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Studies on a Three-Phase Extraction Nickel in the Systems with Cyanex 301

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Abstract

Phase formation was studied for the systems of Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid)–organic solvent (toluene, heptane, octane)–sodium hydroxide–water–trioctylamine. It is demonstrated that the Cyanex 301 transition into a salt form (three-phase extraction) results in achieving the separation of the organic extraction agent solution into the solvent phase and a cation-exchange extraction agent. The sodium salt of Cyanex 301 is almost completely transformed into a new aqueous micellar solution. Conditions have been determined for the efficient separation of the organic phase components and for the isolation concentrated Cyanex 301. An effect of trioctylamine additives exerted on nickel extraction in the systems with Cyanex 301 was studied. A scheme has been proposed for the extraction of nickel using a three-phase extraction, wherein nickel is extracted by means of the concentrated solution of Cyanex 301 from acidic solutions resulted from leaching the ore, the extract is mixed with an organic amine solution to be re-extracted with sulphuric acid, whereas the organic phase is separated into initial components via treatment by sodium hydroxide solutions.

Key words: Cyanex 301, nickel, three-phase extraction, binary extraction, concentrating the extraction agent

INTRODUCTION

In order to process the technological solutions of acidic leaching the ores and concentrates one widely uses metal extraction by organic acids or their salts. However, the recovery of metals from the solutions with high acidity involves, as a rule, the use of concentrated cation-exchange extraction agents, which makes the re-extraction of metals extremely difficult and impossible for concentrated re-extracts. An example of such a problem could be presented by the extraction of nickel and cobalt from the solutions of sulphuric acid leaching the laterite nickel ores. In order to solve the problem it was proposed to use cation-exchange nickel extraction by means of Cyanex 301, bis(2,4,4-trimethyl)dithiophosphinic acid (Goro process) [1, 2]. Nickel re-extraction is carried out using concentrated hydrochloric acid solutions (about 6 mol/L), which complicates to a significant extent the further flow sheet for producing metallic nickel. This process is applied to recovery the metal using a cation-exchange technique, when at the extraction stage the extraction reaction equilibrium

$$Ni^{2+}(aq) + 2HA(org) = 2H^{+}(aq) + NiA_2(org) \qquad (1)$$

is shifted to the right due to a low acid concentration, whereas at the re-extraction stage the equilibrium is shifted to the left caused by increasing the acid concentration. In the eq. (1) indices (aq) and (org) indicate belonging the component under consideration to the aqueous phase or the organic phase, respectively.

The process control at the stages of metal extraction and re-extraction in this case is performed *via* simply changing the composition of the aqueous solutions (pH). The analysis of continuous extraction re-extraction processes demonstrates that a better solving of the problem of this kind involves changing the composition of the organic phase in order to control the process, for example, using a concentrated solution of organic acid in the course of metal extraction, and a diluted organic phase at the re-extraction stage. To change the composition of the organic phase one could perform via transferring the cation-exchange component into any form slightly soluble in an organic diluent.

The formation of the third phase can be often observed in the course of a liquid extraction procedure, which could be caused not only by a low solubility of extraction products in an organic solvent, but also by the formation of a stable aqueous organic micellar solution, as it is, for example, in the case of alkali metal salts of organic acids. The formation of a third phase in the course of solvent extraction is well known. This phenomenon has always been considered undesirable to complicate the process (phase delamination problems and of mass transfer complications in extractors). Now, more and more researchers' attention is paid to the use of three-phase extraction (TPE) for purifying the extraction agents, making ultrafine powders, as well as in analytical chemistry [3–5].

The potentiality of separating the organic phase into the constituent components thereof (extraction agent phase and diluents phase) allows one to develop fundamentally novel continuous processes for the extraction of metals from strongly acidic solutions with obtaining concentrated products. The efficiency of the extracting and concentrating processes could be increased not only *via* changing the concentration of a cation-exchange extraction agent in the organic phase at different stages of continuous process, but also *via* changing the type of extraction process, when at the extraction stage a cation-exchange extraction agent is used, whereas the re-extraction stage involves a binary extracting agent. At a final stage the organic solution of the binary extraction agent (organic acid salt and an amine in a diluent) is separated again using a three-phase extraction *via* the organic phase treatment by aqueous sodium hydroxide.

In this work we demonstrated the possibility to separate organic solutions based on bis (2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), and an organic diluent (toluene, octane), as well as more complex systems with trioctylamine additives, into the initial components in the course of TPE and to use this phenomenon for qualitative and quantitative changing the composition of the organic phase within a continuous extraction process of cation-exchange metal extraction from acidic solutions.

EXPERIMENTAL

For the experiments we used high-purity (kh. ch.) grade and special purity (os. ch.) grade mineral acids, salts and alkali. As the components of the organic phase we used high-purity grade octane, toluene, trioctylamine Technical and technical grade Cyanex 301, containing up to 20 % of different kind impurities.

The separation of the extraction agent solution into components was carried out via contacting the organic phase with aqueous sodium hydroxide in a calibrated test tube graduated at various proportions and compositions of solutions and ratios between the phases. The contact between phases lasted for 3–5 min. The volume of each phase was evaluated after the centrifugation of the emulsion. To determine the concentration of Cyanex 301 in the form of the sodium salt in octane or toluene, the organic phase was treated with 1 M HCl solution, with further evaluating the content of sodium cations in the aqueous phase by means of atomic absorption spectroscopy. The total content of Cyanex 301 (in acid and salt forms), as well as the concentration of Cyanex 301 in the aqueous and aqueous organic micellar solution was determined by means of iodometric titration. In order to isolate Cyanex 301 from the aqueous organic micellar solution the latter was destroyed *via* adding the stoichiometric amounts of a mineral acid (1–2 M HCl). From the concentrating level of the cation exchange extraction agent we evaluated the transition of the organic solvent (octane or toluene) in the micellar aqueous organic solution.

Nickel extraction was carried out at the temperature ranging within 20–60 °C, different pH values of the aqueous phase and the compositions of organic extraction agent solutions. The concentration of nickel in the aqueous phase was determined by means of atomic absorption spectrometry.

RESULTS AND DISCUSSION

In order to separate the components of the organic phase, we used a low solubility of Cyanex 301 sodium salt in non-polar diluents (toluene, octane, *etc.*), which salt is formed upon contacting the extraction agent solution with aqueous sodium hydroxide. The sodium salt is separated in the composition of separate phases, both liquid and solid, as determined by the conditions of extraction agent processing.

The separation conditions for the organic phase components were studied for the systems such as organic acid (Cyanex 301)–solvent (toluene or octane)–NaOH–water, and organic acid–rioctyl amine (R_3N)–solvent (toluene or octane)–NaOH–water.

The most important factors affecting the process involve the initial concentration values of organic acids and alkali, as well as the relationship between these components. The interaction between the solutions of the organic acid under investigation and the solutions a sodium hydroxide at different relationship between the components result in flowing heterogeneous reaction to occur:

Na^+ (aq) + OH^- (aq) + HA (org) → NaA (org)+ H_2O (2)

Since Cyanex 301 is a sufficiently strong acid ($pK_a \sim 2.6$), the reaction (2) proceeds almost quantitatively, thus with adding sodium hydroxide in an amount close to the stoichiometric one, the pH value of aqueous micellar solution is close to neutral value.

In the systems with Cyanex 301, the acidic form (HA) and the salt form (NaA) of the extraction agent behave in an independent manner: the HA remains in the organic diluent phase, whereas NaA forms a new phase, as a rule, an aqueous organic micellar solution containing a prevailing amount of the cation exchange extraction agent (Fig. 1). With a complete transition of the extraction agent into the salt form the content thereof in the diluent phase ranges from 10^{-3} to 10^{-4} mol/L.

The second phase containing the sodium salt of Cyanex 301 represents a typical oil-in-water micellar solution that exhibits opalescence. The micelles are destroyed under acidification to form the initial extraction agent Cyanex 301 in the H^+ form and an aqueous salt solution. The concentration of the extraction agent isolated from the aqueous micellar solution ranges within 1.6–2 mol/L (the content of the extraction agent in the organic solution being equal to 60–80 %). This indicates a partial solubilization of the solvent (toluene, octane) including trioctylamine by the micelles of the sodium salt.

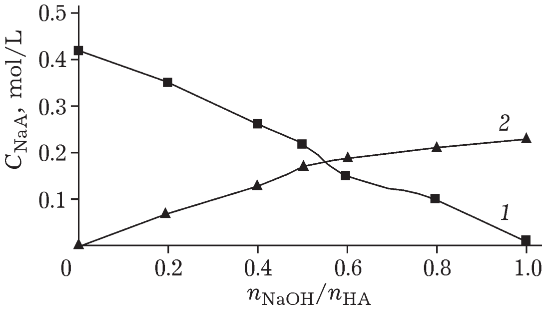

Fig. 1. Cyanex 301 concentration in the organic phase (*1*) and in the aqueous micellar phase (*2*) depending on the molar ratio of $n_{(NaOH)}/n_{(HA)}$.

Thus. the Cyanex 301 concentration in the final product could be an indicator of the micellar solubilization capacity under various conditions. For example, Fig. 2 demonstrates the concentration of Cyanex 301 isolated from the micellar solution depending on Cyanex 301 sodium salt concentration in the aqueous micellar solution. The micellar solutions were prepared by means of contacting the stoichiometric amounts of HA with NaOH at equal volume ratio between the amounts of aqueous and organic phases, but at different concentration values of Cyanex 301 in the initial organic so-

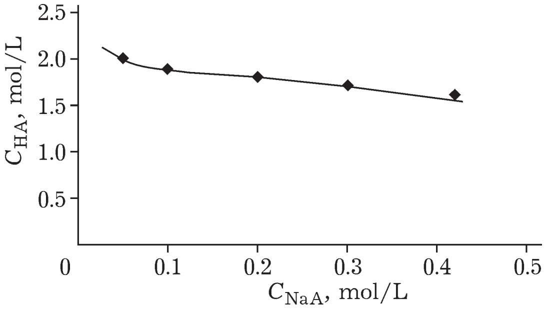

Fig. 2. Effect of NaA concentration in aqueous micellar solution exerted on Cyanex 301 content in the product extracted from acidified solutions.

lution (ranging from 0.05 to 0.5 mol/L). It can be seen that with decreasing the concentration values of NaA in the aqueous micellar solution obtained in such a way the solubilization capacity of micelles decreases, and this results in releasing a more concentrated solution of Cyanex 301 from the solution. In this case the concentrating level of the extraction agent is 10?50 times greater than the starting concentration to demonstrate an increase with the use of more dilute solutions.

At the same time, the solubilization capacity is insignificant, and depends to an insignificant extent on the total concentration of the sodium salt. A certain increase with increasing the overall NaA concentration in the solution could be associated with coarsening the spherical micelles under the assumption that the neutral solvent molecules are concentrated in the bulk of the micelle, whereas the NaA molecules are located on the micellar surface.

Further increasing the concentration of the sodium salt in the solution results in qualitative changing the structure of the aqueous micellar solution and in the formation of a gelatinous precipitate.

Gel formation is observed at the concentration of NaA in aqueous micellar solution higher than 4.0 mol/L.

The introduction of electrolyte salts in the solution, including an excess of sodium hydroxide solution (Fig. 3), is accompanied by a partial dehydration of aqueous micellar solution and the formation of a new phase of aqueous electrolyte that does not contain the extraction agent (micelles). Accordingly, the content of Cyanex 301 sodium salt in the aqueous micellar solution exhibits an increase. However, upon further increasing the electrolyte concentration (NaOH) in the solution the system exhibits an abrupt transition of into another state, NaA passes into the organic phase to form a water-in-oil type micellar solution. In this case the system becomes a two-phase one. This is reflected by the concentration of Cyanex 301 sodium salt in the phases (see Fig. 3).

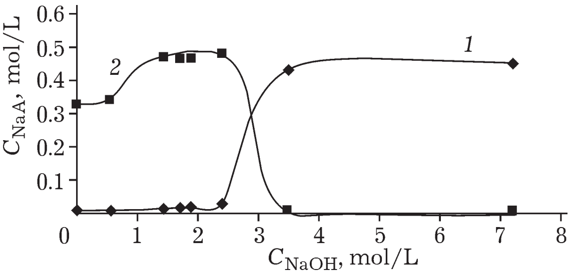

Fig. 3. Effect of excess NaOH concentration on the distribution of Cyanex 301 sodium salt between the aqueous phase (*1*) and the organic (*2*) phase (C_{NaA} = 0.5 mol/L).

Changing the nature of the solvent (toluene replacing by octane) exerts an insignificant effect on the process. In the case of passing to a three-component organic solution system such as organic acid–solvent–trioctylamine the treatment of the organic phase with aqueous sodium hydroxide solution results in the separation of the extraction agent solution into the two phases of Cyanex 301 sodium salt and the organic solution of the tertiary amine. In this case the trioctylamine behaves as a non-polar organic diluent being solubilized by micelles to an insignificant extent.

A small amount of the amine remains in the organic solution of the extraction agent, therefore we assessed an effect of this impurity exerted on the cation-exchange extraction of nickel and first of all on the rate of extraction. At a room temperature, the extraction of nickel occurs at a low rate, and in this connection, according the Goro process [1] one recommends to carry out the extraction at 60 °C. Dependences are obtained for nickel extraction (from the solution of $NiSO_4$) by the solution of Cyanex 301 and the mixtures thereof with trioctylamine. It has been established that the addition of a tertiary amine to the system (up to 25 % of the amount of HA) does not worsen the kinetic parameters of the process. At 60 °C the quantitative extraction of the metal in these systems can be achieved within the time interval less than 2 min.

Trioctylamine impact on the distribution of nickel in the Cyanex 301 system was studied under equilibrium conditions. As expected, the addition of the amine and the transition to the extraction of the organic acid salts and of the organic base by binary extraction agents [6] results in a substantial decrease in the coefficient of nickel distribution due to reducing the concentration of free cation-exchange extraction agent (Fig. 4). When the content of trioctylamine in the system is either stoichiometric (TOA/HA = 1 : 1, the initial content of acidic

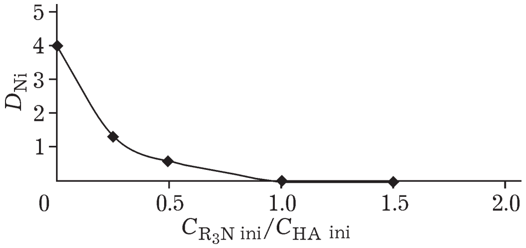

Fig. 4. Nickel distribution coefficient (D_{Ni}) depending on the ratio of $C_{R_3N\ ini}/C_{HA\ ini}$ in the system ($C_{HA\ ini}$ = 0.35 mol/L).

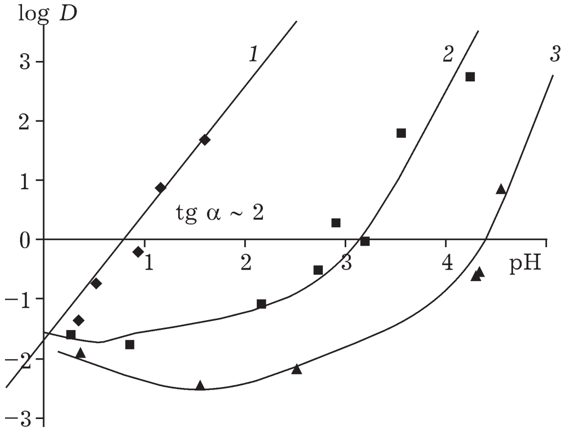

Fig. 5. Log D_{Ni} depending on the solution pH in the case of the extraction by the following solutions: *1* − Cyanex 301, C_{HA} = 0.4 mol/L; *2* − Cyanex 301 + R_3N, $C_{R_3N \cdot HA}$ = 0.33 mol/L; *3* − Cyanex 301+ R_3N, $C_{R_3N \cdot HA}$ = 0.41 M, C_{R_3N} = 0.06 mol/L.

form being equal to 0.35 mol/L) or greater than stoichiometric, the distribution coefficient is reduced by 2−3 orders of magnitude, amounting to approximately 10^{-2}–10^{-3}.

In this case the nature of the extraction process changes from the cation-exchange to the binary (both cation and anion are extracted into the organic phase).

This is reflected in the metal extraction level depending on the solutions pH (Fig. 5). Curve *1* demonstrates log D_{Ni} depending on pH value for acidic Cyanex 301form (in a diluent). The value of the slope for this curve is close to 2, which corresponds to the charge of the metal under cation-exchange extraction. Curve *2* corresponds to log D_{Ni} depending on pH value in the system with $R_3N \cdot HA$. At pH values ranging within 0.5−2 there are low nickel distribution coefficients observed. Thereby, the Ni recovery is insignificantly affected by the solution pH value, since the cation-exchange mechanism of the extraction exhibits changing by a binary mechanism (the extraction of nickel sulphate or bisulphate). With increasing the content of trioctylamine in the system (up to 1.5-fold excess of the amine with respect to the extraction agent, $C_{R_3N \cdot HA}$ = 0.41 mol/L, C_{R_3N} = 0.06 mol/L), the range of re-extraction increases up to pH ~ 4 (curve *3*): D_{Ni} value varies by 5−6 orders of magnitude. In a strongly acid environment (pH ~ 0) the curves approach to each other, since the amines are bound with a mineral acid (in this case, sulphuric acid), and the nickel is extracted *via* a cation-exchange mechanism. Within the region of pH > 3−4, the cation-exchange nature of extraction again appears again, which is reflected in the log D_{Ni} depending on the pH of the solution.

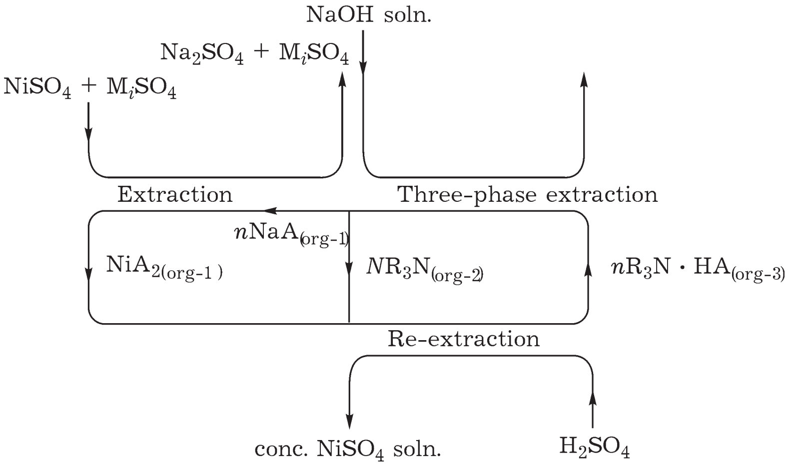

Fig. 6. Scheme for the flows of solutions in the course of nickel extraction by means of Cyanex 301 solution using a three-phase extraction process.

Potentialities were analyzed concerning the use of the TPE process as well as the systems based on Cyanex 301 and trioctylamine in an organic diluent in order to extract nickel from sulphuric acid leaching solutions with obtaining concentrated re-extracts. The general flow chart of the process is demonstrated in Fig. 6. At the first stage, nickel is extracted by the concentrated solution of Cyanex 301 (or its sodium salt) coming from the TPE stage. In the case of the metal extraction from sulphuric acid solutions (pH 1.2, nickel content amounting to 2 g/L) by Cyanex 301 solution with the concentration of 1.6 mol/L, one achieves a greater than 98 % nickel extraction level in a 12-staged extraction procedure, with obtaining nickel extracts containing more than 20 g/L of nickel. At the next stage the nickel extract is mixed with the organic solvent phase containing the amine that is also supplied from the TPE stage. The re-extraction of nickel is carried out by a sulphuric acid solution. It has been demonstrated that at this stage, in the case of the stoichiometric supply of sulphuric acid, one can achieve a complete nickel re-extraction with obtaining the solution containing 60 g/L of nickel.

In the mentioned continuous extraction process the nickel is extracted and concentrated resulting from a series of heterogeneous interfacial chemical reactions as it follows:

1. Extraction:

$$\mathrm{Ni^{2+}\,(aq\text{-}1) + 2HA\,(org\text{-}1) \rightarrow 2H^{+}\,(aq\text{-}1) + NiA_2\,(org\text{-}1)} \quad (3)$$

2. Re-extraction:

$$\mathrm{NiA_2\,(org\text{-}1) + 2R_3N\,(org\text{-}2) + 2H^{+}\,(aq\text{-}2) \rightarrow Ni^{2+}\,(aq\text{-}2) + 2R_3NHA\,(org\text{-}3)} \quad (4)$$

3. Three-phase extraction (extraction agent regeneration):

$$\mathrm{R_3NHA\,(org\text{-}3) + (Na^{+} + OH^{-})\,(aq\text{-}3) \rightarrow R_3N\,(org\text{-}2) + NaA\,(aq\text{-}m) + H_2O} \quad (5)$$

$$\mathrm{NaA\,(aq\text{-}m) + H^{+}\,(aq\text{-}4) \rightarrow HA\,(org\text{-}1) + Na^{+}\,(aq\text{-}4)} \quad (6)$$

In the equations (3)–(6), the indices (aq-1)–(aq-4), (org-1)–(org-3), (aq-m) denote aqueous, organic and aqueous micellar phases, respectively, at different stages of the process.

In general, in the continuous extraction processes such as extraction–re-extraction the major changes in the system occur in the aqueous phase of the initial technological and re-extracted solutions. In the course of steady-state conditions onset in the system, the organic phase in the cycle remains unchanged, and, in fact, serves as a selective carrier of the element under extraction, whereas in realty a complicated reaction occurs between the components aqueous phases such as (aq-1), (aq-2), (aq-3), (aq-4) according a complex heterogeneous process scheme:

$$\mathrm{Ni^{2+}\,(aq\text{-}1) + 2H^{+}\,(aq\text{-}2) + 2(Na^{+} + OH^{-})\,(aq\text{-}3) + 2H^{+}\,(aq\text{-}4) \rightarrow 2H^{+}\,(aq\text{-}1) + Ni^{2+}\,(aq\text{-}2) + 2Na^{+}\,(aq\text{-}4) + 2H_2O} \quad (7)$$

The thermodynamics of the process can be calculated as that for a conventional heterogeneous reaction [7, 8].

From generalized reaction (7) one could see that a high extraction level and a high concentration of nickel in this process are in fact achieved at the expense of the energy of alkali neutralization by acid.

CONCLUSIONS

Phase formation studied in the systems Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid)–organic solvent (toluene, heptane, octane)–sodium hydroxide–water–trioctylamine was studied. It has been demonstrated that with transferring the Cyanex 301 into sodium salt (three-phase extraction) there can be a separation achieved of the organic extraction agent solution into the solvent phase and the organic acid phase. The sodium salt of Cyanex 301 is almost completely converted into a new aqueous organic solution to form micelles. The micelles partially solubilize the organic solvent. Upon acidification, the solution exhibits the segregation of 1.6–2 M Cyanex 301 solution. The presence of organic solvent in the product indicates a partial solubilization of the solvent in the micelles. The solubilization capacity increases to somewhat extent with increasing the concentration of the sodium salt of the extraction agent in the micellar solution, which, to all appearance, indicates an enlargement of spherical micelles. Introducing the surplus of electrolyte (NaOH) into the aqueous phase results in the formation of three phases, whereas at the concentration of 4 mol/L this results in the transition of Cyanex 301 sodium salt to the organic solvent phase with the formation of a “water in oil” micellar solution.

The influence of trioctylamine additives on nickel extraction in the systems with Cyanex 301 was investigated. A scheme has been proposed for the extraction of nickel with the use of three-phase extraction, wherein nickel is extracted with the concentrated solution of Cyanex 301 from acidic ore-leaching solutions, the extract is mixed with an organic solution of amine to be re-extracted with sulphuric acid solution, whereas the organic phase was separated into initial components *via* treating thereof by the solution of sodium hydroxide. This process allows one to extract nickel with high distribution coefficients with obtaining concentrated nickel sulphate re-extracts.

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