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

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Abstract

In the past few years there has been an increase in environmental awareness. This has forced industries to be more careful with the waste they generate. The cleaning and upgrading of metal-containing wastes have become a very demanding assignment. The reclamation of nickel from waste streams has the additional advantage that it is a very valuable metal and the process can be profitable. A new approach to supported liquid membrane extraction, whereby the strip solution is encapsulated within a microporous membrane capsule, was used for the experiments. The capsule constitutes an unconfined reactor and does not have the disadvantage of an excessively high cost to configure the required packing density (m^2/m^3). The capsule has the additional advantage that very high acid concentrations can be used in the strip solution without the risk of high corrosion.

The research shows that there is a correlation between the extraction of nickel with capsule membrane- and supported liquid membrane extraction, except at high acid strip concentrations, where osmosis occurs. Extraction of 95 g/m^2 was obtained at an initial rate of 10 g/m^2·h.

Nomenclature

AA	Atomic absorption spectrophotometer
A_{mem}	Area of membrane capsule
Cir_{mem}	Circumference of membrane capsule
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

Introduction

In the past few years there has been an increase in environmental awareness. This forced industries to be more careful with the waste they generate. The removal and upgrading of metal-containing waste have become not only a very demanding assignment but a lucrative business. The reclamation of nickel from waste streams is no exception. Nickel has the additional advantage that it is a very valuable metal (R32.38/kg (Anon., 1995)).

Supported liquid membranes represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions from solution. The permeation of metal species through SLMs can be described as the simultaneous extraction and stripping operation combined in a single stage. A thin layer of an organic extraction reagent (extractant) is immobilised in a microporous inert support. This support is interposed between the feed solution (aqueous phase), in which the valuable metal is dissolved and the second (stripping) phase, in which enrichment of the metal occurs by transmembrane diffusion (Erlank, 1994).

The biggest obstacle for the use of SLMs to extract ionic species is that the sophistication of the various SLM reactors implies high costs to manufacture, maintain and operate. The advantage of CME is that the concept of an unconfined reactor is introduced, which implies that no fixed geometry (reactor containment) is required. An unconfined reactor is thus not restricted to a certain location or geometry. The capsules can be transferred to a different location while extracting the nickel. The capsule has the additional advantage that very high acid or alkaline concentrations can be used in the strip solution without the risk of high corrosion to the reactor.

A big disadvantage of SLM is the loss of the extractant from the membrane structure. This is a minor problem with the extraction of nickel, because both the extractant (di-2(ethylhexyl) phosphoric acid) and the membrane (Celgard® 4510) are highly hydrophobic.

The purpose of this research was therefore to determine the influence of conditions like the pH and nickel concentration of the feed solution and the hydronium and nickel concentration of the strip solution on capsulated membrane extraction. Another objective was to determine the optimum extractant concentration and the influence of the above-mentioned conditions on this optimum. These results could be used to determine the similarity (if any) between CME and SLM.

Experimental

The membrane capsule

The 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 for one. The capsule was then impregnated by leaving the capsule in the extractant and allowing the extractant to load 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 dia. of approximately 40 mm (refer to Fig. 1). The average contact area of a membrane capsule is approximately 26 cm^2. A string was used to keep the capsule suspended in the bulk aqueous feed solution

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(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. Di-2(ethylhexyl) phosphoric acid (D2EHPA) was used as an extractant.

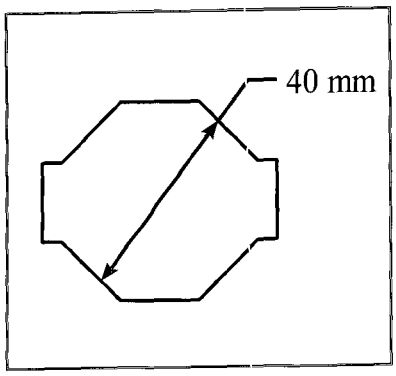
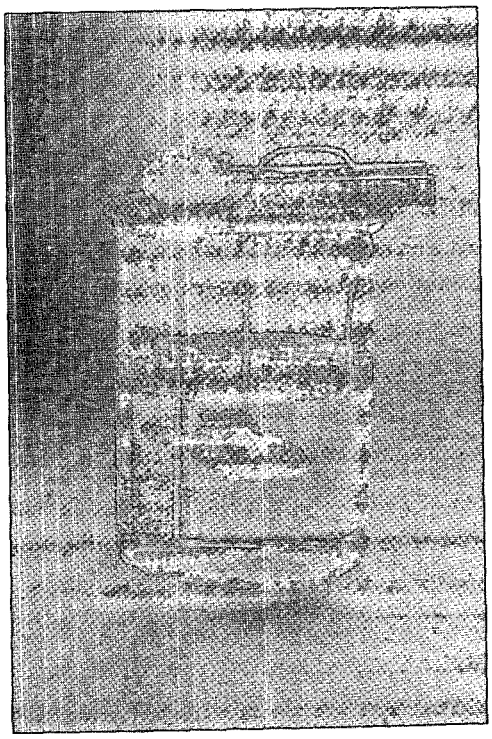


Figure 1
Diagram of membrane capsule



Photograph 1
Experimental configuration

Factorial design of experiment

A second-order central composite experimental design was performed to establish the conditions under which each experiment was to be performed. The purpose of the experimental design was to minimise the number of experiments that had to be performed. The factors and the range over which their variables were studied can be seen in Table 1. Forty-six different experiments were done at different combinations of variables.

Experimental approach

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 with a certain hydronium concentration. The capsule is suspended in the feed solution with a piece of string (see Photograph 1).

Samples were taken from the feed solution at 5 h intervals for the first 25 h with a micropipette. The pH of the feed solution was readjusted to the initial pH every 2 h the first 25 h of the experiment with a diluted sodium hydroxide solution. The nickel concentration was readjusted every 5 h (if extraction had occurred) to the initial feed nickel concentration with a 10 000 mg/dm^3 nickel solution. An example of the measuring results can be seen in Table 2.

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

$$A_{mem} = \frac{\frac{1}{2}(Cir_{mem})^2}{\pi} \qquad (1)$$

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 information was used to fit the following equation through the data, using the least squares method:

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

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

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

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

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

$$\begin{aligned} Rate &= \frac{d}{dt}(a - b\,e^{-ct}) \\ &= b\,c\,e^{-ct} \end{aligned}$$

TABLE 1
THE VALUES OF THE EXPERIMENTAL FACTORS

Factors	Variables					Units
pH (feed)	1.12	2.5	3.5	4.5	5.88	
[H] (strip)	1.351	11	18	25	34.649	Mol/dm^3
[Ni] (feed)	524	800	1000	1200	1475	mg/dm^3
[Ni] (strip)	0	689	1189	1689	2378.2	mg/dm^3
[Extractant]	48.1	55	60	65	71.9	Vol%

TABLE 2
AN EXAMPLE OF MEASURING RESULTS

Time (h)	$[Ni]_{feed}$ (mg/dm³)	Volume (feed solution) (dm³)	Adjustment with 10 g/dm³ [Ni] (dm³×10³)
0	1145	0.405	0.0
5	1010	0.400	0.0
10	912	0.395	3.0
15	962	0.390	1.0
20	1000	0.390	0.0
25	938	0.380	1.0
50	885	0.400	-

If t = 0:
Rate = b c(1)
= b c (4)

Results and discussion

The main effects and interaction of the different factors on the maximum (final) extraction (g/m² nickel) were evaluated. Two obvious outlier data points were overlooked and the following second-order function was fitted through the remaining data:

$$Extr_{Max} = -31.721\ pH - 6.959\ [H]_s + 0.4892\ [Ni]_f - 3.604\times10^{-3}\ [Ni]_s + 13.502\ [Ex] - 1.997\times10^{-2}\ pH^2 + 0.1868\ [H]_s^2 - 7.537\times10^{-5}\ [Ni]_f^2 + 2.329\times10^{-5}\ [Ni]_s^2 - 2.121\times10^{-2}\ [Ex]^2 - 0.2545\ pH\ [H]_s + 2.003\times10^{-2}\ pH\ [Ni]_f + 1.405\times10^{-3}\ pH\ [Ni]_s + 0.2433\ pH\ [Ex] + 2.080\times10^{-3}\ [H]_s\ [Ni]_f + 1.641\times10^{-3}\ [H]_s\ [Ni]_s - 4.974\times10^{-2}\ [H]_s[Ex] + 9.793\times10^{-5}\ [Ni]_f\ [Ni]_s - 8.458\times10^{-3}\ [Ni]_f[Ex] - 2.896\times10^{-3}\ [Ni]_s\ [Ex] - 503.445 \quad (5)$$

The accuracy of this equation will be discussed later in this article. In similar fashion three outlier data points were overlooked and the following second-order function was fitted through the remaining data:

$$Rate = -0.5464\ pH - 3.065\ [H]_s - 2.653\times10^{-2}\ [Ni]_f + 1.155\times10^{-2}\ [Ni]_s - 4.875\times10^{-2}\ [Ex] + 0.1259\ pH^2 + 2.198\times10^{-2}\ [H]_s^2 + 1.237\times10^{-5}\ [Ni]_f^2 + 1.136\times10^{-6}\ [Ni]_s^2 + 2.499\times10^{-4}\ [Ex]^2 + 1.052\times10^{-2}\ pH\ [H]_s + 1.857\times10^{-3}\ pH\ [Ni]_f + 1.907\times10^{-4}\ pH\ [Ni]_s - 3.747\times10^{-2}\ pH\ [Ex] + 3.710\times10^{-4}\ [H]_s\ [Ni]_f - 8.814\times10^{-5}\ [H]_s\ [Ni]_s + 2.996\times10^{-2}\ [H]_s[Ex] + 3.684\times10^{-6}\ [Ni]_f\ [Ni]_s - 2.466\times10^{-4}\ [Ni]_f\ [Ex] - 2.711\times10^{-4}\ [Ni]_s[Ex] + 42.817 \quad (6)$$

The experimental data together with calculated data for Eq. (5) and Eq. (6) are given in Table 3. The data points which were overlooked are printed in bold italics.

The main effects and interaction of different factors on the maximum (final) extraction (g/m²) and the rate of extraction (g/m²h) will subsequently be discussed in greater detail. The graphical representation of the rate of extraction is not shown here since it closely resembles the maximum extraction.

The effect of pH_{feed} and $[H^+]_{strip}$

The effect of the pH of the feed and the $[H^+]$ of the strip solution on the final extraction can be seen in Fig. 2. It is clear that the final amount of nickel which can be extracted with the CME decreases with an increase of $[H^+]$ in the strip solution up to a point where the $[H^+]$ is approximately 21 mol/dm³. If the $[H^+]$ is further increased,

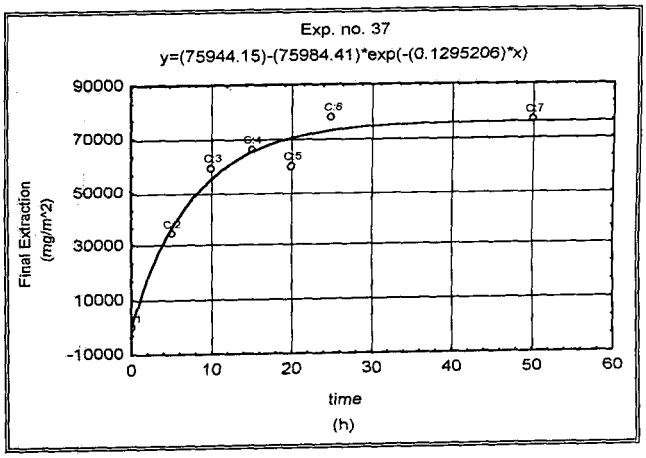


Figure 2
Example of curve fit

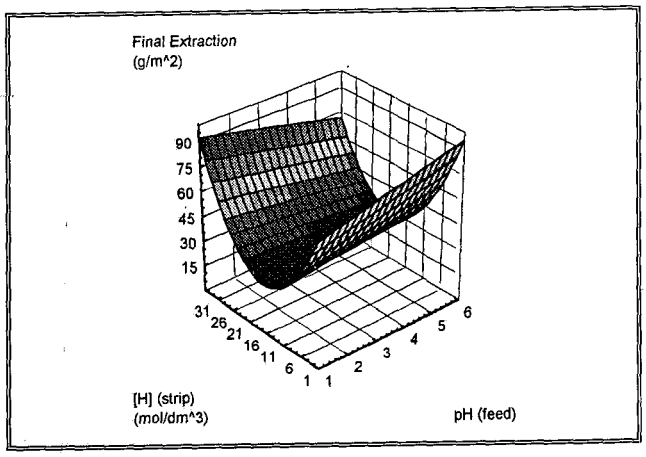


Figure 3
The effect of pH_{feed} and $[H^+]_{strip}$ on the final extraction of nickel

the final amount of extraction also increases. This result can be explained by the fact that the H^+ is transported through the membrane with the complexation reaction and the diffusion of H^+ through the membrane. If the $[H^+]$ is increased, the rate of diffusion increases and fewer H^+ ions are available for the complexation reactions. At the point of approximately 21 mol/dm³ maximum diffusion of H^+ ions occurs. If the concentration of the sulphuric acid is further increased, the acid does not dissociate completely and the undissociated acid forms an H^+ ion reserve. This theory is supported by the following:

- At low $[H^+]$ the maximum extraction occurs at the highest pH, since the complexation reaction is then the controlling reaction and this reaction increases if the pH increases. At higher $[H^+]$ the diffusion of hydronium is the controlling factor. The diffusion of H^+ ions is promoted by a high pH and less H^+ is available for the complexation reaction. The result is that at high $[H^+]$, the maximum extraction occurs at low pH.
- The capsules bulged during the experiment. This is an indication that osmosis had occurred.
- At certain periods during the experiment retro-extraction occurred (Fig. 2). This phenomenon was noted in all 46

TABLE 3
OBSERVED AND PREDICTED DATA

Exp. no	pH_{feed}	$[H]_{strip}$ (mg/dm³)	$[Ni]_{feed}$ (mg/dm³)	$[Ni]_{strip}$ (mg/dm³)	[Ex] (Vol %)	Max. extraction (g/M²)	Eq. 5 (g/M²)	Rate of extraction (g/M²·h)	Eq. 6 (g/M²·h)
1	2.50	11	800	689	55	27.028	34.994	3.548	5.257
2	4.50	11	800	689	55	20.481	26.421	3.716	5.272
3	2.50	25	800	689	55	41.307	23.633	1.354	0.168
4	4.50	25	800	689	55	12.998	7.934	2.090	0.477
5	2.50	11	1200	689	55	43.951	40.474	***11.570***	***3.621***
6	4.50	11	1200	689	55	55.449	47.924	5.432	5.121
7	2.50	25	1200	689	55	11.833	40.761	0.522	0.609
8	4.50	25	1200	689	55	34.593	41.085	3.431	2.403
9	2.50	11	800	1689	55	21.351	27.401	9.425	7.053
10	4.50	11	800	1689	55	25.002	21.638	8.592	7.448
11	2.50	25	800	1689	55	44.854	39.014	***36.472***	***0.729***
12	4.50	25	800	1689	55	15.546	26.125	0.720	1.419
13	2.50	11	1200	1689	55	73.543	72.053	6.525	6.890
14	4.50	11	1200	1689	55	95.259	82.313	11.034	8.771
15	2.50	25	1200	1689	55	100.669	95.314	***12.795***	***2.644***
16	4.50	25	1200	1689	55	***35.367***	***98.448***	4.132	4.820
17	2.50	11	800	689	65	61.545	57.556	3.913	3.588
18	4.50	11	800	689	65	53.159	53.848	4.310	2.853
19	2.50	25	800	689	65	13.349	39.231	0.790	2.693
20	4.50	25	800	689	65	24.306	28.398	1.355	2.252
21	2.50	11	1200	689	65	35.946	29.203	1.544	0.965
22	4.50	11	1200	689	65	23.987	41.520	0.947	1.716
23	2.50	25	1200	689	65	25.058	22.527	1.300	2.147
24	4.50	25	1200	689	65	36.574	27.717	1.600	3.192
25	2.50	11	800	1689	65	27.577	21.003	1.466	2.672
26	4.50	11	800	1689	65	33.407	20.105	1.680	2.319
27	2.50	25	800	1689	65	20.108	25.652	0.586	0.543
28	4.50	25	800	1689	65	20.882	17.629	1.218	0.484
29	2.50	11	1200	1689	65	19.630	31.822	0.744	1.523
30	4.50	11	1200	1689	65	45.106	46.949	1.710	2.655
31	2.50	25	1200	1689	65	52.292	48.120	2.190	1.471
32	4.50	25	1200	1689	65	50.323	56.120	4.542	2.898
33	3.50	18	1000	1189	60	29.293	28.993	1.021	1.033
34	3.50	18	1000	1189	60	27.099	28.993	0.696	1.033
35	1.12	18	1000	1189	60	38.108	29.221	1.643	0.889
36	5.88	18	1000	1189	60	24.893	28.539	.624	2.603
37	3.50	1.351	1000	1189	60	75.984	82.074	9.842	10.007
38	3.50	34.649	1000	1189	60	90.780	79.470	4.185	4.244
39	3.50	18	524	1189	60	***48.129***	***-14.246***	3.317	3.373
40	3.50	18	1475	1189	60	43.321	38.096	4.114	4.286
41	3.50	18	1000	0	60	63.957	49.547	3.013	1.747
42	3.50	18	1000	2378.2	60	65.140	74.304	2.041	3.532
43	3.50	18	1000	1189	48.1	35.956	37.751	1.234	3.205
44	3.50	18	1000	1189	71.9	21.263	14.229	0.678	-1.068
45	3.50	18	1000	1189	60	28.085	28.993	1.030	1.033
46	3.50	18	1000	1189	60	35.090	28.993	1.201	1.033

experiments as well as in the experiments done by Erlank (1994) and Steyn & Janse van Rensburg (1994).

No confirmation of this result could be found in the literature and further research will have to be done on this phenomenon.

The effect of pH_{feed} and $[Ni]_{feed}$

The effect of the pH_{feed} and the $[Ni]_{feed}$ on the final extraction can be seen in Fig. 4. It is clear that the amount of nickel which can be extracted increases with an increase in the pH of the feed and the [Ni] of the feed. This result is confirmed by Verhaege et al. (1987), who derived the following equation from conventional liquid-liquid equilibrium expressions:

$$\frac{[Ni^{2+}]_{feed}}{[Ni^{2+}]_{strip}} = \left(\frac{[H^+]_{feed}}{[H^+]_{strip}} \right)^2 \quad (7)$$

The effect of $[Ni]_{strip}$

It seems as if there is a point where the nickel concentration of the strip results in a minimum final extraction. This result is unexpected and thus far unexplainable. It also contradicts previous results in the literature (Verhaege et al., 1987). This result is not pronounced and will be investigated and reported on in more detail in a subsequent publication as it probably suggests an osmotic dependence.

The effect of pH_{feed} and [Ex]

The effect of these two variables can be seen in Fig. 5. At a lower feed pH, the optimum extractant concentration is also lower, at a higher feed pH the opposite happens. The results are compatible with those of Verhaege et al. (1987).

The effect of $[H^+]_{strip}$ and $[Ni]_{feed}$

The effect of these two variables can be seen in Fig. 6. The final amount of extraction is a maximum at high and low $[H^+]$ in the strip solution. The final extraction increases as the $[Ni]_{feed}$ increases and again a minimum final extraction is obtained at a certain $[H^+]$.

The effect of $[H]_{strip}$ and [Ex]

The effect of these two factors can be seen in Fig. 7. The $[H^+]_{strip}$ does not have a major effect on the optimum extractant concentration. The final extraction is the highest at high and low $[H^+]_{strip}$.

The effect of $[Ni]_{feed}$ and [Ex]

The effect of these two variables on the final extraction can be seen in Fig. 8. As previously

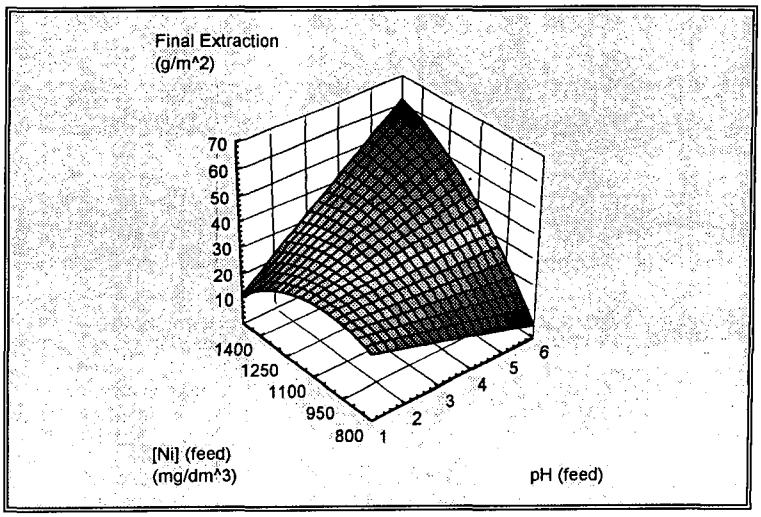


Figure 4
The effect of pH_{feed} and $[Ni]_{feed}$ on the final extraction of nickel

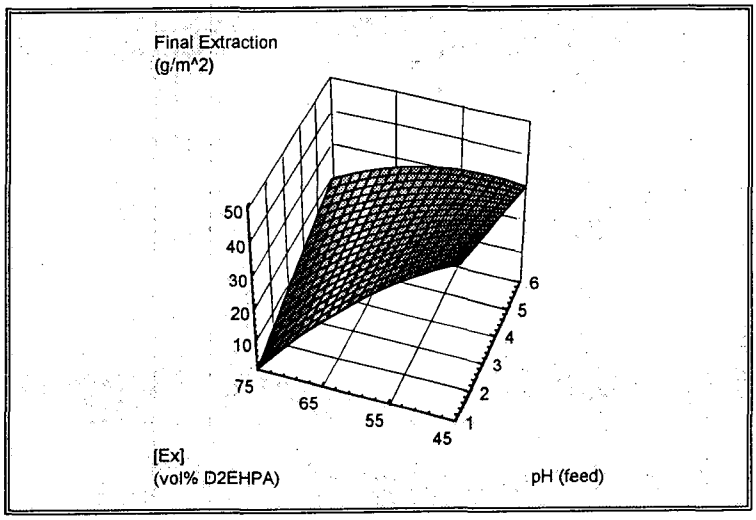


Figure 5
The effect of pH_{feed} and [Ex] on the final extraction of nickel

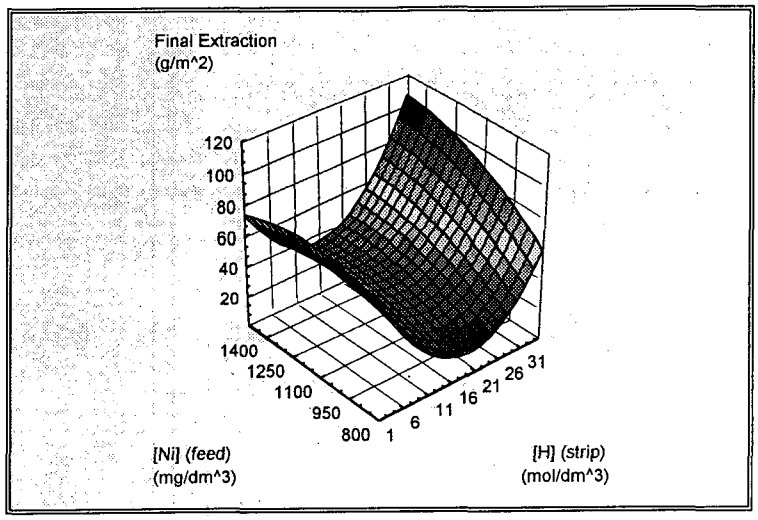


Figure 6
The effect of $[H^+]_{strip}$ and $[Ni]_{feed}$ on the final extraction of nickel

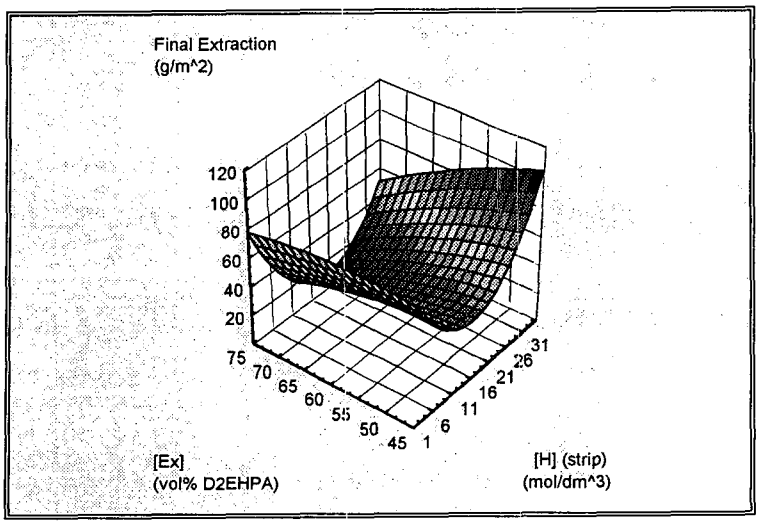


Figure 7
The effect of $[H^+]_{strip}$ and [Ex] on the final extraction of nickel

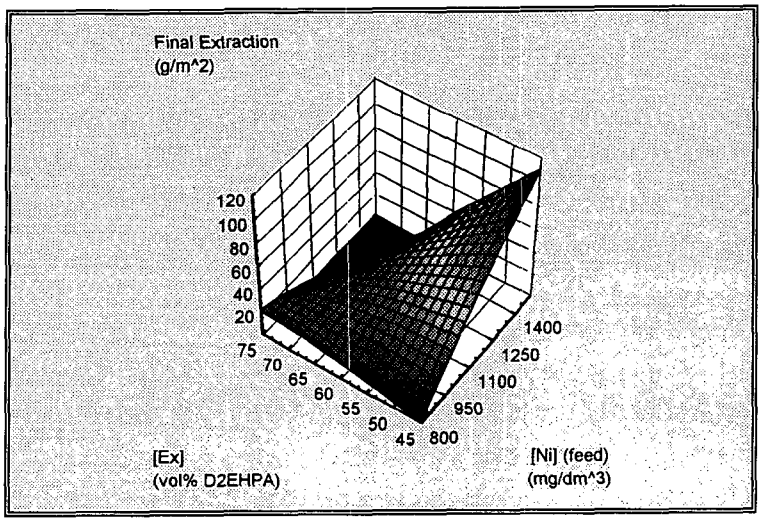


Figure 8
The effect of $[Ni]_{feed}$ and [Ex] on the final extraction of nickel

mentioned the final extraction increases if the $[Ni]_{feed}$ increases. The concentration of the nickel in the feed does seem to have a major effect on the optimum extractant concentration. At lower $[Ni]_{feed}$ the optimum extractant concentration occurs at a higher volume percentage than at higher $[Ni]_{feed}$.

Accuracy

The two most important influences on the accuracy of the experiments were the accuracy of the analytical methods and the influence of temperature on the experiments. An AA spectrometer was used to analyse the feed concentrations. The AA had an accuracy of 95% and higher, but the average drop in the nickel concentration was about 100 mg/dm^3 (10%). Thus, the accuracy that could be obtained with the AA was 9.5%. Statistical methods were used to perform a curve fit on the data. This increased the accuracy, since inaccurate data points, where obvious experimental deviations had occurred, could be identified and were omitted. This is a current statistically verified and accepted procedure. The final curve fit of the data could explain at least 85% of the variance for every experiment.

The temperature of the experiments could have been another cause of inaccuracy. The experiments were performed over a three-month period which stretched through the winter period and there is a difference in the temperature between the first and last experiments. The influence of temperature will be investigated and reported in more detail in a subsequent publication.

A second-order function was fitted through the data for the maximum (final) extraction. Two outliers were omitted and another second-order function (Eq. 5) was fitted through the remaining data. This equation could explain 81.0% of the variance. In similar fashion three outlier data points were omitted and a second-order function (Eq. 6) was fitted through the remaining data. This equation could explain 81.7% of the variance. The variance explained for different data points omitted is displayed in Table 4. It is clear that the equation for the initial rate of

TABLE 4
ACCURACY WITH OUTLIERS OMITTED

Number of data (outliers) ignored	Variance explained (Eq. 5)	Variance explained (Eq. 6)
0	0.6398	0.4949
1	0.7311	0.6817
2	0.8098	0.7603
3	0.8772	0.8170
4	0.9305	0.8480

TABLE 5
REPRODUCIBILITY TEST FOR EXPERIMENTS

Experiment no.	Eq. 5 (g/m^2)	Eq. 6 ($g/m^2 \cdot h$)
33	29.293	1.021
34	27.099	0.696
45	28.085	1.030
46	35.090	1.201
Average:	29.8918	0.987
Std	3.5798	0.1827
Std (%)	11.98	18.51

extraction is more inaccurate than the equation for the maximum extraction. This can be explained by the fact that the rate of extraction is more dependent on temperature than the maximum extraction is.

The following statistical criteria were used to determine whether a point is an outlier or not (Statistica, 1993):

- Standard residual value: This is the standardised residual value (observed value minus predicted value divided by the square root of the residual mean square).
- Deleted residual: The deleted residual is the standardised residual value for the respective data point (case), had it **not** been included in the regression analysis, that is, if one would exclude this case from all computations. If the deleted residual differs greatly from the respective standardised residual value, then this case is possibly an outlier because its exclusion changed the regression equation.
- Cook's distance is another measure of the impact of the respective case on the regression equation. It indicates the difference between the computed coefficients and the coefficients one would have obtained, had the respective case been excluded. All distances should be of about equal magnitude; if not, then there is reason to believe that the respective case(s) biased the estimation of the regression coefficients.

Four of the experiments in the experimental design were repeated to determine the reproducibility of the experiments. The results of these four experiments can be seen in Table 5. The standard deviation for Eq. (5) was found to be 3.5789 (11.98%). The standard deviation for Eq. (6) was found to be 0.1827 (18.51%).

Conclusions

The influence of different conditions on CME was determined. A central composite experimental design was executed to evaluate the influence of the different factors on the extraction of nickel with CME. The research was focused on high hydronium strip concentrations, which is a prominent advantage of CME over SLM. The two equations (Eqs. (5) & (6)) were shown to fit the experimental data to a highly acceptable accuracy and explained 81.0% and 81.7% of the variance respectively. The accuracy and reproducibility were both discussed and the experimental protocol showed an inherent accuracy of approximately 85%. In the light of these results it is possible to make the following conclusions on nickel extraction with CME:

- It is obvious that the extremely high acidity difference (ΔH^+) which is tolerated between the strip solution and the feed solution is advantageous for the extraction of ionic species.
- This driving force (ΔH^+) creates a system in which extraction proceeds against a concentration gradient of at least 1000:1 when considering the ratio between $[Ni^{2+}]$ in the strip- and feed solutions at final extraction.
- It is obvious from the fact that no extraction occurs at an H^+ ion concentration of 0 mol/dm^3 and from Fig. 7, that an optimum $[H^+]$ in the strip solution exists. This optimum must be explored in greater detail to clarify, amongst others the exact mechanism of extraction.
- The CME yields at least two orders of magnitude higher extraction rates compared to traditional SLM configurations reported in literature (Verhaege et al., 1987).
- Substantial further research is necessary on the effects of osmosis when extraction takes place at such high ionic transmembrane concentrations.
- A detailed study of the influence of both temperature and the extractant concentration in the membrane will shed more light on the possible techno-economic feasibility of this extraction technique.
- It is shown (Table 3) that an extraction of 95 g/m^2 (nickel) can be obtained at an initial rate of approximately 10 $g/m^2 \cdot h$.

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