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Electrochemical treatment of low-level nuclear wastes

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Electrochemical reductions of Hg(II), $[RuNO(NO_2)_4OH]^{2-}$, CrO_4^{2-}, and NO_3^- in 1.33 NaOH solution were studied at packed bed electrodes with a view to application of the electrochemical technique to treat nuclear waste solution. The reductions of Hg(II), $[RuNO(NO_2)_4OH]^{2-}$, and CrO_4^{2-} were mass-transfer controlled while nitrate reduction was activation controlled. Based on the data obtained, scale-up for each reduction is proposed and discussed. The experimental data obtained have been used in the design of a plant and detailed calculations have been made. An economic analysis has been made to point out the advantages of the electrochemical treatment.

1. Introduction

Nuclear wastes arise both from the peaceful uses of atomic energy and from the manufacture of nuclear weapons [1]. Such wastes can be conceptually regarded in two divisions: (i) high level nuclear wastes which consist largely of radioactive mixtures of fission products and end up as precipitates to be put into glassified bricks, and (ii) low level wastes which have large volume but low radioactivity.

Water soluble radioactive active species, such as cesium and strontium, are dealt with by means of ion exchange resins. There remains over from this so-called low level waste about 100 million gallons at the Savannah River Plants [2] which contains hydroxide, nitrate, nitrite, aluminate, sulfate, carbonate ions, etc. The main components, nitrate and nitrite, have to be transformed to gaseous nitrogen or ammonia to prevent nitrate and nitrite from entering ground water (underground streams, lakes, rivers, eventually the sea) because of the potential effect on plant life. The liquid waste also contains ruthenium ($\sim 40\,\mu$M), mercury ($\sim 2\,\mu$M), chromate (~ 3 mM). Ruthenium is regarded as a valuable material; mercury and chromate are environmentally hazardous. All these metals must be removed from the wastes.

It is clear that electrochemical treatments, with their ability to utilize the potential of an electrode as an extra variable to aid separation, offer a viable possibility for the treatment of these wastes. Denitrification of the nuclear waste by an electrochemical treatment has been addressed [3–5]. Three-dimensional electrodes, packed bed and fluidized bed electrodes, are attractive for industrial applications since they provide an extensive interfacial surface area and involve forced convection by means of flow through the electrodes. Packed bed electrodes have been used in many industrial applications [6–10] and the current and potential distributions in packed bed electrode have been analysed [11–16].

On the basis of the electrochemical behaviour at planar electrodes recently reported [17], the electrochemical reduction of a low level nuclear waste solution was studied at packed bed electrodes. Separation of metal species (eg., Hg, Ru, and Cr(III)) from the waste and nitrate reduction to gaseous products were major concern of this manuscript in respect to economic consideration.

2. Experimental details

A schematic of the electrochemical cell for the packed-bed electrode is shown in Fig. 1. On a fritted glass disc (ASTM 145–175 μ) was placed a current collector (Ni gauze, Electrosynthesis Co.) on which the electrode particles of the packed bed rested. The cathode compartment was connected through a Nafion® 117 film to the anodic compartment which has a counter electrode (Pt gauze). The electrolyte in the anodic compartment was stagnant while the electrolyte in the cathodic compartment was made to flow through the bed electrodes. The reference electrode used was the saturated calomel electrode (Fisher Scientific Co., +0.24 V in the normal hydrogen scale).

The bed material was Ni (99.9%) particles (Johnson–Matthey Co.) which was grouped into five particle size ranges (50–75 μm, 75–150 μm, 125–250 μm, 250–370 μm and 430–590 μm radius) by means of appropriate sieves (Gilson Inc.). Before each experiment, the Ni particles were washed with 30% HNO_3 and rinsed with distilled water thoroughly, then packed into the cell. Pb shot (99%, 1.3×10^{-3} m from the Alfa Chemical Co.) and Fe powder (99%, 40–70 mesh from the Alfa Chemical Co.) were used occasionally as alternative electrode materials. These particles were immersed in 30% HNO_3 for 10 s and washed with distilled water thoroughly, then packed into the cell. The apparent cross-sectional area of the bed electrode was 1.3×10^{-3} m^2. The length of the bed in the cell was 0.02 m.

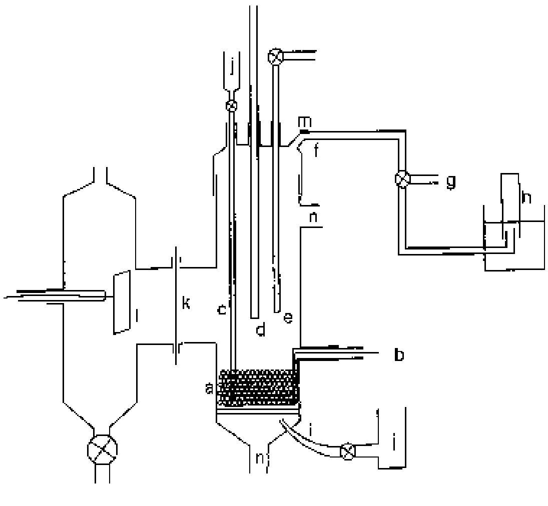

Fig. 1. Schematic for the laboratory scale packed bed electrode. Key: (a) bed of particles, (b) current collector, (c) Luggin capillary, (d) thermometer, (e) purging gas in, (f) gas out, (g) bubbler, (h) gas collector, (i) Luggin capillary, (j) reference electrode, (k) Nafion® film, (l) counter electrode, (m) septum for gas analysis and (n) solution flow-in or flow-out.

The electrolyte in the cathodic compartment was circulated by means of a pump (March Manufacturing Inc.). The flow rate was controlled by adjusting the inlet of the pump and was measured with a flow meter (Cole–Parmer Co.) the upper limit of which was $10^{-5}\,m^3\,s^{-1}$. The electrolytic solution in the electrochemical cell was purged for 1 h with Ar (99.998%) before every run to remove oxygen.

The chemicals for preparing the electrolytic solutions were $Hg(NO_3)_2.H_2O$ (Fisher Inc., GR grade), K_2CrO_4 (Fisher Inc., GR grade), NaOH (EM Inc., GR grade), $NaNO_3$ (EM Inc., GR grade), and $NaNO_2$ (Spectrum Chemical Co, ACS reagent). Water purified by means of a Millipore Q system was used to make the electrolytic solutions. Among the nitrosyl ruthenium compounds, $[Ru(NO)(NO_2)_x\,(OH)_y\,(H_2O)_z]^{q+}$, where $x+y+z=5$ and $q=3-x-y$, is known to be present in the nuclear waste solution [2], and sodium tetranitronitrosyl ruthenate(II), $Na_2[RuNO(NO_2)_4OH].2H_2O$, was prepared by the procedure suggested by Fletcher *et al.* [18].

The temperature of the system undergoing electrolysis was controlled between 15 °C to 76 °C with an ice–water bath or a glass tubing wrapped around with a resistance heater through which the electrolytic solution was passed. The temperature was measured by means of a thermometer or a chromel–alumel thermocouple.

An AMEL potentiostat (model 550) was used to control the potential of the collector in the bed electrodes and current was obtained by means of an AMEL interface (model 560). The currents were recorded by means of a Hewlett-Packard 7044B *X-Y* recorder or a Phillips 8271 *X-Y-t* recorder.

Quantitative analysis by u.v./vis. spectroscopy was carried out to determine the concentrations of nitrate, nitrite, and chromate in the electrolysis at the packed bed electrode. The characteristic wavelengths for nitrate, nitrite and chromate are 300, 353 and 372 nm, respectively. The molar absorptivities for nitrate, nitrite, and chromate at the wavelengths were estimated in 1.33 M NaOH solution (Table 1).

Table 1. Molar absorptivity ($M^{-1}\,cm^{-1}$)

Wavelength /nm	*Nitrate* (NO_3^-)	*Nitrite* (NO_2^-)	*Chromate* (CrO_4^{2-})
300	7	9	660
353	0	23	3630
372	0	13.8	5038

Since the gaseous products of the electrolysis of nitrate and nitrite contains ammonia and nitrogen, GC analysis was carried out. For the analysis of ammonia in the electrolysed solution, 10 μL of the solution was injected into a Porapak N column (Alltech Co.) which was installed in Varian 3400 gas chromatograph. For the analysis of nitrogen gas, 400 μL of gaseous sample was injected into a 13X molecular sieve column (Alltech Co.), which was also installed in a Varian 3400 gas chromatograph. A stainless steel tube inserted between injector and column was frequently washed with distilled water to remove salts originated from injecting of the electrolyte.

Since there were traces of gaseous products such as nitric oxide and nitrogen dioxide which could not be detected with a GC, a Matheson–Kitagawa gas detector system was employed to analyse these gases. The amounts of the gases were determined by the chemical reactions of chromophoric groups with the gases inside a tube through which 100 mL of the gas sample passed. The nitrogen oxides length-of-stain detector tubes were supplied from Matheson Co.

3. Results

3.1. *Reduction of Hg*(*II*)

Figure 2 (full line) shows a typical *I*/*V* curve for the reduction of a solution (300 mL) containing 0.4 mM $Hg(NO_3)_2$, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH at a Ni (particle radius: 110 μm) packed bed electrode by potential sweep technique. The solution was circulated through the packed bed electrode with a flow rate of $3.3\times10^{-6}m^3\,s^{-1}$. By subtracting the current in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH (dashed line) a plateau is found at –0.1 V vs NHE.

3.2. *Reduction of the Ru-nitrosyl complex*

The current–time response in a solution (300 mL) containing 0.4 mM $Na_2[RuNO(NO_2)_4OH]$, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH at a Ni (particle radius: 110 μm) packed bed electrode was obtained at a constant potential (–0.6 V vs NHE at the collector). The solution was circulated through the packed bed electrode with different flow rates. The dependence of the current–time relation on flow rate is shown in Fig. 3.

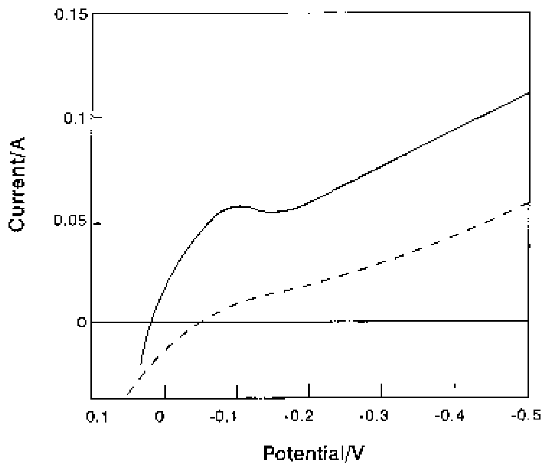

Fig. 2. I/V curve for the reduction of a solution (300 mL) containing 0.4 mM $Hg(NO_3)_2$, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) by potential sweep technique (2 mV s^{-1}). Flow rate: 3.3×10^{-6} m^3 s^{-1}.

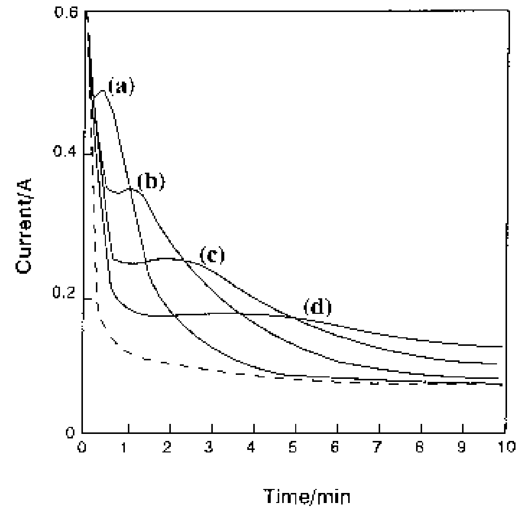

Fig. 3. I/t curves for the reduction of a solution (300 mL) containing 0.4 mM $Na_2[RuNO(NO_2)_4OH]2H_2O$, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) by potential step technique (open to -0.6 V vs NHE). Flow rate: (a) 6.6×10^{-6}, (b) 3.3×10^{-6}, (c) 1.7×10^{-6} or (d) 8.5×10^{-7} m^3 s^{-1}. Dotted line represents a background current obtained in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH.

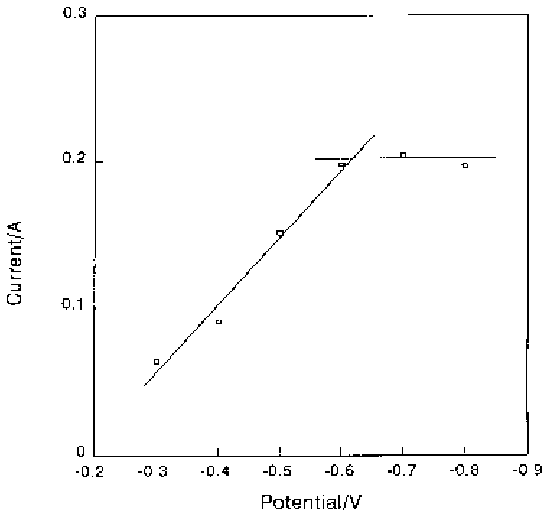

Fig. 4. I/E curve for the electrochemical reduction of the Ru-nitrosyl complex (0.4 mM) in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH was obtained at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) by a potentiostatic technique. Flow rate of 3.3×10^{-6} m^3 s^{-1}.

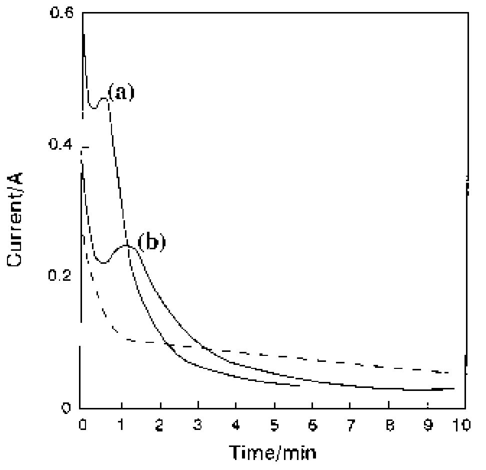

Fig. 5. I/t curves for the reduction of a solution (300 mL) containing 0.3 mM K_2CrO_4, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) by a potential step technique (open to –0.6 V vs NHE). Flow rate = (a) 3.3×10^{-6} or (b) 1.7×10^{-6} m^3 s^{-1}. Dotted line represents a background current obtained in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH.

The current–potential response for the reduction of the Ru-nitrosyl complex in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH was obtained at various potentials at a Ni (particle radius: 110 μm) packed bed electrode (Fig. 4) with a constant flow rate. The mass transfer limiting current was around 0.2 A at a potential more cathodic than –0.6 V vs NHE.

3.3. *Chromate reduction*

The current–time response at a constant potential of –0.6 V vs NHE in a solution (300 mL) containing 0.3 mM K_2CrO_4, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH at a Ni (particle radius: 110 μm) packed bed electrode with two different flow rates (see Fig. 5). The current–potential response in the reduction at a constant flow rate of 3.3×10^{-6} m^3 s^{-1} of the chromate in a solution containing 0.3 mM K_2CrO_4, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH was examined at a Ni (particle radius: 110 μm) packed bed electrode over a potential range of –0.3 to –0.8 V vs NHE (Fig. 6). The mass transfer limiting current was found to be about 0.4 A at a potential more cathodic than –0.6 V vs NHE.

With a packed bed electrode of fixed length, 0.5 L of a solution containing 0.1 M $NaNO_3$ and 1.33 M NaOH with three different chromate concentrations was electrolysed at –0.7 V vs NHE (Fig. 7). When the initial concentration is less than 0.3 mM, the chromate in the solution can be removed (as the hydroxide [17]) to an extent of greater than 99%.

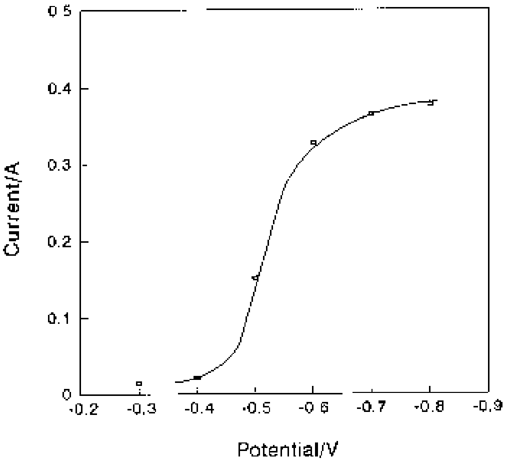

Fig. 6. I/E curve for the electrochemical reduction of the chromate (0.3 mM) in a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH was obtained at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) by a potentiostatic technique. Flow rate of 3.3×10^{-6} m^3 s^{-1}.

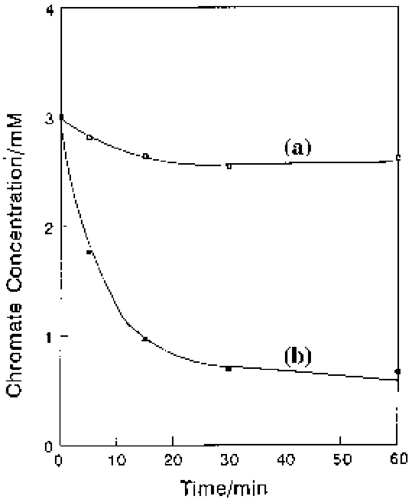

Fig. 8. Reduction of the chromate concentration in 0.25 L of a synthetic nuclear waste solution containing 2 μM $Hg(NO_3)_2$, 40 μM $Na_2[RuNO(NO_2)_4OH]$, 3 mM K_2CrO_4, 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH) at (a) a Ni and (b) a Pb packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) at –0.7 V vs NHE.

Figure 8 shows the reduction of chromate in a synthetic nuclear waste solution at a Ni (particle radius: 110 μm) packed bed electrode and at a Pb (particle radius: 650 μm) packed bed electrode at −0.7 V vs NHE. The concentration of the chromate (3 mM) dropped only 10% at Ni electrodes in 1 h, but when the Ni was replaced by Pb shot, the concentration dropped to 70% in the same time.

3.4. *Nitrate and nitrite reduction*

The steady current for the reduction of a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH at a Ni (particle radius: 110 μm) packed bed electrode was plotted as a function of potential (Fig. 9). There are two Tafel slopes for the nitrate and nitrite reduction: 120 mV in the potential region from –0.5 to –0.7 V and 340 mV in the region from –0.7 to –1.0 V vs NHE.

Figure 10 shows the variation of the concentrations of nitrate, nitrite, and ammonia at a constant potential (–0.8 V vs NHE) as a function of time for the reduction of a solution containing 0.1 M $NaNO_3$ and 1.33 M NaOH at a Ni (particle radius: 110 μm) packed bed electrode. The concentration of the nitrate diminished exponentially and the concentration of nitrite increased to 0.018 M in 2 h and then decreased.

Table 2 shows the results of the electrolysis of a solution (1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH) at various applied potentials at various packed bed electrodes. Ammonia is the major product at all packed bed electrodes and rises at 65% at an Fe packed bed electrode. The yield per cent for the nitrogen is near to 10% at the Pb or Fe packed bed electrode.

Table 3 shows the results of the electrolysis of a solution (1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH) at various temperatures at a Pb (particle radius: 650 μm) packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.01 m). As the temperature increases, both the fraction of nitrate consumed and the ammonia production increase substantially.

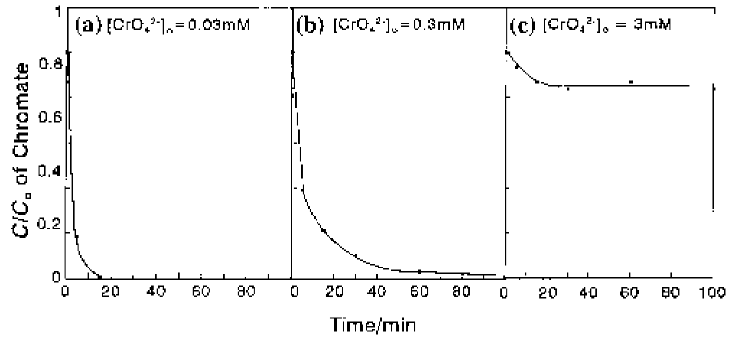

Fig. 7. Reduction of the chromate concentration in 0.5 L of a solution containing 0.1 M $NaNO_3$ and 1.33 M NaOH with the initial chromate concentration of (a) 0.03, (b) 0.3 or (c) 0.3 mM K_2CrO_4 at a Ni packed bed electrode (cross-sectional area: 1.3×10^{-3} m^2, bed length: 0.02 m) at –0.7 V vs NHE.

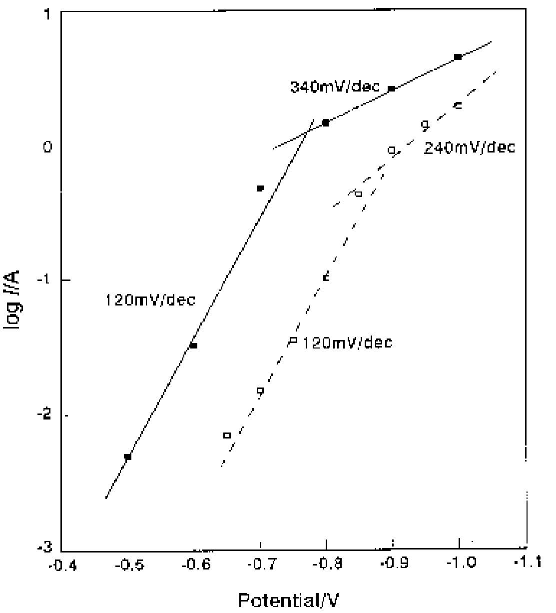

Fig. 9. I/E curves for the reduction of (solid line) a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH and of (broken line) a solution containing 1.33 M NaOH only at a Ni packed bed electrode (cross-sectional area: $1.3 \times 10^{-3}\,m^2$, bed length: 0.02 m).

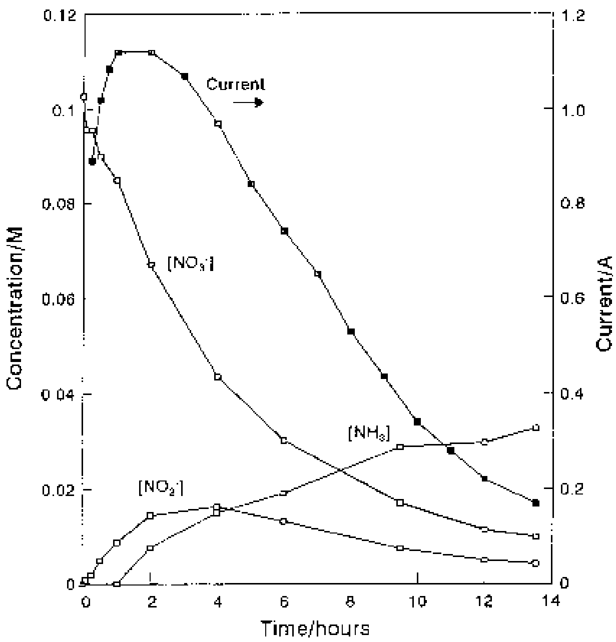

Fig. 10. Variation of the concentrations of nitrate nitrite, ammonia, and the current as a function of time in the reduction of a solution containing 0.1 M $NaNO_3$ and 1.33 M NaOH at a Ni packed bed electrode (cross-sectional area: $1.3 \times 10^{-3}\,m^2$, bed length: 0.02 m) at –0.7 V vs NHE.

4. Discussion

4.1. *Reduction of Hg*(II)

At potentials more negative than –0.1 V vs NHE (see Fig. 2), the deposition of Hg(II) is clearly mass transfer controlled. The current at a packed bed electrode is then represented by [16]

$$I = nFauC_i\left[1 - \exp\left(-\frac{AD\varepsilon L}{\delta u}\right)\right] \qquad (1)$$

where n is the number of electrons in the overall reaction, F is the Faraday constant, a is the cross-sectional area of the packed bed electrode, u is the flow rate of the solution in $cm\,s^{-1}$, C_i is the concentration of an electroactive species at the inlet of the bed, D is the diffusion coefficient of the depositing entity, L is the bed length, δ is the diffusion layer thickness, ε is the voidage of the bed, and A is the specific area per unit volume of the bed which is defined as

$$A = \frac{3(1-\varepsilon)}{r} \qquad (2)$$

where r is the particle radius. With $r = 1.1 \times 10^{-4}$ m (110 μm) and $\varepsilon = 0.4$ (the voidage of randomly packed bed [19]), A is $1.6 \times 10^4\,m^{-1}$.

Table 2. Potentiostatic electrolysis of the synthetic waste (1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH) at packed bed electrodes

Material	*Particle radius* /cm	E_{appl} /V vs NHE	*Solution volume* /L	*Time* /h	$\Delta C(NO_3^-)$ /M	$\Delta C(NO_2^-)$ /M	NH_3 /%	N_2 /%	*NO* /%	NO_2 /%
Ni	0.0113	−0.6	0.5	24	−0.46	+0.18	32	–	–	–
Ni	0.0113	−0.7	0.5	21	−0.88	+0.23	33	–	–	–
Ni	0.0113	−0.8	0.5	19	−0.85	+0.19	35	–	–	–
Ni	0.0113	−0.9	0.3	18	−1.13	+0.04	57	–	–	–
Ni	0.0113	−1.0	0.3	12	−0.89	−0.16	56	–	–	–
Pb	0.065	−1.1	0.3	16	−0.56	+0.18	18	9	0.02	0.003
Pb	0.065	−1.2	0.3	7	−0.77	+0.16	18	8	0.48	0.15
Pb	0.065	−1.3	0.25	4.5	−0.72	+0.28	20	8	0.005	trace
Fe	0.016	−1.0	0.3	24	−0.35	−0.27	61	6	0.04	0.004
Fe	0.016	−1.1	0.3	24	−0.70	−0.32	57	7	0.032	trace
Fe	0.016	−1.2	0.3	24	−0.89	−0.38	65	11	0.012	trace
Ni	0.0063	−0.9	0.25	12	−0.62	−0.21	55	1	0.044	0.01
Ni	0.0113	−0.9	0.25	12	−0.68	−0.16	54	1	0.3	0.036
Ni	0.017	−0.9	0.25	12	−0.68	−0.19	55	2	2	0.28
Ni	0.036	−0.9	0.25	12	−0.46	−0.25	62	1	0.05	0.005
Ni	0.05	−0.9	0.25	12	−0.36	−0.14	58	3	0.016	trace

Cross-sectional area of the bed: 12.6 cm^2; bed length: 2 cm; flow rate: 200 $cm^3\,min^{-1}$

Table 3. Potentiostatic electrolysis of the synthetic waste (1.95 M *$NaNO_3$, 0.66* M *$NaNO_2$, and 1.33* M *NaOH) at Pb (particle radius 0.065 cm) packed bed electrodes at −1.2 V vs NHE for 6 h*

Temperature /°C	$\Delta C(NO_3^-)$ /M	$\Delta C(NO_2^-)$ /M	NH_3 /%	N_2 /%	$10^5 k_1$ /s^{-1}	$10^5 k_2$ /s^{-1}
15	−0.23	+0.11	15	5	14	18
39	−0.33	+0.16	19	4	18	24
46	−0.35	+0.13	20	6	20	28
61	−0.39	+0.13	27	4	22	34
76	−0.56	+0.08	31	2	32	56

Cross-sectional area of the bed: 12.6 cm^2; bed length: 1 cm; flow rate: 200 $cm^3 min^{-1}$; volume of solution: 0.25 L

The diffusion layer thickness in a packed bed has been empirically formulated as [20]

$$\delta = 2r\left[2 + 1.1\left(\frac{\mu}{\rho D}\right)^{1/3}\left(\frac{2u\rho r}{\mu}\right)^{0.6}\right]^{-1} \qquad (3)$$

where r is the particle radius, μ is the viscosity of the solution and ρ is its density. From the handbook [21] the viscosity and the density of the solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$ and 1.33 M NaOH were given as $1.5 \times 10^{-3}\,kg\,m^{-1}\,s^{-1}$ and $1.2 \times 10^3\,kg\,m^{-3}$, respectively. The diffusion coefficient of Hg(II) was calculated by the Wilke–Chang estimation method [22] and found to be $1.7 \times 10^{-9}\,m^2\,s^{-1}$. With $r = 1.1 \times 10^{-4}$ m (110 μm) and $u = 3.3 \times 10^{-6}\,m^3\,s^{-1} = 2.5 \times 10^{-3}\,m\,s^{-1}$, the diffusion layer thickness, calculated using Equation 3, was 2.5×10^{-5} m.

There are two types of reactors in industrial electrochemical processes: the batch reactor and the continuous reactor [23]. When the concentration of an electroactive species is low enough so that the electroactive species can be removed by one pass through the electrochemical cell, the continuous reactor is preferred. For the continuous reactor case, the output concentration is given by [13]

$$C_o = C_i \exp\left(-\frac{AD\varepsilon L}{\delta u}\right) \qquad (4)$$

where the symbols used are the same as those in Equation 1. For the output concentration to be one hundredth of the input concentration, the term $AD\varepsilon L/\delta u$ has to be larger than 4.6. With $r = 1.1 \times 10^{-4}$ m (110 μm), $\varepsilon = 0.4$, $u = 2.5 \times 10^{-3}\,m\,s^{-1}$, $D = 1.7 \times 10^{-9}\,m^2 s^{-1}$, $\delta = 2.8 \times 10^{-5}$ m, the bed length has to be longer than 3×10^{-2} m (3 cm).

The amount of the nuclear waste solution requiring treatment at the Savannah River Plant site is about 4×10^8 L [24]. Suppose the nuclear waste solution be treated in 20 years, the amount of solution to be treated per year is about 2×10^7 L and the flow rate is $6.3 \times 10^{-4}\,m^3\,s^{-1}$. The cross-sectional area of a packed bed electrode is determined by the flow rate. If the flow rate of $2.5 \times 10^{-3}\,m\,s^{-1}$ is adapted to take advantage of the experimental data, the cross-sectional area has to be 0.25 m^2. The determination of the cross-sectional area and the flow rate for scale-up is arbitrary. In this calculation, the flow rate used in the experiment was assumed for the calculation of scale up.

At a packed bed electrode with a cross-sectional area of 2.5 m^2, a flow rate of $2.5 \times 10^{-3}\,m\,s^{-1}$, and a bed length of 3×10^{-2} m, the current for the reduction of Hg(II) in the nuclear waste solution within the time stated is calculated to be 0.25 A from Equation 1 and the output concentration drops to 0.02 μM (one hundredth of the initial concentration) from Equation 4.

4.2. *Reduction of the Ru–Nitrosyl complex*

When a batch quantity of electrolyte is circulated a few times through a packed bed, the current for a mass transfer controlled reaction at potentials negative to –0.6 V vs NHE (see Fig. 4) is represented by [13]

$$I = nFauC_i\left[1 - \exp\left(-\frac{AD\varepsilon L}{\delta u}\right)\right] \times \exp\left[-\frac{aut}{V}\left(1 - \exp\left(-\frac{AD\varepsilon L}{\delta u}\right)\right)\right] \qquad (5)$$

where V is the volume of the batch of solution circulated, t is the time after the first pass, and other symbols are described above. In Fig. 3, subtracted by the background current (i.e., current for a solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH, dotted line in the figure), the current corresponding to the reduction of the ruthenium nytrosyl complex decreases exponentially, which is well represented in Equation 5. The initial spikes were due to the double layer charging and the peaks after the spikes seem due to the increase of electrode surface in the packed bed by the deposition of Ru. For the reduction of the ruthenium nitrosyl complex, the diffusion coefficient is $0.5 \times 10^{-9}\,m^2\,s^{-1}$ [17]. With $r = 1.1 \times 10^{-4}$ m (110 μm), $u = 2.5 \times 10^{-3}\,m\,s^{-1}$ and $a = 1.3 \times 10^{-3}\,m^2$, the diffusion layer thickness, calculated from Equation 3, is 1.9×10^{-5} m. Then, the current at $t = 0$ is calculated to be 0.19 A from Equation 5 and is in a good agreement with the experimental value of Fig. 3(b). The reduction of the ruthenium complex in the waste becomes mass transfer controlled at –0.6 V vs NHE (Fig. 4). Thus, similar calculations to Hg(II) reduction case are used for the reduction of the ruthenium complex. Since the ruthenium complex concentration in the waste is initially 0.04 mM [2], the current at a packed bed electrode ($a = 0.25\,m^2$, this value was decided assuming that the continuous reactor is employed for the reduction of the ruthenium complex) is calculated to be 5 A from Equation 1 and the bed length has to be longer than 7.2×10^{-2} m (7.2 cm) from Equation 4 for the output concentration to be 1% of the input concentration. The IR drop through the solution phase in the packed bed electrode is then calculated from the relation:

$$IR = I\frac{L}{\sigma_s a} \qquad (6)$$

where σ_s is the conductivity of the solution phase and is about $10\,\Omega^{-1}\,m^{-1}$ [21]. With $I = 5\,A$, $a = 0.25\,m^2$, and $L = 7.2 \times 10^{-2}\,m$, the *IR* drop is calculated to be 0.14 V. When the applied potential at the bottom of the bed is –0.6 V vs NHE, the effective applied potential at the top of the bed will be –0.75 V vs NHE when the *IR* drop through the electrode is negligible. The effective applied potential at the top of the bed is also in the mass transfer controlled region (Fig. 4) so that the fundamental assumption that the Ru-nitrosyl complex reaction as being mass transfer controlled is valid.

For practical application, the clogging of packed bed electrodes have to be taken into account because the amount of Ru deposited is large enough to fill up the voids in the packed bed electrode during a 20 year operation. At every six months, the average thickness of the Ru deposited on the electrode particles would become $\sim 40\,\mu m$. Thus, replacement of packed bed electrode at every 6 months is recommended.

4.3. *Chromate reduction*

At a potential negative to –0.6 V vs NHE (see Fig. 6), a flow rate of $3.3 \times 10^{-6}\,m^3\,s^{-1}$ (or $2.5 \times 10^{-3}\,m\,s^{-1}$) and a cross-sectional area of $1.3 \times 10^{-3}\,m^2$, the current, calculated from Equation 1, is 0.289 A when the chromate reduction is mass-transfer controlled. This is in good agreement with the experimental value (Fig. 5(a) or Fig. 6). However, the chromate reduction at a Ni electrode produces chromic hydroxide which (because of its high resistivity) inhibits further chromate reduction as well as other reductions [17]. As seen in Fig. 7, 0.5 L of 0.3 mM chromate was enough to cover the entire surface of the packed bed electrode in 1 h. It is impractical, therefore, to use a nickel packed bed electrode because the chromate concentration in the nuclear waste is 3 mM.

At a Pb packed bed electrode, on the other hand, chromate reduction was found not to produce chromic hydroxide but CrO_2^- because such an inhibition was not observed when a Pb packed bed electrode was used. There are two reduction pathways for the chromate reduction [25]:

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3 + 5OH^-$$

and

$$CrO_4^{2-} + 2H_2O + 3e^- \rightleftharpoons CrO_2^- + 4OH^-$$

CrO_2^- is soluble and does not deposit on the electrode surface. Thus, CrO_2^- is considered to be the reduction product at Pb. Pb should be used as the electrode material for chromate reduction. Also, since the hydrogen evolution overpotential is higher at a Pb than at a Ni, the potential can be shifted in the cathodic direction until the chromate reduction becomes entirely mass-transfer controlled. If this reasoning is right, the chromate concentration in the electrolysis at a Pb packed bed electrode (Fig. 8) has to be dropped to 0. This discrepancy is elucidated in terms of that the chromate reduction was not 100% because there were co-depositions of Hg and Ru, which changed the electrocatalytic effect of the Pb surface. In Fig. 8, however, the difference of the electrocatalytic effect on the chromate reduction at between Ni and Pb has to be stressed.

Some approximate idea for the potential at which the chromate reduction would become diffusion controlled could arise from experiments which would have to be carried out on the reduction of chromate at Pb at lower current densities outside the diffusion controlled limit. If the i_o for the reduction of chromate at Pb is known, then one may obtain the overpotential for the condition at which the limiting current becomes rate determining from the equation

$$i = \frac{i_{\text{lim}} i_o \exp\,(-\alpha F\eta/RT)}{i_{\text{lim}} + i_o \exp\,(-\alpha F\eta/RT)} \tag{7}$$

where i_o is the exchange current density, α is the transfer coefficient, F is the Faraday constant, η is the overpotential, and i_{lim} is the limiting current. It seems likely by analogy to other reactions of this kind to be in the range of $10^{-5} - 10^{-3}\,A\,m^{-2}$ and applying this range of i_o values* to Equation 7, using the value of $1.8\,A\,m^{-2}$ for i_{lim}, one calculates an overpotential for the beginning of diffusion control –0.75 V and –0.51 V. With the equilibrium potential for chromate reduction as –0.24 V vs NHE, the reduction is diffusion controlled at –0.9 V vs NHE.

Since the chromate concentration is 3 mM in the nuclear waste of the Savannah River Plant, when a Pb ($r = 10^{-4}$ m) packed bed ($a = 0.25\,m^2$) electrode is employed as a continuous reactor, the current is calculated from Equation 1 to be 580 A with an applied potential of –0.9 V vs NHE at which the reduction is assumed to be mass transfer controlled. For the output concentration to be 1% of the input concentration, from Equation 4, the bed length has to be longer than 3.8×10^{-2}m with $r = 10^{-4}$ m, $\varepsilon = 0.4$, $u = 2.5 \times 10^{-3}\,m\,s^{-1}$, $D = 1.1 \times 10^{-9}\,m^2\,s^{-1}$[26], $\delta = 2.2 \times 10^{-5}$ m. The *IR* drop through the solution phase† in the packed bed is then 8.74 V and the electricity loss by the *IR* drop is 5 kW.

To reduce the electricity loss or the *IR* drop, the bed length can be reduced to be 8.1×10^{-3} m which is the so called 'characteristic length', defined as $\delta u/AD\varepsilon$. The current is then 360 A, the *IR* drop is 1.2 V, and the electricity loss is 0.4 kW. However, the output concentration is calculated to be 1.1 mM from Equation 4. As shown in Fig. 11 (this is a schematic not showing whole configuration of the reactor), another packed bed electrode could be connected in series to have a current of 130 A, an *IR* drop of

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[*] The value of i_o for the reduction of chromate on Pb could not be obtained experimentally because Pb itself dissolves at potentials near to the equilibrium potentials for the chromate reduction. The analogous reaction used was the reduction of chromate at a Ni electrode.

[†] In the calculation of the *IR* drop, that in the packed bed was focused because the drop between the packed bed and the counterelectrode can be made negligible in any configuration of cell.

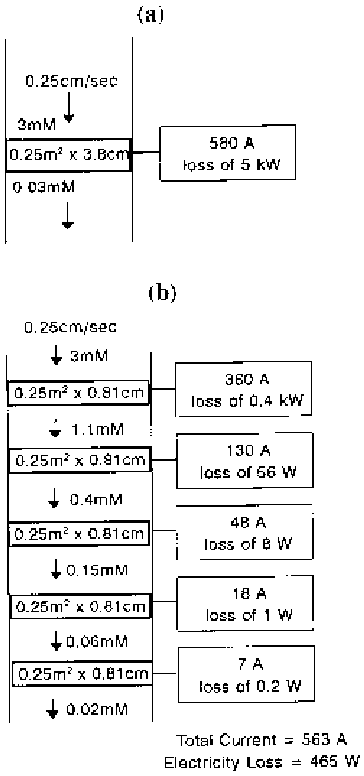

Fig. 11. Comparison of two options for the chromate reduction. Electrodes: (a) one packed bed and (b) serial connection of five packed bed.

0.43 V, an electricity loss of 56 W, and an output concentration of 0.4 mM. The results of further calculations for an expanded system of five packed bed electrodes in series are given in Fig. 11. In this setup, the total electricity loss is 0.47 kW, much less than the electricity loss by one long packed bed electrode (5 kW). A serial connection of shorter packed bed electrodes is more effective than a longer packed bed electrode as far as the electricity loss is concerned.

4.4. *Nitrate and nitrite reduction*

4.4.1. Packed bed electrode. From Fig. 9, the nitrate and nitrite reduction is not mass-transfer controlled when the applied potential is as cathodic as –1.0 V vs NHE at a Ni packed bed electrode. The exchange current density for the reduction of the solution containing 1.95 M $NaNO_3$, 0.66 M $NaNO_2$, and 1.33 M NaOH at Ni was found to be $5.2 \times 10^{-3}\,\mathrm{A\,m^{-2}}$ [17] with ammonia being the principal reduction product. The transfer coefficient was measured to be 0.33. The reactions of nitrate reduction are:

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$$

$$NO_2^- + 5H_2O + 6e^- \longrightarrow NH_3 + 7OH^-$$

$$2NO_2^- + 4H_2O + 6e^- \longrightarrow N_2 + 8OH^-$$

Nitrite is an intermediate of the nitrate reduction and is further reduced to ammonia or nitrogen. The nitrite reduction mechanism is not clearly understood in alkaline solutions [17]. Combination of a nitrogen containing intermediate will produce nitrogen whilst a further reduction of the intermediate produces ammonia [27]. The yield for ammonia or nitrogen is dependent on the electrocatalytic effect of the electrode material (see Table 2). The analysis of the nitrogen containing products did not give 100% balance because all probable products (for example, hydroxyl amine or nitrous oxide) were not analysed. It was not possible to decide the exact reaction mechanism, thus, the phenomenological data such as potential and current were used to calculate the scale up process as follows. The overpotential was determined based on an assumption that the ammonia is the main product.

The current at a packed bed electrode is calculated as

$$I = aA \int_{x=0}^{x=L} i_x \mathrm{d}x \tag{8}$$

where a is the cross-sectional area of the packed bed electrode, A is the specific area per unit volume (Equation 2), L is the length of the packed bed electrode, and i_x is the current density at a position x in the packed bed electrode and is represented (cf. Equation 7) as

$$i_x = \frac{i_{\lim,x} i_o \exp\left(-\alpha F \eta_x / RT\right)}{i_{\lim,x} + i_o \exp\left(-\alpha F \eta_x / RT\right)} \tag{9}$$

where $i_{\lim,x}$ and η_x are the limiting current density and the overpotential at a position x, respectively. The overpotential at a position x above the current collector is represented as [11, 28]

$$\frac{\mathrm{d}^2 \eta_x}{\mathrm{d}x^2} = -A\left(\frac{1}{\sigma_s} + \frac{1}{\sigma_m}\right) \frac{i_{\lim,x} i_o \exp\left(-\alpha F \eta_x / RT\right)}{i_{\lim,x} + i_o \exp\left(-\alpha F \eta_x / RT\right)} \tag{10}$$

where σ_s and σ_m are the specific conductivities through the solution phase and through the metallic phase in the packed bed electrode, respectively. Since the concentration varies through the packed bed electrode, the limiting current density at a position x is expressed as

$$i_{\lim,x} = \frac{nFDC_x}{\delta_{PBE}} = \frac{nFD}{\delta_{PBE}}\left[C_{x=L} - \frac{A}{nFu} \int_{x=x}^{x=L} i_x \mathrm{d}x\right] \tag{11}$$

where the last term represents the decrease of the concentration of an electroactive entity by the faradaic reaction from the top of the bed $(x = L)$ to the position x. From Equations 8–11, the current at a packed bed electrode can be calculated with $a = 0.25\,\mathrm{m}^2$, $L = 10^{-2}\,\mathrm{m}$, $r = 10^{-4}\,\mathrm{m}$, $u = 2.5 \times 10^{-3}\,\mathrm{m\,s^{-1}}$, $\sigma_s = 10\,\Omega^{-1}\,\mathrm{m}^{-1}$ as a function of the applied potential at the collector (Fig. 12). In the calculation, the average conductivity for the metal phase, σ_m, was taken as $1.3\,\Omega^{-1}\,\mathrm{m}^{-1}$, based on the particle-particle contact resistance [29] which is a function of the weight of the particles. In Fig. 12, the

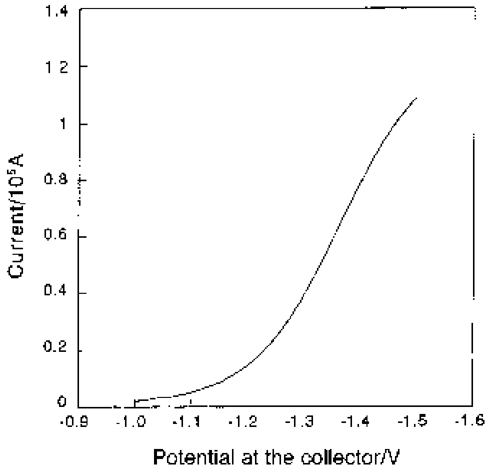

Fig. 12. Current at a packed bed electrode ($a = 10\,\mathrm{m}^2$, $L = 0.01\,\mathrm{m}$, $r = 10^{-4}\,\mathrm{m}$, $u = 2.7 \times 10^{-3}\,\mathrm{m\,s}^{-1}$) for the nitrate and nitrite reduction as a function of the applied potential at the bottom of the packed bed electrode. $\sigma_s = 10\,\Omega^{-1}\,\mathrm{m}^{-1}$ and $\sigma_m = 1.3\,\Omega^{-1}\,\mathrm{m}^{-1}$.

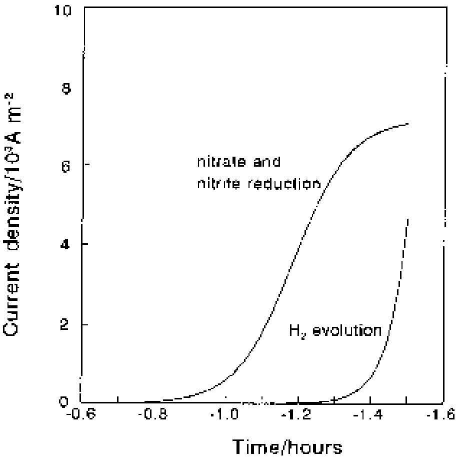

Fig. 13. i/E for the reduction of nitrate and nitrite at a planar Ni electrode.

current at a potential of –1.3 V vs NHE is 4×10^4 A. With this very large value, the *IR* drop through the solution phase in the packed bed electrode, calculated from Equation 6, is 160 V and the electricity loss is 6.4×10^3 kW. Thus, it is impractical to use a packed bed electrode with such a high current because of heat generation and excessive electricity cost. Using

$$I^2R = c_p m \Delta T \tag{12}$$

where c_p is the specific heat capacity, m is the mass and ΔT is the temperature elevation. With roughly estimated values for a heat capacity of $4.2 \times 10^{-3}\,\mathrm{J\,kg^{-1}\,K^{-1}}$ (for the solution inside the bed) and a mass of 25 kg of a packed bed electrode (from the dimension of the packed bed), the temperature of the cell is calculated to increase by as much as 61 °C.

4.4.2. Parallel plate electrode. For the alternative reduction of nitrate and nitrite at a planar electrode, the exchange current density of $5.2 \times 10^{-3}\,\mathrm{A\,m^{-2}}$, the transfer coefficient of 0.33, and the equilibrium potential of –0.085 V vs NHE [17] were still available. Thus, the current density for the reduction of nitrate and nitrite at a planar electrode was calculated from Equation 7 as a function of the potential applied (Fig. 13). At –1.3 V vs NHE, the current density for the nitrate and nitrite reduction is $5.8 \times 10^3\,\mathrm{A\,m^{-2}}$ and is much higher than the competing current density for hydrogen evolution.

Electrochemical removal of nitrate and nitrite at a parallel planar electrodes has been recently studied extensively with a distributed parameter model [4] or a boundary-layer model [5]. The simulated data by the models were in a good agreement with the experimental data obtained in this study. Here, designing of the electrochemical cell is discussed using the experimental data obtained previously [17].

The amount of the nuclear waste solution to be treated per day for the overall treatment time of 20 years is 5.5×10^4 L for a total amount of waste of about 4×10^8 L. In the electrochemical process, the anolyte as well as the catholyte is considered to be supplied from the waste. Then, the amount of waste to be electrolysed at the cathode is 2.8×10^4 L and at the anode 2.8×10^4 L. Since the concentration is high enough, a batch reactor is considered. In a batch, the concentration of nitrate (and nitrite) during electrolysis is [13]

$$C_t = C_{t=0} \exp\left(-\frac{Dat}{\delta V}\right) \tag{13}$$

where a is the area of the planar electrode. With $D = 1.9 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ [34], $V = 2.8 \times 10^4$ L and $t = 1$ day (8.6×10^4 s), the geometric area of the electrode must be 200 m^2 for the concentration to be dropped to 10% of the initial concentration (1.95 M $NaNO_3$ and 0.66 M $NaNO_2$).

With the solution flowing through a parallel plate cell, the effect of the flow rate and the distance between two plates have to be examined. For a parallel plate cell, $Re > 2000$, the mass transfer phenomena are described as [12]

$$Sh = 0.023\, Re^{4/5} Sc^{1/3} \tag{14}$$

where Sh is the Sherwood number ($= L/\delta$ where L is the length of the plate, δ is the diffusion layer thickness), Re is the Reynolds number ($= \rho L u/\mu$ where ρ is the density of the solution, L is the length of the plate, u is the flow rate and μ is the viscosity of the solution), and Sc is the Schmidt number ($= \mu/\rho D$ where μ is the viscosity of the solution, ρ is the density of the solution and D is the diffusion coefficient). From Equation 14, the diffusion layer thickness is a function of the length of the electrode plate and the flow rate, and is simplified to

$$\delta = 6.2 \times 10^{-5} \left(\frac{L}{u^4}\right)^{1/5} \tag{15}$$

with the viscosity of the solution (1.5×10^{-3} $\mathrm{kg\,m^{-1}\,s^{-1}}$) and the density of the solution ($1.2 \times 10^3\,\mathrm{kg\,m^{-3}}$). When a plate of 1 m long is used for the reduction of nitrate with a flow rate of $10^{-1}\,\mathrm{m\,s^{-1}}$, the diffusion layer thickness becomes 3.9×10^{-4} m which is near to the stationary solution diffusion layer thickness. Using Equation 13, the required electrode area is calculated as $160\,\mathrm{m^2}$. With the length of the plate of 1 m, the width of the plate has to be 160 m. This can be achieved by employing layered structure as shown in Fig. 14. The overall height is assumed to be 1 m and the length 1 m. The width would be determined by the spacing between the two plates and the number of electrodes in the layered cell of Fig. 14. A number of electrodes equal to 160 give rise to a total area of $160\,\mathrm{m^2}$. The spacing between two plates is engineered to be $0.02\,\mathrm{m^{-1}}$, the overall width of the reactor would be 3.2 m.

The *IR* drop is calculated to be initially $9.2 \times 10^3\,\mathrm{A\,m^{-2}} \times 0.02\,\mathrm{m}/40\,\Omega^{-1}\,\mathrm{m^{-1}} = 4.6\,\mathrm{V}$; the cell potential is initially 7.4 V and then decreases as time passes because the current decreases (Fig. 15). The electricity requirement per day is 8×10^4 kW h.

4.5. *Economic consideration*

The products of the electrochemical treatment considered are Hg, Ru, Cr(III), ammonia, and nitrogen. Among the products, Ru is considered to be a valuable material to recover. The amount of Ru recovered in the electrochemical treatment is about $40\,\mu\mathrm{M} \times 5.5 \times 10^4\,\mathrm{L} \times 101\,\mathrm{g\,mol^{-1}} = 0.22$ kg per day. With the estimated current price of the Ru, \$5 per g, the earned capital will be \$1100 per day if the ruthenium in the waste is not a radioactive nuclide. A radioactive ^{106}Ru decays to ^{106}Rh by β-decay with half-life of 1 year and ^{106}Rh decays to ^{106}Pd with halflife of 30 s. Since the waste has been collected for 30 years, the Ru present in the waste is not considered as a radioactive nuclide.

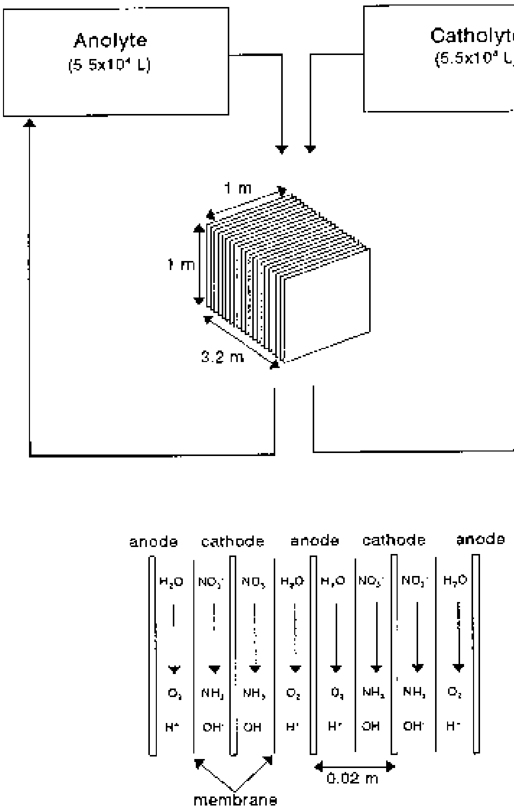

Fig. 14. Designing of a parallel plate flow cell.

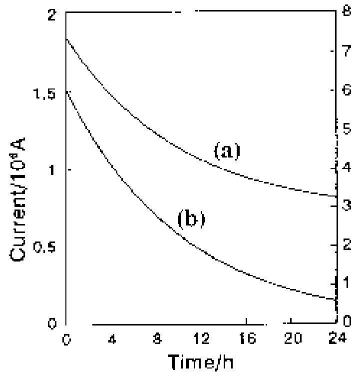

Fig. 15. Cell potential (a) and current (b) at the parallel plate flow cell at –1.3 V vs NHE. Flow rate: $0.1\,\mathrm{m\,s^{-1}}$.

To claim an advantage for the electrochemical treatment of nuclear wastes over other technologies, the operation cost has to be figured out. The electricity needed for one day electrochemical operation is about 8×10^4 kW h and the cost of \$3200 per day with the electricity rate of 4 cents per kW h. Such costs may appear to be too large to be offset by the production of Ru. The cost, however, can be compensated if the cell divided by means of a conducting membrane so that NaOH and HNO_3 could be produced as byproducts. When a nuclear waste solution is electrolysed in a divided cell (i.e., the catholyte is not mixed up with the anolyte during the electrolysis), the catholyte becomes a concentrated NaOH solution:

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$$
$$NO_2^- + 5H_2O + 6e^- \longrightarrow NH_3 + 7OH^-$$
$$2NO_2^- + 4H_2O + 6e^- \longrightarrow N_2 + 8OH^-$$

and the anolyte becomes a concentrated nitric acid:

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$
$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$
$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

In one day's electrolysis of nuclear waste solution, when a cation exchange membrane is employed to separate the anolyte and the catholyte, all sodium nitrate (1.95 M) and sodium nitrite (0.66 M) in the catholyte (1.33 M NaOH) are reduced to ammonia and nitrogen and the concentration of remaining NaOH reaches upto 7.9 M (assuming all sodium cations in anolyte is transferred to catholyte). On the other hand, nitrite is oxidized to nitrate and the concentration of remaining HNO_3 is 2.6 M, which is calculated from the total concentration of nitrogen containing anions (nitrate and nitrite) in the anolyte.

About 2.5×10^4 L of 7.9 M NaOH and 2.5×10^4 L of 2.6 M HNO_3 are produced daily. The nitric acid and sodium hydroxide are needed in the process of dissolution, extraction, and precipitation of the high-level waste. Though they are not pure, the sodium hydroxide and nitric acid can be used in the processes. When the electrochemical reactions of the impurities such as aluminate, sulfate, and carbonate are studied, the purities of NaOH and HNO_3 produced from the nuclear waste can be determined. The amount of NaOH to be recycled per day is 7.8×10^3 kg and the cost recovered is \$7800 at an estimated rate of only \$1 per kg. The amount of nitric acid to be recycled per day is 2.5×10^4 L and the cost is \$2500 at an estimated unit price of \$0.1 per L. Though, the evaluation of the costs for NaOH and HNO_3 are very crude, the electrochemical treatment of nuclear waste may give rise to positive balance (including electricity costs) in the order of $\$10^3$ a day (plus possible cost benefit from the Ru recovery).

5. Conclusion

The electrochemical reduction of Hg(II) from a nuclear waste solution can be treated as a mass-transfer controlled reaction at a packed bed electrode at –0.1 V vs NHE because of its low concentration in the solution.

Ru-nitrosyl complex can be reduced to Ru metal at a Ni packed bed electrode at –0.6 V vs NHE and the reduction is also mass transfer controlled.

A Pb packed bed electrode could be used for the reduction of chromate to avoid the formation of resistant chromic hydroxide films as occurs with Ni. Since the chromate concentration in the waste solution is relatively concentrated, the applied potential must be shifted to –0.9 V vs NHE for the reduction to be mass transfer controlled. A serial connection of shorter packed bed electrodes is better than a long packed bed electrode in respect to the *IR* drop calculation.

The nitrate and nitrite reductions are activation controlled at a potential of –1.2 V vs NHE. When an electrochemical reaction is activation controlled and the current density is high, the use of a packed bed electrode is prohibited because of the *IR* drop. A design has been calculated using a parallel plate cell for the reduction of nitrate and nitrite at –1.3 V vs NHE at which the reaction becomes mass transfer controlled. The process can be made to give rise to byproducts HNO_3 and NaOH. The economics are favourable.

A schematic of a possible plant is in Fig. 16.

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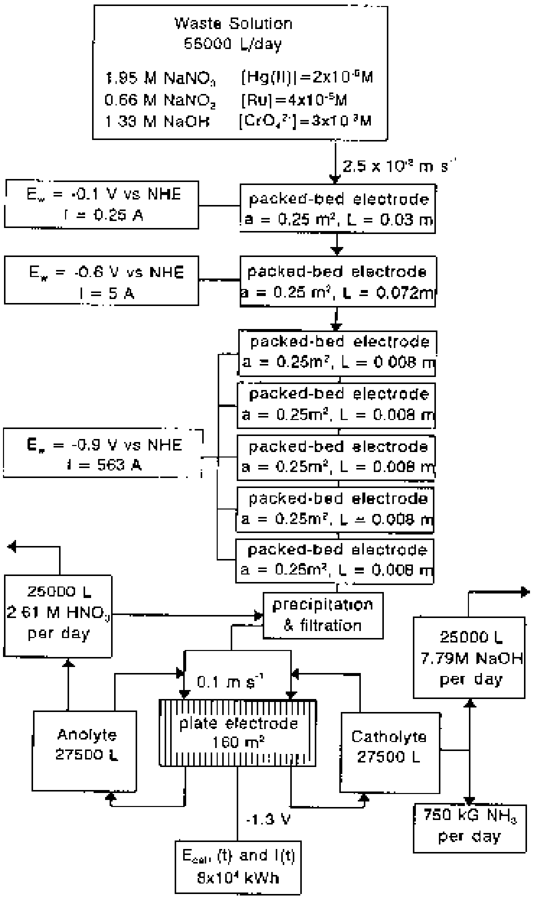

Fig. 16. A schematic of a possible plant for the electrochemical treatment of low-level nuclear waste.

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