JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 811–817

Electrochemical reduction of nitrates and nitrites in alkaline media in the presence of hexavalent chromium

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Received 1 November 1997; revised 26 January 1998

Electrochemical reduction of nitrates and nitrites in alkaline media at constant current is rendered inoperable in the presence of hexavalent chromate. Even at chromate concentrations as low as 9 mg dm^{-3}, the chromium hydroxide film, formed by the reduction of chromate, interferes with the reduction of nitrate and nitrite. We show that reversing the polarity of the electrodes at constant time intervals minimizes the adverse effects of the chromium hydroxide film, enabling the electrochemical reduction of nitrates and nitrites to proceed efficiently. The optimum current and reversal time are coupled through an optimum charge density of 625 C cm^{-2} per cycle. We also demonstrate through long-term studies that the reversal technique can be operated on a continuous basis.

Keywords: *alkaline media*, *electrochemical reduction*, *hexavalent chromium*, *nitrates*, *nitrites*

1. Introduction

Treatment strategies are needed to process the large volume of radioactive waste that has accumulated during the production of nuclear materials. For example, at the Savannah River Site (SRS) in Aiken, SC, approximately 35 million gallons of highly radioactive waste has accumulated over the past 50 years. Recently, treatment processes have initiated at SRS to separate and concentrate the radionuclides for vitrification in the Defense Waste Processing Facility. The remaining decontaminated waste is incorporated into a cement waste-form (Saltstone) and placed in an engineered onsite landfill. It has been proposed to send the low-level waste to an electrochemical reactor prior to solidification to reduce the quantity of nitrate and nitrite, which represent the largest source of groundwater contamination. The average composition of the decontaminated waste is presented in Table 1. Previous studies have shown that feeding a waste simulant containing nitrate, nitrite and caustic to a parallel-plate electrochemical reactor produces ammonia, nitrogen and hydrogen at the nickel cathode [1–8]. The desired reduction can occur in both a divided [1–6] and an undivided [7, 8] cell according to the following reactions:

$$U^{\theta}\text{(V vs SHE)}$$

$$NO_3^- + H_2O_{(1)} + 2\,e^- \leftrightarrow NO_2^- + 2\,OH^- \qquad 0.01 \qquad (1)$$

$$NO_2^- + 5\,H_2O_{(1)} + 6\,e^- \leftrightarrow NH_{3(g)} + 7\,OH^- \qquad -0.165 \qquad (2)$$

$$2\,NO_2^- + 4\,H_2O_{(1)} + 6\,e^- \leftrightarrow N_{2(g)} + 8\,OH^- \qquad 0.406 \qquad (3)$$

$$2\,H_2O_{(1)} + 2\,e^- \leftrightarrow H_{2(g)} + 2\,OH^- \qquad -0.828 \qquad (4)$$

In an undivided cell or in a divided cell with a nonselective separator, the oxidation of nitrate to nitrite via Reaction 1 can occur at the anode thus decreasing the electrochemical efficiency of the overall process. The evolution of oxygen is the dominant reaction at the anode and is given by:

$$U^{\theta}\text{(V vs SHE)}$$

$$4\,OH^- \leftrightarrow O_{2(g)} + 2\,H_2O_{(l)} + 4\,e^- \qquad 0.401 \qquad (5)$$

Unfortunately, the presence of hexavalent chromium effectively stops Reaction 1 at the cathode [6, 8]. The passivating effect of hexavalent chromate is most likely due to the reduction of CrO_4^{2-} to trivalent chromium hydroxide at the cathode according to the following reaction [6, 8–13]

$$U^{\theta}\text{(V vs SHE)}$$

$$CrO_4^{-2} + 4\,H_2O + 3\,e^- \leftrightarrow Cr(OH)_3 + 5\,OH^- \qquad -0.11 \qquad (6)$$

Since the $Cr(OH)_3$ species is insoluble in caustic solution [10], the solid deposits on the cathode and virtually stops Reaction 1 [6, 8].

Adding bismuth salts to the electrolyte improves the current efficiency of Reaction 1, but the effect is temporary since the bismuth eventually deposits on the anode [8]. Lead electrodes have been proposed by Bockris and Kim [6] as capable of reducing the nitrates and nitrites in the presence of chromate. However, environmental considerations as well as lead corrosion renders this alternative undesirable. Removing the chromate prior to the electrochemical reactor is a possible solution, but the relatively low concentration of CrO_4^{2-} among numerous other

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Table 1. Average composition of the decontaminated salt-solution at the Savannah river site [*1*]

Component	*Concentration*/M
$NaNO_3$	1.95
$NaNO_2$	0.6
NaOH	1.33
$NaAl(OH)_4$	0.31
Na_2SO_4	0.14
Na_2CO_3	0.16
NaCl	0.022
NaF	0.015
Na_2CrO_4	0.0033
Na_3PO_4	0.0085
Na_2SiO_3	0.0038
$NaB(C_6H_5)_4$	0.0026

waste constituents suggests that a removal step would be very costly.

We hypothesize that the trivalent chromium hydroxide film can be reoxidized to the soluble hexavalent form by periodic reversal of the electrodes' polarity. Therefore, the objective of this work is to verify this hypothesis in an undivided batch reactor, and to determine the optimum current and reversal time that minimizes the adverse effect of chromate. The polarity reversal technique can be only used in an undivided cell as either electrode acts as an anode or a cathode for a period of time. This is not a major restriction since appreciable efficiencies (~70%) have been found for undivided cells [7, 8] in absence of chromate. The small reduction in current efficiency is offset by the elimination of a costly cation-selective membrane and the cost savings in the assembly and operation of an undivided cell compared to a divided cell.

2. Experimental details

All experiments were performed in the undivided cell shown in Fig. 1. The cell was filled with 100 cm^3 of electrolyte which contained 1.95 M $NaNO_3$, 0.6 M $NaNO_2$, 1.33 M NaOH and varying concentrations of $Na_2Cr_2O_7$. All the chemicals used were of analytical grade and were dissolved in deionized water. The desired concentration of CrO_4^{2-} was obtained by dissolving the requisite amount of $Na_2Cr_2O_7$ in the electrolyte. The predominant hexavalent chromium species is CrO_4^{2-} in concentrated caustic solutions [10]. The anode and cathode were 99.9% nickel with a front face area of 16 cm^2. The backsides of the electrodes were assumed inactive. Unless otherwise noted, the nickel electrodes were polished with 800-grit sandpaper, rinsed with 0.05 M HCl and washed with distilled water prior to placing them in the cell. An electrode prepared by this procedure will be referred to as a new electrode.

Constant current was provided by a Bitrode Multicell Charger, and electric timers together with double-pole double-throw switches were used to reverse the electrode polarity at constant intervals. The current densities used here are in the range used in large flow reactors [5, 7]. Sample volumes of 1.0 cm^3 were withdrawn throughout a run, and the nitrate and nitrite concentration was measured using an ion chromatograph (Dionex 500IC). The temperature of the solution was recorded as a function of time. The temperature rises to a steady-state value in approximately 30 min. The water losses due to evaporation were replenished by periodic addition of deionized water to maintain the desired electrolyte volume in the cell (i.e., 100 cm^3 minus the cumulative sample volume). Approximately 25 cm^3 of deionized water were added during a 50 h run. The solution was constantly stirred by natural convection due to gas evolution at the two narrowly spaced electrodes. The color and the pH of the solution were not observed to change significantly with time during an experiment. Also, no precipitates were observed in any of the experiments.

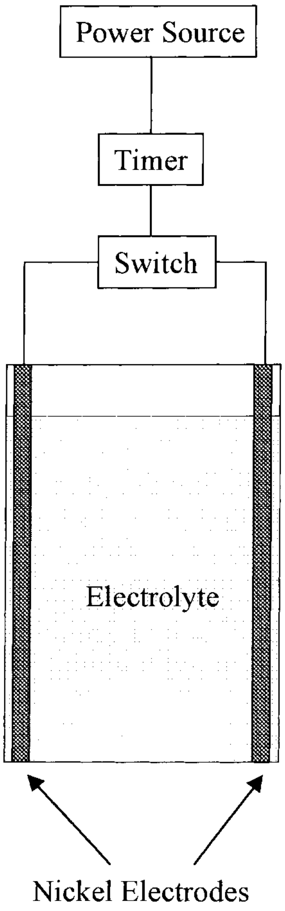

Fig. 1. A schematic of an undivided electrochemical cell. The anode and cathode were 99.9% nickel with a front area of 16 cm^2. The backsides of the electrodes were assumed inactive. The cell contained 100 cm^3 of the simulated waste solution.

3. Results and discussion

The effect of chromate on the electrochemical destruction of nitrites and nitrates is shown in Fig. 2. When a constant current of 2.5 A (160 mA cm^{-2}) is applied in the absence of CrO_4^{2-}, the nitrate concentration decreases slowly during the first five hours. This slow decrease in nitrate concentration is most

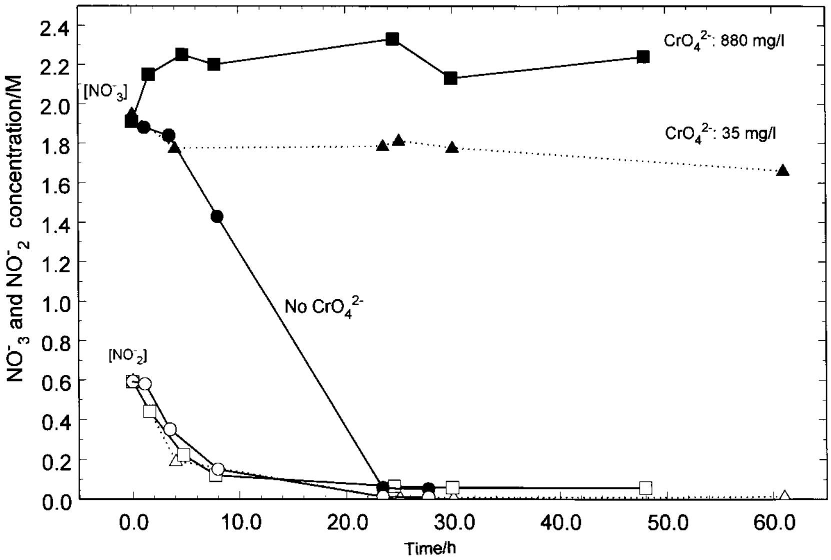

Fig. 2. The effect of hexavalent chromium on the reduction of nitrates and nitrites. The applied current is 2.5 A (160 mA cm^{-2}) which results in a electrolyte temperature of 43 °C.

likely due to the production of nitrate (i.e., oxidation of nitrite) at the anode offsetting the consumption at the cathode. As the nitrite concentration decreases, the net rate of nitrate reduction increases indicating that the nitrite oxidation at the anode becomes negligible. Adding 35 mg dm^{-3} and 880 mg dm^{-3} of CrO_4^{2-} to the electrolyte should not affect the oxidation of nitrites to nitrates, but it effectively stops the nitrate reduction reaction. At 880 mg dm^{-3} of CrO_4^{2-}, the nitrate concentration actually increases from 1.95 to about 2.3 M, due to the oxidation of nitrites to nitrates coupled with negligible nitrate destruction.

The formation of a solid film at the cathode surface was confirmed by the observance of a black cathode following an experimental run. The anode was dulled by the experiment, but it did not turn black. The black film on the cathode was smeared by touch and easily removed either by washing with a dilute acid or reversing the polarity of the electrode. Even at CrO_4^{2-} concentration as small as 35 mg dm^{-3}, the $Cr(OH)_3$ film is capable of inhibiting Reaction 1 at the cathode as shown in Fig. 2. Although Reaction 1 at the cathode is severely inhibited by the film, the oxidation via Reaction 1 will still occur at the anode. The result is a decrease in the nitrite concentration regardless of the amount of CrO_4^{2-} present in the electrolyte.

To understand the redox reaction of hexavalent chromate at a nickel electrode, cycle voltammograms (CV) in 1.33 M NaOH with and without chromate are shown in Fig. 3. The large currents at −1.3 and 0.9 V correspond to hydrogen and oxygen evolution, respectively, and the peaks on nickel between 0.3 and 0.45 V correspond to the nickel hydroxide redox reaction. A scan rate of 100 mV s^{-1} was used for the voltammetry on nickel. Figure 3 also shows a CV at a

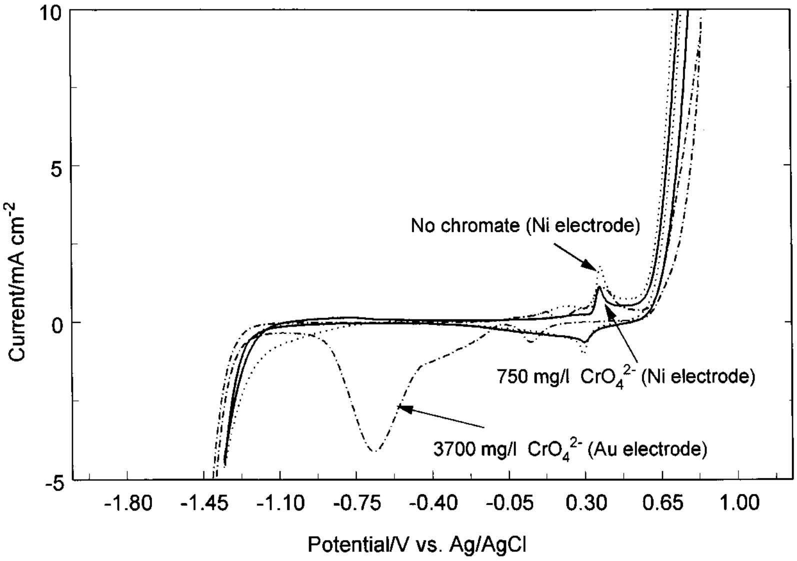

Fig. 3. Cycle voltammograms (CV) for hexavalent chromate on nickel and gold electrodes in 1.33 M NaOH with and without chromate. The voltage range of the CVs was −1.3 to 0.7 V vs Ag/AgCl, and the scan rate was 100 mV s^{-1} for nickel and 50 mV s^{-1} for gold electrode. Anodic currents are positive.

gold electrode with 3700 mg dm^{-3} of CrO_4^{2-} dissolved in 1.33 M NaOH. A scan rate of 50 mV s^{-1} was used for voltammetry on gold. The peak at −0.7 V is attributed to the reduction of Cr(VI) to Cr(III) via Reaction 6 [11–13]. The peak current of approximately 4 mA cm^{-2} is limited by the passivating effect of the trivalent chromium hydroxide on the electrode surface [11–13]. A diffusion-limited peak at CrO_4^{2-} concentration of 3700 mg dm^{-3} and a sweep rate of 50 mV s^{-1} would result in a peak current equal to 30 mA cm^{-2}. No chromate reduction peak is present on the nickel electrode between −1.1 and −0.4 V, and yet Fig. 2 clearly indicates an inhibiting effect of the hexavalent chromate. The negligible effect of chromate on the nickel CV in Fig. 3 is most likely due to the small time constant in the CV experiment compared to the batch experiments in Fig. 2. The time constant of the CV is of the order of 10 s whereas that of the batch experiments is on the order of 10 h. During a CV on nickel, the trivalent chromium hydroxide film formed on the nickel surface is probably very thin.

The conclusion from Fig. 2 is that it is not possible to reduce nitrates and nitrites in the presence of CrO_4^{2-} by applying a constant current. However, when the electrodes polarity is reversed every 30 min, Fig. 4 shows that the nitrate/nitrite destruction may proceed at an acceptable rate. Seven CrO_4^{2-} concentrations were tested ranging from 8.8 to 15 000 mg dm^{-3}, and three of the runs are shown in Fig. 4. The SRS waste stream contains an average concentration of 380 mg dm^{-3} of CrO_4^{2-} (0.0033 M).

The seven runs performed at constant current and with reversal of electrode polarity every 30 min, are summarized in Fig. 5 by plotting the nitrate concentration after 24 h of operation versus the hexavalent chromium concentration. In all three runs, the initial $NaNO_3$ and $NaNO_2$ concentrations are 1.95 M and 0.6 M, respectively, and the final nitrite concentration is practically zero. If CrO_4^{2-} is not present, Fig. 5 shows that the nitrate concentration after 24 h is approximately 0.05 M which corresponds to a 98% destruction of nitrate and nitrite. Without polarity reversal and a CrO_4^{2-} concentration of 8.8 mg dm^{-3}, the nitrate concentration after 24 h is approximately 1.8 M (29% destruction of nitrite and nitrate), and at CrO_4^{2-} concentrations over 500 mg dm^{-3}, the nitrate concentration is approximately 2.35 M (7.8% nitrate and nitrite destruction). Even when reversal of the electrode polarity was used, the efficiency of the process decreases with an increase in CrO_4^{2-} concentrations up to 1000 mg dm^{-3}. At CrO_4^{2-} concentrations over 1000 mg dm^{-3}, the nitrate concentration after 24 h is approximately 0.70 M, which corresponds to a 73% destruction of nitrate and nitrite. Further increases in chromate concentration have no effect on the efficiency of the process. Figure 5 emphasizes that even small amounts of chromate affect the nitrate and nitrite reduction process.

Different reversal times were studied in order to maximize the rate of the reduction of the nitrates and nitrites. Figure 6 presents the effect of different reversal times on a test solution containing 7000 mg dm^{-3} of CrO_4^{2-}. The results for the cases with no chromium present and no reversal of the electrode polarity are also shown for comparison. The nitrite concentrations are not shown since they are approximately the same as those presented in Fig. 4. The runs with a reversal time of 1 and 2 h resulted in a faster destruction of nitrate than the runs with either larger or smaller reversal times. This indicates that there is an optimum reversal time for the operation of the undivided cell. At very large times, the electrode spends most of the time passivated by the chromium hydroxide film resulting in low efficiencies. Small reversal times also result in low efficiencies. It is

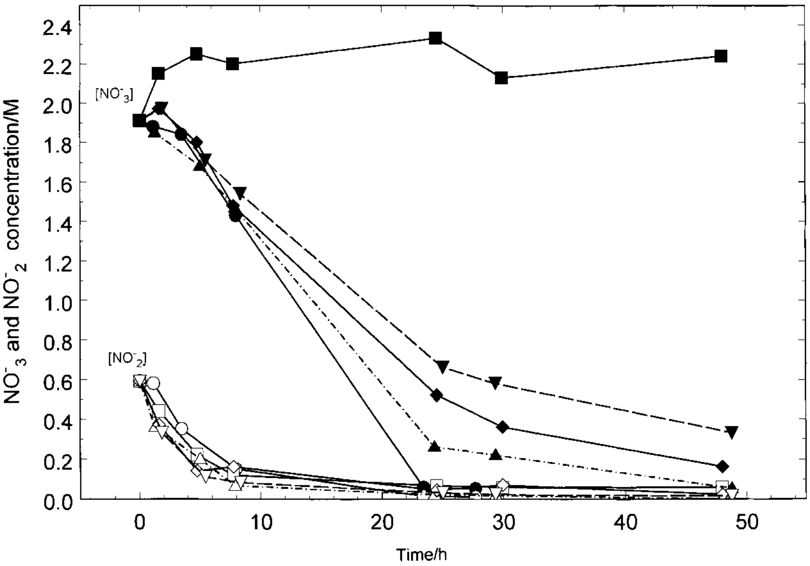

Fig. 4. The effect of hexavalent chromate concentration on the reduction of nitrates and nitrites. The applied current is 2.5 A (160 mA cm^2) which results in a electrolyte temperature of 43 °C. The reversal time is 30 min for the runs with the following chromate concentration: (●) 0, (▲) 8.8, (◆) 88 and (▼) 7000 mg dm^{-3}. The polarity was not reversed in the 880 mg dm^{-3} run (■).

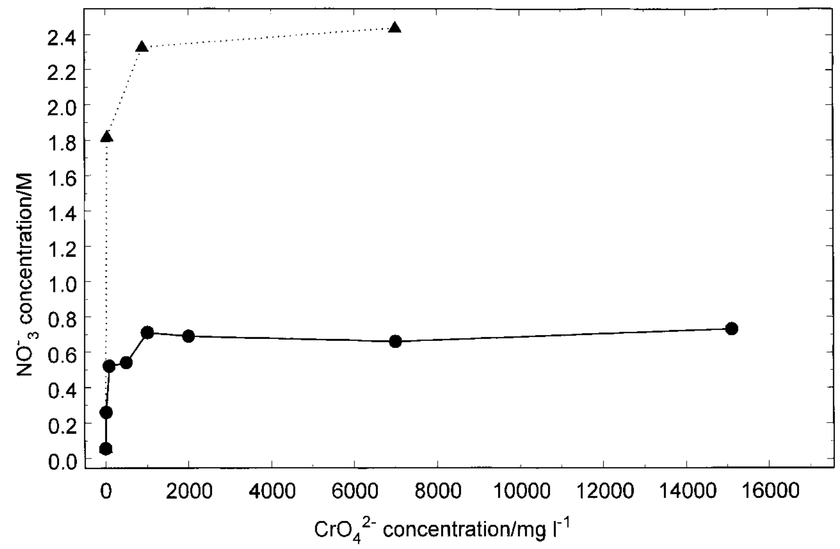

Fig. 5. Reduction of nitrates as function of the hexavalent chromate content with and without reversal of the electrode polarity. The nitrate concentrations plotted are after 24 h of electrolysis. The initial nitrate and nitrite concentrations are 1.95 M and 0.6 M, respectively. The applied current is 2.5 A (160 mA cm^{-2}). Key: (●) 30 min reversal time; (▲) no reversal.

believed that the trivalent chromium hydroxide film forms slowly on the surface of the electrode and it dissolves at an even slower rate. Therefore, very short reversal times will result in a cathode surface that retains a large fraction of the passive film.

Figure 7 shows the $NaNO_3$ concentration after 24 h of cell operation as a function of charge passed per cycle. Two different current densities were tested in a solution containing 7000 mg dm^{-3} of hexavalent chromium. The curve at 160 mA cm^{-2} and 43 °C is a summary of the results presented in Fig. 6. A similar summary is presented for runs at 320 mA cm^{-2} and 75 °C. The temperature in the two runs described above was not controlled, and therefore, the higher current resulted in a higher steady-state temperature due to ohmic heating. To ensure that the optimum reversal time is due to a change in current rather than a change in temperature, the run at 320 mA cm^{-2} was repeated with the cell in a cooling bath. The steady-state temperature for this run was 62 °C. The optimum switching time at 160 mA cm^{-2} and 43 °C (▲), and 320 mA cm^{-2} and 62 °C (■) occurs at the same amount of charge passed per half cycle. This optimum charge per half cycle is 10 000 C (i.e., 625 C cm^{-2}). This charge corresponds to an optimum time per half cycle of approximately 60 and 30 min for a current of 160 and 320 mA cm^{-2}, respectively. The optimum charge per half cycle at 320 mA cm^{-2} and 75 °C is also approximately 10 000 C, although there is no data point exactly at this optimum. The efficiency is slightly higher (i.e., the concentration is slightly lower) at the higher temperatures.

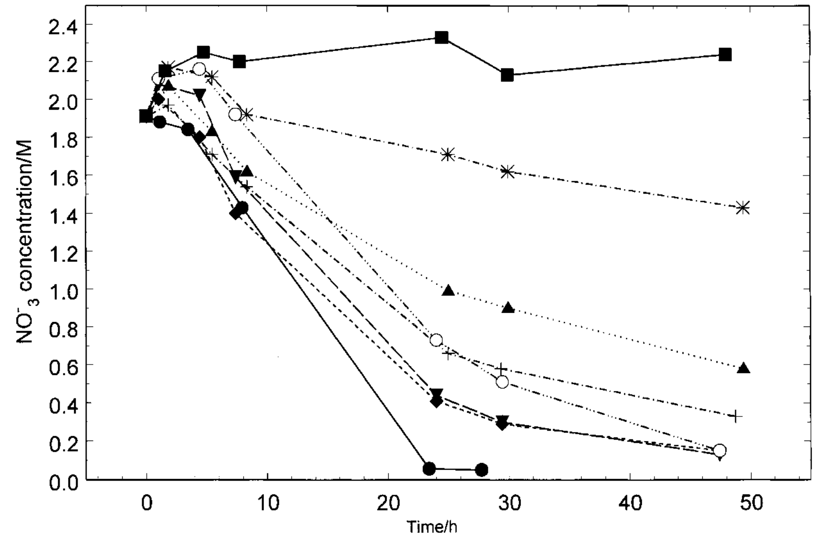

Fig. 6. The effect of different reversing times on the reduction of nitrates and nitrites. The applied current is 2.5 A (160 mA cm^{-2}) which results in a electrolyte temperature of 43 °C. The chromate concentration is 7000 mg dm^{-3} except for the no Cr case. The nitrite concentrations are not shown, as they are similar to those shown in Fig. 4. Reversal time: (*) 5 min; (▲) 15 min; (+) 30 min; (◆) 1 h; (▼) 2 h; (○) 5 h. For comparison purposes, runs are also shown with no reversal: (●) no Cr, (■) with Cr.

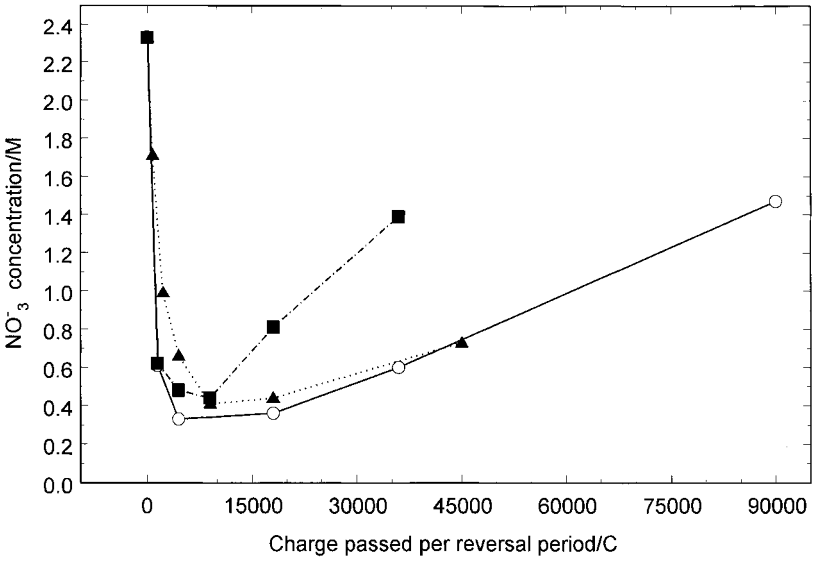

Fig. 7. Reduction of nitrates as a function of the charge per cycle. Charge per cycle is the amount of charge passed every time the electrode polarity is reversed. The average temperature for the run at 160 mA cm^{-2} is 43 °C. For the experiments at 320 mA cm^{-2}, the average temperature is either 75 °C or 62 °C. The Chromate concentration is 7000 mg dm^{-3}. Current density: (○) 320 mA cm^{-2} (T = 75 °C); (▲) 160 mA cm^{-2} (T = 43 °C); (■) 320 mA cm^{-2} (T = 62 °C).

Long-term performance of the nickel electrode was studied to investigate the possibility of any long-term poisoning of the nickel electrodes. Figure 8 compares the performance of a set of new electrodes to electrodes after 300 and 500 h of operation. Also shown are the results from electrodes after 750 h of operation after rinsing with 0.05 M oxalic acid. The long-term experiments consisted of continuously operating the cell with optimum polarity reversal for the indicated number of hours. The nitrate and nitrite concentrations were measured every few hours, and nitrate and nitrite was replenished to maintain their concentration at 1.95 M and 0.6 M, respectively. After this long-term conditioning, fresh solution was placed in the cell and a standard experiment was performed. There is a small long-term decrease in the efficiency of the electrodes over time. However, the efficiency does not seem to decrease any further after 300 h of operation. In addition, the oxalic acid wash regenerates the electrode close to its initial state. Thus it is not necessary to disassemble the reactor to clean and reactivate the electrodes.

4. Conclusions

The following conclusions resulted from this study:

(i) Hexavalent chromium concentration as low as 9 mg dm^{-3} inhibits the electrochemical reduction of nitrates and nitrites when the cell is operated at constant current.

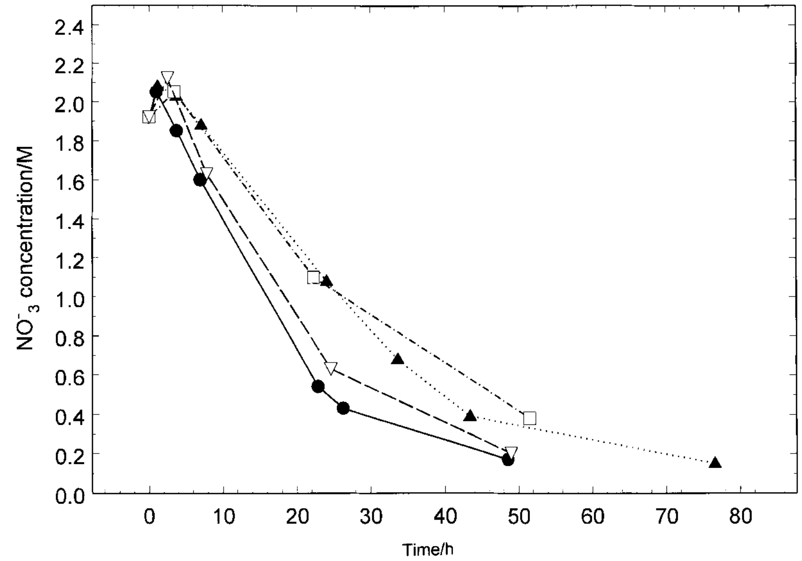

Fig. 8. The long-term performance of nickel electrodes run at 160 mA cm^{-2} in an electrolyte containing 1.95 M $NaNO_3$, 0.6 M $NaNO_2$, 1.33 NaOH and 880 mg dm^{-3} of CrO_4^{2-}. Comparison is made among a new electrode, electrodes after 300 and 500 h of operations, and a set cleaned with oxalic acid after 750 h of operation. The nitrite concentrations are not shown, as they are similar to those shown in Fig. 4. Key: (●) new electrode; (▲) electrode after 300 h; (□) electrode after 500 h; (▽) electrode after 750 h (cleaned with oxalic acid).

(ii) The reduction process can proceed at acceptable rates in the presence of hexavalent chromate by reversing the polarity of the electrodes at constant time intervals.

(iii) The optimum current and reversal time are coupled through an optimum charge density of $625\,\mathrm{C\,cm^{-2}}$ per cycle. The current densities used here are in the range used in large flow reactors. Therefore, the reversal times will be of the order of one hour, a condition that can be implemented on a large scale.

(iv) Any loss in efficiency over extended periods of operation (>300 h) can be recovered by washing the nickel electrodes with dilute acid (e.g., 0.05 M oxalic acid).

Acknowledgements

This work was funded by the US Department of Energy, Office of Technology Development, Office of Environmental Management through the Efficient Separations and Processing Crosscutting Program under contract DE-AC0988SR18035 to Westinghouse Savannah River Company and SCUREF Contract No. AA0009-00T, Task Order 118. The authors also thank Dr D. T. Hobbs for his valuable contribution to this work. The University of South Carolina assisted in meeting the publication costs of this article.

References

[1] D. T. Hobbs, 'Electrochemistry for a Cleaner Environment' (edited by J. D. Genders and N. L. Weinberg), The Electrosynthesis Company, Amherst, New York (1992).
[2] H. Li, D. H. Robertson and J. Q. Chambers, *J. Electrochem. Soc.* **135** (1988) 1154.
[3] S. Prasad, J. W. Weidner and A. E. Farell, *ibid.* **142** (1995) 3815.
[4] D. H. Coleman and R. E. White, *ibid.* **142** (1995) 1152.
[5] J. D. Genders, D. Hartsough and D. T. Hobbs, *J. Appl. Electrochem.* **26** (1996) 1.
[6] J. O'M. Bockris and J. Kim, *ibid.* **27** (1997) 623.
[7] H. Li, J. Q. Chambers and D. T. Hobbs, *ibid.* **18** (1988) 454.
[8] D. T. Hobbs and M. Ebra, *AIChE Symp. Series No. 254* **83** (1987) 149.
[9] D. Sazou and G. Kokkinidis, *J. Electroanal. Chem.* **271** (1989) 221.
[10] M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions', 2nd edn, NACE, Houston, TX (1974), p. 261.
[11] G. Lindenbergh and D. Simonsson, *Electrochim. Acta* **36** (1991) 1985.
[12] A. Cornell, G. Lindbergh and D. Simonsson, *ibid.* **37** (1992) 1973.
[13] G. Lindbergh and D. Simonsson, *J. Electrochem. Soc.* **137** (1990) 3094.