The optimisation of nickel extraction with the use of supported liquid membrane capsules

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Abstract

In a previous publication the authors described the investigation and characterisation of a new approach to supported liquid membranes, whereby the strip solution is encapsulated within a microporous membrane capsule. The research in this article is a continuation of the earlier article and focuses on the influence of the hydronium ion concentration of the strip solution on the extraction of nickel, as well as the influence of temperature, agitation and ligand enhancement on the extraction process. The optimum conditions for the extraction of nickel with the use of capsuled membrane extraction were determined. Extraction of approximately 109 g/m² was obtained at an initial rate of 44.7 g/m²·h. It was estimated that the membrane capsules would have to be recycled at least 14 times to break even under current economic conditions.

Abbreviations

AA	Atomic absorption spectrophotometer
A_{mem}	Area of membrane capsule
Cir_{mem}	Circumference of membrane capsule
D	Impeller diameter (m)
D2EHPA	Di-2(ethylhexyl) phosphoric acid
Ex	Extractant
Extr	Extraction of nickel
Rate	Rate of nickel extraction
SLM	Supported liquid membranes
CME	Capsuled membrane extraction
μ	Viscosity (N s/m²)
ρ	Density (kg/m³)
ω	Rate of rotation

Introduction

In an earlier publication (Smit and Koekemoer, 1996) a new approach to supported liquid membranes was described, whereby the strip solution is encapsulated within a microporous membrane capsule. In that publication the research had been focused on the extraction of nickel at high hydronium strip concentrations, which is a major advantage of CME over SLM. This led to a better understanding of this extraction method, but certain questions still remained, e.g.:

- What is the optimum hydronium ion concentration for the strip solution?
- What is the influence of temperature on the extraction of nickel with CME?
- What is the influence of feed solution agitation on the extraction of nickel with CME?
- Will different anion ligands enhance the extraction of nickel with CME?

The research in this article was focused on answering these questions and on finding the optimum conditions for the extraction of nickel with the use of CME. Such optimisation should facilitate the determination of the techno-economic feasibility of this extraction technique.

Experimental

The membrane capsule

A membrane in capsule configuration was used for the experiments (Erlank, 1984). The membrane was folded double and a hot wire sealer was used to seal all the edges, except one. The capsule was then impregnated by leaving the capsule in the extractant and allowing the extractant to permeate into the membrane pores. The excess extractant (on the outside) was removed by blotting. The capsule was filled with strip solution at the open edge and then completely sealed. The capsules varied in size, but had an average diameter of approximately 40 mm (Fig. 1). The average contact area of a membrane capsule was approximately 26 cm². A string was used to keep the capsule suspended in the bulk aqueous feed solution (cf. Photograph 1). It was vital that the sealed edges of the capsule did not leak since that would defeat the integrity of the extraction system. The membrane used for the experiments was Celgard® 4510 film, manufactured by Celanese Separations Products. Di-2(ethylhexyl) phosphoric acid (D2EHPA) was used as an extractant.
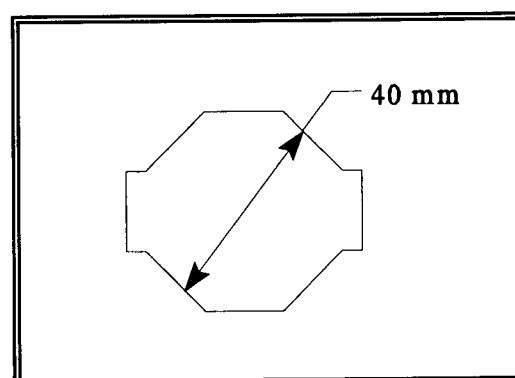

Figure 1
Diagram of membrane capsule

TABLE 1 TYPICAL RESULTS		
Time (h)	$[Ni]_{feed}$ (mg/dm^3)	pH_{feed}
0.00	1022	4.5
2.95	970	3.42
5.10	977	3.5
6.92	957	3.82
10.78	913	3.37
16.17	880	3.13
24.18	860	3
27.87	799	3.28
35.30	725	3.08
50.87	708	2.81

Photograph 1
Experimental configuration

Experimental method

An experiment involved filling a beaker with a feed solution of known pH and concentration. A capsule was prepared with a certain extractant concentration and was filled with a strip solution at a certain hydronium concentration. The capsule was suspended in the feed solution, using a piece of string (Photograph 1). A thermally controlled water bath was used to minimise the effect of temperature variation.

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to the initial pH at these sampling points with a diluted sodium hydroxide solution. The nickel concentration was not readjusted. Typical experimental results may be seen in Table 1, showing the variation of the pH and the nickel concentration of the feed solution with time.

The area of the membrane capsule was approximated to be the area of a circle with the same circumference as the membrane capsule:

$$A_{mem} = \frac{1/2(Cir_{mem})^2}{\pi}$$ (1)
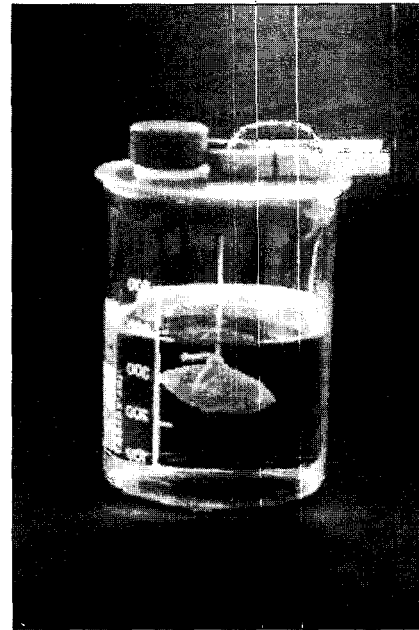
Mathematical background

The above-mentioned information was used to calculate the extraction of nickel (in mg/m^2 of membrane) at the different time intervals. This data were used to fit the following equation, using the method of least squares:

$$Extr_{Ni} = a - be^{-ct}$$ (2)

In this equation a, b and c are constants for every experiment. A selected example of such a curve fit may be seen in Fig. 2, using a set of experimental results.

The maximum extraction for each experiment can be obtained from Eq. (2) by calculating $Extr_{Ni}$ at $t = \infty$ and by subtracting $Extr_{Ni}$ at $t = 0$:

$$
\begin{aligned}
Extr_{max} &= Extr_{Ni,\infty} - Extr_{Ni,0} \\
&= (a - be^{-\infty}) - (a - be^{-c0}) \\
&= (a - b(0)) - (a - b(1)) \\
&= (a) - (a - b) \\
&= b
\end{aligned}
$$ (3)

Exp. no. C 2 a
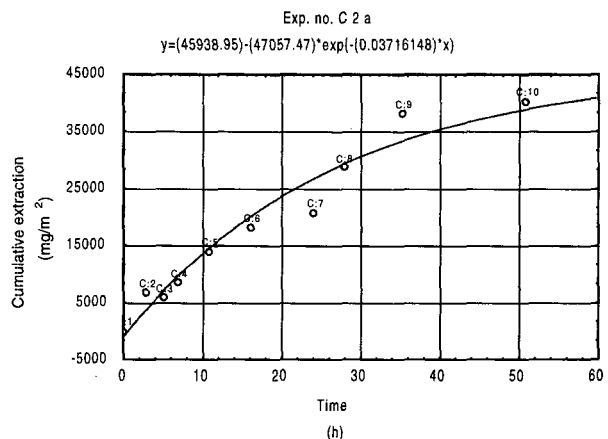y=(45938.95)-(47057.47)*exp(-(0.03716148)*x)

Figure 2
*Cumulative extraction as a function of time
(example curve fit)*

The initial rate of extraction can be obtained by differentiating Eq. 2:

$$
\begin{aligned}
Rate &= d/dt \, (a - b \, e^{-ct}) \\
&= b \, c \, e^{-ct} \\
If \quad t &= 0: \\
Rate &= b \, c(1) \\
&= b \, c
\end{aligned}
$$ (4)

Results and discussion

The hydronium ion concentration of the strip solution

It was shown in the previous publication (Smit and Koekemoer, 1996) that osmosis has a negative effect on the extraction of
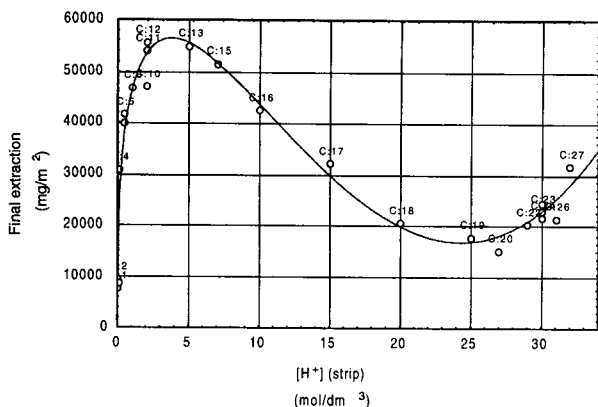
Figure 3
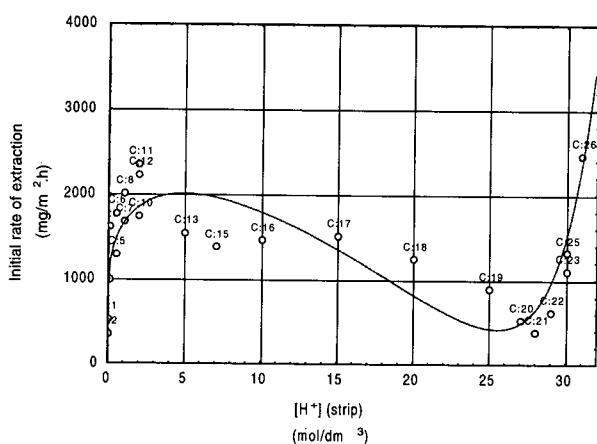The effect of $[H^+]_{strip}$ on the final extraction of nickel

Figure 4
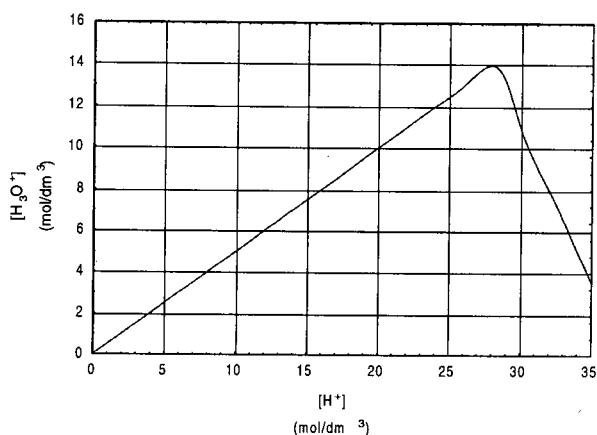The effect of $[H^+]_{strip}$ on the initial rate of extraction

Figure 5
Calculated $[H_3O^+]$ at different H_2SO_4 concentrations
(expressed as $[H^+]$)

nickel with CME. Osmosis has the additional disadvantage that it dilutes the hydronium ion concentration of the strip solution (the main driving force of CME). The conclusion was drawn that an optimum hydronium ion concentration is necessary in the strip solution. It is vital to establish this optimum point quantitatively before any applications of CME will be possible in industry.

Several experiments were conducted with a strip solution, using different hydronium ion concentrations of the strip solution. The graphical representations of the influence of the hydronium ion concentration of the strip solution on the final extraction and initial rate of extraction may be seen in Figs. 3 and 4, respectively. As anticipated, an optimum hydronium ion concentration in the strip solution is necessary. The final amount of extraction and initial rate of extraction increases when the hydronium ion concentration of the strip solution is increased. Maximum extraction of nickel occurs at approximately 4 mol/dm³·a. If the hydronium ion concentration of the strip solution is increased further, the osmotic pressure becomes greater than the hydrophobicity of the liquid membrane and osmosis occurs. This has a negative effect on the extraction process. The extraction of nickel decreases and there is a large loss of hydronium ions. The hydronium ions are extremely mobile and they migrate to the feed solution as soon as osmosis occurs. The osmotic effect can also result in the transport of contaminants to the strip solution in an industrial application, due to so-called hydraulic short-circuiting.

The osmotic effect reaches a maximum at a hydronium ion concentration of approximately 25 mol/dm³. If the concentration of the sulphuric acid is increased further, the acid does not dissociate completely and the undissociated acid forms a hydronium ion reserve. The hydronium ion concentration in these experiments is given as hydronium ions available if H_2SO_4 dissociates completely. The actual hydronium ion concentration may be calculated with the use of dissociation constants. It is generally accepted that the diprotonic H_2SO_4 dissociates in two steps (Cruywagen et al., 1981):

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^{2-}$$
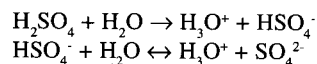
The first step is a complete dissociation, but the second step is only a partial dissociation with the following dissociation constant:

$$Ka_{HSO4-} = 2.162 \times 10^{-4} = \frac{[H_3O^+][SO_4^{2-}]}{[H_2O][HSO_4^-]}$$

The H_2SO_4/H_2O system is an equimolar solution at a concentration of 14 mol/dm³ H_2SO_4. In other words, if the sulphuric acid concentration is lower than 14 mol/dm³, the solution consists of H_2SO_4 diluted in water. However, if the H_2SO_4 concentration is higher than 14 mol/dm³, the solution consists of water diluted in H_2SO_4. The concentration of the hydronium ions may be calculated from the stoichiometric reactions and the dissociation constant. Figure 5 shows the hydronium ion concentration at different H_2SO_4 concentrations (expressed as $[H^+]$).

The observed turning point for the osmotic effect in the experiments occurs at a hydronium ion concentration of approximately 25 mol/dm³ (which is less than the 28 mol/dm³ reflected in Fig. 3). This can be explained by the fact that the hydronium ion concentration of the strip solution is diluted as soon as osmosis occurs. A comparison of the results between this set of experiments and the experiments in the previous article, for the final extraction, may be seen in Fig. 6. The values of the final
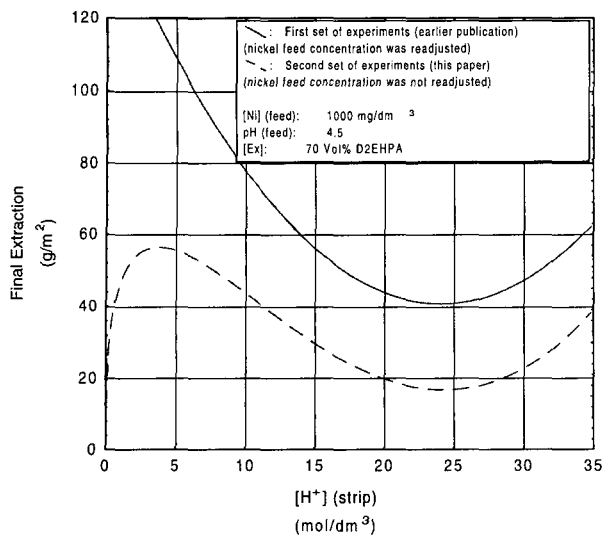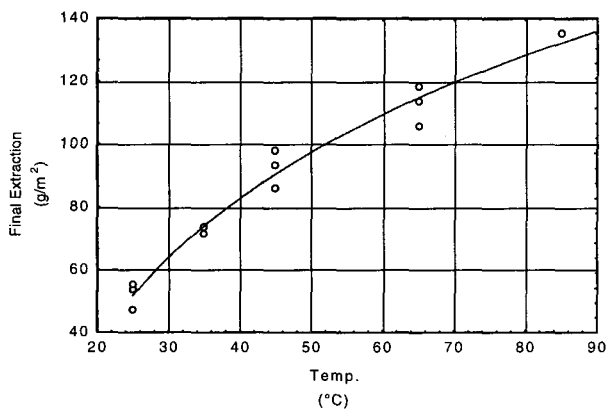
Figure 6
Comparison between two sets of experiments

Figure 7
The influence of temperature on the final extraction of nickel
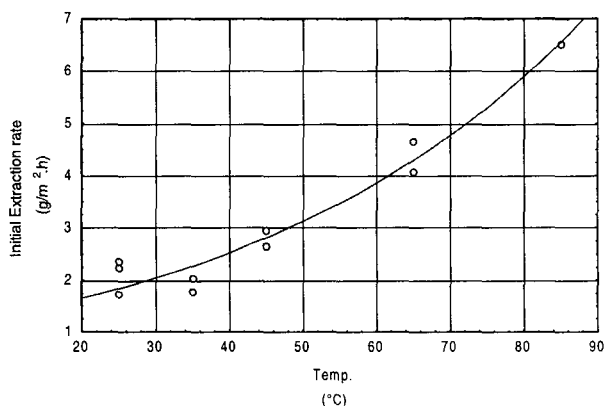

Figure 8
The influence of temperature on the initial rate of extraction

extraction for the experiments in the earlier publication are higher than this set of experiments, because the nickel concentration of the feed solution was not readjusted to the initial concentration in the latter case. It is clear, however, that the general form of the graphs and the minimum final extraction points of are identical for the two sets of experiments.

The optimum hydronium ion concentration is very important for any industrial applications of CME and it may be concluded from Fig. 6 that the optimum hydronium ion concentration is approximately 3.8 mol/dm³, for the current set of experiments.

The influence of temperature on CME

The graphical representation of the influence of the temperature of the feed solution on the final extraction and the initial rate of extraction may be seen in Figs. 7 and 8, respectively.

The final amount of nickel extracted with CME increased by 154% when the temperature is increased from 25°C to 85°C. The initial rate of extraction increased by 253% when the temperature is increased from 25°C to 85°C. This confirms the suspicion, expressed in the previous publication, that the initial rate of extraction is more dependent on temperature, than the final extraction of nickel.

The influence of agitation on CME

A factor which was not investigated previously is the influence of agitation on the extraction of nickel. Hofman (1991) did research on the influence of agitation on SLM and found that the rate of extraction increased up to a Reynolds number of 7 000. A further increase in the agitation had little or no effect on the rate of extraction. This may be explained by the fact that at low agitation the liquid boundary layer of the feed solution is relatively large. If the agitation is increased, this boundary layer becomes thinner and results in a lower resistance to ion transport through the membrane, which implies that this resistance to mass transfer is then not the controlling resistance.

The rotational speed of the impeller was measured with a digital tachometer. The Reynolds number of the feed solutions was calculated with the following equation (Bird et al., 1960):

$$Re = \frac{D^2 \omega \rho}{\mu} \tag{6}$$

In this equation D is the diameter of the impeller, ω is the rate of rotation, ρ is the density of the feed solution and μ is the viscosity of the feed solution.

The graphical representation of the influence of the agitation of the feed solution on the final extraction and the initial rate of extraction may be seen in Figs. 9 and 10 respectively.

The final amount of nickel extracted with CME increased by 61% and the initial rate of extraction increased by 88% if the feed solution is agitated vigorously.

The most dramatic increase occurred when the Reynolds number of the feed solution is increased from 0 to ± 9000. This result correlates well with the result obtained by Hofman (1991) for SLM systems.

The influence of anion ligands on CME

Gu and Wasan (1986) found that SLM extraction can be enhanced by the addition of anion ligands to the feed solution.They tested several ligands and found that acetate gave the best results. The

optimum acetate concentration was found to be 0.10 mol/dm³. The authors of this paper suspected that the same enhancement would apply to CME.

The graphical representation of the influence of anion ligands in the feed solution on the final extraction and the initial rate of extraction may be seen in Figs. 11 and 12, respectively.

It is clear from Figs. 11 and 12 that calcium acetate inhibits the extraction of nickel with CME, while sodium acetate enhances the extraction. This can be explained by the fact that the divalent calcium acetate is a much larger ion than the monovalent sodium acetate. This larger ion causes a steric hindrance in the ligand-accelerated mechanism proposed by Gu and Wasan (1986). The reduction of nickel extraction due to this hindrance can be as high as 92% for the final extraction of nickel and 78% for the initial rate of nickel extraction.

The addition of sodium acetate did enhance the extraction of nickel with CME. The optimum acetate concentration was found to be ±0.05 mol/dm³ for the final extraction and ±0.10 mol/dm³ for the initial rate of extraction. These results correlate with the results obtained by Gu and Wasan (1986).

The addition of sodium acetate to the feed solution resulted in a maximum enhancement of 63% in the final extraction of nickel and an extremely high enhancement of 218% in the initial rate of nickel extraction.

The optimum extractant concentration

The optimum conditions for the extraction of nickel with CME were determined in the sections above. It was shown in Smit and Koekemoer (1996) that the optimum extractant concentration is heavily dependent on other factors. It is thus necessary to determine the optimum extractant concentration under these optimum extraction conditions.

A graphical representation of the influence of the extractant concentration on the final extraction and the initial rate of extraction may be seen in Figs. 13 and 14, respectively.

The optimum extractant concentration for the final extraction of nickel is approximately 70 vol.% D2EHPA dissolved in Escaid 100. The optimum extractant concentration for the initial rate of extraction is approximately 60 vol.% D2EHPA dissolved in Escaid 100. It is clear that the maximum nickel which can be extracted with CME is 109 g/m². This is equivalent to R3.46/m², using the current nickel price. The membranes used cost approximately US$10/m² (R45.65/m²). This implies that the membrane capsules should be recycled at least 14 times to show a profit under these circumstances.

The time needed to extract 90% of the nickel can be calculated from Eq. (2):

$$Extr_{Ni} = b(1 - e^{-ct})$$
$$\therefore 0.9\, b = b(1 - e^{-ct})$$
$$\therefore 1 - e^{-ct} = 0.9$$
$$\therefore -ct = \ln 0.1$$
$$\therefore t = -\frac{\ln 0.1}{c}$$

and amounts to 3.45 h when the extractant concentration is 60 vol% D2EHPA.

Conclusions

The research in this article was focused on clarifying the remaining uncertainties of CME and to find the optimum extraction conditions
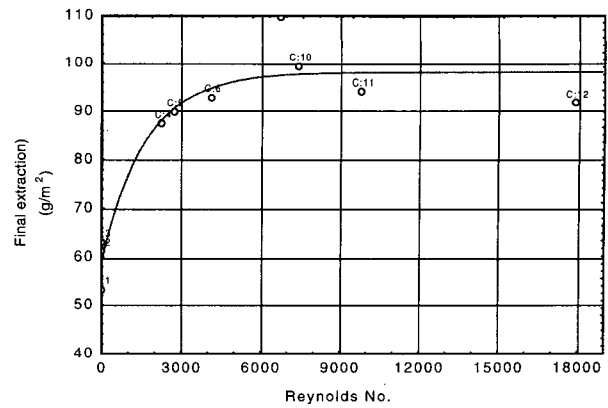

Figure 9
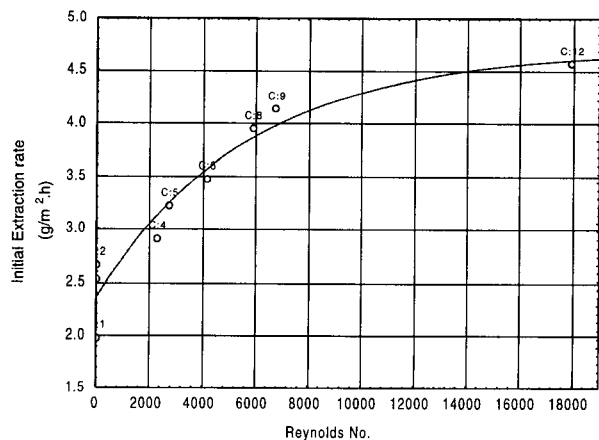The influence of agitation on the final extraction of nickel

Figure 10
The influence of agitation on the initial rate of extraction
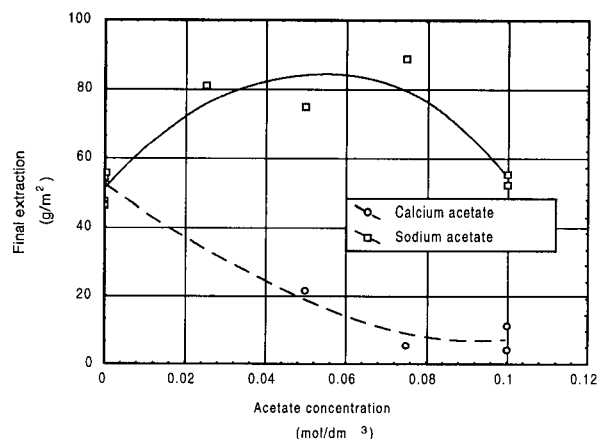

Figure 11
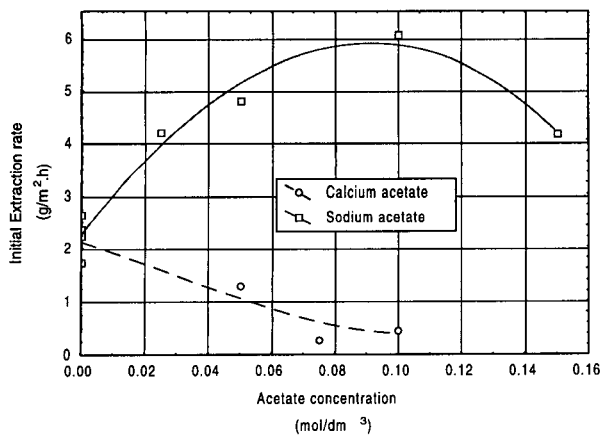The influence of anion ligands on the final extraction
of nickel

Figure 12
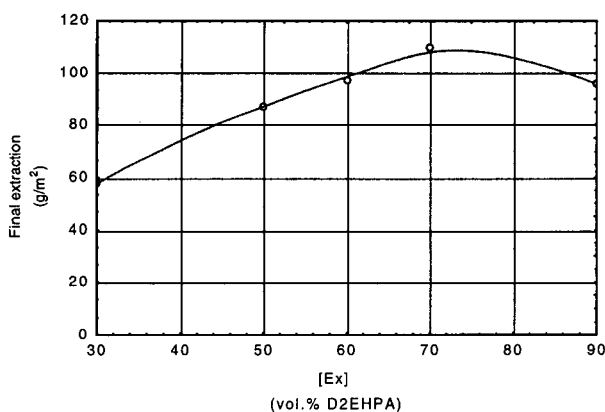*The influence of anion ligands on the initial rate of extraction*

Figure 13
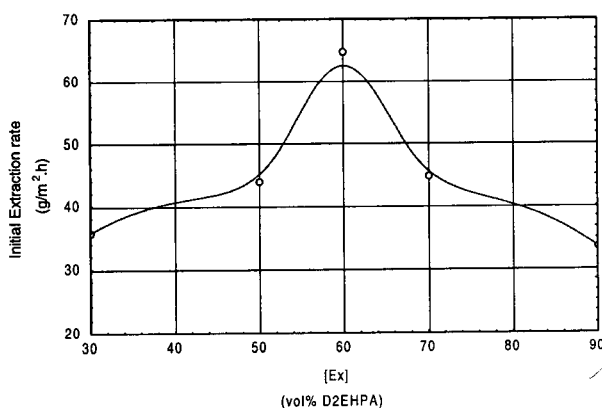*The influence of [Ex] on the final extraction of nickel*

Figure 14
The influence of [Ex] on the initial rate of nickel extraction

for CME. The following conclusions may be drawn from the results obtained:

• The final amount of extraction and initial rate of extraction increased when the hydronium ion concentration of the strip solution was increased. At approximately 4 mol/dm³ a maximum extraction of nickel occurs.

• The hydronium ion concentration of the strip solution was increased further, the osmotic pressure became greater than the hydrophobicity of the liquid membrane and osmosis occurred. This had a negative effect on the extraction process. The extraction of nickel decreased and there was a large loss of hydronium ions.

• This osmotic effect could also result in a transport of contaminants to the strip solution due to so-called hydraulic short-circuiting.

• The final amount of nickel extracted with SLM increased by 154% and the initial rate of extraction by 253% when the temperature was increased from 25°C to 85°C.

• The final amount of nickel extracted with CME increased by 61 % and the initial rate of extraction increased by 88% when the feed solution was agitated vigorously.

• The most dramatic increase occurred when the Reynolds number of the feed solution was increased from 0 to approximately 9 000.

• Calcium acetate inhibited the extraction of nickel with CME, while sodium acetate enhanced this extraction.

• The optimum acetate concentration was approximately 0.10 mol/dm³ and resulted in a 63.5% improvement in the final extraction of nickel and a 218.9% improvement in the initial rate of extraction.

• The optimum extractant concentration was found to be approximately 60 vol% D2EHPA dissolved in Escaid 100.

• Under the above-mentioned optimum conditions, it was possible to obtain a final extraction of approximately 109 g/m² at a rate where 90% of the extraction occurred within the first 3.45 h.

• The membrane capsules would have to be recycled at least 14 times to break even under current economic conditions.

Acknowledgements

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