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Status of Test Results of Electrochemical Organic Oxidation of a Tank 241-SY-101 Simulated Waste

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TERMS

EDTA	ethylenediamenetetraacetic acid
TOC	Total organic carbon

Units of Measure

kwH/D	kilowatt hours per day
amps/cm^2	amperes per square centimeter

STATUS OF TEST RESULTS OF ELECTROCHEMICAL ORGANIC OXIDATION OF A TANK 241-SY-101 SIMULATED WASTE

1.0 INTRODUCTION

This report presents scoping test results of an electrochemical waste pretreatment process to oxidize organic compounds contained in the Hanford Site's radioactive waste storage tanks. Electrochemical oxidation was tested on laboratory scale to destroy organics that are thought to pose safety concerns, using a nonradioactive, simulated tank waste.

Minimal development work has been applied to alkaline electrochemical organic destruction. Most electrochemical work has been directed towards acidic electrolysis, as in the metal purification industry, and silver catalyzed oxidation. Alkaline electrochemistry has traditionally been associated with the following: (1) inefficient power use, (2) electrode fouling, and (3) solids handling problems.

Tests using a laboratory scale electrochemical cell oxidized surrogate organics by applying a DC electrical current to the simulated tank waste via anode and cathode electrodes. The analytical data suggest that alkaline electrolysis oxidizes the organics into inorganic carbonate and smaller carbon chain refractory organics. Electrolysis treats the waste without adding chemical reagents and at ambient conditions of temperature and pressure. Cell performance was not affected by varying operating conditions and supplemental electrolyte additions.

Direct scale-up of the analytical data indicates that 110,000 kilowatt hours per day (KWh/d) of power, and 268 m^2 of anode surface area at a current density of 0.34 amperes per square centimeter (amps/cm^2) would be required to treat 20 million liters of tank 241-SY-101 waste per year. Note scale-up assumes 3:1 dilution of waste with water to enable retrieval and a 180 d/yr operation.

2.0 SCOPE

This preliminary study evaluated the fundamental premise of alkaline electrochemistry to oxidize tank waste organics based on the $10,000 of available funding from the Tank Waste Remediation System (EM-30). Deficiencies in ferrocyanide analysis techniques have delayed tests with simulated waste from tanks containing ferrocyanide. A comprehensive program based on the results of this initial study is outlined below.

- Tests are needed using actual tank waste to verify the preliminary results obtained testing nonradioactive simulants.

- Tests are needed that increase the current density between electrodes. These tests may prove to substantially reduce the cell bed size.

- Long-duration testing is needed to quantify electrode fouling. If the electrodes become fouled a technique to clean the electrodes (i.e., acid leach) should be developed.

- Other electrode types should be evaluated for organic destruction efficiency and electrode fouling/life.

- Offgases created from processing should be sampled and analyzed for constituents and flammability potential (explosion potential in cell from electrical arcing).

- Additional analysis of the treated product is needed to identify metal valence changes and organic byproducts.

Work has been started on these tasks and is scheduled for completion in FY 1993.

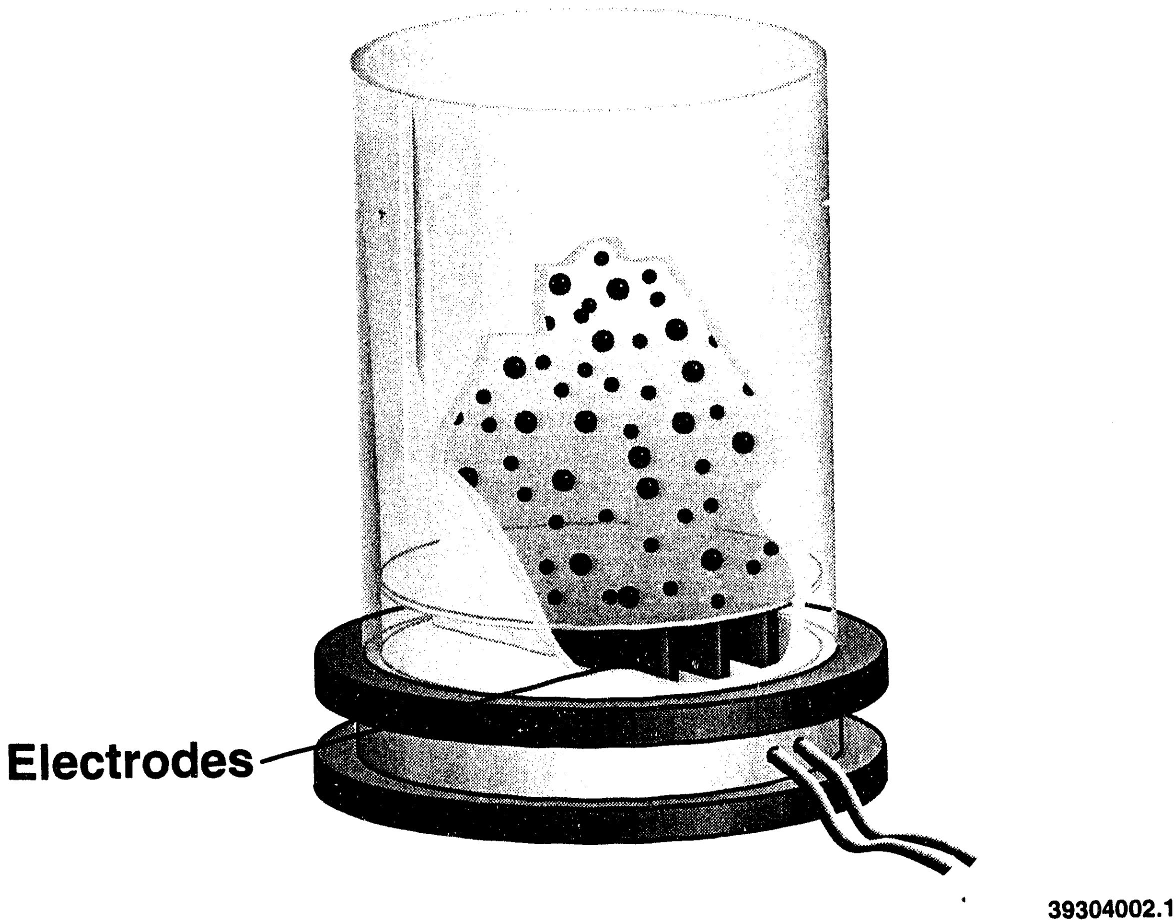
3.0 EXPERIMENTAL

Testing was performed using 200 mL of tank 241-SY-101 simulated waste diluted with 800 mL of water and placed into the Brinecell* Model 101 electrochemical cell (Figure 1). The procedure to prepare the waste simulant is listed in Appendix A. The electrochemical cell was typically operated for 6 to 8 hours at 5 volts and 20 amps to produce a current density of 0.34 amps/cm^2 at the 58 cm^2 anode. The cell uses a multipatented long-lasting anode that can potentially handle high current densities (~0.5 amps/cm^2) in caustic solutions (Brinecell 1992).

High shear mixing to aid oxidant/organic mass transport was obtained using an electric powered teflon stirrer. A polypropylene cooling coil placed inside the cell maintained the simulant temperature at 60 ± 5 °C. The free hydroxide concentration was maintained between 0.1 to 0.5 molar during the tests. Adjustment of pH was needed to replace hydroxide consumed by oxidation of organic. Samples (5 mL) of the simulant solution were taken approximately every hour. Total organic carbon (TOC) analysis was used to measure the amount of organic oxidized during testing. Total solution volume was measured and used to compensate analytical results for concentration caused from evaporation of water.

*Brinecell is a trademark of Brinecell, Inc.

Figure 1. Electrochemical Oxidation Cell.



4.0 ANALYTICAL RESULTS

Figure 2 shows the reduction in TOC from electrochemical processing of sodium salts of the following: (1) formate, (2) oxalate, (3) acetate, (4) citrate, and (5) ethylenediamenetetraacetic acid (EDTA). The analytical data suggest that alkaline electrolysis oxidizes these organics into inorganic carbonate and small carbon chain refractory organics. Acetate and citrate appear to be the most difficult to oxidize.

The effects of varying electrolyte composition on cell performance are depicted in Figure 3 using EDTA as the surrogate organic. Tests encompassed supplemental additions to the simulant of 10 grams of the following: (1) sodium chloride, (2) ferrous sulfate, and (3) chromic oxide. Also 10 mL of 27 normal hydrofluoric acid was added to the simulant. No appreciable change in cell efficiency was measured.

A test was performed with no chloride or fluoride present in the simulant (the baseline simulant contained small quantities of both). Even in the absence of chloride and fluoride, the reaction proceeded indicating that chloride and fluoride ions do not act as significant oxidants and/or catalysts.

The required level of organic destruction to resolve tank safety issues is not well defined; however, a grout waste feed specification of 1.5 g/L TOC (assuming a 1.0 specific gravity) is shown for reference (Hendrickson 1991). In principle, the degree of organic destruction should be linked directly to the safe storage of treated tank waste as follows:

1. Quantify the maximum gas generation rate.

2. Quantify the maximum exotherm caused from an organic reaction.

3. Quantify grout performance using treated product, i.e., compressive strength and toxic characteristic leach procedure tests.

Table 1 shows the energy requirements for oxidation based on meeting the existing grout specification.

Table 1. Energy Requirements for Oxidation to Meet Grout Specification.

Organic	Wh/L simulant
EDTA	540
Acetate	1,400*
Oxalate	440
Formate	540
Citrate	1,100

*Projected.

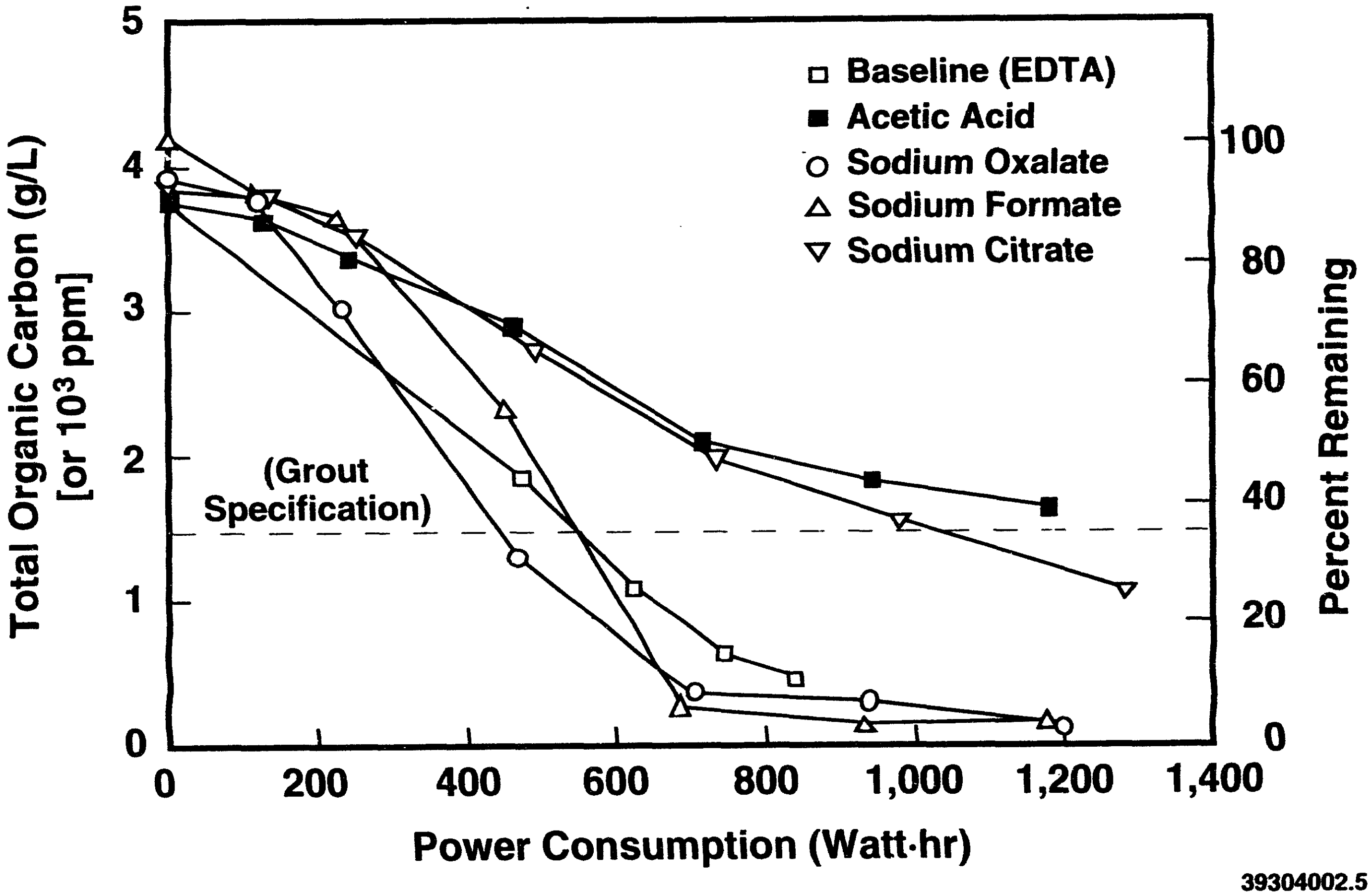


Figure 2. Electrochemical Oxidation of Organics in Tank 241-SY-101 Simulant--Comparison of Various Surrogate Organics.

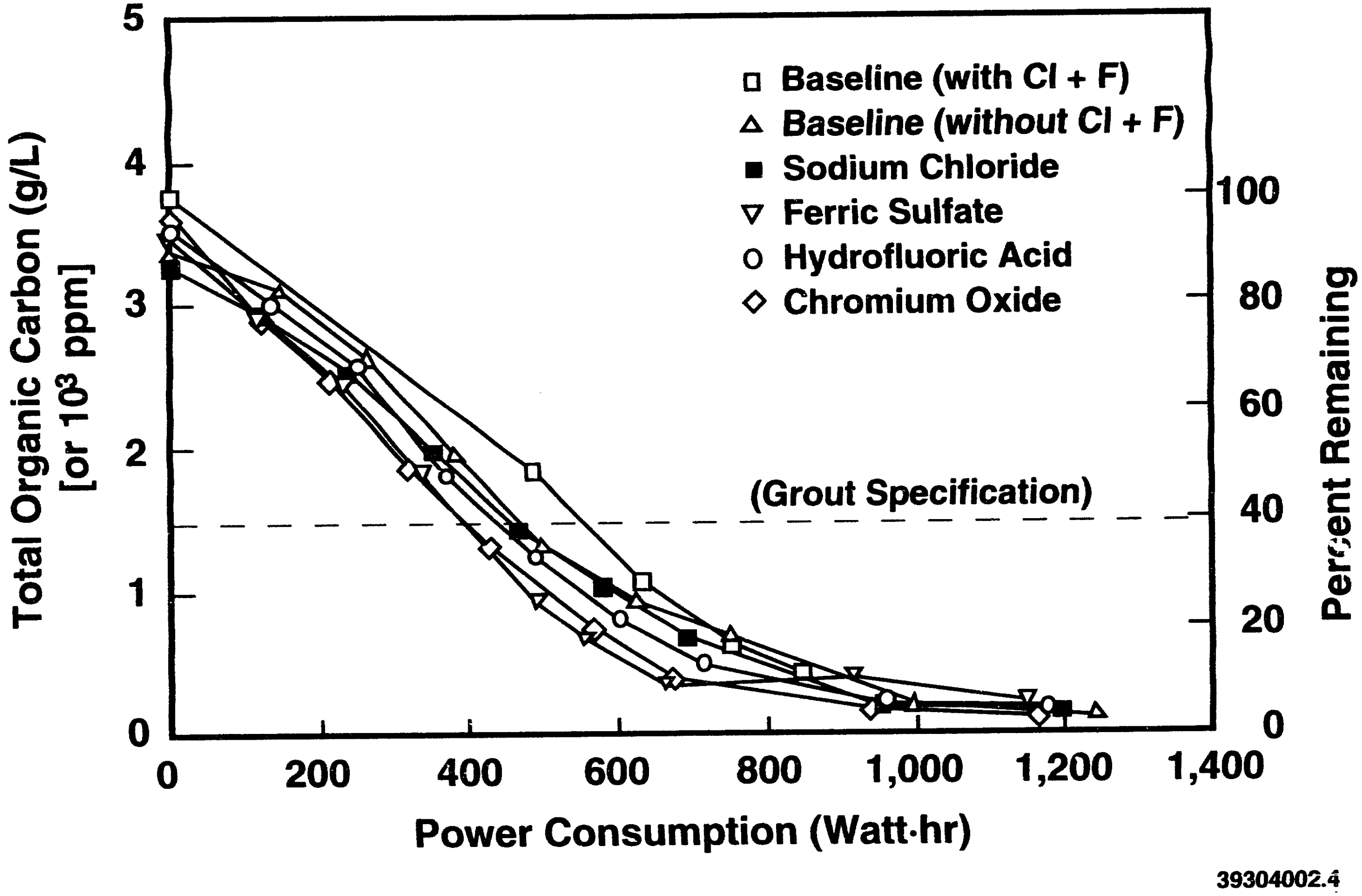


Figure 3. Electrochemical Oxidation of Ethylenediamenetetraacetic Acid in Tank 241-SY-101 Simulant--Comparison of Various Electrolyte Additions.

Several observations were made during testing that provide insight into the applicability of large-scale alkaline electrochemistry. First, although the degree of electrode fouling was not measured, minimal fouling of the electrodes was observed. Secondly, if the hydroxide concentration dropped below roughly 0.01 normal, aluminum compounds precipitate which substantially increased the total volume of solids, which may impact cell efficiency. The inorganic carbon produced during organic oxidation consumes free hydroxide and therefore additions of hydroxide may be needed to prevent excessive solids generation.

5.0 APPLICATION OF RESULTS

A proposed cell design that considers radioactive equipment maintenance and insoluble solids processing is depicted in Figure 4. A bank of cells would be used to obtain the necessary electrode surface area. The proposed concept uses an inner pipe (i.e., platinum coated) as the anode and an outer pipe (i.e., stainless steel) as the cathode. Process slurry is pumped through the annulus of the two pipes. The inner anode pipe also serves to cool the process via cooling water.

Direct scale-up of the analytical data indicates that 110,000 kWh/d of power, and 268 m^2 of anode surface area at a current density of 0.34 amps/cm^2 would be required to treat 20 million liters of tank waste per year. The proposed full-scale cell design has 81 cells (9 x 9), each cell having a 0.75-m diameter and 2-m length. Only 60 cells need to be operating to meet the 20 gallons per minute processing rate requirement. Twenty-one redundant cells are included in the design to facilitate cleaning or replacing individual cells without process downtime. Waste is single pass fed through the 60 cells connected in series. Scale-up assumes 3:1 dilution of waste with water to enable retrieval, a 180 d/yr operation, and a 800 Wh/L of energy consumption, shown in Figures 2 and 3. Appendix B contains calculations for estimated full-scale plant from the analytical results.

In the event of cell failure, each individual cell would be sufficiently small for remote replacement. The cells will likely require periodic acid leaching to remove electrode fouling. Using the proposed geometry, a group or row of cells could be acid leached while the remaining cells continue to treat waste.

Figure 5 portrays a simplified process mass and energy balance for the scale-up of the laboratory electrochemical cell to process 20 million liters of 3:1 diluted tank waste/year. A DC power station would supply the electricity to the cell bed located in a small vault. Waste would be pumped from a feed reservoir through the cell bed to a product reservoir. Offgas handling could include equipment to presumably remove or dilute potential flammable gas concentrations of hydrogen and filtration to remove particulate before venting to the atmosphere. No offgas samples were taken during the tests to establish concentrations of hydrogen and other gases.

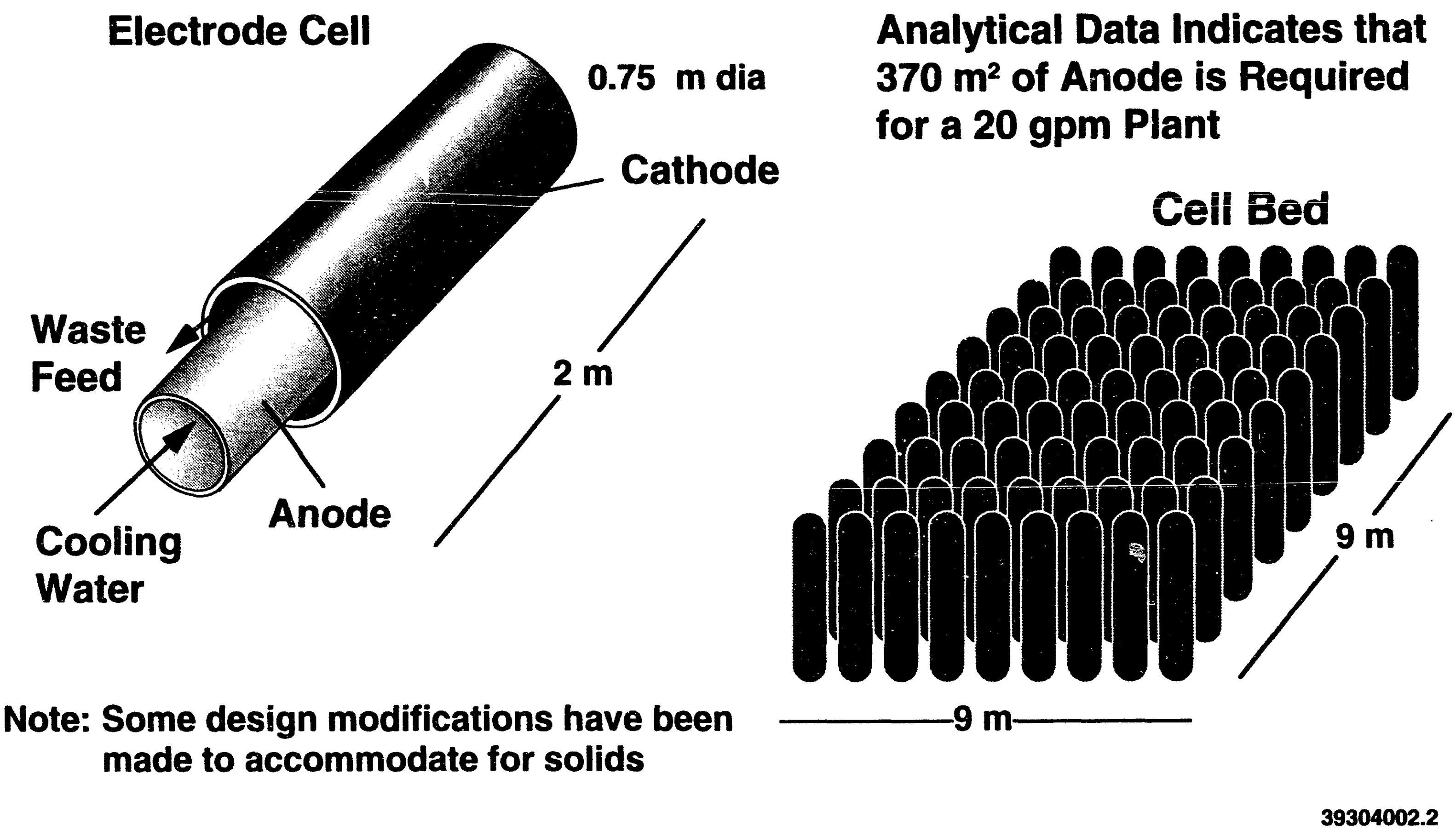
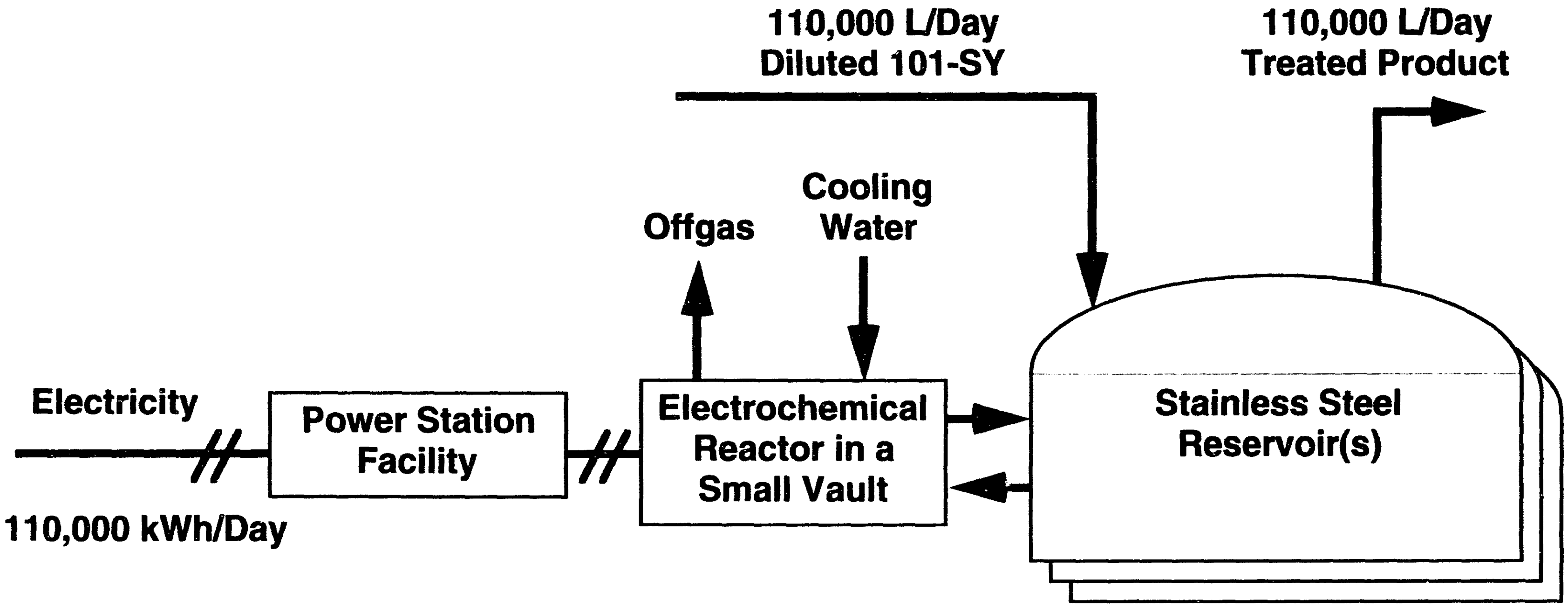


Figure 4. Proposed Brinecell Electrochemical Equipment Design.



Note: Data obtained from bench scale tests using nonradioactive simulated tank waste.

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Figure 5. Preliminary Electrochemical Process Mass and Energy Balance.

6.0 CONCLUSION

Preliminary scoping tests show that alkaline electrolysis can oxidize surrogate organics contained in a tank 241-SY-101 nonradioactive waste simulant into inorganic carbonate and smaller carbon chain refractory organics. Scale-up of the analytical results indicate that an electrochemical process is a potential candidate to resolve tank safety issues regarding organic compounds (and the accompanied hydrogen/flammable gas accumulation).

7.0 REFERENCES

Brinecell Inc., 1992, *Equipment Model 101*, Brochure, P.O. Box 27488, Salt Lake City, Utah 84127.

Hendrickson, D. W., 1991, *Grout Treatment Facility Waste Feed Acceptance Criteria*, WHC-SD-WM-RD-019, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

PROCEDURE FOR MAKING UNDILUTED TANK 241-SY-101 WASTE SIMULANT

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APPENDIX A
PROCEDURE FOR MAKING UNDILUTED TANK 241-SY-101 WASTE SIMULANT
(Based On Window C Sample Analysis)

1. Mix the following acids into a 4-L beaker.

Chemical	Molarity	mL
HNO_3	16	245.
HCL	12	34.
HF	27	1.

2. Add the following chemicals to the acid solution.

Chemical	Grams
$NaAlO_2$	150.
$FeSO_4$-$7H_2O$	0.25
$Ca(NO_3)_2$-$4H_2O$	6.25
Cr_2O_3	1.16
ZnO	0.18
$NiSO_4$-$6H_2O$	0.45
NaH_2PO_4-H_2O	12.7
$Mo(OH)_3$	0.21
$Sr(NO_3)_2$	0.21
CsCl	0.84

NOTE: Testing was started in October 1992, before the approved simulant of tank 241-SY-101 was defined.

3. Slowly add NaOH to pH 9 to 12.

4. Add the following chemicals to the solution:

Chemical	Grams
Na_2CO_3	62.4
NaOH	100.
KOH	8.21
$NH_4(OH)$	1.67
$NaNO_2$	330.

5. Add <u>ONE</u> of the following organic compounds, depending on the test.

Organic Compound	Test Sequence	Grams
Na_4EDTA	1	57.
Sodium Oxalate	2	103.
Sodium Citrate	3	49.
Sodium Acetate	4	58.

6. Add water to make 1 L.

7. Blend the solution at 60 °C for one hour.

The simulant composition is listed in Table A-1.

Table A-1. Undiluted Tank 241-SY-101 Simulant Composition.

Chemicals	Concentration (gmol/L)
Na	14.5
NO_3	3.97
SO_4	0.0026
NO_2	4.78
CO_3	0.59
OH	2.63
Cr	0.15
Fe	.0009
K	0.15
Mo	0.0015
Zn	0.0022
Al	1.83
Cl	0.41
Ca	0.27
F	0.01
NH_4	0.048
Ni	0.025
PO_4	0.092
TOC	1.54
Sr	.001
Cs	.005

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APPENDIX B

DIRECT SCALE-UP OF ELECTROCHEMICAL REACTOR

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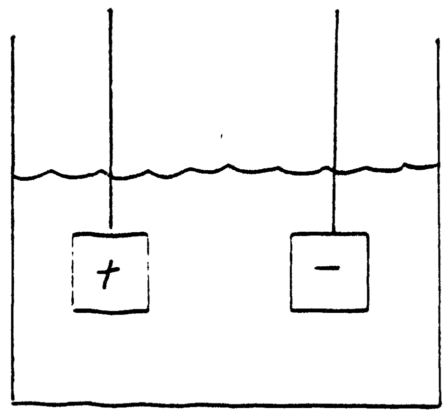
APPENDIX B
DIRECT SCALE-UP OF ELECTROCHEMICAL REACTOR

Given:

Anode Surface Area: 58.8 cm^2
Cell Voltage: 5V
Cell Current: 20 Amps

Assumptions:

1. 800 Wh are needed to treat 200 mL of undiluted waste.
2. 180 days per year operation.



Simplified Cell Diagram

Basis: One Day

Calculate: Power for full-scale plant

$$\frac{(5 \times 10^6 \text{ L 101-SY undiluted waste})(800 \text{ Wh})}{(\text{year})} \cdot \frac{(\text{year})\ (\text{day})\ (\text{kW})}{(.2\text{L simulant})(180 \text{ day})(24 \text{ h})(1{,}000 \text{ W})}$$

Power ⇒ 4629 kW ←
or ⇒ 111,000 kWh/d

Calculate: Anode surface area for full scale plant

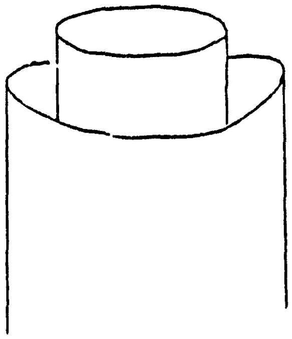
$$P = VI$$
$$4.629 \times 10^6 \text{ W} = (5 \text{ Volts})(3{,}448 \text{ Amps/m}^2)(x\text{m}^2)$$

Anode Area ⇒ 268 m^2 ←

Calculate: Electrochemical Cell Dimensions

Given:

2 m cell height
0.36 m cell radius (inner pipe)



Calculate: Anode surface area per cylindrical cell

$$\text{Anode} = 2\pi rh$$

$$= (2)(\pi)(0.36\text{ m})(2\text{ m})$$

Anode surface area per cell ⇒ 4.5 m^2 ←

Calculate: Number of cells for full scale plant reactor

$$\frac{(268\text{ m}^2\text{ total surface})}{(4.5\text{ m}^2/\text{cell})} = 60\text{ cells}$$ ←
operating in series

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