Research Paper

# Extraction-Stripping Patterns during Co-Extraction of Copper and Nickel from Ammoniacal Solutions into Emulsion Liquid Membranes Using LIX 84I®

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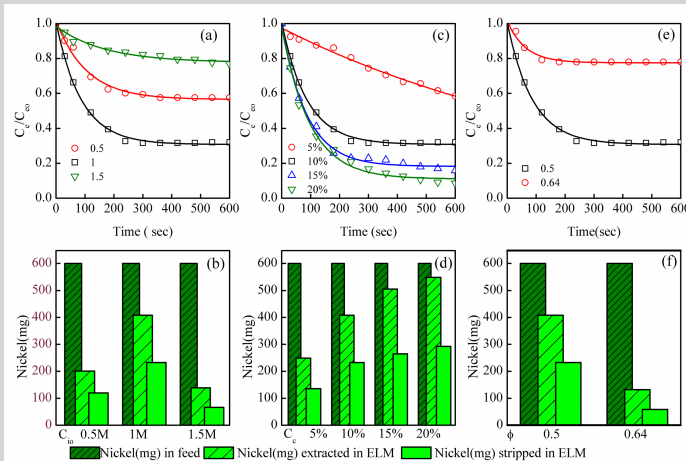
# ARTICLE INFO

# KEYWORDS

# GRAPHICAL ABSTRACT



# HIGHLIGHTS

• Nickel was extracted from ammoniacal media using LIX 84I into ELMs.
• Optimal pH for extraction was 8.1.
• Nickel stripping was slow and equivalent to ~55 % of the amount extracted.
• During co-extraction nickel extraction declined in the presence of copper.
• Copper stripped was equivalent to nickel uptake.

# ABSTRACT

Extraction of nickel and its co-extraction with copper from ammoniacal media into emulsion liquid membrane systems (ELMs) was investigated using LIX 84I as the carrier. Measurement of the solute stripped in the internal phase of emulsion opened a new dimension in the study of the ELM extraction processes. The effect of operating parameters such as feed pH, initial feed concentration, and treat ratio of emulsion to feed and the effect of emulsion parameters such as internal phase stripping acid concentration, carrier concentration, and internal phase volume fraction were investigated. The optimal pH for extraction was 8.1. The overall extraction process was strongly favored by the factors that lead to enhancement of uptake of metal ions such as increase in the carrier concentration and the treat ratio. Investigations on the stripping patterns in W/O emulsions revealed that sulfuric acid of 1.0 M concentration was optimal for nickel stripping in ELMs but the process was slow. Stripping of copper was relatively fast and was favored by higher acid concentrations. The amount of nickel extracted declined in the presence of copper during co-extraction of copper and nickel and the amount of copper stripped in the internal phase of the emulsion was equivalent to the amount of nickel loaded by the emulsion. In general, almost 55% of the metal loaded in the emulsion was found to get stripped in the duration of the runs. Hence, there is scope to formulate emulsions and tune other operating parameters to achieve selective separation of one of the two metals co-extracted in the internal phase of the emulsion.

## 1. Introduction

Increasing interest in metal recovery from Indian Ocean manganese nodules led to the development of hydrometallurgical processes for simultaneous separation of nickel, copper, manganese and other metals from ammoniacal leach solutions. Ammoniacal leaching is otherwise also an attractive approach to process laterite ores, electronic wastes, spent catalysts and other raw materials and concentrates containing nickel, copper, zinc, cobalt and other heavy metals. Merigold and Jensen [1] were the first to describe the coextraction of copper and nickel from ammoniacal laterite leach solutions. The separation of copper and nickel and other metals from

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ammoniacal solutions has been extensively studied with the objective to recover metals from deep-sea nodules [2, 3].

Siemens and Corrick [4] described the co-extraction-selective stripping process as applied to nickel laterite leach liquors. The co-extraction and selective stripping of copper and nickel from ammoniacal-ammonium sulphate leach liquors using LIX 64N has also been investigated by Siemens and coworkers [5, 6] and Bhaskara Sarma et al.[7]. Sandibigraha and Bhaskara Sarma [8] used LIX 87QN to extract both Cu and Ni from ammoniacal solutions. They observed that Ni extraction is extremely sensitive to equilibrium pH. Algucil and Cobo [9] co-extracted copper and nickel using ACORGA PT5050, further using LIX 973N for selective separation of Cu and Ni and they observed that Ni extraction was very sensitive to extractant concentration [10]. Parija *et al.* [11] extracted nickel using LIX 84I. Parija and Bhaskara Sarma [12] optimized process parameters for the separation of nickel and copper from an ammoniacal leach liquor obtained by leaching a Cu-Ni-Fe sulfide concentrate using LIX84. Selective separation of Cu and Ni using LIX 984N from ammoniacal ammonium carbonate solutions was carried out by Sridhar *et al.* [13]. Hu *et al.* [14] investigated the extraction behavior of Ni from ammonium sulfate solution using sterically hindered β diketone.

Emulsion liquid membrane (ELM) technology invented almost fifty years ago is a means for intensification of liquid extraction processes, because ELMs involve extraction and stripping simultaneously. Metal extraction from ammoniacal solutions has been sparingly investigated using ELM systems. Aouarram *et al.* [15] reported a permeation liquid membrane system for pre-concentration and separation of nickel from natural and sea-water. Copper was extracted by Gamerio *et al.* [16] using LIX 54 as a carrier. A detailed investigation on copper extraction using commercial copper extractant LIX 84I as carrier was reported by Sengupta *et al.* [17]. Selective extraction of nickel from its mixtures with cobalt in ammoniacal solutions using ELMs with hydroxyquinolines as carrier has also been reported [18-20]. Recently nickel was extracted from Cr-Ni plating bath solutions using LIX 63 and 2BDA as carriers [21]. In our earlier work on the extraction of zinc as well as the co-extraction of copper and zinc from ammoniacal solutions into ELMs using LIX 84I as carrier it was observed that the extraction process was governed by loading of both the metals in the membrane phase [22]. The stripping patterns in ELMs during Cu and Zn extraction from ammoniacal solutions was also reported.

Since nickel and copper extraction from ammoniacal solutions has been investigated continuously over the last thirty five years, hence there exists considerable interest and potential to co-extract Ni and Cu from ammoniacal solutions and to apply process intensification techniques to this separation. The stripping behavior during carrier-mediated transport of metals in ELM systems is an unexplored area. The presence of a stripping media inside the emulsions makes one anticipate that a fair amount of solute gets stripped in the internal phase but experimental quantification is missing.

Often ELMs are used to recover solutes from feeds where the amount of solute is quite low and it could get loaded in the emulsion and reside in the membrane phase without getting stripped. The effectiveness and utility of ELMs as a process intensification tool is lost if stripping is not significant. In the present investigation using LIX 84I as carrier nickel extraction from ammoniacal solutions and the co-extraction of Ni and Cu from binary solution into ELMs in ammoniacal media is reported. A further attempt is made to quantify the magnitude of metal stripped in the internal phase of the emulsion for different parametric variations.

## 2. Experimental

### 2.1. Materials

The membrane phase consisted of kerosene (Indian Oil Corporation Limited) having a boiling range of 152 °C – 271 °C containing n-paraffins (27.1%), naphthenes (55.9%), aromatics(16%) and olefins (1%) having a density $\rho_{15}$ of 821.3 kg/m³) as the oil phase, Span 80 (S.D Fine Chemicals Ltd.) as the emulsifier and LIX 84I (Cognis Inc.) as the extractant. The kerosene, emulsifier and the carrier were used directly as received from the manufacturer. Sulfuric acid was used as the internal stripping phase. All the reagents copper and nickel sulfate salts, ammonia and ammonium sulfate were of AR grade.

### 2.2. Experimental procedure

W/O emulsions were formulated by blending kerosene containing a requisite amount of carrier LIX 84I (5% – 20% by volume), emulsifier Span80 (3% by weight of the oil phase) and internal stripping phase sulfuric acid (0.5 M – 1.5 M) using a high-speed blender at 12,000 rpm. The resulting

milky white W/O emulsion was cured for 30 min prior to dispersion in the feed phase.

Ammoniacal feed solutions of the desired concentration for nickel extraction and copper-nickel co-extraction were prepared by dissolving the requisite amount of metal salt and ammonium sulfate (50 gm/L) in deionized water. The feed pH was adjusted to the desired value using ammonium hydroxide. Extraction experiments were carried at 30±2 ºC by dispersing the requisite amount of the emulsion in the feed solution (600 ml) in a four-baffled batch reactor equipped with a six bladed turbine impeller at 160 rpm to achieve the required treat ratio (ratio of volume of emulsion to feed). Samples from the feed were withdrawn at definite time intervals and analyzed for the metal content. On completion of the extraction run, the emulsion phase was separated from the feed phase. Further, the emulsion was transferred to a 250 ml Erlenmeyer flask and dipped in a water bath maintained at 60⁰C. This mild heating aided in the splitting of the emulsion and within almost 30 minutes time the internal phase distinctly separated from the oil phase. The metal content in the internal phase was measured and the amount in the oil phase was determined by mass balance. The extraction data was plotted as the ratio of instantaneous metal concentration to initial metal concentration ($C_e/C_{eo}$) versus time.

### 2.3. Analytical methods

#### 2.3.1. Measurement of metal ion concentration

Nickel and copper ion concentrations were measured using an atomic absorption spectrophotometer (AAS) (Chemito Make Model AA 203) at 232.10 μm and 324.8 μm, respectively.

#### 2.3.2. Emulsion globule size measurement

Emulsion globule sizes were measured by the photographic technique [22]. The emulsions were characterized by measurement of viscosity, internal drop size distribution and interfacial tension between the emulsion and feed phase using methods discussed earlier [23].

Table 1 and Table 2 list the parametric variations studied for nickel and copper nickel co-extraction in ELMs. To determine the effect of parametric variations on metal stripping patterns in the internal droplets of ELMs, an assessment was made of the initial metal in feed, total metal extracted by ELMs and the total metal stripped in the internal phase of the emulsion after completion of the extraction runs. This required the emulsion to be separated from feed phase, demulsified and then the internal aqueous phase was analyzed for the metal content. The stripping patterns gave an overall idea of the dynamics of extraction in ELMs and are discussed in the following sections.

**Table 1**
Range of parametric variations studied for nickel extraction from ammoniacal media into ELMs.

| Variable | Process variables | | | Emulsion variables | | |
|---|---|---|---|---|---|---|
| | pH | $C_{eo}$ (mg/L) | TR | $C_{io}$ (M) | $C_c$ (%v/v) | φ |
| pH | 7, 8.1 | 1000 | 1:6 | 1 | 10 | 0.5 |
| $C_{eo}$ | 8.1 | 500,1000, 1500 | 1:6 | 1 | 10 | 0.5 |
| TR | 8.1 | 1000 | 1:8, 1:6,1:5 | 1 | 10 | 0.5 |
| $C_{io}$ | 8.1 | 1000 | 1:6 | 0.5,1,1.5 | 10 | 0.5 |
| $C_c$ | 8.1 | 1000 | 1:6 | 1 | 5,10,15,20 | 0.5 |
| φ | 8.1 | 1000 | 1:6 | 1 | 10 | 0.5, 0.64 |

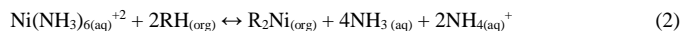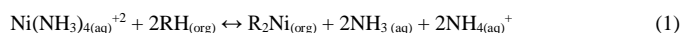Stirring speed (N) = 160 rpm, Surfactant concentration ($W_{surf}$) = 3% wt of oil phase

**Table 2**
Range of parametric variations studied for co-extraction of copper and nickel from ammoniacal media into ELMs.

| Variable | pH = 8.1, TR = 1:6 | | | | |
|---|---|---|---|---|---|
| | $C_{io}$(M) | $C_{eo}$(mg/L) | | φ | $C_c$(%v/v) |
| | | Cu | Ni | | |
| $C_{io}$ | 0.5,1 | 1000 | 1000 | 0.5 | 10 |
| $C_c$ | 1 | 1000 | 1000 | 0.5 | 10,15,20 |
| φ | 1 | 1000 | 1000 | 0.5.0.64 | 10 |
| $C_{eo}$ | 1 | 1000 4440 5760 | 1000 1230 1570 | 0.5 | 10 |

Stirring speed (N) = 160 rpm, Surfactant concentration ($W_{surf}$) = 3% wt of oil phase

## 3. Results and discussion

The extraction of nickel from ammoniacal solutions proceeds either by the mechanism of nickel tetramine complex or the nickel hexamine complex depending upon the amount of ammonia present in the reaction system. The reactions can be described by the equations listed below:

$$Ni(NH_3)_{4(aq)}^{+2} + 2RH_{(org)} \leftrightarrow R_2Ni_{(org)} + 2NH_{3\,(aq)} + 2NH_{4(aq)}^+ \quad (1)$$

$$Ni(NH_3)_{6(aq)}^{+2} + 2RH_{(org)} \leftrightarrow R_2Ni_{(org)} + 4NH_{3\,(aq)} + 2NH_{4(aq)}^+ \quad (2)$$

Sandibigraha and Bhaskara Sarma [8] observed that Ni extraction using the ketoxime LIX87QN is extremely sensitive to equilibrium pH and extraction falls sharply at pH values > 9. Similar observation has also been reported using ACORGA PT5050 [9]. Free ammonia in the solution functions as a coordinating ligand and competes favorably with the organic extractant for binding the metal ion; as a result the extent of extraction declines with an increase in free ammonia in the solution [25]. It was shown by Lee and Chen [26] that ammonia transport across the membranes becomes severe when the aqueous phase pH > 11. They reported that at a pH of 9.5 free ammonia was 50% while at a pH of 8 it was just 10%.

### 3.1. Effect of process variables on nickel extraction and its associated stripping patterns

The parameters affecting the rate of extraction in ELM systems can be classified in two groups. Feed phase pH, initial metal concentration in the feed and the treat ratio of emulsion to feed are the process parameters. On the other hand, parameters depending on the emulsion characteristics such as concentration of stripping acid in the internal phase of the emulsion, carrier concentration in the emulsion, volume fraction of the internal phase are the emulsion parameters. The effects of these parametric variations were studied sequentially, and the effect of feed phase pH was initially evaluated to establish the basic operating conditions of the ELM separations. In our earlier investigation on copper [17] and zinc extraction [21] from ammoniacal solutions we observed that a pH of 8.1 was optimal for the recovery of these metals. Hence, for Ni extraction as well, the pH of extraction was investigated at 8.1 and at a lower pH value to assess the pH effect on the rates of extraction.

### 3.1.1. Effect of pH

Figure 1(a) shows the rate of extraction of nickel in ELMs from ammoniacal-ammonium sulfate solutions at pH values of 7 and 8.1. It can be seen that the nickel uptake is initially rapid and more than 50% of the nickel in the feed stream gets extracted in just three minutes at both pH values. The rate of extraction at a pH of 8.1 was faster than at a pH of 7 although the extent of extraction was nearly the same.

Apparently it seems that the emulsion phase gets saturated at 6–8 minutes of contact at both the pH values in view of the plateau in the curves; however, the amount of nickel was removed at a pH of 8.1 after ten minutes of contact was 4.08 gm/L of the emulsion, while the maximum loading capacity of 10% (v/v) of hydroxy oxime based extractant (2-hydroxy -5 nonyl benzaldehyde oxime) in the solvent as reported by Alguacil and Cobo [9] is 5.2 gm/L of the solvent. Hence, one liter of emulsion having φ = 0.5, i.e. having 500 ml of oil phase should have a maximum loading capacity of 2.6 gm/L of emulsion if the solute does not strip from the oil membrane phase, but emulsion loading capacities are much larger indicating that simultaneous stripping of solute is taking place and therefore the question of saturation of the membrane phase does not arise. It is very much likely that the stripping rate is slow which will further decline as the internal acid strength in the emulsion gets depleted.

Figure 1(b) gives a relative assessment of the amount of nickel present at the end of the run in the emulsion, as well as in the stripping phase of the emulsion at the two pH conditions. It is observed that the amount of nickel loaded in the emulsion is nearly the same in both cases and corroborates with Figure 1(a), but the amount of nickel stripped in the aqueous phase is more at a pH of 8.1 in comparison with a pH of 7.0 which again corresponds to the sharper decline of the extraction profile observed at a pH of 8.1.

### 3.1.2. Effect of initial feed concentration ($C_{eo}$)

The effect of $C_{eo}$ on the rates of nickel extraction was investigated for nickel concentrations ranging from 500 mg/L to 1500 mg/L as shown in Figure 1(c). It is seen that almost 75% of initial nickel gets loaded at $C_{eo}$ = 500 mg/L, which reduces to 68% when $C_{eo}$ = 1000mg/L and further reduces to 42% when $C_{eo}$ = 1500 mg/L. For $C_{eo}$ 1000 mg/L and 1500 mg/L the net amount of nickel loaded per 100 ml of emulsion turns out to be 408 mg and 398.7 mg, respectively that are quite close, indicating that the membrane phase almost reaches a plateau with respect to its loading capacity for both these cases. Analysis of the internal aqueous phase of the emulsion, subsequent to emulsion breakage, also showed that the amount stripped in these cases were quite close to 57% and 51% of the respective amount loaded.

The flux of the nickel-carrier complex within the globules is dependent on the nickel concentration in the aqueous phase as well as on the carrier concentration in the oil membrane phase. When carrier concentration is held constant, the flux depends largely on the initial metal complex and the permeation process is solely dependent on the diffusion of nickel species within the globule. Saturation of the binding capacity of the carrier at the globule interface causes the feed concentrations to level off.

The extent of stripping of the loaded nickel at the end of the run is shown in Figure 1(d). It is clear that the extent of stripping is more or less similar in all the three cases accounting for ~55% of the loaded nickel concentrations, irrespective of the initial feed concentration. These results suggest that the rate of stripping is a slow process and therefore, the overall rates are governed by the loading pattern of ELMs.
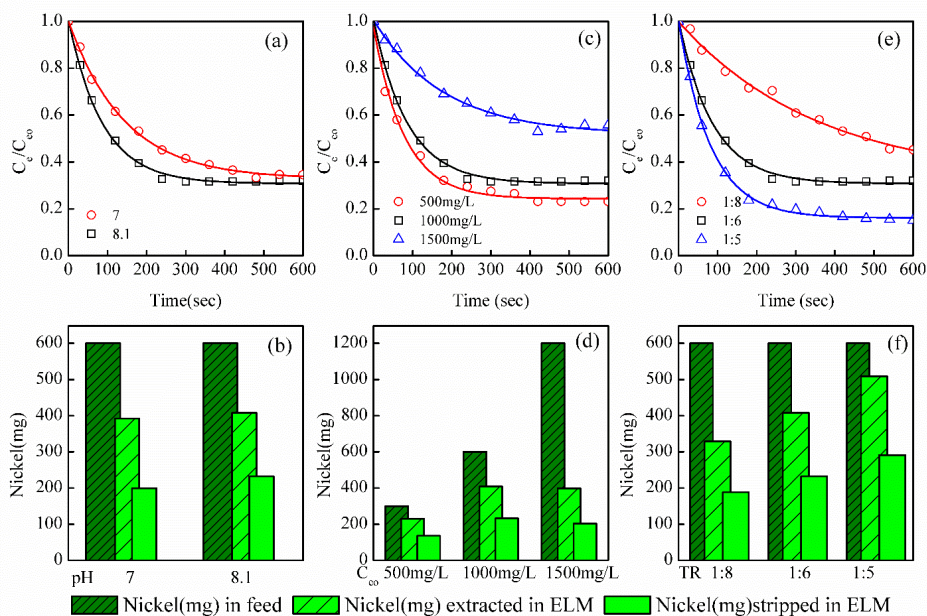


**Fig. 1.** Effect of process parameters on the extraction and stripping patterns of nickel from ammoniacal media into ELMs. (a), (b) Effect of pH, (c), (d) Effect of initial feed concentration ($C_{eo}$), (e), (f) Effect of treat ratio (TR) (Conditions as in Table 1).

### 3.1.3. Effect of treat ratio (TR)

Treat ratio is a measure of emulsion hold up in an ELM system. The increase in TR functions on the same lines as that of an increase in solvent in an extraction system. It always results in an increase in the extent and rates of extraction due to an increase in the amount of carrier as well as the amount of stripping phase in the system and also the mass transfer areas at both the external and internal interfaces. Figure 1(e) shows the extraction curves. It is seen that there is a considerable increase in the rates and extent of extraction with an increase in the treat ratios. Almost 85% of nickel gets extracted in 10 minutes when TR = 1:5 but only 55% of nickel is extracted for TR = 1:8. The observed difference in extraction rates for the lower treat ratio stems from the reduction in loading capacity of the oil membrane, due to reduction in the amount of carrier in the oil phase. Loading of nickel in the ELMs and the amount stripped from the oil membrane phase is shown in Figure 1(f). It is seen that almost 57% of the loaded nickel gets stripped in all three cases in the time span of the experimental runs.

### 3.2. Effect of emulsion variables on extraction of nickel

#### 3.2.1. Effect of internal phase acid concentration ($C_{io}$)

The internal phase acid concentration was varied to study the influence of stripping rates on overall extraction rates. Solvent extraction studies by Parija and Bhaskara Sarma [12] for the co-extraction and selective stripping of nickel and copper from ammoniacal solutions using LIX 84 showed that reasonable nickel stripping from ammoniacal solutions to the tune of 65% per stage could be obtained by using stripping phase pH of 1.75. Further, as pH values increased there was a decline in Ni stripping but there was a greater decline in Cu stripping. At low pH values the extent of Cu stripping was excessive and the selectivity of stripping was lost. We correlated the sulfuric acid concentrations with pH values and noted that acid concentrations 0.05 M, 0.5 M, 1.0 M and 1.5 M resulted in a pH of 1.72, 1.06, 0.89, 0.79 respectively. The influence of concentration of $H_2SO_4$ in the internal phase of the emulsion on the rates of extraction was evaluated at acid concentrations ranging from 0.5 M to 1.5 M.

The extraction profiles using $H_2SO_4$ concentration of 0.5 M, 1.0 M and 1.5 M in the stripping phase are shown in Figure 2(a). It is seen that using 0.5 M acid for stripping in the ELMs resulted in almost 40% removal of nickel in four minutes followed by plateau. With 1.0 M acid in the stripping phase almost 68% extraction took place in about four minutes. When 1.5 M acid was used as the stripping phase of the emulsions only 22% extraction was recorded in 10 minutes of contact. This behavior is attributed to a pH swing that is likely to have taken place during the initial dispersion of the emulsion in the feed phase. Changes in pH values could result from minor breakage of emulsion taking place during initial dispersion of the emulsion or due to the adherent aqueous phase on the surface of W/O emulsions. Since the emulsion

was formulated with 1.5 M acid, even a minor degree of breakage or small amount of adherent aqueous phase could result in reasonable shift of pH below the value of 8.1 giving rise to conditions not conducive to the transfer of nickel in the ELMs.

The final nickel distribution in the stripping phase of the ELM is shown in Figure 2(b). It is clearly observed that for the case of $C_{io}$ = 0.5 M, although the loading was low, almost 60% of the total Ni loaded got stripped while with $C_{io}$ = 1.0 M the extent of stripping was 57% of the nickel loaded and for $C_{io}$ = 1.5 M about 48% of the loaded Ni got stripped.

#### 3.2.2. Effect of carrier concentration ($C_c$)

Carrier concentration in the membrane phase has considerable influence on the overall extraction rates in ELMs. The effect of carrier concentration on nickel extraction from ammoniacal solution investigated at four LIX 84I concentrations in the membrane phase ranging from 5% (v/v) to 20% (v/v) is shown in Figure 2(c). Extraction rates steadily increased with oxime concentration in the membrane phase. Carrier concentration of 5% (v/v) LIX 84I in the membrane phase resulted in a linear decline in the nickel concentration in the feed over the entire span of the experimental run but increasing the carrier concentrations to 10% (v/v) led to a sharp decline in the nickel concentration in the feed phase within the initial four minutes of contact with the ELMs. Thereafter, a plateau in feed concentration was observed. Increasing the carrier concentration in the ELMs to 15% (v/v) showed a similar initial trend, although almost 15% enhancement in the extent of extraction at any time interval was recorded when compared with carrier concentration of 10% (v/v). A further increase in carrier concentration to 20% (v/v) in the first four minutes resulted in almost identical rates as observed with $C_c$ = 15% (v/v), but in the second half of the experimental run, the rate and extent of extraction both got enhanced resulting in almost 91.5% recovery of nickel about 8% more than the case with $C_c$ = 15% (v/v).

The effect of variation of the amount of carrier is implicit in other effects as well, for example, the variation of treat ratio induces corresponding variation in carrier concentration in the system. When the treat ratio is 1:6, for 600 ml of feed there is 100 ml of emulsion in which the membrane phase is 50 ml. There is 10% (v/v) carrier, i.e. 5 ml of carrier in the system which reduces to 3.75 ml when treat ratio is changed to 1:8 with the same amount of feed. It can be easily figured out that a carrier concentration of 7.5% (v/v) with TR = 1:6 and 600 ml of feed results in 3.75 ml of carrier in the system. By comparing the extraction profile for TR=1:8 shown in Figure 1(c) with the extraction profiles obtained for variation in carrier concentration shown in Figure 2(c), it is observed that the profile in Figure 1(c) is intermediate to the profiles of 5% and 10% carrier concentration shown in Figure 2(c), thereby implying the influence of the carrier concentration in other parametric variations.
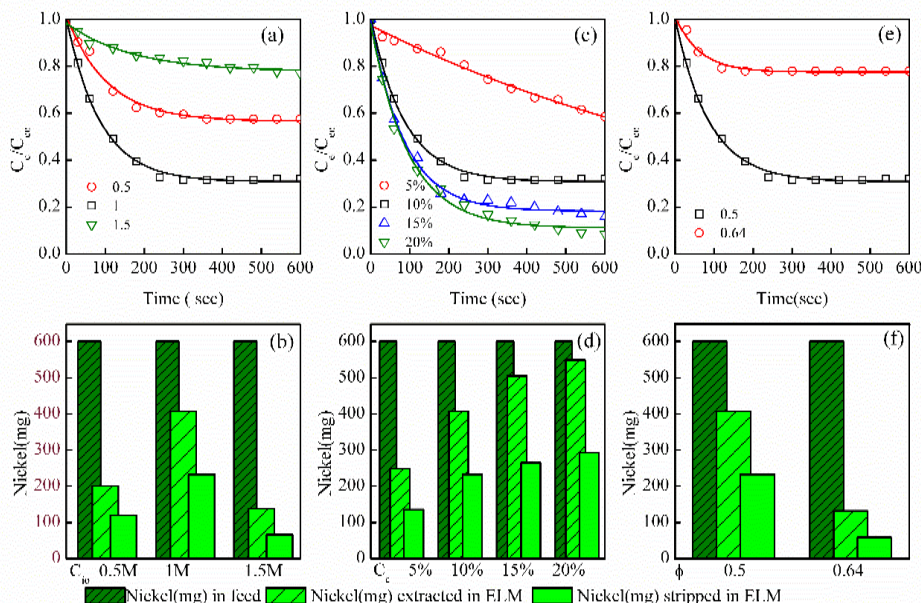


**Fig. 2.** Effect of emulsion parameters on the extraction and stripping patterns of nickel from ammoniacal media into ELMs, (a), (b) Effect of internal phase acid concentration ($C_{io}$), (c), (d) Effect of carrier concentration ($C_c$), (e), (f) Effect of internal phase volume fraction (φ) (Conditions as in Table 1).

The distribution of nickel at the end of the run in the oil and aqueous phase of the emulsion is shown in Figure 2(d). It is evident from the figure that in all the cases, the extent of stripping is about 55% ± 2% of the nickel loaded in the emulsion. An increase in the carrier concentration primarily enhances the nickel loading capacity of the ELMs and consequently the nickel flux within the globules; therefore, at high carrier concentrations the nickel flux penetrates deep within the globules resulting in the internal phase droplets located in the core of the globules becoming more effective in stripping the loaded nickel from the extractant complex.

### 3.2.3. Effect of internal phase volume fraction (ϕ)

A change in the internal phase volume fraction ϕ changes the emulsion morphology and in turn influences the rates of extraction as well as the stability of the emulsion. All sensible properties of the emulsions change with changes in ϕ. In the present study, experiments were carried out at ϕ = 0.5 and ϕ = 0.64 while maintaining all other parameters at a constant value. Figure 2(e) shows the effect of variation of ϕ on the extraction of nickel. It is seen that there is considerable decline in the extraction rates with an increase in ϕ.

Although an increase in ϕ increases the storage capacity of the ELMs due to an increase in the amount of stripping phase in the emulsion, it also leads to an increase in the viscosity of the emulsion. Hence, under the same degree of agitation, large emulsion globules are formed. It is appropriate to note that an increase in ϕ also results in a decline in the membrane phase volume of the emulsion and therefore the amount of carrier in the system. The combined effect of decline in extractant, decline in the mass transfer area due to large globule sizes and large internal droplet size contribute to the decline in overall extraction rates. This issue is fairly complicated because an increase in ϕ also leads to the formation of thinner membranes that result in lower diffusional resistances, therefore the exact reason for the decline in extraction rates cannot be pinned to any single effect and the optimality of a particular value of ϕ appears to be a sort of tradeoff between the contradictory effects. The extent of nickel stripped by the internal phase is only 44% of the total nickel loaded for ϕ = 0.64 as shown in Figure 2(f), which is primarily due to the substantial reduction in the stripping surface areas. Further, large globules formed due to an increase in the viscosity of the emulsion cause a decline in the external surface area and increase the diffusional path length.

### 3.3. Co-extraction of nickel and copper into ELMs

Co-extraction of nickel and copper from ammoniacal-ammonium sulfate solutions was also investigated using ELMs at a pH of 8.1. The effect of the emulsion parameters such as internal phase acid concentration, internal phase volume fraction, carrier concentration as well as the initial feed concentration of nickel and copper, on the rates of extraction of copper and nickel from the feed was investigated. Table 2 shows the parametric variables studied.

### 3.3.1. Effect of stripping acid concentrations ($C_{io}$)

Two acid concentrations of 0.5 M and 1.0 M were used in the internal phase of the W/O emulsions to evaluate the effect of stripping acid concentration on the extent and rates of copper and nickel extraction from feed solutions into ELMs. It is known that nickel gets stripped rather easily even with low acid strengths while copper gets stripped at relatively higher acid strength of 1.0 M and above. It was anticipated that low acid strengths would preferentially favor nickel removal while higher acid strengths would favor copper removal, however this was not observed (Figure 3(a)).

The rate of extraction of both nickel and copper increased with stripping acid concentration from 0.5 M to 1.0 M. However, the rates of copper extraction were much faster than that observed for nickel. Moreover, while copper was almost quantitatively extracted in 3 minutes into ELMs having $C_{io}$ = 1.0 M, even in the best case only 49% Ni was extracted in the contact time of 10 minutes with emulsions having $C_{io}$ = 1.0 M. Comparing Figure 2(a) with Figure 3(a), the effect of $C_{io}$ on nickel extraction in the presence of copper is identified. There was significant decline in the extent and rates of nickel extraction in the presence of copper. This decline is expected and attributed to two factors:

LIX 84I, which was used as the carrier in this investigation, is primarily a copper extractant. The selectivity of LIX84I for various metals follows the order Cu > Ni > Zn. Therefore, it is apparent that LIX 84I loads Cu preferentially and more rapidly than Ni. Secondly, the rate of stripping of Cu appears to be faster than Ni at both internal acid concentrations as shown in Figure 4(a), which presents the extraction and stripping profiles at both acid concentrations.

It is very likely that copper ions, which complexes more rapidly and preferentially with LIX84I, diffuses rapidly inside the ELM globules and encounters the peripheral internal droplets where the Cu gets stripped and depletes the acid in those droplets. The loaded nickel complex has to diffuse much deeper within the emulsion globule to encounter the stripping reagent to get stripped. Hence, the aspect of enhanced diffusional path length also contributes to the decline in observed extraction rates for nickel in the presence of copper.

### 3.3.2. Effect of carrier concentration ($C_c$)

Carrier concentration in the membrane phase strongly influences the overall extraction rates of nickel in ELMs. The effect of carrier concentration on the extraction of copper and nickel mixture from ammoniacal solution is shown in Figure 3(b). Extraction rates of copper from the feed mixture were identical for emulsions containing 15% (v/v) and 20% (v/v) oxime concentration in the membrane phase while they were marginally slower for $C_c$ = 10% (v/v). However, quantitative extraction of copper was observed in these extractions but at different time intervals.
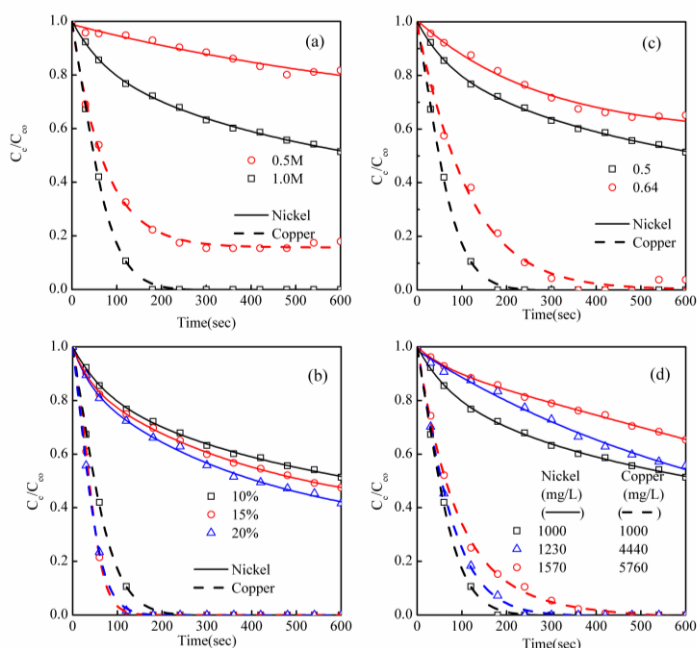


**Fig. 3.** Effect of parametric variables on the co-extraction of copper and nickel from ammoniacal media in ELMs. (a) Effect of internal phase acid concentration ($C_{io}$), (b) Effect of carrier concentration ($C_c$), (c) Effect of internal phase volume fraction (ϕ), (d) Effect of initial copper and nickel concentration in feed ($C_{eo}$) (Conditions as in Table 2).
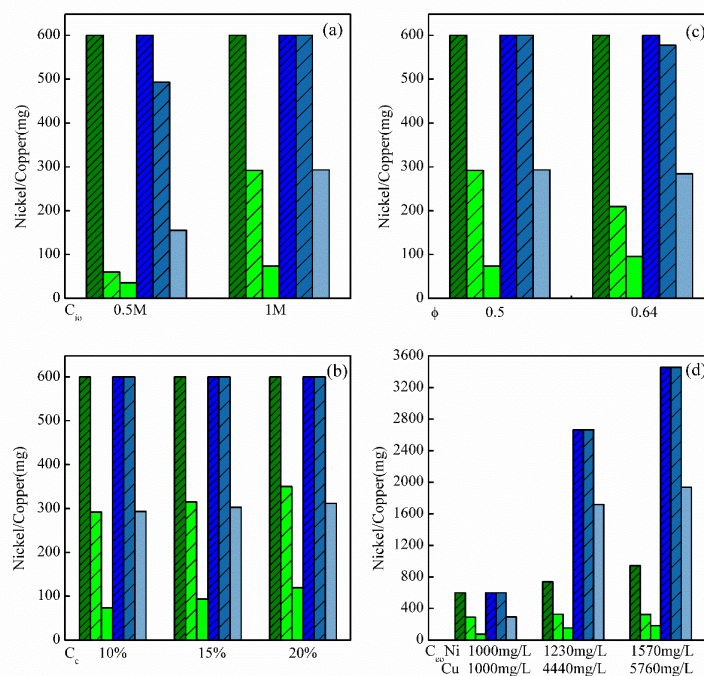
**Fig. 4.** Copper-nickel, extraction-stripping patterns in ELMs, (a) Effect of internal phase acid concentration ($C_{io}$), (b) Effect of carrier concentration ($C_c$), (c) Effect of internal phase volume fraction ($\phi$, (d) Effect of initial copper and nickel concentration in feed ($C_{eo}$).

Due to the preferential complex formation of LIX 84I with copper, its uptake by ELM is very rapid and as a consequence the rate of uptake of nickel that is relatively slow gets even more retarded in the presence of copper. It can be seen from Figure 3(b) that only after copper is quantitatively loaded in the ELMs, the rate of nickel loading gets enhanced for $C_c$ of 15% (v/v) and 20% (v/v) of LIX 84I while for $C_c$ = 10% even that is not observed.

The decline in the rates of Ni extraction from the mixed solute system can largely be attributed to the shortage of free carrier within the ELM system available to bind with nickel. This becomes amply clear from Figure 4(b) that shows almost ~ 50% of the loaded Cu remains non-stripped at the end of the run in all three cases, implying that a considerable amount of extractant remains bound with copper and is not free for loading nickel. This shortage of free extractant results in a decline in nickel loading. It is seen from Figure 4(b) that the amount of Cu stripped has a good correlation with the amount of Ni loaded. These results suggest that copper strongly complexes with LIX 84I and does not get displaced easily, and the stripping of Cu is slow even with the acid of concentration 1.0 M. If higher acid strength had been used then it is likely that Cu could have gotten stripped to a greater extent, resulting in a greater amount of free extractant to load Ni, but at the same time Ni stripping would have been even more retarded.

### 3.3.3 Effect of internal phase volume fraction ($\phi$)

The effect of the internal phase volume fraction on the rates of co-extraction of copper and nickel is shown in Figure 3(c). It is observed that the extraction rates of both metals are considerably faster when $\phi$ = 0.5 in comparison to $\phi$ = 0.64. A decline in extraction rates is caused primarily because the increase in the internal phase volume causes a decline in the membrane phase volume to the extent of 32%. and correspondingly a similar decline in the extractant content in the system, which leads to a sharp decline in loading capabilities of the ELMs. This effect is augmented by a shift in the internal droplet size distribution to larger sizes, and the Sauter mean diameter shifts from 2.72 μm for $\phi$ = 0.5 to 10.75 μm for $\phi$ = 0.64, and large internal droplets result in lower internal surface areas in ELMs having $\phi$ = 0.64 that leads to slow rates of stripping and eventually an overall decline in the extraction rates is observed.

Analysis of the internal phase of the ELMs after emulsion breakage at the end of the experimental run reveals an interesting feature of the overall dynamics of the process. From Figure 4(c), it is observed that with $\phi$ = 0.5, all of the copper in the feed mixture is loaded in the emulsion, but only half of it is stripped. When $\phi$ = 0.64, nearly 95% of the feed copper is loaded in the ELMs and again almost half of it is stripped. The amount of copper stripped remains almost the same irrespective of $\phi$. However, for Ni extraction it was found that ELMs having $\phi$ = 0.5 load only ~ 50% of the Ni from the feed and only a quarter of it gets stripped. While with ELMs having $\phi$ = 0.64 only one

third of the initial Ni in the feed gets extracted by the emulsion, it is observed that a 32% decline in the extractant content in the system when $\phi$ = 0.64 contributes to almost ~ 27% decline in the amount of Ni extracted in ten minutes establishing almost a linear correlation between the extractant content in the system and amount of Ni extracted. However, contrary to expectations almost half the nickel extracted by these emulsions gets stripped in the internal phase. This fairly large extent of stripping is attributed to the large amount of internal phase present within the ELMs that make available a lot of acid for stripping the Ni from the loaded complex.

### 3.3.4. Effect of initial feed concentration ($C_{eo}$)

Variation of copper and nickel in the initial feed concentration were explored to gain an understanding of the pattern of co-extraction of both the metals in ELMs from fairly concentrated feeds. The idea was to test the efficacy and stability of the ELMs to extract such feeds and also to identify restrictions – if any, that high solute concentration is imposed on the co-extraction of metals by the ELMs. The copper concentration in these feeds varied widely in the range of 1000–5760 mg/L while that of nickel was varied moderately in the range of 1000–1570 mg/L.

Extraction results are shown in Figure 3(d). For all three cases, copper extraction was much faster than nickel extraction, and an almost quantitative removal of copper took place within seven minutes at a maximum copper concentration of 5760 mg/L, while a maximum of 34% nickel removal took place with an initial nickel concentration of 1570 mg/L in the same time duration. This pattern is attributed to the same factors discussed in the previous section. Copper gets loaded faster, and this induces a large flux of copper-oxime complex directed inwards within the emulsion. All peripheral internal phase droplets are depleted of their acid content to strip the copper, and hence nickel has to diffuse deeper to get stripped. The slow rate of extraction observed for nickel is additionally contributed by the slow stripping rates of nickel in ELMs. The histogram shown in Figure 4(d) bears testimony to these ideas.

It is distinctly observed that ELMs with LIX 84I as extractant show a preference for the selective removal of copper from Cu–Ni mixtures. Other aspects including stripping kinetics of copper and nickel, physicochemical features such as diffusion of the oxime complex within the emulsion globule, etc. all get completely masked by the affinity of the oxime for copper.

## 4. Conclusions

A new dimension in ELM extraction was revealed by the assessment of the solute stripped in the internal phase of the emulsion at the end of the run. The significant findings in light of both extraction and stripping behavior of nickel and copper–nickel mixtures in ELMs are:

i. The optimal pH for extraction was found to be a pH of 8.1 as found earlier for copper, zinc and copper – zinc mixtures. Ni extraction was most favored when internal phase acid concentration was 1.0 M. The increase in $\phi$ was deleterious for the extraction with the amount of nickel extracted and stripped declining sharply at $\phi = 0.64$.

ii. The magnitude of nickel extraction increased with the carrier concentration in the emulsion indicating that loading governs the overall extraction process. The effect of initial feed concentrations and the treat ratio on the extraction rates also led to the same conclusions. Loading of nickel governs the overall process and the amount of nickel stripped in all cases was ~55 % of the amount extracted.

iii. Co-extraction of copper and nickel using LIX 84I from ammoniacal media showed that internal phase acid strength of 0.5 M was inadequate for the stripping of copper as well as nickel from the membrane phase, and a minimum acid strength of 1.0 M acid was found appropriate. The rate of copper extraction was much greater than the rate of nickel extraction. In the experimental range of concentrations investigated copper could be quantitatively loaded in the emulsion even when its concentration was very large. Nickel loading declined further in the presence of copper, and copper stripped to a far greater extent in the internal phase of the emulsion in comparison to nickel.

iv. The increase in carrier content increased the rates of copper and nickel uptake by the ELMs but did not affect the net copper uptake, while marginally improving the nickel uptake. It was interesting to find that the amount of copper stripped in the internal phase was equivalent to the amount of nickel uptake by the ELMs.

v. It was found that ELMs loaded with LIX 84I had the efficacy of removing nickel as well as mixtures of copper and nickel from aqueous ammoniacal media. Further, they could be used for selective removal of copper from Cu–nickel mixtures in ammoniacal media.

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