

ELECTROLYTIC DENITRIFICATION OF ALKALINE NITRATE
AND NITRITE SOLUTION

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ABSTRACT

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

INTRODUCTION

High-level radioactive waste is currently stored at the Savannah River Plant 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 Fig. 1. This process will separate the water soluble radionuclides from the non-radioactive 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.

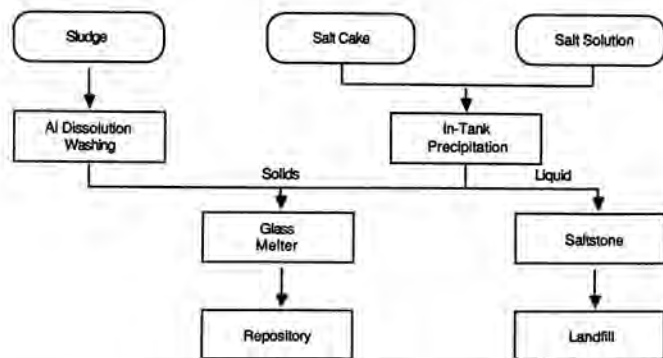


Fig. 1. Defense Waste Processing.

A program was initiated recently to investigate technologies to reduce the volume of decontaminated salt solution requiring disposal in saltstone, and to reduce the release of nitrate and nitrite from saltstone into the groundwater. Electrochemical reduction of alkaline solutions containing sodium nitrate have been previously reported.^{1,2} The nitrate is reportedly reduced to a mixture of nitrogen, ammonia, oxygen, and sodium hydroxide. If the sodium hydroxide produced during electrochemical reduction could be recycled, significant cost savings to saltstone opera-

tions would be realized by reducing the volume of solution requiring incorporation into saltstone. In addition, cost savings for the purchase of fresh sodium hydroxide would be realized and the landfill acreage requirements for the saltstone landfill would be reduced. Because of the lower nitrate and nitrite concentrations after electrolysis, reduced leaching of nitrate and nitrite would be expected for the saltstone monolith.

EXPERIMENTAL

Experiments were carried out in single and multi-cell equipment using a nonradioactive, synthetic salt solution of approximate composition expected for decontaminated salt solution. Chemical composition of the synthetic salt solution used in the experimental program 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.

TABLE I

Chemical Composition of Synthetic Salt Solution

Component	Weight %
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

^aOther salt include NaCl, NaF, Na₂CrO₄, Na₃PO₄, Na₂SiO₃, and NaB(C₆H₅)₄.

The single cell apparatus was constructed from 0.5" plexiglass and had the following inside dimensions; 12" height, 7.785" width, and 2.5" depth. The multicell apparatus was constructed from 0.5" polypropylene and had the following inside dimensions; 14" height, 12" width, and 12" depth. Electrodes were placed in the multicell tank with two-inch spacing, producing seven individual electrochemical cells.

Because of the excellent chemical stability of nickel in concentrated alkaline solutions, electrodes of nickel 200 alloy were selected for use in 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. Off-gases were collected and ammonia scrubbed by passing through a dilute sulfuric acid solution. Unless otherwise specified, reaction temperatures were allowed to vary according to the input current and resistivity of the salt solution. Water was added periodically during electrolysis to maintain a constant volume.

RESULTS AND DISCUSSION

Single Cell Electrolysis Experiments

Electrolytic reduction of nitrate and nitrite in the synthetic salt solution was found to be negligible under the initial experimental conditions investigated. Based on the electrode potentials, it was postulated that chromate was inhibiting electrolysis by reoxidizing nitrite to nitrate, reducing the chromate to a chromium(III) species. To complete the cycle, the reduced chromium species would be reoxidized to chromate at the anode. The inhibiting effect of chromate was experimentally verified by conducting an experiment with a salt solution containing no sodium chromate. Electrolysis proceeded rapidly in the absence of sodium chromate. Upon addition of 60 ppm sodium chromate to the electrolysis bath, further reduction of the nitrate and nitrite was immediately stopped.

The addition of bismuth salts during the electrolysis was found to block the inhibiting effect of the chromate, allowing electrolysis to proceed to completion. Figure 2 shows a plot of hydroxide ion concentration versus time (cumulative ampere hours) for experiments using salt solutions with and without chromate, and with bismuth. This figure shows the inhibiting effect that chromate has on the electrolysis, and the effectiveness of bismuth in blocking the chromate inhibition. A negligible increase in the hydroxide ion concentration is observed during the electrolysis of the chromate-containing solution. Without chromate ion present, the hydroxide ion concentration increases rapidly, indicating reduction of the nitrate and nitrite. The addition of a bismuth salt to the chromate-containing salt solution results in a rapid increase in the hydroxide ion concentration, equal to the rate observed for the chromate-free salt solution.

Greater than 95% of the nitrate and nitrite in the chromate containing salt solution could be destroyed in the synthetic salt solution with relatively good current efficiency. Greater than 99% of the nitrate and nitrite could be reduced, but at significantly greater power consumption. Current density and electrode spacing did not appear to affect the rate of electrolysis. However, the temperature of the salt solution increased as the current density increased, resulting in faster evaporation rates.

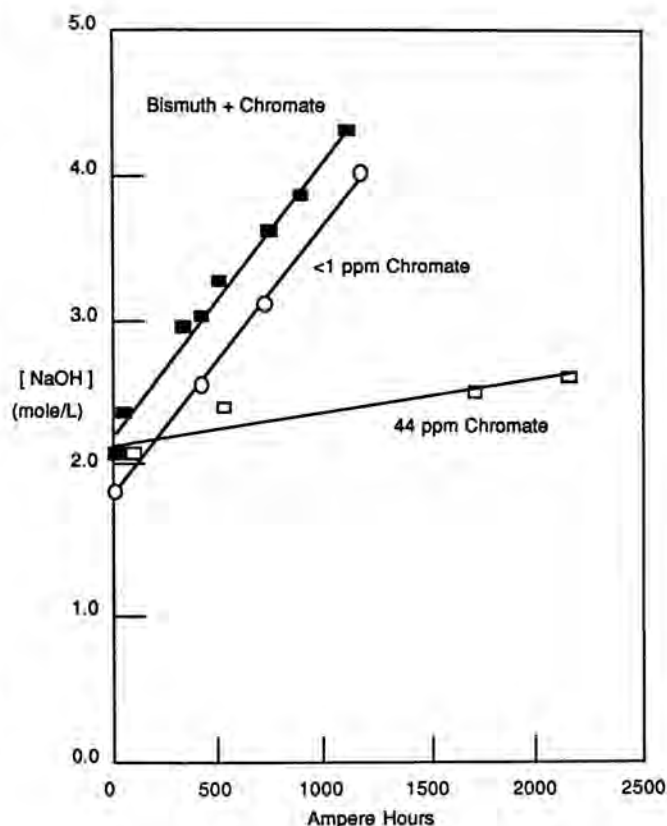


Fig. 2. Change in NaOH Concentration During Electrolysis.

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 Fig. 3.

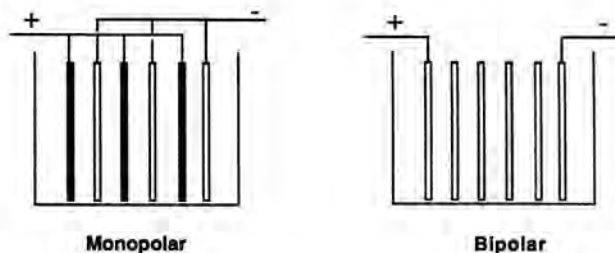


Fig. 3. Electrolytic Cells.

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 6.6 ± 0.5 kWh/gallon and 8.0 ± 1.0 kWh/gallon 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.

Based on the amount of sulfuric acid neutralized by ammonia in the off-gases, an average 90% of the nitrate and nitrite was reduced to nitrogen. Seventy percent was the lowest value observed for the amount of nitrogen generated during electrolysis. The concentration of sodium hydroxide in the final electrolyzed solution was approximately 13% by weight. Considerable evaporation of the water occurs during electrolysis, which results in a variable sodium hydroxide concentration. As observed in the single cell experiments, the rate of water evaporation increased with an increase in the current density.

During the course of electrolysis, the effectiveness of bismuth in blocking the chromate inhibition decreases. Apparently, the bismuth is depositing and forming a nonconductive oxide layer on the anode surface. Periodic addition of bismuth will maintain good current efficiency for a brief time. However, after sufficient deposition has occurred, the efficiency becomes very poor. The oxide deposit can be removed by reversing the current for several minutes. The bismuth oxide sloughs off the anode and eventually settles to the bottom of the cell. The volume of sludge produced during electrolysis was approximately 1% of the original volume of salt solution. The sludge consisted of approximately 40 wt % solids. Elements identified in the solids included bismuth (70 wt %), nickel (15 wt %), and chromium (1 wt %).

Saltstone Volume Reduction

One equivalent of sodium hydroxide is generated per equivalent of sodium nitrate or sodium nitrite reduced during electrolysis. If the sodium hydroxide produced by electrolysis was recycled, considerable reduction in the volume of saltstone would be realized. Table II shows the percent of reduction in the volume of saltstone that would be realized if increasing percentages of the 1984 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 1984 usage of sodium hydroxide would provide a reduction in the volume of saltstone ranging from 24-64%. Significant cost savings to saltstone operations and to the purchase of fresh sodium hydroxide would be realized.

TABLE II

Volume Reduction to Saltstone

% NaOH Recycled	% Volume Reduction
0	11
25	24
50	37
75	50
100	64

Concentration of Electrolyzed Salt Solution

Sodium hydroxide solution used at SRP contains 50% by weight (19.1 M) NaOH. Concentrations as high as 40 wt % (15M) have been obtained by evaporation of electrolyzed salt solutions. During evaporation crystallization of salts occurs, which is first detected at a sodium hydroxide concentration of approximately 20 wt %. Initially, sodium carbonate and sodium sulfate crystallize, 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, are observed in the crystalline solids.

Incorporation of Electrolyzed Salt Solution Into Saltstone

Initial experiments have indicated 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 did not appear to affect the preparation or the physical properties of the saltstone. Preliminary data indicated that leaching of nitrate and nitrite ions was lower than the reference formulation, which is consistent with decreased nitrate and nitrite concentrations.

Preliminary Process Flow Diagram

A preliminary process-flow diagram incorporating an electrolytic reduction facility for treating decontaminated salt solution is presented in Fig. 4. Decontaminated salt solution 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.

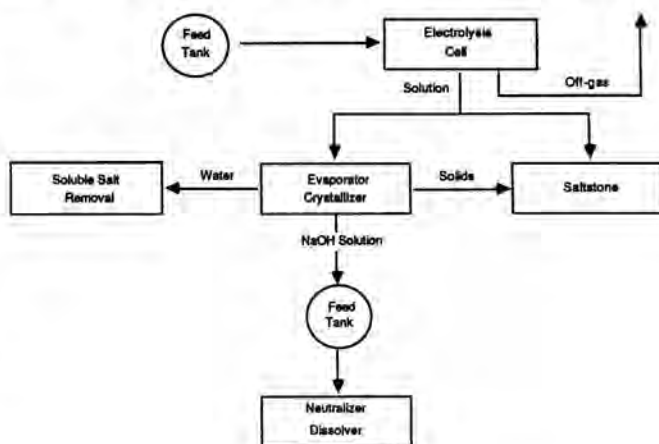


Fig. 4. Electrolytic Reduction Process.

After electrolysis, the salt solution would be sent to either the saltstone facility or to an evaporator/crystallizer to increase the sodium hydroxide concentration for recycle. Solids generated during concentration would be sent to saltstone after dissolution in condensed water from the evaporator. Excess evaporated water would be sent to a facility for removal of soluble salts before discharge to groundwater sources. The concentrated sodium hydroxide would be stored in shielded tanks. As needed, the concentrated sodium hydroxide solution would be transferred to the desired tank for neutralization of acidic waste streams.

CONCLUSIONS

An electrochemical process has been demonstrated that is capable of destroying greater than 95% 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. The concentrated sodium hydroxide solution produced by the electrolysis can be incorporated into the reference saltstone formulation and may be suitable for recycling in waste processing operations. Bipolar electrolysis appeared to be more attractive than monopolar electrolysis based on the reaction rate and power consumption.

REFERENCES

1. 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.
2. 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.

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