

248728

RECORDS ADMINISTRATION

ACUM

DP-MS-86-10

**ELECTROCHEMICAL PROCESSING OF ALKALINE NITRATE
AND NITRITE WASTES**

by

D. T. Hobbs and M. A. Ebra

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

A paper proposed for presentation at the
AIChE 1986 Meeting
Miami, Florida
November 2-7, 1986

**SRL
RECORD COPY**

and for publication in The Symposium Series

This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

**ELECTROCHEMICAL PROCESSING OF ALKALINE NITRATE
AND NITRITE WASTES***

by

D. T. Hobbs and M. A. Ebra

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

ABSTRACT

Processing of high-level waste at the Savannah River Plant (SRP) will produce, as a by product, a low-level, alkaline salt solution containing approximately 17% sodium nitrate and sodium nitrite. This solution will be incorporated into a cement formulation, saltstone, and placed in an engineered landfill. Electrochemical methods have been investigated to decrease the nitrate and nitrite in this solution in order to lower the leaching of nitrate and nitrite from saltstone and to reduce the volume of saltstone. Laboratory experiments have demonstrated the technical feasibility of electrolytically reducing the nitrate and nitrite in a synthetic salt solution similar in composition to that expected to be produced at SRP. Greater than 99% of the sodium nitrate and sodium nitrite can be reduced, producing ammonia, nitrogen, oxygen, and sodium hydroxide. In addition, significant reductions in the volume of saltstone may be realized if the sodium hydroxide produced by electrolysis can be recycled.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

INTRODUCTION

High-level radioactive waste is stored at the Savannah River Plant (SRP) in underground carbon steel tanks. The high-level waste, which is comprised of water soluble and water insoluble species, will be processed as shown in Figure 1. This process will separate the water soluble radionuclides from the nonradioactive species. The highly radioactive slurry will be combined with the sludge and vitrified in the Defense Waste Processing Facility. The decontaminated salt solution will be incorporated into a cement wasteform, saltstone, and placed in an engineered landfill.

A program was recently initiated to investigate electrochemical methods of reducing the release of nitrate and nitrite from saltstone and of reducing the volume of decontaminated salt solution requiring disposal in saltstone. Electrolytic reduction and electrochemical separation of alkaline sodium nitrate solutions have been previously reported.¹⁻³ During electrolysis, nitrate and nitrite are reported to be 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.

In the electrochemical separation process, the decontaminated salt solution is separated into a nitric acid stream and a sodium hydroxide stream. If either or both of these streams could be

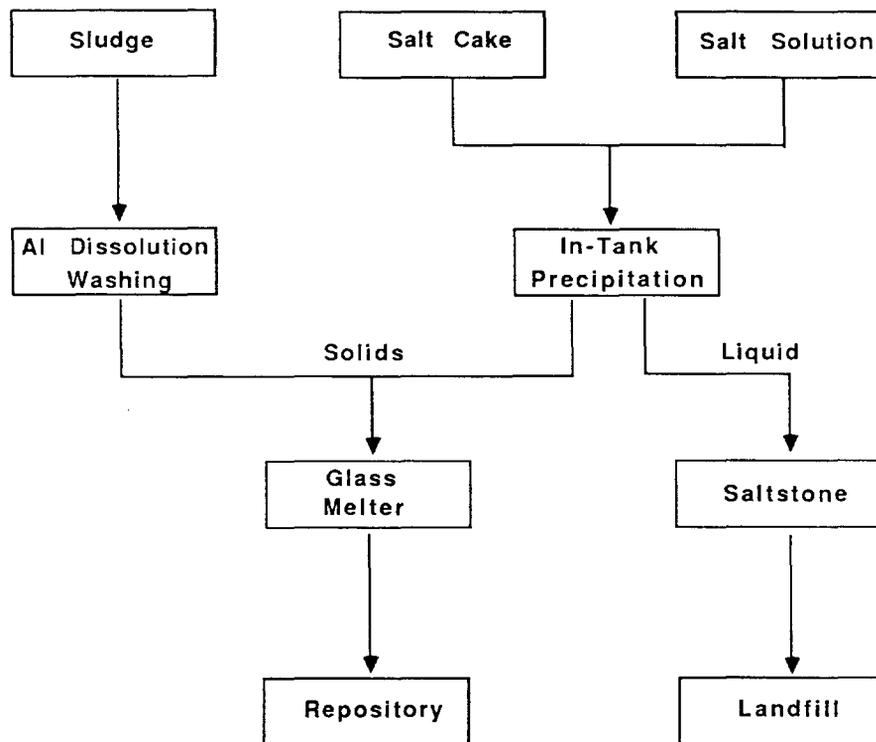


FIGURE 1. Defense Waste Processing

recycled, significant cost savings to saltstone operations would be realized by a reduction in the volume of solution requiring incorporation into saltstone. In addition, cost savings for the purchase of fresh nitric acid and sodium hydroxide would be realized and the acreage requirements for the saltstone landfill would be reduced, as in the case with the electrolytic process. Because of the lower nitrate and nitrite concentrations after processing, reduced leaching of nitrate and nitrite would be expected for the saltstone monolith.

EXPERIMENTAL

A synthetic salt solution of approximate composition expected for decontaminated salt solution was utilized in the experiments. Chemical composition of the solution is given in Table I. Chemical analyses for nitrate, nitrite, hydroxide, and other cationic and anionic species were determined by a combination of titrimetric, spectroscopic and chromatographic methods.

Technetium-99 was obtained as an aqueous solution of ammonium pertechnetate from Du Pont New England Nuclear of Boston, MA. Technetium-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 CaF_2 detector in conjunction with a Canberra Series 85 multichannel analyzer. Sodium hydroxytetranitronitrosylruthenium(II) was prepared by a modification of the procedure of Fletcher, et. al.⁴

TABLE I**Chemical Composition of Synthetic Salt Solution**

<u>Component</u>	<u>Wt %</u>
H ₂ O	68.8
NaNO ₃	15.6
NaNO ₂	3.9
NaOH	4.2
NaAl(OH) ₄	3.6
Na ₂ SO ₄	1.9
Na ₂ CO ₃	1.7
Other ^a	0.3

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

Electrochemical separation experiments were conducted in a three-cell stack assembly built by Ionics, Inc. of Watertown, MA as shown in Figure 2. In this membrane cell, the catholyte and anolyte compartments are separated from the feed compartment by cationic and anionic selective membranes, respectively. An Ionics Cr-62 cationic membrane was used in all of the experiments. Ionics type Ar-108 and Ar-204 anionic membranes were used for the sodium nitrate solution and synthetic salt solution experiments, respectively.

Electrolysis experiments were conducted in single-cell and multicell apparatus constructed of either 0.5-inch plexiglass, 0.6-inch polypropylene, or 0.25-inch, high-density polyethylene. Nickel 200 alloy 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 V three-phase AC power input, or a Hewlett-Packard Model 6011A power supply operating off of a 100 V AC power input. Water was added periodically during electrolysis to maintain a constant volume.

Off-gases were collected in one of two ways. In one method, a slight negative pressure was maintained above the cell. The off-gases were collected and passed through a dilute sulfuric acid scrubber of known concentration to remove the ammonia. The amount of ammonia generated was determined by titrating the unreacted sulfuric acid with a standardized solution of sodium hydroxide. The remaining gases were vented to the atmosphere. The second

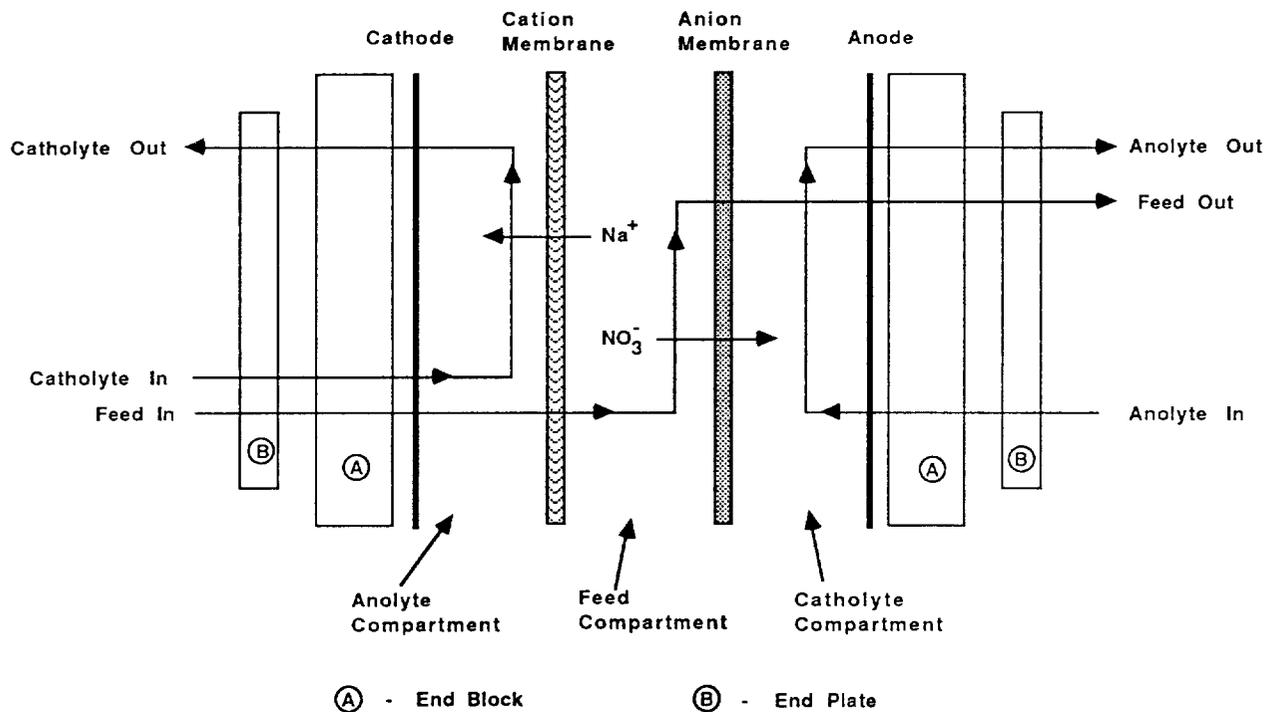
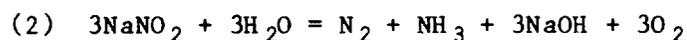
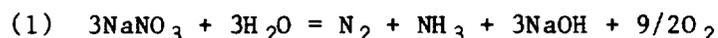


FIGURE 2. Ionics Electrochemical Cell

method utilized an all-glass apparatus isolated from the atmosphere by a water trap. Gas samples were collected in 100 mL glass bulbs that had a sidearm and rubber septum. Gas identification was determined by a combination of gas chromatography and Fourier transform infrared spectroscopy using a Hewlett-Packard 5880 gas chromatograph with a Carbosieve S-II column in a temperature programmed profile, and a Nicolet 20-DX spectrometer with a three-inch cell and NaCl windows.

RESULTS AND DISCUSSION

Two types of electrochemical processes, electrolysis and electrochemical separation, were studied. Nitrate and nitrite are reduced during electrolysis to nitrogen and ammonia with the simultaneous formation of hydroxide and oxygen. The net chemical reactions are given in equations 1 and 2. One equivalent of hydroxide ion is formed per equivalent of nitrate or nitrite reduced. Oxygen is produced at the anode from the oxidation of hydroxide to complete the electrical circuit.



Electrochemical separation utilizes an electrochemical cell separated into three compartments (feed, anolyte, and catholyte) by ion-selective membranes. An electrical potential across the electrodes induces the migration of ions from the feed compartment across the membranes to the anolyte or catholyte compartment. Cations migrate into the catholyte. Hydrogen and hydroxide ion

are formed in the catholyte compartment by the reduction of water at the cathode. Anions migrate into the anolyte compartment. Oxygen and protons are produced in the anolyte compartment by the oxidation of water at the anode.

Electrolysis produces a highly concentrated sodium hydroxide solution containing other salts not electrochemically reactive under the conditions used to reduce nitrate and nitrite. Electrochemical separation produces three product streams; a depleted feed stream, an acid stream composed primarily of nitric acid, and a sodium hydroxide stream. Both the nitric acid and sodium hydroxide streams could be recycled to reprocessing operations. In addition, electrochemical separation would require less power than an electrolysis process because only one equivalent of electrons is consumed per equivalent of sodium nitrate, as compared to five to eight electrons for electrolysis.

Single-Cell Electrolysis Experiments

Electrochemical reduction of nitrate and nitrite proceeded smoothly with the nonradioactive synthetic salt solution. Greater than 99% of the nitrate and nitrite were reduced during electrolysis. 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. It is believed that chromate ion is participating in a catalytic cycle that, at proper

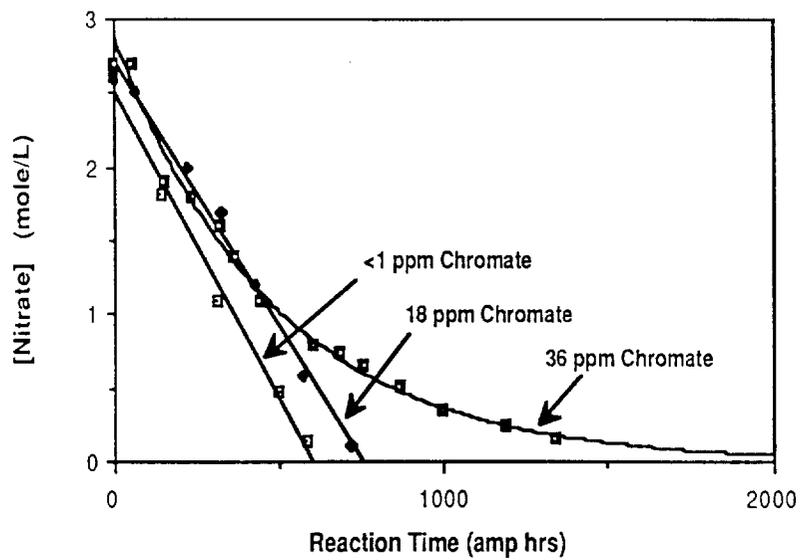


FIGURE 3. Effect of Chromate on Nitrate Reduction

conditions, results in the effective inhibition of the electrolytic process. Apparently, chromate ion is reoxidizing nitrite and nitrate with chromate being reduced to a chromium (III) species. To complete the cycle, the reduced chromium species would be reoxidized to chromate at the anode.

From Figure 3, electrolysis is effectively stopped when the concentration of chromate is sufficiently high such that the rate of nitrate reduction is less than the rate of reoxidation of nitrite to nitrate. At high nitrate levels, a higher chromate concentration can be tolerated. However, at lower nitrate concentrations, only low levels of chromate can be tolerated.

Several methods have been developed to overcome the inhibiting effects of chromate ion on the electrolytic process. The addition of bismuth salts to the salt solution was found to block the effects of chromate.⁵ A slight excess of the stoichiometric amount of bismuth salt will temporarily block the effect of chromate. However, over the course of electrolysis, bismuth eventually deposits on the anode increasing the overvoltage and thus decreasing the electrical efficiency. Reversing the polarity of the electrodes to remove the bismuth deposit will restore the electrode, allowing for good electrical efficiency and nitrate reduction. Fresh bismuth salts must be added periodically because, during the course of the electrolysis, some of the bismuth precipitates from solution and no longer is effective in blocking the effects of chromate ion.

Because of the additional cost, process complexity, and formation of a solid phase in the electrolysis cell as the result of adding bismuth, alternate methods for the removal of chromate were investigated. Chromate ion can be selectively removed from the synthetic salt solution by treating with ferrous ion. The ferrous ion reduces the chromate ion to a Cr(III) species, which precipitates as a hydrated chromous oxide, $\text{Cr}_2\text{O}_3 \cdot x \text{H}_2\text{O}$. The ferrous ion is oxidized to ferric ion, which also precipitates in the alkaline solution as hydrated oxides, $\text{FeO}(\text{OH})$ and $\alpha\text{-Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$. The precipitation of chromium is compatible with the precipitation and adsorption of radionuclides during salt processing. Thus, chromate ion could be removed from the salt solution prior to the electrolysis step using the current equipment.

Alternatively, the chromate ion can also be removed electrochemically using a steel electrode. In this method, the decontaminated salt solution would be passed through an electrochemical cell to remove sufficient chromate ion to allow for the efficient reduction of the nitrate and nitrite. This method has the advantage of not adding additional chemicals to the waste stream.

Electrochemical Separation Experiments

In addition to electrolytic denitrification, experiments were conducted to determine if nitric acid and sodium hydroxide could be separated from salt solution by a three-compartment electrochemical cell. It was found that a 2.1 M solution of sodium nitrate could

be separated into nitric acid and sodium hydroxide with an overall current efficiency of 70% and a specific energy consumption of 3.7 kWh per kilogram of sodium hydroxide produced. The maximum concentrations of the nitric acid and sodium hydroxide solutions were 0.9 M and 1.0 M, respectively. When the feed concentration was increased to 3.9 M in sodium nitrate, the efficiency decreased to 26%. At the higher salt concentrations, sodium ion is apparently passing through the anionic membrane resulting in the lower efficiency. The maximum nitric acid and sodium hydroxide solution concentrations were 1.2 M and 1.6 M, respectively.

Separation of a synthetic SRP-type salt solution using the electrochemical cell was not possible due to fouling of the anionic membrane. Fouling was caused by aluminate ion precipitating as aluminum hydroxide within the interstitial volume of the membrane upon contact with pH conditions of less than 10. Even though the acid concentration of the anolyte stream is sufficiently high to dissolve the aluminum hydroxide, the precipitate would not completely redissolve resulting in an excessively high pressure drop across the anionic membrane.

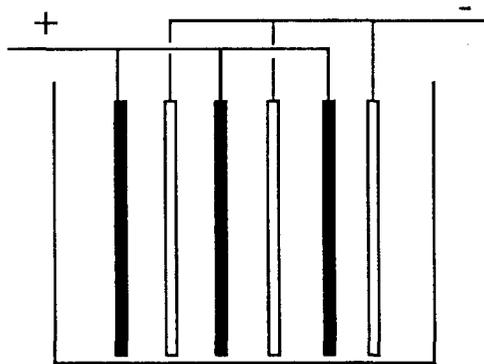
Two modifications were tried in order to separate the synthetic salt solution. First, the feed solution was diluted 10:1. Second, the system was modified to allow feed to pass through both the feed and the anolyte compartments. This modification prevents the fouling of the membrane by maintaining a sufficiently high pH in the anolyte compartment.

During the experiment, the pH of the anolyte stream was slowly lowered due to production of protons at the anode. However, the pH was not allowed to drop below 11. A current efficiency of 92% was obtained for the separation of sodium into the catholyte stream, producing a 0.6 N sodium hydroxide solution. The current efficiency of the separation of nitrate was 52%; however, this calculation does not consider the transport of other anions, hydroxide, aluminate, carbonate, sulfate, etc., which also cross through the membrane.

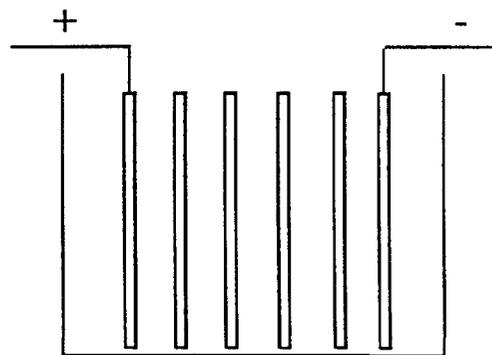
Because of the large dilution necessary to prevent weeping of cations and the increased complexity of the equipment and process to accommodate the chemistry of the aluminate ion, no further experimental work was conducted with the electrochemical separation process. Improved bipolar membranes currently under development may allow for more efficient treatment of concentrated salt solutions not achieved with the membranes tested.

Multicell Electrolysis Experiments

With the establishment of the technical feasibility of the electrolytic process in destroying nitrate and nitrite in a simulated salt solution, experiments were conducted in a larger multicell apparatus to determine a more accurate power consumption, current efficiency, and mass balance for the process. Two arrangements for connecting the electrodes to the external power supply were investigated. The two arrangements were monopolar (parallel) and bipolar (series). Diagrams of both arrangements are given in Figure 4.



Monopolar



Bipolar

FIGURE 4. Electrolytic 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 was approximately 13% by weight. Considerable evaporation of the water occurs during electrolysis. The amount of water evaporated ranged from 50-100% of the original salt solution volume. Because of the high salt content of the waste stream, crystallization of solids will occur after approximately 20% of the water volume has been evaporated. Therefore, water must be added to prevent crystallization in the electrolysis cells.

Radionuclide Decontamination

Actual decontaminated salt solution will contain a number of radionuclides. The major radionuclides are ^{137}Cs , ^{99}Tc , ^{106}Ru , and ^{124}Sb . Based on the reduction potentials, technetium and ruthenium species should be electrochemically active under conditions used to reduce the nitrate and nitrite. Thus, electrolysis may provide a means to reduce the level of these nuclides in solution and, subsequently, in saltstone. Experiments have shown that pertechnetate ion and an anionic complex of ruthenium are electrochemically active.

Figure 5 shows a plot of nitrate concentration and the decontamination factor for ^{99}Tc 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. A 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.

The technetium deposit is easily removed from the cathode by a combination of soaking and reversed polarity electrolysis. 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 is re-oxidized 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 used in the reversed polarity electrolysis for 96 hours.

Initial investigations into 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

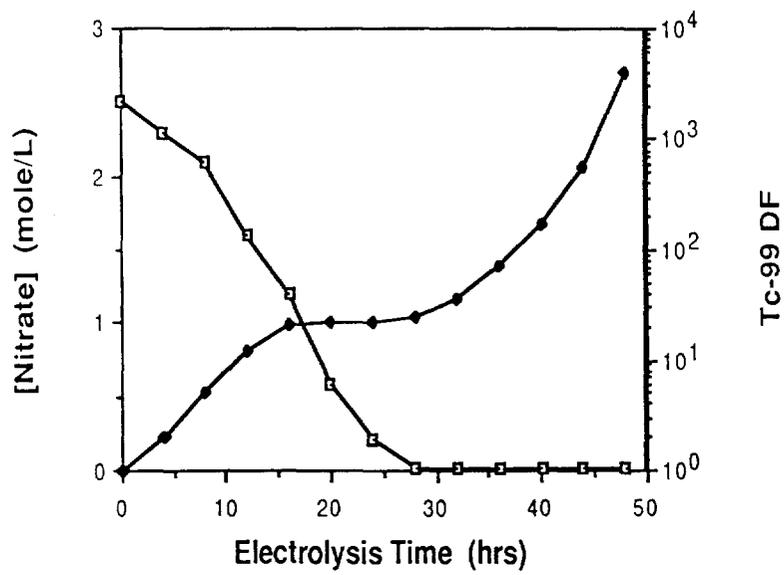


FIGURE 5. Nitrate Reduction and Technetium Decontamination

ruthenium complexes to reduce. 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. Analysis of the solution indicated that 69% of the ruthenium had been removed from solution after 77% of the nitrate had been reduced.

Integration of Electrolytic Reduction Process

A preliminary process flow diagram incorporating an electrolytic reduction facility for treating decontaminated salt solution is presented in Figure 6. Decontaminated salt solution from salt processing would be transferred from the hold tank to the electrolysis cell for nitrate and nitrite destruction. An off-gas system would be provided to treat gases generated during electrolysis.

After electrolysis, the salt solution would be sent to either the saltstone facility or to an evaporator to increase the sodium hydroxide concentration for recycle. Solids generated during concentration would be sent to saltstone. Evaporator condensates would be sent either to the electrolysis cell to maintain constant volume or to a facility for removal of soluble salts before discharge. The concentrated sodium hydroxide 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.

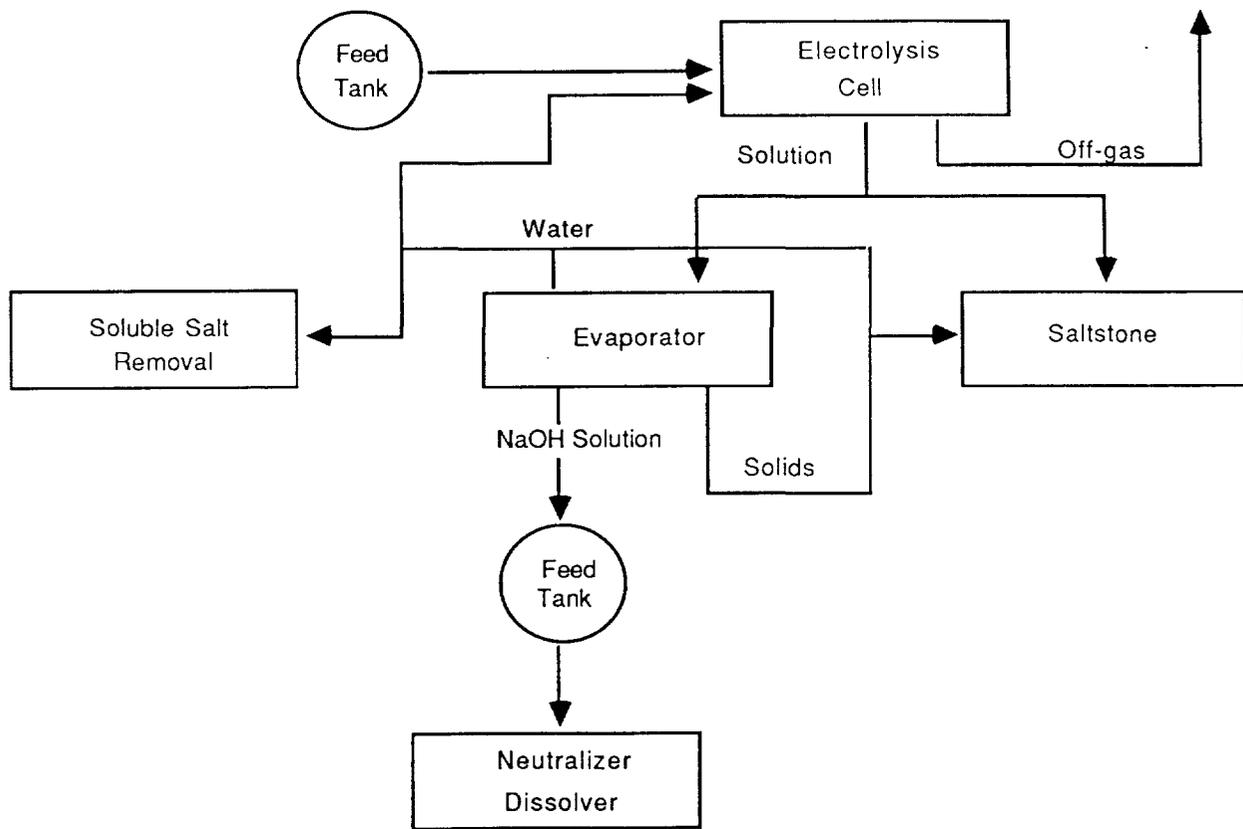


FIGURE 6. Electrolytic Processing Flow Diagram

Table II shows the percent of reduction in the volume of saltstone that would be realized if increasing percentages of the 1985 usage of sodium hydroxide at SRP were provided by recycled sodium hydroxide. With no recycling, an 11% reduction in the volume of saltstone would be realized by solids reduction alone. Recycling 25-100% of the 1985 usage of sodium hydroxide would provide a reduction in the volume of saltstone ranging from 57 to 64%. Significant cost savings to saltstone operations and to the purchase of fresh sodium hydroxide would 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 occurred. Crystallization was 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 other sodiums salts, some of the electrolyzed salt solution must be incorporated into saltstone for disposal. Initial experiments have indicated that

TABLE II

Volume Reduction to Saltstone

<u>% NaOH Recycled</u>	<u>% Volume Reduction</u>
0	11
25	57
50	62
100	64

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 did 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.

CONCLUSIONS

Electrochemical separation of decontaminated supernate was not feasible due to fouling of the membranes by precipitation of aluminum hydroxide and weeping of cations at high salt concentrations. An electrolytic process has been demonstrated that is capable of destroying greater than 99% of the nitrate and nitrite in an alkaline salt solution similar in composition to that expected to be produced during processing of high-level waste at SRP. In addition, the electrolytic process will provide for decontamination of technetium-99 and ruthenium-106 radionuclides from the salt solution. 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.

References

1. H. W. Alter, D. L. Barney, J. K. Davidson, A. C. Schafer, Jr., and E. J. Witt, Electrolytic Recycle Method For the Treatment of Radioactive Nitric Acid Waste, KAPL-1721, June 26, 1957.
2. A. F. Messing and I. R. Higgins, An Electrolytic Procedure for the Removal of Ruthenium and Nitrate From Alkaline Waste Solutions, ORNL-2532, September 19, 1958.
3. A. B. Mindler and S. B. Tuwiner, "Electrolytic Reduction of Nitrate from Solutions of Alkali Metal Hydroxide," U.S. Patent 3,542,657, November 24, 1970.
4. J. M. Fletcher, I.L. Jenkins, F.M. Lever, F. S. Martin, A. R. Powel and R. Todd, J. Inorg. Nucl. Chem., 1, 378 (1955).
5. D. T. Hobbs, M. A. Ebra, and A. B. Mindler, "Electrolytic Denitrification of Alkaline Nitrate and Nitrite Solution," Proceedings of the Symposium on Waste Management, Volume 1, Tuscon, Arizona, March 2-6, 1986, 643-646.