Integrated Membrane Process for Gold Recovery from Hydrometallurgical Solutions

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This work reports the nondispersive solvent extraction (NDSX) of gold cyanide from aqueous alkaline cyanide media with LIX79 and stripping of gold from the organic complex simultaneously using two microporous hydrophobic polypropylene hollow-fiber contactors for extraction and stripping, respectively. Extraction was studied under different hydrodynamic conditions and mass-transfer correlations for shell and tube sides. The mass-transfer process was compared with experimental results. The HFNDSX was operated with 12–18% LIX 79 in n-heptane by contacting alkaline cyanide feed containing gold through the tube side and organic extractant through the shell side, which was recirculated between extraction and stripping hollow-fiber modules through the shell side countercurrently. In the second HF contactor, the stripping solution, 1M NaOH flowed through the tube side countercurrently. Modeling of the system identified rate-controlling steps under different experimental conditions. The interfacial chemical reaction rate at the dominant surface, and mass-transfer resistance caused by this reaction controlled the entire extraction process. Several experiments with synthetic solutions of different compositions of gold hydrometallurgical solutions established optimum conditions to achieve a clean separation of Au(I). It was possible to separate Au(I) in the presence of other metal cyanide salts, such as Fe(II), Cu(II), Ni(II), Ag(I), and Zn(II) (NaCN = 1,000–5,000 ppm), which was concentrated in the stripping phase containing NaOH.

Introduction

Separation of metals by solvent extraction using conventional equipment, such as mixer–settlers, extraction columns, and centrifugal equipment, or by membrane extraction using hollow-fiber contactors, has been an important technique in pollution control, as well as in hydrometallurgical processes. Membrane extraction can outperform conventional mixer–settlers and extraction columns, as it provides a surface area per volume that is 30–100 times larger than for the latter two systems (Yang and Cussler, 1986; Daiminger et al., 1996). The extraction rate of hollow fibers can also be comparable to that of contrifugal extractions (Yang and Cussler, 1986), which are more expensive (Hafez, 1983). In view of this, recently developed membrane-extraction processes using microporous hollow fibers are of particular interest because of their versatility and in the way they overcome problems encountered in conventional liquid–liquid extraction (LLE). Membrane extraction is carried out using microporous membranes to immobilize the aqueous/organic interface with the porous structure. The solute is transported from the feed to the extractant phase, through the membrane, without phase dispersion, thus avoiding the formation of stable emulsions that may hinder the process. The technique also overcomes other shortcomings of conventional liquid extraction such as flooding limitations on the independent variation of phase flow rates, the density-difference requirement, and inability to handle particulates. Further, membrane-extraction processes have been applied in a large number of systems, including the extraction of metals, pollutants, proteins, antibiotics, and pharmaceutical products (Gabelman et al., 1999; Sirkar, 1997; Ho and Sirkar, 1992; Sastre et al., 1998; Kumar and Sastre, 1998, 2000). Although the NDSX technique has been used for some years, applications of this technique in hydrometallurgy are rare as compared to their applications in biosepara-

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tions (Ho and Sirkar, 1992). Among the few studies performed for hydrometallurgical applications, the nondispersive solvent-extraction pilot plant for removal of Cr(VI) from galvanic process wastewaters, tested by Alonso et al. (1999) in Spain, brought this technique to a level of commercialization.

Among several precious metals, gold has always been at the center of attention owing to its versatility in many industries throughout the world. Therefore, its recovery from several diverse sources is of great importance. In the present scenario, recovery of gold from alkaline cyanide solutions is accomplished by well-established procedures of zinc cementation and carbon absorption (Mooiman et al., 1984), but this process is energy intensive, particularly with regard to the regeneration of the spent carbon. Little attention has been given to the development of alternative processes for gold recovery. There are a number of situations in which the NDSX process could be employed for gold recovery from these cyanide leach solutions. These possibilities include: (1) heap and agitation leach solution from low-grade ores (1–10 ppm); (2) eluate solution from carbon strip (100–2,000 ppm); and (3) waste electroplating solutions (1,000–2,000 ppm). The recovery of gold from cyanide media has been attempted by several researchers using conventional liquid–liquid extraction. Riveros et al. (1990) performed recovery of gold from real cyanide solutions using commercial quaternary amines (Aliquat-336 dissolved in Solvesso-150) in order to develop a complete pilot-plant campaign. The stripping process seems to be complicated on an industrial scale, because (1) acidic thiourea was suggested as a stripping agent, and (2) incineration of gold-loaded quaternary amine salt was advised in order to obtain pure gold metal. Kordosky et al. (1992) have developed a solvent extraction (SX) process for gold(I) recovery using an SX circuits with reagent *N-N'*-bis (2 ethylhexyl) guanidine and *N-N'*-bis (tridecyl) guanidine (similar to LIX79 containing guanidine functionality). In spite of good performance, third phase and crud formation were reported by the authors. Similarly, in further studies Virning and Wolfe (1996) performed conventional SX studies with a real mine solution of Au(I) from cyanide media using LIX79, a circuit configuration consisting of three stages of extraction and two stages of stripping. Third-phase formation was reported by the authors, and a modifier was added in order to eliminate this problem. In view of this, present studies deal with HFNDSX for extraction separation of Au(I) from hydrometallurgical solutions.

To obtain the optimum operational conditions for this process, it is necessary to have a reliable design model of the system that includes the separation selectivity of the components to be used as a reference parameter. Based on the previous studies, LIX79 containing a guanidine functionality (Henkel Co.) was chosen as an extractant that has a good extractability at pH > 9 and stripping of Au(I) in highly basic (pH > 12) solutions (Sastre et al., 1999; Kordosky et al., 1992; Virning and Wolfe, 1996).

The aim of the present work is to characterize the extraction of Au(I) with LIX79/*n*-heptane using membrane contactors with microporous membranes. Hydrodynamic and chemical conditions were established for this process in order to separate gold from synthetic hydrometallurgical solutions. Results performed for the extraction of Au(I)–LIX79 with one module and in an integrated process (extraction and stripping together in two HF modules) were also compared.

Table 1. Physical Conditions, Equilibrium Parameters, and Hollow-Fiber Membrane Characteristics

Symbol	Property	Value
H	Partition coefficient	4.44 5.00*
D_m	Pore liquid diffusivity (cm^2/s)	2.5×10^{-6}
D_s	Shell liquid diffusivity (cm^2/s)	2.5×10^{-5}
D_t	Aqueous diffusion coefficient of Au(I) (cm^2/s)	7.2×10^{-6}
η_s	Shell fluid viscosity (g/cm·s)	4.47×10^{-3}
K_{ex}	Extraction equilibrium constant	$2.19 \pm 0.5 \times 10^{11}$
k_e	Forward reaction-rate constant of Eq. 5 (cm/s)	6.57×10^{10}
k_i	Effective rate of interfacial reaction defined in Eq. 5	6.18×10^{-7}** 1.85×10^{-6}†
	Hollow fiber membrane details	
	Fiber ID (cm)	24.0×10^{-3}
	Fiber OD (cm)	30.0×10^{-3}
	Fiber wall thickness (cm)	3.0×10^{-3}
	Fiber length (cm)	15.0
	Active interfacial area (m^2)	1.4
	Porosity (%)	30
	Pore size (μm)	0.03
	Polymeric material	Polypropylene

*Partition coefficient for stripping.
**Value estimated at 12% LIX79 and feed pH 10.3.
†Value estimated at 18% LIX79 and feed pH 10.3.

Experimental Procedure

Reagents

A stock solution of Au(I) (5 g/L) was prepared from pure solid $KAu(CN)_2$, and 1 g/L of each cyanide salt, such as $KAg(CN)_2$, $Zn(CN)_2$, $KNi(CN)_4$, and CuCN (Johnson Mattey Chemicals, Karlsruhe, Germany), and $K_4Fe(CN)_6 \cdot 3H_2O$ (Merck, Darmstadt, Germany), were dissolved in NaCN (Merck). $KNi(CN)_4$ and CuCN salts were dissolved in excess of NaCN in deionized water. The organic solvent used in HFNDSX studies was *n*-heptane, which is a commercially available solvent. All chemicals were used as received. LIX 79 (*N*, *N'*-bis(2-ethyl hexyl) guanidine) was kindly donated by Hankel Co. and Cytec Inc., Canada.

Hollow-fiber apparatus

The hollow-fiber device used for the two steps was a commercially available unit purchased from Hoechst Celanese (now known as Celgard GmbH), Charlotte, NC (Liqui-Cel, 8×28 cm 5PCG-259 contactor and 5 PCS-1002 Liqui-cel laboratory LLE). The module details and hollow-fiber membrane characteristics are listed in Table 1.

Partition coefficients of Au(I) extraction equilibrium

Details of the liquid–liquid distribution measurements are essentially the same as those published elsewhere (Sastre et al., 1999; Madi, 1998).

Density and viscosity measurements

Densities and viscosities of the LIX79/*n*-hetane solutions were measured in order to relate Au(I) extraction with their physical properties using HFNDSX techniques. Viscosities were measured at 25 ± 1°C using a Cannon-Ubelhode Semimicro 100 Viscosimeter (Cannon Instruments Co., USA), and densities were determined by weighing a known volume of solution using a pycnometer.

Nondispersive membrane extraction setup

The nondispersive separation process comprises two membrane modules, one for the extraction and the other for the backextraction (stripping), plus a stirred tank for the organic solution and two stirred tanks for the aqueous phases. The experimental setup for the metal separation experiments consists of two gear pumps capable of flows of 1 L/min for the organic and BEX phases, powered by a variable speed dc motor, and a peristaltic pump for the aqueous feed phase capable of flows of 1 L/min. The organic phase wet the porous wall of the fiber because of its hydrophobic nature. The interface was immobilized at the pore by applying a higher pressure to the aqueous stream than to the organic stream. The differential pressure was always kept below the breakthrough pressure. In the aqueous phase, the pressure was held at 0.2–0.5 bar higher than in the organic phase. The membrane-based solvent extraction and stripping process of Au(I) using two hollow-fiber contactors in recirculation mode is shown in Figure 1. The HFNDSX operation was carried out with 12–18% LIX 79 in *n*-heptane by contacting alkaline cyanide feed containing gold through the tube side and organic extractant through the shell side, which was recirculated between the extraction and stripping hollow-fiber modules though the shell side in countercurrent mode. In the second HF contactor, stripping solution, 1 M NaOH flowed through the tube side in countercurrent mode.

The organic phase is a 1500-mL solution of 12–18% LIX 79 in *n*-heptane. One thousand mL of aqueous feed solution of the desired Au(I) concentration was prepared by taking a suitable aliquot from the stock solution. Further, the desired feed pH was adjusted by adding 1 M NaOH solution. The stripping solution, 1 M NaOH, was used when backextraction of Au(I) was carried out in the hollow-fiber module. At predetermined times during the procedure, small aliquots of the feed stream (aqueous solution for the extraction and organic solution for the stripping) were taken and analyzed for metal concentration by standard atomic absorption spectrometry. Au(I) was stripped with 1 M NaOH for analyzing gold in the organic phase.

In the experiments dealing with gold separation there are similar chemical conditions, that is, pH (9–11) and NaCN (1,000–5,000 ppm) concentration, that are encountered in hy-

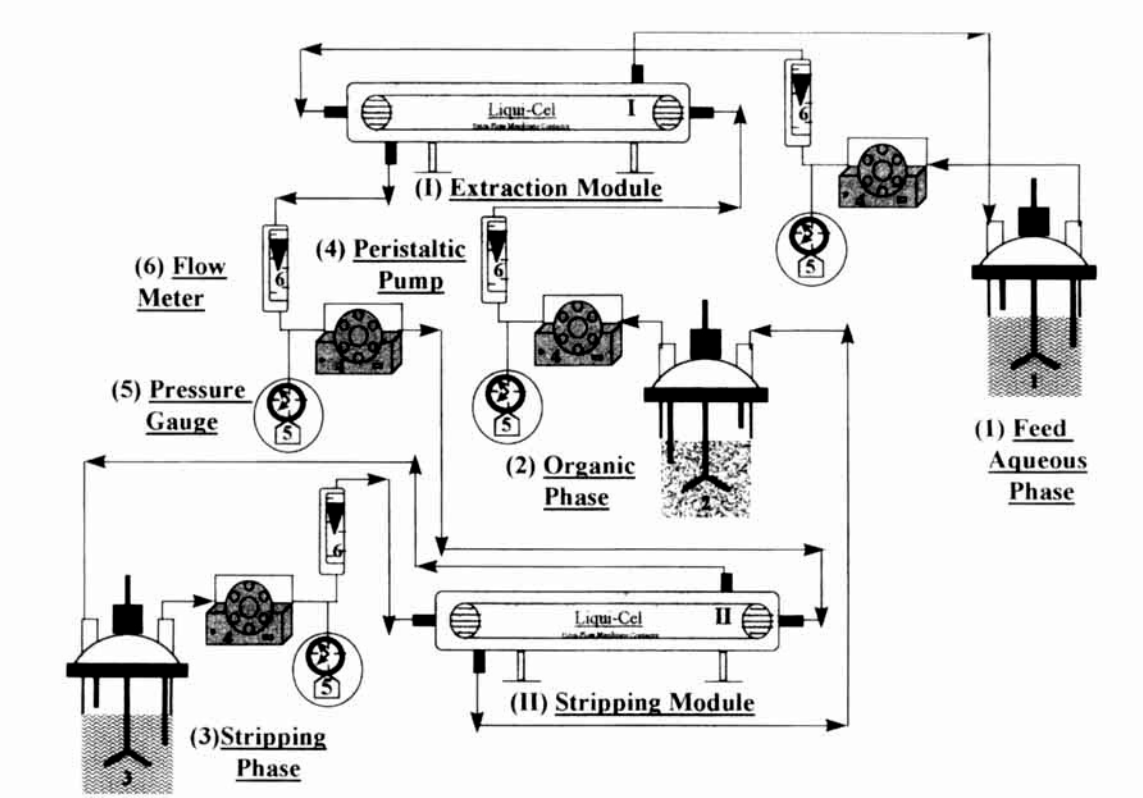

Figure 1. Integrated membrane-based process for Au(I) recovery from cyanide media using two hollow-fiber contactors.

drometallurgical leach solutions from low-grade ores (Virnig et al., 1996; Mooiman and Miller, 1990). The samples containing the Au(I), Cu(I), Fe(II), Ni(II), and Zn(II) mixture were analyzed by ICP (Spectroflame by Spectro Analytical Instruments) to determine each metal concentration.

The presence of bicarbonate in LIX79/(*n*-heptane was analyzed by FTIR (Fourier transform, FTIR, spectroscopy, Perkin-Elmer System 2000).

Theoretical Background

Extraction equilibrium

The extraction mechanism of gold with LIX79 is based on the ion pair type (Virning et al., 1996). The extraction of Au(I) by organic extractant LIX 79 dissolved in *n*-heptane has been studied and described elsewhere (Madi, 1998; Kumar and Sastre, 2000; Sastre et al., 1999). The Au(I) ions in alkaline cyanide media (present as $\mathrm{Au(CN)_2}^-$) form a complex with the extractant LIX 79 (*N*, *N'*-bis(2-ethyl hexyl) guanidine, RH), expressed as

$$\mathrm{R_{org} + H^+_{aq} + Au(CN)^-_{2aq} \Leftrightarrow [HAu(CN)_2R]_o} \qquad \mathrm{K_{ex}}, \quad (1)$$

and the stripping of Au(I) from loaded LIX79 phase is shown as

$$\mathrm{[HAu(CN)_2R]_o + NaOH_s \Leftrightarrow Au(CN)_2{}^-{}_s + R_o + H_2O + Na^+}. \quad (2)$$

The extraction equilibrium can be described by the following reactions and extraction constants

$$K_{\mathrm{ex}} = \frac{\mathrm{[HAu(CN)_2R]_{org}}}{\mathrm{[Au(CN)_2{}^-][H^+][R]_{org}}}, \quad (3)$$

where R is the organic extractant. More details on extraction equilibrium reactions are described in our earlier work (Sastre et al., 1999; Kumar and Sastre, 2000). The values of K_{ex} for Au(I) with LIX 79/*n*-heptane were found to be $2.19 \pm 0.15 \times 10^{11}$. The partition coefficient could be presented as

$$\log \mathrm{H} = \log K_{\mathrm{ex}} + \log[\mathrm{H}^+] + \log[\mathrm{R}]_{\mathrm{org}}. \quad (4)$$

Nondispersive membrane extraction

As derived by D'Elia et al. (1986), for cocurrent flow, the key equation for the calculation of K^E_{Au} or K^S_{Au} is

$$\left[\frac{\dfrac{1}{Q_f} + \dfrac{1}{Q_{e/s}H}}{\dfrac{1}{V_f} + \dfrac{1}{V_{e/s}H}}\right] \ln\left[\frac{C^0_{e/s}/\left(H - C^0_f\right)}{\left(C^0_{e/s} - C^0_f\right) + \left(V_f/HV_{e/s}\right)\left(C^0_f - C_f\right)}\right] \quad (5)$$

For countercurrent contact, the following equation was used (D'Elia et al., 1986):

$$\ln\left[\frac{\left(C^0_{e/s}/H - C^0_f\right)}{\left(C^0_{e/s}/H - C^0_f\right) + \left(V_f/HV_{e/s}\right)\left(C^0_f - C_f\right)}\right] = t$$
$$\times \frac{\left[1 - \exp\left(-4K^E_{\mathrm{Au}}V_m/d\left(1/Q_f - 1/Q_{e/s}H\right)\right)\right]\left[1/V_f + 1/V_{e/s}H\right]}{\dfrac{1}{Q_f} - \dfrac{1}{Q_{e/s}} \exp\left[-\dfrac{4K^E_{\mathrm{Au}}V_m}{d}\left(\dfrac{1}{Q_f} - \dfrac{1}{Q_{e/s}H}\right)\right]}; \quad (6)$$

where Q_f and $Q_{e/s}$ are the feed and extract/strip flows; V_f and $V_{e/s}$ are the feed and extract/strip volumes; C^0_f and $C^0_{e/s}$ are the concentrations of the solute in the feed and in the extract/strip solutions at time zero; C_f is the concentration of the solute in the feed at time *t*; V_m is the volume of all the hollow fibers; and *d* the diameter of one fiber.

Model Development

The system consists of an aqueous phase containing $\mathrm{Au(CN)_2^-}$ flowing in the tube side of microporous hollow-fiber membranes whose pores are filled with the organic extractant and the organic extractant flowing cocurrently or countercurrently in the shell side (Figure 1). The reaction takes place on the inside of the wall of the membrane where the phase interface is located. To determine the rate-controlling step, we consider the commonly used hypothesis that the extraction involves four sequential steps: the effective rate of the interfacial reaction at surface, mass transfer from the bulk aqueous feed to the inside surface of the hollow-fiber membrane, diffusion across the membrane itself, and mass transfer into the organic solution surrounding the fiber. From the bulk-loaded organic LIX79 phase in the stripping module, the gold complex is transferred to the membrane–strip interface at the pore mouth, and finally transferred to the bulk aqueous stripping phase (Yun et al., 1993).

Assuming a resistance in the series model, the reciprocal of the overall mass-transfer coefficient is the total resistance to mass transfer and can be described as the sum of the mass-transfer resistances inside the fiber (feed phase), across the fiber wall (membrane resistance), and outside the fibers (organic phase). Therefore, the expression for overall mass-transfer coefficient, K^E_{Au}, can be written as (Cussler, 1984, 1995).

$$\frac{1}{K^E_{\mathrm{Au}}} = \frac{1}{k_i} + \frac{1}{k_f} + \left(\frac{d_i}{d_{lm}}\right)\frac{1}{k_m H} + \left(\frac{d_i}{D_h}\right)\frac{1}{k_s H}. \quad (7)$$

The following expression takes into account the empirical relations for k_f and k_s, which depends on the hydrodynamics of the feed and organic phases, respectively:

$$\frac{1}{K^E_{\mathrm{Au}}} = \frac{1}{k_i} + \frac{1}{(D_t/d_i)\left(d_i^2 v_t/LD_t\right)^{1/3}} + \left(\frac{d_i}{d_{lm}}\right)$$
$$\times \frac{\tau t_m}{K_{\mathrm{ex}}[\mathrm{H}^+][\mathrm{R_{org}}](D_m \epsilon)} + \left(\frac{d_i}{D_h}\right)$$
$$\times \frac{1}{K_{\mathrm{ex}}[\mathrm{H}^+][\mathrm{R_{org}}]\,\beta[(L)](v_s D_h/\eta_s)^{0.6}(\eta_s/D_s)^{0.33}(D_s/D_h)}, \quad (8)$$

where

$$\frac{1}{k_i} = \frac{1}{k_e[\mathrm{H}^+][\mathrm{R}_{\mathrm{org}}]} \tag{9}$$

$$H = K_{\mathrm{ex}}[\mathrm{H}^+][\mathrm{R}_{\mathrm{org}}],$$

thus

$$[\mathrm{H}^+][\mathrm{R}_{\mathrm{org}}] = \mathrm{H}/\mathrm{K}_{\mathrm{ex}}$$

on suitable substitution in Eq. 9,

$$1/k_i = 1/(ke[\mathrm{H}/\mathrm{K}_{\mathrm{ex}}]),$$

and k_i is the effective rate of interfacial reaction at the surface: k_f, k_m, and k_s are the mass-transfer coefficients in the aqueous feed, membrane, and the organic solvent, respectively; d_i, D_h, and d_{lm}, respectively, are the internal, external, and logarithmic mean fiber diameters. Equation 9 was derived to estimate the value of k_i similar to the methods published in the literature (Yun et al., 1993; Yang et al., 1996, 2000). The first term on the righthand side of Eq. 8 represents the resistance owing to interfacial reaction; the second term indicates the mass-transfer resistance in the aqueous phase; the third term is the membrane resistance; and the fourth term is the resistance of the organic extraction solvent. The partition coefficient, $H = [\mathrm{H}^+][\mathrm{R}_{\mathrm{org}}][K_{\mathrm{ex}}]$, appears in the membrane resistance, because in our experiments the organic solvent wets the membrane but water does not.

The overall mass-transfer coefficient can be calculated from the individual transfer coefficients k_i, k_f, k_m, and k_s. The tube- and shell-side mass-transfer coefficients are known to depend on the flow conditions in the fiber lumen and shell fluid, respectively, and correlations expressing these dependencies are available in the literature.

The flow through the fibers in the membrane modules will always be laminar. Within this general context, the individual mass-transfer coefficient for the tube side is dependent on the mean flow velocity v_f, according to (Prasad and Sirkar, 1988; Hann et al., 1989; Dahuron and Cussler, 1988)

$$N_{sh} = (k_f d_i/D_t) = 1.64(D_t/d_i)(d_i^2 v_f/LD_t)^{1/3}. \tag{10}$$

In general, the preceding correlation predicts mass-transfer coefficients with reasonable accuracy for $N_{Gz} > 4$, but overestimates them for $N_{Gz} < 4$ (Lévêque, 1928). In the present experimental conditions, N_{Gz} ranges from 5.5 to 8.2. Similarly, for the shell-side mass-transfer coefficient, the following correlation was given (Prasad and Sirkar et al., 1988; Basu et al., 1990; Yun et al., 1993)

$$N_{sh} = \frac{k_s D_h}{D_s} = \beta[D_h(1-\phi/L)]N_{re}^{0.6}N_{Sc}^{0.33} \tag{11}$$

where

$$N_{Re} = \frac{v_s D_h}{\eta_s}, \qquad N_{Sc} = \frac{\eta_s}{D_s},$$

β is 5.85 for hydrophobic membranes, $0 < N_{Re} < 500$, and $0.04 < \phi < 0.4$. In the present system both conditions are fulfilled, as N_{Re} ranges from 3.0 to 11.0 and $\phi = 0.35$, and the notations D_h = hydraulic diameter, D_t = diffusion coefficient of solute in the tube side; d_i = inner fiber diameter; L = fiber length; D_s = diffusion coefficient of solute in the shell side; v_t and v_s are the velocity of the liquid in the fiber side and the shell side, respectively. An estimate of the membrane mass-transfer coefficient can be determined by the following equation (Kiani et al., 1984; Prasad et al., 1986):

$$k_m = \frac{D_m \varepsilon}{\tau[(d_o - d_i/2)]} \tag{12}$$

For the membrane and solvent here: t_m = membrane thickness = 30 μm; τ = tortuosity = 3 (the value obtained from Celgard GmbH); D_m = diffusion coefficient of gold complex in membrane = 2.5×10^{-6} cm²/s (Kumar and Sastre, 1999); $\varepsilon = 0.30$; and $H = 4.44$. The membrane tortuosity was also determined by the Wakao-Smith model, expressed as the inverse of the membrane porosity, which almost matches the value suggested by Hoechst Celanese (now known as Celgard GmbH) (Iverson et al., 1994).

The membrane mass-transfer coefficient does not depend on the hydrodynamics; it is only related to the membrane properties and to the diffusion coefficient of the solute in the organic phase present in the pores.

Results and Discussion

Optimization of hydrodynamic conditions

The details of hollow-fiber module, hollow-fiber membrane characteristics, physical properties, and chemical equilibrium parameters are presented in Table 1. It is well established in the NDSX technique (Kiani et al., 1984; Daiminger et al., 1995) that, in order to keep the interface within the pores of a hydrophobic membrane, it is necessary to maintain a higher local pressure in the aqueous phase. It is interesting to note that the overall mass-transfer coefficient obtained in the integrated process (in two simultaneous HF module extraction and stripping) was observed to be higher than the values of K_{Au}^E obtained with the single module (no stripping). This is probably due to the equilibrium limitation, which was eliminated when the stripped organic was in continuous contact with the feed owing to the fast stripping of the LIX79–Au(I) complex in the backextraction module. Similar equilibrium limitations were observed by Hu Shih-Yao and Wiencek (1998) while performing liquid membrane emulsion of copper with hollow-fiber contactors using LIX84 as an extractant. The previous work on nondispersive extraction was performed with the LIX79–Au(I) system, using one hollow-fiber module in order to optimize this process in batch experiments (Kumar et al., 2000). Although the performance of this system was satisfactory, the LIX79 became loaded with bicarbonate through exposure to air during the experimental runs. Also, with one module, when the feed was replaced with fresh feed and the organic LIX79/*n*-heptane phase was maintained the same, this could have resulted in a raffinate pH of 7.5 from the initial pH of 10.3 (after three batches of experiments), which could be unsafe for the process in the cyanide medium. To overcome this problem, the LIX79/*n*-heptane phase was preloaded with a carbonate/bicarbonate buffer having a pH of around 10. Figures 2a–2c show the FTIR spectra, which confirmed the presence of bicarbonate in the LIX79/*n*-heptane organic phase, collected from the batch experiment. Figure 2 shows (1) FTIR spectra of LIX79 alone; (2) FTIR spectra of LIX79/*n*-heptane after the three continuous batch experiments, and (3) FTIR spectra of LIX79/*n*-heptane after the three continuous batch experiments where the aqueous phase contains 500 ppm NaCN. The FTIR spectra exhibited bands at 1,600–1,800 cm^{-1} and at 2,000–2,500 cm^{-1} assigned to C=O, O=C=O stretching, respectively. Comparing these spectra to pure LIX79, we can conclude the loading of bicarbonate into LIX79 due to its exposure to air during the experimental run. Interestingly, this problem could be eliminated in the currently studied integrated membrane process, as bicarbonate-loaded LIX79 comes into contact with NaOH in the stripping module, where it becomes neutralized and the pH of raffinate turned out to be 10.6–10.8 (constant). As can be seen from Figure 3, the reduction in Au(I) concentration in the feed over time was faster with the increase in Reynolds numbers in cocurrent mode with 12% LIX79. The theoretically calculated values of k_f from Eq. 6 was two to three orders of magnitude higher compared to the experimentally obtained overall mass-transfer coefficient, K_{Au}^{E}. Hence, feed resistance ($1/k_f$) does not dominate the overall mass-transfer coefficient. As expected, Au(I) removal from the feed was not efficiently accomplished in the extraction module when the *Re* for the feed was 1.84, which leaves the Au(I) concentration in raffinate 0.44×10^{-7} mol/cm^3 (initial concentration 2.8×10^{-7} mol/cm^3) compared to the value of 0.06×10^{-7} mol/cm^3 in raffinate for the Reynolds number =

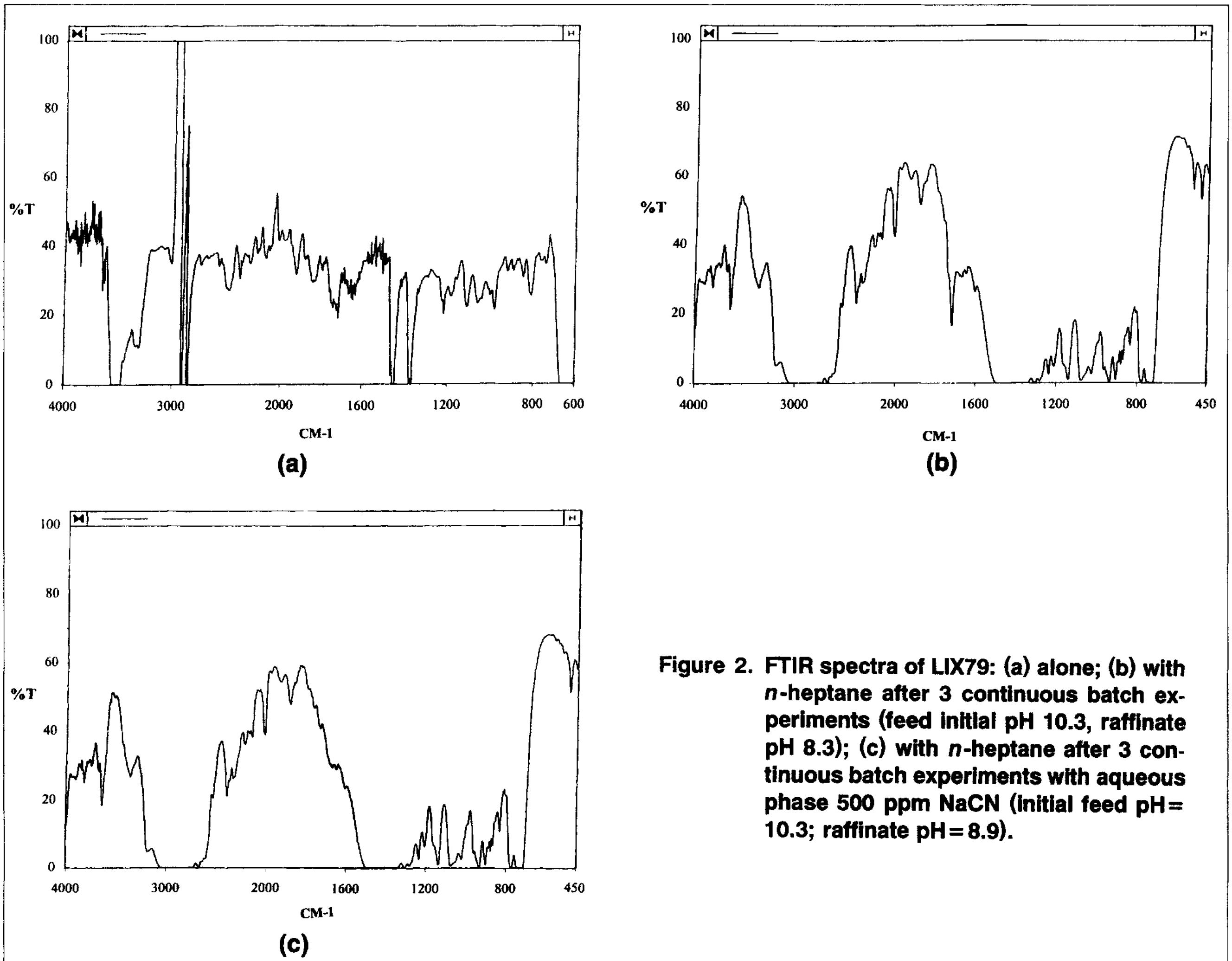

Figure 2. FTIR spectra of LIX79: (a) alone; (b) with *n*-heptane after 3 continuous batch experiments (feed initial pH 10.3, raffinate pH 8.3); (c) with *n*-heptane after 3 continuous batch experiments with aqueous phase 500 ppm NaCN (initial feed pH = 10.3; raffinate pH = 8.9).

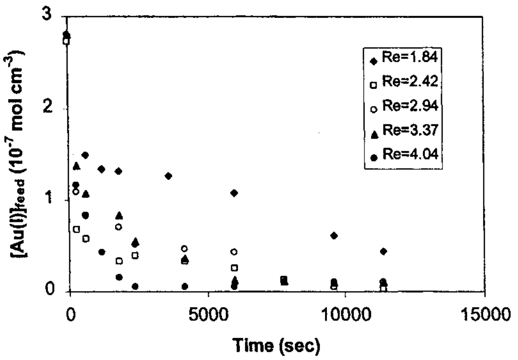

Figure 3. Variations of gold cyanide concentration in feed as a function of time for different Reynolds numbers of aqueous feed phase in cocurrent mode.

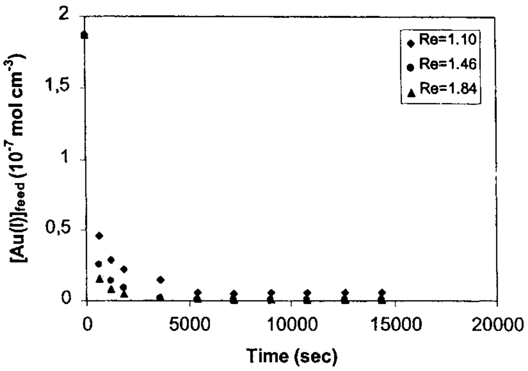

Figure 5. Variations of gold cyanide concentration in aqueous feed as a function of time for different Reynolds numbers of feed phase in countercurrent mode.

4.04 in a similar elapsed period. Hence, Reynolds numbers for feed ranging between 2.94 and 4.04 could provide better mass transfer and almost 100% extraction of gold under similar experimental conditions.

Figure 4 shows the effect of the changing shell-side organic-phase flow rate ($Re = 3.67$–14.66) while keeping the aqueous flow rate constant for 12% v/v LIX79/*n*-heptane. Module extraction efficiency changes dramatically below 2.78 cm^3/s of the organic flow rate (not shown in Figure 3). The gold concentration in the feed dropped from 2.6×10^{-7} mol·cm^{-3} to 0.07×10^{-7} mol·cm^{-3} in raffinate after around 100 min for Reynolds numbers = 3.67 whereas for Reynolds numbers = 9.16–14.66 the same value of Au(I) in raffinate was achieved in 40 min. This behavior indicates that most gold cyanide can be transferred easily into the organic phase by the interfacial reaction when the concentration of the LIX79 is in excess due to an increase in the organic-phase flow rate, since the aqueous inlet concentration of gold is only 10–50 mg/L and the aqueous stream flow rate, Q_f, is around 11.1 cm^3/s ($v_f = 2.5$ cm/s).

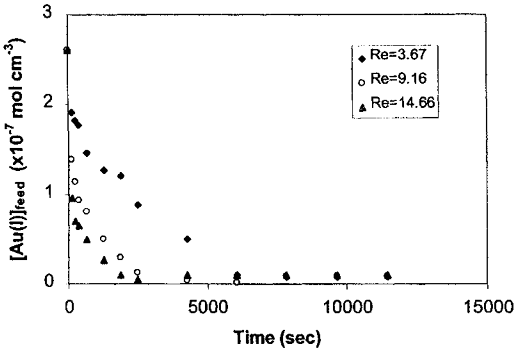

Figure 4. Variations of gold cyanide concentration in aqueous feed as a function of time for different Reynolds numbers of organic phase in cocurrent mode.

Figure 5 indicates that the countercurrent mode was more suitable for efficient mass transfer of Au(I) than the cocurrent mode. The increase in the Reynolds number from 1.46 to 1.84 in countercurrent mode indicates that the feed raffinate value reached 0.06×10^{-7} mol·cm^{-3} in around 30 min, while for Reynolds numbers = 1.1, the same value was achieved in 90 min. On the other hand, K_{Au}^{E} was found to be of the same order of magnitude irrespective of the contacting mode (countercurrent mode or cocurrent mode). As can be seen in Figure 5, at low flow rates ($Re = 1.1$), the Au(I) reduction in feed was more in the countercurrent mode than that of a similar flow rate operated in cocurrent mode (Figure 4). At $Re = 1.84$, the mass transfer was better in countercurrent mode, as the raffinate value reached 0.05×10^{-7} mol·cm^{-3} in 30 min, whereas for the same Reynolds numbers in cocurrent mode, it took more than 150 min to achieve similar

Table 2a. Mass-Transfer Coefficient of Feed, Membrane, and Organic and Interfacial Reaction-Rate Constant in Extraction Module

K_{Au}^{E} (cm/s) Exp.	k_i (cm/s)	k_f (cm/s)	k_m (cm/s)	k_s (cm/s)
2.510^{-6}–1.0×10^{-5}	1.85×10^{-6}	10^{-3}	8.33×10^{-5}	6.0×10^{-5}–10.3×10^{-5}

Table 2b. Mass-Transfer Resistance Due to Interfacial Reaction, Feed, Membrane, and Organic Phase in Extraction Module Defined in Eq. 8

$1/K_{\mathrm{Au}}^{E}$ (s/cm) Exp.	$1/k_i$ (s/cm)	$1/k_f$ (s/cm)	$(r_i/r_m)1/k_m[\mathrm{H}^+][R_{\mathrm{org}}][K_{\mathrm{ex}}]$ (s/cm)	$(r_i/r_o)1/k_s[\mathrm{H}^+][R_{\mathrm{org}}][K_{\mathrm{ex}}]$ (s/cm)	$1/K_{\mathrm{Au}}^{E}$ Model Eq. 4 (s/cm)
1–4×10^5	3–5×10^5	10^3	2,000–3,000	1.7×10^3–3.0×10^3	3–5×10^5

values in raffinate. Based on these studies, countercurrent mode was selected for the integrated membrane process. The feed and strip flow rate were 6.94 cm^3/s and organic extractant was recirculated between the extraction and stripping module at a flow rate of 4.72 cm^3/s.

Identification of the limiting step of the mass-transfer process in the extraction module

The forward reaction kinetic constant (k_e) in Eqs. 8 and 9 has been evaluated while performing mathematical modeling of a supported liquid membrane goldcyanide–LIX79 system and was found to be 6.57×10^{10} cm/s (Benzal et al., 1999). As the first attempt was with LIX79, it was not possible to compare this value with earlier published values. Also, LIX79 is a new reagent developed very recently by Henkel. Table 2a presents mass-transfer coefficients values of k_i, k_s, k_m, and k_f, while Table 2b lists all four terms of Eq. 8, which guide us in identifying the rate-controlling step. The overall resistance in the experiments calculated from Eq. 7 or Eq. 8 was observed to be between 1 and 4 10^5 s/cm compared to the values of the overall resistance of 3–5 10^5 s/cm estimated from the model. The second, third, and fourth terms are thus negligible. In this regard, the fractional resistance of each step in the overall process (R_m^0, R_f^0, R_s^0, and R_i^0) could be calculated by the following the equation; for example, R_m^0 is defined as

$$R_m^0 = R_m / (R_i + R_m + R_s + R_f), \tag{13}$$

where R_i, R_m, R_s, and R_f are mass-transfer resistances due to interfacial reaction, membrane, organic phase, and feed. Under the present experimental conditions, the values of $\%R_m^0$, $\%R_f^0$, $\%R_s^0$, and $\%R_i^0$ were 0.5, 0.2, 4.8, and 94.5 at a low organic flow rate. This clearly indicates that the rate-controlling step was an interfacial reaction on the membrane surface. At a high organic flow rate, values of $\%R_m^0$, $\%R_f^0$, $\%R_s^0$, and $\%R_i^0$ were 0.5, 0.2, 0.3, and 99.0, respectively. The mass-transfer coefficient evaluated in the present studies was in good agreement with earlier values ($K^E = 2.2 \times 10^{-6}$ cm/s) determined while performing nondispersive extractions of chromium from galvanic process wastewater using Aliquat 336 in an integrated membrane process (Alonso et al., 1999; Alonso and Pantelides, 1996; Ortiz, 1996). The obtained value of K_{Au}^E is 7.6×10^{-6} cm/s (LIX79 = 18% and NaCN = 5,000 ppm), which is around 3.5 times higher than the value obtained for the Cr(VI)–Aliquat 336 system ($K^E = 2.2 \times 10^{-6}$ cm/s) in a similar hollow-fiber module. This difference is attributed to the different values of liquid diffusivities for different chemical systems, which have a strong dependence on the organic solution viscosity. Since the viscosity of Aliquat 336 (2.459 g/cm·s) is higher than that of LIX79 (0.447 gm/cm s for 12% LIX79) /*n*-heptane), the difference in the values of the mass-transfer coefficient for extraction (K_E) was justified.

The overall resistance in the extraction module would could be reduced by optimization of suitable chemical parameters. At pH 9, the overall resistance is minimal, but separation factors of Au(I) against other base metals were poor. However, application of this technique at pH 9 could be problematic, as the separation of gold from base metals at this pH will not be possible in practice in spite of high mass transfer (Figure 6). Hence, pH 10.3–10.6 was selected for the best separation where we have to compromise with mass transfer.

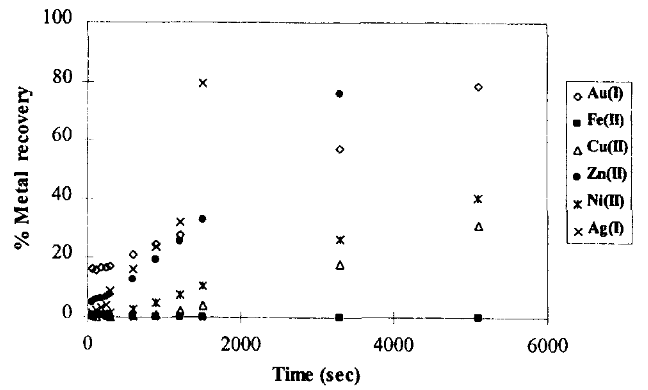

Figure 6. Separation of Au(I) from Fe(II), Cu(II), Ag(I), Ni(II), and Zn(II) using 18% (v/v) LIX79 at pH 9; Au(I); 10 mg/L, Fe(II): 30 mg/L, Cu(II): 30 mg/L, Ni(II): 10 mg/L, Ag(I): 3 mg/L. and Zn(II): 5 mg/L; stripping solution: 1.0 M NaOH; NaCN 5,000 ppm.

The estimated values of k_i at pH 9, 10 and 10.3 were 2.5×10^{-5}, 2.0×10^{-5}, and 1.85 cm/s, respectively. Although the value of k_i at pH 9 was observed to be almost 20 times that of the value estimated at pH 10.3, separation factors of Au(I) at pH 9 with respect to Cu(I), Ag(I), Zn(I), and Ni(II) were quite poor. Further increases of pH could provide better separation factors against those metals with small increases in overall resistance. Membrane resistance reached a maximum at pH 11 with moderate separation factors. On the other hand, by increasing concentrations of LIX79, overall membrane resistance was reduced significantly, independently of the increase in NaCN concentration.

The deviation observed in the theoretical and the experimental values of the mass-transfer coefficient could be due to several reasons as explained by several researchers (Alexander and Callahan, 1987; Park and Chang, 1986; Prasad and Sirkar, 1988, 1990; Rogers, 1997; Costello et al., 1993; Takeuchi et al., 1990; Wikramasinghe et al., 1992; Cussler, 1995). In the hollow-fiber contactor, the tube-side flow regime is likely to be laminar due to the very small lumen diameter. Otherwise, the pressure drop along the fiber would be exceedingly high. In any such developed correlation, the effects of any flow maldistribution on the tube-side resulting from particular inlet design and outlet headers are hidden (Park, 1986). Similarly, the effects of any fiber inlet crimping or fiber inlet plugging at the tube sheet are unknown. On the other hand, hollow-fiber modules usually exhibit channeling, bypassing, and stagnant regions on the shell side due to nonuniform distribution of the fibers and their elongation by the use of organic solvents (Prasad and Sirkar, 1990; Wikramasinghe et al., 1992; Costello et al., 1993). The hydrodynamics of the organic phase circulating in the shell side will be affected by these deviations from the ideal flow, thus causing an incorrect evaluation of the mass-transfer coefficient. This deviation could also be due to the inaccuracy associated with the evaluation of a diffusion coefficient of solute in the organic phase that is directly linked to Eqs. 10, 11 and 12. Therefore, inaccuracy in diffusion coefficient values can results in significant deviation of mass-transfer coefficients (Alexander, 1987).

Evaluation of the rate-controlling step in the stripping module

As described in the experimental section (Figure 1), stripping was performed simultaneously in the second module by recirculating LIX79 in the shell side of the extraction and stripping module, while the NaOH solution flowed through the tube side in the second module. The stripping rates of Au(I) can be estimated by assuming that the chemical reaction is fast relative to the diffusion-controlled mass transfer, and the overall mass-transfer coefficient was estimated by following the model equation using k_f, k_m, and k_s (Alexander et al., 1987):

$$\frac{1}{K_{\mathrm{Au}}^{s}} = \frac{1}{k_s} + \frac{1}{k_m} + \frac{1}{k_{st} H}, \tag{14}$$

where k_s = mass-transfer coefficient in the organic feed; k_m = mass-transfer coefficient in the membrane; k_{st} = mass-transfer coefficient in the aqueous stripping solution; H = partition coefficient of stripping; $1/K_{\mathrm{Au}}^{s}$ = overall resistance to mass transfer; $1/k_s$ = resistance to mass transfer in the organic feed; $1/k_m$ = resistance to mass transfer in the membrane; and $1/k_{st}H$ = resistance to mass transfer in the aqueous stripping solution. The values of k_s (organic feed) (calculated from Eq. 11), k_m for the membrane (calculated from Eq. 12), and k_{st} for the stripping solution (calculated from Eq. 10) are listed in Table 3a. The overall mass-transfer coefficient (K_{Au}^{S}) for stripping ranged from 3.8×10^{-5} cm/s to 4.8×10^{-5} cm/s. The overall resistance due to organic feed, membrane, and stripping solution are presented in Table 3b. The overall mass-transfer resistance was experimentally found to be between $2.1\text{–}2.6 \times 10^{4}$ compared to the overall resistance calculated from Eq. 14, that is, $2.5\text{–}3.0 \times 10^{-4}$. Data in Table 3b show that resistance due to the organic phase is dominant at low organic flow rates. In this respect, the fractional resistance of each step to the overall process was calculated under the present experimental conditions and the values of $\%R_m^0$, $\%R_s^0$, and $\%R_{st}^0$ were 48, 51, and 1, respectively, at high flow rates, and 40, 59, and 1 at low flow rates. This clearly indicates that mass-transfer resistance was dominated in both the organic solution and the membrane at high flow rates, while mass-transfer resistance due to the organic solution was enhanced slightly at low flow rates, as suggested by Eq. 11. The order of magnitude of the K_{Au}^{S} values in our experiments was observed to be higher ($K_{\mathrm{Au}}^{S} = 3.8\text{–}4.8 \times 10^{-5}$ cm/s) than that determined by Alonso and Pantelides (1996) while carrying out the stripping of cadmium in a ceramic module contactor (mass-transfer coefficient for stripping = 3.33×10^{-6} cm/s). This is probably due to two reasons: first, the type of extractant used was acidic in nature and the back extraction of the complex from the loaded organic solution was difficult due to the strong complexation of metal with extractant (poor H for stripping). Second, the operation of the ceramic module used for stripping cadmium from the loaded Cyanex 302 was not as efficient as the Liqui-Cel contactor.

Optimization of chemical conditions for Au(I) separation from hydrometallurgical solutions and performance evaluation

The separation of gold from copper and iron is particularly important. These two metals, which are usually associated with gold in many ores, give rise to several contamination problems in the refining of gold. Some experiments were conducted to demonstrate the selectivity of the gold in order to examine the effect of several other metal ions generally accompanying $\mathrm{Au(CN)_2^-}$ and their interferences with the overall extraction of Au(I). Among the metal ions examined, Fe(II) (30 mg/L), Cu(II) (30 mg/L), Ni(II) (5 mg/L), Ag(I) (3 mg/L), and Zn(II) (10 mg/L) were tested in the form of a mixture with Au(I) (10.0 mg/L). The cyanoions that exist with Au(I) were $\mathrm{Ag(CN)_2^-}$, $\mathrm{Cu(CN)_4^{3-}}$, $\mathrm{Zn(CN)_4^{2-}}$ $\mathrm{Ni(CN)_4^{2-}}$, and $\mathrm{Fe(CN)_6^{4-}}$. Table 4 presents the K_{Au}^{E} values at different concentrations of NaCN in the feed when extraction and stripping of Au(I) was performed simultaneously using two hollow fiber modules. Table 5 presents the K_{Au}^{E} and K_{Au}^{S} values at different pH for the extraction and stripping of Au(I) from synthetic hydrometallurgical solutions in an integrated process using two hollow-fiber modules, one each for extraction and stripping. Table 6 lists the separation factors of Au(I) against other metal cyanides with variations in pH and NaCN concentrations in feed. Figure 6 shows that separation of gold cyanide from other metal cyanide complexes at pH 9 was practically impossible, as Zn(II) and Ag(I) were extracted in considerable amounts. Their recovery was around 80% in the stripping phase (1 M NaOH). As seen from Table 6, the separation factors of Au(I) with respect to Ag(I) and Zn(II) at pH 10.6 were, respectively, around 85 and 190 times those obtained at pH 9 under similar experimental conditions (NaCN = 5000 ppm and LIX79 18%). Moreover, copper and nickel recovery during the stripping phase was between 30 and 40%. As indicated in Figure 7, the increase in pH from 9 to 10.6 could provide better separation of Au(I) over other metal cyanides in spite of lowering the mass-transfer coefficient at pH 10.6. Although some extraction of Zn(II) and Ag(I) was observed in this pH range in the extraction module, their backextraction during the stripping phase was observed to be slower, as gold reaches the stripping phase faster than these metals. When gold was at around 2 ppm in feed (in 45–60 min), the feed was replenished with a fresh one in order to avoid Zn(II) and Ag(I) contamination during the

Table 3a. Mass-Transfer Coefficient of the Feed, Membrane, and Organic Phase in Stripping Module

K_{Au}^{S} (cm/s) Exp.	k_{st} (cm/s)	k_m (cm/s)	k_s (cm/s)	K_{Au}^{S} (cm/s) (model)
$3.8 \times 10^{-5}\text{–}4.8 \times 10^{-5}$	10^{-3}	8.33×10^{-5}	$6 \times 10^{-5}\text{–}8 \times 10^{-5}$	$2.5\text{–}3.3 \times 10^{\ 5}$

Table 3b. Mass-Transfer Resistance Due to Feed, Membrane, and Organic Phase in Stripping Module

$1/K^S_{Au}$ (s/cm) Exp.	$1/k_{st}H^*$ (s/cm)	$1/k_m$ (s/cm)	$1/k_s$ (s/cm)	$1/K^S_{Au}$ Model Eq. 9 (s/cm)
$2.1-2.6\times10^4$	2×10^2	1.2×10^4	$1.3\times10^4-1.8\times10^4$	$2.5\times10^4-3.0\times10^4$

*Partition coefficient for stripping.

Table 4. Mass-Transfer Coefficients for Extraction of Au(I) from Aqueous Alkaline Cyanide Media as a Function of Initial NaCN Concentration with LIX 79 in *n*-Heptane Using NDSX Technique Countercurrently

Run	Init. NaCN Conc. in Aqueous Feed	K^E_{Au} ($\times10^{-6}$ cm/s) (Cocurrent)
1	0	7.6
2	1,000	3.5*
3	1,000	6.0
4	2,000	7.1
5	5,000	7.6

Note: Feed composition: Fe(II) (30 mg/L), Cu(I) (30 mg/L), Ni(II) (10 mg/L), Ag(I) (3 mg/L), and Zn(II) (5 mg/L) were tested in the form of a mixture with Au(I) (10 mg/L); *extractant phase:* 18% LIX79; feed pH: 10.6.
*Value at 12% LIX79.

stripping phase. This observation is also supported by kinetic analysis performed using conventional liquid–liquid extraction by Virnig and Wolfe (1996) showed that gold could be extracted up to 70% in one minute, whereas Ag(I), Zn(II), and Cu(I) could be extracted to 16%, 47%, and 2%, respectively, using 8% LIX79 in Escaid 110 at pH 10.5 (NaCN = 100 ppm). Figure 8 depicts the extraction and stripping results when feed pH was maintained at 11. As suggested by the extraction mechanism, recovery of Au(I) plummeted from 80% to 40% with an increase in pH from 10.5 to 11, respectively. The separation factors of Ag(I) and Zn(II) decreased slightly at pH 11 (raffinate pH 11.4), as the effective gold extraction rate in the feed phase was reduced and took more time for 70–80% recovery during the stripping phase, which ultimately increased the extraction of Ag(I) and Zn(II) and reduced the separation factors (Table 6). Figures 7, 9, and 10 show gold recovery during the stripping phase when NaCN concentration in the feed was 1,000, 2,000, and 5,000 mg/L, respectively, using 18% LIX79/*n*-heptane at a feed flow rate of 6.94 cm^3/s, an organic flow rate of 4.72 cm^3/s, and a stripping solution flow rate of 6.94 cm^3/s at pH 10.6. In the presence of 1,000–2,000 ppm NaCN, extraction of Au(I) was between 90 and 95% (45 min), whereas recovery of Au(I) during the stripping phase varied between 75% and 85% (60 min). At high NaCN concentration (5000 ppm), separation factors of gold with respect to Ag(I) improved slightly. This was possibly due to the formation of $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$, which were not extractable in significant amounts, as lower coordination number complexes ($Ag(CN)_2^-$) were preferred to higher coordination silver complexes ($Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$) (Marsden and House, 1992; Martin and Al-

Table 5. Mass-Transfer Coefficients for Extraction and Stripping of Au(I) from Aqueous Alkaline Cyanide Media (Synthetic Hydrometallurgical Solution) as a Function of Initial Feed pH With LIX 79/*n*-Heptane Countercurrently Using NDSX technique

Run	Init. pH of Aqueous Feed	K^E_{Au} ($\times10^{-6}$ cm/s) Extraction Module	K^S_{Au} ($\times10^{-5}$ cm/s) Stripping Module
1	9.0	9.8	4.8
2	10.3	7.6	4.7
3	11.0	2.5	3.8

Note: Feed composition: Fe(II) (30 mg/L), Cu(I) (30 mg/L), Ni(II) (10 mg/L), Ag(I) (3 mg/L), and Zn(II) (5 mg/L) were tested in the form of a mixture with Au(I) (10 mg/L); *Extractant phase:* 18% LIX79; *NaCN concentration:* 5,000 ppm.

Table 6. Separation Gold Factors of Other Cyanide Metal Salts Using LIX79/*n*-Heptane Countercurrently With a Synthetic Hydrometallurgical Solution

Exp. Conditions	$S_{Au/Cu}$	$S_{Au/Fe}$	$S_{Au/Zn}$	$S_{Au/Ni}$	$S_{Au/Ag}$
LIX79 12% NaCN = 1,000 pH = 10.6	895	359	23	1,144	76
LIX79 18% NaCN = 1,000 pH = 10.6	775	370	9	203	16
LIX79 18% NaCN = 2,000 pH = 10.6	573	295	11	97	12
LIX79 18% NaCN = 5,000					
pH = 9	6	2,136	0.1	0.2	0.5
pH = 10.6*	2,534	713	19	87	44
pH = 11*	352	283	16	37	21

Feed composition: Fe(II) (30 mg/L), Cu(I) (30 mg/L), Ni(II) (10 mg/L), Ag(I) (3 mg/L), and Zn(II) (5 mg/L) were tested in the form of a mixture with Au(I) (10 mg/L); *Stripping Phase:* 1 M NaOH; *Feed flow rate:* 6.94 cm^3/s; *Organic flow rate:* 4.72 cm^3/s; *stripping solution flow rate:* 6.94 cm^3/s.
*LIX79 and NaCN concentrations are the same as in the pH 9 experiment.

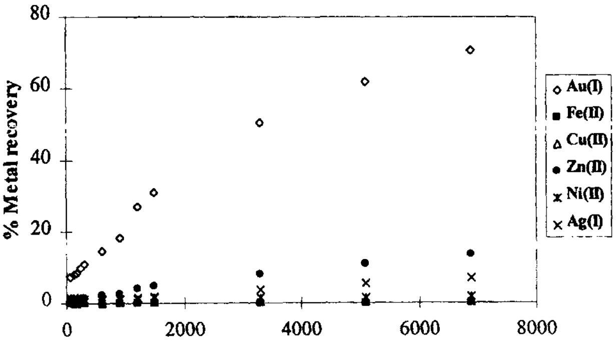

Figure 7. Separation of Au(I) from Fe(II), Cu(II), Ag(I), Ni(II), and Zn(II) using 18% (v/v) LIX79 at pH 10.5; Au(I): 10 mg/L, Fe(II): 30 mg/L, Cu(II): 30 mg/L, Ni(II): 10 mg/L, Ag(I): 3 mg/L, and Zn(II): 5 mg/L; stripping solution: 1.0 M NaOH; NaCN 5,000 ppm.

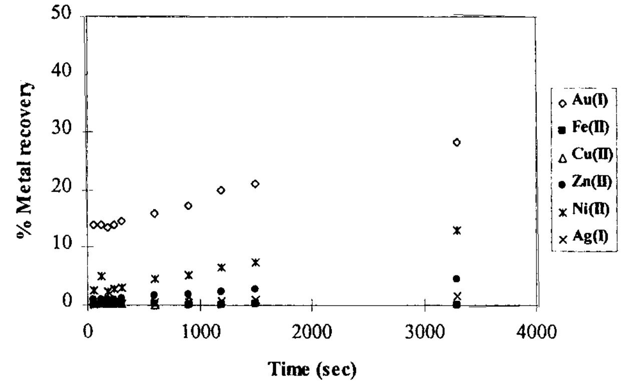

Figure 8. Separation of Au(I) from Fe(II), Cu(II), Ag(I), Ni(II), and Zn(II) using 18% (v/v) LIX79 at pH 11; Au(I): 10 mg/L, Fe(II): 30 mg/L, Cu(II): 30 mg/L, Ni(II): 10 mg/L, Ag(I): 3 mg/L, and Zn(II): 5 mg/L; stripping solution: 1.0 M NaOH; NaCN 5,000 ppm.

guacil, 1998). In the presence of 5,000 ppm NaCN in feed at pH 10.6, recovery of Au(I) during the stripping phase was around 50% in 1 h, which indicated that large amounts of NaCN will probably affect the gold recovery. This is as expected, as free gold cyanide will compete with the reagent for gold. The other reason for this decrease could be higher complexes of gold ($Au(CN)_4^-$), which are probably less extractable by LIX79. However, the existence of this gold species is still controversial, in spite of the fact that the recent literature reported the possibility of such a species in 0.02 M KCN at pH 7 (Safavi and Shams, 1999). The same value of gold recovery, that is, 80% could be achieved in a little more time (2 h), but the amounts of Zn(II) and Ag(I) would also be increased during the stripping phase. The same behavior was also observed by Virnig and Wolfe (1996) while performing conventional liquid–liquid extraction with a real mine solution at gold mine sites in the United States using SX circuits. The authors have used as high a LIX79 concentration as 30% for the effective recovery of gold in the presence of several other metal cyanides.

Based on the preceding results, the following order of selectivity with 18% LIX79 was obtained at pH 10.6 while maintaining NaCN 5000 in the feed (Table 6):

$$Au(CN)_2^- > Zn(CN)_4^{2-} > Ag(CN)_2^- > Ni(CN)_4^{2-}$$
$$> Fe(CN)_6^{4-} > Cu(CN)_4^{3-}.$$

These results agree with previous works, which indicates that LIX79 has a higher affinity for univalent ions, such as $Au(CN)_2^-$, than for multivalent ions, such as $Cu(CN)_4^{3-}$, $Fe(CN)_6^{4-}$, $Cu(CN)_3^{2-}$ (Virnig and Wolfe, 1996; Kordosky, 1992). Also, the extraction of these complexes strongly depends on the metal coordination number; from the results shown in Table 6, it is seen that the extraction order follows the series $Me(CN)_2^- > Me(CN)_4^{n-} > Me(CN)_6^{n-}$. Those complexes with lower coordination numbers were extracted, preferably over those with higher numbers, and, in general, the same deduction can be made with respect to the complex charge: lower change complexes are extracted in preference to higher charge complexes (Alguacil and Caravaca, 1996).

The separation factor of each base metal was calculated by the following equation; for example, $SF_{Au/Cu}$ is defined as (Campderrós et al., 1998)

$$SF_{A/B} = \left(\frac{[Au(I)]_{0,strip}}{[Au(I)]_{0,feed}} \right) \left(\frac{[Cu(I)]_{0,feed}}{[Cu(I)]_{0,strip}} \right). \qquad (15)$$

Also, to concentrate Au(I) the feed was continuously replaced with a fresh one, and the stripping solution was maintained the same throughout these experiments; it flowed through the tube side (6.94 cm^3/s) and the organic phase was passed through the shell side at (4.72 cm^3/s). The gold cyanide was concentrated at 400 ppm. In this separation process, the

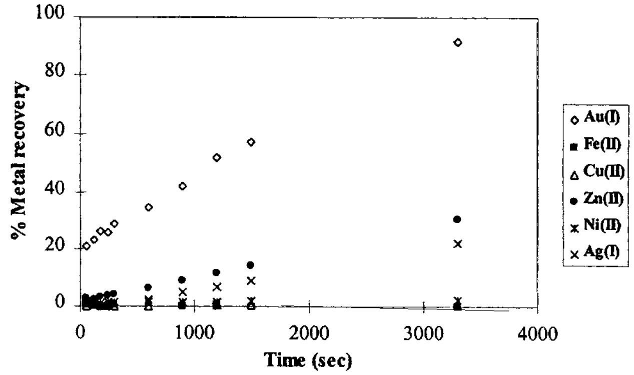

Figure 9. Separation of Au(I) from Fe(II), Cu(II), Ag(I), Ni(II), and Zn(II) using 18% (v/v) LIX79 at pH 10.6; Au(I): 10 mg/L, Fe(II): 30 mg/L, Cu(II): 30 mg/L, Ni(II): 10 mg/L, Ag(I): 3 mg/L, and Zn(II): 5 mg/L; stripping solution: 1.0 M NaOH; NaCN 1,000 ppm.

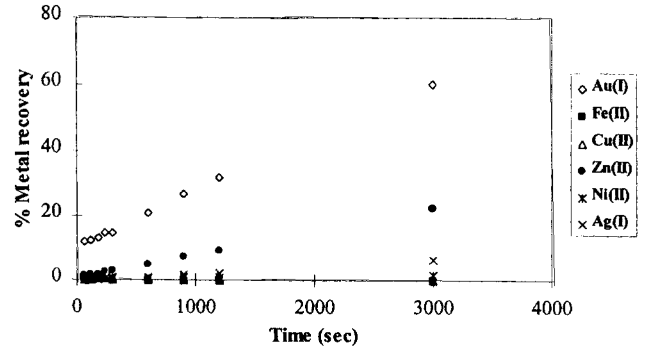

Figure 10. Separation of Au(I) from Fe(II), Cu(II), Ag(I), Ni(II), and Zn(II) using 18% (v/v) LIX79 at pH 10.6; Au(I): 10 mg/L, Fe(II): 30 mg/L, Cu(II): 30 mg/L, Ni(II): 10 mg/L, Ag(I): 3 mg/L, and Zn(II): 5 mg/L; stripping solution: 1.0 M NaOH; NaCN 2,000 ppm.

K_{Au}^{E} value was found to be $5.0-7.1 \times 10^{-6}$ cm/s and K_{Au}^{S} was $3.8-4.8 \times 10^{-5}$ cm/s.

Conclusions

Simultaneous extraction and stripping of gold cyanide from alkaline hydrometallurgical cyanide solutions was accomplished to extract the solute and to concentrate it by using a novel extractant, LIX79. In this way, saturation of the carrier does not occur, as it is continuously regenerated in the stripping module and gives better performance. The problem faced (loading of LIX79 with bicarbonate by exposure to air in previous experiments) in batch studies with one module could be resolved in an integrated membrane process. Several experiments with synthetic solutions of different compositions of gold hydrometallurgical solutions were performed to establish optimum conditions for this process in order to achieve clean separation of Au(I). It was possible to separate/concentrate Au(I) in the presence of other metal cyanide salts, such as Fe(II), Cu(II), Ni(II), Ag(I), and Zn(II) (NaCN = 1,000–5,000 ppm), which showed a good selectivity of Au(I) against other metal cyanide salts. The separation factors based on the experimental results obtained for the following cyanoions give the following order of selectivity:

$$\text{Au(CN)}_2^{-} > \text{Zn(CN)}_4^{2-} > \text{Ag(CN)}_2^{-} > \text{Ni(CN)}_4^{2-}, > \text{Fe(CN)}_6^{4-} > \text{Cu(CN)}_4^{2-}.$$

The use of a stripping solution containing NaOH provided efficient and fast backextraction of Au(I) in the stripping (product) module. The step that limited the mass-transfer process could be identified by independently varying the hydrodynamics of both aqueous and organic phases and evaluating the overall mass-transfer coefficients. In this integrated process, the mass-transfer resistance resulting from a chemical extraction reaction at the surface was observed to be dominated during the entire extraction process, whereas the stripping reaction was fast and instantaneous, and the mass-transfer coefficient for stripping was found to be more than extraction. The validity of this model was evaluated with experimental data and found to tie in well with theoretical values.

Acknowledgments

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Notation

C = metal concentration, g/cm^3
d = diameter of one fiber, cm
D_t = diffusion coefficient of solute in the tube side, cm$^2 \cdot$s^{-1}
D_s = diffusion coefficient of solute in the shell side
D_m = diffusion coefficient of metal complex in the membrane
D_h = hydraulic diameter, cm
d_i = inner fiber diameter
H = partition coefficient of extraction/stripping
k_f = mass-transfer coefficient of the aqueous feed, cm/s
k_e = forward reaction-rate constant of Eq. 9, cm/s
k_i = rate of interfacial reaction defined in Eq. 9
k_m = membrane mass-transfer coefficient, cm/s
k_s = organic mass-transfer coefficient, cm/s
k_{st} = mass-transfer coefficient for stripping, cm/s
K_{Au}^{E}, K_{Au}^{S} = overall mass-transfer coefficient for extraction and stripping, respectively, cm/s
L = fiber length, cm
N_{Re} = Reynolds number for the feed, $N_{Re} = (vd/\eta)$
N_{Sc} = Schmidt number, $N_{Sc} = \eta/D$
N_{Gz} = Graetz number, $N_{Gz} = d^2v/DL$
N_{Sh} = Sherwood number for the tube side, $N_{sh} = k_f/d_i/D_t$, and shell side, $N_{Sh} = k_s D_h/D_s$, respectively
Q = flow rate, cm^3/s
r = hollow-fiber radius, cm
$R_m^0, R_f^0, R_s^0, R_i^0, R_{st}^0$ = fractional resistance due to membrane, feed, solvent, interfacial reaction, and stripping, respectively
t_m = thickness of the fiber membrane, cm
V_e = organic tank volume, cm^3
V_f = feed-tank volume, cm^3
V_s = stripping tank volume, cm^3
V_m = volume of hollow fibers, cm^3

Greek letters

τ = tortuosity of the membrane
η_t = viscosity of the aqueous feed/stripping solution, cp or g/cm$\cdot s$
η_s = viscosity of the organic solution, cp or (g/cm$\cdot$s)
v_t and v_s = the velocity of the liquid in the fiber side and shell side, cm/s
ϕ = packing fraction of the HF module
ϵ = porosity

Subscripts and superscripts

i = for inner radii
o = for outer radii
e/s = for extract/strip
t = tube side
s = strip side or shell side
f = feed
m = membrane
0 = refers to concentration at time zero

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