Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Urtiaga, A. M. , Zamacona, S. and Ortiz, M. I.(1999) 'Analysis of a NDSX Process for the Selective Removal of Cd from Phosphoric Acid', Separation Science and Technology, 34: 16, 3279 — 3296
To link to this Article: DOI: 10.1081/SS-100100836
URL: http://dx.doi.org/10.1081/SS-100100836

SEPARATION SCIENCE AND TECHNOLOGY, **34**(16), pp. 3279–3296, 1999

Analysis of a NDSX Process for the Selective Removal of Cd from Phosphoric Acid

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ABSTRACT

In this work an analysis of the separation process of Cd from phosphoric acid by means of nondispersive solvent extraction technology and by using Aliquat 336 as the selective extractant and water as the backextractant solution is presented. Based on the results of a previous literature report for a different type of extractant, experimental planning has been carried out to determine the feasibility of cadmium removal in a continuous process that includes a regeneration step of the extractant to its chloride form. A chemical mechanism for the separation process has been proposed. Analysis of the steady-state results of Cd transport from the feed acidic phase to the stripping phase led to evaluation of the membrane mass transport parameter, $K_m = 1.76 \times 10^{-8}$ m/s.

Key Words. Phosphoric acid; Cadmium; Aliquat 336; Nondispersive solvent extraction; Hollow fiber

INTRODUCTION

Cadmium is one of the heavy metals present in wet phosphoric acid. In the manufacture of phosphate fertilizers the cadmium in the acid is transferred to the fertilizer and finally to soils. Due to the high toxicity of cadmium, it is environmentally desirable to reduce the cadmium content in wet phosphoric acid.

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The concentration of cadmium in phosphoric acid depends on the nature of the phosphate rock, on the manufacturing process, and on the concentration of P in the end product. According to the literature (1), the cadmium content in commercial phosphate rocks varies between 1 and 340 ppm, and in processing with sulfuric acid, 80% of this cadmium is found in the acid. In this low range of concentrations, liquid–liquid extraction seems to offer the best efficieny for the removal of cadmium from phosphoric acid among all the available technologies, provided a suitable extraction system is employed.

The literature refers to several cadmium removal methods. CFB Rudolf A. Oetker (2) investigated a conventional multistage liquid–liquid process using a tertiary amine as the extraction agent and an aqueous solution of sodium sulfate or sodium carbonate as the stripping agent. The same company also patented a process using phosphenes, phosphane salts, or phosphonium compounds as selective cadmium extractants. A similar procedure was developed by J. R. Simplot Co. (3) using the same class of solvents. Hoechst (4) patented a process that uses dialkyldithiophosphoric acid esters as extractants and NaOH, HCl, and HBr as stripping agents. Copper stripping was not quantitatively achieved in any of these cases, indicating the tendency of Cu to remain in the organic phase. The performance of two thiophosphinic acids, Cyanex 301 and Cyanex 302, in the extraction of Cd, Zn, Co, Mn, Ni, and Cu from acidic aqueous solutions is reported by the manufacturer (5). Ercros SA (6) patented a new process of cadmium separation from phosphoric acid by means of emulsion liquid membranes, using Cyanex 302 as the extractant and a 20% hydrochloric acid solution as the backextraction agent. Most of these references ignore other heavy metals in phosphoric acid which affect the behavior of the organic extractant phase on a long-term scale.

The literature survey revealed that thiophosphinic acids could be suitable Cd extractants. The efficiency of Cyanex 302 was successfully checked in previous work using a synthetically prepared cadmium solution in purified phosphoric acid (30% P_2O_5) and innovative nondispersive extraction in membrane contactors as the separation method (7, 8). The cadmium concentration was reduced from the initial 100 mg/L to 2 mg/L by using hydrochloric acid as the stripping phase. However, these results could not be repeated when working with industrial grade phosphoric acid. After several experiments it was concluded that the simultaneous presence of copper in the industrial acid, influenced the ability of Cyanex 302 to extract Cd because of the formation of a copper-loaded organic phase where a redox reaction takes place which leads to oxidation of the organic compound and the simultaneous reduction of copper, yielding to an extractant which is no longer active (9, 10). Under these circumstances, a change in the extraction agent was required.

An extensive literature survey concerning the extraction of cadmium with amines, preferably tertiary amines, was presented by Strenström and Aly (11). With regard to the use of Aliquat 336, separation of cadmium from environmental water samples (12), from halide media (13, 14), and from industrial effluents (15, 16) was reported.

Strenström (11, 17–19) tested a wide group of primary, secondary, tertiary, and quaternary amines as extractants. By using the distribution coefficient as the comparison parameter, tertiary and quaternary amines (Alamine 336 and Aliquat 336, respectively) showed the best results. The distribution coefficients of Aliquat 336 were somewhat higher than those of Alamine 336, but the tendency of Aliquat 336 to form a third organic phase and the poor separation of aqueous and organic phases obliged us to discard this extractant.

The nondispersive solvent extraction (NDSX) process is an alternative to the conventional extraction in mixer settlers and countercurrent columns. NDSX is characterized by stabilization of the aqueous–organic interface at a porous material, avoiding the dispersion of the phases and thus eliminating emulsion formation and phase entrainment. NDSX technology has been applied successfully using Aliquat 336 as the extractant agent to the separation-concentration of Cr(VI) (20, 21) and amino acids (22).

Because of the importance for environmental as well as health concerns of research on a technological alternative that will allow the removal of heavy metals from phosphoric acid, the aim of this work is to analyze the separation-concentration of cadmium, one of the most toxic metals, from wet phosphoric acid by means of nondispersive solvent extraction in hollow fiber membrane contactors using Aliquat 336 as the organic extractant.

EXPERIMENTAL

The NDSX experimental setup consisted of two or three hollow fiber contactors as required in the different steps of the experimental work. The characteristics of the contactor are given in Table 1. It is a commercially available

TABLE 1
Characteristics of the Hollow Fiber Contactor

Type of fiber	Celgard X-30
Number of fibers	10,000
Material, fibers	Polypropylene
Material, shell	Polypropylene
Inner diameter of the fibers	2.4×10^{-4} m
Wall thickness of the fibers	3.0×10^{-5} m
Pore size	3×10^{-8} m
Porosity	40%
Diameter of the shell	0.08 m
Effective length	0.15 m
Hold-up of the fibers	7.7×10^{-5} m^3
Hold-up of the shell space	2.05×10^{-4} m^3
Mass transfer area	1.4 m^2

device from Hoechst Celanese (Liqui-Cel Extra-Flow 2.5 × 8) and mounted with Celgard X-30 porous polypropylene membranes.

Several types of pumps were employed to draw the fluids through the system. The selection of an adequate pumping element was made by considering the flow-rate requirements and the chemical compatibility of the materials. Peristaltic pumps (GILSON Minipulse 3 and EYELA MP-3) fixed with Viton tubing were used to draw the phosphoric acid and the water stripping streams at the low range of volumetric flow rates. A gear pump (Micropump 020-000) was used to pump the organic phase. The hydrochloric acid equilibration phase was pumped using a diaphragm pump (ALLDOS M220-75D02) with a chemically inert polypropylene diaphragm, body, and valve seat, powered by a variable speed DC motor. A pulse dampener (COLE PALMER) eliminated pulsation in the output flow. Teflon flowmeters (AALBORG) were used to monitor the flow rates of the fluid phases. The flowmeters were equipped with a backpressure control valve in order to maintain the appropriate differential pressure for the control of the aqueous–organic interface at each module. The inlet and outlet pressures of each stream were measured in each of the modules using stainless steel pressure gauges (WICA). The differential pressure between the aqueous phases (feed, stripping, and equilibration were maintained in the range $0.1\ \mathrm{kg/m^2} < \Delta P < 0.3\ \mathrm{kg/m^2}$). Connections among the different elements of the experimental apparatus were by Teflon tubing.

The feed phase was industrial-grade phosphoric acid, supplied by Fertiberia S.A. (Spanish company) The initial cadmium content in the acid was 1.42×10^{-4} M (16 mg/L). This concentration was increased to 50 mg/L in all experiments by the addition of $CdSO_4 \cdot {}^8/_3H_2O$ (AnalaR, Probus). A preliminary filtration step was used to remove the suspended solid impurities of the industrial-grade phosphoric acid. The organic extractant phase was a solution of Aliquat 336, a commercial mixture of trialkylmethylammonium chlorides (trialkyl = C_8–C_{10}, mainly capryl) supplied by Henkel and used as received without further purification. The composition of the organic phase was, in volume percentages, 30% Aliquat 336, 30% isodecanol (Exxon), and 40% kerosene (Petronor S.A). The addition of isodecanol is necessary in order to avoid the formation of a second organic phase when the aqueous and organic phases are in contact. The regeneration of the extractant was performed using water as the stripping agent (11, 18, 19). A solution of hydrochloric acid (Probus), 1 M, was used as the equilibration phase.

In the first set of experiments two membrane modules were employed, one for the Cd extraction operation and the second one for Cd stripping and regeneration of the organic extractant. In this layout the feed phosphoric acid and the water-stripping phase were circulated either in a batch mode or in a continuous mode, as shown schematically in Fig. 1. In the final layout (Fig. 2), a third membrane module was added in order to perform an equilibration step,

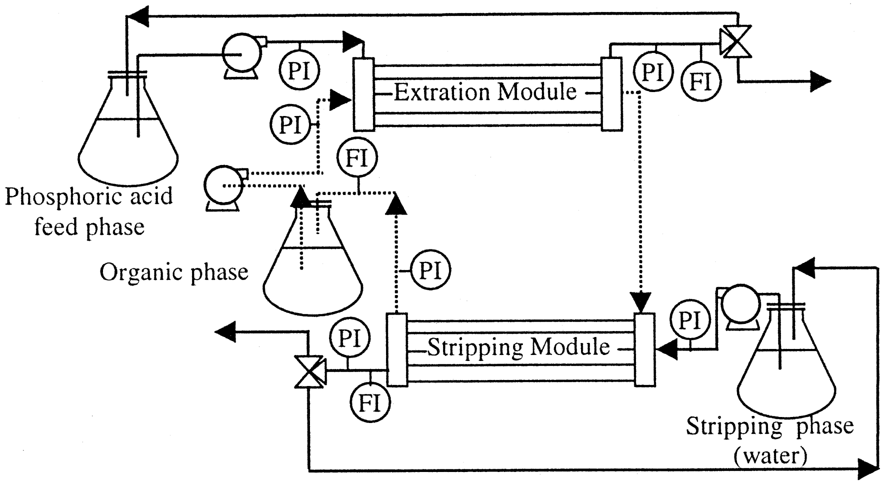

FIG. 1 Experimental setup with two hollow fiber modules, employed in the preliminary experiments. The feed and stripping phases could be circulated either in a batch mode or in a one-through mode.

needed to convert the Aliquat 336 hydroxide to the chloride salt needed for the extraction process. The equilibration phase was pumped past the membrane module and then returned to the reservoir, and the feed and stripping phases were always operated in a continuous mode.

The organic extractant phase was always circulated in a closed circuit, flowing through the extraction, stripping, and equilibration modules. The flow of

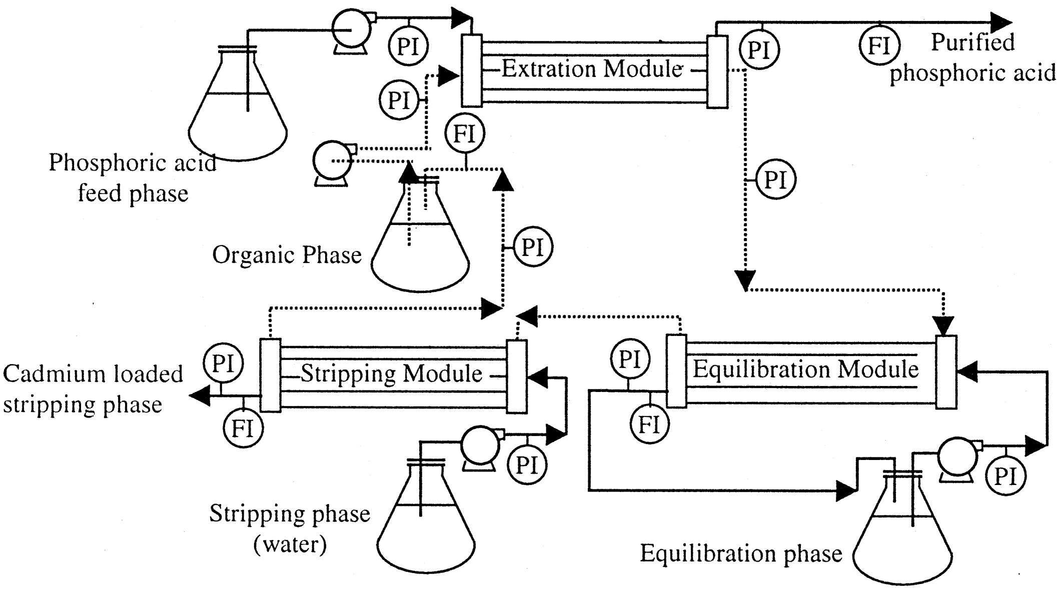

FIG. 2 Experimental setup with three hollow fiber modules, including the equilibration step of the organic phase.

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TABLE 2
Metallic Content in the Industrial
Phosphoric Acid

Metal	Concentration (mg/L)
Cadmium	16
Chromium	292
Copper	34
Iron	2013
Nickel	48
Lead	8
Zinc	335

the organic phase was through the inside of the fibers in the extraction module, while it was circulated through the shell-side in the stripping and equilibration modules. This layout facilitated the simultaneous control of the differential pressure between the aqueous and organic streams in all three modules

Samples of phosphoric acid and the stripping phases were either taken from the tanks or collected at the outlet of the extraction and stripping modules at regular time intervals. The cadmium concentration in these samples was determined using an inductively coupled plasma atomic emission spectrometer (ICP, Perkin-Elmer). When Cd was the only metal to be measured, the aqueous samples were analyzed by atomic absorption spectroscopy (Perkin-Elmer 3110). Metal concentration in the organic phase was calculated from the mass balance. Table 2 presents the concentration of metals in the raw phosphoric acid. Analytical determination of chloride anions in the aqueous stripping phase was carried out by ion chromatography in a Waters 501 HPLC provided with a Waters 430 conductivity detector using an IC-Pack A anionic analytical column. The pH of the stripping phase was measured with a pH-meter.

RESULTS AND DISCUSSION

This paper reports analysis of the separation-concentration process of cadmium from phosphoric acid by means of nondispersive solvent extraction in hollow fiber membrane contactors. This required the performance of experiments in various configurations of the experimental apparatus until the chemical features of the system were known in detail and the proper operating conditions were obtained. In this section we describe the different parts of the experimental work and the partial conclusions obtained in each phase.

Three sets of experiments were performed in order to test the viability of cadmium removal from industrial phosphoric acid using Aliquat 336 as the extractant and NDSX as the separation technique. The experimental conditions are detailed in Table 3.

Preliminary Experiments

The initial experiments were performed in a batch operating mode using the experimental configuration shown in Fig. 1. Two modules, one for extraction and one for stripping, and three liquid phases (feed phosphoric acid, organic extractant, and water stripping phase) were employed. Four consecutive extraction cycles were performed by changing the feed phase at the beginning of each run while maintaining the same the organic and stripping phases. In the first three cycles the feed solution was changed after 4 hours of running while it was kept longer in the fourth experiment. The evolution of all the metals in the feed phosphoric acid and in the water stripping tanks was measured (Table 1).

It was found that the water stripping stream became acidic and loaded with cadmium, zinc, and iron, as shown in Figs. 3, 4, and 5. Figure 3 shows the evolution with time of the concentration of cadmium in the feed, organic, and stripping tanks. It can be seen that the efficiency of Cd extraction decreases with time, a fact that was initially attributed to progressive loading in Cd in the organic extractant.

Figures 4 and 5 show that there was coextraction of Zn and Fe. Moreover, analysis of the stripping phase by means of ion chromatography revealed that chloride and phosphate anions were also transported from the feed phosphoric acid to the water stripping phase. Finally, the pH of the stripping phase was acidic, with a value close to 1. This result led to the idea that Aliquat 336 was performing the extraction and transport of phosphoric acid from the feed phase into the stripping phase, which occurs with other acids reported in the literature (23, 28).

TABLE 3
Scheme of the Experimental Conditions

Experiment	Initial volume (m^3)	Flow rate (m^3/s)
Figures 3, 4, and 5	$V_f = 1.5 \times 10^{-3}$	$F_f = 6 \times 10^{-6}$
	$V_o = 0.75 \times 10^{-3}$	$F_o = 6.2 \times 10^{-6}$
	$V_s = 0.5 \times 10^{-3}$	$F_s = 8.3 \times 10^{-6}$
Figure 6	Continuous flow	$F_f = 3.3 \times 10^{-8}$
	$V_o = 0.75 \times 10^{-3}$	$F_o = 4.8 \times 10^{-6}$
	Continuous flow	$F_s = 3.3 \times 10^{-8}$
Figure 7	Continuous flow	$F_f = 2.5 \times 10^{-7}$
	$V_o = 1 \times 10^{-3}$	$F_o = 1 \times 10^{-6}$
	Continuous flow	$F_s = 1.67 \times 10^{-7}$
	$V_e = 1 \times 10^{-3}$	$F_e = 8.3 \times 10^{-6}$

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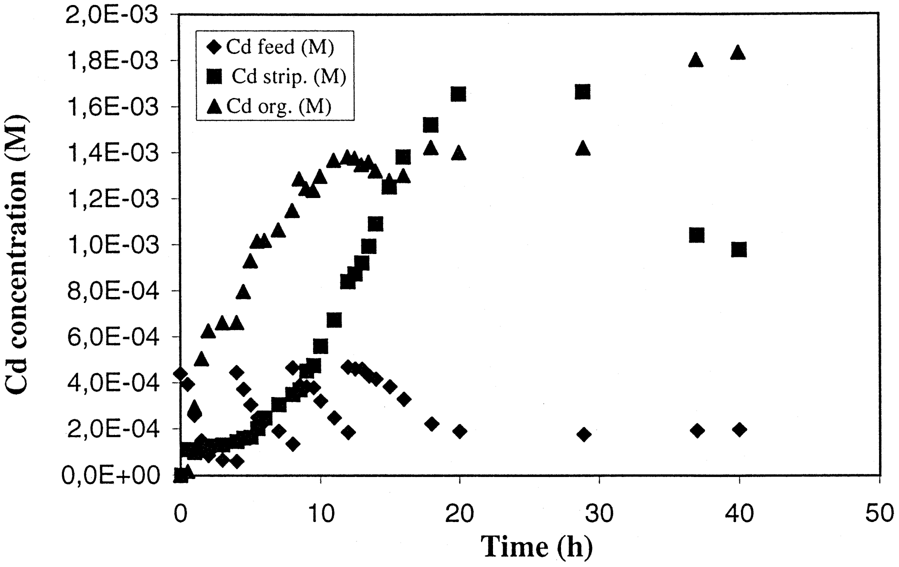

FIG. 3 Cadmium evolution with time in the feed, organic, and stripping tanks.

Concerning the results of cadmium separation and considering previous studies reported in the literature (12, 29, 30), it was postulated that the organic extractant Aliquat 336 was responsible for the extraction of cadmium by liberating it in the backextraction solution in its chloride salt. This conclusion was reached after checking for the presence of chloride in the stripping phase, by ion chromatography.

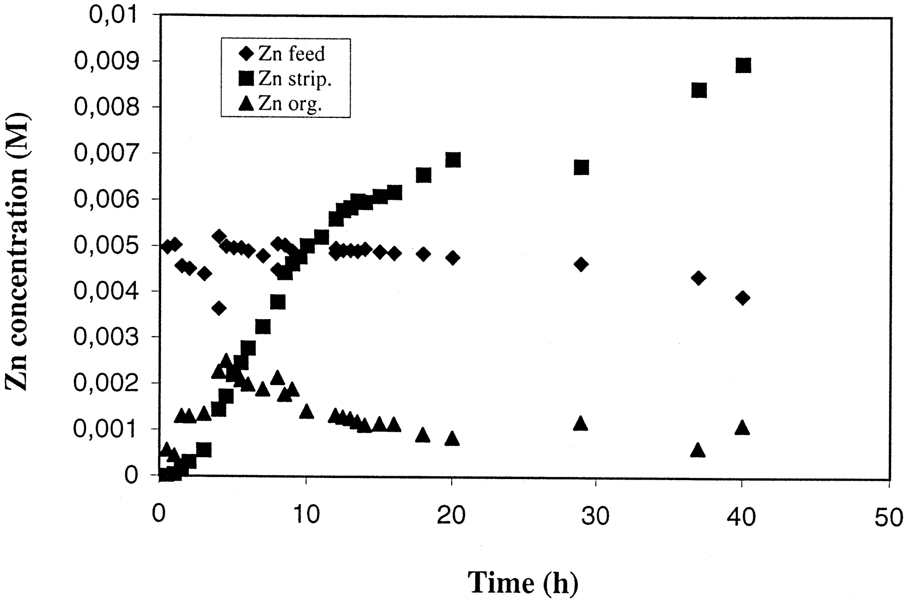

FIG. 4 Zn evolution with time in the feed, organic, and stripping tanks.

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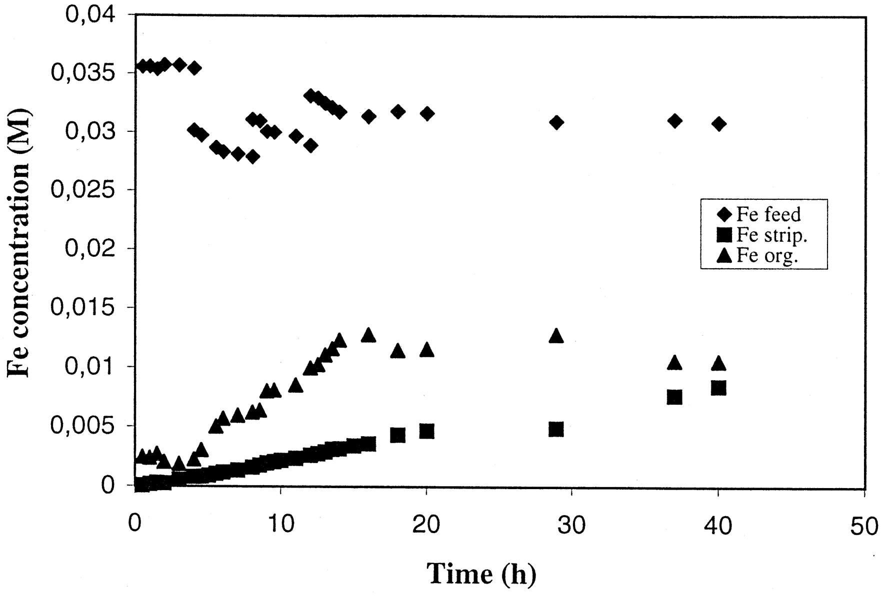

FIG. 5 Iron evolution with time in the feed, organic, and stripping tanks.

Next, a different set of experiments was performed in order to test the efficiency of the process. The feed and the stripping phases were circulated in a continuous mode with a single pass of the aqueous fluids through the contactors. The organic flow was maintained in a closed circuit. The results are given in Fig. 6.

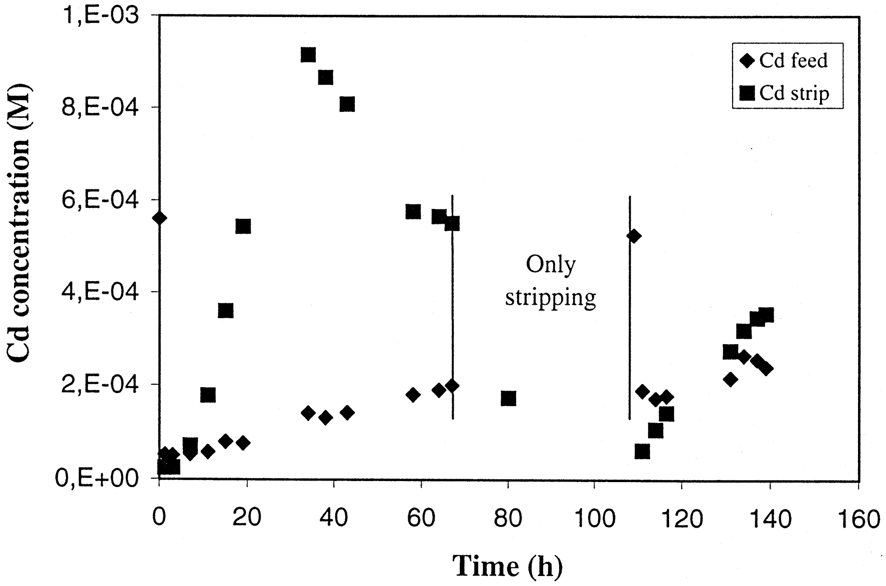

FIG. 6 Cadmium concentration in the feed and stripping phases at the outlet of the extraction and stripping modules, without equilibration of the Aliquat 336 extractant.

Again, the loss of efficiency of the process with time is clear, since the cadmium concentration at the outlet of the extraction module is continuously increasing. After 67 hours of experimental run the flow of the feed phase was interrupted and the organic phase was submitted to a stripping period of 42 hours with the aim of regenerating the metal-loaded extractant and continuing the extraction runs after this step. However, the efficiency of the process was not improved, since the yield of cadmium extraction was the same as before the stripping period.

It was concluded that there was a loss in extractant efficiency, probably due to the loss of chemical properties of the extractant, and that it occurred parallel to the increase in chloride concentration in the backextraction phase. Therefore, it was next decided to check the role of the chloride ions. Strenström and Aly (17) assumed that the chloride ions were responsible for the formation of cadmium chloride as a previous step in the cadmium extraction with tertiary amines. In their work, hydrochloric acid was added to the phosphoric acid to improve the extraction efficiency of Alamine 336, and they concluded that the formation of cadmium chloride in the aqueous phase allowed the metal to be extracted.

In order to check wether the chloride anions initially present in the phosphoric acid were responsible for the extraction of Cd, a synthetic solution of phosphoric acid (30% P_2O_5) free of chloride and containing 50 mg/L of Cd was put into contact with a freshly prepared organic extractant solution in a rotary stirrer. After equilibrium was reached, 96% of the cadmium had been extracted. So that it was concluded that it is not necessary to have chloride anions in the phosphoric acid to perform cadmium extraction with Aliquat 336. The cadmium-loaded organic phase obtained in this experiment was later put into contact with water, and the resulting aqueous phase was analyzed. The presence of phosphate and chloride anions was determined by ion chromatography, thus checking that the origin of the stripped chloride was in the organic extractant Aliquat 336, a quaternary alkyl ammonium salt that is commercialized in its chloride form.

Extraction Mechanism

On the basis of the previously reported results and with the experimental evidence of the high acidity of the stripping phase, a chemical mechanism for the extraction of Cd from phosphoric acid with Aliquat 336 and stripping with water is postulated as follows.

Extraction Step

$$H_3PO_4 + 3\overline{AlCl} \quad \leftrightarrow \quad \overline{Al_3PO_4} + 3HCl \tag{1}$$

$$Cd_3(PO_4) + 6HCl \quad \leftrightarrow \quad 3CdCl_2 + 2H_3PO_4 \tag{2}$$

$$CdCl_2 + 2\overline{AlCl} \quad \leftrightarrow \quad 3\overline{Al_2CdCl_4Cd_3(PO_4)_2} \tag{3}$$

$$\overline{+\ 12\overline{AlCl} \quad \leftrightarrow \quad 3\overline{Al_2CdCl_4} + 2\overline{Al_3PO_4}} \tag{4}$$

Stripping Step

$$\overline{Al_2CdCl_4} \quad \xleftrightarrow{H_2O} \quad 2\overline{AlCl} + CdCl_2 \tag{5}$$

$$\overline{Al_3PO_4} + H_2O \quad \leftrightarrow \quad 3\overline{AlOH} + PO_4H_3 \tag{6}$$

where *Al* denotes Aliquat 336. The Aliquat 336 extractant exchanges the chloride ions with the phosphate ions of the feed phosphoric acid, generating hydrochloric acid in the feed phase that provides the required chloride ions for the formation of cadmium chloride. As a result, the cadmium chloride species is formed. The cadmium chloride is readily extracted by Aliquat 336. Thus, in the extraction step the organic phase becomes loaded with cadmium chloride and phosphate ions. In the stripping step the cadmium chloride is released into the water stream and the phosphate form of Aliquat 336 is transformed into its hydroxide form by equilibrium with the hydroxide ions in the aqueous phase (24), therefore reducing the pH of the stripping solution. The progressive decrease in the efficiency of the process is due to the formation of the hydroxide form of Aliquat 336, which is not active in the extraction of cadmium chloride.

Equilibration Step

$$\overline{AlOH} + HCl \quad \leftrightarrow \quad \overline{AlCl} + H_2O \tag{7}$$

The addition of a third step for the regeneration of the Aliquat 336 by equilibration with hydrochloric acid will bring the extractant back to its original chloride form, allowing the separation of cadmium from phosphoric acid.

Experiments with Extraction, Stripping, and Equilibration Steps

We next turn to a check of the validity of the chemical mechanism proposed above by Reactions (1)–(7). In order to achieve the equilibration of Aliquat 336, it was necessary to perform an equilibration step of the organic extractant. Equilibration with hydrochloric acid was carried out in a third hollow fiber membrane contactor, as described in the Experimental section (Fig. 2). The aqueous and organic phases were circulated in a once-through mode, while the organic and equilibration phases flowed in closed circuits. All phases were renewed in each experimental run.

Figure 7 shows the evolution of cadmium concentration at the outlet of the extraction and stripping modules in a long-term experiment. It can be seen that the concentration of cadmium was reduced from 50 mg/L at the inlet of the module to values below 2 mg/L at the outlet of the module. The percentage of cadmium extraction remained constant over the whole period, proving that the efficiency of Aliquat 336 extractant was not altered. The concentration of Cd in the stripping phase followed a different pattern, showing an increase with time until the steady state was reached. The reason is that the mass transport rate of cadmium in the stripping step is lower than the rate of the extraction step, leading to the accumulation of cadmium in the organic phase.

The influence of the flow rates of the feed and stripping phases was investigated. Two groups of experiments were performed. In the first group the flow rate of the stripping phase was maintained constant and the flow rate of the feed phase was varied, and inversely in the second group of experiments. Each experimental run proceeded until the steady state of the Cd concentration in the stripping phase was reached. The volumes and flow rates of the organic and equilibration phases were the same as reported in Fig. 7.

Table 4 shows the percentage of extraction obtained in each experimental run as a function of the flow rate of the aqueous phase. It can be seen that the flow rate of the stripping phase has no influence on the extraction percentage whereas the variation of the flow rate of the feed phase introduces a remarkable effect which is due to the influence of the cadmium concentration of the organic phase on the extraction process.

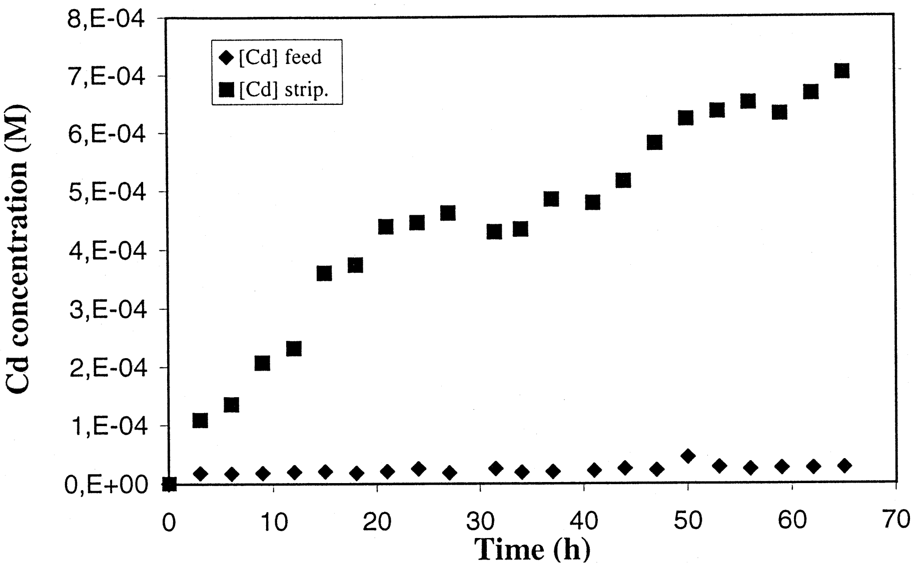

FIG. 7 Cadmium concentration in the feed and stripping phases at the outlet of the extraction and stripping modules, with the equilibration step of the Aliquat 336 extractant.

TABLE 4
Percentage of Cd Extraction as a Function of the Flow Rates of the Feed and Stripping Phases

Feed phase flow rate (mL/min)	Stripping phase flow rate (mL/min)	% Extraction
15	10	94
60	10	77
120	10	63
10	15	97
10	30	96
10	60	96
10	120	96

Mass Transfer Parameters

A steady-state mass balance to the fluids circulating through the module is given by

$$(\pm)F\,\frac{dC}{dz} = \frac{A_{\mathrm{m}}}{L}\,J \tag{8}$$

where F is the flow rate of the fluid, C is the cadmium concentration in the phase, J is the flux of Cd per unit mass transfer area and per unit time, and A_{m} is the mass transfer area of the membrane, calculated as $A_{\mathrm{m}} = n2\pi rL$.

In the extraction module the phosphoric acid phase is losing cadmium, thus the sign of the left-hand-side term must be negative. For the stripping aqueous phase which is gaining cadmium as it flows through the stripping module, the sign of the LHS term must be positive.

Phase boundary resistances in the aqueous and organic phases in the modules of these HF contactors are usually considered negligible, and therefore it is assumed that the main resistance to mass transfer is located in the transport across the membrane (7, 21, 25). With this assumption, the flux of cadmium in the extraction module is given by

$$J = K_{\mathrm{m}}\,\Delta\overline{C} \tag{9}$$

where K_{m} is the membrane mass transfer coefficient and $\Delta\overline{C}$ is the concentration difference of the Aliquat–cadmium complex across the membrane. In the extraction module $\Delta\overline{C} = (C_{\mathrm{eq,f}} - \overline{C})$ and in the stripping module $\Delta\overline{C} = (\overline{C} - \overline{C}_{\mathrm{eq,s}})$. Under the assumption of equilibrium conditions at the aqueous–organic interface, the concentration of cadmium in the organic phase can be related to the concentration of cadmium in the aqueous phase by the corresponding equilibrium expression. In the literature (23, 24, 26, 27), nonlinear expressions have been reported for the equilibrium reactions between Aliquat 336 and different species. After substitution in Eq. (9), the system of Eqs. (8) and (9) could be integrated to determine the evolution of cadmium with the length of the hollow fiber.

The high concentration of the stripping agent in the backextraction phase, in this case water, usually allows the equilibrium description to be simplified to the definition of a distribution coefficient, the ratio of the concentration of cadmium in the organic phase to the concentration of cadmium in the stripping phase at the interface:

$$H_s = \overline{C}_{eq,s}/C_s \tag{10}$$

Substitution of Eqs. (9) and (10) into Eq. (8) leads to

$$\frac{dC_s}{dz} = \frac{A_m K_m}{F_s\, L}(\overline{C} - H_s C_s) \tag{11}$$

That is, the macroscopic cadmium mass balance to the water stream in the stripping module. The subscript “s” denotes the stripping phase.

Equation (11) can be simplified if we consider that Reaction (5) is totally shifted to the right, leading to the expression

$$\frac{dC_s}{dz} = \frac{A_m K_m}{F_s\, L}\overline{C} \tag{12}$$

As can be seen from the modeling equations, in order to describe the experimental results it is necessary to know the membrane mass transfer coefficient K_m and the equilibrium parameters.

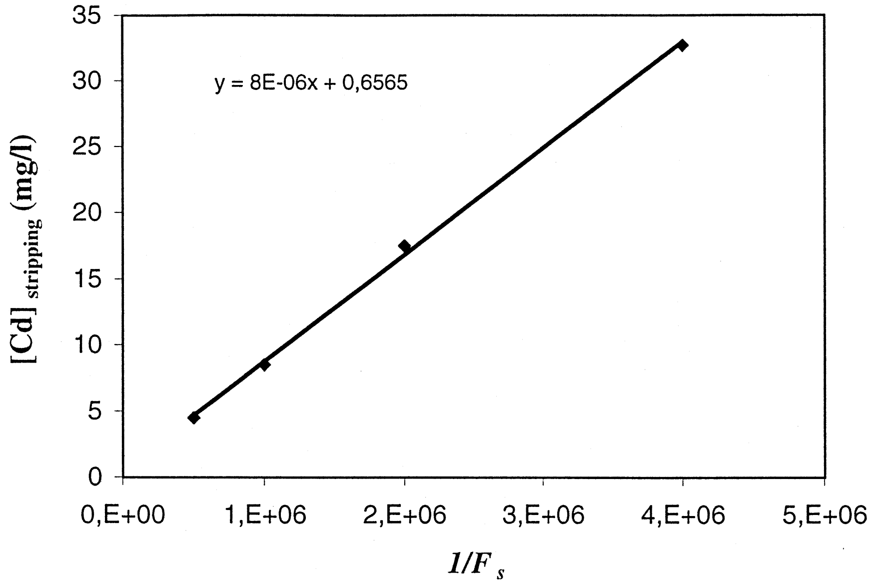

FIG. 8 Cadmium concentration in the stripping phase vs $1/F$s.

By integration of Eq. (12) between the limits in $z = 0$, $C_s = 0$ and in $z = L$, $C_s = C_s$ we obtain

$$C_s = \frac{A_m K_m}{F_s} \overline{C} \tag{13}$$

The steady-state cadmium concentration in the stripping phase is plotted vs the inverse of F_s in Fig. 8, data corresponding to constant values of F_f. The data are linear, consistent with Eq. (13). The slope of this plot includes the cadmium concentration in the organic phase; that is, constant and independent of F_s once the steady state is reached. $\overline{C}$ was calculated by a mass balance of all the phases in the system. The value of K_m is obtained from the slope of this plot, $K_m = 1.76 \times 10^{-8}$ m/s.

Future work will deal with verification of the proposed model and determination of the equilibrium parameter of the extraction reaction, which could include a more involved expression of the Cd extraction equilibrium.

CONCLUSIONS

Analysis of the separation process of Cd from phosphoric acid by means of nondispersive solvent extraction technology and using Aliquat 336 as the selective extractant and water as the backextractant solution is presented in this work. The continuous process requires a regeneration step of the Aliquat 336 extractant to its chloride form in order to obtain long-term stability.

Based on previous reports in the literature (4–7), Cyanex 302 and other phosphorous-based extractants could be suitable Cd extractants from a highly acidic media. The complex metallic content of industrial-grade phosphoric acid induces the oxidation of Cyanex 302 by Cu(II), yielding an extractant that is no longer active (9, 10). The amine group of extractants has also been investigated as selective cadmium extractants (11–19). Among then, Aliquat 336, a quaternary ammonium salt, seemed to offer the highest extraction efficiency.

In this work the chemical mechanism of the separation process of cadmium from phosphoric acid using Aliquat 336 and water as stripping agent has been proposed. The Aliquat 336 extractant exchanges the chloride ions with phosphate ions of the feed phosphoric acid. As a result, the cadmium chloride species is formed in the acid. The cadmium chloride is extracted by Aliquat 336. Thus, in the extraction step the organic phase becomes loaded with cadmium chloride and phosphate ions. In the stripping step the cadmium chloride is released into the water stream and the phosphate form of Aliquat 336 is transformed into its hydroxide form by equilibrium with the hydroxide ions in the aqueous phase, therefore reducing the pH value of the stripping solution. The addition of a third step for the regeneration of Aliquat 336 by equilibration with hydrochloric acid brings the extractant back to its original chloride form, allowing the separation of cadmium from phosphoric acid to be performed on a long-term scale.

Finally, analysis of the steady-state results of Cd transport from the feed acidic phase to the stripping phase led to evaluation of the membrane mass transport parameter, $K_\mathrm{m} = 1.76 \times 10^{-8}$ m/s.

NOTATION

A_m	mass transfer area of the membrane (m^2)
C	cadmium concentration in the aqueous phases (mol/L)
C_0	initial cadmium concentration (mol/L)
C	cadmium concentration in the bulk of the organic phase (mol/L)
$\overline{C}_\mathrm{eq}$	cadmium concentration in the organic phase at the interface (mol/L)
F	volumetric flow rate (m^3/s)
H_s	distribution coefficient
J	cadmium flux ($\mathrm{mol/m^2 \cdot s}$)
K_m	mass transfer coefficient of the organic phase impregnated in the membrane (m/s)
L	effective length of the hollow fiber module (m)
n	number of hollow fibers in the module
r_i	inner radius of the hollow fiber (m)
r_o	outer radius of the hollow fiber (m)
z	axial coordinate

Subscripts

eq	equilibration phase
f	feed phase
o	organic phase
s	stripping phase

ACKNOWLEDGMENT

Financial support from the European Commission under Project AVI*-CT94-0014 is gratefully acknowledged.

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Received by editor November 23, 1998
Revision received February 1999

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