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Viability of the separation of Cd from highly concentrated Ni–Cd mixtures by non-dispersive solvent extraction

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Abstract

The separation of nickel and cadmium from highly concentrated solutions by means of non-dispersive solvent extraction (NDSX) has been studied in this work. Extraction and back-extraction processes were carried out simultaneously in a batch mode using two parallel modules and the organic phase flowing in a closed circuit. Starting with concentrations of 0.37 M of Cd and 0.37–0.68 M of Ni in the feed aqueous phase, 1 M of H_2SO_4 in the back-extraction phase, and using D2EHPA as extractant, the viability of the separation–concentration of Cd from that mixture has been confirmed. Under the experimental conditions, the separation process was run at a constant rate of mass transport, thus leading to a selectivity factor in the concentration step $\rho = 67$ mol Cd/mol Ni. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Separation of metals by solvent extraction has been an important technique in pollution control as well as in hydrometallurgical processes. Conventional-practice solvent extraction relies on dispersion, which causes loss of extractant as well as solutes. Microporous membrane-based non-dispersive solvent extraction technology (NDSX) has been developed recently; the main difference between both technologies lies in the way of contacting the organic and the aqueous phases. In the hollow fiber modules one phase flows through the lumen of the fibers and the other through the shell side. In this way both phases get in contact through the pores of the fiber without mixing and therefore the dispersion of the organic phase into the aqueous stream or vice versa is eliminated and also the emulsion formation and phase entrainment [1,2]. To achieve this type of contact a differential static pressure has to be applied in one of the phases: in the aqueous solution for hydrophobic membranes and in the organic phase for hydrophilic membranes. Apart from this, the NDSX technology presents several advantages, such as, very large interfacial area and reduction in the equipment volume and space.

Many applications of non-dispersive liquid–liquid extraction in hollow fiber contactors to the removal and/or concentration of one solute from aqueous solutions are found in the literature [3,4]. Metals have been widely extracted into an organic compound using NDSX: Au, Cd, Co, Cr, Cu, Zn, etc., [5–7] and among other solutes, proteins, aminoacids and fermentation based pharmaceutical products have also been removed [2,8,9]. However, in some cases the objective of the process is not only the removal but the separation of the components of a mixture. Individual metal removal/recovery from mixtures of cations or mixtures of cations and anions using NDSX has been also studied [10,11].

The separation of nickel and cadmium from highly concentrated solutions generated during the leaching step of the recycling process of Ni–Cd batteries is one practical example where the objective is the separation of the components of a mixture since two of them can be reused. Among all small secondary batteries, Ni–Cd accumulators are currently the most important systems since the long life, high reliability and minimal maintenance requirements have made them very popular. After use, the management of the resulting waste presents several problems, and recycling is an attractive solution since it implies material conservation as well as important economical and environmental benefits. The latter are specially important considering the toxicity of the metals present in the batteries.

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Hydrometallurgical processes of Ni–Cd recovery from batteries are based on the leaching of shredded nickel–cadmium scrap followed by series of separation steps including solvent extraction and stripping, among others. The application of non-dispersive solvent extraction technologies in these separation steps presents several advantages as mentioned earlier.

D2EHPA has been shown in the literature to be a good extractant for divalent metals like: Cd, Ni, Pb, Co, U, Cu... Several works have been reported for the separation of Cd and Ni using D2EHPA as extractant. Ritcey [12] showed a process for the separation and recovery of cadmium and nickel by solvent extraction from this type of wastes using ammonia pre-equilibrated D2EHPA. Clark et al., [13] studied the purification of nickel from concentrated solutions (2 M) using D2EHPA (20%). More recently, Preston [14] investigated the synergistic effects of carboxylic acids and trialkylphosphine sulphides in the selective solvent extraction of cadmium (0.01 M) from mixtures of zinc and nickel. Also, according to Preston et al. [15] cadmium (0.04 M) can be selectively separated in the presence of nickel (0.42 M) by D2EHPA (0.5 M). Finally, Soler et al. [16] reported some preliminary results of the separation of Cd and Ni from sulphate solutions using hollow fiber modules, analyzing the influence of the feed solution variables, namely pH and Cd concentration on the separation process.

The complexity of the description of the extraction behaviour of phosphorus compounds has also been widely mentioned [17,18]. The reaction between the metal and the organic carrier is an ion exchange reaction described by the following equation:

$$Me^{2+} + n\overline{(HX)_2} \Leftrightarrow \overline{MeX_2(HX)_{2n-2}} + 2\,H^+ \qquad (1)$$
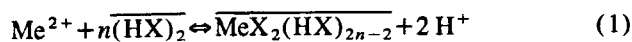
where n is the stoichiometric coefficient. Different values of n have been reported in the literature: 2 and 2.5 for Cd and 2, 2.5 and 3 for Ni [19–23].

Taking into account the interest and complexity of the separation of Cd and Ni from highly concentrated solutions, this work has been focused on the viability of the application of the non-dispersive solvent extraction technology to achieve the separation of both metals. Batch experiments have been performed determining the separation selectivity.

2. Experimental setup

All the experiments have been performed using as organic phase a mixture of 1.7 M of di(2-ethylhexyl) phosphoric acid (Merck) called D2EHPA, and kerosene (Petronor) as solvent. It was also necessary to add a third component: tributylphosphate TBP (Aldrich Chemicals) at 0.3 M to avoid the segregation of a second organic phase. The feed aqueous solutions were prepared with $CdSO_4$ 8/3 H_2O and $NiSO_4$ $6H_2O$ (AR grade) and the stripping phase was a solution of H_2SO_4 (1 M).

Two commercial modules manufactured by Hoechst Celanese containing polypropylene hollow fibers were used as contactor systems. Characteristics of the modules are given in Table 1. As those fibers were hydrophobic it was necessary to circulate the aqueous streams at higher pressure than the organic phase.

Both aqueous phases utilised PTFE diaphragm pumps, capable of pumping up to 0.8 l/min and powered by a variable speed DC motor, and the organic phase utilised a gear pump capable of flows up to 1 l/min.

Three teflon flowmeters were used to monitor the flow rates of the feed, stripping and organic streams. The flowmeters were equipped with back pressure control valves in order to maintain the appropriate differential pressure for the control of the aqueous organic interface at each module.

Adjustment of pH was carried out by a pH controller system (Metrohm 691-01). The pH was continuously monitored in the feed and back-extraction aqueous solution (BEX). The pH-meter signal activated a peristaltic pump for the addition of a sodium hydroxide (18 M) solution to the feed aqueous solution, whereas in the back-extraction a solution of H_2SO_4 (1 M) was used. The volume added to the aqueous phases was about 20 ml and therefore the change in the total volumes was considered negligible.

The set-up of the experimental system based on two hollow fiber (HF) modules is shown in Fig. 1. The aqueous feed phase is contacted with the organic extractant phase in the extraction module. The loaded organic phase then flows to the back-extraction module where it is contacted with the BEX agent. Thus the organic extractant phase flows in a closed cycle between the extraction and the back-extraction modules. Feed and back-extraction phases were operated in a batch mode.

Samples were taken out at different times from the aqueous reservoirs, and cadmium and nickel concentration were analysed after preparation. Both concentrations were measured on a Perkin-Elmer 1100 B Atomic Absorption Spectrophotometer.

Table 1
Hollow-fiber membrane module characteristics

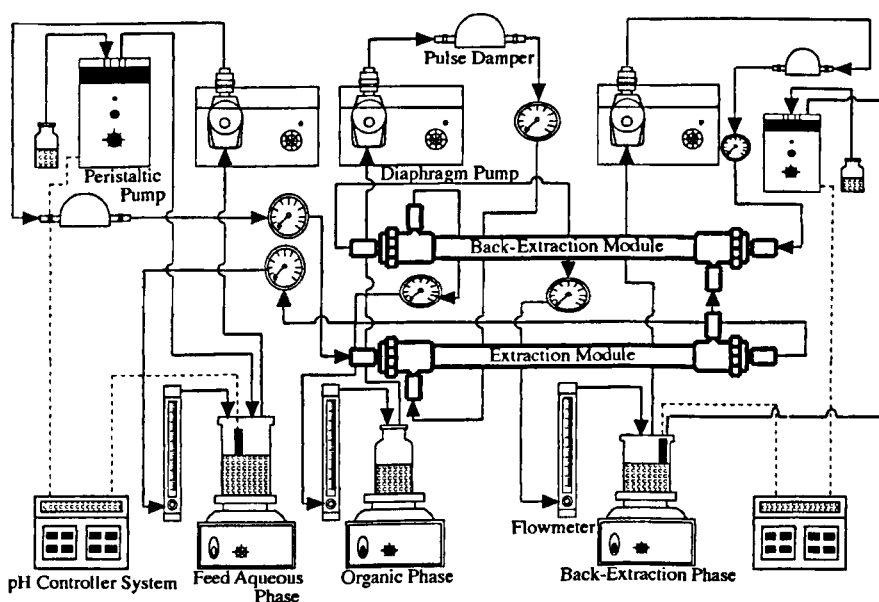| Characteristics of the modules	Values
fiber	X-10/polypropylene
internal diameter	240 μm
wall thickness	30 μm
number of fibers	2100
nominal porosity	30%
shell material	polypropylene
potting material	epoxy resin
shell inner diameter	25 mm
shell length	200 mm
effective mass-transfer length	160 mm
effective mass-transfer area	0.23 m²

Fig. 1. Set-up diagram of the simultaneous hollow fiber EX and BEX processes.

Table 2
Working conditions for the separation/recovery experiments of Ni–Cd mixtures

Set of experiments	Number of cycles	Initial/final Cd concentration in the feed aqueous phase (M)	Initial/final Ni concentration in the feed aqueous phase (M)	Initial/final Cd concentration in the BEX aqueous phase (M)	Initial/final Ni concentration in the BEX aqueous phase (M)	pH in the extraction solution
I	5	0.36/0.18	–	0.092/0.9	–	3.5
II	6	0.38/0.2	–	0/1.14	–	3.5
III	2	0.42/0.029	0.38/0.28	0/0.5	0/0.002	3.5
		0.36/0.035	0.355/0.31	0.5/1.09	0.002/0.02	
IV	1	0.37/0.043	0.36/0.34	0.5/1.59	0.02/0.03	2.5
V	1	0.38/0.039	0.67/0.57	1.59/1.95	0.03/0.057	2.5

3. Results and interpretation

3.1. Cadmium recovery

Being the aim of the work, the separation of Ni–Cd mixtures by extracting one of the metals and keeping the other in the feed aqueous phase, the first step presented in this paper is the study of the viability of the application of the NDSX technology to the separation–concentration of cadmium from aqueous solutions containing $CdSO_4$.

Kinetic experiments were conducted starting with concentrations of Cd(II) of 0.37 M in the feed solution, working with an organic mixture of D2EHPA (1.7 M), TBP (0.3 M), and kerosene and using H_2SO_4 (1 M) as the back-extraction agent. During the whole experiment the pH value of the aqueous phases remained constant: 3.5 in the extraction tank and 0.5 in the back-extraction tank; those pH values were selected to facilitate the separation of Cd–Ni mixtures [16]. Experimental conditions are shown in Tables 2 and 3. The experiments were run for 10 h (one cycle); at this moment a new batch with a fresh aqueous solution was replenished

Table 3
Volume of the aqueous and organic phase used in the set of experiments

Set of experiments	Number of cycles	Volume in feed aqueous phase (l)	Volume in organic phase (l)	Volume in stripping aqueous phase (l)
I	5	0.5	1	0.5
II	6	0.5	1	0.5
III	2	cycle one 0.5	1	0.5
		cycle two 0.6	1.2	0.3
IV	1	0.6	1.2	0.3
V	1	0.6	1.2	0.3

while keeping the same BEX solution. Two sets of experiments were carried out starting with different cadmium concentrations in the organic phase: 0.11 M in experiment I and 0.22 M for experiment II.

At defined time intervals, samples of the aqueous feed and back-extraction solutions were taken out and prepared for analysis of cadmium. The results of the evolution of the

dimensionless cadmium concentration with time in the feed and back-extraction tanks are shown in Figs. 2 and 3 for experiment I and in Figs. 4 and 5 for experiment II. Final concentrations of $CdSO_4$ found in the BEX solutions were higher than 0.9 M (100 g/l) for the first set of experiments and 1.14 M (128 g/l) for the second set. Therefore, the viability of the hollow fiber extraction process for the removal and concentration of Cd(II) using D2EHPA as organic extractant was confirmed. It is also important to remark that the Cd concentration courses in the extraction and back-extraction solutions are linear, indicating that the Cd flux remains constant along with the experiments.

Fig. 6 reports the evolution of the Cd concentration in the organic phase obtained as a mass balance between the extraction and back-extraction solutions for experiments I and II. It is noticed that in the experiment I the concentration of Cd increases with time from 0.13 M to 0.19 M, however during experiment II the concentration keeps constant around a value

Fig. 4. Experimental dimensionless Cd(II) concentration in the feed aqueous phase vs. time for experiment II. (●) Cycle 1, (○) Cycle 2, (■) Cycle 3, (□) Cycle 4, (▲) Cycle 5, (△) Cycle 6.
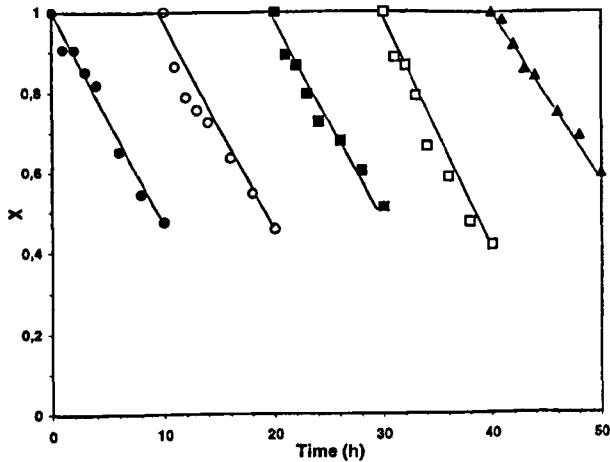

Fig. 2. Experimental dimensionless Cd(II) concentration in the feed aqueous phase vs. time for experiment I. (●) Cycle 1, (○) Cycle 2, (■) Cycle 3, (□) Cycle 4, (▲) Cycle 5.

Fig. 5. Experimental dimensionless Cd(II) concentration in the back-extraction aqueous phase vs. time for the experiment II. (●) Cycle 1, (■) Cycle 2, (○) Cycle 3, (□) Cycle 4, (▲) Cycle 5, (△) Cycle 6.
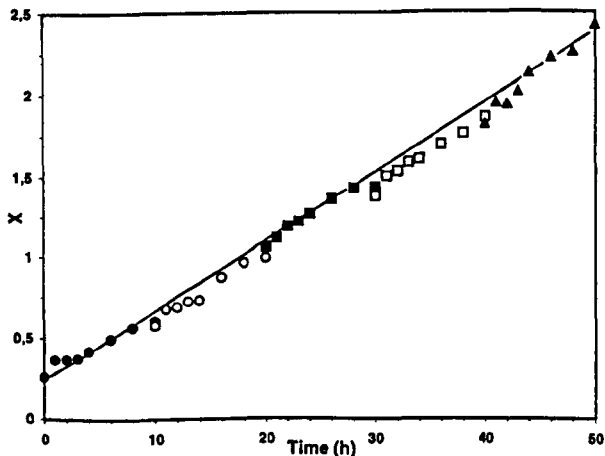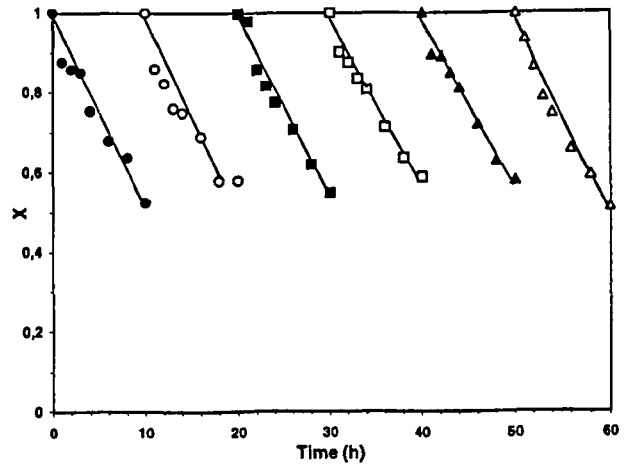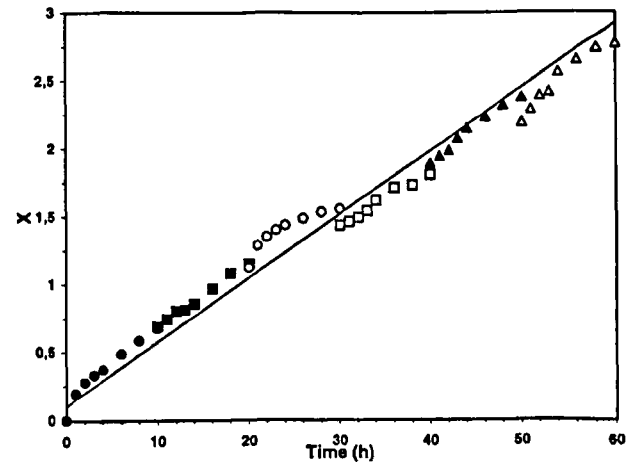

Fig. 3. Experimental dimensionless Cd(II) concentration in the back-extraction aqueous phase vs. time for experiment I. (●) Cycle 1, (○) Cycle 2, (■) Cycle 3, (□) Cycle 4, (▲) Cycle 5.
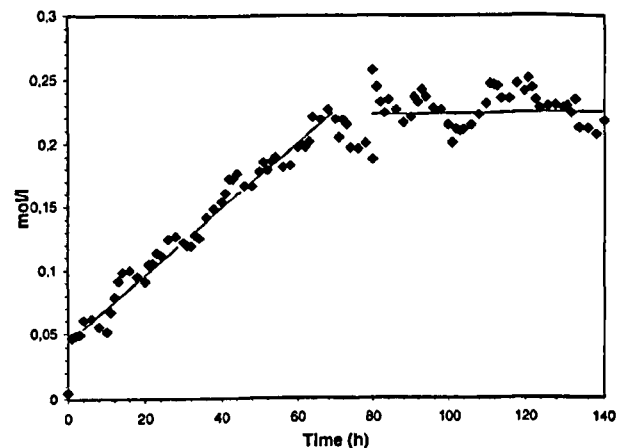

Fig. 6. Experimental Cd(II) concentration in the organic phase for experiments I and II.

of 0.22 M. This behaviour is explained by the fact that in experiment I the flux is higher in the extraction process than in the back-extraction process, (1.17E-5 mol/m² s in the extraction and 8.5E-6 mol/m² s in the BEX), whereas in the experiment II, the fluxes are similar: 0.97E-5 mol/m² s in the extraction and 1.0E-5 mol/m² s in the back-extraction.

After the analysis of the viability of the separation and concentration of Cd, the following experiments were directed towards the analysis of the separation of two components (Cd–Ni) present in a mixture by means of non-dispersive solvent extraction. Considering that Ni can also be extracted by D2EHPA, the extraction and back-extraction of the two solutes cannot be considered independently since both are coupled through the organic phase.

3.2. Separation of Cd–Ni mixtures

Several experiments were done in order to study the separation of Ni–Cd mixtures; Table 2 shows the experimental conditions. All the kinetic experiments were conducted starting with concentrations of Cd(II) around 0.36 M (40 g/l) in the feed solutions and working with an organic mixture of 60% (v/v) D2EHPA, 10% TBP (v/v) and kerosene. The organic phase was used previously in the individual experiments of Cd separation–concentration, so that the initial concentration of cadmium in the organic solution was 0.22 M. The separation experiments were run until the concentration of Cd in the feed solution dropped below 0.04 M (one cycle); at this moment a new batch with a fresh solution was replenished, and a second cycle with the same conditions was performed as it is referred in Table 2.

The kinetic results of experiment III are presented in Figs. 7 and 8 for the extraction and the back-extraction, respectively. First, it is important to observe that after 30 h 90% of cadmium was extracted whereas 20% of nickel had been *coextracted*. In the back-extraction phase, the separation of both metals is even higher since the concentration of cadmium after 60 h is about 1.1 M while the concentration of Ni is only about 0.02 M, since the working conditions (0.22 M of Cd in the organic solution) favour considerably the back-extraction process of Cd. It is also observed that the presence of Ni in the aqueous phase influences the Cd extraction when compared to the experiments performed with CdSO₄ solutions since the extraction flux decreases down to 1.5E-6 mol/m² s, which represents a decrease of more than 10 times.

In order to study the influence of the pH value a new experiment (IV) was carried out working with a feed solution with lower pH. Fig. 9, where the evolution of the concentration-time data at different pH values is plotted, shows the influence of the latter variable value on the extraction rates of Ni and Cd. It is noticed that the extraction of both metals decreases when the pH decreases and therefore the Cd flux also decreases down to 9.0E-7 mol/m² s. It is also observed that the final concentration of Ni in the feed aqueous phase is reduced to 5% of the initial value.

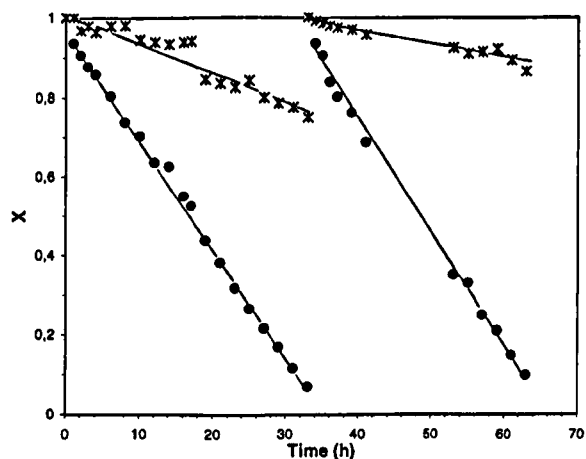Fig. 7. Experimental dimensionless Cd(II) and Ni(II) concentrations in the EX aqueous phase vs. time for experiment III. (●) Cadmium, (*) Nickel.
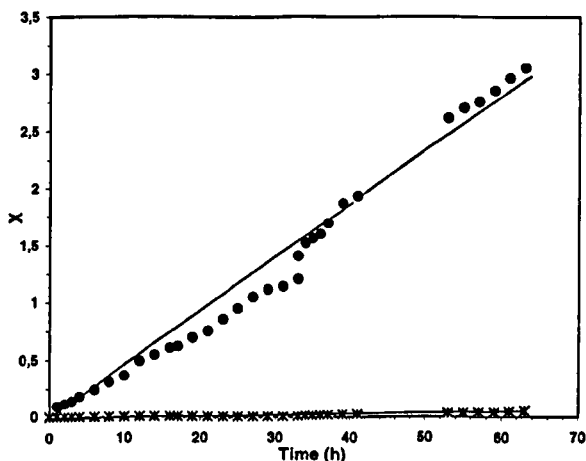

Fig. 8. Experimental dimensionless Cd(II) and Ni(II) concentrations in the BEX aqueous phase vs. time for experiment III. (●) Cadmium, (*) Nickel.
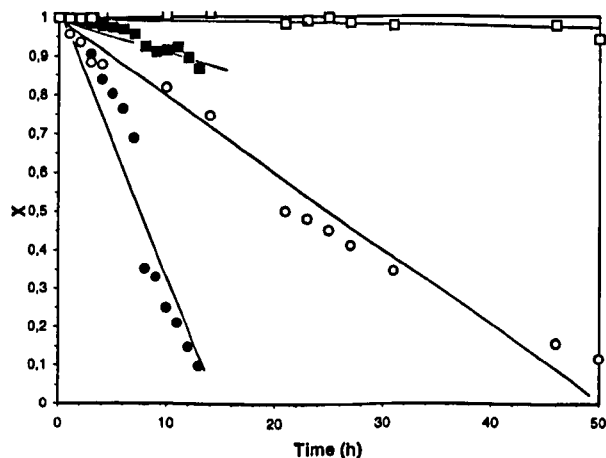

Fig. 9. Experimental dimensionless Cd(II) and Ni(II) concentrations in the EX aqueous phase vs. time for experiment III and experiment IV. (●) Cadmium pH = 3.5, (○) Cadmium pH = 2.5, (■) Nickel pH = 3.5, (□) Nickel pH = 2.5.

Once the separation of Cd was confirmed at pH = 2.5, the viability of the process was also checked working under more adverse conditions, i.e., by increasing the Ni initial concentration in the feed aqueous phase to 0.68 M (experiment V). Similar results were obtained under these conditions. Fig. 10 plots the results of the concentration of Ni and Cd vs. time in the BEX solution corresponding to experiments III, IV and V.

These results indicate that after the last experiment, the purity of the Cd and Ni products were 98.5% and 93.5%, respectively. In a batch counter-current process working under the initial conditions: 0.04 M of Cd and 0.4 M of Ni as sulfate solutions, Preston et al. [15] obtained 97% and 99.1% of Cd and Ni purity, respectively, in the final solutions after three stages.

3.3. Separation selectivity

The results obtained in this work led to the analysis of the selectivity of the separation process of Cd–Ni mixtures. In a batch process the separation selectivity is defined as the ratio of the differential concentration of Cd divided by the differential concentration of nickel and, thus equal to the ratio of the separation rates of both metals. The following equation expresses mathematically this concept.

$$\rho(t) = \frac{dC_{Cd}/dt}{dC_{Ni}/dt} \qquad (2)$$

The integration of Eq. (2) over the whole operation time of the experiments would lead to the global selectivity that can be defined both for the extraction tank and for the back-extraction tank as,
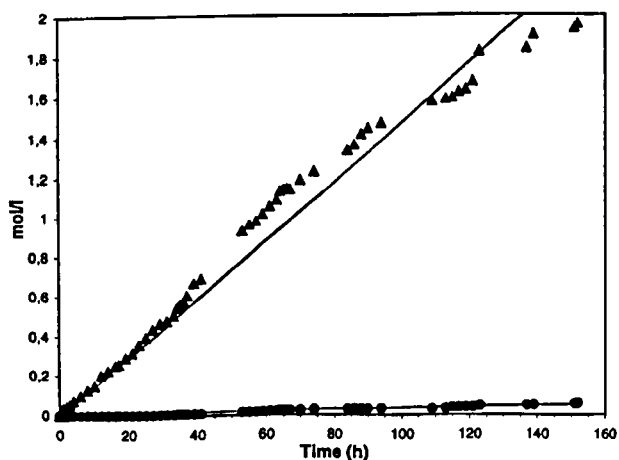
$$\phi = \int_{0}^{t} \rho(t)dt. \qquad (3)$$

Fig. 10. Experimental dimensionless Cd(II) and Ni(II) concentrations in the BEX aqueous phase vs. time for experiments III, IV and V. (▲) Cadmium, (●) Nickel.

Under the experimental conditions used in this work, and taking into account that the evolution of Ni and Cd concentration in the stirred tank took place with constant rates for the BEX process (see Fig. 10), Eq. (2) was transformed into:

$$\rho = \frac{\Delta C_{Cd}}{\Delta C_{Ni}} \qquad (4)$$

Using Eq. (4) the selectivity factor for experiments III, IV and V has been calculated by obtaining a constant selectivity value equal to 67 mol of Cd/mol of Ni referred to the BEX stirred tank, i.e., during the whole experiment 67 mol of Cd have appeared in the BEX tank per mol of Ni.

4. Conclusions

In this paper, the viability of the application of the non-dispersive solvent extraction technology to the separation of nickel and cadmium from highly concentrated solutions has been checked using D2EHPA as organic extractant working in a batch mode, and carrying out the extraction and back-extraction processes simultaneously.

Working under the experimental conditions previously reported by the authors [16], the kinetics of the separation of Cd (0.37 M) from aqueous solutions with D2EHPA as selective extractant was studied initially. Using an organic phase loaded with 0.22 M of Cd, the extraction and back-extraction rates of Cd are equal, and therefore no accumulation of Cd in the organic phase occurred.

Working with mixtures of both metals in the feed aqueous phase, Cd 0.4 M and Ni 0.37–0.67 M; 1 M of H_2SO_4 in the BEX phase, and using D2EHPA as extractant, the viability of the separation of Cd by NDSX has also been checked. Under the experimental conditions a batch process with a constant mass transport flux was developed. The analysis of the separation selectivity under the studied conditions led to a constant value equal to 67 mol Cd/mol Ni in the BEX solution.

Therefore, in this work it has been shown that the NDSX technology can be applied to the separation of highly concentrated mixtures of Cd and Ni, simulating the conditions that can be found in a leaching step of shredded nickel-cadmium batteries, and defining a process with a constant separation selectivity.

Acknowledgements

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