

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### RECOVERY OF NICKEL VIA LIQUID EMULSION MEMBRANE PROCESS USING METHANE SULFONIC ACID AS A STRIPPANT

P. S. Kulkarni<sup>a</sup>; K. K. Tiwari<sup>a</sup>; V. V. Mahajani<sup>a</sup>

<sup>a</sup> Chemical Engineering Division, Department of Chemical Technology, University of Mumbai, Mumbai, India

Online publication date: 31 March 2001

**To cite this Article** Kulkarni, P. S. , Tiwari, K. K. and Mahajani, V. V.(2001) 'RECOVERY OF NICKEL VIA LIQUID EMULSION MEMBRANE PROCESS USING METHANE SULFONIC ACID AS A STRIPPANT', *Separation Science and Technology*, 36: 4, 639 — 656

**To link to this Article:** DOI: 10.1081/SS-100102951

**URL:** <http://dx.doi.org/10.1081/SS-100102951>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## RECOVERY OF NICKEL VIA LIQUID EMULSION MEMBRANE PROCESS USING METHANE SULFONIC ACID AS A STRIPPANT

P. S. Kulkarni, K. K. Tiwari, and V. V. Mahajani\*

Chemical Engineering Division,  
Department of Chemical Technology,  
University of Mumbai, Matunga, Mumbai 400019, India

### ABSTRACT

A liquid emulsion membrane (LEM) process is considered for the enrichment of nickel ions from dilute aqueous solutions. The liquid emulsion membrane consisted of a carrier di-2 ethylhexyl phosphoric acid (D2EHPA), an organic diluent, an emulsifying agent, and an aqueous stripping agent thereby having water in oil emulsion. Various stripping agents (hydrochloric, sulfuric, nitric, and methane sulfonic acid) were tested for the stability of membrane. The swelling, breakage, osmotic pressure, and particle size of LEM containing various stripping acids were compared. Methane sulfonic acid (MSA) outperformed the other acids as a stripping agent. The recovery of nickel depends on pH of aqueous feed phase. The other important variables affecting the LEM process of nickel such as acid strength, speed of agitation, organic diluent, and treat ratio were systematically investigated by using methane sulfonic acid as a strippant. It was found that nickel extraction was maximum when concentration

---

\*Corresponding author. E-mail: vvm@udct.ernet.in

of MSA was 1M and treat ratio was 1:3. It was also observed that dodecane as a diluent resulted in better extraction of nickel as compared to other diluents such as heptane, toluene, and xylene.

## INTRODUCTION

Liquid emulsion membrane (LEM) separation process is an advanced version of solvent extraction process wherein extraction and stripping is accomplished in one contactor. The LEM process has an advantage over conventional extraction particularly if the concentration of material being extracted is very low and transport process is governed by the mass-transfer rate. The organic emulsion membrane provides a very large interfacial area despite the fact that there is a tendency to form globules. Thus LEM extraction has a very good commercial potential (1–5). The block diagram of LEM process is depicted in Fig. 1.

An important problem in the practical application of LEM process is the stability of the liquid membranes. The instability of liquid membrane leads to breakage and hence unselective release of already separated components (6–9). The swelling of membrane is due to transport of water from the feed phase to the strip phase. The swelling ultimately results in breakage of the membrane. Therefore, proper selection of stripping agent (strippant) is vital in the success of LEM process.

The mineral acids such as  $H_2SO_4$ ,  $HCl$ , and  $HNO_3$  are well-known stripping agents for metal ions. In the present investigation, the effect of various strippants on the membrane stability and extraction of metal ion in LEM system was studied. Along with the mineral acids, it was decided to use methane sulfonic acid as a strippant, which has a low  $pK_a$  value. Methane sulfonic acid has a very high affinity for metal ions and therefore can be an ideal electrolyte for recovery. For instance, MSA has been reported to be suitable for Pb (lead) recovery from scrap batteries (10). In our opinion, there is practically no information available on the use of methane sulfonic acid (MSA) as a stripping agent in LEM extraction process of enriching metal ions. It was, therefore, thought desirable to study enrichment of nickel, a model ion for LEM study, with the help of MSA as a stripping agent. The performance was compared with other stripping acids such as  $HCl$ ,  $H_2SO_4$ , and  $HNO_3$ . The extraction, emulsion swelling, breakage, internal particle size, and osmotic pressure in the presence of all these acids were compared.

## EXPERIMENTAL

### Chemicals

The main chemical extractant, di-2-ethyl hexyl phosphoric acid (D2EHPA) [CAS No. 298-07-7] having 98.5% purity and surfactant, sorbitan monooleate



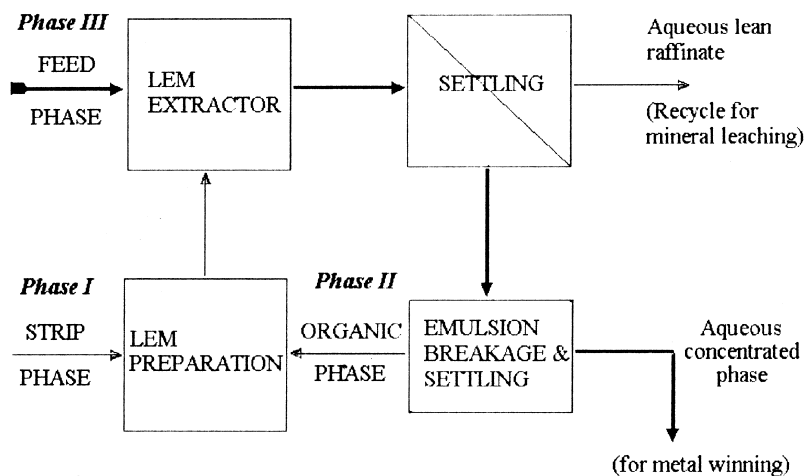
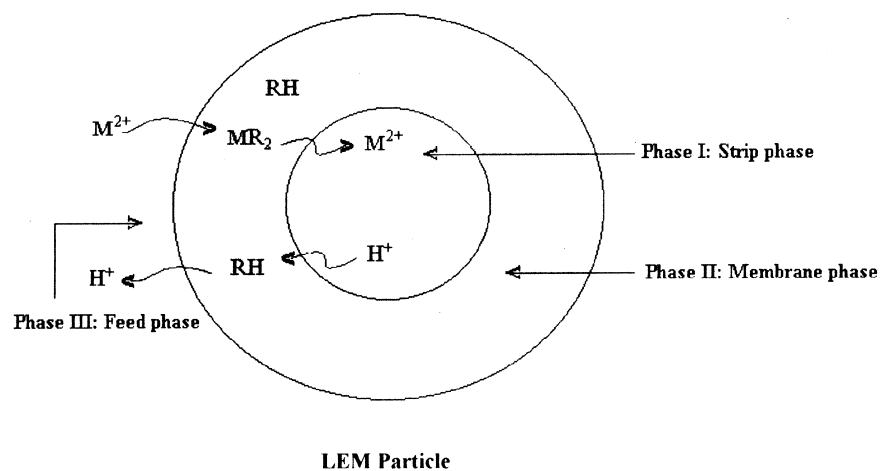


Figure 1. Block diagram of liquid emulsion membrane process.

(Span 80/Monemul 80) [CAS No. 1338-43-8] were obtained from local suppliers of repute. Methane sulfonic acid (MSA) [CAS No. 75-75-2] was a free gift by The Dharamsi Morarji Chemical Co. Ltd., Mumbai. All chemicals were used without any further purification. A local vendor supplied nickel salt of minimum 99% purity. Mixed xylene, heptane, toluene, and dodecane were used as organic solvents for the membrane preparation. All other reagents used were of analytical reagent grade and were used as received.



### Apparatus and Procedure

Emulsion was prepared by emulsifying aqueous solution of acid (strip phase) with an organic phase (membrane phase). The membrane consists of varying proportions of nonionic surfactant SPAN 80, a carrier reagent D2EHPA, and an organic solvent. The internal strip phase was added dropwise into a glass reactor containing an organic phase. A predetermined volume ratio of 1:1 was maintained for organic phase (membrane phase) to the internal strip phase. The contents were simultaneously stirred at 3000 rpm for 15 min with a six-blade turbine impeller of 30 mm in diameter in a glass vessel of 70 mm in diameter. An excellent milky white stable emulsion was obtained, which has a mean diameter of the encapsulated droplets varying from 2 to 10  $\mu\text{m}$  as measured on Coulter's particle size analyzer. The emulsion was dispersed in feed phase of nickel salt from which nickel is to be extracted. The emulsion stability was tested by examining the phase separation over time. A six-blade paddle impeller of 50 mm in diameter rotating at 250 rpm was used for stirring, and extraction was carried out in a glass vessel of 80 mm in diameter. The individual size of emulsion droplet varies from 2 mm to 4 mm. The internal droplet size and emulsion globule size depend on concentration of the reagents used under study and hydrodynamics.

In the LEM extraction of nickel, pH plays a critical role. Kulkarni et al. (11) have experimentally observed that for good extraction rates of nickel, pH should be equal to or below 4. Therefore, pH of the feed phase was maintained at 4 by using 2 M sodium hydroxide solution. Samples of about 5  $\text{cm}^3$  were withdrawn from the extractor at different intervals of time and were filtered through a sintered glass plug to separate emulsion and aqueous feed phase. At the end, the emulsion phase was separated from feed phase by simple gravity separation in separating funnel, and finally the emulsion was broken down by heating to about 80°C for the analysis of strip phase. We have observed that Ni concentration in strip phase during high temperature de-emulsification was the same as that observed during de-emulsification by acetone (de-emulsifying agent) at 30°C. Experiments for accounting breakage involved in extraction process were carried out simultaneously. All experiments were carried out at 30°C, and the reproducibility of each experiment was checked at least twice.

Osmotic pressure measurements were carried out to determine the stability of LEM. A Reverse Osmosis (SEPA, ST) cell with a nylon membrane was used for measuring flux of the feed and strip phase. It consisted of a magnetically stirred cell having provision to hold a flat membrane. The housing was made of SS 316 and was capable of taking pressure of gas up to 72  $\text{kg}/\text{cm}^2$ . The magnetic stirring minimizes resistance due to concentration polarization.



## RECOVERY OF NICKEL VIA LIQUID EMULSION

643

Following are the operating parameters for the reverse osmosis study:

Type of membrane	: RO Nylon
Membrane size	: 49 mm diameter (1.93 inches)
Active membrane area	: 16.9 cm <sup>2</sup> (2.9 inches <sup>2</sup> )
Processing volume	: 300 cm <sup>3</sup>
Pressure applied	: 10 kg/cm <sup>2</sup>

The flux of permeate through a membrane is given by

$$\text{Flux } (F) = \frac{(\Delta P - \Delta \Pi)}{R} \quad (1)$$

Downstream of the membrane was at atmospheric pressure. The N<sub>2</sub> pressure was applied upstream of membrane in the unit. Deionized water was used to determine the membrane resistance ( $R$ ). Aqueous nickel nitrate solutions were used for measurement of osmotic pressure. Because the resistance ( $R$ ) of the polymeric membrane (nylon), pressure ( $\Delta P$ ) applied, and the osmotic pressure difference ( $\Delta \Pi$ ) between upstream and downstream sides of the membrane were known and because no solute was in the downstream,  $\Delta \Pi$  represents osmotic pressure only calculated from Eq. (1).

### Analytical

The internal droplet size of emulsion was measured at the start and end of the experiment by using Coulter LS 230 particle size analyzer. The outer size of the emulsion globule was analyzed by using an Image Analyzer instrument. The measurements of viscosity and pH were carried out as usual.

Analysis of the metal ion was carried out by "Dionex High Performance Ion Chromatograph" using a CS2 column and a post column reactor. The metal left behind in the organic phase was calculated by using mass balance.

## RESULTS AND DISCUSSION

The major limitation of the LEM process is breakage of the membrane caused by swelling, which in turn depends upon cotransportation of water along with the metal ion under consideration, into the strip phase. The osmotic pressure difference is the main driving force for cotransportation of water. The selection of stripping agent in turn depends on the factors influencing breakage of the membrane. It was, therefore, thought desirable to evaluate the performance of methane sulfonic acid as a stripping agent and compare the same with other acids.



### Methane Sulfonic Acid as a Stripping Agent: Comparative Study

#### Osmotic Pressure (II)

The stability of liquid emulsion membrane depends on the osmotic pressure difference in the feed and strip phase. The increase in initial osmotic pressure difference between feed phase and strip phase leads to transport of water from feed to strip phase. The higher the initial osmotic pressure difference, the higher the swelling of emulsion. As the internal phase swells, the stability of the emulsion suffers, ultimately leading to the breakage of the internal phase. It was, therefore, thought desirable to carry out measurements of osmotic pressures of the feed and strip phases.

The osmotic pressure (II) values were measured by using "Reverse Osmosis" (SEPA ST) unit. From this, the initial osmotic difference was calculated, which can be deemed as an indication of membrane stability. The values are shown in Table 1. The initial osmotic pressure difference in methane sulfonic acid is lower as compared to the other acids, meaning, thereby, lower rates of cotransportation of water in the strip phase containing MSA.

The driving force for water transport is the osmotic pressure difference between the external and internal phases. The swelling can be suppressed by decreasing the osmotic pressure difference. The addition of inert species such as glucose to the external feed phase was reported to decrease the osmotic pressure difference (12). The reduced initial osmotic pressure difference values (with the addition of 1% glucose) are given in Table 1. It was found that the difference was almost 40% lowered by addition of 1% glucose in the external phase. The reduction in initial osmotic pressure difference (with or without addition of glucose) increases membrane stability and hence makes the LEM process more efficient. It is seen that osmotic pressure difference between feed and enriched strip phase is

**Table 1.** Initial Osmotic Pressure Difference

Acid	Initial Osmotic Pressure Difference kg/cm <sup>2</sup>	Initial Osmotic Pressure Difference with Addition of 1% Glucose kg/cm <sup>2</sup>
MSA	1.94	1.02
HCl	2.12	1.25
HNO <sub>3</sub>	2.23	1.37
H <sub>2</sub> SO <sub>4</sub>	2.41	1.51

Note: Initial osmotic pressure difference is a difference between strip phase (2000 ppm Ni + 1N acid) and feed phase (400 ppm Ni + distilled water).



## RECOVERY OF NICKEL VIA LIQUID EMULSION

645

lower in the case of MSA as compared to  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$  at the same concentration of acid (N is identical). Thus, we can conclude while using MSA as a strip phase, swelling can be less and hence breakage as compared to other acids. However, in subsequent experiments, glucose was not added.

### Internal Particle Size

The increase in swelling of the strip phase, due to cotransportation of water was also analyzed by particle size analyzer (Coulter Counter LS 230). Recently, Chang et al. (13) have also studied internal particle size analysis for liquid emulsion membrane separation of enzymes. The particle size of the strip phase containing all acids was practically the same ( $\sim 2.37 \mu\text{m}$ ) before extraction. From Table 2, it is seen that the strip phase containing sulfuric acid swelled highest, and that containing MSA exhibited lowest swelling under otherwise identical conditions.

This makes LEM process with MSA more efficient from an enrichment point of view. The larger particle size of the strip phase bearing  $\text{H}_2\text{SO}_4$  observed after extraction means  $\text{H}_2\text{SO}_4$  resulted in dilution of the separated product, thereby making the process inefficient.

### Swelling

The swelling mechanism is also mediated by a hydrated surfactant; that is, the surfactant solubilizes the water of external phase into membrane phase. The hydrated surfactant then diffuses to the internal phase. Finally, the water is released to the internal phase. This phenomenon is driven by the osmotic pressure

**Table 2.** Internal Particle Size of Emulsion Membrane

Acids	Internal Particle Size Before Extraction ( $\mu\text{m}$ )	Internal Particle Size After Extraction ( $\mu\text{m}$ )
MSA	2.37	4.33
HCl	2.39	5.06
$\text{HNO}_3$	2.35	5.63
$\text{H}_2\text{SO}_4$	2.37	5.99

Note: Internal particle size of the emulsion; constituting strip phase (1N acid) and organic phase 3% surfactant (Monemul 80) +5% D2EHPA in xylene.



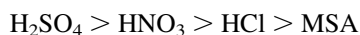


difference between the external phase and internal phase. The disadvantages of swelling in LEM separation system are the dilution of the separated product in the internal phase, the increase of membrane rupture (breakage), and the increase in agitation power required to disperse the emulsion (7). This makes the LEM process inefficient. Therefore, the application of a LEM process for metal recovery largely depends on the swelling of the emulsion caused by the internal acid used. The swelling can be quantified as:

$$S_w = \frac{V_{i,t} - V_{i,0}}{V_{i,0}} \times 100 [\%] \quad (2)$$

In this definition of swelling please note that change in volume is considered and not breakage of emulsion. While swelling occurs, it is possible that some membrane particles might have broken thereby causing leak of Ni in feed phase. Therefore, the swelling is deemed as "apparent swelling," and further it is global swelling and not individual particle swelling. Henceforth, we use "swelling" for this apparent swelling. In the process-engineering point of view, "swelling" is important to size volume of the contactor.

A series of experiments were conducted at a constant treat ratio of 1:5, 3% (v/v) surfactant Monemul 80 (equivalent to Span 80; sorbitan monooleate) and 5% (v/v) D2EHPA as the extractant in xylene. The internal strip phase concentration of various acids was kept 1*N*, and the resulting emulsion was contacted with the feed phase containing deionized water. Figure 2 exhibits the effect of swelling caused as a function of time by different acids as a strippant. It is seen that the initial rate of swelling is higher, and it further increases steadily with respect to time. Methane sulfonic acid (MSA) as the stripping phase yielded minimum swelling than the other acids. On the other hand, sulfuric acid yielded maximum swelling of emulsion, due to its more affinity towards water. Thus we have a swelling order as :



This order could have been expected from the increase in internal droplet size due to cotransport of water as outlined earlier.

### Breakage

The breakage/leakage due to swelling of internal phase culminating into rupture is a serious problem in LEM process. Experiments for accounting breakage were done by using 5 gm/L of nickel in the internal phase (phase 1) consisting of 1*N* sulfuric, methane sulfonic, nitric, and hydrochloric acids, while keeping other parameters constant. This was then dispersed in the organic phase to prepare the emulsion phase. The emulsion was treated with the external aqueous phase (deionized water). Finally, metal leaked during the course of the extraction process in the external phase was analyzed. The percentage breakage (*Bk*) was estimated by using following formula:



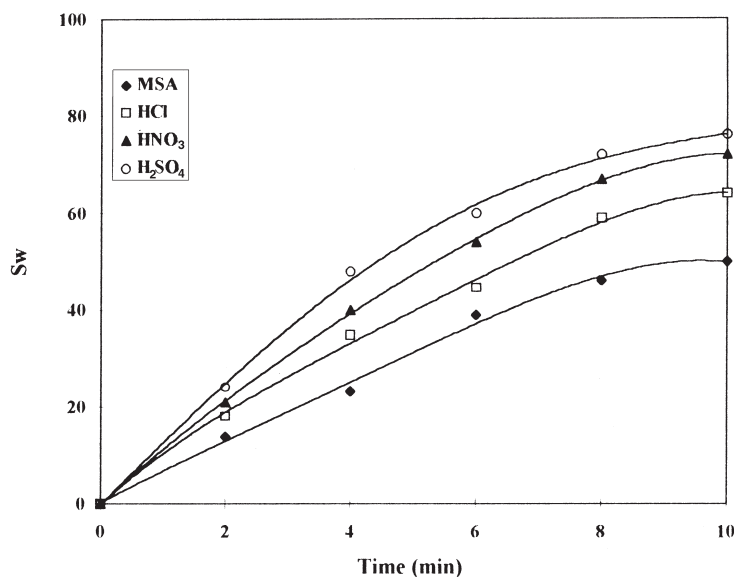


Figure 2. Effect of acids on the swelling of emulsion.

$$Bk = \frac{C_{e,f}V_{e,f}}{C_{i,o}V_{i,o}} \times 100 [\%] \quad (3)$$

Figure 3 depicts how the breakage increased with elapsed time in different stripping phase. The breakage,  $Bk$  [%] increased significantly when acid was sulfuric. The maximum swelling occurred when sulfuric acid was used as stripping agent in comparison with the other acids. Therefore, increase in the water transport to the internal phase appeared to increase the breakage by making the emulsion increasingly unstable. Methane sulfonic acid has lowest swelling compared to the other acids, so it produces minimum breakage of the emulsion.

From the foregoing, it is seen that methane sulfonic acid outperforms other acids. The breakage and swelling was least when MSA was used as a stripping agent. It was, therefore, decided to have studies of process parameters for extraction of nickel using MSA as a stripping phase.

### Extraction of Nickel by LEM Process

As extraction of Ni is pH dependent (14–17), distribution coefficient of nickel increases with an increase in feed phase pH. Thus, it requires external addition of alkali while performing LEM experiments.



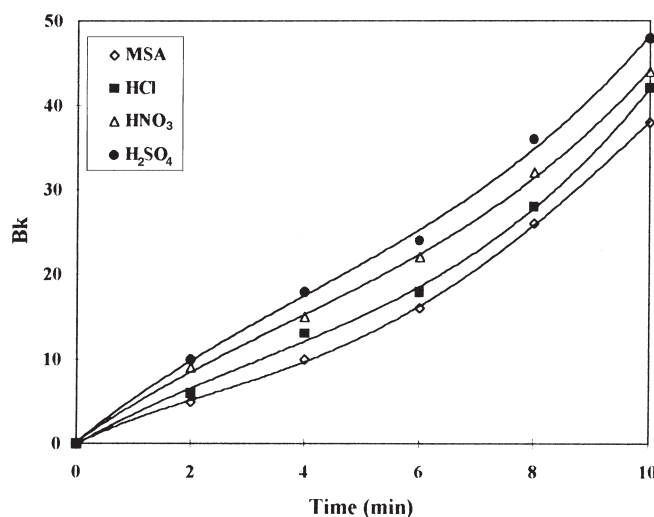


Figure 3. Effect of acids on the breakage of emulsion.

In the LEM process not only the value of distribution coefficient  $K_D$  [ $K_D = (\bar{Ni})/(Ni)$ ] is important but also stability of membrane phase is very important. Kulkarni et al. (11), have reported data on  $K_D$  as a function of pH of aqueous feed phase. Further, they observed that the liquid emulsion membrane was unstable above pH 5 when pH was varied between 2 to 6. In our experiments also, when MSA was used as a stripping agent, we observed the membrane to be unstable above pH 5.

Therefore, the aqueous phase was maintained at pH of 4 by adding caustic solution externally, during the LEM process. Kulkarni et al. (11), have also observed that this addition of alkali while extraction of nickel decreased the initial osmotic pressure difference and thus reduced the swelling of emulsion up to 50%.

The extraction and stripping reactions of nickel occurring in LEM process can be listed as;



where  $RH$  represents the protonated form of an extractant that is used as a carrier.

The complexation reaction, taking place at the membrane-external aqueous phase interface, is presented by Eqs. (4) and (5) and exhibits stripping via decomplexation at the membrane-internal aqueous phase interface. The overall reaction represents an exchange of nickel ion for two hydrogen ions.

Because methane sulfonic acid (MSA) was found to be the best strippant among all other acids used, it was thought desirable to carry out extraction and stripping of nickel by using the MSA. A residence time of 4 min was selected for



## RECOVERY OF NICKEL VIA LIQUID EMULSION

649

the extraction run of nickel, based on our prior experience. It was observed that breakage of emulsion commenced (as indicated by increase in concentration of Ni in feed phase) after 4 min. The extent of extraction ( $Ex$ ) and enrichment ( $En$ ) were estimated as follows:

$$Ex = \frac{M_0 - M_t}{M_0} \times 100 \quad (6)$$

$$En = \frac{M_i}{M_0} \quad (7)$$

### Effect of Acid Strength on the Extraction of Nickel

The applications of a membrane process for nickel recovery will not only depend on extraction efficiencies but also on the concentration of the strip solution. Clearly, it would be most desirable for strip acid solutions produced from a membrane process to be amenable to direct electrowinning to produce metallic nickel. In order to investigate the influence of strip acid concentration on nickel transfer and to check the feasibility of using concentrated strip solution, a series of experiments were carried out. The experiments were conducted at a constant treat ratio of 1:5 and 5% D2EHPA as the extractant in xylene. The strip phase acid concentration of acid was varied from 0.5N to 3N. Figure 4 exhibits the effect of

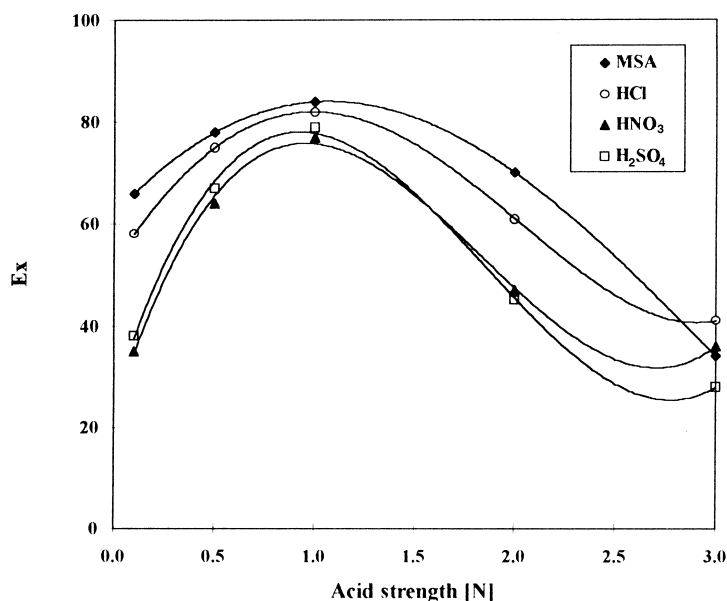


Figure 4. Effect of strength of acids on the extraction of nickel at the end of 4 min.

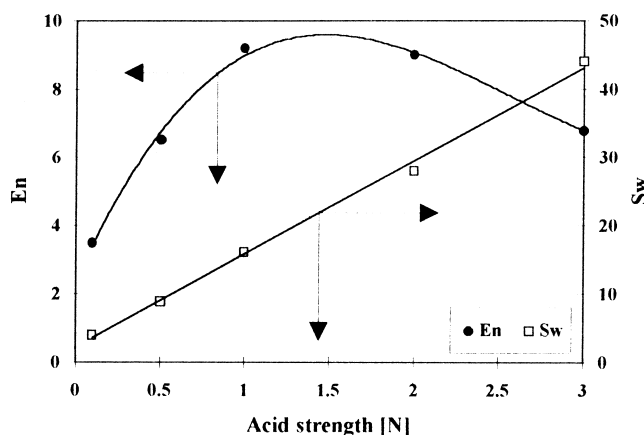


strip acid concentration on the extraction of nickel. The extent of extraction increased when the acid concentration was increased from 0.5*N* to 1*N*. However, further increase in the strip acid concentration from 1*N* to 3*N* was found to reduce the extent of extraction. Please note that the extraction experiments were conducted for 4 min in all cases as mentioned earlier. The unexpected behavior is explained by the swelling of the liquid emulsion membrane due to water transport in the presence of acid. The water permeates through the membrane and causes the internal droplets to swell and then break. The breakage of LEM reduces the mass-transfer area for nickel transportation, thereby having less enrichment of nickel. A similar effect was also observed for transport of copper in a LEM process (18).

It was found that maximum extraction occurred when methane sulfonic acid was used as an internal stripping phase. The other acids also exhibited similar behavior. However, it is seen from Fig. 4 that MSA is the best among all acids studied, even from an extraction point of view.

#### Effect of Acid Strength on the Water Transport and Final Recovery/Enrichment of Nickel

The goal of LEM process lies in fruitful recovery of the metal. The final swelling and the final nickel concentration in the stripping phase are shown in Fig. 5 as a function of methane sulfonic acid concentration. As acid concentration ( $H^+$ ) increased, enrichment increased because the driving force increased. But when acid concentration exceeded about 2*N*, concentration of nickel in strip phase started falling. The decrease in enrichment at 3*N* concentration of methane sulfonic acid is attributed to the swelling of strip phase. On the other hand,



**Figure 5.** Effect of strip phase MSA concentration on the emulsion swelling and final recovery of nickel.

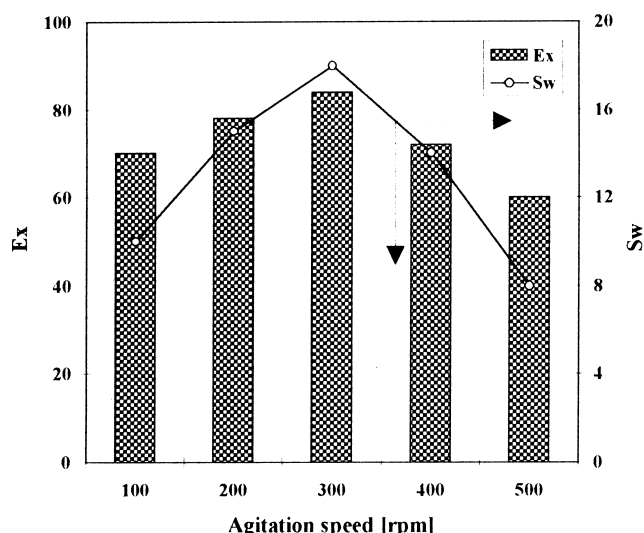


swelling linearly increased as acid concentration increased. This is because the difference of osmotic pressure between the internal strip and external feed phase increased and because the water was transported by the hydrated surfactant. A similar effect was also observed for transport of amino acid in a LEM process (7). The swelling causes the dilution of the strip phase and unless the swelling is taken into account, the concentration of strip phase will be overpredicted.

#### Effect of Speed of Agitation on Extraction

The speed of agitation of the feed phase affects the performance of LEM process to a great extent. The effect of speed of agitation on extraction and emulsion swelling was studied in the range of 100 rpm to 500 rpm and is shown in Fig. 6.

It was observed that with an increase in speed of agitation from 100 rpm to 300 rpm, the rate of extraction increased. This is due to an increase in volumetric mass-transfer coefficient  $k_L a$  in aqueous feed phase (between the emulsion "globules" and aqueous solution), but further increase in speed of agitation from 300 rpm to 500 rpm resulted in decrease in the extent of extraction, which was contrary to the general expectation (19). This was attributed to hydrodynamic instability of emulsion at higher speed. It was observed that with an increase in speed of agitation, the rate of swelling of the internal phase increased. But at



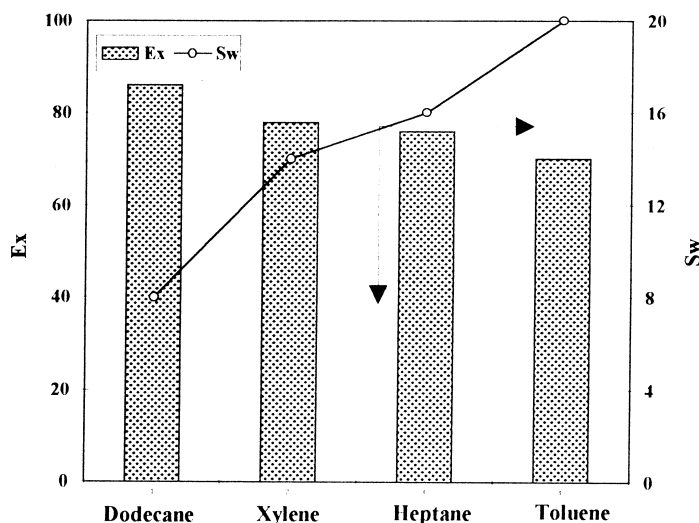
**Figure 6.** Effect of agitation speed on emulsion swelling and extraction of nickel with MSA as a strippant.



higher speeds of agitation at 400 and 500 rpm the emulsion phase was broken and its final volume decreased after 3 min. As the speed of agitation increased, the co-transport of water was also increased, thereby resulting in swelling and ultimately breaking of emulsion membrane. Further, the increased speed might have caused shear on emulsion globules and then particles. The resulting shear might be sufficient to cause the breakage of emulsion. A combination of these two resulted in breakage of the emulsion at speeds exceeding 300 rpm in our experimental setup. Every system is thus expected to have optimum speed (tip speed) of agitation.

#### Effect of Organic Solvents (Diluent)

Change in organic solvent during preparation of emulsion produced changes in the stability of emulsion and percentage of extraction. The viscosity of the diluent is the main parameter, which decides the thickness of the membrane and permeability of the membrane for the solute to diffuse through it. Various organic solvents tried were dodecane, toluene, xylene, and heptane. The extraction of nickel with the help of 5% v/v extractant (D2EHPA) and 3% v/v surfactant (Monemul 80) and various organic solvents is depicted in Fig. 7. It was found that dodecane has the lowest swelling impact. On the other hand, toluene has highest swelling impact among the solvents used. This was attributed to hydrophobic na-



**Figure 7.** Effect of organic solvent on emulsion swelling and extraction of nickel with MSA as a strippant.



**Table 3.** Organic Solvent and Viscosity

Organic Solvent	Viscosity ( $\mu$ ) cp at 30°C
Dodecane	1.41
Xylene	0.97
Heptane	0.92
Toluene	0.64
(D2EHPA concentration = 5% v/v; surfactant concentration = 3% v/v)	

ture of aliphatic hydrocarbons, thereby having lower water transportation. The membrane prepared by aromatic solvents tends to break down under shearing conditions (6). It was observed that there was very little difference of swelling between xylene and heptane.

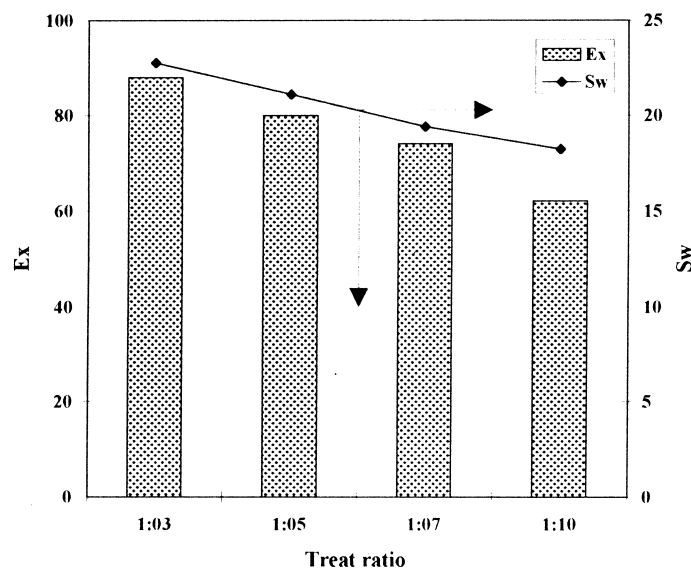
The data on viscosity of these organic diluents used for making the emulsion of 5% D2EHPA with 3% surfactant are given in Table 3. This clearly indicates that dodecane has higher viscosity produces higher extraction and lower percentage of swelling than the others. The success of LEM system is based on the stability of membrane and transport of water through the organic membrane. The higher number of carbon atoms (dodecane = 12, heptane = 7) in dodecane means more hydrophobicity, which results in less transport of water across the membrane. Therefore, we strongly recommend experimental screening of solvent for LEM system.

#### Effect of Treat Ratio (TR)

The treat ratio defined as the ratio of emulsion phase volume ( $V_e$ ) to aqueous feed phase volume ( $V_v$ ), plays an important role in determining effectiveness of liquid emulsion membrane. Experiments were conducted to study the effect of treat ratio on the percentage of extraction, the enrichment factor, and swelling of emulsion. The treat ratio was varied by changing the amount of emulsion added to the feed phase and by keeping the volume of the later constant. Figure 8 exhibits the effect of treat ratio on extraction and swelling of nickel. The treat ratio was varied from 0.1 ( $V_e:V_v = 1:10$ ) to 0.33 ( $V_e:V_v = 1:3$ ). As shown in Fig. 8, there was a steady increase in the fraction of metal extracted with increasing values of  $V_e/V_v$  whereas the swelling of emulsion had no profound effect. With an increase in the treat ratio, the volumes of both the carrier and the stripping agent, i.e., the volume of emulsion as a whole, increased. Therefore, the surface area for mass transfer owing to the formation of a larger number of emulsion globules increased. As a result, a higher degree of extraction was obtained but the enrichment was less. The lower treat ratio means less amount of emulsion is used to extract nickel,







**Figure 8.** Effect of treat ratio on emulsion swelling and extraction of nickel with MSA as a strippant.

which is desired from the process point of view to have maximum enrichment with respect to feed phase nickel. Thus, there exists a trade-off between the rate of mass transfer and concentration of metal in the strip phase. For this system a treat ratio of 1:5 or 1:7 appears to be acceptable.

### CONCLUSION

1. Methane sulfonic acid was observed to be a better stripping agent for enrichment of nickel than the other mineral acids.
2. The diluent plays an important role in the stability of membrane. A high molecular weight paraffin is recommended as a diluent than aromatics.
3. There exists a trade-off between speed of agitation of the feed phase and hydrodynamic stability of membrane phase.

### NOMENCLATURE

Bk      breakage (%)  
cp      centipoise



## RECOVERY OF NICKEL VIA LIQUID EMULSION

655

Ex	extraction (%)
En	enrichment (recovery)
F	(m <sup>3</sup> of permeate/h)/(m <sup>2</sup> of membrane)
K <sub>D</sub>	distribution coefficient
k <sub>L</sub> a	mass-transfer coefficient
M	metal ion concentration (mol m <sup>-3</sup> )
M <sub>e</sub>	concentration of metal in external feed phase (mol m <sup>-3</sup> )
M <sub>i</sub>	concentration of metal in internal phase (mol m <sup>-3</sup> )
M <sub>0</sub>	initial metal ion concentration
M <sub>t</sub>	metal ion concentration at time <i>t</i>
(Ni)	concentration of nickel in organic phase (mol m <sup>-3</sup> )
(Ni)	concentration of nickel in aqueous phase (mol m <sup>-3</sup> )
Δ P	pressure difference between upstream and downstream of membrane, applied pressure (kg/cm <sup>2</sup> )
R	resistance offered by membrane (P/F) (kg/cm <sup>2</sup> )/[(m <sup>3</sup> /h)/(m <sup>2</sup> )]
RH	extractant
Sw	swelling (%)
TR	treat ratio
V <sub>i</sub>	volume of internal phase (m <sup>3</sup> )
V <sub>e</sub>	volume of emulsion phase (m <sup>3</sup> )
V <sub>v</sub>	volume of aqueous feed phase (m <sup>3</sup> )
μ	viscosity of membrane phase in centipoise
Π	transmembrane osmotic pressures (kg/cm <sup>2</sup> )

### Subscripts

Aq.	aqueous phase
e	external phase
f	final
i	internal phase
0	initial
Org.	organic phase
t	time

### ACKNOWLEDGMENTS

We acknowledge the financial support by Board of Research in Nuclear Sciences, (BRNS) Govt. of India Mumbai, INDIA, under the grant no. 36/10/96—R & D II/877. P. S. Kulkarni is also thankful to BRNS for the fellowship. The authors are grateful to Mohini Organics (P) Ltd. for the supply of sorbitan monooleate (Monemul 80). The authors are also grateful to Dr. A. K. Shah of The Dharamsi Morarji Chemical Co. Ltd. for the sample of MSA.



# REFERENCES

1. Li, N.N U. S. Patent 3,410,794, 1968. Cf, Chemical Abstr. 70: 39550z (1969).
2. Hayworth, H.C.; Ho, W.S.; Li, N.N. Sep. Sci. Technol. **1983**, *18* (6), 493.
3. Frankenfeld, J.W.; Cahn, R.P.; Li, N.N. Sep. Sci. Technol. **1981**, *16* (4), 385.
4. Weiss, S.; Grigoriev, U.; Muhl, P. J. Membr. Sci. **1982**, *12*, 119.
5. Draxler, J.; Furst, W.; Marr, R. J. Membr. Sci. **1988**, *38*, 281.
6. Kinugasa, T.; Watanabe, K.; Takeuchi, H. J. Chem. Eng. Jpn. **1989**, *22* (6), 593.
7. Itoh, H.; Thien, M.P.; Hatton, T.A.; Wang, D.I.C. J. Membr. Sci. **1990**, *51*, 309.
8. Ding, X.; Xie, F. J. Membr. Sci. **1991**, *59*, 183.
9. Mok, Y.S.; Lee, K.H.; Lee, W.K. J. Chem. Tech. Biotechnol. **1996**, *65*, 309.
10. MSA in Electrochemical Applications. Atochem (Elf Aquitaine).
11. Kulkarni, P.S.; Tiwari, K.K.; Mahajani, V.V. J. Chem. Tech. Biotechnol. **2000**, *75*, 553.
12. Scholler, C.; Chaudhuri, J.B.; Pyle, D.L. Biotech. & Bioeng. **1993**, *42*, 50.
13. Chang, J.H.; Lee, S.C.; Lee, W.K. Chem. Eng. J. **1999**, *73*, 43.
14. Yamashita, K.; Kakoi, T.; Kosaka, H.; Goto, M.; Nakashio, F. Sep. Sci. Technol. **1998**, *33* (3), 369.
15. Juang, R.S.; Jiang, J.D. J. Membr. Sci. **1995**, *100*, 163.
16. Kakoi, T.; Ura, T.; Kasaini, H.; Goto, M. Sep. Sci. Technol. **1988**, *33* (8), 1163.
17. Nemeh, A.; Van Peteghem, A.P. Hydrometallurgy **1992**, *31*, 149.
18. Martin, P.; Davies, G.A. Hydrometallurgy **1977**, *2*, 315.
19. Thien, M.P.; Hatton, T.A.; Wang, D.I.C. Biotech. & Bioeng. **1990**, *35*, 853.

Received November 17, 1999

Revised May 2000



## **Request Permission or Order Reprints Instantly!**

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

**[Order now!](#)**

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081SS100102951>