{99} Tc (ICP-MS) [b,d]	4.70E+07	N/A	4.91E+07	N/A	4.28E+07

(a) Analyses are corrected for dilution occurring to catholyte during test due to transport of water through membrane with sodium ions.

(b) Concentrations of radionuclides are given in picocuries/liter (pCi/L). All others are in mg/L.

(c) N/A = not analyzed. Reduced sample size; limited waste volume restricted the number of analyses performed.

(d) PHA = gamma peak height analysis; ICP/MS = ICP with mass spectroscopy to analyze for "mass 99" species.

Table 4.2. Analyses of Radioactive Waste as Anolyte During Divided Cell Tests[a]

Component	Anolyte Concentrations (mg/L) or (pCi/L)[b]				
	Initial	1 h	2 h	3 h	4 h
Total Organic Carbon	3360	3088	2598	1853	2409
Nitrite	4830	219	0	0	0
Nitrate	4360	7354	5889	4993	5940
SO_4	639	N/A[c]	N/A	N/A	514
PO_4	676	N/A	N/A	N/A	266
Al	359	N/A	N/A	N/A	243
Ca	48.6	N/A	N/A	N/A	4.5
Cr	33.3	N/A	N/A	N/A	22.1
Fe	4.7	N/A	N/A	N/A	1.6
Ni	10.7	N/A	N/A	N/A	0.23
Zn	0.292	N/A	N/A	N/A	0.435
^{90}Sr[b]	6.64E+06	4.44E+06	2.18E+06	1.55E+06	1.10E+06
^{137}Cs [b]	1.21E+11	N/A	N/A	N/A	1.33E+09
^{99}Tc (PHA) [b,d]	4.88E+07	N/A	N/A	N/A	3.81E+07
^{99}Tc (ICP-MS) [b,d]	3.87E+07	N/A	2.94E+07	N/A	2.29E+07

(a) Analyses are corrected for concentration effect occurring during test due to transport of water through membrane with sodium ions from anolyte side to catholyte side.

(b) Concentrations of radionuclides are given in picocuries/liter (pCi/L). All others are in mg/L.

(c) N/A = not analyzed. Reduced sample size; limited waste volume restricted the number of analyses performed.

(d) PHA = gamma peak height analysis; ICP/MS = ICP with mass spectroscopy to analyze for "mass 99" species.

Table 4.3. Analyses of Radioactive Waste During Undivided Cell Test

Component	Waste Concentrations (mg/L) or (pCi/L)[(a)]				
	Initial	**1 h**	**2 h**	**3 h**	**4 h**
Total Organic Carbon	5620	11200	9200	4440	5940
Nitrite	12100	3640	929	255	176
Nitrate	10700	19300	23600	24700	25500
SO_4	1850	N/A[(b)]	N/A	N/A	2480
PO_4	660	N/A	N/A	N/A	790
Al	9540	N/A	N/A	N/A	11400
Ca	79.7	N/A	N/A	N/A	53.4
Cr	54.1	N/A	N/A	N/A	71.2
Fe	23.5	N/A	N/A	N/A	24.0
Ni	8.7	N/A	N/A	N/A	5.1
Zn	0.08	N/A	N/A	N/A	0.08
^{90}Sr[(a)]	7.06E+05	6.06E+05	4.89E+05	5.30E+05	2.62E+05
^{137}Cs [(a)]	9.25E+09	N/A	N/A	N/A	1.11E+10
^{99}Tc (PHA) [(a,c)]	8.41E+07	N/A	N/A	N/A	1.07E+08
^{99}Tc (ICP-MS) [(a,c)]	8.31E+07	N/A	8.87E+07	N/A	1.09E+08

(a) Concentrations of radionuclides are given in picocuries/liter (pCi/L). All others are in mg/L.

(b) N/A = not analyzed. Reduced sample size; limited waste volume restricted the number of analyses performed.

(c) PHA = gamma peak height analysis; ICP/MS = ICP with mass spectroscopy to analyze for “mass 99” species.

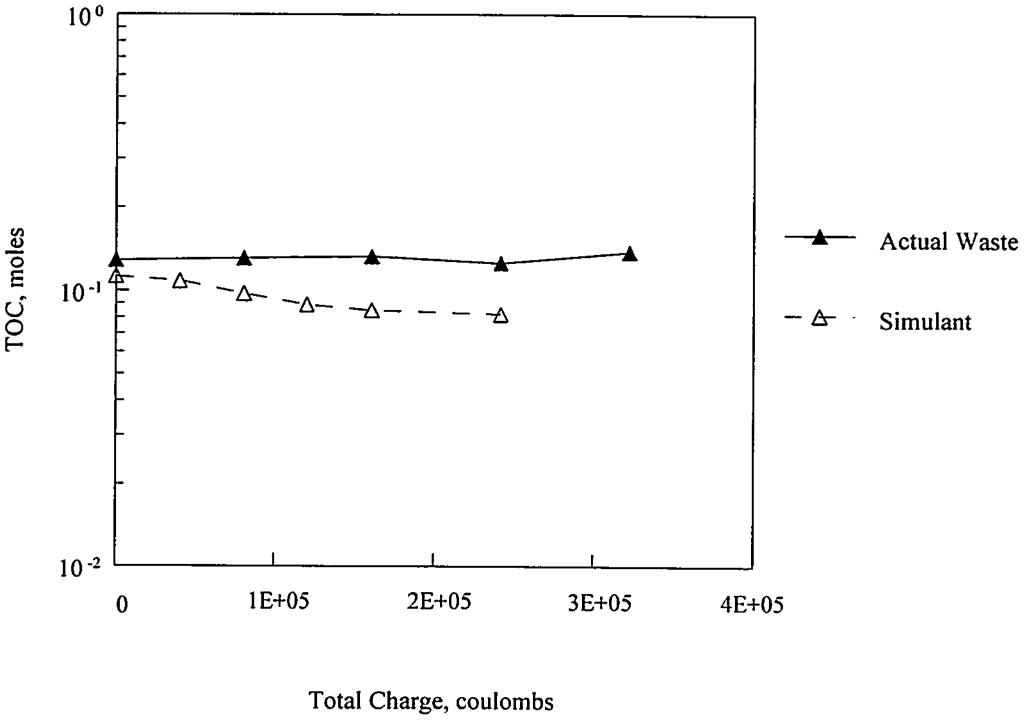

Figure 4.1. Moles of Total Organic Carbon in the Catholyte as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

Figures 4.2 and 4.3 show only a small decrease in nitrite (14.4%) and nitrate (5.3%) in the catholyte compartment for the actual waste test. The destruction rates show a two to three times increase after 3 h, which may be indicative of the induction period observed by Chai et al. (1995) during testing with Savannah River and Hanford tank simulant wastes. The overall nitrate and nitrite destruction rate is on the order of 2.7 E-8 moles/C, which is two orders of magnitude lower than that observed for the simulant. The explanation put forth by ESC for the lower destruction rate is that a chromium hydroxide film may form on the cathode and inhibit the rate of nitrate and nitrite reduction. ESC has obtained overall nitrate and nitrite destruction rates on the order of 7.7 E-07 moles/C with Hanford simulants (Chai et al. 1995), which differ by less than an order of magnitude from the PNNL results. The actual waste contains a much higher concentration of chromium than the simulated waste, which would support the induction-period hypothesis and, therefore, the lower destruction rate in the actual waste versus the simulant. Further support is provided by the fact that inspection of the cathode after testing showed a fine black/dark brown film adhered to the electrode surface. Figure 4.4 shows a photograph of the film adhered to the cathode after completion of Test #1. This film was smearable but could not be removed from the cathode by soaking in deionized water. A smear of the film was taken, although not enough film was available to provide a sample for chemical analysis.

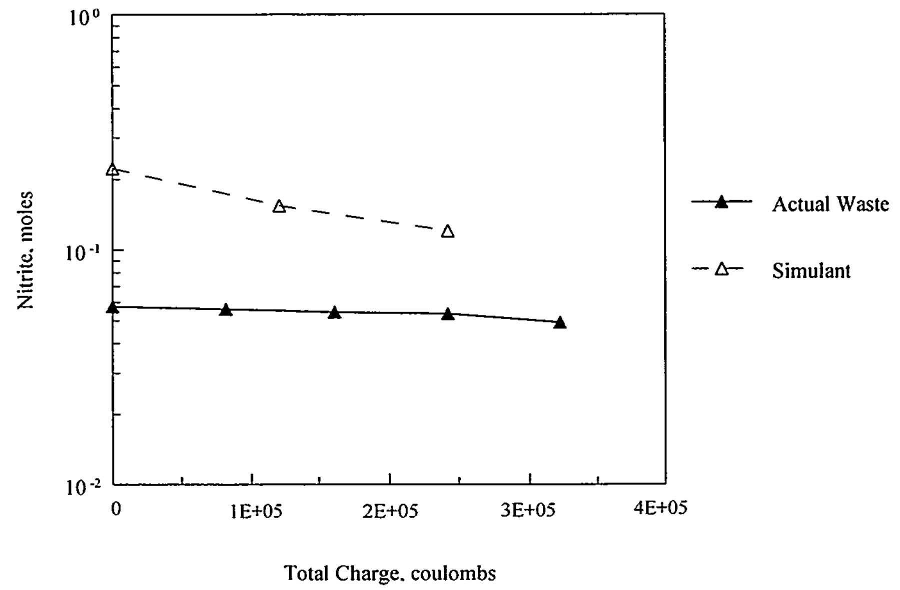

Figure 4.2. Moles of Nitrite in the Catholyte as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

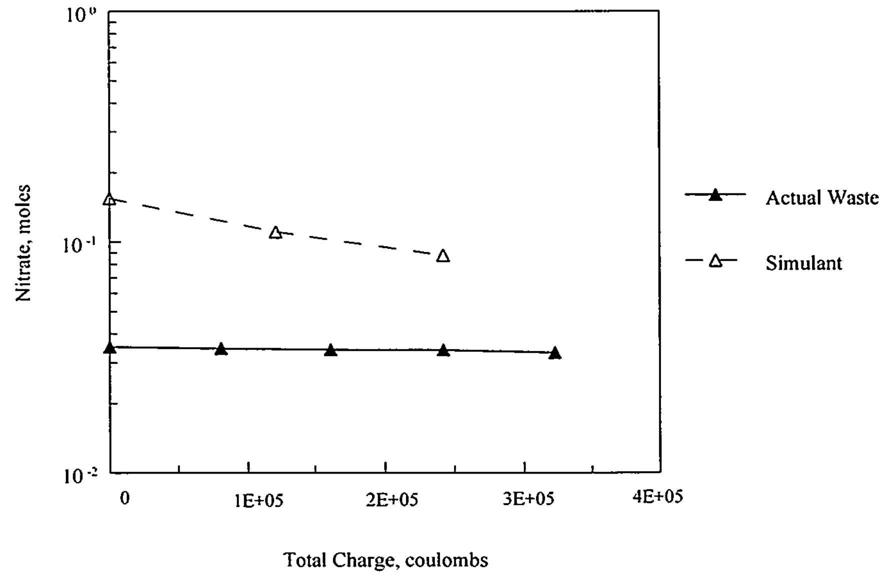

Figure 4.3 Moles of Nitrate in the Catholyte as a Function of Total Charge Passed Comparing the Simulatnt and Actual Waste Tests.

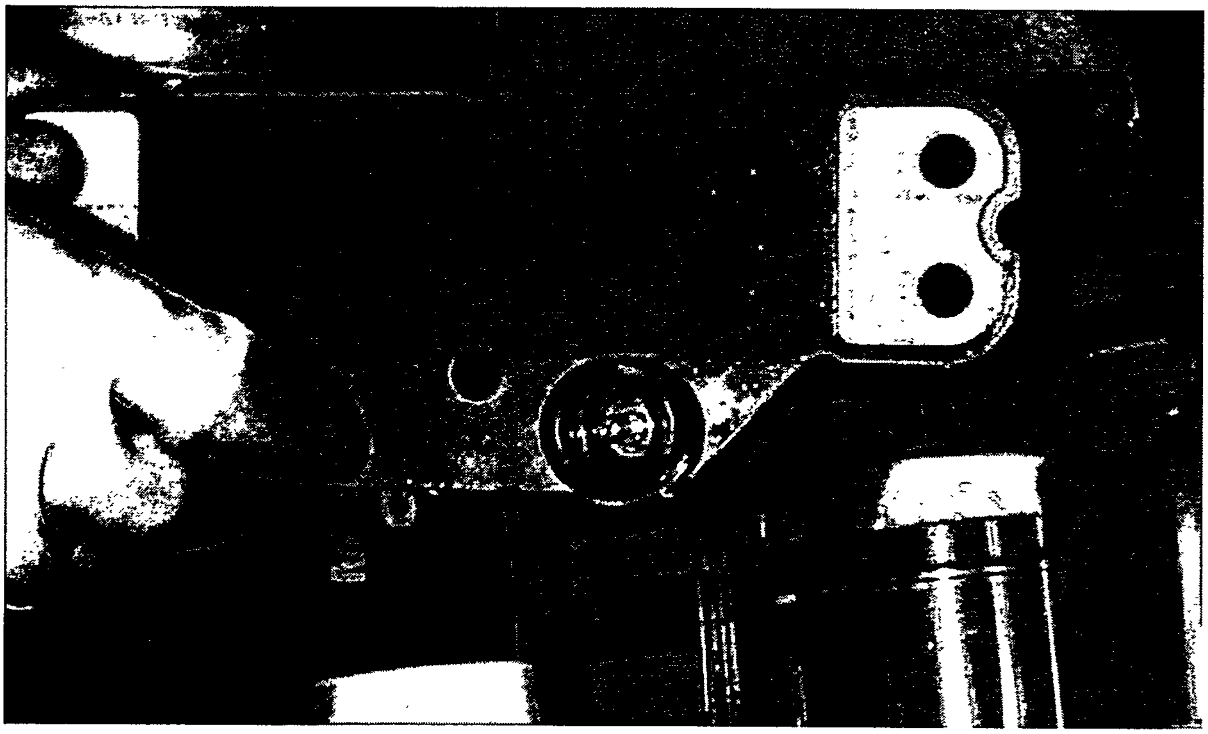

Figure 4.4. Photograph of Cathode After Completion of Actual Waste Catholyte Test. A fine smearable black/dark brown film formed on the cathode during testing.

Figure 4.5 shows the gases (H_2 and NH_3) generated in the catholyte loop during testing, and Figure 4.6 shows the current efficiency for hydrogen generation. The offgas was nearly all hydrogen with a small amount of ammonia. The hydrogen current efficiency ranges from 48% to 100%. The volume of ammonia slightly exceeds the amount expected based solely on nitrate and nitrite reduction. This points to other reactions and/or to degassing of ammonia in the tank waste.

4.3.2 Test 2 - Divided Cell - Anolyte

Figure 4.7 shows the destruction of TOC as a function of the charge passed for the simulant and actual waste tests. The organic destruction appears to be constant over the duration of the test (1E-07 mole/C) for the actual waste. The simulant tests showed very little TOC destruction for the first 2 h, followed by a very significant drop over the next hour, resulting in essentially complete TOC destruction (2.2 E-07 mole/C). This initially low TOC destruction would indicate some competing reaction was occurring during the first 2 h, for example, the oxidation of nitrite or the breakdown of more complex organics into smaller molecules, without going to complete TOC destruction (e.g., EDTA going to other simpler degradation products that are still aqueous-soluble species).

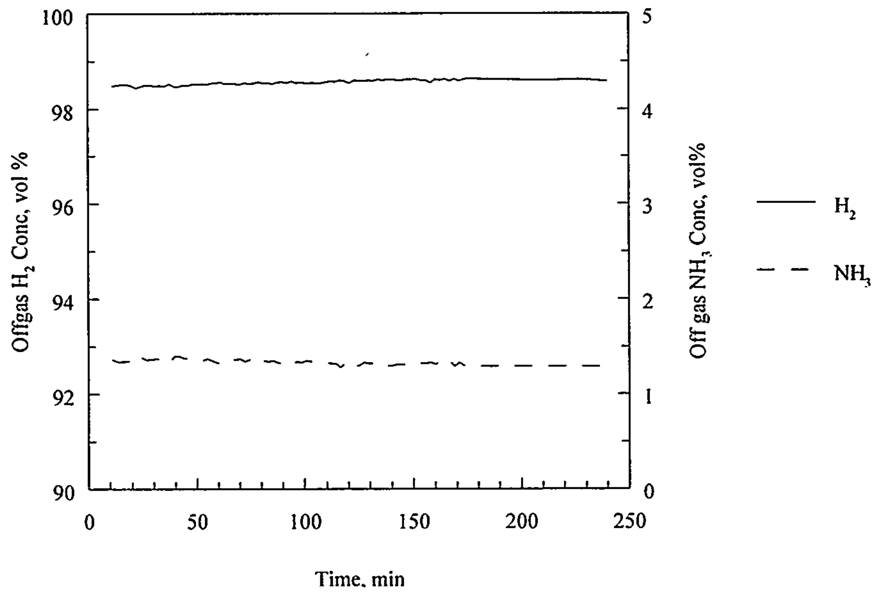

Figure 4.5 Concentrations of Offgas Components (H_2 and NH_3) Evolved During Catholyte Test With Actual Waste

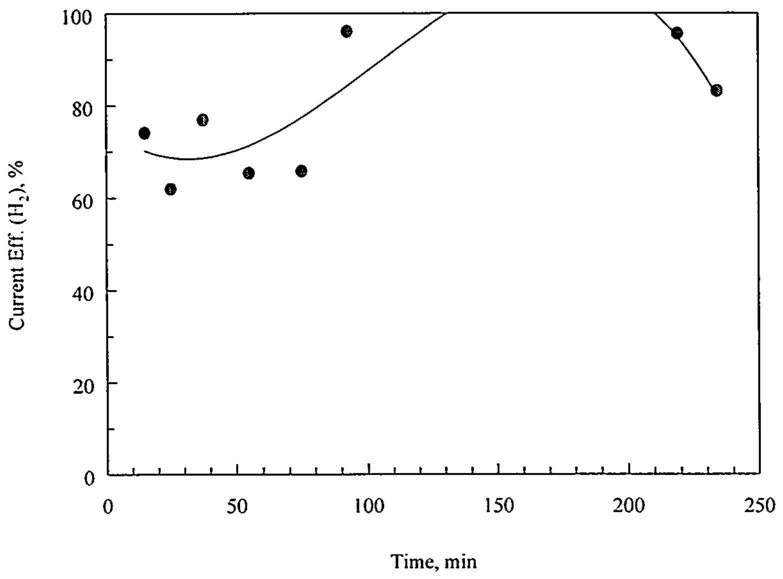

Figure 4.6 Current Efficiency Based on H_2 Generation in Catholyte Test With Actual Waste.

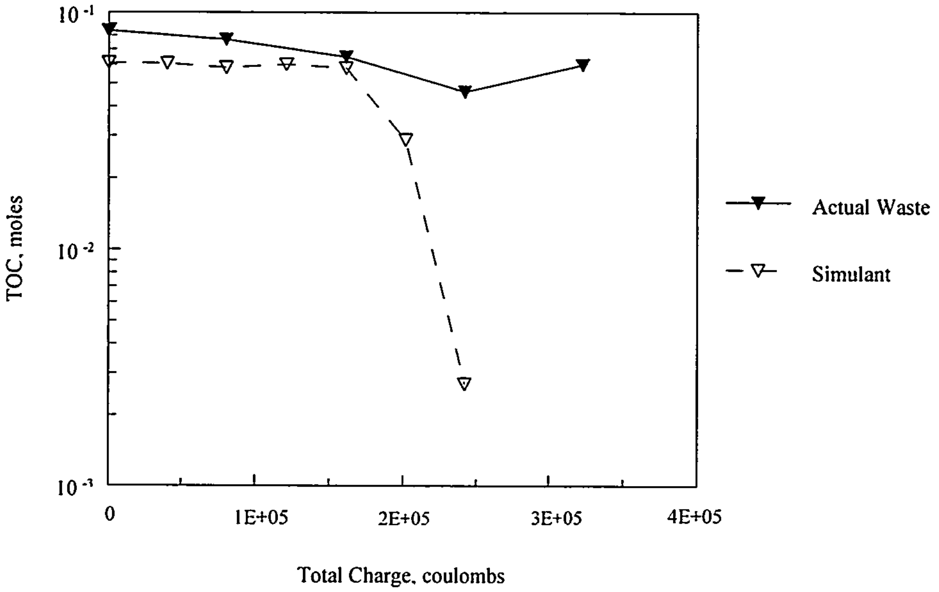

Figure 4.7. Moles of Total Organic Carbon in the Anolyte as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

These differences in destruction rates were not unexpected. For instance, the degree of organic destruction has been shown in previous testing at PNNL with simulants to vary depending on the nature of the initial organic compounds [(a)]. Certain organic materials are more refractory than others, requiring more time and energy to destroy them. Formate and oxalate have been observed to have high destruction rates, while citrate and acetate are much more refractory. EDTA and HEDTA were found to lie somewhere in between. Characterization of individual organic species in these complex tank wastes is extremely difficult, and has only been partially successful in the past. Results indicate that all the above organic species may exist in the Tank 101-SY waste. No attempts were made to characterize the organic species in the supernatant as part of this effort. For the simulated waste, EDTA was used as the only source for organic carbon. Therefore, part of the difference in organic destruction between simulant and actual waste tests is likely attributable to differences in organic species.

It is observed that in both the simulant and actual waste, nitrite is quickly oxidized to nitrate. The depletion of nitrite shown in Figure 4.8 indicates that the oxidation of nitrite to nitrate competes with the organic destruction. The corresponding nitrate concentration data for the actual waste tests are shown in Figure 4.9.

(a) Unpublished PNNL letter report "Electrochemical Organic/Complexant Destruction in Hanford Tank Waste Simulants," submitted by W. E. Lawrence et al. (PNNL) to D. T. Hobbs (WSRC) under subcontract AA71980V, December 1994.

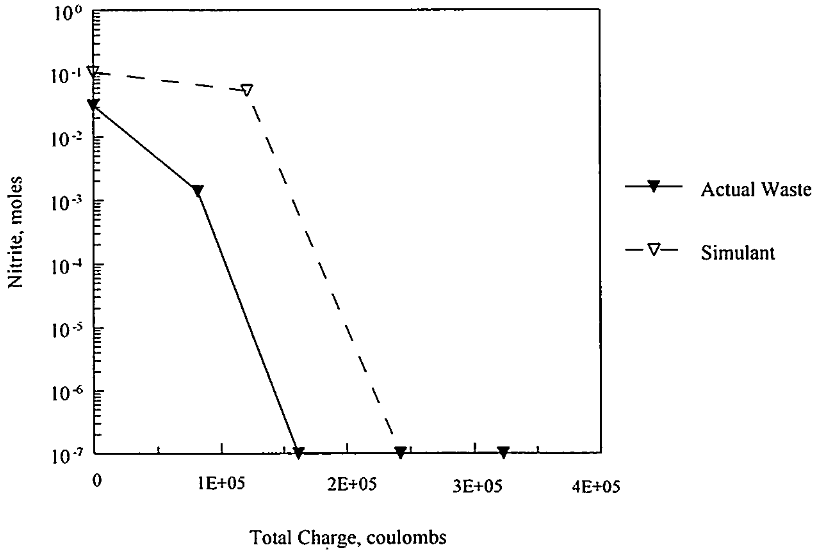

Figure 4.8. Moles of Nitrite in the Anolyte as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

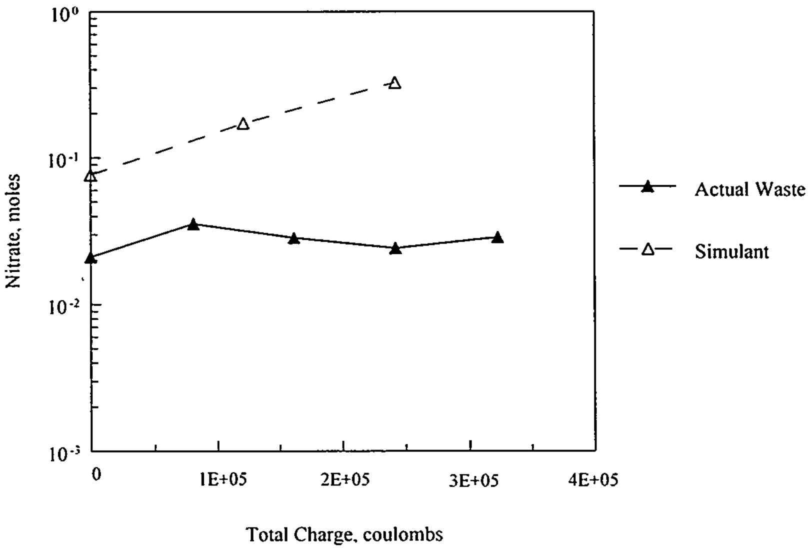

Figure 4.9. Moles of Nitrate in the Anolyte as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

Figures 4.10 and 4.11 show the gases generated in the anolyte loop during testing and the current efficiency for oxygen generation. Oxygen is the primary gas generated at the anode at current efficiencies ranging from 14% to near 100%. The offgas data also indicate the presence of ammonia, which may be attributed to ammonia generation from organic destruction and/or offgassing from solution. This amount of ammonia measured can be accounted for through either source.

Inspection of the electrodes after testing showed only a slight discoloration and no formation of a film or coating. Photographs of the electrodes and membrane after completion of Test 2 are shown in Figures 4.12 and 4.13, respectively.

4.3.3 Test 3 - Undivided Cell

Figure 4.14 shows the TOC concentration as a function of the charge passed. The TOC destruction rates were 5.6 E-07 moles/C and 6.2 E-07 moles/C for the simulant and actual waste tests, respectively. Due to uncertainty with the undivided cell TOC data, the destruction rate and current efficiency (23%) are reported for Hours 1 to 4 because the initial TOC value is uncertain. This difficulty in accurately measuring TOC in the Hanford simulant and actual tank waste has been observed in other studies (Chai et al. 1995). The shape of the curve, TOC concentration versus time, is the same as reported by Chai et al. (1995) during simulant testing. Therefore, the first data point was omitted from the rate and efficiency calculations.

The undivided cell test shows similar trends to the anolyte test for nitrite and nitrate (Figures 4.15 and 4.16). Nitrite is consumed by oxidation to nitrate, although at a slower rate than in Test 2. Inspection of the electrodes after testing showed no visible changes to the cathode and anode and no evidence of film formation. Photographs of the electrodes after testing are shown in Figure 4.17.

Figure 4.18 shows the gases generated during testing, and Figure 4.19 shows the current efficiency for oxygen and hydrogen generation. The primary gases generated are hydrogen and oxygen. As expected, the current efficiency for both hydrogen and oxygen are below 100% primarily as a result of the nitrite/nitrate electron shuttle and organic destruction. A small amount of ammonia was detected in the process offgas. If organic destruction pathways through the formation of ammonia are assumed, the amount of TOC destroyed is adequate to account for all of the ammonia being detected. However, waste degassing is another potential source for ammonia. Ammonia is known to be present in the tank waste and may be offgassed as the process operates at temperatures up to 65 C and provides solution mixing.

4.3.4 Radionuclide Behavior

As was described in Section 1.0, a main reason for destroying organics in the waste is to destroy, or at least defunctionalize, organic compounds that complex and solubilize otherwise insoluble radionuclides in the waste supernatant. Consequently, the concentrations of certain radionuclides in the actual waste were monitored throughout these tests.

Strontium-90 is a radionuclide with normally very low solubility in caustic solutions. However, in the presence of a suitable complexant such as EDTA or other organic species, its solubility can be greatly increased. Therefore, destroying the complexing ability of the organic should cause the non-complexed ^{90}Sr to precipitate. Figure 4.20 shows the change in ^{90}Sr concentration over time for each of the actual waste tests in the different cell configurations. With the exception of the initial sample where the low ^{90}Sr analysis is suspect, the concentration of ^{90}Sr in the catholyte is relatively constant for the 4-h test, as was the TOC concentration (Figure 4.1). This is not conclusive in itself, since complexants could be defunctionalized

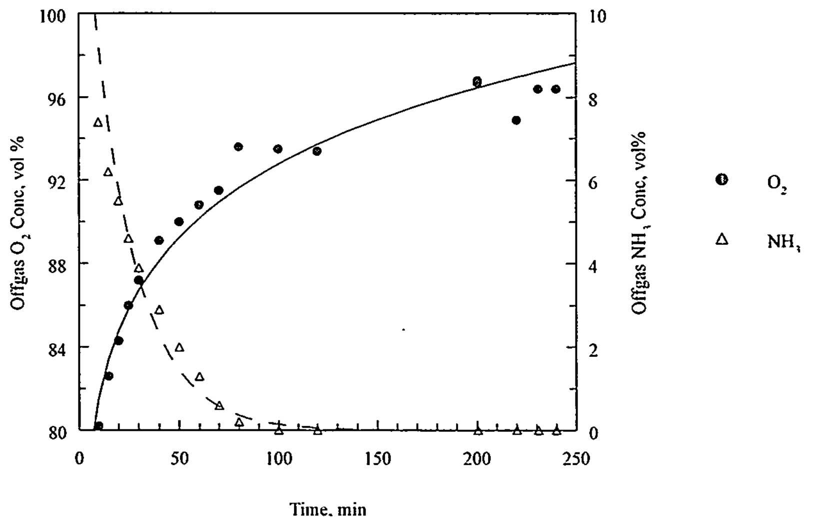

Figure 4.10. Concentrations of Offgas Components (O_2 and NH_3) Evolved During Anolyte Test With Actual Waste.

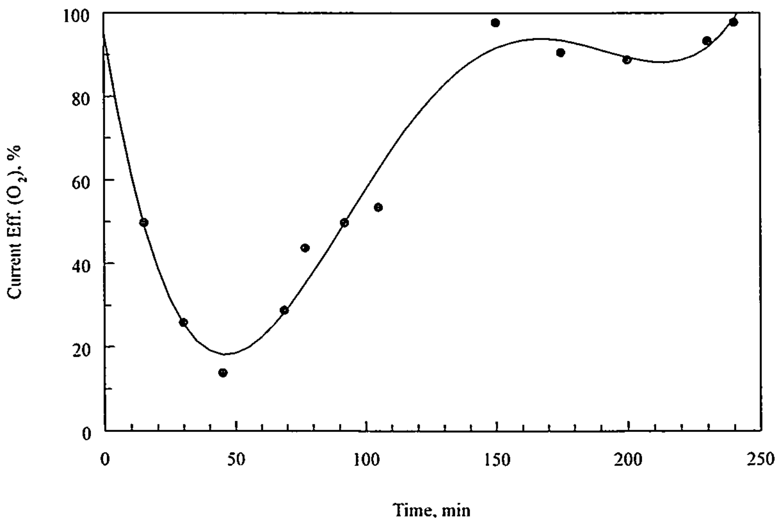

Figure 4.11. Current Efficiency Based On Oxygen Genteration During Anolyte Test With Actual Waste.

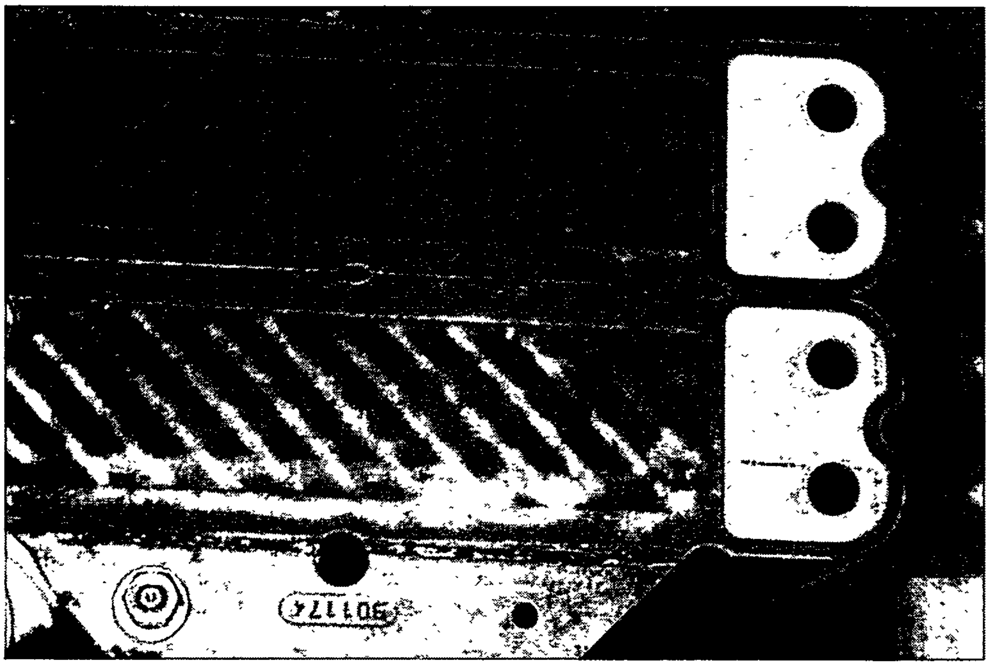

Figure 4.12. Photograph of Cathode (Top) and Anode (Bottom) After Anolyte Test With Actual Waste. Both electrodes showed a slight darkening, but no film was observed.

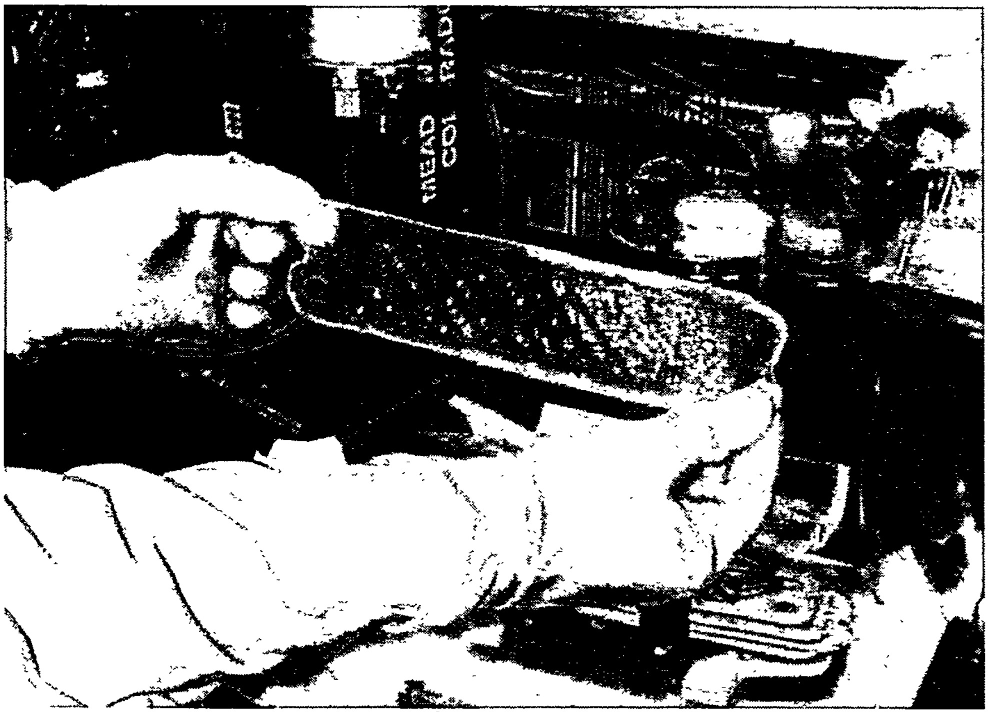

Figure 4.13. Photograph of Nafion® Membrane After Anolyte Test With Actual Waste. The membrane showed no signs of fouling or degradation.

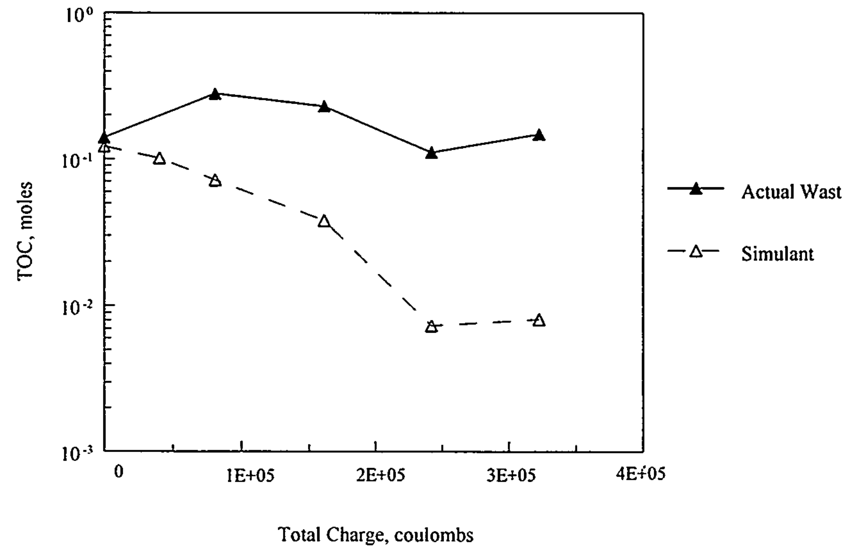

Figure 4.14. Moles of Total Organic Carbon in the Undivided Cell as a Function of Total Charge Passed Comparing Simulant and Actual Waste Tests.

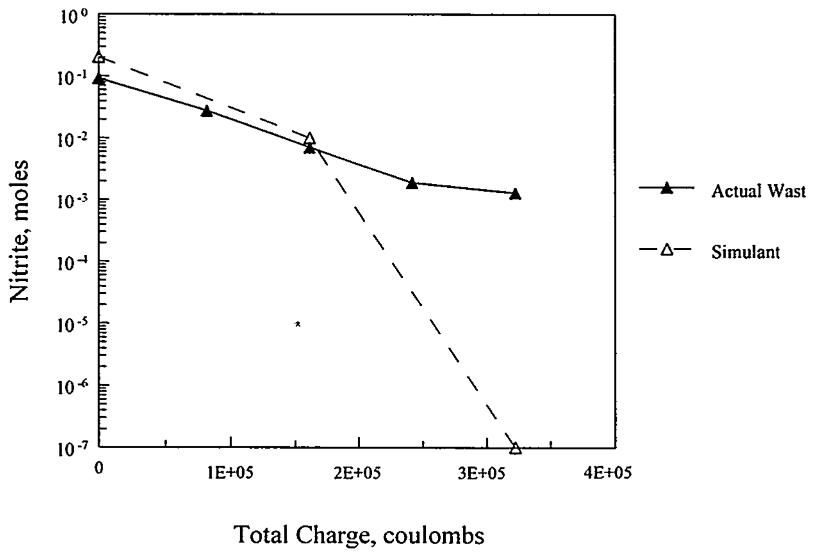

Figure 4.15. Moles of Nitrite in the Undivided Cell as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

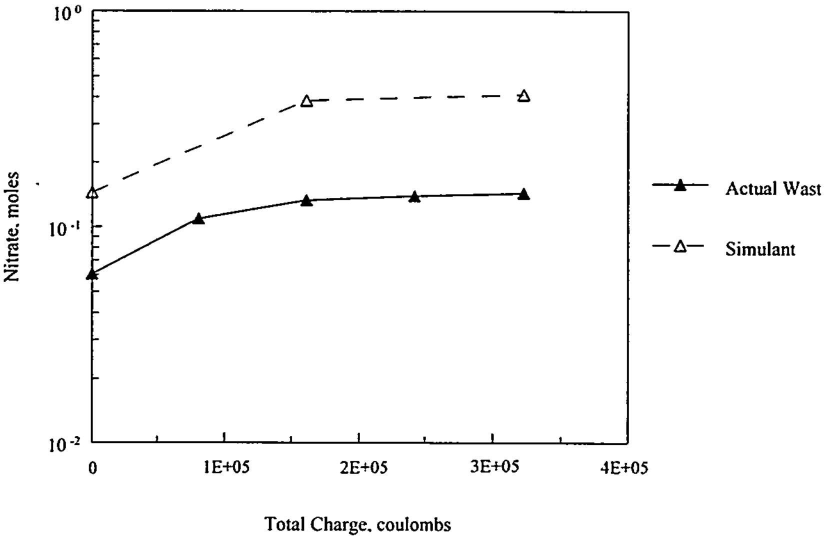

Figure 4.16. Moles of Nitrate in the Undivided Cell as a Function of Total Charge Passed Comparing the Simulant and Actual Waste Tests.

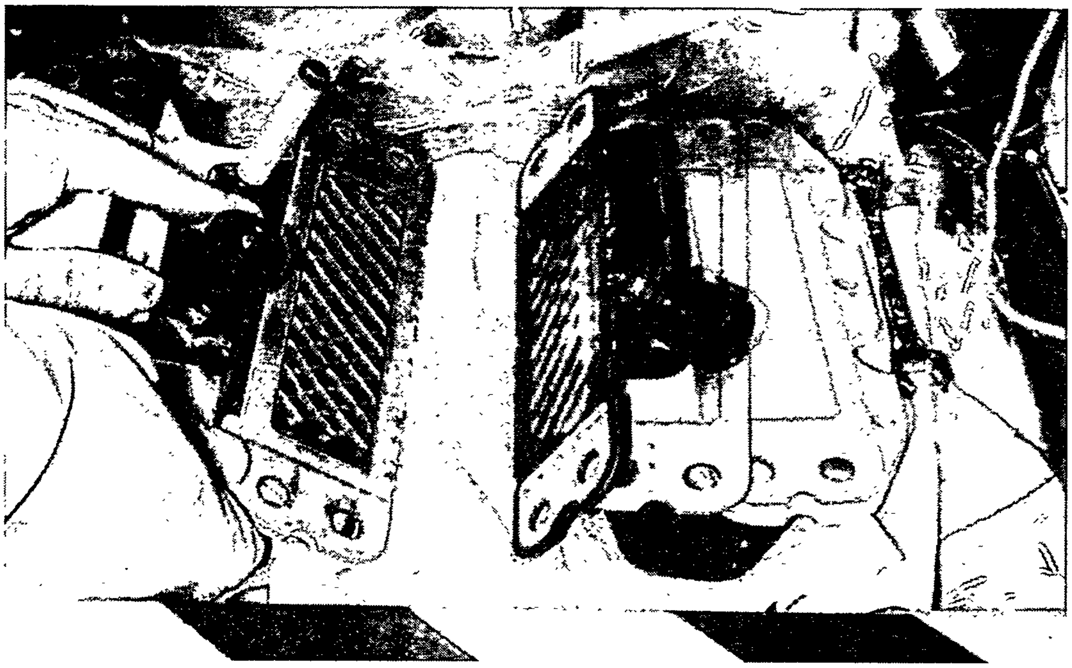

Figure 4.17. Photograph of Cathode (Left) and Anode (Right) After Undivided Cell Test With Actual Waste. No significant change in electrode appearance was observed

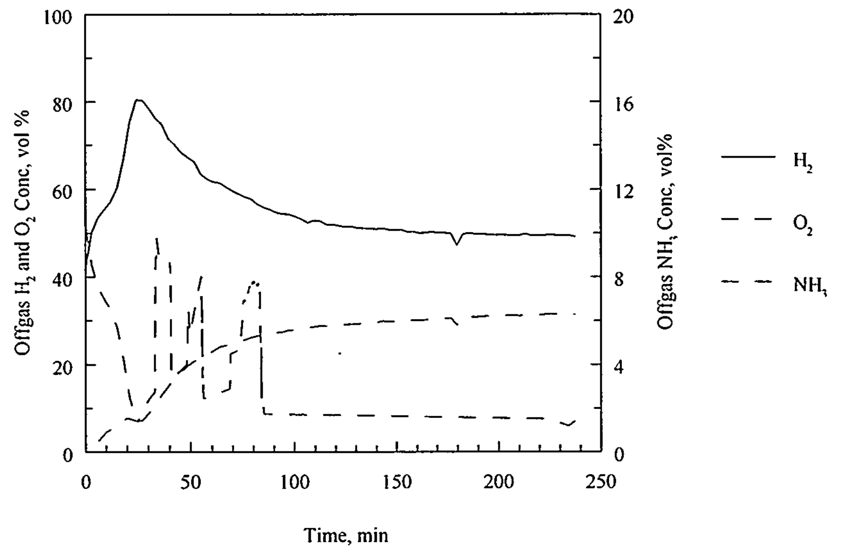

Figure 4.18. Concentrations of Offgas Components (H_2, O_2, and NH_3) Evolved During Undivided Cell Test With Actual Waste.

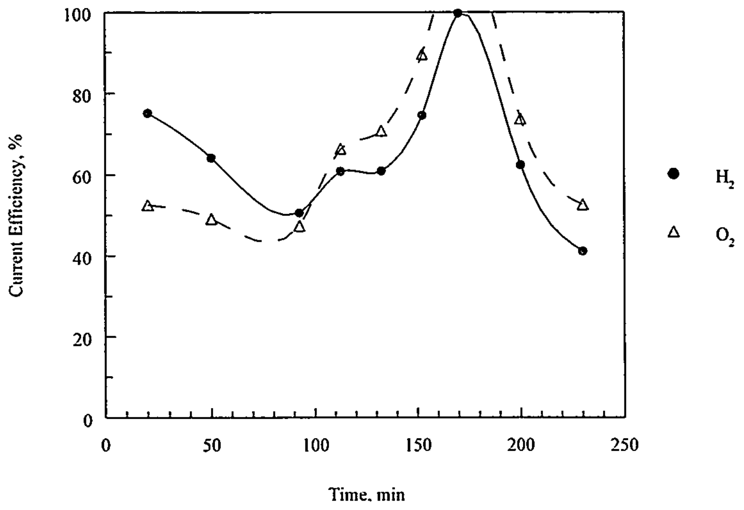

Figure 4.19. Current Efficiencies Based on Hydrogen and Oxygen Generation During Undivided Cell Test With Actual Waste.

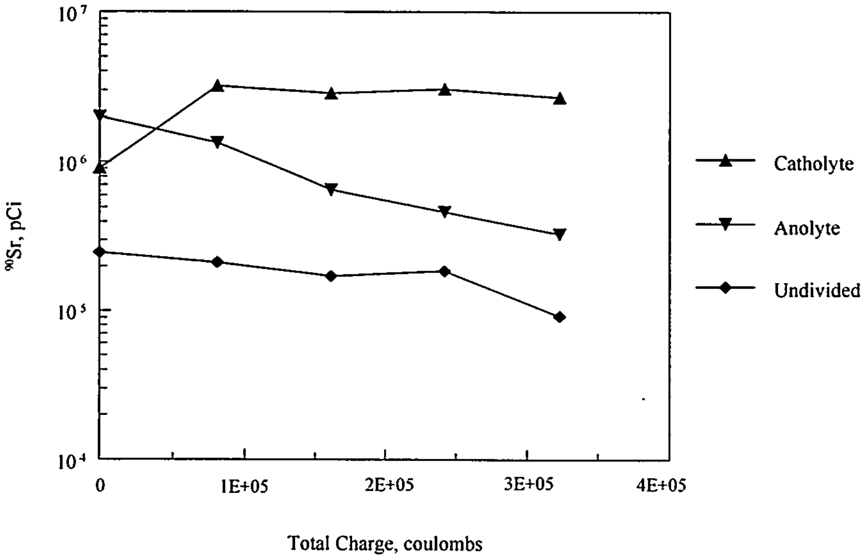

Figure 4.20. Picocuries of ^{90}Sr in Catholyte, Anolyte, and Undivided Cell TestsWith Actual Waste as Functions of Total Charge Passed.

without a detectable loss of solution TOC. Note, however, that the ^{90}Sr concentration does decrease in both the anolyte and undivided cell tests where the environment is oxidizing and organics are either destroyed or at least degraded.

The behavior of ^{99}Tc was also evaluated in the actual waste tests. Figure 4.21 shows the concentration of ^{99}Tc in the waste supernatant throughout the tests for the different cell configurations. The results do not provide conclusive evidence that nonpertechnetate species were oxidized or that ^{99}Tc was electrodeposited. A longer-term run past the the induction period described above is recommended. During the induction period it is known that minimal nitrate and nitrite reduction occur, which would potentially preclude the electrodeposition of the ^{99}Tc.

4.4 Future Directions

These test results indicate that on a short-term basis the simulant adequately reflects the characteristics of the actual waste with respect to TOC. However, inorganic species such as chromium, which are believed to influence cathode reactions, will require further investigation in future electrochemical testing activities. Other inorganic species such as Tc, Pb, Sr, etc., are of interest from a disposition. Therefore, longer duration (50 to 100 hour) actual waste testing is recommended to investigate the system performance with respect to film formation, complexant defunctionalization, and metal disposition. A long-term test would allow evaluation of effects of more significant changes in species concentrations, and would minimize effects of the induction period on overall performance.

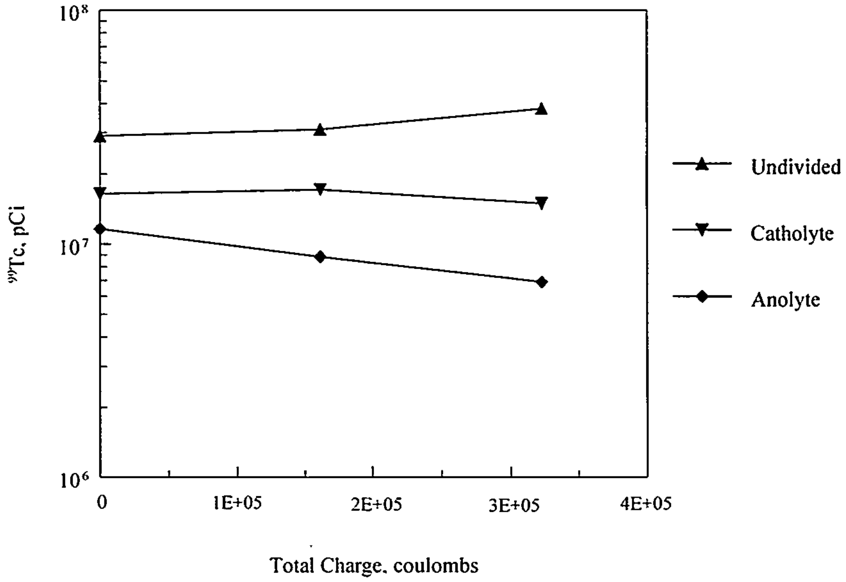

Figure 4.21. Picocuries of ^{99}Tc in Catholyte, Anolyte, and Undivided Cell Tests With Actual Waste as Functions of Total Charge Passed

The complexant defunctionalization and organic destruction results are encouraging, although the longer-term stability must be addressed with respect to the performance issues described above. The rates of TOC destruction are in agreement with simulant testing, although are not conclusive as to the potential for additional destruction, since the speciation of the organics in the waste is not well known. Refractory species may be present or generated that cannot be easily destroyed, possibly leading to changes in the rate of TOC destruction. A longer-term test would provide answers to these questions by evaluating the observed asymptotic change in the rate of destruction with respect to organic concentration.

5.0 References

Chai, D., et al. 1995. *Final Report on the Large Scale Demonstration for the Electrochemical Processing of Hanford and Savannah River Site High-Level Waste Simulants.* WSRC-TR-95-0405, Westinghouse Savannah River Company, Aiken, South Carolina.

Hobbs, D. T. 1995. *Electrolytic Denitration of Radioactive Savannah River Site Waste.* WSRC-TR-95-0176, Westinghouse Savannah River Company, Aiken, South Carolina.