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## **LABORATORY SIMULATION OF NICKEL(II) AND COBALT(II) ION SEPARATION IN A CONTINUOUS COUNTER-CURRENT EXTRACTOR**

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In the paper studies were presented related to application of CYANEX 272 (di(2,4,4-trimethylpentyl)phosphine acid) extractant in the extractive separation of nickel(II) and cobalt(II) ions originating from a sulphate solution. Values of  $pH_{0.5}$  amounted to 4.6 and 5.7 for cobalt(II) and nickel(II) ions, respectively, which permitted selective separation of the ions. Simulation of the three-stage extraction process, performed in laboratory conditions, permitted to conclude that such a process allows for a selective separation of cobalt(II) and nickel(II) ions although it requires appropriate modification only when pH of the aqueous phase is controlled.

*Key words: ions separation, extraction, counter-current extractor, simulation*

### INTRODUCTION

Various industrial processes water streams contain nickel(II) and cobalt(II) ions at relatively low concentrations. One of the ways in which they are processed involves application of extraction techniques, aimed at their selective separation and isolation. In a counter-current apparatus, such a process can be conducted in a continuous way and such procedure as waste utilization is advantageous since it allows to adjust size of the installation to current needs of the producer.

Literature contains several examples of equilibrium studies on extractive separation of nickel(II) and cobalt(II) using phosphoorganic extractants such as di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethyl-pentyl)-phosphinic acid (CYANEX 272) and its sulphuric derivatives, di(2,4,4-trimethylpentyl)dithio-

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phosphinic acid (CYANEX 301) and di(2,4,4-trimethylpentyl)thiofosfinic acid (CYANEX 302) (Fu and Golding, 1987; Komasa et al., 1981, 1983, 1984; Gajda and Apostoluk, 2000, 2002; Reddy et al., 2005; Devi et al., 1998). All the above mentioned extractants of the CYANEX series may be used to extraction of both Co(II) and Ni(II) ions but selectivity of separation of the ions decreases in the following order: Cyanex 302 > Cyanex 272 >> Cyanex 30 (Sole and Hiskey, 1992).

Most of presented studies involve equilibrium studies. Their results point to the potential of separation of nickel(II) and cobalt(II) ions at a single stage of extraction. Such results are of high importance in basic studies but manifest restricted applicability in designing multi-step processes running in a continuous manner. In the latter case not only the efficiency of individual extraction stage of 85-95% is important but also progression of several side reactions which may decrease extracting ability of the extractant.

Present study aimed at examining the potential for separation of nickel(II) and cobalt(II) ions in a three-stage counter-current extractor operating in a continuous manner.

## EXPERIMENTAL

The raw material involved a sulphate solution containing 0.01 and 0.015 mol/dm<sup>3</sup> of nickel(II) and cobalt(II), respectively. Adding appropriate amounts of sodium sulphate, ionic strength of the original solution was adjusted to 0.10 M. The preliminary pH in the starting solution of 8.00 was obtained adding appropriate amounts of 1 M NaOH solution. The reagents were obtained from POCh (Poland). CYANEX 272 (CYTEC, Canada), containing 85 % di(2,4,4-trimethyl)phosphinic acid was used as the extractant. The organic phase was obtained dissolving 0.02 M of the extractant in a kerosene of 0.85 g/dm<sup>3</sup> in density (ALDRICH). Flasks, each containing 40 cm<sup>3</sup> of aqueous and organic phases, were mechanically agitated at constant temperature of 25±1°C for 15 min. After separation of the phases, metal ion concentrations were estimated in the aqueous phase using AAS Solar 939 spectrophotometer (Unicam). pH of the equilibrium was estimated in the aqueous phase using a combined electrode (type ERH-136, Hydromet) coupled to a pH-meter (CX-731, Elmetron). Concentration of metal ions in the organic phase was calculated from the mass balance.

The multi-step, counter-current extraction was performed in a cascade of apparatuses of a mixer/settler type. Scheme of such a process is shown in Figure 1. The essence of the system involves counter-current type of contact between the aqueous and the organic phases, which assures the maximum loading of the organic phase. The reaction of metal ion transfer from the aqueous to the organic phase was accompanied by increase in acidity of the aqueous phase, in line with the following reaction:



Such a course of the reaction denoted an increasing acid concentration in the aqueous phase after every step of the extraction. Since the extraction process was strongly influenced by acidity of the raw solution the amounts of metal ions transferred at sequential stages of the extraction should be expected to decrease.

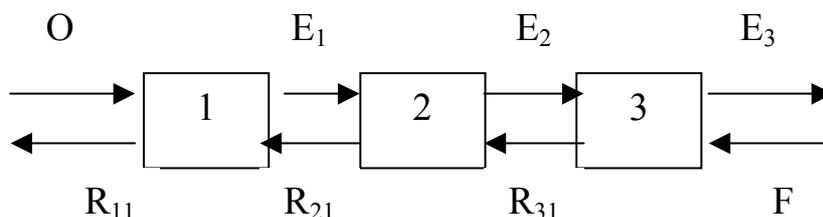


Fig. 1. Scheme of three-step counter-current extraction.  $O$  – supplied organic phase;  $F$  – supplied aqueous phase;  $R_i, E_i, i=1,2,3$  – the consecutively obtained raffinates and extracts following the first, second and third steps of extraction

In laboratory simulation of the multi-step counter-current extraction was conducted in vessels (flasks or separators) subjected to multifold, consecutive mixing and phase separation (Figure 2). As the result of the extraction, the raffinates were obtained (denoted in the scheme as  $R_1^I, R_1^{II}, \dots, R_1^{VI}$ ), and extracts ( $E_3^I, E_3^{II}, \dots, E_3^{VI}$ ). The superscripts indicate consecutive approximations of the final raffinate and extract concentrations following the first, second and third step of extraction (subscript). The process was conducted until properties of the consecutively obtained  $E$  and  $R$  products stabilized. The scheme of the extraction corresponded to a three-step counter-current extraction performed in a continuous manner, presented in Figure 1. It was assumed that equilibrium was reached at individual steps of the extraction.

The principles of the procedure were as follows (Fig. 2): the measured volume of the raw solution  $F$  (aqueous phase containing  $0.01 \text{ mol/dm}^3$  of Ni(II) and  $0.015 \text{ mol/dm}^3$  Co(II) ions, of  $\text{pH} = 8.00$ ) was mixed at the step  $3^I$  with appropriate volume of the organic phase  $O$  (extractant,  $0.02 \text{ mol/dm}^3$  solution of CYANEX 272 in kerosene). After settling, the organic phase,  $E_3^I$  extract, and the aqueous phase,  $R_3^I$  raffinate were separated from each other. The raffinate phase was transferred to step  $2^I$  and mixed with a new dose of the fresh extractant,  $O$ . The obtained extraction phase,  $E_2^I$ , was mixed at the step  $3^{II}$  with a new dose of the raw solution  $F$ , and the  $R_2^I$  raffinate with a new dose of the extractant  $O$  at the step  $1^I$ , etc. Termination of the extraction process was signified by absence of changes in the composition of  $R_1^I, R_1^{II}, \dots, R_1^{VI}$  raffinates.

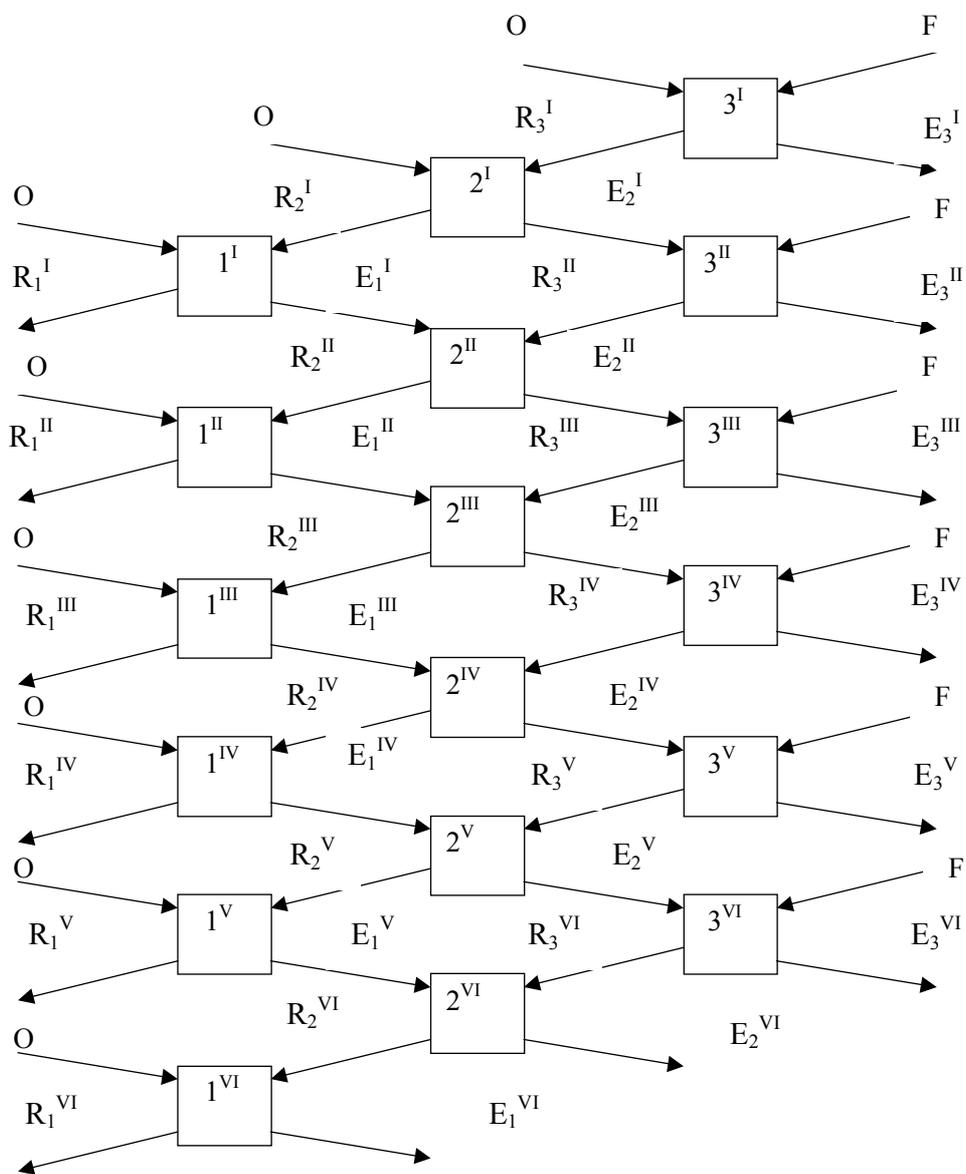


Fig. 2. Scheme of three-step counter-current extraction under laboratory conditions. Six steps of the extraction were assumed.  $O$ : the supplied organic phase,  $F$ : the supplied aqueous phase,  $R$ : raffinate,  $E$ : extract. Superscripts correspond to consecutive approximations of the extraction system. Subscripts correspond to numbers of steps in the extractor battery

## DISCUSSION

Preliminary experiments showed that the extraction equilibrium was reached after 5 min of contact of the phases. Separation of phases was complete. In order to define conditions under which the extraction process of separating nickel(II) from cobalt(II) ions should be conducted, equilibrium experiments were performed. The relationships between  $\log D$  and pH for nickel(II) and cobalt(II) ions are shown in Figure 3. The arrangement of lines in the figure was influenced by conditions in which the extraction process was conducted, i.e. by concentration of reagents both in the aqueous and in the organic phases and by the type of solvent. Cobalt(II) ions could be noted to be extracted better than nickel(II) ions. This was indicated by the difference in values of  $\text{pH}_{0.5}$ , which amounted to 4.6 and 5.7 for cobalt(II) and nickel(II) ions, respectively. This pointed to the potential of separating the two metal cations in the extraction process. However, separation of the studied ions should be strongly dependent upon pH of the raw solution. It should be expected that the lower is pH, the less pronounced will be the separation. Therefore, in the studies on the counter-current extraction process pH of the raw solution was set at 8.

Taking advantage of the preliminary results from extraction studies, the McCabe – Thiele graph was drawn (Fig. 7 and 8). This provided grounds for the conclusion that two extraction steps should be sufficient for separation of the studied metal ions. However, taking into account a lowered efficiency of extraction steps in further studies a three-step counter-current extraction was employed.

Changes in pH and metal ions concentrations in the organic phase,  $E_1^I, E_1^{II}, \dots, E_1^{VI}$  at individual steps of the simulation are shown in Figs. 4 and 5. As can be noted, already at the step 4 of the simulation pH of the aqueous phase approximated the value of 4 and did not practically change in the subsequent steps. Similarly, concentrations of cobalt(II) and nickel(II) ions in the organic phase asymptotically approached the values of, respectively, 250 and 100 mg/dm<sup>3</sup>. The values were reached already in the 4<sup>th</sup> step of the simulation. This demonstrated that the counter-current extraction process reached a stable condition. Alterations in the separation coefficient in the course of the extraction process are shown in Fig. 6. The separation coefficient stabilized at the level of approximately 5 already at the second step of the extraction.

In the presented here counter-current extraction process of separating nickel(II) from cobalt(II) ions a relatively good coefficient of ion separation was obtained. Nevertheless, the transfer of cobalt(II) ions to the organic phase was accompanied by transfer of small amounts of nickel(II) ions. This was related to the relatively pronounced drop in pH of the aqueous phase, to the level of around 4.0, following consecutive steps of the extraction. Such a result pointed to the need of controlling pH following every step of the extraction.

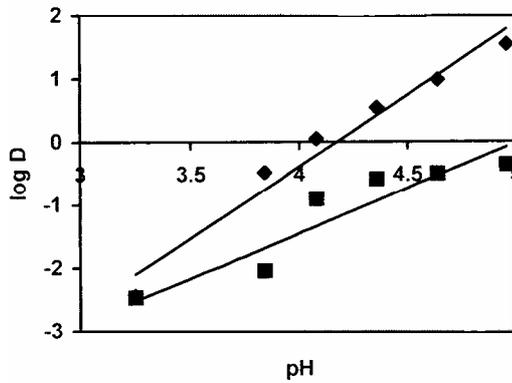


Fig. 3. Cobalt(II) (◆) and nickel(II) (■) separation coefficient between the aqueous and organic phases. Original concentrations of Ni(II) and Co (II): 0.01 mol/L

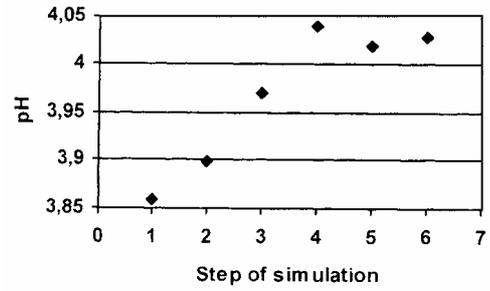


Fig. 4. Change in raffinate pH after third step of the extraction at individual steps of the simulation.

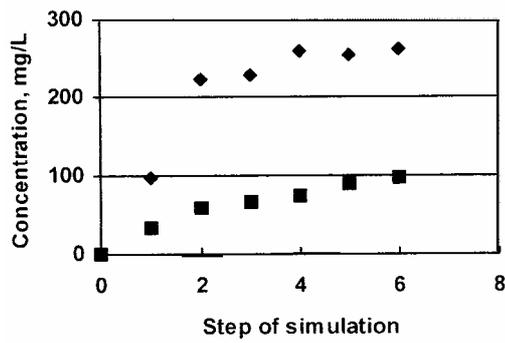


Fig. 5. Changes in concentration of Co(II) (◆) and Ni(II) (■) in the extract after third step of extraction

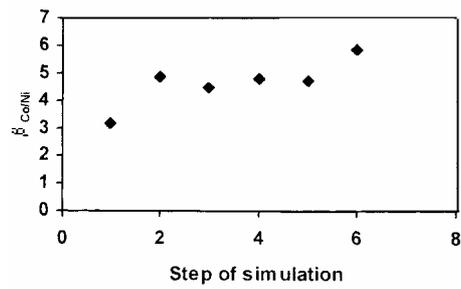


Fig. 6. Separation coefficient  $\beta_{Co/Ni}$  for nickel(II) and cobalt(II) ions

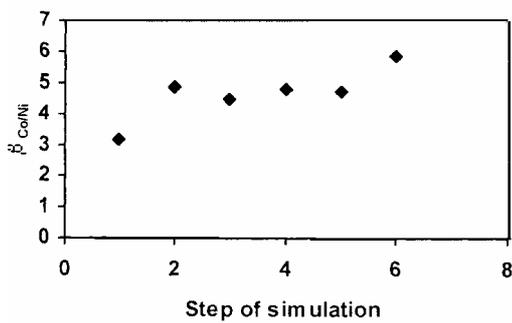


Fig. 7. McCabe – Thiel graph. Nickel(II) extraction

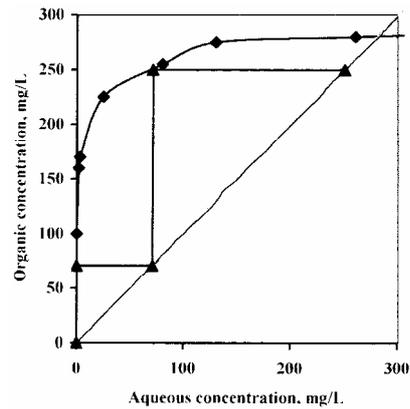


Fig. 8. McCabe – Thiel graph. Cobalt(II) extraction

## CONCLUSIONS

Laboratory simulation of the counter-current extraction process points to the potential of using CYANEX 272 extractant for selective separation of cobalt(II) ions in presence of nickel(II) ions from sulphate solutions in the counter-current extraction process. The obtained results indicate the need for pH control following every step of the extraction and for setting it at such a level which prevents against the parallel transfer of nickel(II) ions. The performed studies on the counter-current extraction process on a laboratory scale allow to draw significant technological conclusions related to the way in which the process should be conducted.

## ACKNOWLEDGEMENTS

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W pracy przedstawiono badania związane z zastosowaniem ekstrahenta CYANEX 272 (kwas di(2,4,4-trimetylopentylo)fosfinowy) do ekstrakcyjnego rozdzielania jonów niklu(II) i kobaltu(II) z roztworu siarczanowego. Stwierdzono, że wartości  $pH_{0.5}$  wynoszą 4.6 i 5.7 odpowiednio dla jonów kobaltu(II) i niklu(II), co pozwala na selektywny rozdział tych jonów. Przeprowadzona symulacja w warunkach laboratoryjnych przeciwnieprądowego trzystopniowego procesu ekstrakcyjnego pozwala stwierdzić, że w procesie takim możliwe jest selektywne rozdzielanie jonów kobaltu(II) od jonów niklu(II) jedynie w przypadku kontroli pH fazy wodnej.