

ELECTROCHEMICAL PROCESSING OF LOW-LEVEL WASTE SOLUTIONS

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ABSTRACT

The feasibility of treating low-level Savannah River Plant (SRP) waste solutions by an electrolytic process has been demonstrated. Although the economics of the process are marginal at the current densities investigated at the laboratory scale, there are a number of positive environmental benefits. These benefits include: 1) reduction in the levels of nitrate and nitrite in the waste, 2) further decontamination of Tc-99 and Ru-106 and 3) reduction in the volume of waste.

INTRODUCTION

High-level radioactive waste (HLW) is currently stored at the Savannah River Plant in underground carbon steel tanks. The HLW, which is comprised of water soluble and water insoluble species, will be processed as shown in Fig. 1. This process will concentrate the highly radioactive species as a solid phase for vitrification into a borosilicate glass in the Defense Waste Processing Facility. The remaining water soluble species will comprise a low-level waste (LLW). This LLW, or decontaminated salt solution, will be incorporated into a cement wasteform, saltstone, and placed in a lined vault.

Because of the composition and volume of the decontaminated salt solution, several technologies were considered to decrease levels of species in

conversion and the potential for significant volume reduction by recycle of the sodium hydroxide (1-3). Also, there may be additional radionuclide decontamination by deposition of electrochemically active species on the electrodes.

During electrolysis, nitrate and nitrite are reduced to a mixture of nitrogen and ammonia. Oxygen and sodium hydroxide are also produced. If the sodium hydroxide could be recycled to neutralize fresh waste, a significant reduction in the volume of solution requiring disposal in saltstone could be realized.

EXPERIMENTAL

Synthetic salt solutions of approximate composition expected for decontaminated salt solution were prepared from reagent-grade chemicals and either deionized or deionized and distilled water. Chemical composition ranges of synthetically prepared solutions are provided in Table I. A combination of titrimetric, spectroscopic and chromatographic methods were employed for determining the chemical composition of solutions before and after electrolysis. The chemical composition of the SRP low-level waste used in the experiments is also given in Table I.

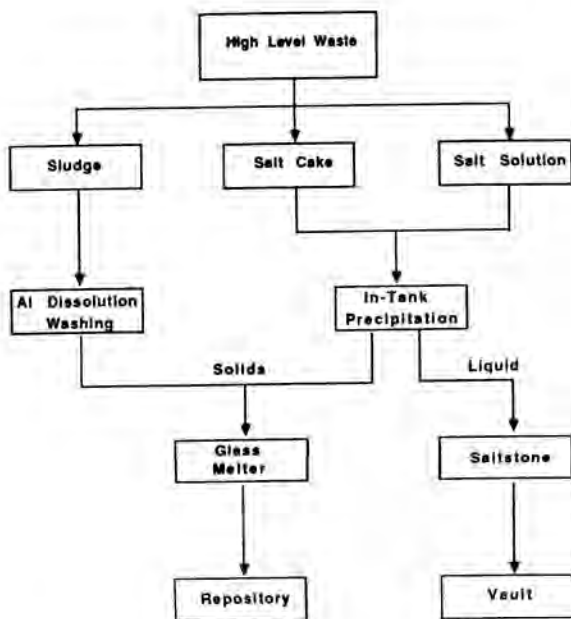


Fig. 1. Processing of SRP High-Level Waste.

the waste that are of an environmental concern and to reduce the volume of waste requiring disposal in saltstone. Electrolytic reduction appeared particularly attractive because of the high nitrate and nitrite

TABLE I

CHEMICAL COMPOSITION OF SALT SOLUTIONS

COMPONENT	CONCENTRATION (mole/L)	
	Synthetic	SRP
NaNO ₃	2.6-3.0	2.6
NaNO ₂	0.5-0.8	0.27
NaOH	1.4-1.5	1.4
NaAl(OH) ₄	0.30-0.33	0.25
Na ₂ SO ₄	0.09-0.16	0.14
Na ₂ CO ₃	0.23-0.27	0.29
other ^a	<0.01	<0.01
Specific Gravity (g/cm ³)	1.25-1.27	1.17

^a other salts include NaCl, NaF, Na₂CrO₄, Na₂MoO₄, Na₃PO₄, Na₂SiO₃, and NaB(C₆H₅)₄.

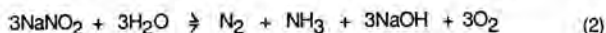
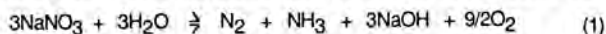
Technetium-99 was obtained as an aqueous solution of ammonium pertechnetate from Du Pont New England Nuclear of Boston, MA. Sodium hydroxytetranitronitrosylruthenium(II) was prepared by a modified procedure of Fletcher et al. (4). Tc-99 concentrations in salt solutions were determined by a liquid scintillation technique using a United Technologies Packard Minaxi Tri-Carb[®] 4000 Series instrument. Technetium-99 levels deposited on electrodes were determined using a solid state CaF₂ detector in conjunction with a Canberra Series 85² multichannel analyzer. Ru-106 and other gamma-emitting radionuclides were determined using a germanium detector in conjunction with a Canberra Series 80 multichannel analyzer.

Electrolysis experiments were conducted in single cell and multicell apparatus constructed of either 0.5 inch plexiglass, 0.5-inch polypropylene, or 0.25-inch, high-density polyethylene. Nickel 200 alloy (21 mil) was used for both the cathode and anode in all of the experiments. DC power was supplied by an American Rectifier Model SISA 24200C power supply operating off of a 220-volt, 3-phase AC power input, a Hewlett-Packard Model 6011 A power supply operating off a 110V, AC power input, or a Hewlett, Packard Model 6281A power supply operating off a 110V, AC power input. Water was added periodically during electrolysis to maintain a constant volume.

Offgases were collected and the ammonia was determined either by acid-base titration or by Fourier transform infrared spectroscopy using a Nicolet 20-DX spectrometer with a three-inch cell and NaCl windows. Other gases were identified and quantified by gas chromatography using a Hewlett-Packard 5880 gas chromatograph with a Carbosieve S-II column in a temperature programmed profile.

RESULTS AND DISCUSSION

Nitrate and nitrite are reduced during electrolysis to nitrogen and ammonia with the simultaneous formation of hydroxide ion and oxygen. The net electrochemical reactions are given in Eqs. 1 and 2.



The process requires substantial electrical energy as a result of reducing the nitrogen oxidation state from +5(NO₃⁻) or +3(NO₂⁻) to zero (N₂) or -3 (NH₃). Oxygen is produced at the anode from the oxidation of hydroxide to complete the cell circuit. One equivalent of hydroxide ion is formed per equivalent of nitrate or nitrite reduced resulting in the production of a highly concentrated sodium hydroxide solution.

Electrolysis Experiments

Greater than 99% of the nitrate and nitrite in synthetic salt solutions could be reduced by electrolysis. Figure 2 shows typical changes in the concentration of nitrate, nitrite, and hydroxide as a function of time. As expected, the rate of appearance of hydroxide is very similar to the rate of decrease in nitrate and nitrite. The nitrite concentration decreases exponentially with time, which is consistent with a mass-transfer limited process. The nitrate concentration decreases linearly with time, indicating that the rate is not limited by mass-transfer. The rate-limiting step is probably due to a reaction involving the adsorption of nitrate on the cathode surface.

The efficiency of the reduction was found to be dependent on the current density, presence of chromate ion, temperature, and electrode spacing. Figure 3 shows a plot of nitrate concentration with reaction time at various levels of chromate ion. At high levels of nitrate, chromate ion does not significantly effect the rate of reduction. However, as the nitrate level decreases and/or the level of chromate increases, the rate is markedly decreased. Apparently, chromate ion is reoxidizing nitrite to nitrate with chromate being simultaneously reduced. To complete the cycle, the reduced chromium species would be reoxidized to chromate at the anode.

Figure 4 shows the relationships of percent of nitrate and nitrite reduced and the overall current efficiency with the concentration of chromate. At <36 ppm chromate, complete reaction of the nitrate and nitrite can be achieved. However, as the chromate level is increased above 1 ppm, the current efficiency decreases dramatically. At 36 ppm chromate, approximately 2.5 times as much electrical energy would be required to achieve complete reduction of the nitrate and nitrite as compared to <1 ppm chromate.

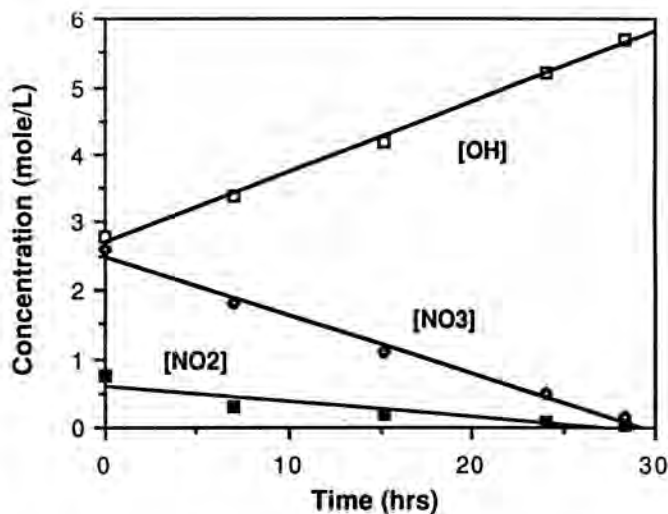


Fig. 2. Concentration Changes During Electrolysis.

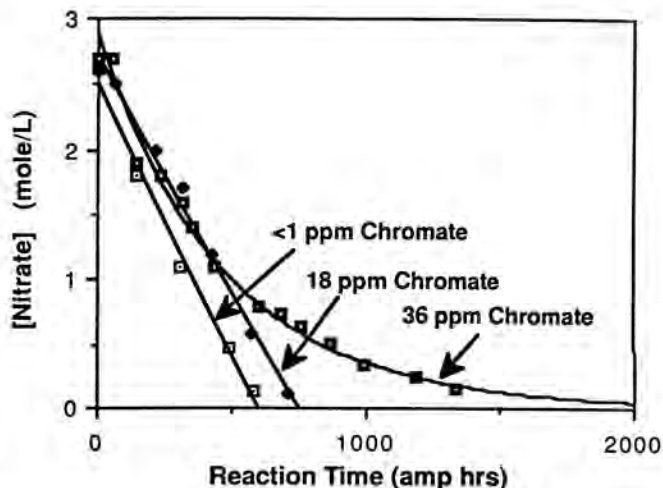


Fig. 3. Effect of Nitrate on Chromate Reduction Rate.

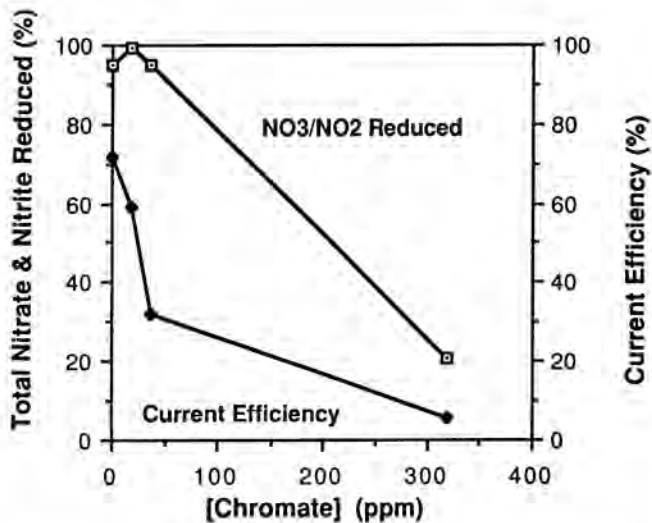


Fig. 4. Effect of Chromate on Extent and Efficiency of Reaction.

The average expected concentration of chromate in decontaminated salt solution is 290 ppm. This level would effectively inhibit the electrolytic reduction of the nitrate and nitrite in the waste solution. To achieve high conversion of the nitrate and nitrite at good current efficiency, the decontaminated salt solution must be treated to reduce the chromate level in solution prior to electrolysis.

Several methods have been developed to mitigate the effects of chromate ion on the electrolytic process. These include the addition of bismuth salts, reduction of the Cr(VI) to insoluble Cr(III), and electrochemical deposition of chromium. Of these methods, the latter is preferred because of the advantages of not adding additional chemicals to the waste and lowest impact on other site operations.

Experiments were conducted in a larger multicell apparatus to determine a more accurate power consumption, current efficiency, and mass balance for the process. Both monopolar and bipolar electrolysis arrangements were investigated. Diagrams of both arrangements are given in Fig. 5.

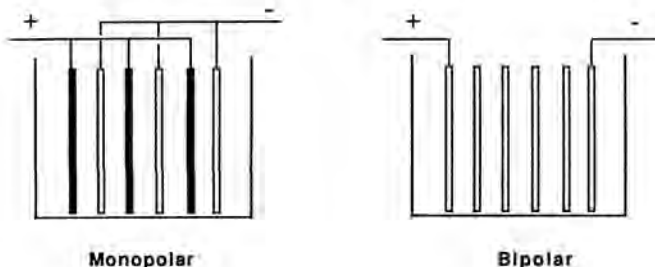


Fig. 5. Types of Electrolysis Cells.

The monopolar arrangement appeared to be slightly more efficient than the bipolar arrangement in the multicell experiments. The average power consumption for the monopolar experiments was 1.7 ± 0.13 kWh/liter and 2.1 ± 0.26 kWh/liter for the bipolar experiments. However, the rate of nitrate and nitrite reduction

in the bipolar arrangement was approximately five times that observed for the monopolar arrangement.

The concentration of sodium hydroxide in the final electrolyzed solution is approximately 13% by weight. Considerable evaporation of the water occurs during electrolysis. The amount of water evaporated ranges from 50% to 100% of the volume of the original salt solution. Because of the high salt content of the waste stream, crystallization of solids will occur after approximately 20% of the volume of water has been evaporated. Therefore, water must be added to prevent crystallization in the electrolysis cells.

Radionuclide Decontamination

The major radionuclides in decontaminated salt solution are Cs-137, Tc-99, Ru-106, and Sb-125. Further decontamination of the long-lived Tc-99 and the Ru-106, which emits high-energy gamma radiation, would be desirable. Per technetate and certain ruthenium species are known to be electrochemically active in alkaline solutions at potentials used to reduce the nitrate and nitrite (2,5). Thus, electrolysis may provide a means to reduce the level of these nuclides in the SRP waste solution and consequently in saltstone. Experiments with synthetic salt solutions have shown that per technetate ion and an anionic complex of ruthenium are electrochemically active.

During electrolysis, the solution concentration of Tc-99 decreases exponentially as shown in Fig. 6. The exponential decrease is consistent with a mass-transfer-limited reaction. Figure 7 shows a plot of nitrate concentration and the decontamination factor for Tc-99 as a function of reaction time. The technetium is reduced concomitantly with nitrate and nitrite and deposited on the cathode. Decontamination factors as high as 4000 have been obtained. Mass balance of the technetium indicated that the technetium either deposited on the cathode or remained in solution. No evidence of volatilized technetium was observed.

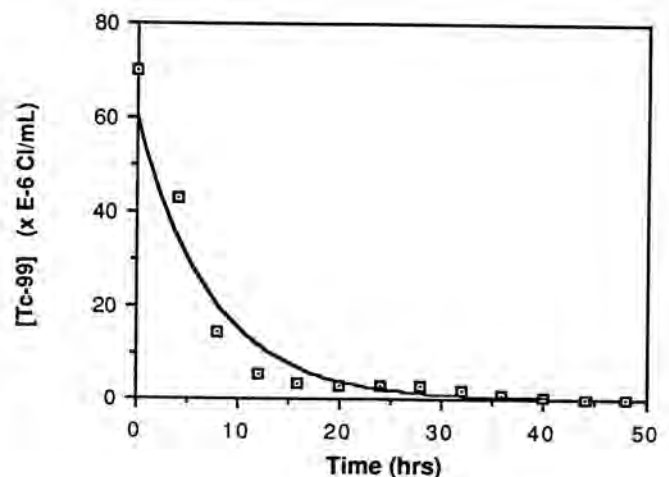


Fig. 6. Tc-99 Solution Concentration during Electrolysis.

The technetium deposit is easily removed from the cathode by a combination of reversed polarity electrolysis and soaking. Up to 89% of the technetium could be removed by reversing the polarity of the electrodes in contact with a dilute alkaline solution of sodium nitrate and nitrite. Presumably the technetium deposit

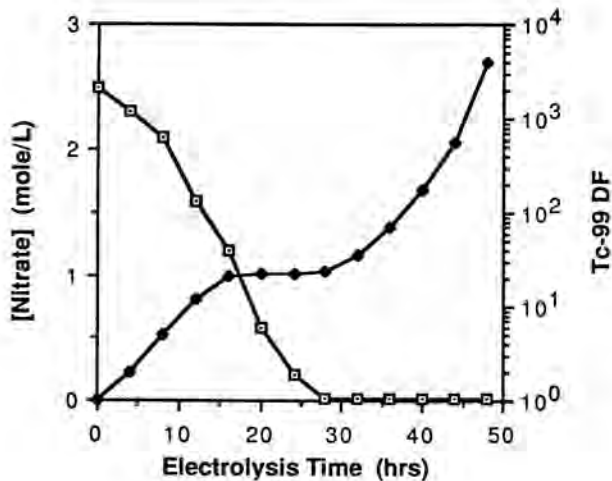


Fig. 7. Nitrate and Tc-99 Removal as a Function of Time.

is reoxidized to pertechnetate, which redissolves in the salt solution. Maximum dissolution of the technetium by reversed polarity electrolysis is achieved at 1.2 hours. After 1.2 hours, the amount of technetium in solution decreases due to reduction of the soluble technetium onto the cathode. The remaining technetium can be recovered in solution by soaking the electrodes with the solution for 96 hours.

Initial experiments to determine the electrochemical activity of ruthenium utilized an anionic complex of ruthenium, the disodium salt of hydroxytetranitronitrosylruthenium (II), $\text{Na}_2 \text{Ru}(\text{NO})(\text{NO}_2)_4\text{OH}$. This stable complex is believed to be one of the forms of ruthenium in SRP waste and would also represent one of the more difficult ruthenium complexes to reduce because of its chemical stability. During electrolysis, the bright yellow color of the solution due to the ruthenium complex gradually fades and a black deposit appears on the cathode. Analysis of the deposit revealed it to contain elemental ruthenium. This is consistent with the reduction of the ruthenium (II) complex at the cathode to form elemental ruthenium. Figure 8 shows the solution concentration of ruthenium as a function of reaction time. As in the case of technetium, an exponential decrease was observed indicating a mass-transfer-controlled reaction. Decontamination factors as high as 200 have been obtained with the synthetic solutions.

SRP Waste

Two electrolysis experiments have been conducted using an SRP waste solution. Major chemical components are given in Table 1. The level of chromate in the waste was determined to be 23 ppm. No measures were taken to mitigate the effect of chromate during electrolysis. In the two experiments, 79% and 91% of the total nitrate and nitrite in the waste solution were converted, respectively. In both of the experiments, 58% of the Tc-99 was removed from solution. In each experiment, 30% and 72% of the Ru-106 were removed, respectively.

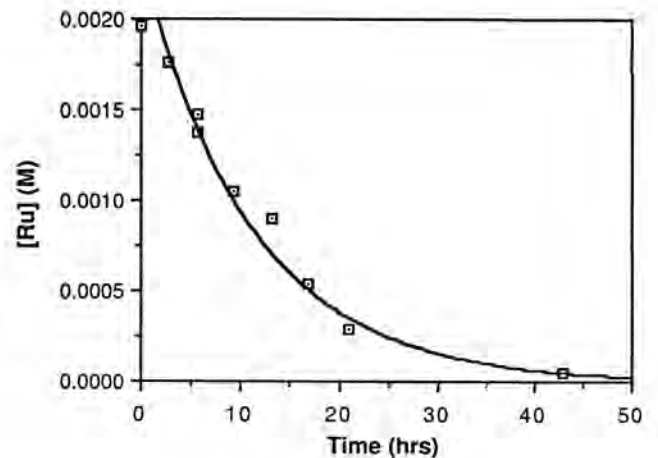


Fig. 8. Ruthenium Concentration in Solution as a Function of Time.

The initial experiment utilized the same nickel electrodes previously used in several of the synthetic salt solution experiments. The second experiment utilized virgin nickel electrodes. Faster and more complete conversion of the nitrate and nitrite was observed with the virgin electrodes. However, the virgin electrodes were poorer in removing Ru-106. No difference was observed between the electrodes with respect to removal of Tc-99. The rate of nitrate and nitrite reaction was similar to that observed for synthetic solutions at similar chromate concentrations. The extent of reduction was perhaps somewhat lower than that predicted by the earlier experiments using synthetic salt solutions. These results do confirm the influence surface features of the electrode have on the adsorption and electrochemical reactions occurring during the process.

Integration of Electrolytic Reduction Process

Figure 9 shows a simple flow diagram for an electrolytic reduction process to treat decontaminated salt solution. In addition to the electrolysis cell facility, an evaporator would be necessary to increase the sodium hydroxide concentration in the electrolyzed waste solution to a suitable level for recycle.

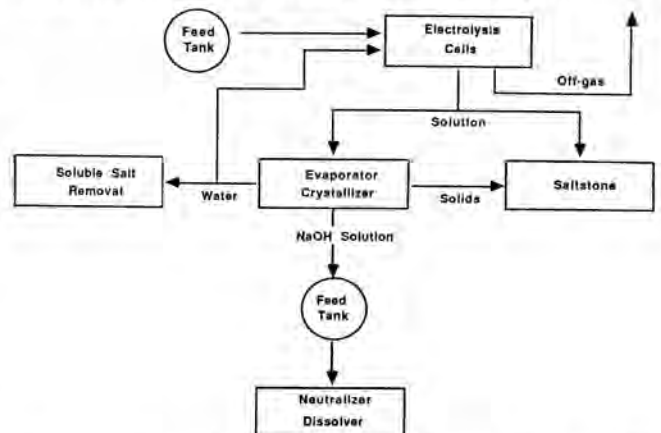


Fig 9 Electrolytic Reduction Process Flow Diagram.

Decontaminated salt solution from salt processing operations would be transferred from the saltstone hold tank to the electrolysis cell for nitrate and nitrite destruction. An offgas system would be provided to treat gases generated during electrolysis prior to release to the environment. After electrolysis, the salt solution would be transferred either to the saltstone facility or to an evaporator for concentration of the sodium hydroxide for recycle. Solids generated during evaporation would be disposed of in saltstone. Evaporator condensates would be either recycled to the electrolysis cell to provide for evaporative losses and water consumption during electrolysis or released to groundwater sources after removal of residual soluble salts and radionuclides. The concentrated sodium hydroxide solution would be stored in shielded tanks. As needed, the concentrated sodium hydroxide solution would be transferred into fuel reprocessing facilities for neutralization of acidic waste streams.

With no recycling, the volume of saltstone would be reduced by approximately 11%. Recycling sodium hydroxide would provide considerable reduction in the volume of saltstone. Based on the average volume of LLW solution that will be produced and the projected usage of sodium hydroxide for the next 20 years, it is estimated that recycling the sodium hydroxide would reduce the volume of saltstone by up to 75%. Significant cost savings to saltstone operations and to the purchase of fresh sodium hydroxide would thus be realized.

Fifty weight percent sodium hydroxide solution is currently used at SRP in fuel reprocessing operations. To minimize impact on current equipment and process operations, the concentration of the recycled sodium hydroxide should be as high as possible. Concentrations as high as 40 wt% (15M) in sodium hydroxide have been obtained by the evaporation of electrolyzed salt solutions. During evaporation crystallization of salts occurs. Crystallization is first detected at a sodium hydroxide concentration of approximately 20 wt%. Initially, sodium carbonate and sodium sulfate crystallized, which is consistent with the solubility of these salts. Upon further evaporation, increasing amounts of the more-soluble salts; sodium aluminate, sodium nitrate, and sodium hydroxide, were observed in the crystalline solids.

Because of excess sodium hydroxide and the crystallization of other sodium salts, a portion of the electrolyzed salt solution will require disposal in saltstone. Experiments indicate that electrolyzed salt solutions containing 13-23 wt% sodium hydroxide can be incorporated into the reference saltstone formulation using standard laboratory equipment and procedures. The increased level of sodium hydroxide does not appear to affect the preparation or the physical properties of the saltstone. Leaching data indicate that the leaching of nitrate and nitrite ions is reduced as compared to the reference formulation. This is consistent with decreased nitrate and nitrite concentrations in the electrolyzed salt solution as compared to the reference salt solution.

Process Economics

Based on the flowsheet shown in Fig. 9 and energy requirements and mass balances found in the laboratory for the electrolysis and evaporation steps, capital and annual operating costs have been estimated. Assuming a current density of 0.43 amps/cm², a current efficiency of 75%, and recycling 100% of annual sodium hydroxide usage, the permanent investment and annual operating costs are \$19.8 MM and \$3.3 MM, respectively. Annual cost savings to saltstone and the purchase of

fresh sodium hydroxide are \$4.6 MM. This results in annual cost savings of \$1.3 MM or a 6% return on the investment.

Although, the return on the investment is low, the permanent investment may be significantly decreased by optimizing the process. For the purposes of the present evaluation, a current density of 0.43 amps/cm² was selected. Previously reported work has indicated that the electrolysis can be carried out at current densities as high as fifty times greater than that used in the economic evaluation (1,2). Because the permanent investment is directly related to the electrode surface area, lower capital costs could be realized by increasing the current density resulting in lower electrode surface area requirements. For example, if the current density could be increased by a factor of two, the cell facility costs would be decreased by approximately 50%.

The higher current densities may provide for higher conversion of the nitrate and nitrite to ammonia and less to nitrogen. This would result in increased electrical energy costs and may possibly require more-extensive offgas treatment facilities. Current research activities are directed at determining the optimum electrode composition for maximizing current density and current efficiency while minimizing formation of ammonia.

CONCLUSIONS

The feasibility of treating low-level SRP waste has been clearly demonstrated. Greater than 90% of the nitrate and nitrite in SRP wastes can be electrolytically destroyed. Although the economics are marginal, there are a number of positive environmental benefits. These benefits include: 1) reduction in the levels of nitrate and nitrite in the waste; 2) further decontamination of Tc-99 and Ru-106; and 3) reduction in the volume of waste. The concentrated sodium hydroxide solution produced by the electrolysis can be incorporated into the reference saltstone formulation and may be suitable for recycling in fuel reprocessing and waste processing operations.

ACKNOWLEDGMENT

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