

Removal of cobalt(II) and zinc(II) from sulphate solutions by means of extraction with sodium *bis*(2,4,4-trimethylpentyl)phosphinate (Na-Cyanex 272)

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Abstract The removal of Co(II) and Zn(II) from model and real crude nickel sulphate (CNS) solutions by extraction with sodium *bis*(2,4,4-trimethylpentyl)phosphinate (Na-Cyanex 272) is studied and compared with the effect of using *bis*(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). The proposed novel approach to manage both hazardous metal ions from CNS with sodium salt of Cyanex 272 focuses on the following issues: (i) effect of the initial pH of feeds on the extraction efficiency, (ii) leaching of metal ions from CNS, (iii) efficiency and selectivity of metal ion extraction from real CNS, and (iv) FT-IR analysis of structure of complexes formed by the metal ions with the extractant studied. It is concluded that converting Cyanex 272 into its sodium salt greatly improves the efficiency of the extraction in comparison to the conversion into the acidic form of the extractant, regardless of the type of metal ion considered, whether Zn(II) or Co(II). These phenomena occurring in the extraction system are confirmed by the obtained FT-IR spectra of the organic phases after extraction and stripping.

Keywords Cobalt(II) · Zinc(II) · Liquid–liquid extraction · Crude nickel sulphate solution · Cyanex 272 · Hazardous waste management

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Introduction

Hydrometallurgical processing of ores and concentrates (the so-called wet method) involves the use of aqueous solutions for extraction of metals, and the majority of their compounds, from primary deposits (Cole and Sole 2003; Ritcey 2006). Liquid–liquid extraction can be applied to the raw materials that cannot be processed pyrometallurgically because of the chemical nature of the processed metal or its low content in the ore.

The strict environmental regulations, diminishing natural resources of metals, their scarce availability, and the ever-growing demand for them (circuit boards, batteries, capacitors, etc.) stimulate the efforts directed at the recovery of metals from spent batteries (Kang et al. 2010; Li et al. 2015), industrial sludges (Kumar et al. 2013; Sethu et al. 2008) and wastewater streams (Reddy and Park 2007). An example are copper electrorefineries that, besides cathode copper production, produce crude nickel sulphate (CNS) technical grade commercial product sold for its nickel value (Olejnik et al. 2008). Almost all of the nickel contained in copper-bearing ores is concentrated in the final product of smelting process of copper anodes. Spent electrolyte after copper removal is subjected to concentration resulting in the crystallization of nickel sulphate. Its fine crystals after centrifugation form the final product (KGHM 2015). CNS is composed of mainly Ni(II) (25–30 %), about 0.5 % Co(II) and traces of Zn(II), Cu(II), Mg(II) and iron ions (Gotfryd 2006). High purity product can be obtained by removal of all impurities from the crude product. However, recovery of these impurities, i.e. Co(II), Cu(II) and Zn(II) from the wastewater, the CNS solution, coming from one of the biggest Polish companies (copper electrorefinery), seems to be a required and prospective industrial solution that fits the definition of cleaner

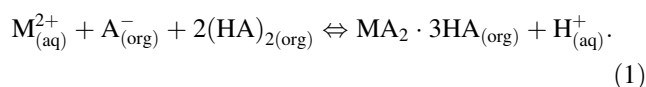
technology as it “approaches to manufacturing that minimize the generation of harmful waste and maximize the efficiency of energy use and material use” (Markusson 2011). On the one hand, the recovery of metal ions from CNS is important because of reduction of environmental risk of release of toxic heavy metals to water or soil, while on the other hand, the application of by-product as a secondary source of valuable (the so called “strategic”) metals is in accordance with the idea of sustainable development.

For many years, multistage processes have been developed to improve the purification of metal-containing streams. They are based mainly on precipitation of metal hydroxides by calcium or barium compounds and pH changes. There are some patents that describe formation of pure nickel sulphate by fractional precipitation of other impurities (Drąg et al. 1989; Kerfoot et al. 2002; Moritomo et al. 2014). However, the main drawback of the procedure is only partial removal of impurities and formation of iron hydroxide contaminated with significant amounts of barium and calcium sulphates.

Although some authors have proposed the removal of heavy metals from industrial wastewater (Mishra et al. 2014; Zinicovscaia et al. 2015) or sewage (Al-Gheethi et al. 2015) by biosorption on microalgae *Spirulina platensis* or various bacteria, these methods are rather suitable for diluted solutions. In addition, those authors have focused on the removal but not on the recovery of the heavy metals that can be also valuable products. Sulphate solutions containing Zn(II), Fe(II), Cu(II) and Co(II) can be processed also with multistage solvent extraction to separate pure NiSO₄ from sulphate contaminants. Some authors have proposed to obtain a purified nickel sulphate solution using extraction of nickel from CNS by stripping the nickel-loaded organic phase containing derivatives of phosphinic acid. However, the application of acidic extractant required neutralization of the aqueous phase to control the pH of the extraction system. Otherwise extraction efficiency of Co(II) and Zn(II) decreased dramatically (Gotfryd 2006).

One of the most frequently investigated acidic extractants is Cyanex 272, and its selectivity of cobalt extraction from solutions containing nickel sulphate has been confirmed by many researchers (Cytex Industries Inc. 2008) not only with conventional liquid–liquid extraction (Ritcey 2006; Sole et al. 2005) but also with use of liquid membranes (Parhi and Sarangi 2008). However, such acidic extractants as Cyanex 272 (Kang et al. 2010; Zhu et al. 2011), Cyanex 301, Cyanex 302 (Sole and Hiskey 1995) and DEHPA (Kongolo et al. 2003; Van de Voorde et al. 2006) can be successfully replaced by their sodium salts to extract Ni(II) and Co(II) from various aqueous solutions (Devi et al. 1994, 1998). Devi et al. (1994, 1997, 1998)

have studied sodium salts of DEHPA, PC-88 (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) and Cyanex 272 for extraction of Co(II), Ni(II) and Zn(II) from model sulphate solutions. On the basis of their research, the authors indicated Na-Cyanex 272 as the best Co(II) extractant from among the extractants studied. Reddy and Park (2007) have proposed a flowsheet of the process aimed at separation of cobalt and nickel from copper sulphate solutions with partly saponified Cyanex 272 and D2EHPA and reported almost 100 % of overall recovery of these metals. On the other hand, Sarangi et al. (1999) have investigated chloride solutions of Co(II) and Ni(II) and noted that increasing Na-Cyanex 272 concentration caused a decrease in the extraction of both metals. The mechanism by which metal ions are transported from the aqueous phase into the organic phase with partially saponified Na-Cyanex 272 is as follows (Kang et al. 2010):



On comparing the effects of the use of acidic Cyanex 272 to those of its sodium salt (Na-Cyanex 272), some advantages of the salt application can be indicated: improvement in the efficiency in the initial pH range between 2.6 and 7 (Devi et al. 1994), the presence of only monomeric form of the extractant (acidic extractant forms dimers resulting in reduction in extraction efficiency). Summarizing, the application of Cyanex 272 salt may improve extraction of divalent metal ions from sulphate secondary sources.

Thus, the paper aimed at carrying out the investigation of the removals of Co(II) and Zn(II) from the model and the real sulphate solutions by extraction with sodium *bis*(2,4,4-trimethylpentyl)phosphinate (Na-Cyanex 272), and comparing the results with those obtained by extraction with acidic Cyanex 272. To the best of our knowledge, the literature data on the use of sodium salts of acidic extractants do not refer to the treatment of real leaching solutions. Extraction of the required compounds from the real solutions generates problems often impossible to predict during the investigation step of model solution, resulting from interactions of ions co-existing in a real mixture. Thus, the novelty of the research presented in this paper is the study of extraction with sodium salt of Cyanex 272 from a real solution after leaching of CNS. The following issues are investigated: (i) the effect of initial pH of feeds on the extraction efficiency, (ii) leaching of metal ions from CNS, (iii) efficiency and selectivity of the extraction of metal ions from real CNS, and (iv) FT-IR analysis of the structure of complexes formed by the metal ions with the extractant studied.

Experimental

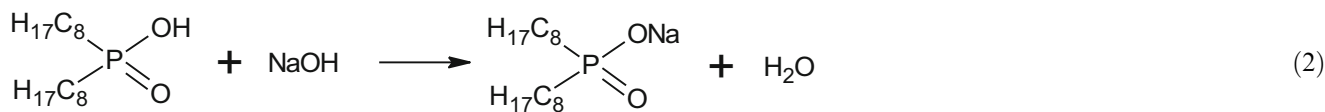
Reagents

Cyanex 272 (*bis*(2,4,4-trimethylpentyl)phosphinic acid) supplied by Cytec Industries Inc. (2008) was used without further purification. The organic phase containing 0.2 mol dm⁻³ Cyanex 272, 1.5 g dm⁻³ butylated hydroxytoluene (BHT), and 5 vol% decan-1-ol in Exxsol D80 (mixture of aliphatic hydrocarbons and cycloparaffins, with aromatics content less than 0.2 wt%, supplied by Brenntag, Poland) was prepared. Some amount of the organic phase was reacted with 2.5 mol dm⁻³ NaOH (o/w = 1) to convert Cyanex 272 into its sodium salt (Na-Cyanex 272).

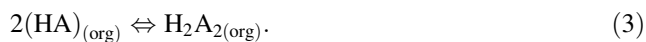
Aqueous feeds used for the determination of pH influence on the extraction contained about 5 g dm⁻³ Co(II) or Zn(II) (as sulphates, POCh, Poland) and their initial pH was adjusted with H₂SO₄ or NaOH (POCh, Poland). All chemicals were used as delivered without any purification.

Preparation of Na-Cyanex 272

Prior to extraction, the organic phase (0.2 mol dm⁻³ Cyanex 272, 1.5 g dm⁻³ BHT, and 5 vol% decan-1-ol in Exxsol D80) was conditioned with 2.5 mol dm⁻³ NaOH (o/w = 1) according to the following reaction:



Sodium salt of Cyanex 272 exists mainly as a monomer, while acidic extractant (HA) forms dimers according to the reaction (Rydberg et al. 2004):



Both forms can act as extractants, however, they differ in the mechanism of extraction (Devi et al. 1994).

The degree of neutralization of Na-Cyanex 272 used in this work was calculated from the mass balance of OH⁻ determined before and after neutralization and was equal to almost 100 % (0.196 mol dm⁻³). It is assumed that the difference in OH⁻ in the aqueous phases refers to Na⁺ transferred into the organic phase to form sodium salt of Cyanex 272.

Extraction procedure

Extraction was carried out in a typical way: aqueous feeds containing 5 g dm⁻³ of Co(II) or Zn(II) sulphate were

mechanically shaken with the organic phase (volume ratio w/o = 1) for 30 min at 20 °C in glass separatory funnels, and then allowed to stand for phase separation. The initial pH was adjusted in the range of 2–4 with H₂SO₄ or NaOH. Stripping was carried out with 2 mol dm⁻³ H₂SO₄.

Three-stage extraction of metal ions from the CNS leach solution containing 28, 0.69, 0.62 and 0.57 g dm⁻³ Ni(II), Cu(II), Co(II), and Zn(II) (resulting from the leaching with hot water), pH 4, was carried out cross-currently at the volume ratio w/o = 1. It means that a raffinate from one stage of extraction was used as a feed in a consecutive extraction stage and made to come into contact for 30 min with the fresh organic phase as shown in Fig. 1. The organic phase was stripped with 2 mol dm⁻³ H₂SO₄ (volume ratio w/o = 1).

Equilibrium pH of the aqueous phases after extraction was measured, and metal ion concentration was determined by voltamperometric method at Computrace VA 727 (Metrohm) (Metrohm 2015a, b).

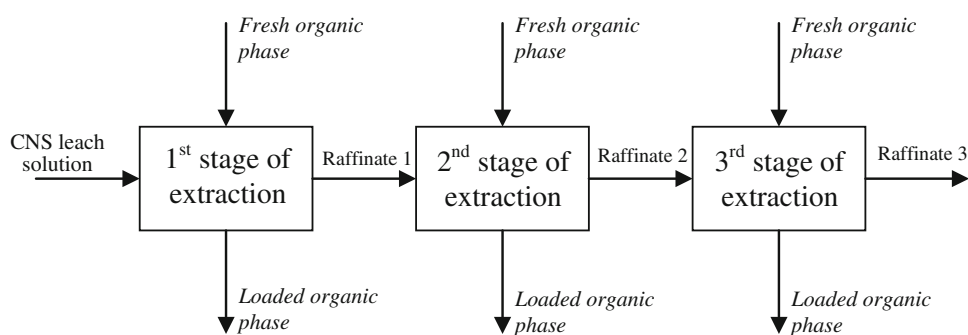
Ni(II), Co(II), Zn(II) and Cu(II) concentrations in CNS were determined with ICP OES (IRIS, Thermo Jarell Ash, USA) at 224.7, 228.6, 237.8, 221.6, 231.6 and 213.8 nm for Cu, Co, Co, Ni, Ni and Zn, respectively.

The voltamperometric and ICP measurements were replicated three times.

Leaching of crude nickel sulphate solution

CNS originated from three Polish smelters: Glogow I HM, Glogow II HM and Legnica HM. The CNS was dissolved in hot demineralized water (60, 70, 80 and 90 °C) and mixed for 3 h (1200 rpm) using a magnetic stirrer upon heating (RCT basic IKA). This process was accompanied by a decrease in pH from 1.8 to 1.02. After cooling, the neutralizing agent (1 mol dm⁻³ NaOH) was added to obtain pH of nearly 4.5. Then, the solutions prepared were stirred over the same operating parameters and temperatures for 2 h. As a result of oxyhydrolysis, a partial precipitation of the impurities such as iron, arsenic, antimony, some aluminium, calcium and lead took place. In the next step, the phases were separated by sedimentation at the low temperature and filtration at the high one. Measurements of pH values of the aqueous solution carried out before leaching of CNS and after its dissolution were considered

Fig. 1 Schematic representation of the three-stage extraction



as reliable when pH values changed by less than 0.1 within a time period of 10 min.

Synthesis of organic complexes

The laboratory synthesis of complexes of Co(II) or Zn(II) with Cyanex 272 and Na-Cyanex 272 was carried out in the following way: the solution of Co(II) and Zn(II) sulphates in ethanol was heated under reflux until complete dissolution. Then, the solution of extractant in ethanol was added (molar ratio metal:extractant 1:1 or 1:2), and the resulting mixture was boiled under reflux for 3 h. The precipitates were filtered off and next washed with ethanol. The yields were for the complex Co:extractant 1:1 76 % (m.p. 69.1–71.9 °C), Co:extractant 1:2 71 % (m.p. 41.8–43.1 and next 71.7–73.1 °C), Zn:extractant 1:1 49 % (m.p. 29.1–30.4 °C) and Zn:extractant 1:2 62 % (m.p. 25.4–27.9 °C).

The synthesis of Na-Cyanex 272 was carried out using ethanol as a diluent. The mixture of Cyanex 272 and NaHCO₃ was boiled under reflux for 6 h. Both mixtures were left to cool to room temperature. After that, the diluent was evaporated under vacuum, dried and washed with chloroform. The white precipitate was recrystallized from ethanol and isolated with 89.5 % yield, m.p. 243.1–249.9 °C.

Spectroscopic analysis

FT-IR analyses of the organic phases obtained from extraction and stripping were carried out on the Vertex 70 Spectrometer (Bruker Optics FT-IR) in the range of IR 400–4000 cm⁻¹. The spectra of the organic phases were recorded using KBr liquid transmission cells or as thin films using NaCl discs (plates). Spectra of the complexes synthesized, as well as, of the Na-Cyanex 272 were recorded in the range of IR 500–4000 cm⁻¹ using the Vertex 70 Spectrometer equipped with a *MIRacle*TM ATR accessory (single reflection diamond ATR crystal).

Calculations

Distribution ratio of metal ions (D_M) was defined as

$$D_M = \frac{C_M^{\text{org}}}{C_M^{\text{aq}}}, \quad (4)$$

where C_M^{org} and C_M^{aq} stand for the concentrations of metal ions after extraction in the organic and aqueous phases, respectively.

Percentage extraction (E) was calculated from the contents of metal ions in the aqueous phases before m_M^0 and after m_M^{aq} extraction:

$$E = \frac{m_M^0 - m_M^{\text{aq}}}{m_M^0} \times 100 \%. \quad (5)$$

The total percentage extraction ($\sum E$) for the three-stage extraction was calculated as follows:

$$\sum E = \frac{\sum m_M^{\text{org}}}{m_M^0}. \quad (6)$$

Selectivity of metal ion extraction was characterized by separation coefficient, $\beta_{M1/M2}$, defined as

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}}, \quad (7)$$

where D_{M1} and D_{M2} denote distribution ratios of respective metals in a mixture.

Results and discussion

Extraction with Na-Cyanex 272 and Cyanex 272

The extractions of Co(II) and Zn(II) with solutions of Cyanex 272 and Na-Cyanex 272 from model aqueous solutions at the initial metal concentration of 5 g dm⁻³ yielded the results as presented in Figs. 2 and 3.

Extraction of Co(II) with Na-Cyanex 272 is efficient and amounts to over 90 % in the range of the initial pH (pH_{ini}) values studied (Fig. 2). The efficiency of Co(II) extraction is much higher at the initial pH lower than that reported by

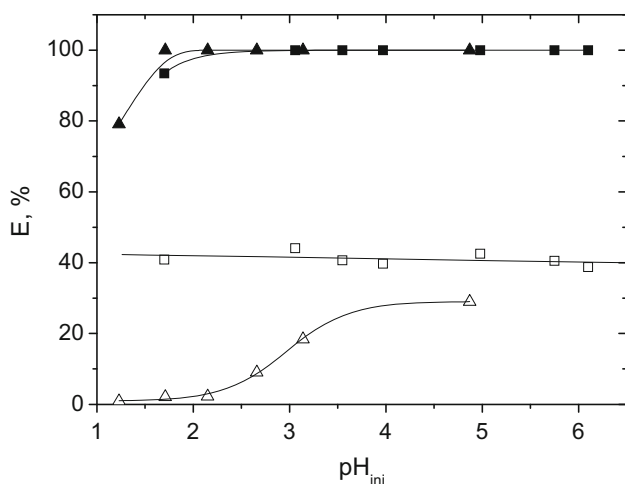


Fig. 2 Influence of the initial pH on extractions of Co(II) (black square, white square) and Zn(II) (black triangle, white triangle) with Na-Cyanex 272 (black square, black triangle) and Cyanex 272 (white square, white triangle)

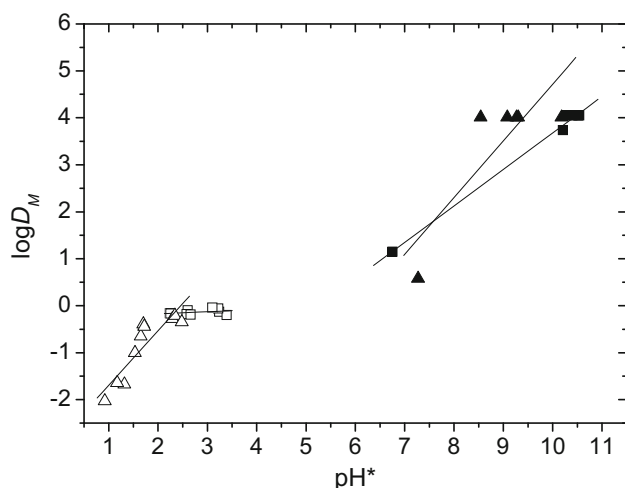


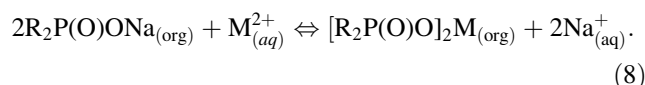
Fig. 3 Dependence of $\log D_M$ on equilibrium pH of the aqueous phase after extraction of Co(II) (black square, white square) and Zn(II) (black triangle, white triangle) with Na-Cyanex 272 (black square, black triangle) and Cyanex 272 (white square, white triangle)

Devi et al. (1994, 1998) who investigated Co(II) extraction also with Na-Cyanex 272. However, the difference between their results and ours stems from different concentrations of metal ions in the feed and also in the degree of neutralization of Cyanex 272. In Devi et al.'s works, Cyanex 272 was not fully saponified which affected the extraction behaviour of the organic phase.

Extraction of Zn(II) at pH 1 equals 80 %, and increases to a constant value of 100 % when pH is increased. The pH change does not affect significantly the percentage extraction; thus, in the case of Na-Cyanex 272, the initial pH does not have to be strictly controlled. It is important to maintain pH below 6.5 to avoid precipitation of metal ion hydroxides.

To compare the efficiencies of Co(II) and Zn(II) extractions with Cyanex 272 salt and the acidic form of the extractant, one-stage extraction was carried out. The percentage extractions of Co(II) and Zn(II) with the acidic Cyanex 272, shown in Fig. 2, are lowered to half of that when compared with its sodium salt. This phenomenon can be explained by the formation of dimers of organophosphoric acid resulting from hydrogen bond interactions between the molecules of the organic acid, as shown in Fig. 4 (Rydberg et al. 2004).

Therefore, the lower the content of acidic form, the lower the number of dimers in the organic phase. As observed from Eq. (1), only partial saponification of the acidic form causes that for each extracted metal ion even five molecules of the extractant are used, while for the extraction with sodium salt of Cyanex 272, it proceeds with two molecules of an extractant according to the following reaction:



As a consequence, higher percentage extraction of metal ions is reported for the extraction with sodium salt than with acidic Cyanex 272 (Figs. 2, 3). Co(II) extraction with Cyanex 272 is at a constant level, i.e. 40–50 %, for pH from the range studied. Zn(II) extraction with Cyanex 272 increases with the increasing pH, and over pH 3, it is constant and equals 30 %. Na-Cyanex 272 performs much better in the extractions of Co(II) and Zn(II) ($\log D_M$ close to 4) than does the acidic form of Cyanex 272 ($\log D_M$ as maximum amounts to 0). Figure 3 confirms that, as a result of Co(II) and Zn(II) extractions with Na-Cyanex 272, the equilibrium pH is shifted to higher pH values because there is no proton release to the aqueous phase. This observation confirms full conversion of Cyanex 272 into its sodium salt before extraction.

Effect of metal ion extraction on pH of the aqueous phase

Changes in the equilibrium pH of the aqueous phase as a consequence of metal ion extraction with solutions of Cyanex 272 or Na-Cyanex 272 are shown in Fig. 5.

Equilibrium pH of the raffinate after extraction with salt of Cyanex 272 increases significantly to pH 10, and does

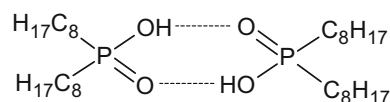


Fig. 4 Dimeric form of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272)

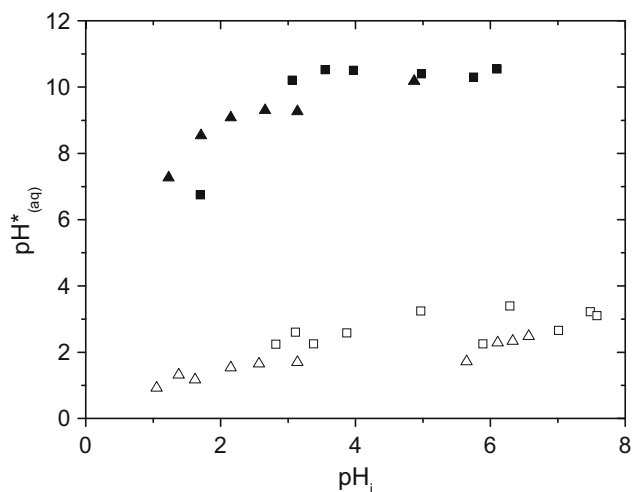


Fig. 5 Changes in equilibrium pH ($\text{pH}^*_{(\text{aq})}$) for various initial pH values of the feed after extraction of Co(II) (black square, white square) and Zn(II) (black triangle, white triangle) with Na-Cyanex 272 (black square, black triangle) and Cyanex 272 (white square, white triangle)

not depend on the initial pH (Fig. 5). The reason for this drastic pH change can be explained by Na^+ exchange from Na-Cyanex 272 into ions of the metal extracted (Kang et al. 2010). Most possibly, the excess of the sodium salt undergoes hydrolysis to be converted into the acidic form of the extractant, resulting in the formation of sodium hydroxide in the aqueous phase. The reaction of the process has been proposed in an earlier work of the authors (Staszak et al. 2012). On the contrary, pH values after extraction with acidic Cyanex 272 decrease as a result of proton transfer from acidic extractant in the organic phase to the aqueous phase and simultaneous extraction of Co(II) or Zn(II) to the organic phase.

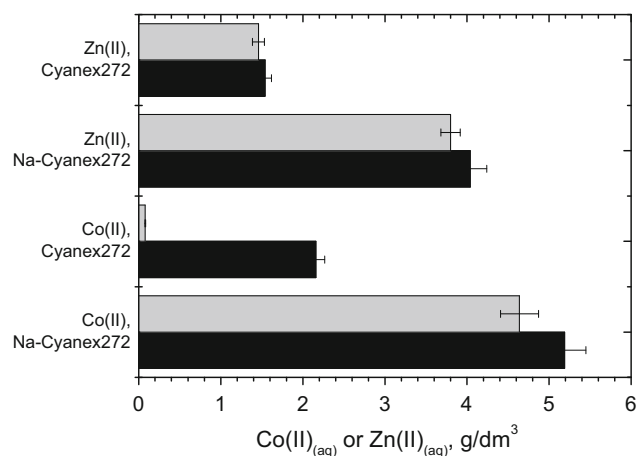
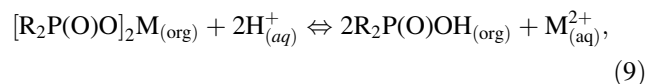


Fig. 6 Co(II) or Zn(II) content in the extract (black square) or strippant (grey square)

Stripping of Co(II) and Zn(II) from the organic phases

Stripping of both metal ions from the extracts (the organic phases) was carried out with 2 mol dm^{-3} solution of H_2SO_4 , and the efficiency of Co(II) or Zn(II) stripping is shown in Fig. 6.

The Co(II) and Zn(II) stripping from Na-Cyanex 272 organic phase is efficient and attains 80–90 % efficiency of stripping of the metal ions. Co(II) stripping from acidic Cyanex 272 almost does not occur (2–3 %). On the contrary, Zn(II) is stripped from Cyanex 272 very effectively, to reach almost 100 %. As the stripping runs according to the following reaction,



the acidic form of the extractant is obtained as a result of stripping, regardless of the original form of Cyanex 272 before extraction.

Extractions of Co(II) and Zn(II) from their mixture

As the next step, to investigate separation of both metal ions, extractions of Co(II) and Zn(II) were carried out from the sulphate solution containing about 0.1 mol dm^{-3} of each metal ion, i.e. 5.6 and 5.7 g dm^{-3} of Co(II) and Zn(II), respectively, pH 4.

The results shown in Fig. 7 evidence that Zn(II) is almost quantitatively extracted (96 %) to the organic phase containing Na-Cyanex 272, while almost half of Co(II) remains in the aqueous solution. Selectivity coefficient of Zn(II) extraction in the presence of Co(II) is equal to almost 25. On the one hand, it means that the majority of

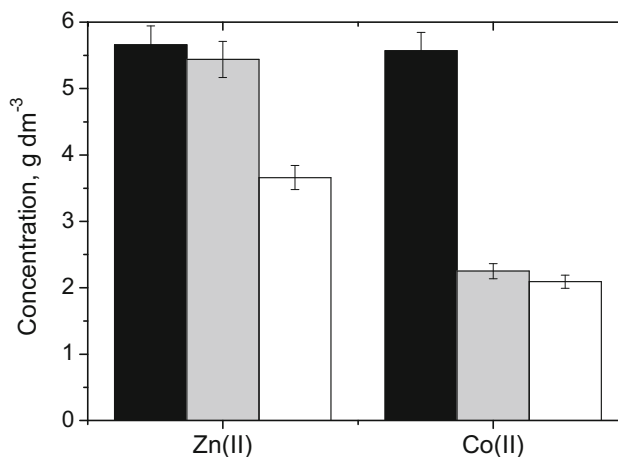


Fig. 7 Comparison of Co(II) and Zn(II) concentrations in the feed (black square), organic (extract) (grey square) and stripping phase (white square) (organic phase: Na-Cyanex 272)

Zn(II) is transported to the organic phase, but it cannot be selectively separated from Co(II). On the other hand, almost 50 % of Co(II) that remained in the aqueous solution is almost completely free from Zn(II).

Crude nickel sulphate

Leaching of crude nickel sulphate

Finally, extraction of metal ions from real CNS solution was investigated. Solid CNS was leached according to the procedure described in the Experimental section to obtain solution containing metal ions for further extraction. At first, CNS was mixed with water, and the colour was observed to change from dull greyish green to clear dark green. This operation resulted in separation of the insoluble residues. The resulting green colour of the solution indicated the high concentration of nickel ions in the solution.

Table 1 shows the pH values of the aqueous solution measured before leaching of CNS and after its dissolution at the four temperatures analysed. Regardless of the leaching temperature, a decrease in pH of the solution is observed. These pH changes are caused by leaching of metal sulphates present in the CNS supplied from the foundry to the aqueous phase.

After each leaching experiment, the mass of sediment was measured (Table 1, the initial amount of CNS was 20 g). It was noted that the mass decreases with the increasing temperature during the process. This shows a much better leaching of metal salts from CNS at high temperatures.

As a result of the leaching, the following concentrations of metal ions were obtained: 28, 0.69, 0.62 and 0.57 g dm⁻³ of Ni(II), Cu(II), Co(II) and Zn(II), respectively.

Extraction of metal ions from CNS solution

The focus was on the extractive technique used for the recovery of the metal ions present in CNS in three consecutive stages of extraction with the organic phase containing 0.2 mol dm⁻³ Na-Cyanex 272, 1.5 g dm⁻³ BHT and 5 vol% decan-1-ol in Exxsol D80. The pH value of the

Table 1 pH of the aqueous samples at the beginning and at the end of mixing (initial and final pH) for the first stage of CNS leaching and mass of sediment left (*m*)

<i>T</i> (°C)	Initial pH	Final pH	<i>m</i> , g
60	1.8	1.02	4.17
70	1.8	0.98	4.33
80	1.8	1.07	3.69
90	1.8	1.06	2.55

feed containing 28, 0.69, 0.62 and 0.57 g dm⁻³ Ni(II), Cu(II), Co(II), Zn(II) (obtained from the leaching with hot water at 60 °C) was initially established as 4. After the first and second stages of extraction with Na-Cyanex 272, the pH increased up to 6.7 and 6.9, while after the third stage, it decreased to 4.8. One-step stripping of the metal ions from the organic phase after the first and the second extraction stages was carried out using 2 mol dm⁻³ H₂SO₄.

The results of three-stage extraction are presented in two separate figures (Figs. 8, 9) because of large difference in the concentrations of Ni(II) and the other metals.

In each consecutive stage, the Ni(II) concentration in the aqueous phase decreased, and the total percentage of extraction after three stages was equal to 76 %. However, the three stages were not enough to deplete it completely; still nearly 8 g dm⁻³ of Ni(II) remained in the aqueous phase (Fig. 8). In the mean time, Cu(II) and Co(II) were fully extracted with 0.2 mol dm⁻³ Na-Cyanex 272 (Fig. 9). After stage one of extraction, copper(II) is almost completely removed, while the least extraction efficiency is noted for Zn(II). However, Zn(II) percentage extraction after the three stages is high enough to reach almost 90 %.

Stripping of Zn(II), Co(II) and Cu(II) with 2 mol dm⁻³ H₂SO₄ is effective, and yields between 40 and near 60 % of the stripped metal ions in stage one (Fig. 10).

Selectivity of extraction of metal ions from CNS solution

Selectivity of extraction is an important issue to separate various metal ions. Selectivity factors of Ni(II) over the other metal ions are rather low because of the great amount of excess of Ni(II) in the aqueous feed (Table 2). Thus, no selective separation of Ni(II) and the other metals is possible in the presented system.

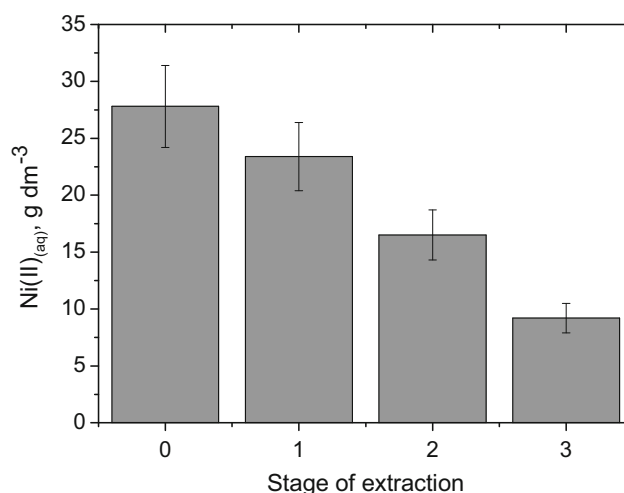


Fig. 8 Concentration of Ni(II) in sulphate mixture: 0 feed, 1 after one stage of extraction, 2 after second stage of extraction, 3 after third stage of extraction; the organic phase: 0.2 mol dm⁻³ Na-Cyanex 272

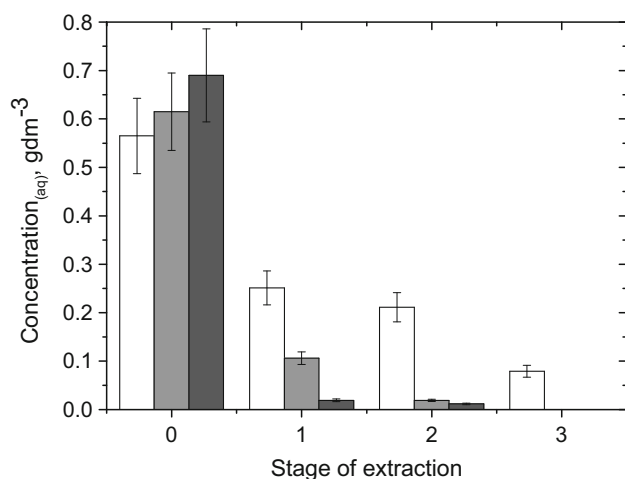


Fig. 9 Concentrations of (white square) Zn(II), (grey square) Co(II), and (black square) Cu(II) in sulphate mixture: 0 feed, 1 after one stage of extraction, 2 after second stage of extraction, and 3 after third stage of extraction; the organic phase: 0.2 mol dm⁻³ Na-Cyanex 272

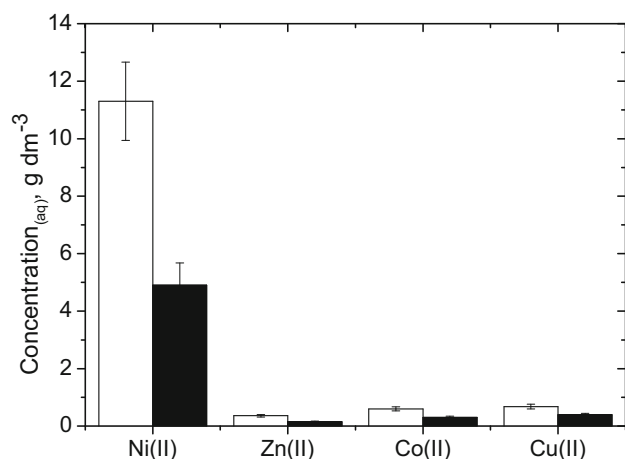


Fig. 10 Stripping of metal ions from the loaded organic phase after the first stage of extraction (white square extracted metal ions, black square stripped metal ions)

Table 2 Selectivity factors of Ni(II) over the other metals in consecutive stages of extraction with 0.2 mol dm⁻³ Na-Cyanex 272

Stage of extraction	$S_{\text{Ni(II)/Zn(II)}}$	$S_{\text{Ni(II)/Co(II)}}$	$S_{\text{Ni(II)/Cu(II)}}$
1	0.16	0.04	0.01
2	2.71	0.09	0.38
3	0.49	0.01	0.01

According to the selectivity factors of Ni(II) over the other metals, Ni(II) should be removed from the aqueous mixture prior to the extraction with Na-Cyanex 272. Next, the mixture of Zn(II), Co(II), and Cu(II) can be processed. Selectivity factors of Co(II) separation over Zn(II), presented in Table 3, are high and increase after each

Table 3 Selectivity factors of Co(II) separation over Zn(II) in consecutive stages of extraction with 0.2 mol dm⁻³ Na-Cyanex 272

Stage of extraction	$S_{\text{Co(II)/Zn(II)}}$	$S_{\text{Co(II)/Cu(II)}}$	$S_{\text{Zn(II)/Cu(II)}}$
1	3.78	0.15	0.04
2	28.0	4	0.14
3	34.5	1	0.008

extraction stage. Thus, they indicate good separation of Co(II) from sulphate mixture in the presence of Zn(II). However, it is important to remove first Cu(II) because it can be more easily extracted than both Co(II) and Zn(II).

FT-IR analysis of the organic phases

FT-IR analysis was carried out to confirm the results obtained in the study of extraction. The FT-IR spectra of the organic phases containing Cyanex 272 and its sodium salt (Na-Cyanex 272) are shown in Fig. 11.

FT-IR spectrum of Cyanex 272 shows broad bands in the region of phosphinic group with the maxima at 2305 and 1713 cm⁻¹, which correspond to the bonded PO-H (stretching and deformation vibrations, respectively) and very strong bands in the range of 1200–900 cm⁻¹ with the maximum region near 1177 cm⁻¹ (P=O stretching band) and at 1055 and 956 cm⁻¹ corresponding to P-OH stretching bands. As a result of Cyanex 272 being transferred into its sodium salt, the FT-IR spectra differ especially in the range near 2300 cm⁻¹, where the strong absorption of O-H band is markedly reduced. In addition, the absorption peaks in the regions of P=O, PO-H, and P-OH vibration bonds upon formation of sodium salts shift from 1178 to 1129 cm⁻¹, from 1713 to 1660 cm⁻¹, and from 956 to 1026 cm⁻¹, respectively. The FT-IR analysis also shows the disappearance of the O-P-O wagging and rocking vibrations initially observed at 566 and 545 cm⁻¹.

The spectra of the organic phases containing Na-Cyanex 272 before and after extraction, and after stripping of individual Co(II) or Zn(II) and their mixture, are also studied and shown in Figs. 12 and 13 in Supplementary data.

The FT-IR analysis of the organic phase after Zn(II) extraction shows further changes in the Cyanex 272 spectra due to the metal chelation: the P-O⁻ stretching band shifts from 1026 to 1041 cm⁻¹, P=O stretching band shifts from 1129 to 1136 cm⁻¹, and an increase in the intensity of the signal in the 538–546 cm⁻¹ region, which is attributed to Zn-O stretching band.

In the case of the extraction of Co(II), the spectral analysis also shows the changes in the P-O⁻ and the P=O stretching bands, which are shifted to 1041 and 1136 cm⁻¹, respectively. However, the signal at 1041 cm⁻¹ has lower

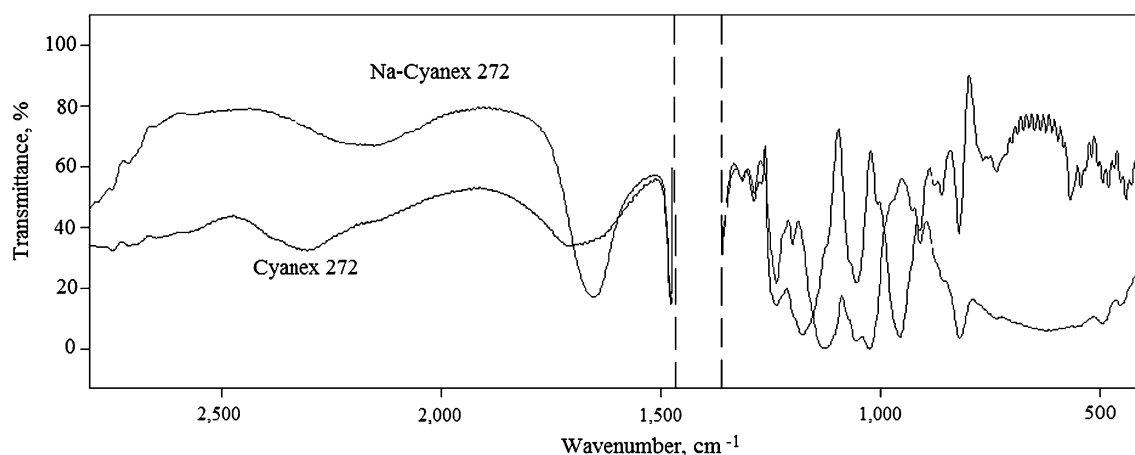


Fig. 11 FT-IR spectra of the organic phases containing acidic form of Cyanex 272 and its sodium salt, Na-Cyanex 272

intensity than that of the corresponding uncomplexed Na-Cyanex 272. After stripping, the signals being attributed to the changes resulting from the complexation process return to the positions of free Cyanex 272, and this confirms the efficient back extraction of the metals to the aqueous solution. The most characteristic changes noted after stripping are for the band at 1026 cm^{-1} , which is shifted towards lower frequencies (956 cm^{-1}); for the P=O stretching bands, the band shifts from 1129 cm^{-1} to 1177 cm^{-1} ; and the appearance of the signals at 545 and 566 cm^{-1} which are attributed to O–P–O vibrations.

Changes in the FT-IR spectra of the organic phase similar to those shown in Fig. 12 are noted after extraction of both metals from model mixture solution. However, after extraction of metals from CNS, the changes suggest a hydrolysis of Na-Cyanex 272 to the acidic form of Cyanex 272 (Fig. 13b, Supplementary Data).

FT-IR (ATR) spectra of the Co(II) and Zn(II)-Na-Cyanex 272 complexes synthesized at 1:1 and 1:2 molar ratios in comparison with the synthesized Na-Cyanex 272 are shown in Figs. 14 and 15 in Supplementary data. The analysis, as expected, shows characteristic spectral changes resulting from the zinc(II) and cobalt(II) coordination; however, no differences between the complexes synthesized at the Na-Cyanex 272:metal molar ratios of 1:1 and 2:1 were observed. The most characteristic effect confirming zinc(II) complexation is the shift of the signals attributed to the P–O⁻ and the P=O stretching bands observed in the spectral range of $1200\text{--}1000\text{ cm}^{-1}$ (signal observed at 1049 is shifted to 1124 cm^{-1} ; that observed at 1057 shifted to 1049 cm^{-1} ; and the signal observed at 1028 cm^{-1} to 1024 cm^{-1}). The FT-IR spectra of the loaded organic phase and of the synthesized complexes differ from each other; however, the difference does not result from formation of different complexes but from the presence of BHT and decan-1-ol in the organic phase.

The complexation of cobalt(II) is also combined with the P–O⁻ and the P=O stretching bands changes, but the presented results suggest the difference between the structures of Na-Cyanex 272-cobalt(II) and Na-Cyanex 272-zinc(II) complexes. The most important changes resulting from complexation of cobalt ions with Na-Cyanex 272 is the shift of the signal observed at 1149 cm^{-1} to lower frequencies at 1126 cm^{-1} and the merger of the two signals noted at 1057 and 1028 cm^{-1} to form one broad signal with a peak at 1036 cm^{-1} . Similarly, with regard to the complex with zinc(II), the structural arrangement of Na-Cyanex 272-cobalt(II) complex does not depend on the ligand:metal molar ratio.

Conclusions

Converting Cyanex 272 into its sodium salt significantly improves the efficiency of extraction in comparison to that performed with the acidic form of the extractant, regardless of the type of metal ion considered, Zn(II) or Co(II). Stripping of metal ions from Na-Cyanex 272 causes transformation of the salt into the acidic form of the extractant. The phenomena occurring in the extraction system are confirmed by the obtained FT-IR spectra of the organic phases after extraction and stripping. A comparison of FT-IR spectra shows the contribution of BHT and decan-1-ol to the coordination of metal ions extracted.

This novel approach to extraction of metal ions from CNS with sodium salt of Cyanex 272 proved that the change in initial pH of feeds does not have a negative effect on the extraction efficiency, which is a great advantage of the basic form of the extractant over its acidic form. Regarding the presence of other metal ions in real CNS, negative effect of high content of Ni(II) on the efficiency and selectivity of other metal ion extraction from the solution is indicated. Although Co(II) separation from

Zn(II) is possible from model solution, the selectivity of their separation from real CNS solution is not efficient. Results of the selectivity of extraction with Na-Cyanex 272 for an industrial solution indicate that Ni(II) should be removed from the aqueous mixture prior to extraction with Na-Cyanex 272. Further, the mixture of Zn(II), Co(II), and Cu(II) can be processed.

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