BACK-EXTRACTION OF Ni-Cd FROM HIGHLY LOADED ORGANIC PHASES.

EQUILIBRIUM MODELING.

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INTRODUCTION

Definition of the mixtures

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 economic and environmental benefits. The latter are specially important considering the toxicity of the metals present in the batteries.

Hydrometallurgical processes for the recovery of Ni-Cd 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 viability of the separation of nickel and cadmium from highly concentrated solutions by means of non-dispersive solvent extraction (NDSX) has been studied in a previous work where the pH of the aqueous solution and the metallic concentration where shown to be the most important variables in the separation process (1).

Technology description

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. To achieve this type of contact a differential static pressure has to be applied in one of the phases. In the actual practice NDSX processes include two different steps, the first one where the extraction of the selected compounds is achieved by means of a suitable extractant and a second step where the extracted compounds go to a back-extraction (BEX), phase and at the same time the organic phase regeneration takes place.

Objectives of the work

D2EHPA has been shown in the literature to be a good extractant for Cd and Ni (1, 2). The complexity of the description of the extraction behaviour of phosphorus compounds has been also widely mentioned (3). The reaction between the metal and the organic carrier is an ion exchange

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reaction; different values of stoichiometric coefficient of the extractant have been reported in the literature: 2 and 2.5 for Cd and 2, 2.5 and 3 for Ni (4, 5).

In previous papers the viability of the application of the non-dispersive solvent extraction technology to the separation of nickel and cadmium from highly concentrated solutions (2) and the kinetics and modelling of the non-dispersive extraction and back-extraction of Cd from high concentration aqueous solutions and using D2EHPA as selective extractant has been reported. (4)

In the present work the back-extraction process of highly loaded organic phase with Cd and Ni is studied making a proposal the mechanism of the liquid-liquid chemical reaction equilibrium. The results of this study present high interest in the modelling of the whole process of extraction and back-extraction of the metals.

EXPERIMENTAL SET-UP AND PLANNING

Although this work is focused on the BEX process analysis, the experimental results were obtained from whole separation runs incorporating both the extraction and back-extraction steps.

All the experiments have been performed using as organic phase a mixture of 1.7 M of di(2-ethylhexyl) phosphoric acid called D2EHPA, and kerosene as solvent. A third component: tributylphosphate 0.3 M was added to avoid the segregation of a second organic phase. The feed aqueous solutions were prepared with $CdSO_4$ 8/3 H_2O and $NiSO_4$ $6H_2O$ and the stripping phase was a solution of H_2SO_4 (1M). The experimental set-up is fully described in previous works (2,4).

Adjustment of pH was carried out during the whole experiment in the feed and back-extraction aqueous solution (BEX) in order to work with pH=3.5 and pH=0.5 in the feed aqueous phase and in the back-extraction phase respectively. Those pH values were selected to facilitate the separation of Cd-Ni mixtures (3).

The initial concentrations of each metal in the aqueous, organic and back-extraction solutions are shown in Table 1. In order to load the organic phase to the concentration values shown in Table 1 the following procedure was carried out: the feed aqueous phase containing 0.2 M of Cd was contacted with 1.7 M D2EHPA for 20 hours until the concentration of Cd in the organic phase is about 0.2 M. Then the aqueous phase is changed to an aqueous phase containing 0.2 M of Ni but the organic phase keeps the same solution. This second part of the experiment runs for 20 hours. In those two steps the back-extraction part of the experimental system was not working.

Table 1: Experimental conditions

	Cd Ext. (M)	Cd Org. (M)	Cd Back-ext. (M)	Ni Ext. (M)	Ni Org. (M)	Ni Back-ext. (M)
EXP. 1	0.2	0.2	0.2	0.2	0.2	0
EXP. 2	0.2	0.2	0.2	0.2	0.2	0.2

Once the organic phase is loaded with Cd and Ni, the feed aqueous phase is renewed with a solution containing 0.2 M of Cd and Ni as shown in the upper table and the process of simultaneous extraction and back-extraction works it is 2 hours.

KINETIC RESULTS

Figures 1 and 2 show the kinetics of the extraction and back-extraction process when the Cd and Ni initial concentration are 0.2 M in all the solutions involved in the process. It is observed in Figure 1 that the concentration of Cd decreases with time whereas the Ni concentration keeps the initial value due to the pH value of the feed (pH=3.5). In Figure 2 it is observed that the concentration of both metals in the back-extraction solution increases with time until a value about 0.3M. It is also important to notice that the evolution in the BEX solution of Cd and Ni is similar.

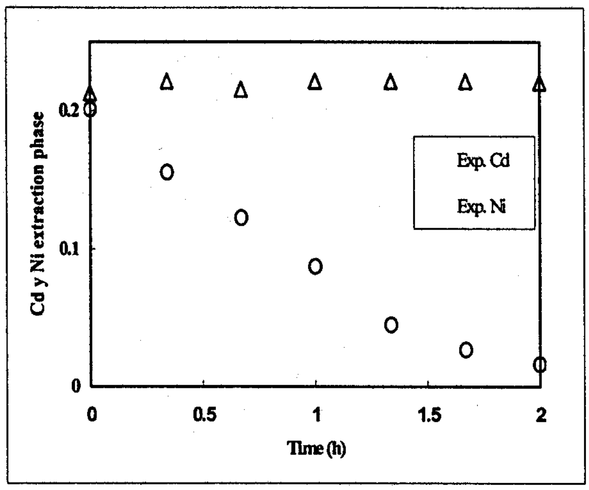

Figure 1:Evolution of Cd and Ni concentration in the extraction tank corresponding to experiment 2.

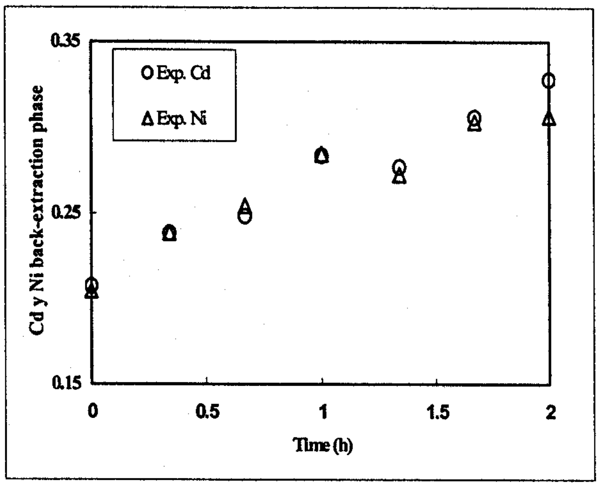

Figure 2:Evolution of Cd and Ni concentration in the back-extr. tank corresponding to experiment 2.

EQUILIBRIUM MODELLING IN THE BEX PROCESS

In a previous work (2) it was reported the mathematical model of Cd recovery by a NDSX process Considering that the membrane mass transfer governed the kinetic control the proposed kinetic model consisted of a system of partial differential and algebraic equations describing the mass balances of Cd in the fluid phases of the hollow fiber contactors and homogenisation tanks. The design parameters, Km, membrane mass transport coefficient, and Ke, equilibrium parameter of the extraction and back-extraction reaction of Cd (Eq. 1 and 2) were calculated from the correlation of the experimental results to the simulated results with the reported models:

$$\text{Extraction:} \quad Cd^{+2} + 2\overline{(HX)_2} \Leftrightarrow \overline{CdX_2(HX)_2} + 2H^{+} \tag{1}$$

$$\text{Back- Extraction:} \quad \overline{CdX_2(HX)_2} \Leftrightarrow Cd^{+2} + \overline{2(HX)_2} \tag{2}$$

$$K_{Ext(Cd)}=1.82E\text{-}5$$

$$K_m=1.57e\text{-}7 m/s$$

Working with mixtures of Cd and Ni the extraction of the latter metal has been avoided working at a pH lower or equal to 3.5 in the feed phase, however initially loaded organic phases with Ni led to the back-extraction of this metal. Thus, it is necessary to be able to describe the BEX reaction of Ni. Starting from the stoichiometric equations reported in the literature (5), in this work it has been performed a discrimination of the equilibrium model as well as the optimization of the corresponding equilibrium parameter following the same procedure previously developed for the kinetic modelling of the Cd recovery process (4). Table 2 gives a summary of the stochiometric expressions proposed to describe the BEX reactions of Cd and Ni.

Table 2: Stoichiometric equations of the back-extraction of Ni^{+2} and Cd^{+2}.

Model number	Back-extraction stoichiometric	
I	$\overline{CdX_2(HX)_2} \Leftrightarrow Cd^{+2} + \overline{2(HX)_2}$	Eq. 1 (5)
	$\overline{NiX_2(HX)_3} \Leftrightarrow Ni^{+2} + \overline{2.5(HX)_2}$	Eq. 2 (5)
II	$\overline{CdX_2NiX_2(HX)} \Leftrightarrow Cd^{+2} + \overline{NiX_2(HX)_3}$	Eq. 3
	$\overline{NiX_2(HX)_3} \Leftrightarrow Ni^{+2} + \overline{2.5(HX)_2}$	Eq. 4
III	$\overline{CdX_2NiX_2} \Leftrightarrow Cd^{+2} + \overline{NiX_2(HX)_2}$	Eq. 5
	$\overline{CdX_2NiX_2} \Leftrightarrow Ni^{+2} + \overline{CdX_2(HX)_2}$	Eq. 6
	$\overline{CdX_2(HX)_2} \Leftrightarrow Cd^{+2} + \overline{2(HX)_2}$	Eq. 7
IV	$\overline{CdX_2NiX_2} \Leftrightarrow Cd^{+2} + Ni^{+2} + \overline{2(HX)_2}$	Eq. 8
	$\overline{CdX_2(HX)_2} \Leftrightarrow Cd^{+2} + \overline{2(HX)_2}$	Eq. 1
V	$\overline{CdX_2NiX_2} \Leftrightarrow Cd^{+2} + Ni^{+2} + \overline{2(HX)_2}$	Eq. 9

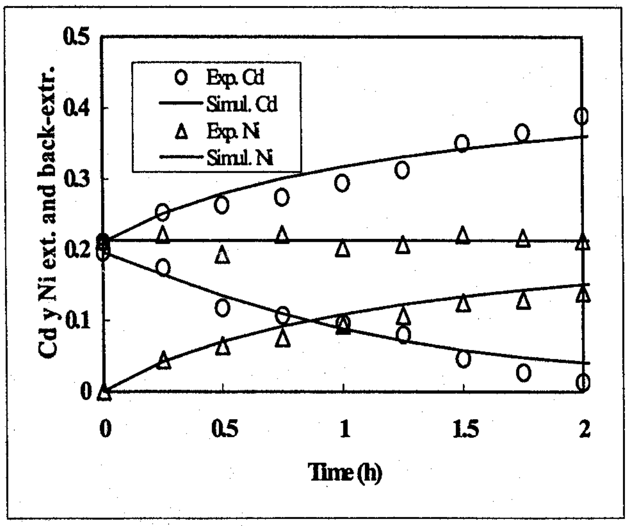

Figure 1: Simulated and experimental concentrations of Cd and Ni for the experiment 1.

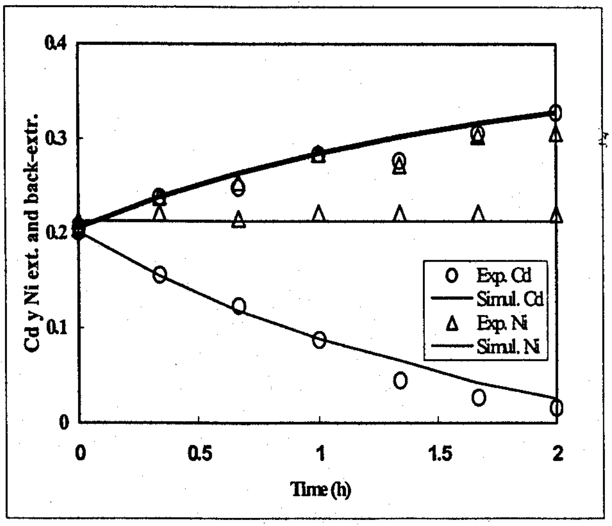

Figure 2: Simulated and experiment concentrations of Cd and Ni for the experiment 2.

Figures 3 and 4 show the comparison of the experimental and simulated results when equation (9) was used in the mathematical modelling. A good fitting of the experimental results is observed, thus checking the validity of the reported model.

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