

Pseudo-Emulsion Based Hollow Fiber Strip Dispersion: A Novel Methodology for Gold Recovery

J. V. Sonawane and A. K. Pabby

PREFRE, Nuclear Recycle Group, Bhabha Atomic Research Centre, Tarapur, Maharashtra 401502, India
Dept. d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, E-8028 Barcelona, Spain

A. M. Sastre

Dept. d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, E-8028 Barcelona, Spain

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This article presents the study of Au(I) extraction from synthetic cyanide media through pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) containing LIX-79/n-heptane as extractant in the form of a pseudo-emulsion with NaOH. The permeation of Au(I) is investigated as a function of various experimental variables: hydrodynamic conditions, feed pH, LIX-79 concentration in pseudo-emulsion, cyanide concentration in feed phase, NaOH concentration in pseudo-emulsion as a strippant, and initial Au(I) concentration in feed phase. In PEHFSD, pseudo-emulsion is an emulsion that is formed temporarily between organic and stripping solutions. The organic and aqueous solutions are separated when the stirring device is stopped. In this study, feed was circulated through the tube side in counter current mode. The linear flow velocity of the feed was varied between 0.74 and 2.58 cm/s and the linear flow velocity of the pseudo-emulsion was maintained at 0.28 cm/s. The value of the permeation coefficient obtained under standard experimental conditions was 8.19×10^{-5} cm/s. The selectivity of LIX-79/n-heptane based PEHFSD toward different metal cyanide salts such as Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I) was also examined. © 2007 American Institute of Chemical Engineers AIChE J, 54: 453–463, 2008

Keywords: gold(I), PEHFSD, LIX-79, permeation coefficient

Introduction

Membrane technologies currently play an increasingly important role in resource recovery, pollution prevention, energy production, environmental monitoring, and quality control.^{1,2} Among these technologies, liquid membranes (LMs) have shown certain potential, and several configurations of LMs are currently being investigated for various applications. Various supported liquid membrane (SLM) techniques in flat-sheet (FSSLM), hollow fiber (HFSLM), and spiral-wound configurations are also under considera-

tion.^{3–10} Hollow fiber and spiral-wound modules are best suited to providing high surface-area-to-volume ratios. The removal of metal ions from dilute or concentrated solutions has received a great deal of attention in terms of its potential for the recovery of valuable metals or decontamination of effluents using HFSLM mode. Although these techniques are very attractive possibilities, their lack of stability means that scale-up of these processes is infrequent. Improvements and modifications are suggested continuously for the use of LM techniques in industrial applications in various fields. Sastre et al. have published a state-of-the-art review on LM techniques and their improvements and modifications in the last few years, covering bulk liquid membrane (BLM), HFSLM, emulsion liquid membrane (ELM), and non-dispersive solvent extraction (NDSX), among others.

In view of this, it was necessary to find a more stable technique, which can utilize the advantages of LM techni-

J. V. Sonawane: On leave from PREFRE, Nuclear Recycle Group, Bhabha Atomic Research Centre, Tarapur 401502, India.

Correspondence concerning this article should be addressed to A. M. Sastre at ana.maria.sastre@upc.edu.

ques and become suitable for industrial use. The pseudo-emulsion based strip dispersion technique fulfils these criteria. It can be operated using a hollow fiber contactor (high surface-area-to-volume ratio) and performs the stripping in a single module. This could be done by passing pseudo-emulsion of organic extractant (in diluent) mixed with the stripping solution (mixing device at 600 rpm), which facilitates stripping of the metal ion from loaded organic in the stripping phase in a single module. Consequently, this technique facilitates simultaneous extraction and stripping in a single module with good stability (pores are always filled by organic (extractant) with continuous flow of carrier/extractant) and could be used for micro to macro concentration (HFSLM is limited to macro concentration due to loss of organic in subsequent runs) with consistent performance for low to higher feed flow rates.

Gold has always been the most highly regarded precious metal, owing to its variety of uses in industry. Therefore, its recovery from different sources is of great importance. It can be recovered from pregnant solutions by well-defined techniques such as cementation, carbon adsorption, and solvent extraction.¹¹ A lack of selectivity is found when activated carbon is used in the presence of mixtures of other metal cyanides.¹²

The present research deals with the removal of Au(I) in the presence of base metals from cyanide medium by pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) using a single hollow fiber module for extraction as well as stripping. In PEHFSD, the feed solution containing $\text{Au}(\text{CN})_2^-$ with other base metals in a cyanide medium is circulated through the tube side. A dispersion prepared by continuous stirring of the organic phase (12% LIX-79 dissolved in *n*-heptane) and the aqueous stripping phase (0.2 M NaOH) forming a water-in-oil pseudo-emulsion is passed continuously through the shell side in counter current mode. The influence of different hydrodynamic and chemical parameters such as pH of feed, cyanide concentration in feed, LIX-79 concentration in *n*-heptane, NaOH concentration in the pseudo-emulsion phase, and initial Au(I) concentration in feed were investigated. The selectivity of Au(I) against metal cyanide salts such as Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I) ions was evaluated in detail. This study is of particular importance as all the chemical parameters were examined using a synthetic hydrometallurgical alkaline solution containing a mixture of gold with other metal cyanide salts and base metals. This was done to optimize the conditions, which are similar to those encountered for gold recovery from hydrometallurgical leach solutions containing mixtures of other metal cyanide salts such as Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I).

Experimental

LIX-79 (Henkel Canada) was used as carrier for transport experiments in the present investigation; *n*-heptane (Sigma-Aldrich Logistik Kappelweg, Germany) was used as diluent. Stock gold(I) (1 g/L) solution was prepared by dissolving the required amount of $\text{KAu}(\text{CN})_2$ (Johnson Matthey Chemicals, Karlsruhe, Germany) in NaCN (Merck). All other chemicals used in the present study were of analytical reagent grade (AR) grade. The organic membrane phase was prepared by dissolving the appropriate volume of LIX-79 (carrier) in *n*-heptane (diluent) to obtain organic solutions of different concentrations.

Hollow fiber apparatus used for PEHFSD

The hollow fiber device used for the single step was a commercially available unit purchased from Hoechst Celanese (now known as Celgard), Charlotte, NC (Liqui-cel, 8 × 28 cm 5PCG-259 LLE contactor). The module details and hollow fiber membrane characteristics are described in our previous work.^{13,14}

Partition coefficients of Au(I) extraction equilibrium, density, and viscosity measurements

Details of the liquid-liquid distribution measurements are essentially the same as those published elsewhere.^{13,15–20}

PEHFSD preparation and methods

The hollow fiber strip dispersion process comprises a single membrane module for extraction and stripping and one stirred tank for preparing a pseudo-emulsion of LIX-79/*n*-heptane and NaOH. The experimental set-up for the separation of metals consists of two gear pumps capable of flows of 1 L/min for both phases, powered by a variable speed DC motor. The organic phase wet the porous wall of the fiber because of its hydrophobic nature. The interface was maintained at the pore by applying a higher pressure to the aqueous stream (Feed) than to the pseudo-emulsion stream. The differential pressure was always kept below the breakthrough pressure. In the aqueous feed phase, the pressure was maintained 0.2 bar higher than in the pseudo-emulsion phase. The schematic view of PEHFSD using a single hollow fiber contactor in recirculation mode is shown in Figure 1. The PEHFSD operation was carried out with 12% LIX-79/*n*-heptane by passing alkaline cyanide feed containing gold through the tube side and pseudo-emulsion (LIX-79/*n*-heptane and 0.2 M NaOH) through the shell side in counter current mode. The stirring rate was kept at 400 rpm. This stirring speed was fixed as best suited for our experiments. Also, the character of emulsion should be such that it should have clear and fast phase separation (aqueous strippant and organic) when mixing is stopped (pseudo-emulsion takes around 30 s to reach back to emulsion reservoir without breaking/splitting). The recovery of metals from pseudo-

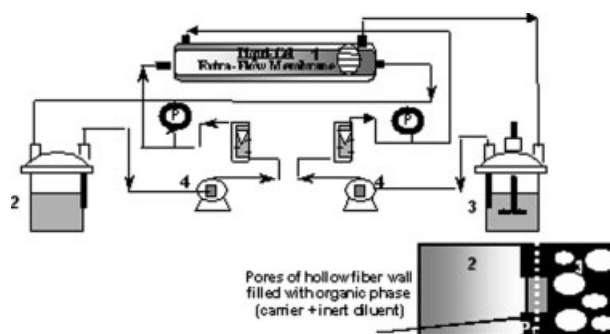


Figure 1. Schematic view of PEHFSD fiber strip dispersion operated in recycling mode for recovery of Au(I) from aqueous cyanide media.

(1) Hollow fiber membrane contactor, (2) Aqueous feed solution into tube side, (3) Pseudo-emulsion (LIX-79/*n*-heptane + 0.2 M NaOH) into shell side, (4) Feed and pseudo-emulsion pumps.

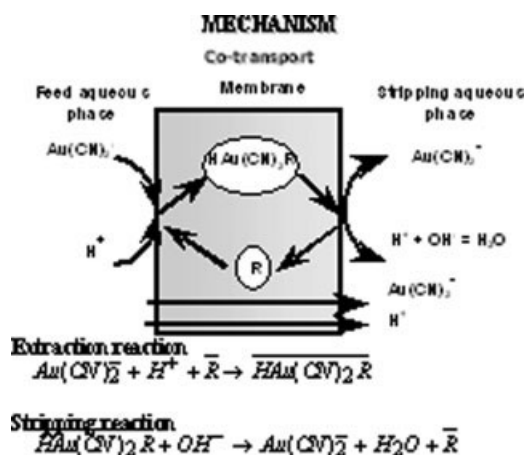


Figure 2. Transport mechanism of gold(I) cyanide with LIX-79 by PEHFS with single hollow fiber module.

emulsion can be accomplished [pseudo-emulsion breaks down soon after the mixing of solution (strippant + extractant) stopped] and aqueous and organic phases separates automatically. The volume of pseudo-emulsion phase is 2000 cm³ (solution of 1000 cm³ of 12% LIX-79/*n*-heptane + 1000 cm³ of aqueous 0.2 M NaOH); 1000 cm³ 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 0.2 M NaOH was used for the stripping of Au(I) in pseudo-emulsion. At a predetermined time, small aliquots of the feed stream and a small aliquot from the pseudo-emulsion tank were taken and analyzed for metal concentration by standard atomic absorption spectrometry. The presence of bicarbonate in LIX-79/*n*-heptane was analyzed by FTIR (Fourier transform, FTIR, spectroscopy, Perkin-Elmer System 2000) and more details are given in Ref. 13.

Theoretical Background

Extraction equilibrium

Ho and Wang²¹ suggested that PEHFS follows the mechanism of HFSLM as data obtained using this technique fitted the typical LM equation (more details in model development section). For extraction of Au(I) through a PEHFS containing LIX-79 as a mobile carrier, the concentration profile across the hollow fiber membrane pores in the hollow fiber contactor is schematically shown in Figure 2. The Au(I) ions in alkaline cyanide media represented as Au(CN)_2^- form an ion pair type complex with organic extractant LIX-79 (*N,N*, bis(2-ethyl hexyl) guanidine, RH) dissolved in *n*-heptane.¹⁴ The extraction reaction is expressed as:



The organic complex $[\text{HAu(CN)}_2\text{R}]_o$ then diffuses through the pore of the hollow fiber toward the membrane-pseudo-emulsion interface, where the Au(I) is stripped in the

pseudo-emulsion phase after coming into contact with NaOH. This reaction is fast and instantaneous. This stripping reaction is expressed as:



In agreement with the corresponding Au(I) species distribution diagram, a mechanism that explains the Au(I) transport (feed phase) through the hollow fiber membrane pore can be represented by Eq. 2. This reaction shows that it regenerates the carrier and diffuses back to the feed through the pore of the hollow fiber, after which the process is repeated.¹ Such a process is called cotransport (Figure 2), where the counter ion concentration in the feed solution is used as the driving force for metal transport.

The extraction equilibrium and extraction constant can be described by the equation

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

where *R* is the organic extractant. More details on extraction equilibrium reactions are given in our earlier work.¹⁶ 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:

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

Model Development

PEHFS extraction

In the case of PEHFSs, calculation of the overall permeability coefficients of the experimental system is based on a first-order mass transfer model with instantaneous chemical reaction on the stripping side when a recycling mode is employed. The study of the influence of LM composition leads to the evaluation of the mass-transfer parameters.

PEHFS model

For the recycling mode, both feed solution and pseudo-emulsion of LIX-79/*n*-heptane and 0.2 M NaOH as stripping solution are recycled, as shown in Figure 1. To model the recycling mode, in 1984 Danesi^{22,23} proposed a simple model with a constant permeation coefficient. The difficulties involved in describing a nonsteady state process with variation of the concentration in the axial and radial directions, making use of the continuity equation, lead to the use of the macroscopic mass balance of the permeating solute in a certain volume of fiber in a given time interval.^{24–26} The model for transport of Au(I) in a hollow fiber supported LM system operating in recycling mode consists of four equations describing (i) the change of Au(I) concentration in the feed and stripping streams when it is circulating through the membrane module and (ii) the change of Au(I) concentration in the feed and stripping tanks, where the aqueous solutions are continuously recirculated, based on the complete mixing hypothesis.

Assuming linear concentration gradients and absence of back-mixing, these equations are formulated as follows:

1. For the feed solution
module mass balance

$$\frac{\partial C_f^m}{\partial t} = -v_f \frac{\partial C_f^m}{\partial z} - \left(\frac{A}{V_m} \right)_{in} P_{Au} (C_f^m - C_s^m) \quad (5)$$

tank mass balance

$$\frac{dC_f^T}{dt} = \frac{Q_f}{V_f} (C_{f,z=L}^m - C_{f,z=0}^m) \quad (6)$$

2. For the stripping solution
module mass balance

$$\frac{\partial C_s^m}{\partial t} = -v_s \frac{\partial C_s^m}{\partial z} + \left(\frac{A}{V_m} \right)_{out} P_{Au} (C_f^m - C_s^m) \quad (7)$$

tank mass balance

$$\frac{dC_s^T}{dt} = \frac{Q_s}{V_s} (C_{s,z=L}^m - C_{s,z=0}^m) \quad (8)$$

where P_{Au} is the overall permeability coefficient (cm/s), C is the solute concentration (g/cm³), L is the fiber length (cm), Q is the flow rate (cm³/s), v is the linear velocity (cm/s), and V is the tank volume (cm³). The subscripts f and s refer to the feed and stripping solutions, respectively. The superscripts m and T refer to the membrane module and phase tank, respectively.

A/V_m is the ratio of area to volume of mass transfer of the fiber:

1. for the feed phase circulating through the inside of the fiber

$$(A/V_m)_{in} = \frac{2\pi n_f r_i L}{\pi n_f r_i^2 L} = \frac{2}{r_i} \quad (9)$$

2. for the stripping phase circulating along the outside of the fiber

$$(A/V_m)_{out} = \frac{2\pi n_f r_o L}{\pi (R_c^2 - n_f r_o^2) L} = \frac{2r_o n_f}{R_c^2 - n_f r_o^2} \quad (10)$$

where n_f gives the number of fibers contained in the membrane module, R_c is the inner radius of the module cell, and r_i and r_o are the inner and outer radii of the hollow fiber, respectively.

The integration of the system of differential Eqs. 5–8 for concurrent flow can be obtained by numerical methods. When a sodium hydroxide solution is used as the stripping agent, an instantaneous reaction is assumed to occur on the outside of the fiber, leading to $C_s^m = 0$ and $C_s^T = 0$. In this case, the solution to Eqs. 5–8 is simplified to:

$$V_f n \left(\frac{C_{f,t=0}}{C_f} \right) = Q_f \left\{ 1 - \exp \left(\frac{2P_{Au}L}{v_f r_i} \right) \right\} t \quad (11)$$

Experimental results can thus be fitted to a first-order kinetic law

$$V_f \ln \left(\frac{C_{f,t=0}}{C_A} \right) = S t \quad (12)$$

where S is the factor dependent on the geometry of the fibers and the module, the linear velocity of the fluids, and the

overall permeability of the system. The overall permeability coefficient can easily be obtained from the experimental value of the slope S as

$$P_{Au} = \frac{-v_f r_i}{2L} \left[\ln \left(1 - \frac{S}{Q_f} \right) \right] \quad (13a)$$

or

$$P_{Au} = \frac{-Q_f}{2\pi r_i L N} \left[\ln \left(1 - \frac{S}{Q_f} \right) \right] \quad (13b)$$

for a system run in a recycling mode.

The design of the hollow fiber supported LM modules for the separation-concentration of gold using overall permeability coefficient P_{Au} centers on three mass transfer resistances. One of these occurs in the liquid flowing through the hollow fiber lumen. The second corresponds to the gold-complex diffusion across the LM immobilized in the porous wall of the fiber. The third resistance is due to the aqueous interface created on the outside of the fiber.

The reciprocal of the overall permeability coefficient is given by

$$\frac{1}{P_{Au}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{P_m} + \frac{r_i}{r_o} \frac{1}{k_o} \quad (14)$$

where r_{lm} is the hollow fiber log mean radius, and k_i and k_o are the interfacial coefficients corresponding to the inner and outer aqueous boundary layers. P_m is the membrane permeability, which is related to the partition coefficient of gold (D_r) with LIX-79¹⁹ by

$$P_m = D_r k_m = K_{ex} [H^+] [R]_{org} k_m \quad (15)$$

where partition coefficient D_r is defined by

$$D_r = [Au(CN)_2 R]_{org} / [Au(CN)_2^-] \quad (16)$$

Inserting Eq. 15 in Eq. 14 gives P_{Au} :

$$\frac{1}{P_{Au}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{k_m K_{ex} [H^+] [R_{org}]} + \frac{r_i}{r_o} \frac{1}{k_o} \quad (17)$$

When the reaction is instantaneous on the stripping side, the contribution of the outer aqueous phase is removed from Eq. 17 and P_{Au} is determined from:

$$\frac{1}{P_{Au}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{k_m K_{ex} [H^+] [R_{org}]} \quad (18)$$

Membrane diffusion

The effective diffusion coefficients (D_{eff}) of Au(I) extractant complexes through the organic membrane phase were determined using the model. An effective diffusion coefficient (D_{eff}) for the solute in the immobilized organic LM can be defined as follows¹:

$$D_{eff} = k_m t_m \tau \quad (19)$$

Results and Discussion

LIX-79 is a hydrophobic moiety which can form ion pairs with anions such as $Au(CN)_2^-$. Thus, it is a desirable carrier for transport of $Au(CN)_2^-$ cyanide anions. The formation

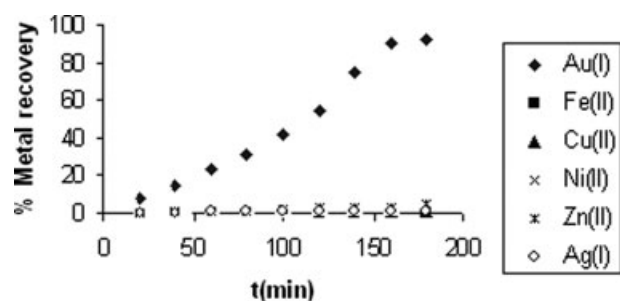


Figure 3. Separation of Au(I) from other metal cyanide salts under standard experimental conditions.

Tube side (Feed): 1000 cm³ of 10 mg/L Au(I), 30 mg/L Fe(II), 30 mg/L Cu(I), 10 mg/L Ni(II), 5 mg/L Zn(II), 3 mg/L Ag(I) in 1000 cm³ of NaCN solution; Pressure difference (bar): 0.20; Rate (L/h): 20; Initial pH = 10.30; Stirring rate: 400 rpm. Shell side: Pseudo-emulsion: 1000 cm³ of 12% LIX-79/*n*-heptane + 1000 cm³ of 0.2 M NaOH; Rate (L/h): 4.5; Initial pH = 12.40.

process of the ion pair at the aqueous feed phase/organic layer membrane fiber interface and the dissociation process of the ion pair at the fiber membrane/pseudo-emulsion phase interface are sufficiently fast. In preliminary experiments, it was found that LIX-79 mediated the transport of Au(CN)₂⁻ to the neutral aqueous receiving phase. This is probably because of the stability of the ion pair in the fiber membrane pore. However, in the presence of sodium hydroxide in the receiving phase (in this case, the pseudo-emulsion phase), Au(CN)₂⁻ is replaced by OH⁻ in the pseudo-emulsion phase, and the efficiency of the transport process is increased.^{14,17} In the next step, different experimental variables such as pH of feed phase, concentration of cyanide in the feed phase, concentration of sodium hydroxide in the pseudo-emulsion phase, concentration of LIX-79 in the pseudo-emulsion phase, and Au(I) concentration in the feed phase were investigated. The different metal cyanide salts such as Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I) ions were examined in comparison with gold to achieve the highest efficiency in the transport of Au(CN)₂⁻ across the PEHFSD by using a single hollow fiber module.

Gold cyanide-LIX-79 PEHFSD extraction system

The LIX-79/*n*-heptane (12% v/v or 0.375 M) system was used to carry out different experiments in counter current mode in presence of other metal cyanide salts as indicated in

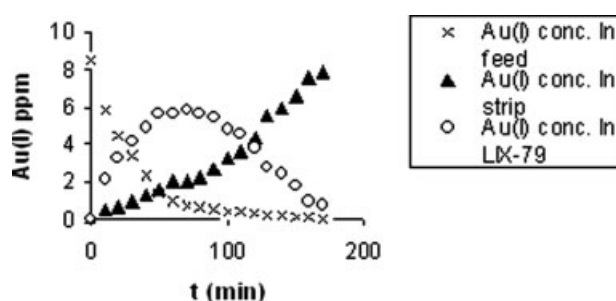


Figure 4. Concentration courses obtained from the feasibility study.

Tube side (Feed): 1000 cm³ of 10 mg/L Au(I), 30 mg/L Fe(II), 30 mg/L Cu(I), 10 mg/L Ni(II), 5 mg/L Zn(II), 3 mg/L Ag(I) in 1000 cm³ of NaCN solution; Pressure difference (bar): 0.20; Rate (L/h): 20; Initial pH = 10.30; Stirring rate: 400 rpm. Shell side: Pseudo-emulsion: 1000 cm³ of 12% LIX-79/*n*-heptane + 1000 cm³ of 0.2 M NaOH; Rate (L/h): 4.5; Initial pH = 12.40.

Figures 3 and 4. It can be seen in Figure 4 that Au(I) ions can be transported against their concentration gradient. As the concentration of Au(I) in feed solution was decreased, it was observed to increase in the stripping phase with elapsed time. Experiments were carried out by taking 1000 cm³ of 10 mg/L Au(I), 30 mg/L Fe(II), 30 mg/L Cu(I), 10 mg/L Ni(II), 5 mg/L Zn(II), and 3 mg/L Ag(I), with a minimum of 1000 ppm of NaCN solution at pH 10.5 in feed and a feed rate of 20 L/h (linear feed flow velocity 1.23 cm/s). The pseudo-emulsion was prepared by mixing 1000 cm³ of 12% LIX-79/*n*-heptane and 1000 cm³ of 0.2 M NaOH (stirred at 400 rpm) and was passed through the shell side. As seen in Figure 3, Au(I) was also separated from a mixture of other metal ions. The percentage transport of other metal ions after 180 min was Fe(II) 3.66%, Cu(II) 0.81%, Ni(II) 1.55%, Zn(II) 4.96%, and Ag(I) 1.37%, while transport of Au(I) within the same time period was >92% (Table 1). This shows that Au(I) can be separated from other metal ions.

Effect of feed pH

To study the influence of feed pH, experiments were performed at various pH, keeping both the LIX-79 concentration and NaOH concentration in the pseudo-emulsion phase constant. The results are shown in Table 2. Figures 5 and 6 pres-

Table 1. Recovery of Au(CN)₂⁻ in Presence of Other Base Metal Cyanides Using the PEHFSD Technique

Time (min)	% Recovery of Au(I)	% Recovery of Ag(I)	% Recovery of Cu(II)	% Recovery of Ni(II)	% Recovery of Zn(II)	% Recovery of Fe(II)
20	8.08	0.76	0.01	0.17	0.48	0.19
40	14.87	0.84	0.02	0.51	0.74	0.27
60	23.06	0.99	0.05	0.51	0.96	0.60
80	30.63	1.33	0.20	0.89	1.23	0.69
100	42.22	1.44	0.32	0.99	1.66	0.75
120	54.52	1.90	0.42	0.95	2.64	0.83
140	74.62	2.27	0.47	0.99	2.81	0.99
160	89.93	3.21	0.57	1.28	3.24	1.08
180	92.56	3.66	0.80	1.54	4.96	1.36

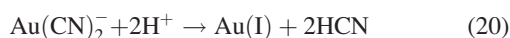
Experimental conditions: experimental conditions: tube side (Feed): 1000 cm³ of 10 mg/L Au(I), 30 mg/L Fe(II), 30 mg/L Cu(I), 10 mg/L Ni(II), 5 mg/L Zn(II), 3 mg/L Ag(I) in 1000 cm³ of NaCN solution; Pressure difference (bar): 0.20; Rate (L/h): 20; Initial pH = 10.30; Stirring rate: 400 rpm. Shell side: Pseudo-emulsion: 1000 cm³ of 12% LIX-79/*n*-heptane + 1000 cm³ of 0.2 M NaOH; Flow rate (L/h): 4.5.

Table 2. Effect of Feed Phase pH on the Transport of $\text{Au}(\text{CN})_2^-$ Using the PEHFS Technique

pH (Feed)	Slope (cm^3/s)	r^2	P_{Au} (10^{-5} cm/s)
9	1.9547	0.991	21.3
1.3	0.8534	0.9897	8.19
10.5	0.5625	0.9846	5.24
11	0.3809	0.9978	3.49

Experimental conditions: tube side (Feed): 1000 cm^3 of 10 mg/L Au(I), 30 mg/L Fe(II), 30 mg/L Cu(I), 10 mg/L Ni(II), 5 mg/L Zn(II), 3 mg/L Ag(I) in 1000 cm^3 of NaCN solution; Pressure difference (bar): 0.20; Flow rate (L/h): 20; Initial pH = 10.30; Stirring rate: 400 rpm. Shell side: Pseudo-emulsion: 1000 cm^3 of 12% LIX-79/*n*-heptane + 1000 cm^3 of 0.2 M NaOH; Rate (L/h): 4.5.

ent the experimental courses of P_{Au} vs. time and $V_f \ln(C_o/C_i)$ vs. time, respectively. The results revealed that the P_{Au} ($\times 10^{-5}$ cm/s) plummeted from 21.3 to 3.49 as feed pH increased from 9.0 to 11.0. These results are similar to those previously observed in flat sheet supported LM studies of Au(I) extraction from alkaline cyanide media (with the same feed composition). This observation is consistent with the theory according to which permeability is directly proportional to concentration of $[\text{H}^+]$ ions in the feed phase:



This equation shows that an increase in proton concentration in the feed solution will result in higher levels of HCN, which is responsible for decreasing the extraction of Au(I). This is particularly unfavorable when the pH of the feed solution is more than 11. To avoid this HCN formation, considering the pH range of the actual hydrometallurgical solution (normally varying between 10 and 11), an aqueous feed pH of 10.3 was selected for further experiments.

Influence of the stripping agent concentration in the pseudo-emulsion phase

This study was carried out using NaOH solutions as the stripping agent in the pseudo-emulsion phase for Au(I) transport and the results obtained are shown in Figure 7. The experimental results were fitted to Eq. 12 and a plot of $V_f \ln(C_o/C_i)$ vs. time for different initial NaOH concentrations

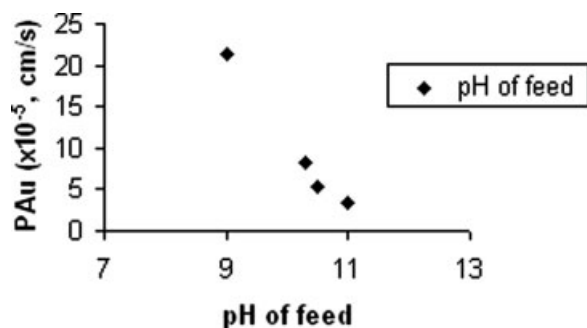


Figure 5. P_{Au} (10^{-5} cm/s) as a function of feed pH in recycle mode in presence of base metals using the PEHFS technique (experimental conditions are as given in Table 1).

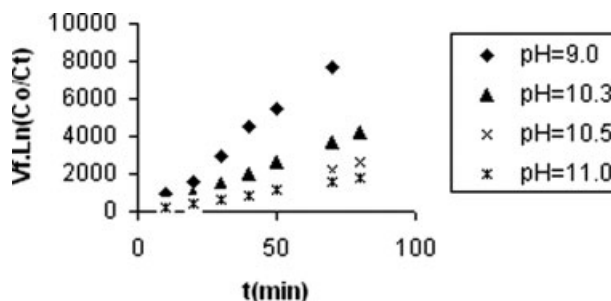


Figure 6. Influence of the initial pH on the permeability of Au(I) in the feed phase in presence of base metals as a function of time in recycle mode (experimental conditions are as in Table 1).

revealed that Au(I) permeability is not greatly influenced by increasing the NaOH concentration in the pseudo-emulsion phase. As seen from Table 3, the effect of NaOH concentration in the pseudo-emulsion phase influenced the separation factor of gold against other metal cyanide salts for Fe(II) was maximum at 0.2 M NaOH, after which it decreased with an increase in NaOH concentration. The same applies for the separation factors of Ni(II), Zn(II), and Ag(I), although for Cu(II) this increased with an increase in NaOH concentration. As seen from Figure 7, Au(I) permeability was not affected significantly by an increase in NaOH concentration. Consequently, 0.2 M NaOH concentration was selected for further experiments. A lower concentration of NaOH was not suitable for the experiments.

Influence of cyanide concentration in the feed phase

To study the influence of cyanide concentration in the feed phase, experiments were performed at various cyanide concentrations, keeping the LIX-79/*n*-heptane and NaOH concentration in the pseudo-emulsion phase constant. Figure 8 shows the effect of the cyanide in the feed phase on the transport of Au(I). Table 4 shows that the value of the permeability coefficient plummeted with an increase in cyanide concentration in the feed phase. The P_{Au} (10^{-5} cm/s) values obtained were 13.32 and 9.69 for 0 and 100 ppm NaCN, respectively, whereas P_{Au} value obtained at 1000 ppm was

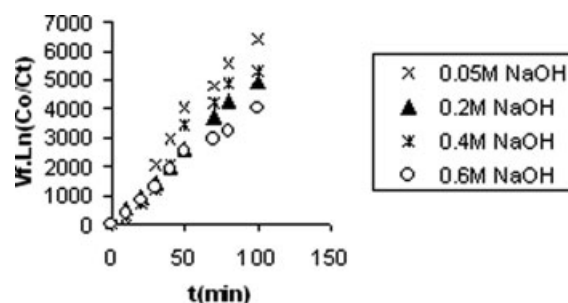


Figure 7. Influence of the stripping agent on the permeability of Au(I) in the pseudo-emulsion phase as a function of time in recycle mode (experimental conditions as in Table 2).

Table 3. Gold Separation Factors of Other Metal Cyanide Salts Using LIX-79/*n*-heptane Counter Currently with a Synthetic Hydrometallurgical Solution as a Function of NaOH Concentration in Pseudo-Emulsion After 3 h of Experiment

NaOH (M)	$S_{Au/Fe}$	$S_{Au/Cu}$	$S_{Au/Ni}$	$S_{Au/Zn}$	$S_{Au/Ag}$
0.05	11.32	40.67	10.17	7.5	3.43
0.2	58.45	40.2	77.93	54.77	97.07
0.4	28.19	58.73	52.86	46.13	7.68
0.6	18.02	86.74	11.88	9.38	7.03

1.5 times lower than the value obtained at 0 ppm NaCN. Since real alkaline solutions containing gold with other metal cyanides are expected to contain NaCN in the same range, 1000 ppm of NaCN was selected. A study was also conducted to observe the effect of sodium cyanide concentration on the transport of other metals, and Table 5 indicates that the separation factors of Au(I) against Fe(II), Cu(I), Ni(II), Zn(I), and Ag(I) for 1000 ppm of NaCN are 58.45, 40.2, 77.93, and 97.07, respectively. The same behavior was also observed when Virnig and Wolfe²⁶ performed liquid-liquid extraction studies with gold mine solutions. The maximum separation factors in presence of 1000 ppm of NaCN in the feed established that other metal cyanide complexes in this range were unable to extract into LIX-79/*n*-heptane because of poor extraction coefficients.

Influence of the feed flow rate on Au(I) transport

The influence of linear feed flow rate was studied to optimize gold cyanide transfer in the tube side by keeping the pseudo-emulsion flow rate constant. Results are shown in Figure 9, plotted as $V_f \ln(C_o/C_i)$ vs. time and P_{Au} vs. linear flow rate, respectively, for testing 10 mg/L of Au(I) concentration using 12% LIX-79/*n*-heptane. P_{Au} ($\times 10^{-5}$) increased (Table 6) from 9.73 to 11.13 for an increase in linear feed flow rate from 3.33 to 4.17 cm³/s and decreased with further increase in linear feed flow rate. As expected, P_{Au} first increased with linear flow rate and then decreased. The increase of P_{Au} with linear flow rate was caused by a decrease in the thickness of the aqueous boundary layer when the linear feed flow rate in the fiber lumen increased. The other reason for a decrease in P_{Au} value could be lower

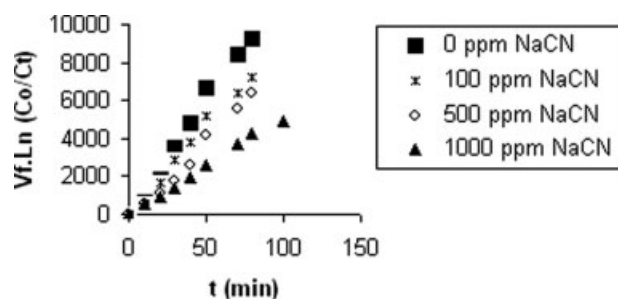


Figure 8. Influence of cyanide on the permeability of Au(I) in the feed phase as a function of time in recycle mode (other conditions are as in Table 2).

Table 4. Effect of Cyanide Concentration in the Feed Phase on the Transport of Au(CN)₂⁻ by PEHFSD Technique (Other Conditions are as in Table 2)

NaCN Concentration (ppm)	Slope (cm ³ /s)	r^2	P_{Au} (10^{-5} cm/s)
0	1.3196	0.991	13.32
100	0.9953	0.9897	9.69
500	0.8879	0.9846	8.55
1000	0.8534	0.9978	8.19

residence time at higher flow rates, which provides insufficient time to complex gold cyanide with LIX-79. This resulted in incomplete loading of LIX-79 with gold, which finally contributed to the lower value of P_{Au} . In our experiments, it was necessary to maintain the interface in the pore of the fiber mouth. To avoid the problem of contaminating the aqueous feed solution with the emulsion at a higher linear flow rate (11.66 cm³/s), a linear flow rate of 5.56 cm³/s was selected throughout the study. Also, as seen in Table 7, the separation factor for other metals reached a maximum at a linear feed flow rate of 4.17 cm³/s. Although a flow rate of 4.17 cm³/s gave the highest permeability of gold, 5.56 cm³/s was selected to provide a stabilized interface, better throughput, and sufficient separation factor of Au(I) against other metal cyanides to obtain a better product. In this work, when the flow rate of the feed is more than 20 L/h, pressure control was found to be better for the long duration experiments. As far as separation factors are concerned, they are also enough at 5.56 cm³/s to accomplish gold separation without any contamination of other metals. Hence, by selecting this flow rate (5.56 cm³/s), separation of gold was not affected maintaining better control of pressure across tube and shell side.

Influence of LIX-79/*n*-heptane concentration in the pseudo-emulsion phase on Au(I) transport

The effect of LIX-79/*n*-heptane concentration on Au(I) permeation was studied. Experimental conditions were established as pseudo-emulsion phase with various concentrations of LIX-79 in *n*-heptane and 0.2 M NaOH, and a feed concentration of 10 mg/L of Au(I) in 1000 ppm of NaCN in presence of other base metal cyanide salts. Results are shown in Figure 10, plotted as $V_f \ln(C_o/C_i)$ vs. time, and show that the permeability of Au(I) transport increased with increasing

Table 5. Separation Gold Factors of Other Metal Cyanide Salts Using LIX-79/*n*-heptane Counter Currently with a Synthetic Hydrometallurgical Solution as a Function of Cyanide Concentration in the Feed Phase After 3 h of Experiment by PEHFSD (Other Conditions are as Table 2)

Feed Cyanide Concentration (ppm)	$S_{Au/Fe}$	$S_{Au/Cu}$	$S_{Au/Ni}$	$S_{Au/Zn}$	$S_{Au/Ag}$
0	6.29	23.7	6.24	1.58	2.31
100	10.98	36.95	19.51	5.48	4.31
500	12.32	40.66	18.55	8.7	6.41
1000	58.45	40.2	77.93	54.77	97.07

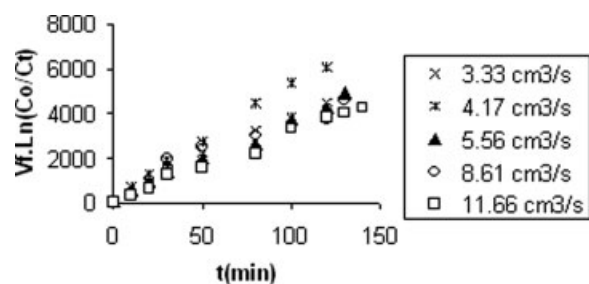


Figure 9. Influence of the linear feed flow rate on the permeability of Au(I) in the feed phase as a function of time in recycle mode using the PEHFS technique (experimental conditions as in Table 2, except variation of flow rate).

LIX-79 concentration, which is consistent with the results obtained using the same technique with synthetic Au(I) solution.²⁷ Figure 11 is a plot of percentage transport of Au(I) against time for different concentrations of LIX-79 from the batch in recycle mode. The percentage transport of Au(I) was seen to increase with LIX-79 concentration of up to 18% (v/v) and the transport rate was therefore limited by diffusion through the aqueous film on the feed side of membrane in this region. Table 8 shows the separation factors for other metals, which reveal that the separation factors increase with increasing LIX-79 concentration in the pseudo-emulsion phase. The higher concentration of LIX-79 contributed to the higher extraction of Au(CN)_2^- complex selectively. Other metal cyanides had lower distribution coefficients and their extraction was lower than that of gold. This shows good agreement with the results obtained in experiments with the same module using a hollow fiber supported LM and nondispersive solvent extraction of Au(I) with the same carrier.^{1,13}

Influence of initial Au(I) concentration in the feed phase and evaluation of diffusional parameters

Figure 2 gives a schematic representation of Au(I) diffusion through the membrane. The mass transfer of Au(I) crossing the membrane is described considering only diffusional parameters. The interfacial transport of Au(I) to the chemical reaction has been disregarded as the chemical reactions seem to take place at the aqueous feed solution-membrane and membrane-pseudo-emulsion phase interfaces, and previous studies suggest that chemical reactions occur simultaneously relative to the diffusion process.^{1,21,28} Therefore, the Au(I) transport rate is determined by the rate of diffusion

Table 6. Effect of Feed Linear Flow Rate on the Transport of Au(CN)_2^- Using PEHFS (Experimental Conditions as Table 2, Except Flow Rates)

Q_f (Feed Flow) (L/h)	Slope (cm^3/s)	r^2	P_{Au} , (10^{-5} cm/s)
12	3.33	0.9886	9.73
15	4.17	0.9952	11.13
20	5.56	0.994	8.19
31	8.61	0.9839	4.57
42	11.66	0.9851	2.16

Table 7. Gold Separation Factors of Other Metal Cyanide Salts Using LIX-79/*n*-heptane Counter Currently with a Synthetic Hydrometallurgical Solution as a Function of Linear Feed Flow Rate After 3 h of Experiment Using the PEHFS Technique (Experimental Conditions as in Table 2, Except Flow Rate)

Feed Flow Rate (L/h)	Slope (cm^3/s)	$S_{\text{Au/Fe}}$	$S_{\text{Au/Cu}}$	$S_{\text{Au/Ni}}$	$S_{\text{Au/Zn}}$	$S_{\text{Au/Ag}}$
12	3.33	35.25	218.28	45.85	44.87	97.07
15	4.17	68.03	92.51	98.89	48.07	61.1
20	5.56	58.45	40.2	77.93	54.77	56.99
31	8.61	40.74	33.38	31.41	30.51	54.69
42	11.66	24.31	20.04	18.64	12.43	27.34

of gold-containing species through the feed diffusion layer and the rate of gold-LIX-79 [$\text{HAu(CN)}_2\text{R}$ in Figure 2] species through the membrane. The aqueous mass transfer coefficient (K_f), the membrane mass transfer coefficient (K_m), and the diffusivity of Au(I) crossing the membrane may then be derived by Eq. 18.^{1,23} By plotting $1/P_{\text{Au}}$ vs. $1/K_{\text{ex}} [\text{H}^+][\text{LIX-79}]$ for different extractant concentrations of LIX-79 (at feed pH = 10.3), and varying pH with 12% LIX-79 concentration, one should obtain a straight line with slope $r_i/r_{\text{lm}}k_m$ and an ordinate to calculate the value of K_i and K_m (Figure 12). The values of $K_i = 2.32 \times 10^{-3}$ cm/s and $K_m = 2.01 \times 10^{-5}$ cm/s were calculated from the proposed model. The calculated value of the effective diffusion coefficient ($D_{\text{eff}} = \tau d_o K_m$) was 1.81×10^{-6} cm²/s for the studied conditions. This closely coincided with the magnitude of diffusion coefficient values discarded by Sastre and coworkers^{1,13} in their previous work.

Separation of Au(I) from Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I)

To examine the effect of several other metal ions that generally accompany Au(I), a systematic investigation was made of their influence on the overall permeation of Au(I). The separation of gold from copper and iron is particularly significant. As these two metals are usually associated with gold in many ores, they give rise to several contamination problems in the refining of gold.¹³ From the metal ions Fe(II) (30 mg/L), Cu(I) (30 mg/L), Ni(II) (10 mg/L), Zn(II) (5 mg/L),

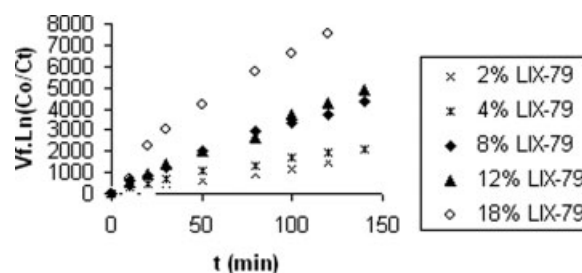


Figure 10. Influence of the LIX-79/*n*-heptane concentration on the permeability of Au(I) in the pseudo-emulsion phase as a function of time in recycle mode (experimental conditions as in Table 2, except LIX79 concentration).

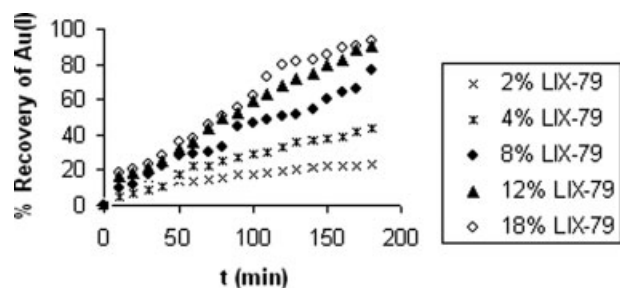
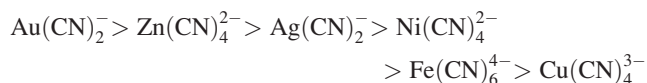


Figure 11. Influence of the LIX-79/*n*-heptane concentration on the percentage transport of Au(I) in the pseudo-emulsion phase as a function of time in recycle mode (experimental conditions as in Table 2, except LIX79 concentration).

and Ag(I) (3 mg/L) tested in the form of a mixture with Au(I) (10 mg/L), the cyano ions which exists with Au(I) were $\text{Ag}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_4^{3-}$, $\text{Zn}(\text{CN})_4^{2-}$, $\text{Ni}(\text{CN})_4^{2-}$, and $\text{Fe}(\text{CN})_6^{4-}$.

The separation of Au(I) using LIX-79, based on the experimental results obtained for the cyano ions, gives the following order of selectivity (Table 2):



Gold selectivity with respect to these anions was determined with 12% LIX79, feed pH = 10.3, linear feed flow rate = 5.56 cm³/s (linear flow velocity = 1.23 cm/s), and 0.2 M NaOH as strippant, NaCN = 1000 ppm. These conditions were similar to those encountered in hydrometallurgical leach solutions from low-grade ores.^{1,13}

These results agree with previous work indicating that LIX-79 has a higher affinity for univalent ions, such as $\text{Au}(\text{CN})_2^-$, than for multivalent ions, such as $\text{Cu}(\text{CN})_4^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Cu}(\text{CN})_3^{2-}$.^{26,29} For anions of the same type, particularly $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$, the larger $\text{Au}(\text{CN})_2^-$ anion is extracted in preference to $\text{Ag}(\text{CN})_2^-$. Furthermore, other highly charged cyano anions were not amenable to extraction, except for zinc complex. Similar results were found in the extraction of cyano ions by quaternary amines.³⁰

The extraction of these complexes depends greatly on the metal coordination number. It is observed here that the

Table 8. Separation Factors of Gold Against Other Metal Cyanide Salts in Counter Current Mode with a Synthetic Hydrometallurgical Solution by PEHFS Technique as a Function of LIX-79 Concentration in the Pseudo-Emulsion Phase After 3 h of Experiment

LIX-79 (v/v) %	$S_{\text{Au/Fe}}$	$S_{\text{Au/Cu}}$	$S_{\text{Au/Ni}}$	$S_{\text{Au/Zn}}$	$S_{\text{Au/Ag}}$
2	6.14	40.85	5	3.3	3.2
4	11.7	44.37	7.72	8.88	6.08
12	58.45	40.2	77.93	54.77	97.07
18	61.14	77.31	81	68.06	95.96

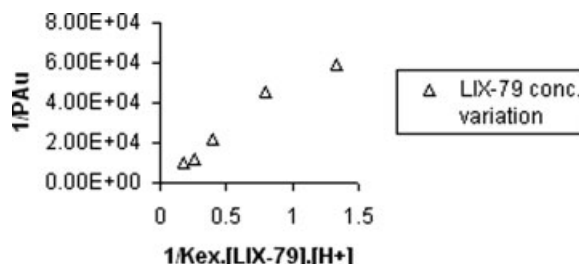


Figure 12. Plot of $1/P_{\text{Au}}$ as a function of $1/K_{\text{ex}} [\text{LIX-79}][\text{H}^+]$ for various LIX-79 concentrations in the pseudo-emulsion phase.

extraction order follows the series: $\text{Me}(\text{CN})_2^- > \text{Me}(\text{CN})_4^{2-} > \text{Me}(\text{CN})_6^{4-}$. 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 charge complexes are extracted preferably to higher charge complexes.³¹

Thus, as seen in Tables 3, 5, 7, and 8, showing the results obtained under different experimental conditions, in these transport studies, the separation factor of each base metal is defined as (representative case of Fe given in equation³²):

$$SF_{\text{Au/Fe}} = \left(\frac{[\text{Au(I)}]_{0,\text{strip}}}{[\text{Au(I)}]_{0,\text{feed}}} \right) \left(\frac{[\text{Fe(II)}]_{0,\text{feed}}}{[\text{Fe(II)}]_{0,\text{strip}}} \right) \quad (21)$$

Figures 6–10 present the results of Au(I) permeability in presence of base metals such as Fe(II), Cu(I), Ni(II), Zn(II), and Ag(I) ions under different experimental conditions. In a previous study carried out without base metals, the P_{Au} value obtained was 5.3×10^{-5} cm/s and the P_{Au} value obtained with base metals under similar experimental conditions was 8.19×10^{-5} cm/s. P_{Au} values were high in presence of base metals due to lesser availability of free cyanide which decrease the competition for gold in alkaline cyanide media. This will probably increase the extraction with LIX79. On the other hand, when Au is alone, free cyanide competition is more and extraction of gold is affected. This is clearly demonstrated in our previous publication¹⁶ showing that the mass transfer coefficient was one tenth of the value obtained when Au was present without base metals in presence of 1000 ppm of NaCN.

The experiments were carried out using 27 L of 10 ppm of Au(I) as a feed (linear flow velocity = 1.23 cm/s) and a pseudo-emulsion formed by 0.2 M NaOH + 12% LIX-79/*n*-heptane to evaluate concentration factor, defined as the ratio of the final concentration of Au(I) in the stripping phase to the initial concentration in the feed solution under similar experimental conditions. In this experiment, feed was continuously replaced with fresh feed without changing pseudo-emulsion. In this way, metal was allowed to concentrate in pseudo-emulsion in recirculation mode (linear flow velocity 0.28 cm/s). After passing 27 L, mixing unit was stopped and pseudo-emulsion was allowed to settle for few minutes. Finally, strip solution was checked for metal concentration. This was around 24.6 times the initial metal concentration in feed. The total time taken for this experiment was around 44

h. The feasibility of recovering Au(I) with PEHFSD using LIX-79 in *n*-heptane as a LM was thus proved.

Conclusions

Gold(I) extraction and stripping was conducted in a single hollow fiber contactor using PEHFSD in presence of other base metals. The three most important features of this technique are (i) to maintain constant supply of the organic membrane solution in the pores, which ensures stable and continuous operation; (ii) the direct contact between the organic and strip phases on the strip dispersion side provides an additional area for stripping; and (iii) the recovery of metals becomes very easy from pseudo-emulsion [emulsion breaks down soon after the mixing of solution (strippant + extractant) stopped and aqueous and organic phases separate automatically]. A predictive model was successfully developed. The present study demonstrates that LIX-79/*n*-heptane can be used effectively as carrier in Au(I) permeation through PEHFSD. This PEHFSD technique was found to be a promising option for the simultaneous separation and concentration of Au(I) from synthetic alkaline cyanide media in presence of other metal cyanides such as $\text{Ag}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_4^{3-}$, $\text{Zn}(\text{CN})_4^{2-}$, $\text{Ni}(\text{CN})_4^{2-}$, and $\text{Fe}(\text{CN})_6^{4-}$ using LIX-79/*n*-heptane. The use of a stripping solution containing NaOH in the pseudo-emulsion phase provided efficient and fast stripping of Au(I). To achieve clean separation of Au(I) in presence of other metals, several experiments with synthetic hydrometallurgical solution were performed and optimum conditions for this process were established. A good selectivity was found, and the separation of Au(I) based on the experimental results obtained for the cyano ions by 12% LIX-79 (v/v), with 0.2 M NaOH as stripping agent, feed pH = 10.3, and feed linear flow velocity = 1.23 cm/s gave the following order of selectivity: $\text{Au}(\text{CN})_2^- > \text{Zn}(\text{CN})_4^{2-} > \text{Ag}(\text{CN})_2^- > \text{Ni}(\text{CN})_4^{2-} > \text{Fe}(\text{CN})_6^{4-} > \text{Cu}(\text{CN})_4^{3-}$. The validity of this model was evaluated with experimental data and found to tie well with theoretical values.

Notation

C = metal concentration (g/cm^3)
 d = diameter of one fiber (cm)
 d_a = thickness of the aqueous feed boundary layer (cm)
 D_r = partition coefficient of gold
 d_i and d_o = inner and outer fiber diameter, respectively
 t_m = thickness of the fiber membrane (cm)
 D_{eff} = effective membrane diffusion coefficient of the gold-containing species
 k_i = aqueous mass transfer coefficient
 k_m = membrane mass transfer coefficient
 L = fiber length (cm)
 n_f = number of fibers
 Q = flow rate (cm^3/s)
 r_i and r_o = inner and outer hollow fiber radius (cm)
 P_{Au} = overall permeability coefficient (cm/s)
 V = tank volume (cm^3)
 V_m = volume of hollow fibers (cm^3)

Subscripts

f = feed solution
 s = stripping solutions
 in = inside the fiber

out = along the outside of the fiber
 i = for inner radii
 o = for outer radii

Superscripts

m = membrane module
 T = phase tank
 o = refers to concentration at time zero

Greek letters

τ = tortuosity of the membrane
 v_f and v_s = velocity of liquid inside fiber and shell side (cm/s)

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