JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 1–9

Electrochemical reduction of nitrates and nitrites in alkaline nuclear waste solutions

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Received 6 January 1995; revised 6 June 1995

Sodium nitrate and nitrite are major components of alkaline nuclear waste streams and contribute to environmental release hazards. The electrochemical reduction of these materials to gaseous products has been studied in a synthetic waste mixture. The effects of electrode materials, cell design, and other experimental parameters have been investigated. Lead was found to be the best cathode material in terms of current efficiency for the reduction of nitrate and nitrite in the synthetic mix. The current efficiency for nitrite and nitrate removal is improved in divided cells due to the elimination of anodic oxidation of nitrite. Operation of the divided cells at high current densities (300–600 $\mathrm{mA\,cm^{-2}}$) and high temperatures (80 °C) provides more efficient reduction of nitrite and nitrate. Nearly complete reduction of nitrite and nitrate to nitrogen, ammonia, or nitrous oxide was demonstrated in 1000 h tests in a divided laboratory electrochemical flow cell using a lead cathode, Nafion® 417 cation exchange membrane, and oxygen evolving DSA® or platinum clad niobium anode at a current density of 500 $\mathrm{mA\,cm^{-2}}$ and a temperature of 70° C. Greater than 99% of the nitrite and nitrate was removed from the synthetic waste mix batch in the 1000 h tests at an overall destruction efficiency of 55%. The process developed shows promise for treating large volumes of waste.

1. Introduction

Production of nuclear materials within the DOE complex has produced large volumes of high-level waste (HLW) that contain nitrate and nitrite as well as radioactive fission products. Processes being developed for the permanent disposal of the HLW are aimed at separating the bulk of the radioactivity, primarily cesium-137 and strontium-90, into a small volume for incorporation into a vitrified wasteform, with the remainder being incorporated into low-level wasteforms. Such low-level waste solutions contain high levels of sodium hydroxide, sodium nitrate and sodium nitrite and lesser amounts of aluminate, sulfate, carbonate, chloride, fluoride, silicate, phosphate, and chromate. Because of the very high concentrations, nitrate and nitrite are major contributors to environmental release and personnel exposure risks. Reduction of nitrate and nitrite to gaseous products could permit evaporation and recovery of the caustic value of the waste, reducing the volume of the low-level waste stream for disposal and providing a source of caustic for neutralization of acid waste clean-up solutions.

Electrochemical reduction of nitrate in alkaline solutions has been studied using various cathode materials. The reduction of nitrite and nitrate in 1 M NaOH at platinized platinum under controlled potentials resulted in ammonia formation at high overpotentials and nitrogen at less negative potentials [1]. Galvanostatic electrolyses in 3 M NaOH and 0.25 M Na_2CO_3 at nickel cathodes gave nitrogen gas as the major product at low current densities (less than or equal to 107 $\mathrm{mA\,cm^{-2}}$) and ammonia as the major product at high current densities (466 $\mathrm{mA\,cm^{-2}}$) in a divided glass cell [2]. Lead and zinc cathodes were found to give higher rates of nitrate removal than nickel and also produced more ammonia in undivided glass cell electrolyses at a constant current density of 173 $\mathrm{mA\,cm^{-2}}$ [3]. Electrolytic denitration of alkaline solutions including radioactive wastes has also been the subject of several patents and government reports [4–7]. Previous studies have shown that it is possible to destroy more than 99% of the nitrite and nitrate in simulated and actual radioactive waste solutions [8, 9].

The present work has sought to demonstrate the feasibility of electrochemical denitration of complex simulated low-level nuclear waste streams using electrochemical flow cells. The effects of electrode materials, cell configuration, and cell operating parameters on the electrochemical reduction of nitrite and nitrate in simulated waste solutions have been investigated to develop a robust process capable of treating large volumes of waste. Toward this end a long term demonstration of the process has also been performed.

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2. Experimental details

2.1. *Analysis of nitrate, nitrite, and off-gases*

Nitrate and nitrite analyses were performed on a Waters 600 HPLC using a micro Bondapak C18 column. The mobile phase was 0.05 M potassium dihydrogen phosphate (HPLC Grade) with one vial of PIC-A reagent (Waters) in 2 dm^3 of buffer, running at a flow rate of 2.5 ml min^{-1}. Detection of the species was by UV at 214 nm. This method gave excellent separation of the products with no interfering peaks.

Gas analyses were performed on a Perkin–Elmer 8500 gas chromatograph using a thermal conductivity detector. Nitrous oxide and ammonia were separated and quantified on a Chromasorb 103 column modified with 10% Versamide 900/8% KOH. Oxygen and nitrogen were separated and quantified on a molecular sieve 5A column. Both columns used helium as the carrier gas at a flow rate of 60 ml min^{-1} (STP). The injector temperature was 120 °C and 0.2 ml of gas was injected. Hydrogen was quantified on the molecular sieve column using argon as the carrier gas. The volumetric percentages of gases present in off-gas samples was determined by using a certified standard gas mix (Scott Specialty Gases) as an external standard for calibration of the GC.

2.2. *Direct reduction in glass H-cell*

Constant current electrolyses were performed in a divided glass cell using various cathode materials. The cathode and anode chambers were separated by a Nafion® 417 (DuPont) cation exchange membrane. The catholyte consisted of 70 ml of 1.95 M sodium nitrate, 0.60 M sodium nitrite, and 1.33 M sodium hydroxide. Only ACS reagent grade chemicals were used in this work. Electrolyses were carried out at a current density of 140 mA cm^{-2} at 5 cm^2 electrodes. The catholyte chamber was sealed so as to be gas tight and gas samples were taken by syringe through a septum. A coulometer (ESC 640) was used to monitor charge. The anolyte was 1.0 M sulfuric acid and the anode a 5 cm^2 platinum flag.

2.3. *Direct reduction in electrochemical flow cell*

Constant current electrolyses were also performed in electrochemical flow cells with the complete simulated waste solution. Electrochemical cells used were the FM01 LC (ICI, 64 cm^2 per electrode face) and the MP Cell (ElectroCell AB, 100 cm^2 per electrode face). The cells were operated in either the undivided or divided configurations, with Nafion® 417 used as the separator in the divided cells. Electrolyte was recirculated through the cells with March centrifugal pumps and the flow rate monitored with rotameters. Glass electrolyte reservoirs were heated by heating tapes. The system was sealed gas tight and the off-gases taken through a condenser and demister to remove water vapour prior to a gas sampling port where gas samples were taken by syringe through a septum.

2.4. *Membrane resistance testing*

Irradiated Nafion® 417 and Nafion® 324 membranes were tested for changes in resistance in a glass H-cell fitted with Luggin capillary probes extending to within 1 mm of either side of the membrane. SCE reference electrodes in the Luggin chambers measured the potential difference corresponding to the potential drop across the membrane as a function of current density. Electrodes were platinum flags placed well away from the membrane and Luggin probes. The electrolyte was 2 M sulfuric acid held at 40 ± 1 °C. The current was slowly increased from 0–2.25 A (0–500 mA cm^{-2}) at a rate of 1.4 mA s^{-1}. Current and potential were sampled every 24 s.

3. Results

3.1. *Cathode materials for nitrate reduction*

3.1.1. Divided glass cell cathode screening with simplified mix. Potential cathode materials were screened by performing galvanostatic electrolyses in a divided glass cell. A simplified mixture ($NaNO_3$, $NaNO_2$, NaOH) was used so that possible interferences from other species present in the complete mix could be eliminated. N_2, N_2O, and NH_3 were the only products identified, formed by the following reactions:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$NO_2^- + 2H_2O + 3e^- \rightarrow \tfrac{1}{2}N_2 + 4OH^- \quad (2)$$

$$2NO_2^- + 3H_2O + 4e^- \rightarrow N_2O + 6OH^- \quad (3)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \quad (4)$$

Table 1 reports data from electrolyses at a series of cathode materials. The results are reported at about 60 000 C, which corresponds to approximately 3/4 of the charge needed to completely reduce all of the NO_2^-/NO_3^- in solution to nitrogen at 100% current efficiency. It can be seen that at all cathode materials, there is a substantial decrease in NO_3^- and NO_2^- concentrations. The off-gas composition is also reported although Table 1 in fact gives only area percentages of product gases and does not take account of component response factors. Hydrogen was not analysed and therefore, was not included in the off-gas composition. It is, however, clear that N_2 is always a major contributor to the gas composition. On the other hand, the importance of the other products, NH_3 and N_2O varies strongly with the cathode. It should also be noted that the amount of off-gas generally increases with time (initially, the reduction of NO_3^- to NO_2^- is the major cathode process) and the ratio of gases is also a function of the charge passed.

Table 1. Glass cell nitrate/nitrite destruction at various electrode materials

	Destruction efficiency /%	*Off-gas /% nitrogen**	*Off-gas /% nitrous oxide**	*Off-gas /% ammonia**
Lead	100	75	24	1
Cadmium	99	69	3	28
Lead alloy	92	67	32	2
316 SS	83	55	32	12
Nickel	81	45	38	17
Copper	79	37	57	6
Porous nickel	78	63	35	2
ATJ graphite	76	43	54	4
Metcote ES-6	64	75	0	25

* Based on relative areas under GC peaks only.

Conditions: catholyte: 1.95 M $NaNO_3$, 0.60 M $NaNO_2$; 1.33 M NaOH, 70 ml. Anolyte: 1 M H_2SO_4, 150 ml. Pt anode, Nafion® 417 membrane, $i = 140\,\mathrm{mA\,cm^{-2}}$, T = ambient, electrode area 5 $\mathrm{cm^2}$. Results reported at 60 000 C.

The objective of this research is to convert the NO_3^- and NO_2^- to gaseous products with the minimum power consumption. The current efficiency for the reduction of NO_3^- and NO_2^- is therefore of concern but its calculation requires a precise knowledge of all products throughout the electrolysis. We have therefore introduced the term 'destruction efficiency' which is defined as

$$\text{Destruction efficiency} = \frac{Q_\mathrm{T}}{Q_\mathrm{exp}} \times 100$$

where

$$Q_\mathrm{T} = (3\Delta m_\mathrm{nitrite} + 5\Delta m_\mathrm{nitrate})F$$

where Δm_i is the change in the number of moles of NO_3^- or NO_2^- in the system and F is the faradaic constant. Q_exp is the experimental charge. Obviously, the calculation of the destruction efficiency assumes that N_2 is the only product. Even so, we believe that the destruction efficiency is a reasonable basis to compare cathodes and the influence of other experimental parameters.

The destruction efficiencies for NO_2^-/NO_3^- destruction show a trend with the hydrogen overpotentials of the metals tested with the most efficient reactions seen at lead and its alloys and cadmium. This agrees with literature reports indicating that better current efficiencies could be obtained with lead as opposed to nickel [3]. This is to be expected since a major competing reaction to nitrate reduction is hydrogen evolution. Lead also produced the lowest level of ammonia. Metcote® ES-6 (ICI proprietary low hydrogen overpotential coating) has the lowest hydrogen overpotential and gives the poorest destruction efficiency as well as a large amount of ammonia production. The other materials tested show various amounts of ammonia production. A zinc cathode corroded severely.

3.1.2. Divided flow cell cathode screening with complete mix. The MP flow cell was used for flow cell cathode screening with a solution whose composition is intended to mimic that seen in the nuclear industry. In the following discussion, this solution is termed the complete mix. The cell was operated in a divided configuration so as to remove possible interferences such as nitrite oxidation at the anode. The composition is shown in Table 2.

(a) *Comparison of cathode materials*

Figure 1 shows the destruction of nitrite and nitrate in the complete mix at lead and nickel cathodes. With a lead cathode, nitrite builds up in solution while nitrate levels decline and, after nitrate depletion, the nitrite level also declines. This suggests that the conversion of nitrite to gaseous reduction products is the slow step in the reaction mechanism. At nickel, the pronounced increase in nitrite levels is not observed, instead, after a slight increase in nitrite concentration, both nitrite and nitrate decrease throughout the experiment. This suggests that the kinetics and/or mechanism for nitrate reduction at nickel is quite different from that at lead. Overall, lead shows a higher rate of removal of NO_3^-/NO_2^-.

A standard gas mix was used during the flow cell experiments so that response factors and actual volumetric percentages could be calculated for the product gases. Figure 2 gives the instantaneous off gas composition at lead and nickel when the complete mix is used. At both cathodes, nitrogen and nitrous oxide are the major nitrogen containing products early in the experiment with ammonia becoming the dominant

Table 2. Composition of the complete simulated mix

Component	*Concentration/M*
$NaNO_3$	1.95
$NaNO_2$	0.60
NaOH	1.33
$NaAl(OH)_4$	0.31
Na_2SO_4	0.14
Na_2CO_3	0.16
NaCl	0.22
NaF	0.015
Na_2SiO_3	0.0038
Na_3PO_4	0.0085
Na_2CrO_4	0.0033
$NaB(C_6H_5)_4$	0.0026
$Na_2\{Ru(NO)(NO_2)_4(OH)\}$	4.5×10^{-5} (= 4.5 mg $\mathrm{dm^{-3}}$ Ru)
$HgCl_2$	2.2×10^{-6} (= 0.45 mg $\mathrm{dm^{-3}}$ Hg)

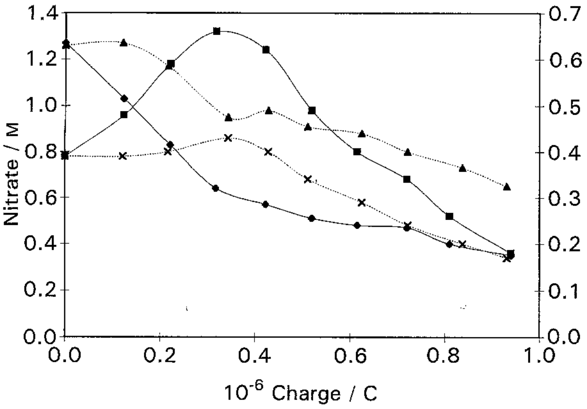

Fig. 1. Effect of cathode material on nitrate and nitrite removal. Conditions: divided MP flow cell, electrode area = 100 cm^2. Nafion® 417 membrane, Pt anode. Catholyte = 700 ml complete mix. Anolyte = 3 M H_2SO_4, i = 500 mA cm^{-2}, T = 70 °C, electrolyte flow = 1 gal min^{-1}. Nitrate: (◆) lead cathode and (▲) nickel cathode. Nitrite: (■) lead cathode and (×) nickel cathode.

gas product in the second half of the experiment. Lead gives greater amounts of the nitrogen containing reduction products than does nickel, as is expected since more destruction of NO_3^- and NO_2^- and better destruction efficiencies were observed at the lead cathode. It should be stressed, however, that the amount of gas evolution increases markedly during the electrolyses. This is especially true at lead, where early in the electrolysis the major electrode process is $NO_3^- \rightarrow NO_2^-$, and little gas is evolved. Indeed, the destruction efficiency shows that at lead, NO_3^-/NO_2^- reduction to NO_2^-/N_2 remains the major cathode reaction but as their concentration drops, ammonia production becomes more important.

Figure 3 shows cumulative destruction efficiencies for all cathode materials tested in the divided flow cell with the complete mix. Lead achieves the most efficient destruction of nitrite and nitrate. The cumulative destruction efficiency at lead starts at about 70% and drops to 55% as nitrite and nitrate are depleted. Roughly 2/3 of the NO_3^-/NO_2^- in the synthetic mix was removed at lead in the flow cell experiment. Cumulative destruction efficiencies at lead with the simplified mix in the glass cell experiments approached 100% after the conversion of about 75% of NO_3^-/NO_2^- to gaseous products. Cumulative destruction efficiencies for nitrite and nitrate removal at nickel and graphite are also worse in the complete mix than in the simplified mix used in the glass cell experiments. The remaining cathode materials tested, copper, 316 stainless steel, and platinum, achieved little nitrate destruction as evidenced by the poor destruction efficiencies. These materials also gave only trace amounts of nitrogen containing reduction products and large amounts of hydrogen. This is in contrast with the results seen in the glass cell (Table 1) where stainless steel and copper performed well. Clearly, other components in the complete mix interfere with the reduction process to a lesser or greater extent at all cathode materials tested.

Solution analyses showed that chromium was almost entirely removed from solution in the successful experiments with lead, nickel, and graphite cathodes, but not removed from the mix when other

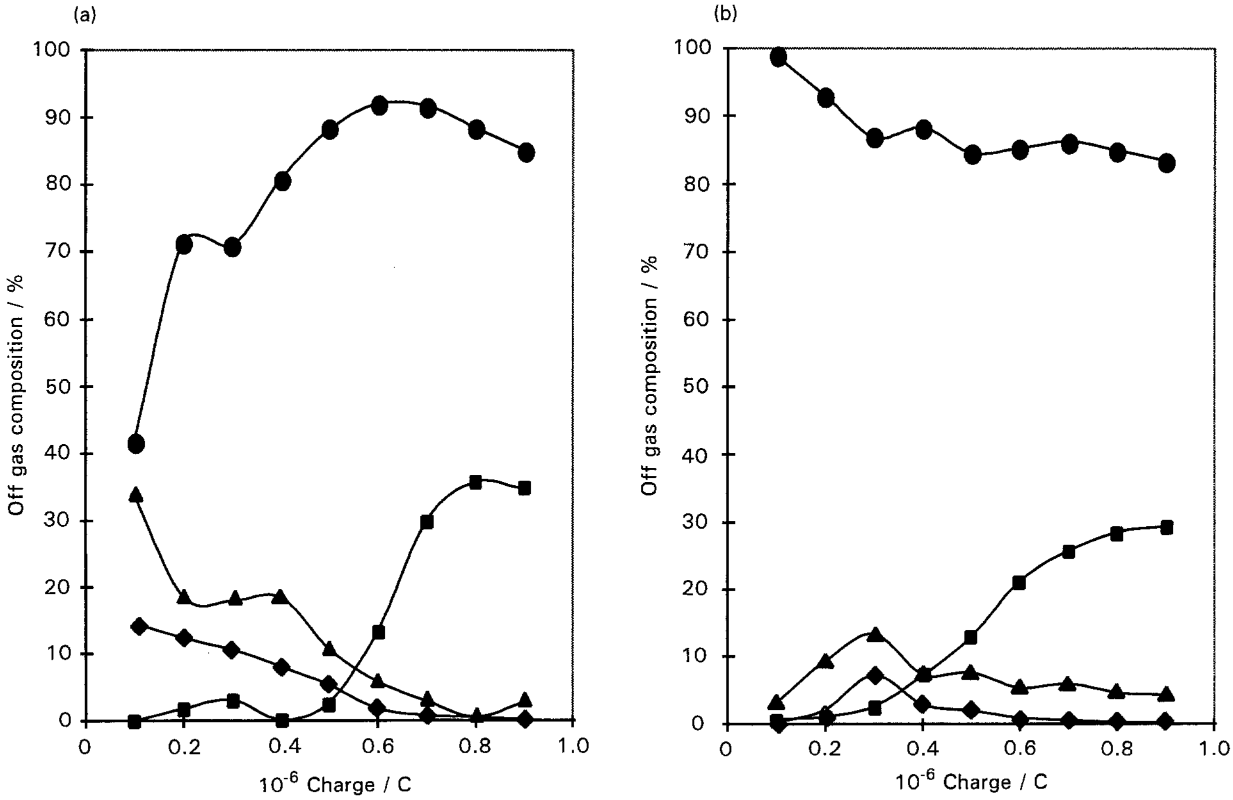

Fig. 2. Off-gas composition in flow cell with complete mix. (a) Lead cathode; (b) nickel cathode. Conditions: divided MP flow cell, electrode area = 100 cm^2. Nafion® 417 membrane, Pt anode. Catholyte = 700 ml complete mix. Anolyte = 3 M H_2SO_4, i = 500 mA cm^{-2}, T = 70 °C, electrolyte flow = 1 gal min^{-1}. Key: (●) %H_2, (■) % NH_3, (▲) % N_2, (◆) % N_2O.

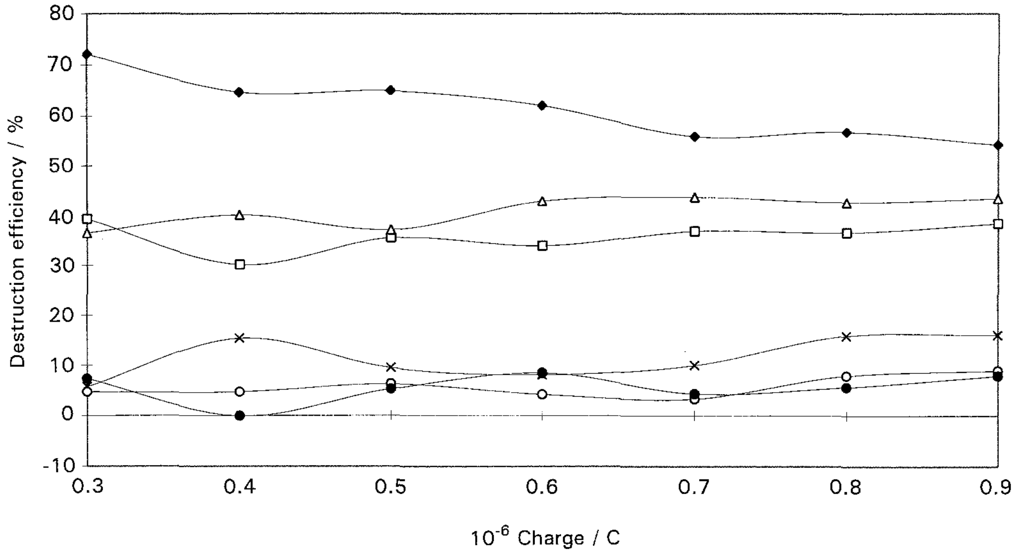

Fig. 3. Comparison of cathode materials for destruction of nitrate/nitrite in a flow cell. Conditions: divided MP flow cell, electrode area = $100 cm^2$. Nafion® 417 membrane, Pt or DSA-$O_2^{®}$ anode. Catholyte = 700 ml complete mix. Anolyte = 3 M H_2SO_4, $i = 500 mA cm^{-2}$, $T = 70$ °C, electrolyte flow = 1 gal min^{-1}. Key: (◆) lead, (□) nickel, (△) graphite, (×) copper, (○) platinum and (●) 316 SS.

cathodes were used. The literature suggests that in base, chromate can form $Cr(OH)_3$ films on platinum cathodes [10]. These films hinder the reduction of large molecules while still allowing hydrogen evolution to occur. Further chromate reduction is also hindered. The industrial process for chlorate electrosynthesis takes advantage of this behaviour. Chromate is added to the electrolyte to prevent the reduction of intermediately formed hypochlorite ions to chloride at the cathode in the undivided cell. Perhaps at platinum, copper, and stainless steel, nitrate reduction, as well as chromate reduction, is hindered by the formation of chromium hydroxide films while nickel, graphite, and lead did not fully support the film formation and reduction continued.

(b) *Longer term flow cell cathode screening experiments*

Since the reduction process seems to be sensitive to other species present in the full waste mix two of the promising cathode materials, nickel and lead, were screened in longer experiments to ensure that their performance remained the same with larger amounts of the mix. Figure 4 shows cumulative destruction efficiencies for electrolyses lasting 50 h. Poor destruction efficiencies and low amounts of nitrogen containing reduction products were seen at nickel through the bulk of the run. Thus nickel performed quite differently in the 50 h test than in the initial short screening tests.

The lead cathode gave cumulative destruction efficiencies similar to those seen in shorter experiments. The destruction efficiency decreased at longer times largely because nitrite and nitrate were substantially removed from solution and hence mass transfer of these reactants to the cathode became limiting. Ammonia was again the dominant reduction product in the latter half of the experiment. Lead appeared stable in these extended tests and is clearly one of the best cathode materials tested for reduction of nitrate/nitrite in the complete mix.

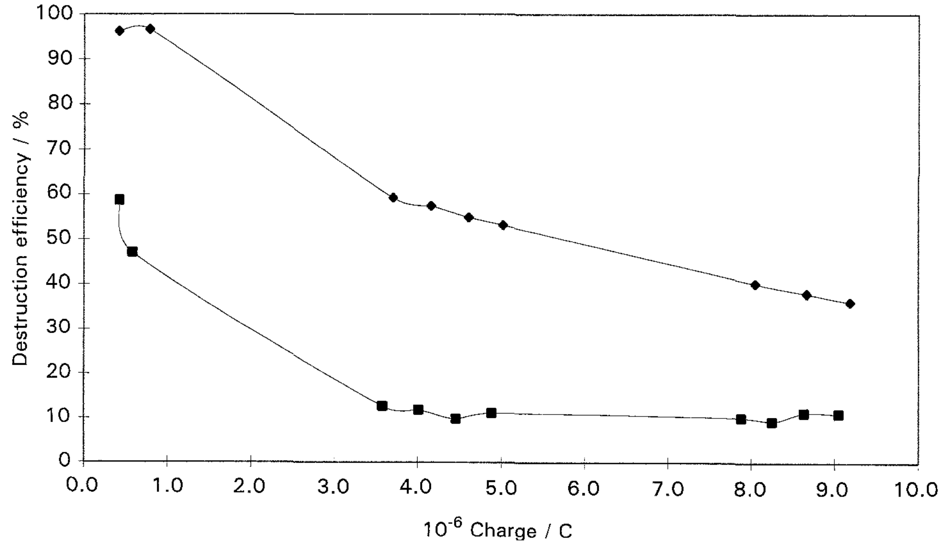

Fig. 4. 50 h cathode screening tests. Conditions: divided MP flow cell, electrode area = $100 cm^2$. Nafion® 417 membrane, DSA-$O_2^{®}$ anode. Catholyte = 3500 ml complete mix. Anolyte = 3 M H_2SO_4, $i = 500 mA cm^{-2}$, $T = 70$ °C, electrolyte flow = 1 gal min^{-1}. Key: (◆) lead cathode and (■) nickel cathode.

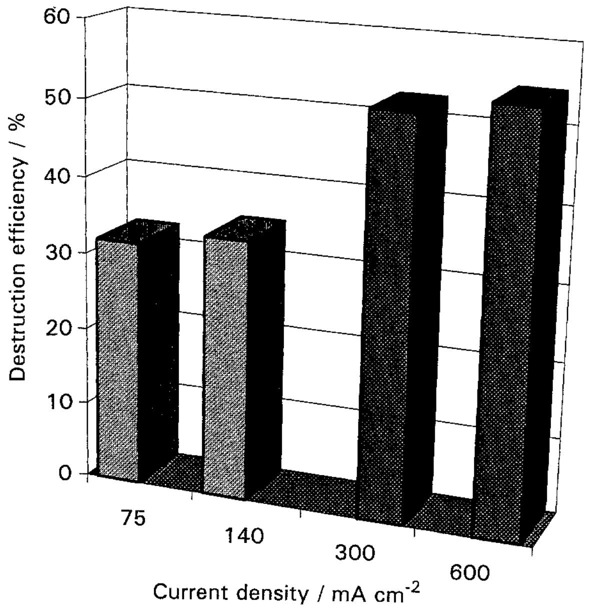

Fig. 5. Effect of current density and temperature on nitrate/nitrite reduction. Conditions: undivided ICI FM01 flow cell, electrode area = 64 cm^2. Pb–Sn–Ca alloy cathode, Ni anode. Electrolyte = 700 ml complete mix, electrolyte flow = 0.8 gal min^{-1}. Key: (▨ light) 50 °C and (▨ dark) 80 °C.

3.2. *Effect of increasing both temperature and current density on nitrate/nitrite reduction*

The combined effects of current density and temperature on the reduction of nitrate in the complete mix were investigated in an undivided flow cell (FM01 LC, ICI) using a lead alloy (ICI Pb/Sn/Ca alloy) cathode and nickel anode. Figure 5 shows that destruction efficiencies were improved in experiments carried out at higher current densities (300 and 600 mA cm^{-2}) and higher temperatures (80 °C). These results are reported at 1 million coulombs, and 40–60% of the NO_3^-/NO_2^- present had been converted to gaseous products. The use of high current densities does not result in loss of destruction efficiency at these NO_3^-/NO_2^- conversions and provides greater *iR* heating of the solution, thus high current density and high temperature are preferred for nitrate/nitrite reduction in the flow cell with the complete mix.

3.3. *Anode materials for direct reduction of nitrates*

Two requirements should ideally be met by potential anode materials for nitrate reduction. First, the material would have to be stable to the complete mix under actual electrolysis conditions. Second, it would be an advantage if the anode reaction did not interfere with the reduction process so that the cell may be operated in an undivided configuration.

3.3.1. Undivided flow cell anode screening tests. Figure 6 summarizes the results of electrolyses with three anodes in an undivided MP flow cell with a lead cathode. In undivided cells with Pt, 316 stainless steel, or nickel anodes, cumulative destruction efficiencies were worse than those seen in the divided cell with a lead cathode. The stainless steel anode gave a large amount of rust coloured solids in solution. No solids were seen in solution with the nickel anode but the anode was coated with precipitate and showed a slight weight loss. The platinum anode did not show physical evidence of corrosion but gave much poorer destruction efficiencies. Negative destruction efficiencies seen early in the experiment reflect a net oxidation of nitrite to nitrate. Two other anode materials tested in the undivided flow cell, graphite and lead, corroded severely. Thus, of the anode materials tested only nickel may be suitable for the direct reduction of nitrate in an undivided cell. However, the possible corrosion of a nickel anode is of concern.

3.4. *Effect of cation exchange membranes on the removal of nitrate/nitrite*

3.4.1. Effect of membrane on nitrate/nitrite removal. Figure 7 shows that the inclusion of a cation

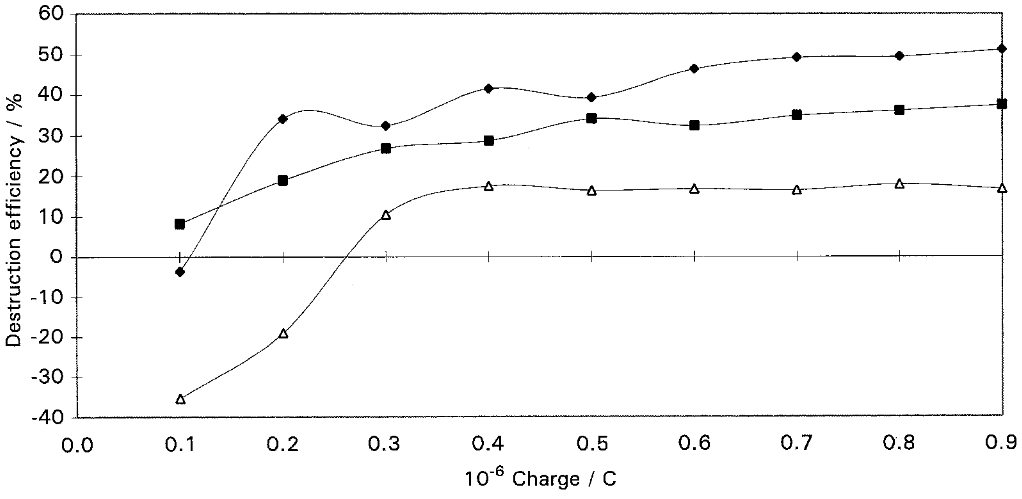

Fig. 6. Comparison of anode materials for reduction of nitrate/nitrite in an undivided cell at a lead cathode. Conditions: undivided MP flow cell, electrode area = 100 cm^2. Lead cathode. Electrolyte = 700 ml complete mix. i = 500 mA cm^{-2}, T = 70 °C, electrolyte flow = 1 gal min^{-1}. Key: (◆) 316 SS, (■) nickel and (△) platinum.

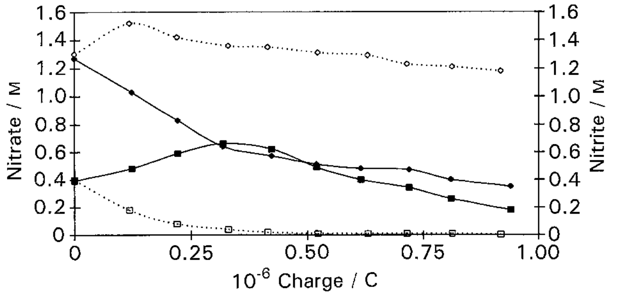

Fig. 7. Effect of membrane on nitrate removal in a flow cell. Conditions: MP divided flow cell, Nafion® 417 membrane, Pb cathode, Pt anode. Catholyte = 700 ml complete mix. Anolyte = 3 M H_2SO_4, $i = 500\,\mathrm{mA\,cm^{-2}}$, $T = 70\,°\mathrm{C}$, electrolyte flow = 1 gal min^{-1}. MP undivided flow cell, lead cathode, Pt anode. Electrolyte = 700 ml complete mix. $i = 500\,\mathrm{mA\,cm^{-2}}$, $T = 70\,°\mathrm{C}$, electrolyte flow = 1 gal min^{-1}. Nitrate: (◆) divided cell and (◇) undivided cell. Nitrite: (■) divided cell and (□) undivided cell.

Charge, C × 10^6	0.12	0.22	0.32	0.42	0.52	0.62	0.72	0.82	0.92
% Destruction efficiency divided cell	75	65	62	56	57	54	54	57	54
% Destruction efficiency undivided cell	−35	−19	11	18	16	17	17	18	17

exchange membrane brings about a significant improvement for nitrate/nitrite reduction with a lead cathode and platinum anode. The membrane isolates the catholyte electrochemistry from interfering oxidation of nitrite at the anode. The figure shows that without a membrane, nitrite was removed, but nitrate levels changed little, suggesting that nitrite was oxidized to nitrate. As a result, cumulative destruction efficiencies for nitrate/nitrite removal are poor or even negative. When a membrane is included both nitrite and nitrate are removed from solution at good destruction efficiencies.

3.4.2. Effect of radiation on membranes. In order for the direct reduction process to be feasible in a divided cell, the cation exchange membrane must not be damaged by radiation from trace amounts of radionuclides found in the waste stream. It is conceivable that radiation could cleave sulfonic acid groups from the membrane's polymer backbone or even damage the fluorinated backbone of the membrane. Any such damage would probably result in changes in membrane resistivity. Nafion® 417 and 324 membranes were exposed to a ^{60}Co radiation source and irradiated at an accelerated dose rate ($(4.7 \pm 0.6) \times 10^4$ rad h^{-1}) at ambient temperature. One hour of irradiation at this dose rate was estimated to correspond to six months of exposure to the actual waste. The membranes were irradiated in deionized water, 0.1 M sulfuric acid, and the complete synthetic mix to determine the effect of the sample matrix. Nafion® 324 was tested because it has a higher equivalent weight layer on one side of the membrane which makes it less permeable to diffusing anions as compared to Nafion® 417. Thus, Nafion® 324 is less likely to allow anions from the complete mix to pass into the anolyte.

Figure 8 plots potential drop across the membrane vs current density for unirradiated Nafion® 324 membranes and membranes irradiated for varying amounts of time in the complete mix. The supporting electrolyte for the membrane potential tests was 2 M H_2SO_4. The potential drop across the membrane includes the solution *iR* drop between the Luggin probes and the membrane. Control experiments with unirradiated membranes gave a variation in membrane potential of about 15 mV at 500 mA cm^{-2}. The graph shows no clear trend in terms of changes of resistivity with irradiation. Similar results were seen with Nafion® 324 membranes irradiated in a sulfuric acid or water matrix and with Nafion® 417. Furthermore, Nafion® 324 irradiated for 4 hours showed similar performance and cell voltage characteristics to unirradiated Nafion® 324 in a 100 h flow cell test using the complete mix at a current density of 500 mA cm^{-2} and a temperature of 70 °C. We conclude that the irradiation did not cause significant

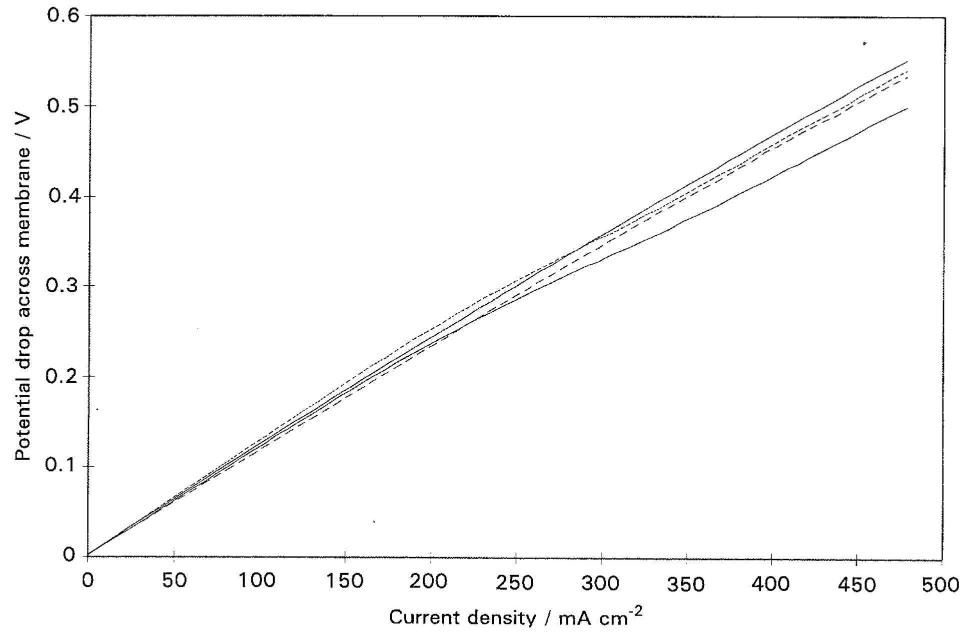

Fig. 8. Effects of irradiation on Nafion® 324 irradiated by exposure to ^{60}Co source. Conditions: irradiation done in complete mix. Key: (——) control, (- - - -) 2 h irradiated, (– – –) 4 h irradiated and (– - - –) 8 h irradiated.

changes in resistivity and hence chemical composition of the membrane at a total dose of up to $(3.8 \pm 0.5) \times 10^5$ rad.

3.5. *Long term flow cell component performance and stability tests*

Based on the short term test results, the conditions found for the most efficient nitrate/nitrite reduction in the complete mix are thought to be as follows: high temperature (70–80 °C), high current density (300–600 mA cm^{-2}), divided cell, and lead cathode. These conditions were examined in long-term performance and stability tests. A divided MP cell with a lead cathode, Nafion® 417 cation exchange membrane, and oxygen evolving DSA®, platinized niobium, or shiny platinum clad niobium anode (cell area 100 cm^2) was used for these tests at a current density of 500 mA cm^{-2} and a temperature of 70 °C. A large batch (70 dm^3) of the complete mix was used as the catholyte.

3.5.1. Acid anolyte. The performance for the direct reduction at a lead cathode at 500 mA cm^{-2} was similar in the long-term studies to that seen in shorter experiments. Greater than 99% of the nitrite and nitrate was removed in the 1000 h tests. Note that the shorter term experiments were intentionally stopped after roughly 2/3 of the nitrite and nitrate had been converted to gaseous products. The overall destruction efficiency in the 1000 h test dropped from an initial value of about 70% to 55% at the end of the experiment as nitrate and nitrite were completely depleted. Thus even at high conversions the destruction efficiency remains fairly high, although mass transfer limitations do reduce the destruction efficiency. These results were repeated in a second 1000 h test using a platinum clad niobium anode. Chromate was completely removed from solution early in the experiments. The lead cathode and Nafion® 417 membrane showed good stability and performance over the 1000 h.

The anodes in these extended trials did not perform well. Each anode tested (oxygen evolving DSA® type, platinized niobium, platinum clad niobium) failed after several hundred hours of operation due to corrosion. Anode failure was evidenced by rising cell voltage as the precious metal coating of these electrodes was etched exposing the titanium or niobium substrate which then passivated in the acidic environment. Solution analyses of the sulfuric acid anolytes all showed high levels of the precious metals used to coat the electrodes as well as the base metal. Scanning electron microscopy done on the anodes also showed that etching had occurred, often to the extent of complete removal of large areas of catalyst coating.

Solution analyses also showed high amounts of fluoride (> 10 ppm) in the anolyte. Fluoride migrated across the cation exchange membrane from the catholyte into the anolyte under the influence of the potential field. Anions are known to diffuse across cation exchange membranes at rates that would readily give 10 ppm F$^-$ in the anolyte [11]. In the acidic anolyte fluoride would form HF, known to attack oxygen evolving DSA-type anodes. Fluoride contamination of the acidic anolyte is likely responsible for the corrosion and failure of the anodes.

3.5.2. Basic anolyte. One means of avoiding anode corrosion in a divided cell would be to use a caustic anolyte. Fluoride migrating into this media would form NaF instead of HF and may not cause corrosion. Furthermore, inexpensive anode materials such as stainless steel could be used. The anolyte chosen was 10 M NaOH and the source of caustic could be NaOH recovered from the spent catholyte by evaporation and recrystallization.

This concept was tested in the MP flow cell using a lead cathode, Nafion® 324 separator, and a stainless steel anode at a current density of 500 mA cm^{-2} and temperature of 70 °C. Destruction efficiencies were similar to those seen with an acid anolyte. The experiment continued smoothly for over 100 h with no indication of anode corrosion. Further long term testing is needed to confirm the performance of the process and stability of cell components where a caustic anolyte is used.

4. Discussion

Glass cell studies of the reduction of nitrate and nitrite in NaOH confirmed literature results demonstrating that destruction efficiencies are better at a lead cathode than at nickel. In general, more efficient reduction of nitrite and nitrate occurred at those cathode materials with higher overpotentials for hydrogen evolution. Flow cell studies of the reduction process in a simulated alkaline low-level nuclear waste stream demonstrated that the destruction efficiencies are lower in the complete mix. For some cathode materials, nitrate/nitrite reduction was almost completely suppressed in the complete mix. Destruction efficiencies in the flow cell with the complete mix were improved when current density and temperature were increased.

Lead maintained good destruction efficiencies when used in the divided flow cell configuration in both short and long term experiments. When a lead cathode was used in the undivided cell configuration, destruction efficiencies were lower and corrosion of nickel and stainless steel anodes was noted. The Nafion® 417 cation exchange membranes and lead cathode demonstrated good stability and destruction efficiencies similar to those seen in shorter tests during a 1000 h test. The membrane was also shown to be unaffected by radiation. All anodes tested in 1000 h experiments corroded when a sulfuric acid anolyte was used. The corrosion was likely due to the migration of fluoride into the anolyte and subsequent formation of HF. Good stability of a stainless steel anode was observed for 100 h when a caustic anolyte was used. If an acidic anolyte is used, it may be possible to complex fluoride by adding borate salts to the anolyte. Alternatively, DSA® coatings on an Ebonex® (conductive TiO_x) substrate may prove to be stable to HF since Ebonex itself is stable in fluoride media.

Acknowledgement

We are grateful for funding provided by the Department of Energy under Contract No. DE-AC09-89SR18035 to Westinghouse Savannah River Corporation.

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