Pilot scale deionisation of a galvanic nickel solution using a hybrid ion-exchange/electrodialysis system

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Abstract

A pilot scale ion-exchange/electrodialysis system was tested on-site at a galvanic plant. The system was used to treat a rinse solution containing approximately $5\,g\,m^{-3}$ Ni^{2+}. It operated continuously without the need of maintenance for a period of 3 months and was able to remove nickel to concentrations less than the analysis detection limit of approximately $0.2\,g\,m^{-3}$. This work also describes the effect of solution pH on various aspects of the deionisation process.
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1. Introduction

The purpose of this work was to establish a new process for the removal of heavy metals from dilute galvanic solutions. The recovery of heavy metals from industrial process solutions has garnered a great deal of attention in recent years. This is mainly due to the rise in environmental awareness and the consequent severity of legislation regarding the disposal of toxic substances; for instance, the effluent limits for nickel ions in Germany, Switzerland and the United States are 0.5 (1991), 2 (1991) and 3.98 ppm (2001), respectively [1,2]. Stringent legislation, however, is not the only reason for industry to invest in such processes. The high cost of water due to its "relationship to environmental management" [3] and the potential for additional cost savings by moving towards a "closed" system provide additional incentives and "put added dollars into the metal finishers pockets" [4]. A continuous process for heavy metal recovery increases the viability of a closed process, a process that itself becomes more cost-effective through the recycling and optimal use of raw materials [5,6].

The pilot scale study presented in this paper follows previous work that focused on the removal of nickel ions from dilute solutions using a hybrid system that combines an ion-exchange column with an electrodialysis cell [7–11].

In this way, the properties of ion-exchange materials are combined with the advantages of electrically driven migration processes. The hybrid system is made by incorporating an ion-exchange resin into the diluate compartment (the compartment in which the metal ions are removed from solution) of an electrodialysis type cell. This compartment is located between two ion-selective membranes that essentially divide the cell into three parts. The ion-exchange resin concentrates the metal ions within its matrix and hence increases the conductivity and efficiency of the cell. The application of an electric potential across two electrodes located in the outer compartments promotes the migration of the metal ions towards the negatively charged electrode (the cathode) and into a separate compartment where they are concentrated; this compartment is termed the "cathode" or "concentrate" compartment. The metal ions are replaced by hydrogen ions from the compartment containing the positively charged electrode or anode; this compartment is termed the "anode" compartment.

Two types of experiments were performed, one on-site and the other in the laboratory. The pilot scale cell was tested on-site at a galvanic plant for a period of approximately 3 months. During this time two experiments, involving the treatment of a $5\,g\,m^{-3}$ Ni^{2+} rinse solution, were carried out. These experiments varied in both solution flow rate and the quantity of solution treated.

Experiments were conducted in the laboratory to determine the effect of pH on various aspects of the process.

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Nomenclature

$\bar{c}_i$	concentration of species i (mol m^{-3})[1]
D_i	effective diffusion coefficient of species i (m^2 s^{-1})
ΔE	potential difference (V)
n_i	quantity of ion i (mol)
N_i	flux of species i into cathode compartment (mol m^{-2} s^{-1})
t	time (day)
u_i	effective mobility of species i (m^2 V^{-1} s^{-1})
V_R	volume of process solution (m^3)
$\bar{X}_i$	fraction of ion i in solution (–)
z_i	valence of ion i (–)

Greek letters

α_H^{Ni}	Ni^{2+}/H$^+$ separation factor (–)
η_i	differential current efficiency for ion i (%)
ν	rate at which the centre of gravity of the pore liquid moves (m s^{-1})
υ	flow rate of process solution through the ion-exchange bed (m^3 min^{-1})
φ	electric potential (V)

Subscripts

a	anode compartment
bed	ion-exchange bed
k	cathode compartment
p	process solution

Over bar indicates values within ion-exchange resin.

Since the process involves the exchange of Ni^{2+} from solution with H$^+$ in the resin, the pH of the process solution will decrease as it is treated. The concentration of ions other than nickel in the feed solution, i.e. H$^+$ and Na$^+$, will affect the sorption equilibrium and hence the efficiency of the system. The conductivity of the interstitial solution will also increase with the addition of other ions to the feed, thereby decreasing the fraction of current carried by Ni^{2+}. This results from the availability of three paths for ionic transport, and therefore current:

1. Solely through the ion-exchange bed.
2. Solely through the solution phase.
3. Alternating through the solution and resin phases.

These terms are additive, and both the second and third transport paths are functions of the interstitial solution conductivity [12].

2. Experimental

2.1. Pilot scale experiments

The pilot scale experiments were carried out with a modified ElectroCell AB Multipurpose Cell. This cell consisted of three vertical compartments including an anode, cathode and centre compartment. The outer anode and cathode compartments both had dimensions of $10 \times 10 \times 0.6$ cm^3 and both contained platinised titanium electrodes with areas of 100 cm^2. The centre compartment was built in-house (Technical University Eindhoven) and designed for the purpose of containing the ion-exchange resin; the vertical cross-section of the centre compartment was 100 cm^2 and it had a width of 1 cm. The compartments were separated by two Nafion 117 ion-exchange membranes, also with active areas of 100 cm^2. The cell was connected to three separate liquid circuits (Fig. 1): an anolyte circuit containing 0.03 m^3 1 M H$_2$SO$_4$, a catholyte circuit of 0.03 m^3 1 M HCl and a process solution circuit that was connected to the centre ion-exchange compartment. The electric potential difference over the bed was applied using a Delta Elektronika E030-3 power supply and measured using a Data Precision 2480 Multimeter; a Metrawatt Multiscript 3 recorder was used to record the current.

Two series of experiments were carried out. They differed mainly in the quantity of process solution treated (i.e. 0.3 and 0.6 m^3) and the flow rate at which these solutions were passed through the ion-exchange compartment (i.e. 233 and 1000 cm^3 min^{-1}, respectively). During both experiments the anolyte and catholyte flow rates were 233 cm^3 min^{-1}. Approximately 125 cm^3 Dowex 50WX-2 100 resin in the hydrogen form was placed in the centre compartment of the cell and a cell voltage of 5 V was applied. The experiments were prepared in such a way as to resemble the treatment of the actual rinse tank (located at the galvanic plant where the pilot cell was tested) as closely as possible; the ionic composition of the rinse solution led to the division of each experiment into several parts.

2.1.1. The 0.30 m^3 experiment

2.1.1.1. Part 1. The 0.30 m^3 experiment was conducted first and can be divided into three parts. The first part involved the batch treatment of 0.30 m^3, 5 g m^{-3} Ni^{2+} process solution prepared by diluting 20 cm^3 of the industrial solution (Watts bath containing 80 kg m^{-3} Ni^{2+} as NiSO$_4$ and NiCl$_2$, H$_3$BO$_3$ and small quantities of organic additions; the SO$_4^{2-}$, Cl$^-$ and H$_3$BO$_3$ molar concentration ratio was 0.39:0.27:0.34, respectively) with 0.30 m^3 of the same water fed to the rinse tank (tap water) in the galvanic plating line. The solution prepared in this step, which resembled that found in the actual rinse tank, also contained other divalent ions such as Mg^{2+} and Ca^{2+} found at concentrations approximately 10 times greater than that of nickel. It has also been found that these divalent ions are essentially removed at a rate relative to their concentrations in solution [6,11]; their presence in the process solution will therefore decrease the efficiency of nickel removal and recovery. This is due to the similar ion-exchange selectivities and diffusivities exhibited by divalent ions [12]. It was therefore assumed that once all nickel ions were removed from the process solution,
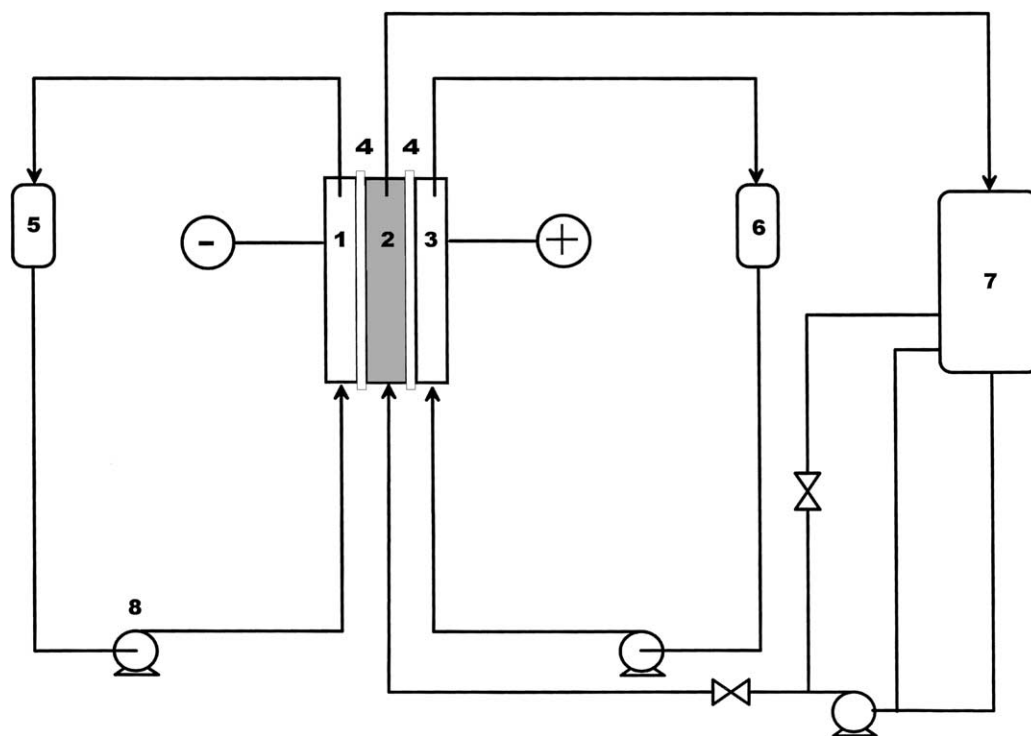
Fig. 1. Pilot scale set-up (cell enlarged for clarity): (1) anode compartment; (2) ion-exchange bed; (3) cathode compartment; (4) cation-selective membranes; (5) anolyte reservoir; (6) catholyte reservoir; (7) process solution reservoir; (8) pump; *I*: current recorder; *V*: voltage source.

the solution was also free of all other divalent ions [11]. The process solution was treated at a flow rate of $233 \, cm^3 \, min^{-1}$ and a cell voltage of 5 V.

2.1.1.2. Part 2. After the nickel had been removed from the process solution, the following procedure was carried out. First, the catholyte was replaced with a fresh 1 M HCl solution; this as the catholyte contained a high concentration of Mg^{2+} and Ca^{2+} and a relatively low concentration of Ni^{2+}. The $20 \, cm^3$ electroplating solution was then added to the previously treated solution in order to raise its nickel concentration back to approximately $5 \, g \, m^{-3}$. Since Ni^{2+} made up the bulk of divalent cations in the resulting solution, and since the concentration of divalent cations was much smaller than in the first treatment step, the process was restarted at a cell voltage of 2.5 V to account for the smaller regeneration rate required to treat it.

2.1.1.3. Part 3. The third step involved the addition of $20 \, cm^3$ electroplating solution to the previously treated solution. It was then treated at a cell voltage of 2.5 V.

The process solution was treated for approximately ten days after each of the three additions of the nickel-plating solution. Samples of the catholyte and anolyte were taken periodically during the first step and at the end of the second and third steps. They were later analysed for nickel and hydrogen content by atomic absorption spectroscopy and pH

measurement, respectively; a description of the AAS method can be found in [7].

2.1.2. The $0.6 \, m^3$ experiment
After the $0.3 \, m^3$ experiment was completed, all three solutions—the anolyte, catholyte and process solutions— were replaced and parts 1 and 2 above were repeated. In this case, however, a $0.6 \, m^3$ process solution with a nickel concentration of approximately $5 \, g \, m^{-3}$ was treated at a flow rate of $1000 \, cm^3 \, min^{-1}$. During this experiment samples were taken from the anolyte, catholyte and process solutions periodically; one sample was also taken directly from the cell effluent 1 h after the second addition of the nickel-plating solution (part 2). The process solution was treated at a cell voltage of 5 V.

2.2. Laboratory experiments

2.2.1. Electromigration experiments
The effect of feed solution pH on the treatment of dilute nickel solutions using a hybrid ion-exchange/electrodialysis process was studied. The experimental set-up consisted of a three-compartment perspex cell and three separate liquid lines; it was similar to that depicted in Fig. 1. The outer compartments were connected to liquid circuits having volumes of approximately $400 \, cm^3$; the liquid in these circuits were pumped using two centrifugal Verder V-MD6 pumps. The centre, ion-exchange compartment was fed with solution

stored in a $0.030\,m^3$ reservoir using a Schmitt MPN 100 centrifugal pump. The flow rate through the central compartment was measured using an F&P Co 2F1/4.20.5/36 flow metre with glass ball.

The effective area of the membrane and electrode inside the cell was $10\,cm^2$ ($1\,cm \times 10\,cm$), while the volume of the anode, central and cathode compartments were 5.0, 10 (bed thickness of $1.0\,cm$) and $5.0\,cm^3$, respectively. The system was kept at a constant temperature, i.e. 298 K, using a M3 Laude thermostatic bath. A constant voltage was applied using a Delta Elektronika Power Supply D 050-10 and regulated between two reference electrodes placed approximately 2 mm from the ion-selective membranes in the anode and cathode compartments.

A conductivity cell was placed at the outlet of the central compartment to monitor the conductivity of the effluent solution; it was connected to a Radiometer Type CDM 2d conductivity metre. A Philips PW 9409 pH metre was used to determine the pH of the treated solution. An Automatic Multimeter PU 2519 and Keithley 177 Microvolt DMM voltmeter were used to measure cell voltage and current, respectively. The pH, conductivity and current metres were connected to a Multilab computer interface (built in-house) for continuous data acquisition. The Multilab system was also capable of continuous bed voltage measurements.

2.2.2. Preparation of the nickel loaded ion-exchange resin

The preparation of the Dowex 50WX2-100 ion-exchange resin, which included its effective conversion to the nickel form, involved the following steps:

1. A quantity of exchanger (approximately $20\,cm^3$) containing nickel and hydrogen was placed in a column with a cross-sectional area of $1\,cm^2$.
2. The exchanger was regenerated with $2\,M\ H_2SO_4$ to convert it to the H^+ form.
3. The exchanger was rinsed with deionised water until the effluent was pH neutral.
4. The resin sample was then loaded with nickel by passing the feed solution used in the corresponding experiment through the column until the pH of the influent and effluent were equal.
5. This procedure was repeated for every feed solution studied.

The feed solutions used in these experiments were varied in pH while the nickel concentration was kept constant at about $1\,mol\,m^{-3}$. The solution was prepared by dilution of a Watts bath solution with deionised water. To obtain the desired pH, the dilution was made by adding deionised water and a mixture of H_2SO_4, HCl and H_3BO_3 in a concentration ratio equal to that of the original industrial solution.

2.2.3. Preparation of the ion-exchange membranes

Two Nafion-117 cation-exchange membranes were used in the electrodialysis cell. The membranes were treated with

1 M sulphuric acid for approximately 2 h and then washed with deionised water before each experiment.

2.2.4. Nickel ion sorption

To determine the resulting fraction of nickel in the ion-exchanger the Ni:S ratio was measured using energy dispersive spectroscopy or EDS (Jeol Superprobe JXA-8600 SX, measurements were made using an acceleration voltage of 20 kV and a beam current between 5 and 7 nA). The experiment included the following steps:

1. The 10–20 ion-exchange particles were equilibrated for 15 min in a $200\,cm^3$ $0.001\,M$ $NiSO_4$ solution at various pH's: 1.0, 1.7, 2.0, 4.0, 6.0 and at a temperature of 298 K.
2. Some of these particles were removed and washed with deionised water after each equilibration step. The particles were then dried at 313 K for a period of 2 days.
3. The dry ion-exchanger was analysed by EDS.

In a similar manner a Ni^{2+}/H^+ isotherm in a solution with a total concentration of $0.1\,M$ ($NiSO_4 + H_2SO_4$) was made. This was done by varying the hydrogen and nickel fractions in the bulk solution and measuring the resulting nickel fraction in the resin by EDS.

2.2.5. Effect of various feed solution pH

The nickel loaded ion-exchanger was placed into the central compartment of the cell between the two cation-exchange membranes. The dilute industrial solutions, containing about $0.001\,M$ Ni^{2+}, were passed "once through" the ion-exchange compartment at a flow rate of $0.42\,cm^3\,s^{-1}$. The anode and cathode circuits were each filled with a 1 M H_2SO_4 solution, these solutions were cycled at a flow rate of approximately $3\,cm^3\,s^{-1}$. A constant voltage of 5 V was applied across the ion-exchange bed and the system was kept at a constant temperature of 298 K. Since the potential drop over the anolyte, catholyte and membranes is negligible, the voltage of 5 V is practically equal to the bed voltage.

Each electromigration experiment was carried out for a period of 6 h. Anolyte, catholyte and effluent samples were taken at regular intervals and analysed for Ni^{2+} using AAS.

At the end of each experiment, the bed voltage was progressively increased to observe the bed voltage at which nickel hydroxide precipitation would occur. The system was allowed to run at each cell voltage for a period of 15 min.

3. Results

3.1. Pilot scale experiments

The pilot scale set-up ran successfully for a period of approximately 3 months. The cell, along with the accompanying equipment, operated continuously and without leakage in the industrial environment in which it was situated. The results presented in this paper represent various measurements taken over these 3 months during which two experiments
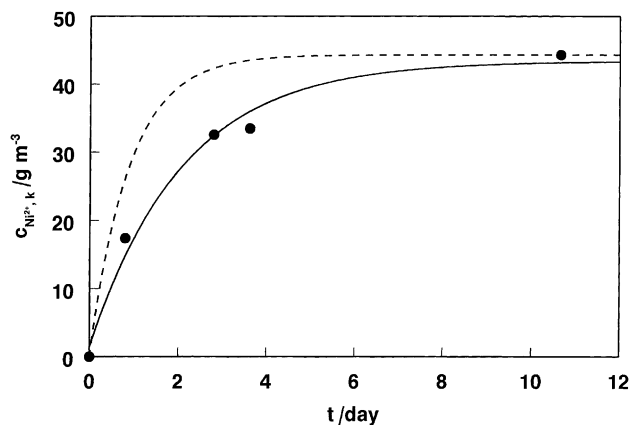
Fig. 2. Concentration of nickel in the catholyte as a function of electrodialysis time; $0.30 \, m^3$ process solution was treated at a flow rate of $233 \, cm^3 \, min^{-1}$, the three phases of the experiment are clearly seen at $t = 0$, 10 and 20 days (cell voltage = 2.5 V). The solid line represents the actual nickel concentration in the catholyte while the dotted line represents Eq. (1).

were conducted. In the first experiment a $0.30 \, m^3$ solution with approximately the same constitution as the rinse bath in the galvanic plating line ($5 \, g \, m^{-3}$ Ni^{2+} in rinse water [13]) was treated at a flow rate of $233 \, cm^3 \, min^{-1}$. Catholyte samples were taken during step 1 of this experiment, and only at the beginning and end of steps 2 and 3. The concentration of nickel in the catholyte during step 1 is given in Fig. 2 as a function of time. The concentration of nickel in the catholyte increased to approximately $44 \, g \, m^{-3}$ during the first part of the experiment, after which the catholyte was refreshed. After the completion of the second part the Ni^{2+} concentration was found to be $45 \, g \, m^{-3}$ while after the third part the catholyte nickel concentration, expected to increase to about $90 \, g \, m^{-3}$, only increased to $65 \, g \, m^{-3}$. The difference is attributed to the quantity found deposited as metallic nickel on the cathode. Anolyte samples were also taken at the end of steps 2 and 3 and they were found to contain 8.23 and $12.06 \, g \, m^{-3}$ Ni^{2+}, respectively.

At the same time that the catholyte samples were taken, the pH of the process solution was measured. These results are shown in Fig. 3. The pH, initially 7.75, decreased rapidly during the first day of the experiment to a value of approximately 2.85. The decrease in pH occurred due to the exchange of cations from the process solution with hydrogen from the ion-exchange bed, and to a lesser degree from the diffusion of acid from the outer electrolyte compartments [7,8].

After the $0.3 \, m^3$ experiment was completed the anolyte and catholyte solutions were replaced and $0.6 \, m^3$ process solution was prepared. This second experiment was run with a process solution flow rate of $1000 \, cm^3 \, min^{-1}$. During this experiment, samples of the process solution were taken on a regular basis and analysed for nickel content; the results are shown in Fig. 4. The initial nickel concentration in the process solution, approximately $7 \, g \, m^{-3}$, decreased to below
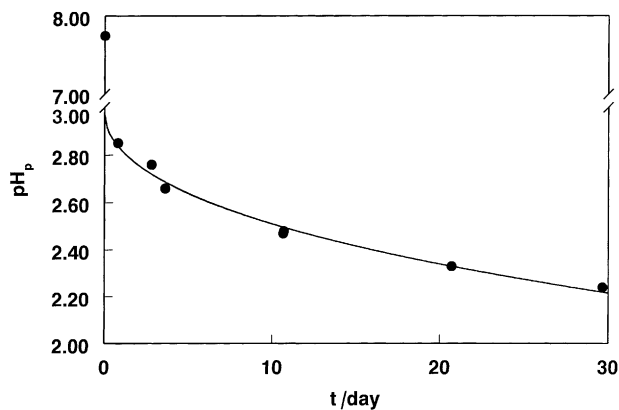

Fig. 3. pH of the process solution as a function of electrodialysis time; $0.30 \, m^3$ process solution was treated at a flow rate of $233 \, cm^3 \, min^{-1}$.

the detection limit of the analysis ($0.2 \, g \, m^{-3}$) after approximately 7 days of treatment. After the second addition of plating solution less than 2 days of treatment was required to bring the nickel concentration in the process solution below the detection limit ($t = 16$–18 days). The difference in the $c_{Ni,p}/t$ curves for steps 1 and 2 was caused by the difference in the concentration of Mg^{2+} and Ca^{2+} ions in the process solution. It was also observed that 1 h after the second addition of plating solution, the nickel concentration at the outlet of the centre compartment was found to be lower than the analysis detection limit. The removal of Ni^{2+} therefore occurred in a single pass of the process solution through the cell during the second step.

After 21 days electrodialysis, the concentration of nickel in the anolyte was found to be $17.8 \, g \, m^{-3}$, which is a factor 3 larger than that in the original process solution. This can be explained by the fact that the nickel concentration in the resin can reach up to 6000 times that found in the original process solution; ion-exchange then occurs across the anode side membrane between sorbed Ni^{2+} and $2H^+$ originating from the anolyte.
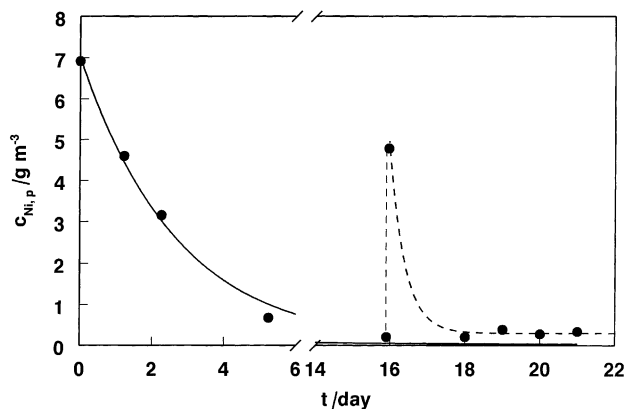

Fig. 4. Concentration of nickel in the process solution for the experiment during which $0.60 \, m^3$ process solution was treated at $0.001 \, m^3 \, min^{-1}$ and a cell voltage of 5 V. The dotted line represents Eq. (1).
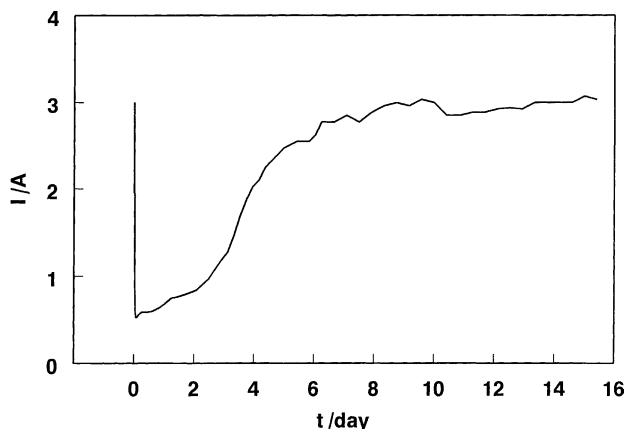
Fig. 5. Current vs. electrodialysis time during the first phase of the experiment during which $0.60\,m^3$ process solution was treated at $0.001\,m^3\,min^{-1}$ and a constant cell voltage of 5 V.

Fig. 6. Fraction of nickel in the Dowex 50WX-2 ion-exchanger loaded in solutions containing $0.001\,M$ $NiSO_4$ and various H_2SO_4 concentrations.

The current for the first step of the experiment is shown in Fig. 5 as a function of time. It decreased sharply during the first 2 h of treatment after which it gradually began to increase to a relatively constant value of approximately 3 A (because the distribution of current over the cell is not uniform, current densities are not given, see [9,10] for a description of the current distribution over the hybrid cell). The change in current was brought about by the conversion of the bed to different ionic forms, i.e. hydrogen to divalent ion form and visa versa, having different resistances [9,10].

After both experiments were complete the cell was disassembled for inspection. One of the most noticeable (but expected) [6,14] observations was the presence of biological growth in the ion-exchange bed. The growth was found to be separable from the particles and was not found on either of the two membranes. The ion-exchange particles were otherwise in good condition and the ion-selective membranes showed no defects. The cathode was tinted black indicating the presence of metallic nickel (such deposition was also observed in previous work [8]) and no metal hydroxide deposits were found within the cell.

3.2. Nickel sorption isotherm

In Fig. 6 the fraction of nickel absorbed by the Dowex 50WX-2 ion-exchanger is given as a function of solution pH where each solution contained $1\,mol\,m^{-3}$ Ni^{2+}. The fraction of nickel in the resin increased with an increase of solution pH from 1 to 2 and remained constant at higher pH. The Ni^{2+}/H^+ isotherm for a $H_2SO_4/NiSO_4$ solution with a total sulphate concentration of 0.1 M, is given in Fig. 7. The positive curve of the isotherm indicates that nickel was strongly preferred by the resin over protons; a common factor used to quantify the preference of one ion over another is called the separation factor and is defined by Eq. (1) [12]. The separation factor increased from 1.95 at an equivalent nickel ionic fraction in solution (X_{Ni}) of 0.93–16.96 at $X_{Ni} = 0.095$
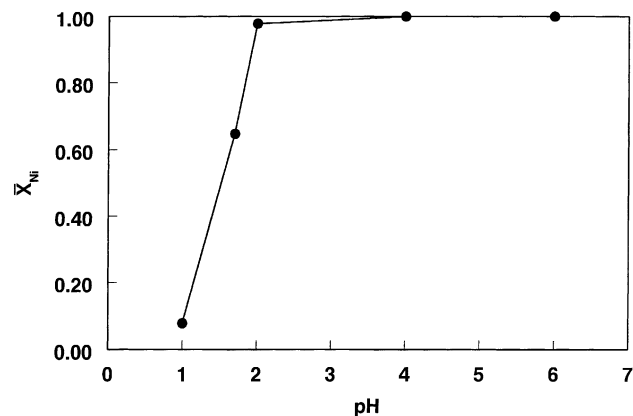
(it has been found that a nickel fraction of 1 in the resin corresponds to an effective concentration of approximately $534\,mol\,m^{-3}$ [9]):

$$\alpha_H^{Ni} = \frac{\bar{X}_{Ni}X_H}{\bar{X}_H X_{Ni}} \tag{1}$$

where

$$X_{Ni} = \frac{2c_{Ni}}{2c_{Ni} + c_H}, \qquad X_H = \frac{c_H}{2c_{Ni} + c_H}$$

3.3. Nickel removal from solutions of different pH

To determine the effect of feed solution pH on the nickel flux to the cathode compartment, experiments were carried out at a constant bed voltage, ΔE_{bed}, of 5 V (regulated between the reference electrodes). During the preparation of the ion-exchange resin, the resin turned from its original light yellow colour (in the H^+ form) to green upon effective conversion to the Ni^{2+} form. The resin turned less green when loaded with the pH 1 and 1.7 nickel solutions, indicating a decrease in nickel sorption. During the experiments with feed solution pH between 2 and 6, the current density
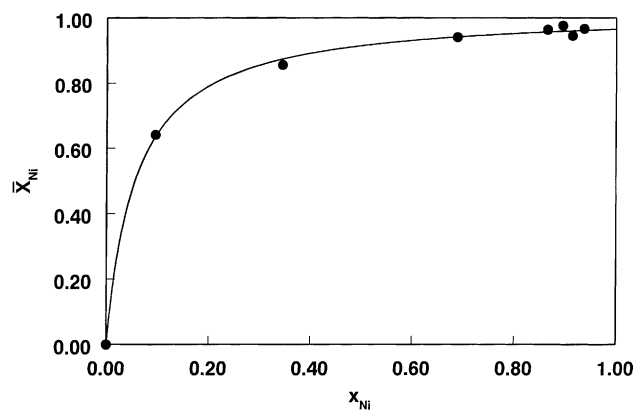

Fig. 7. Ni^{2+}/H^+ (sulphate) isotherm for the Dowex 50WX-2 ion-exchanger in solutions with a total concentration of 0.1 M.
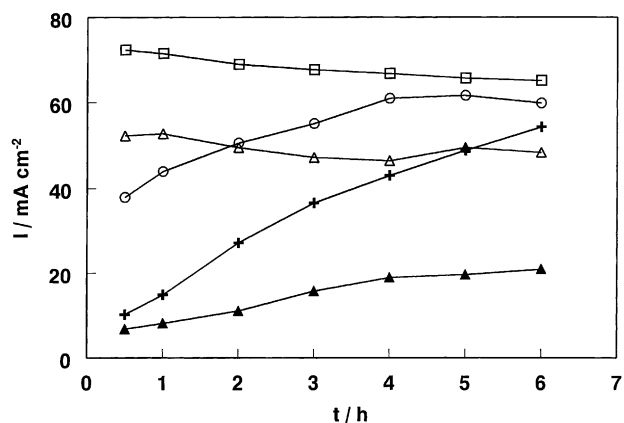
Fig. 8. Current vs. electrodialysis time for the lab scale experiments during which 0.001 M Ni^{2+} solutions with differing pH were treated at a constant cell voltage of 5 V; feed solution pH: 1.0 (□), 1.7 (△), 2.0 (○), 4.0 (+), 6.0 (▲).

Fig. 10. Nickel flux as a function of solution pH for the lab scale experiments during which dilute Watts bath solutions, 0.001 M Ni^{2+}, with differing pH were treated at a cell voltage of 5 V (●); (+) represents the replicate of the pH 2 experiment.

was observed to increase while the current density during the pH 1 and 1.7 experiments (Fig. 8) decreased slightly with time (because the beds were pre-equilibrated with their appropriate feed solutions, the current distribution across the cell for the various experiments can be considered uniform and therefore current densities are given).

During the electrodialysis process, Ni^{2+} ions from the solution exchanged with two equivalents of hydrogen ions in the ion-exchanger. This caused the pH of the feed solution to decrease. The pH of the feed solution at the outlet of the cell was constant for the duration of each experiment. The pH 6 and 4 feed solutions decreased to 2.8 and 2.5 at the outlet of the cell, respectively; no clear differences between the inlet and outlet pH were observed during the other experiments.

The amount of nickel transported into the cathode compartment with respect to electrodialysis time is depicted in Fig. 9. The nickel content of the catholyte increased linearly
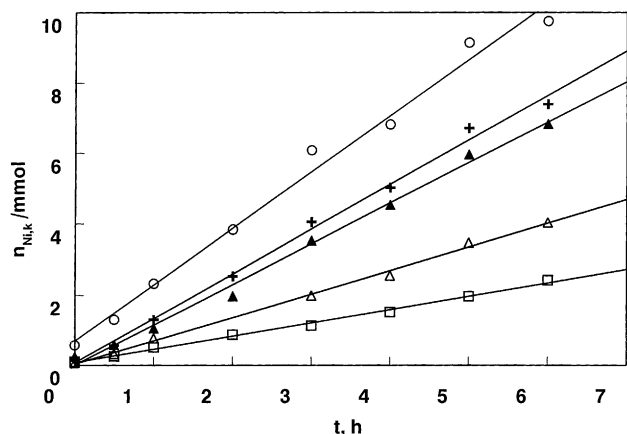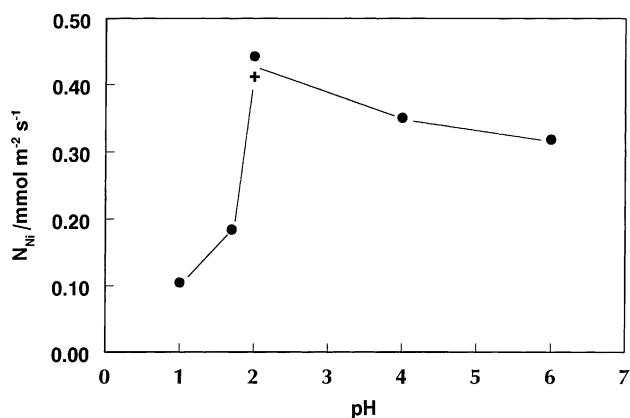
for all feed solutions. The maximum value of Ni^{2+} ions in the catholyte after 6 h of electrodialysis (approximately 10 mmol) was obtained with a feed solution pH of 2.

In Fig. 10 the nickel flux to the cathode compartment is given as a function of the feed solution pH. This figure shows a maximum flux for the feed solution with a pH of 2. The experiment with a feed pH of 2 was carried out twice to verify this result and the nickel fluxes for both trials are given in the figure. Below a pH of 2, the nickel flux decreases substantially.

The differential current efficiency for the removal of nickel is represented as a function of electrodialysis time in Fig. 11 for the various feed solutions. The current efficiency, η_{Ni}, for the electrodialysis process decreased with increasing concentration of H^+ in solution. It decreased with electrodialysis time between pH 6 and 2, and remained constant for pH 1 and 1.7.

Fig. 9. Quantity of nickel in the catholyte as a function of electrodialysis time for the lab scale experiments during which 0.001 M Ni^{2+} solutions with differing pH were treated at a cell voltage of 5 V: 1.0 (□), 1.7 (△), 2.0 (○), 4.0 (+), 6.0 (▲).
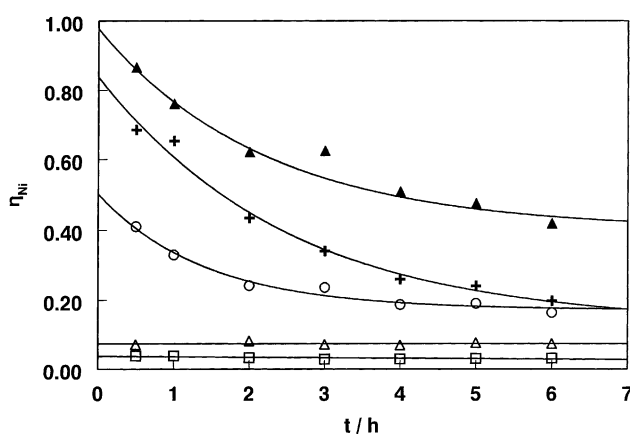

Fig. 11. Current efficiency as a function of electrodialysis time for the lab scale experiments during which 0.001 M Ni^{2+} solutions with different pH were treated at a constant cell voltage of 5 V: 1.0 (□), 1.7 (△), 2.0 (○), 4.0 (+), 6.0 (▲).
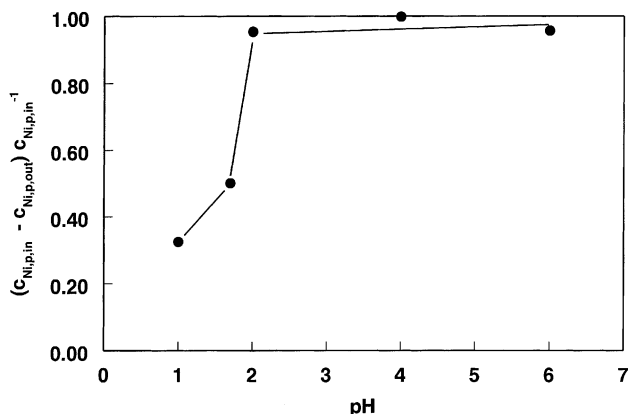
Fig. 12. Fraction of nickel removed from the feed solution for the lab scale experiments during which 0.001 M Ni^{2+} solutions with differing pH were treated at a cell voltage of 5 V. This value was constant for the entirety of the experiments.

The fraction of nickel removed from the feed solutions was determined (Fig. 12). Approximately 95% was removed from feeds with pH values of 2, 4 and 6 while much less was removed from feed solutions with pH values of 1 and 1.7.

3.4. Nickel hydroxide precipitation

After 6 h electrodialysis, the bed voltage was progressively increased in 1 V intervals to determine the approximate bed voltage above which nickel hydroxide precipitation takes place. Nickel hydroxide precipitation was observed on the cathode side ion-exchange membrane at a cell voltage of 9 V with the pH 6 feed solution. No nickel hydroxide precipitation occurred at feed pH values of 1, 1.7, 2 and 4, even at a bed voltage of 20 V. The cell voltage was not increased beyond 20 V because of the high current obtained at this voltage (approximately $0.6 \, A \, cm^{-2}$ for pH 1 and $0.3 \, A \, cm^{-2}$ for pH 4).

4. Discussion

The pilot scale cell operated for a period of approximately 90 days and during this time two experiments were carried out. During the first part of each experiment, all divalent ions were removed from the process solution; these included not only Ni^{2+} but also other divalent ions naturally found in tap water such as Ca^{2+} and Mg^{2+} (the total concentration of which was around 0.001 M, determined by EDTA complexation with eriochrome black indicator [15]). The typical current profile at a constant cell voltage of 5 V is given in Fig. 5 for the first part of the experiment. Since divalent ions have mobilities of about an order of magnitude less than that of hydrogen ions, the resistance of the bed increased upon absorption of these divalent ions during the first 2 h of electrodialysis (this was studied in detail in [9]). After 2 h the current gradually began to increase; during this time the

quantity of divalent ions fed to the cell was less than the amount removed by electrodialysis; the bed therefore began to regenerate to the more conductive hydrogen form. After approximately 7 days the current levelled off at around 3 A, this represents the point at which the bed was practically regenerated and the process solution was essentially free of divalent ions.

During part 2 of the $0.6 \, m^3$ experiment, the process solution contained only Ni^{2+} and monovalent ions such as H^+. The current during this part of the experiment remained constant at around 3 A at a cell voltage of 5 V. Since protons have a much higher mobility in the resin compared to Ni^{2+}, the high current indicates that a large quantity of the bed was not used for nickel transport, even at a flow rate of $1000 \, cm^3 \, min^{-1}$. The initial fraction of the bed used for nickel transport can be estimated by taking the initial flux of nickel in the nickel form of the resin into consideration. For a fully loaded bed the maximum flux was found to be $2.35 \times 10^{-4} \, mol \, m^{-2} \, s^{-1}$ at 5 V in previous work [8]. The initial nickel flux into the central compartment of the cell was approximately 3.3×10^{-7} and $1.4 \times 10^{-6} \, mol \, s^{-1}$ for the 0.30 and $0.60 \, m^3$ experiments, respectively. Theoretically, this means that only a bed area of 1.4×10^{-3} and $6.0 \times 10^{-3} \, m^2$ or bed fractions of 0.14 and 0.6 would be used, respectively. These calculated figures are most likely less than the actual bed area used since it does not take the equilibrium and kinetics of sorption into account (i.e. fraction of nickel ions sorbed under actual conditions as well as the dispersion of the sorption front).

Most of the nickel removed from the process solution could be found in the catholyte. During the first two parts of the $0.30 \, m^3$ experiment, 22 and 23 mmol of the total 25 mmol Ni^{2+} were found in the catholyte, respectively, while the remainder, approximately 2 mmol, had diffused into the anolyte. This accounts for approximately 8% of the nickel in the process solution. Essentially, the same fraction of nickel was transported during the $0.60 \, m^3$ experiment, that is, 0.087 mol of the total 0.102 mol Ni^{2+}, or 8.5%, had diffused to the anolyte during the entire $0.60 \, m^3$ experiment. The diffusion of nickel ions to the anolyte involved the exchange of nickel in the resin with H^+ from the anolyte; it involved no net charge transfer.

The quantity of nickel remaining in the process solution and the catholyte, assuming perfect mixing in the tank and the removal of all nickel ions in one pass through the cell are given by Eqs. (2a) and (2b), respectively:

$$c_{Ni,p}(t) = \frac{n_{Ni,p}(t)}{V_p} = \frac{n^0_{Ni,p} \, e^{(-v/V_p)t}}{V_p} \tag{2a}$$

$$c_{Ni,k}(t) = \frac{n_{Ni,k}(t)}{V_k} = \frac{(n^0_{Ni,p} - n_{Ni,a}(t)) - n^0_{Ni,p} \, e^{(-v/V_p)t}}{V_k} \tag{2b}$$

Eqs. (2a) and (2b) are represented as dashed lines in Figs. 2 and 4, respectively. The removal of all nickel ions in a single

pass during step 1 is clearly incorrect (due to the presence of additional divalent ions), but the assumption is good for part 2 of the $0.6\,m^3$ experiment as no Ni^{2+} was found in solution 1 h after this part was started. Since the feed flow rate during the $0.3\,m^3$ experiment was much lower than that used during the $0.6\,m^3$ experiment, it is proposed that this assumption is also good for parts 2 and 3 of the $0.3\,m^3$ experiment.

The isotherm (Fig. 7) shows that the sorption of Ni^{2+} is favoured over that of H^+ when the total concentration of sulphate ions in the bulk is 0.1 M. The separation factor was found to have values between 2 and 17 for $\bar{X}_{Ni}$ between 0.97 and 0.64. It is well known that in the case of divalent–monovalent exchange, the separation factor is strongly affected by the total concentration of ions in the bulk solution; it decreases with increasing total solution concentration [12]. The nickel concentration was constant in all the solutions used in the remainder of this study (0.001 M), while the concentration of H^+, or pH, was varied. Under these conditions the fraction of nickel in the Dowex 50WX-2 resin was found to be 1 at solution pH values greater than 2 while it was found to decrease significantly to a value of 0.078 at a pH of 1 (Fig. 6).

The flux of nickel into the catholyte is a function of the concentration of nickel in the bed and can be described by the Nernst–Planck relationship [7,12,16,17]:

$$N_i = \bar{D}_i \frac{d\bar{c}_i}{dx} + z_i \bar{c}_i \bar{u}_i \, \text{grad} \, \varphi + v\bar{c}_i \tag{3}$$

It consists of a diffusion, migration and convection terms, respectively. For feed solutions below a pH of 2, the nickel concentration in the resin, and hence the nickel flux to the catholyte decreases. For feed solutions with pH between 2 and 6 the nickel concentration in the resin is practically constant but the nickel flux to the cathode compartment decreases with increasing pH. This may be attributed to the increasing role of the third mechanism of transport in addition to transport solely through the solution and resin phases, namely the alternating transport of Ni^{2+} through both the resin and solution phases. Since increasing interstitial solution conductivity enhances this mechanism, this transport mechanism will increase in importance with decreasing feed solution pH.

The consequence of a lower degree of nickel sorption and flux is a decreased rate of nickel removal from the process solution. The fraction of nickel removed from the feed at pH 1 and 1.7 was found to be 0.32 and 0.50, respectively, while a fraction of approximately 0.95 was removed from the pH 2, 4 and 6 experiments.

Another consequence of a decrease in solution pH is a drop in current efficiency (Fig. 11). This arose from both the increased conductivity of the interstitial solution and the increased H^+ fraction in the ion-exchange bed. Both of these factors led to increased H^+ transport and hence a decrease in the fraction of current carried by Ni^{2+}. During the pH 2, 4 and 6 experiments the current efficiency was observed to decrease with time. This was caused by a partial regeneration of the bed, most likely near the outlet of the cell. The degree of regeneration, however, was small and, as is shown by the linearity of the data in Fig. 9, did not noticeably affect the nickel flux to the catholyte. Since the diffusion coefficient of H^+ in the resin is an order of magnitude greater than that of Ni^{2+}, only a small degree of regeneration will result in a large increase in H^+ transport and hence a large decrease in the current efficiency of the system.

One positive consequence of an increased concentration of H^+ in the feed solution is its tendency to prevent the formation of nickel hydroxide within the centre compartment. The formation of nickel hydroxide precipitate was found to occur between cell voltages of 5 and 10 V with a feed concentration of 0.001 M $NiSO_4$ [9]. The nickel hydroxide was observed to form on the cathode side membrane and, under more extreme circumstances, to form around the ion-exchange particles themselves [7,18]. At the cathode side membrane the hydrated water of the $Ni^{2+}(6H_2O)$ will dissociate to form $Ni(OH)_2(4H_2O) + 2H^+$; the hydrogen is transported to the cathode compartment [19,20]. Also of note is that it has been found that the nickel hydroxide could be removed by running the system with a deionised water feed; the strong acidity of the hydrogen form of the regenerated resin will aid the dissolution of the hydroxide and the re-sorption and transport of the nickel to the catholyte. In this work, nickel hydroxide was observed to form on the cathode side membrane at a cell voltage of 9 V in the case of an industrial 0.001 M Ni^{2+} feed at pH 6. At and below a pH of 4, however, no nickel hydroxide was observed, even at a cell voltage of 20 V and current densities between 0.3 and $0.6\,A\,cm^{-2}$.

5. Conclusions

The H^+ concentration in the process solution was found to significantly affect the efficiency of the hybrid ion-exchange/electrodialysis process. Below a pH of 2, the fraction of Ni^{2+} sorbed by the resin from a 0.001 M Ni^{2+} solution decreased, thereby decreasing its rate of removal. One positive aspect of decreasing process solution pH is its inhibition of nickel hydroxide formation in the ion-exchange compartment.

The treatment of an actual rinse solution containing dilute concentrations of nickel ions using the pilot scale cell was successful. The concentration of nickel in the process solution was found to decrease from approximately 5 ppm to less than the detection limit of the analysis (<20 ppb) after each treatment. The limiting factor of these experiments was not the flux of nickel out of the ion-exchange bed, but the flux of nickel into the cell. The process solution flow rate is therefore critical to the efficiency of the process. The experiments ran continuously without the formation of nickel hydroxide or other solid compounds within the cell and showed that the cell can operate without human intervention.

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