# Detailed investigation of the rejuvenation of a spent electroless nickel solution by electrodialysis with a view to optimizing electrodialysis performance.

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## Abstract

The rejuvenation of spent electroless nickel baths by electrodialysis has received a considerable amount of attention over the past decade and the technique is being increasingly employed to extend electroless nickel bath life. However, thus far there has not been a detailed investigation into the optimum electrodialysis operating conditions and into the best ion selective membranes and cell configuration that could be used. Along with providing a brief review of the progress in the use of electrodialysis to extend the electroless nickel bath life, this paper shall present the results of electrodialysis trials carried out at four different critical cell operating conditions *i.e.* current density, pH, flow rate and temperature. The effectiveness of the electrodialysis technique at each operating condition shall be assessed with regard to parameters such as total ion removal, permselectivity and current efficiency. This work also provides for monitoring the fate of all the anions and cations in the electroless nickel bath during the electrodialysis process by using ion chromatography and inductively coupled plasma spectrosopy as analysis techniques. Once the optimum operating conditions have been established it is then planned to test and compare different ion selective membranes and to experiment with different cell configurations

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## Introduction

The electroless nickel (EN) process is of considerable industrial importance and is the most important catalytic plating process today producing metal deposits with better physical properties than electroplated nickel. The overall equation for the chemical deposition of nickel by hypophosphite is shown in Eqn. 1.

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni + 2H_2PO_3^- + 2H^+ + H_2 \qquad \textbf{(1)}$$

One of the major shortcomings of the electroless nickel process is the inherent limited bath life (and the associated disposal costs) due to the accumulation of harmful anions (sulfate and orthophosphite) and cations (sodium) in the baths (Riedel 1991). The orthophosphite is the product of hypophosphite oxidation during nickel reduction and the sodium and sulfate are counterions to hypophosphite and nickel respectively, which are continuously replenished in the bath. After 6-8 MTOs (MTO = metal turnover), the orthophosphite concentration can be 2.5 M (200 g $L^{-1}$) and the plating solution will turn cloudy due to nickel orthophosphite precipitation producing rough deposits, poor corrosion resistance and the plating rate can decrease from 15 $\mu m\ hr^{-1}$ to less then 8 $\mu m\ hr^{-1}$ (Duncan 1996, Mallory and Parker 1994). Without an effective means to remove these harmful components, the EN bath eventually must be discarded resulting in high disposal and raw material costs (Richmond and Top 1990). The long-term goal of any electroless nickel-plating shop will be to prolong the life of the EN bath for as long as possible. Over the past decade there has been significant progress in extending electroless nickel bath life *via* selective chemical precipitation, ion-exchange, electrodialysis, replacing sodium hypophosphite with nickel hypophosphite and improved in-process bath maintenance (Bolger and Szlag 2000). At the forefront of these EN bath regeneration technologies has been electrodialysis; the technique has been patented for this purpose (Vaughan 1993) and the quality of an EN deposit from an EN bath rejuvenated by electrodialysis has been reported to be as good as a fresh EN bath deposit (Steffani and Meltzer 1995, Li *et al*. 1998, Stencel and O'Donnell 1995). Table 1 presents some of the results of electrodialysis trials carried out by a variety of institutions, universities and plating suppliers (Bolger and Szlag 2000). It is generally accepted that the contaminants in spent EN baths need only be removed to a concentration where they no longer interfere with the rate or quality of the plating process. Table 1 shows that the percentage removal of orthophosphite varies from 15 % to 80 % and the levels of sodium and sulfate removed vary from 50 % to 80 % and invariably where high levels of the harmful components are removed there were also high losses of the useful constituents *i.e*. hypophosphite and the organic acids. In the majority of the cases where electrodialysis was used to remove $H_2PO_3^-$ almost the exact same amount of valuable $H_2PO_2^-$ was removed. The exception to this is a recent study by Born *et al*. who achieved an excellent 30:1 selectivity for $H_2PO_3^-:H_2PO_2^-$ using special mono-permselective membranes and a modified arrangement of the anion and cation ion exchange membranes (Born *et al*. 2000). The paper, however, does not describe how this selectivity was achieved *i.e.* ion selective membranes or electrodialysis cell configuration used. Much of the work that has been done on spent EN bath rejuvenation by electrodialysis does not contain the necessary details on the membranes used, the electrodialysis cell configuration or operating conditions (due perhaps due to proprietary protection concerns). This is one of the reasons we decided to carry out a detailed study of the electrodialysis of a spent electroless nickel solution. This work differs from previous electrodialysis trials as follows:

- We wished to establish a baseline for the removal rates of the various bath components under four critical electrodialysis operating conditions *i.e.* current density, bath pH, bath temperature and solution flow rate for a given number of cell pairs. The pH balance of the cell will be a critical factor in the removal of divalent acids over monovalent acids.
- A complete ion analysis system for an EN solution was developed in order to monitor all of the bath components including the stabilizing organic acids. This required the development of a method for separating and quantifying EN bath anions by ion chromatography and the use of a simulated spent electroless nickel bath. Many of the previous studies on EN bath rejuvenation have assessed the removal of contaminants using crude yardsticks such as total dissolved solids or conductivity.
- Once the optimum operating conditions have been established we hope to test a series of commercial anion and cation exchange membranes to determine their removal efficiency and selectivity in treating spent EN baths. There have been significant advances in ion permselective membrane design over the last decade particularly with membranes intended to pass monovalent ions (Saracco *et al.* 1993, Sata 1994) which shall be used in this work.
- An electrodialysis cell can have a variety of configurations each of which will have a different electrodialysis characteristic; we intend to explore different configurations in order to maximize the permselectivity for bath harmful components over useful components.

In this paper we present the results of electrodialysis trials on a simulated spent electroless nickel bath at the four different operating conditions of current density, bath pH, bath temperature and solution flow rate.

The electrodialysis of the simulated EN solution under the four different operating conditions was evaluated using three separate criteria; the % removal of each ion, the current efficiency and the permselectivity of the membrane. The % removal of the ions was calculated using Eqn. 2.

$$\%\ \text{Ion Removal} = [(C_{FC} - C_{IC})/C_{ID}] \times 100 \qquad \textbf{(2)}$$

$C_{FC}$ = Final ion concentration in the concentrating compartment (anolyte or catholyte)
$C_{IC}$ = Initial ion concentration in the concentrating compartment
$C_{ID}$ = Initial ion concentration in the depleting compartment (spent EN solution)

The current efficiency is the fraction of the electrical charge that is involved in the transport of the EN bath ions from one compartment to the other. The current efficiency can be calculated using Eqn. 3.

$$\text{Current Efficiency} = (\Sigma(C_R \times Z) \times F)/I \times T \qquad \textbf{(3)}$$

$C_R$ = Ion concentration removed (moles)
Z = Ion charge
F = Faraday's number (96,500 A s $mol^{-1}$)
I = Current (A)
T = Time (s)

*Table 1 Percentage removals of EN bath components after electrodialysis (ED) treatment by different authors/institutions*

| Author | CEM[#] | AEM[#] | $Na^+$ | $Ni^{2+}$ | $H_2PO_3^{2-}$ | $H_2PO_2^-$ | $SO_4^-$ | Organic acids | TDS | Metal Turnovers (MTOs) |
|---|---|---|---|---|---|---|---|---|---|---|
| (Bellamare 1997) | - | - | - | 10 % | 77 % | 68 % | 60 % | 45 % | - | Bath quality improved from 6 to 1.5 MTO** |
| (Crotty 1999) | - | - | 80 % | 28 % | 81 % | 85 % | 80 % | 54 - 67 % | - | Bath quality improved from 6.6 to 1.3 MTO |
| (Kuboi and Takeshita 1989) | - | - |  | 8 % | 34 % | 13 % | 34 % | 5 - 11 % | - | Bath life was more than 20 MTOs |
| (Steffani and Meltzer 1995, Steffani 1996) | - | - | - | - | - | - | - | - | 58 - 64 % | Bath quality improved from 6 to 1.5 MTO |
| (Li *et al*. 1998, Li *et al*. 1999) | No. 3361* | No. 3362* | 50 % | 30 % | 50 % | 10 % | 50 % | 40 % | - | Bath life was more than 17 MTOs |
| (Williams and Vogel 1999, AESF 1999) | - | - | - | 10 % | 86 % | 68 % | 59 % | 50 % | - | Bath life was more than 60 MTOs |
| (Renz *et al*. 1999, Renz *et al*. 2000) | Nafion 450 | Neosepta AM1 | - | - | 14 % | 9 % | - | - | - | - |
| (Stencel and O'Donnell 1995*)* | - | - | 80 % | 25 % | 83 % | 83 % | 79 % | - | - | Bath quality improved from 6 to 1.5 MTO |
| (Born *et al*. 2000) | - | - | - | - | ~ 45 % | ~ 1.5% | - | - | - | Bath life was more than 75 MTOs |

[#] CEM = Cation exchange membrane and AEM = Anion exchange membrane

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** Bath quality refers to the bath quality at 1.5 MTO and at 6 MTO; the bath at 1.5 MTO has lower levels of unwanted ions

The permselectivity of the membrane is evaluated by comparing the beneficial removal of bath contaminants (orthophosphite, sulfate and sodium) with the loss of useful components (hypophosphite, propanoic and succinic acid and nickel). The permselectivity ($P_V^C$) of the contaminants over the valuable components (see Eqn. 4) can be calculated by using a modified version of the equations used to calculate ion exchange equilibrium constants and permselectivities by Sata (Sata 1994).

$$P_V^C = (CR_{cont}/CR_{val.})/(CI_{cont.}/CI_{val.}) \qquad \textbf{(4)}$$

$CR_{cont.}$ = conc. of contaminants removed $\quad$ $CI_{cont.}$ = initial conc. of contaminants
$CR_{val.}$ = conc. of valuable components lost $\quad$ $CI_{val}$ = initial conc. of valuable components

The equation for calculating permselectivity includes a concentration factor that accounts for the fact that the concentration of the contaminants is higher than the useful bath components. For example, in the simulated EN bath the orthophosphite concentration is $7^{1}/_{3}$ times higher than the hypophosphite concentration so a permselectivity of 1 for orthophosphosphite/hypophosphite would mean that $7^{1}/_{3}$ times more orthophosphite is removed than hypophosphite.

## Experimental

The composition of the simulated spent electroless nickel bath is shown in Table 2 along with the concentration of each component and the method of analysis for that component. The bath composition is based on a typical real-life spent bath composition (Li *et. al.* 1999, Mallory 1990, Riedel 1991).

*Table 2 Concentration of simulated spent electroless nickel bath components with analysis technique for each component*

| **Component** | **grams/liter** | **moles/liter** | **Analysis** |
|---|---|---|---|
| Nickel | 5 | 0.086 | ICP[1] |
| Sodium | 75 | 3.26 | ICP |
| Orthophosphite | 135 | 1.687 | IC[2] |
| Sulfate | 60 | 0.625 | IC |
| Hypophosphite | 15 | 0.230 | IC |
| Propanoic acid | 10 | 0.135 | IC |
| Succinic acid | 10 | 0.085 | IC |

[1] Inductively coupled plasma spectroscopy [2] Ion chromatography

The bath pH was 4.5 and for the pH variable experiments it was possible to adjust the pH upwards and downwards of 4.5 by using differing proportions of phosphorus acid ($H_3PO_3$) which decreases the pH and sodium orthophosphite ($Na_2HPO_3$) which increases the pH. The concentration of sodium in the bath inevitably will fluctuate slightly depending on the amounts of $H_3PO_3$ and $Na_2HPO_3$ used.

A simplified diagram of the single membrane pair electrodialysis cell used for initial investigations is shown in Figure 1. Under the influence of an electric potential, the anions and cations in the spent EN bath are transported from the center compartment (depleting solution) through anion and cation selective membranes into the anolyte and catholyte respectively (concentrating solutions). An Electrocell MP50 electrolysis cell with a membrane/electrode surface area of 10 $cm^2$ and a 1.2 cm intercompartment gap was used for the electrodialysis trials. The volume of the feed solutions for each compartment was 10 L and a 0.1 M sodium sulfate solution was used as the starting anolyte and catholyte solution. The cation selective membrane chosen for the initial testing of process variables was a Tokuyama Neosepta® CMS membrane that was designed for permselectivity to monovalent cations by forming a thin cationic charged layer on the surface. The anion selective membrane for initial testing was a Tokuyama Neosepta® ACM membrane that reduces proton leakage from the anolyte to the center compartment; it was necessary to use this membrane to control the pH in the center compartment.

The electrodialysis trials were conducted over a 24 hour period and samples were taken from each compartment at regular intervals for analysis of the ions in Table 2 and for pH. The potential drop across the cell was measured by connecting a multimeter to the anode and cathode. A Dionex AS11 anion exchange column with a hydroxide gradient was used to quantify the anions. An ion chromatogram of a simulated spent EN bath is shown in Figure 2. Sodium and nickel were quantified by inductively coupled plasma spectroscopy.

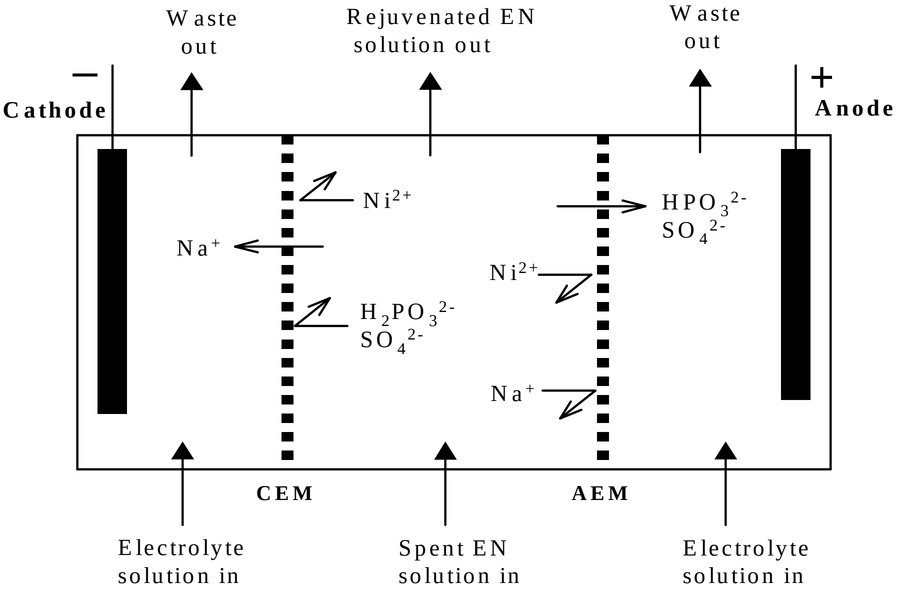

*Figure 1  A single membrane pair electrodialysis cell for regeneration of a spent EN bath*

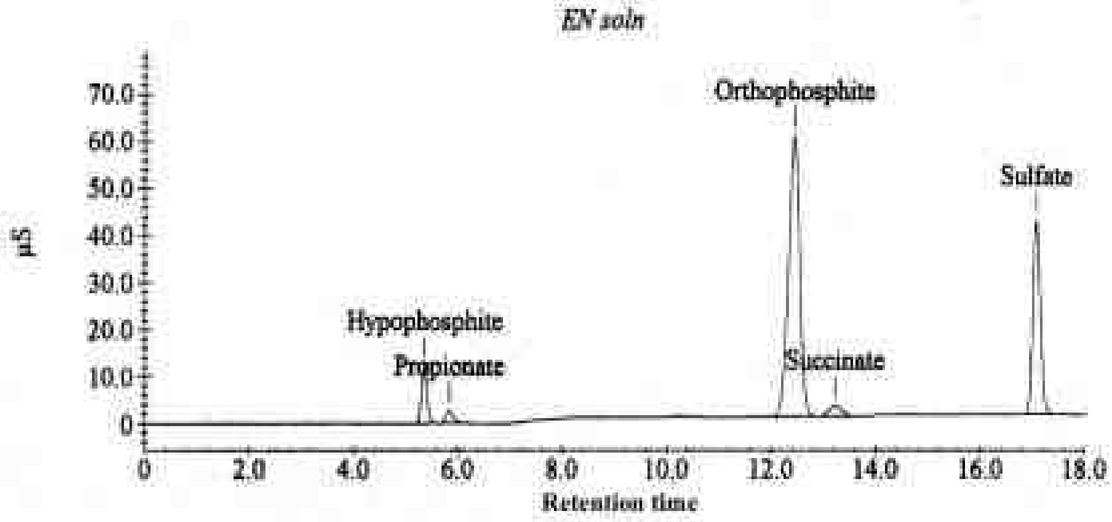

*Figure 2  Typical anion chromatogram of a simulated spent electroless nickel solution*

## Results and discussion

The electrodialysis trials on the simulated EN solution at the various operating conditions showed that the permselectivity of the cation selective membrane was exceedingly in favor of sodium over nickel. In all cases there was less than 2-3 % loss of nickel from the bath. The permselectivity for sodium over nickel can be attributed to (a) the use of a monovalent selective membrane (b) the complexation of nickel by the organic acids and (c) the larger ionic size of nickel. The remainder of the results and discussion shall mostly concern the anion removal although the data for % removals of sodium and nickel shall be given at each different operating condition.

## Current density

*Table 3 The % removals of cations and anions from a simulated spent EN bath on electrodialysis at different current densities at a flow rate of 2 L min$^{-1}$, pH 4.5 and at room temperature.*

| Current dens. / mA cm$^{-2}$ | $Na^+$ | $Ni^{2+}$ | $H_2PO_2^-$ | $C_3H_5COO^-$ | $H_2PO_3^-$ | $C_2H_4(COO^-)_2$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| 100 | 3.9 | 0 | 7.7 | 3.2 | 4.2 | 8.7 | 1.6 |
| 200 | 9.1 | 0 | 12.1 | 9.2 | 8.7 | 14.5 | 2 |
| 400 | 14.1 | 1.1 | 23.6 | 16.6 | 13.6 | 15.6 | 5 |
| 600 | 14 | 0 | 25.8 | 17 | 17.5 | 16.2 | 6.5 |

The limiting current density in a electrochemical system under given conditions can generally be determined from a Cowan-Brown plot, which is a graph of the reciprocal of the current *vs.* voltage divided by current *i.e.* resistance (Cowan and Brown 1957). The plot slope radically changes when the limiting current density is reached as the resistance of the cell increases rapidly. Due to the high concentrations of the salts present in the simulated spent EN bath it was not possible to determine the limiting current density without exceeding the current density range for the ion selective membranes and the power supply. However, a graph of the % removal of anions *vs*. time (see Figure 3) does show that above a current density of 400 mA cm$^{-2}$, the % removal of the lower concentration components (hypophosphite, propanoic and succinic acid) either reaches a plateau or decreases while % removal of the higher concentration components (orthophosphite and sulfate) continues to increase. It is likely that the limiting current density for the lower concentration components (which happen to be the components we wish to keep in the bath) is approximately 200-400 mA cm$^{-2}$ and the limiting current density for orthophosphite and sulfate (and sodium) is above 600 mA cm$^{-2}$. It is apparent that by operating at a higher current density one could optimize the permselectivity of the electrodialysis cell for the bath contaminants over the valuable bath components. This is clearly shown in Figure 4 which shows that operating at a high current density has the advantage of not only increasing the total amount of ions removed but will also favor the permselectivity of orthophosphite and sulfate over the other bath anions. In a similar manner to orthophosphite and sulfate the removal of sodium ions increases linearly with current density from 4 % removal at 100 mA cm$^{-2}$ to 20 % removal at 600 mA cm$^{-1}$. At all operating conditions the % removal of sulfate is low in comparison to the other bath anions; it is likely that low sulfate removal in the presence of these other EN bath anions is a feature of the Tokuyama Neosepta® ACM membrane.

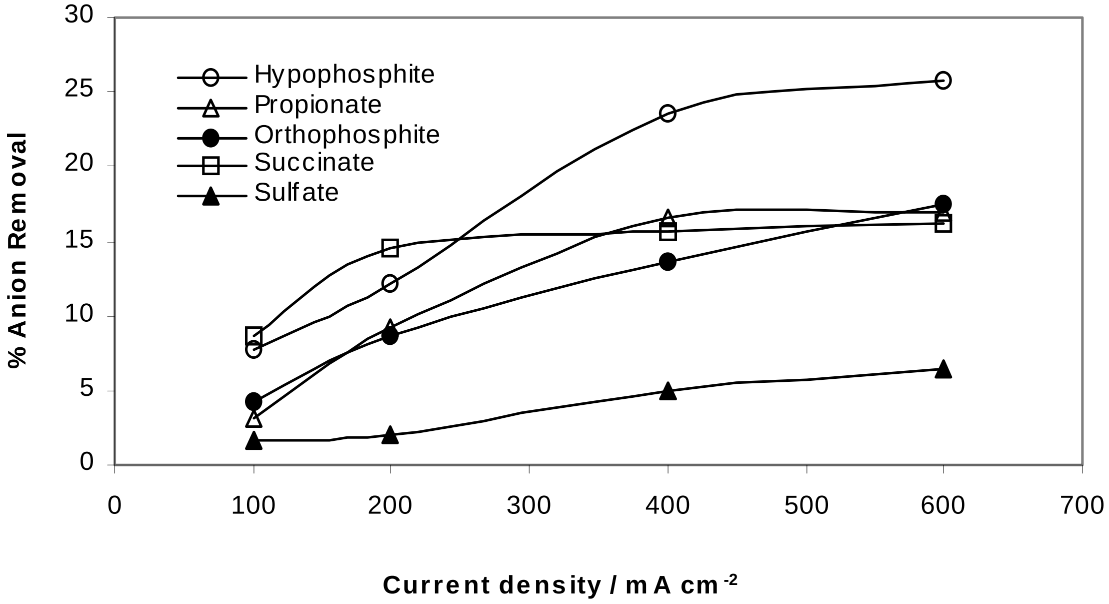

*Figure 3 The percentage of each anion removed from the EN bath as a function of current density on electrodialysis at 2 L min$^{-1}$, pH 4.5 and room temperature*

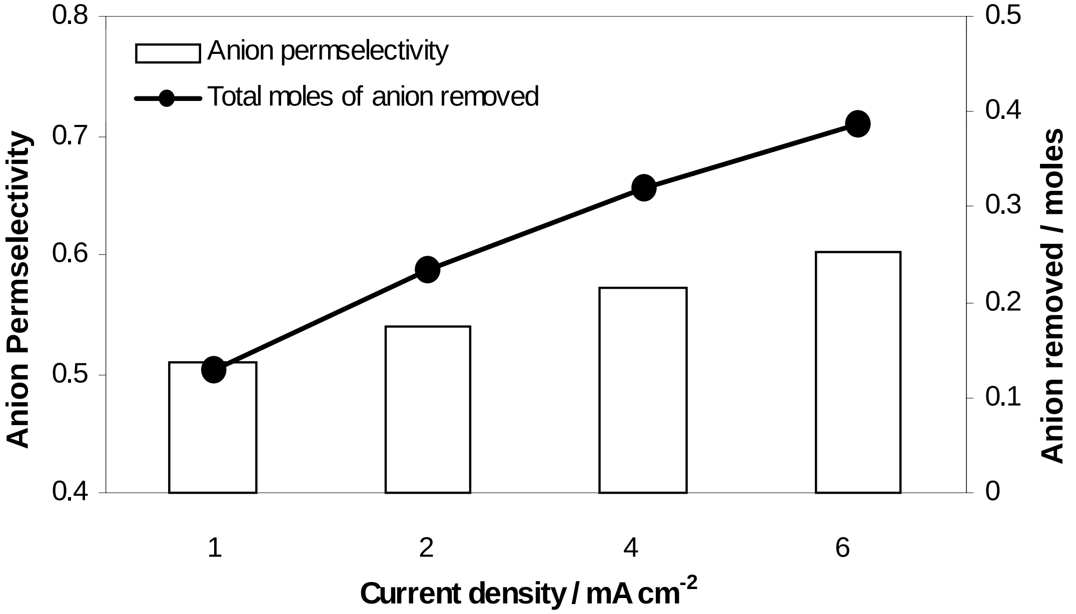

*Figure 4 The total anion permselectivity and total moles of anions removed at different current densities on electrodialysis at 2 L min$^{-1}$, pH 4.5 and room temperature*

## Bath pH

*Table 4 The % removals of cations and anions from a simulated spent EN bath on electrodialysis at different pHs at a flow rate of 2 L min$^{-1}$, current density of 400 mA cm$^{-2}$ and at room temperature.*

| pH | $Na^+$ | $Ni^{2+}$ | $H_2PO_2^-$ | $C_3H_5COO^-$ | $H_2PO_3^-$ | $C_2H_4(COO^-)_2$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| 2.0 | 11.5 | 0 | 9.1 | 2.6 | 10 | 6.6 | 1.7 |
| 3.0 | 13.4 | 0 | 10.6 | 3.7 | 9.3 | 8.3 | 2.6 |
| 4.5 | 14.1 | 1.1 | 23.6 | 16.6 | 13.6 | 15.6 | 5 |
| 5.0 | 12.5 | 0 | 21.4 | 16.8 | 9.9 | 17.3 | 2.3 |

The graph of % removals of the five bath anions as a function on pH in Figure 5 reveals that the pH of the bath has a significant effect on the efficiency of anion removal. In all cases the % removals of all anions are at or close to their highest at the normal bath pH of 4.5. An increase in pH to pH 5 results in decrease in the % removal for the anions except for propanoic and succinic acid. The p*Ka* of propanoic and succinic acid are 4.86 and 4.16 respectively, so an increase in pH from 4.5 to 5 will produce increased amounts of the dissociated form of the acid and will result in greater % removal of the organic acids. Hypophosphorus acid and orthophosphorus acid on the other hand are strong acids (p*Ka* of 1.1 and 1.3 respectively) and are fully dissociated at pH 4.5 and 5 although this does not explain the decrease in % removal from pH 4.5 to 5 for these anions. At the lower pHs of 2 and 3 the organic acids are likely to undergo protonation as borne out by their low % removal from the bath at these pHs. The % removal of the hypophosphite ion from the bath is halved on decreasing the pH from pH 4.5 than pH 3; in comparison the reduction in % removal of orthophosphite is much less. The reduction in % removals of the anions at the lower pHs is likely to be a consequence of preferential transfer of protons across the anion selective membrane due to the higher concentration of hydrogen ions. This is supported by the fact the pH of the center compartment tended to gradually decrease over time at pH 2 and pH 3. The % removal of sodium from the bath is relatively constant compared to the anion removal on changing the pH from pH 2 to pH 5; this may be expected given that $Na^+$ will be unaffected by protonation at the lower pHs.

The total permselectivity of the anions and of orthophosphite/hypophosphite at different pHs are shown in Figure 6. There is an almost linear increase in the total anion permselectivity on decreasing the pH from pH 5 to pH 2 *e.g.* at pH 2 the total anion permselectivity is 1.14 and there is preferential removal of orthophosphite over hypophosphite (orthophosphite/hypophosphite permselectivity is 1.1). It is apparent that by simply decreasing the pH from 4.5 one can improve the electrodialysis permselectivity for the bath contaminants and reduce losses of valuable EN bath components in the system.

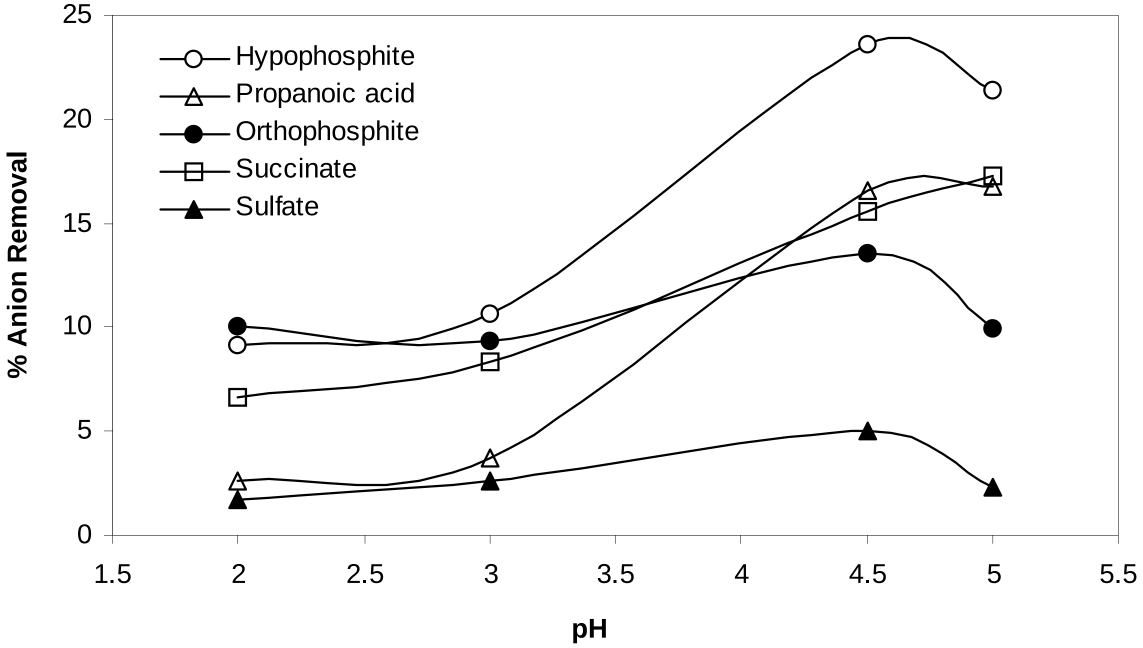

*Figure 5 The percentage of each anion removed from the EN bath as a function of pH on electrodialysis at 2 L min$^{-1}$, current density of 400 mA cm$^{-2}$ and room temperature*

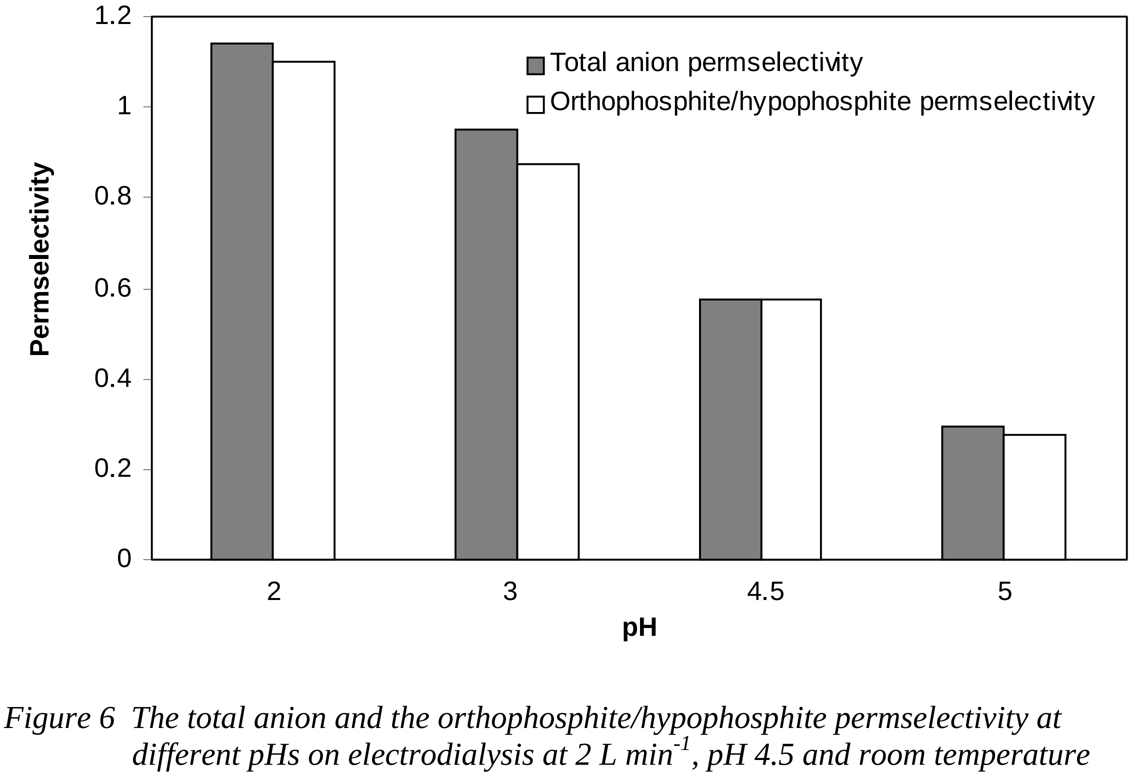

*Figure 6 The total anion and the orthophosphite/hypophosphite permselectivity at different pHs on electrodialysis at 2 L min$^{-1}$, pH 4.5 and room temperature*

## Flow rate

*Table 4 The % removals of cations and anions from a simulated spent EN bath on electrodialysis at different flow rates at a current density of 400 mA cm$^{-2}$, pH 4.5 and at room temperature.*

| Flow rate / L min$^{-1}$ | $Na^+$ | $Ni^{2+}$ | $H_2PO_2^-$ | $C_3H_5COO^-$ | $H_2PO_3^-$ | $C_2H_4(COO^-)_2$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| 0.5 | 13.4 | 0 | 18.6 | 11.2 | 11 | 12 | 2.4 |
| 2.0 | 14.1 | 1.1 | 23.6 | 16.6 | 13.6 | 15.6 | 5 |
| 4.0 | 13.9 | 0 | 24.4 | 19.6 | 15 | 19 | 6 |
| 10.0 | 12.5 | 0 | 26 | 25.5 | 19.5 | 27.6 | 6.6 |

Electrodialysis trials were carried out at flow rates of 0.5, 2 and 10 L min$^{-1}$; the cross-sectional area of the electrodialysis frame was 0.0012 m$^2$ so these flow rates correspond to velocities of 0.0069, 0.027 and 0.139 m$^2$ s$^{-1}$. Manufacturers of sheet-flow electrodialysis stacks have determined the optimum flow velocity in an electrodialysis stack to be about 0.05 m s$^{-1}$ (Davis *et. al.* 1997) so the flow rate/velocity range in this work was chosen to encompass this optimum velocity. The % removal of the EN bath anions on electrodialysis as a function of flow rate is shown in Figure 7. The % removal of all the anions in the bath increases with increasing flow rate. This is in accordance with electrochemical theory that an increase in flow velocity will reduce the boundary layer thickness at the membrane, decrease polarization and increase the limiting current density. Except for succinate, the % removal of the anions as a function of flow rate is not linear; it increases sharply from 0.5 to 2 L min$^{-1}$ and then increases more slowly from 2 to 10 L min$^{-1}$. This is in agreement with the earlier statement that the optimum flow rate for the cell is around 2-4 L min$^{-1}$ (velocity of 0.027 – 0.054 m$^2$ s$^{-1}$). In addition, it was found that at a flow rate of 10 L min$^{-1}$ the membrane lifetime was shorter and there was more likelihood of hydraulic transfer of water across the membranes over time due to the higher pressures in the cell.

The effect of flow rate on the anion permselectivity of the membrane is shown in Figure 8 along with the total anion removal (moles) with flow rate. Although it is not clear from Figure 8 (as the x-axis is not linear), there is a linear relationship between the total removal of anions from the bath and flow rate. However it is apparent from Figure 8 that the total anion permselectivity of the membrane is independent of the flow rate *i.e.* the flow rate merely increases the flux of anions through the membrane but does not improve the transport of one anion over another.

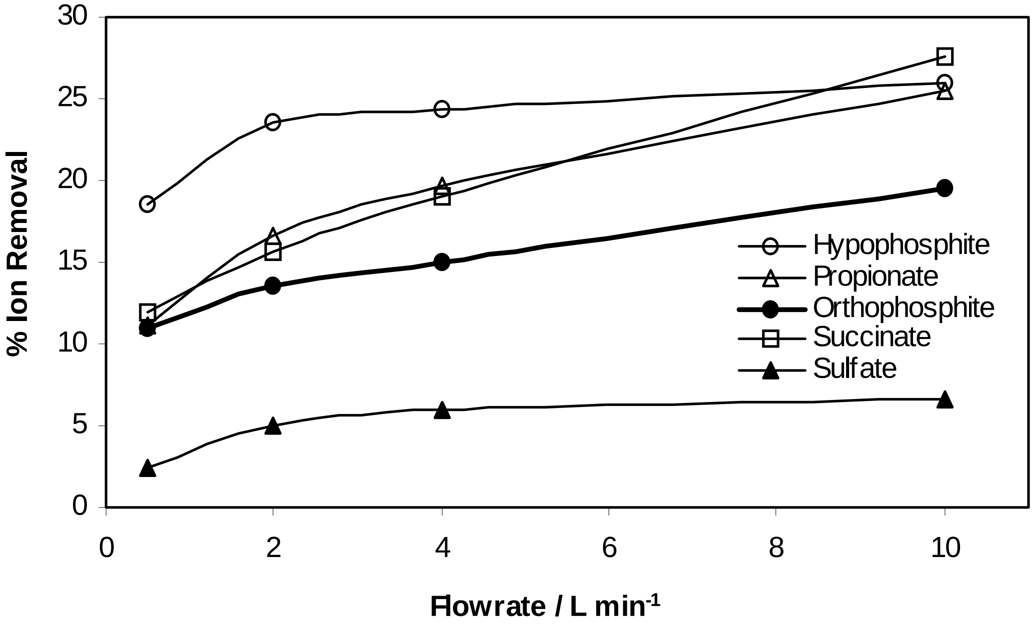

*Figure 7 The percentage of each anion removed from the EN bath as a function of flow rate on electrodialysis at pH 4.5, current density of 400 mA cm$^{-2}$ and room temperature*

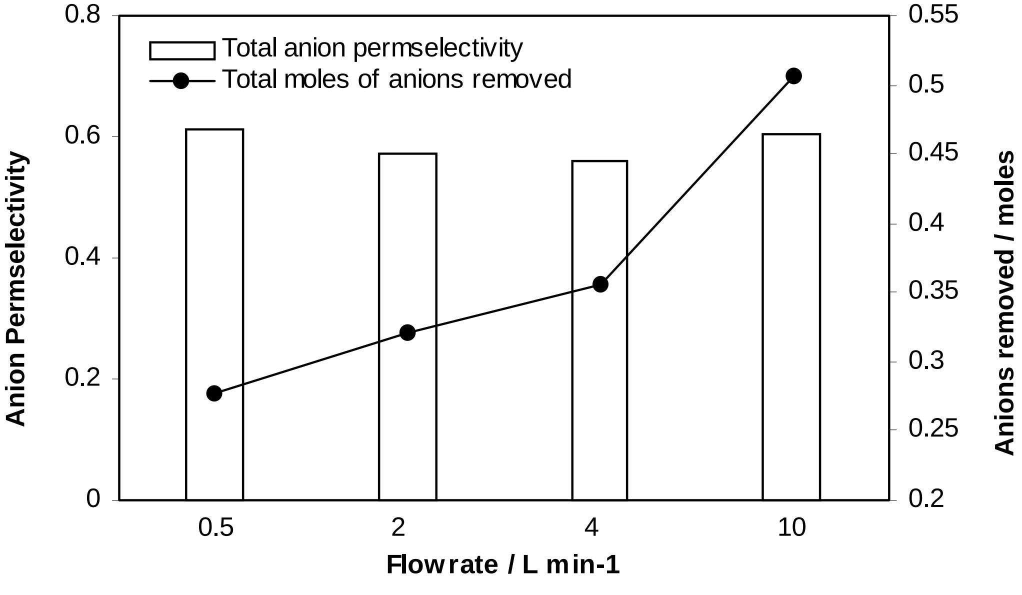

*Figure 8 The total anion permselectivity and total moles of anions removed at different flow rates on electrodialysis at a current density of 400 mA cm-1, pH 4.5 and room temperature*

## Temperature

*Table 5 The % removals of cations and anions from a simulated spent EN bath on electrodialysis at 20 $^0$C and 40 $^0$C at a flow rate of 2 L min$^{-1}$, current density of 400 mA cm$^{-2}$ and pH 4.5.*

| Temperature / $^0$C | $Na^+$ | $Ni^{2+}$ | $H_2PO_2^-$ | $C_3H_5COO^-$ | $H_2PO_3^-$ | $C_2H_4(COO^-)_2$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| 20 | 14.1 | 1.1 | 23.6 | 16.6 | 13.6 | 15.6 | 5 |
| 40 | 13.3 | 0 | 17.1 | 7 | 13 | 20.7 | 5.2 |

An increase in temperature in an electrochemical system usually enhances mass transport rates to electrodes and membranes *via* a combination of decreased solution viscosity and increased diffusion coefficients. However, in this work, we did not find that there was a significant increase in ion mass transport rates on increasing the temperature of the EN solutions and anolyte/catholyte from 20 $^0$C to 40 $^0$C (see Table 5). In fact the % removals for the hypophosphite anion and propanoic acid are lower at 40 $^0$C than at 20 $^0$C. In the case of the organic and phosphorus based acids an increase in temperature will have an effect on the acid dissociation constant ($Ka$) that is dependent on the Gibb's free energy change ($\Delta G$) on proceeding from undissociated to dissociated forms of the acid. The free energy change is different for each acid and may account for the variability in % removal rates for the acids. The sodium ion (and probably the sulfate ion) are unaffected by these free energy changes but the removal rates still do not increase on raising the temperature from 20 $^0$C to 40 $^0$C. The total moles of anions removed at 40 $^0$C (0.3 moles) is not significantly different from that at 20 $^0$C (0.32 moles) but the total anion permeability does change from 0.57 at 20 $^0$C to 0.93 at 40 $^0$C. It is therefore possible improve the total anion permeability in favor of the removal of the bath contaminants by operating the cell at a higher temperature. This would not be a significant inconvenience or cost for a plating shop as the electroless nickel baths are operated at temperatures in excess of 40 $^0$C.

## Current Efficiency

In large-scale electrodialysis, the energy consumed in the process is a critical factor and in trying to minimize the energy required one should attempt to maximize the current efficiency (see Eqn. 3). The current efficiency of the electrodialysis trials at different current densities, flow rate, pH and temperature are presented in Figure 9. It is apparent from Figure 9 that the cation current efficiency does not fluctuate as greatly as the anion current efficiency between different operating conditions. At different current densities both the cation and anion current efficiencies fall off as the current density is increased from 100 to 600 mA cm$^{-2}$. Although increasing the current density will increase the amount of ions removed from the spent EN bath one does has to sacrifice a loss in the cell current efficiency. By increasing the flow rate from 0.5 to 10 L min$^{-1}$ one can almost double the anion current efficiency as the higher velocity will increase the total mass removal of anions for the same applied electrical charge (see Figure 8). Operating the system at different pHs and temperatures produces only slight changes in both the anion and cation current efficiency.

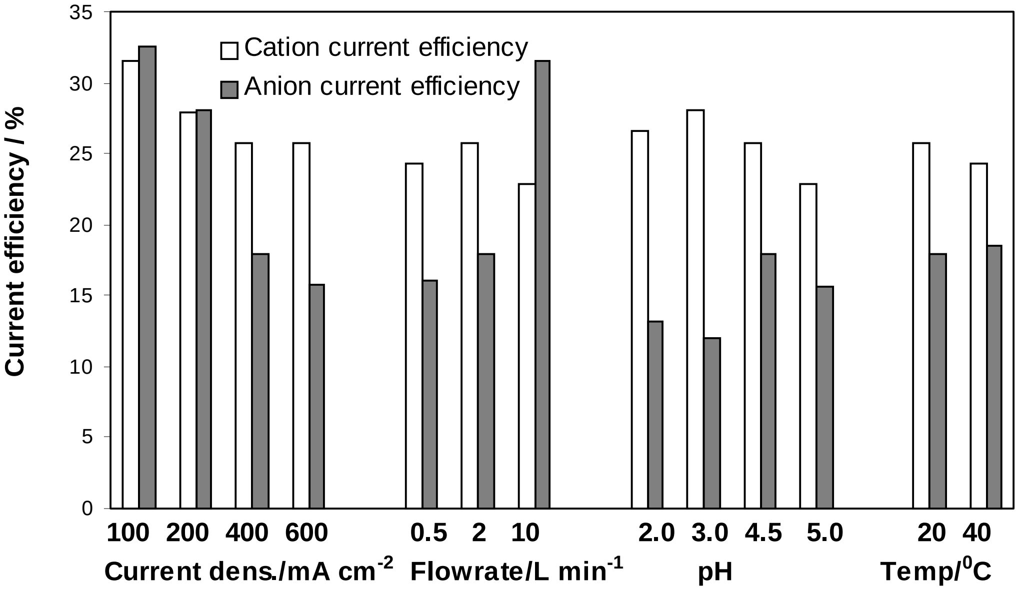

*Figure 9 Cation and anion current efficiency at different current densities, flow rate, pH and temperature in the electrodialysis cell*

## Conclusion

The research conducted by our laboratory on optimizing electrodialysis for the rejuvenation of electroless nickel baths has thus far shown that by varying fundamental operating parameters such as current density, flow rate, pH and temperature, one obtains very different ion removal rates and cell permselectivities. Given the variation in the effectiveness of the electrodialysis technique there is clearly an optimum set of conditions under which to operate the cell which will result in reduced losses of the valuable bath components and improved cell cost-effectiveness. We intend to continue these investigations in our laboratory to further our understanding of EN bath ion removal along with carrying out a comparative study on the effectiveness of a range of ion selective membranes and cell configurations. On completion of this study we hope to transfer the electrodialysis cell to a local plating shop for utilization on an actual spent electroless nickel bath.

## Acknowledgements

This research was supported by an appointment to the Postgraduate Research Participation Program at the National Risk Management Research Laboratory administered at the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the U.S. Environmental Protection Agency.

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