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Separation and concentration of cobalt from aqueous thiocyanate solutions containing cobalt–nickel by emulsion liquid membranes using TBP as extractant

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ABSTRACT

In this work, the zinc plant copper cake (CINKUR Co., Turkey) was leached with hydrochloric acid and main acidic leach solution containing Zn(II), Fe(II), Pb(II), Al(III), Cu(II), Co(II) and Ni(II) ions was obtained. Except for cadmium, cobalt and nickel, the other metals were precipitated by adding various reagents and adjusting the pH of the solution. Then, cadmium was separated by solvent extraction process. After these separation processes, ammonium thiocyanate and water were added to remaining leach solution. Thus, acidic thiocyanate leach solutions used in ELM process were obtained. ELM consists of kerosene as diluent, tributyl phosphate as extractant, sorbitan monooleate (SPAN 80) as surfactant, and 6 M ammonia solution as the stripping solution. Separation and concentration of cobalt by ELM from acidic thiocyanate leach solution containing cobalt and nickel was performed. The important parameters governing the extraction behavior of cobalt have been investigated. These parameters were mixing speed, surfactant concentration, extractant concentration, phase ratio, treatment ratio, stripping solution base concentration, initial cobalt concentration in feed solution, thiocyanate concentration in the feed solution, and the feed solution pH. The results obtained showed that by appropriate selection of the extraction and stability conditions, nearly all of the cobalt ions present in the feed solution were extracted within 10 min. The separation factors of cobalt with respect to nickel, based on initial feed concentration, have experimentally found to be of as high as 310 for non-equimolar Co–Ni feed solutions.

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1. Introduction

Cobalt and nickel are among the most important nonferrous metals. Certain raw materials such as laterite ores are the main sources for their production. Hydrometallurgical methods of leaching applying sulphate, chloride–sulphate, and chloride systems result in leach liquors containing mainly nickel and cobalt in company of some impurities, such as copper, iron, and aluminium. Usually, the majority of these impurities are removed by precipitation with lime, while the copper is cemented out with cobalt powder and recovered by filtration. The obtained purified leach liquors contain both Co(II) and Ni(II) ions. It is very difficult to obtain pure cobalt and nickel compounds from such solutions because of the similar physico-chemical properties of these metals [1].

The separation of cobalt from nickel in aqueous solution above mentioned has always been a problem in hydrometallurgy. Their adjacent positions in the transition metal series in the periodic table result in aqueous somewhat similar chemical behavior but differences do exist. For example, although both cobalt and nickel preferentially exist as divalent hexahydrated ions in dilute aqueous solution, the rate of water exchange on the cobalt ion is very much higher than for nickel. Thus complex ion formation often proceeds much more readily with divalent cobalt than with nickel. On the other hand, the trivalent cobalt ion is much less labile and forms in preference to nickel even though the redox potentials for the Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+}couples are nearly identical. Co also in the divalent state exhibits a marked tendency to form a tetrahedral configuration under more concentrated electrolyte conditions rather than the hexagonal configuration of the six-coordinated species. These general differences help to provide the basis for the various separation processes currently used or proposed for cobalt–nickel separation in hydrometallurgy [2].

Using classical methods, such as precipitation, oxidation, and crystallization, it is impossible to separate the nickel–cobalt pair in a simple and economical way. Solvent extraction seems to be the most efficient method for separation of Co(II) and Ni(II) ions from solutions, including leach liquors [3–6]. Generally, cobalt is preferentially removed with a suitable extractant, leaving nickel behind. A limitation in traditional solvent extraction is that a large inventory of solvent is required, especially when processing dilute solutions. Another limitation in traditional solvent extraction is also high capital cost.

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The use of emulsion liquid membranes containing specific metal ion carriers offers an alternative method to the solvent extraction processes for selective separation and concentration of the metal ions from aqueous dilute solutions [7]. Emulsion liquid membranes have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently, since they combine the processes of extraction and stripping in a single unit operation [8]. The extraction chemistry is basically the same as that found in solvent extraction, but the transport is governed by kinetic rather than equilibrium parameters, that is, it is governed by a non-equilibrium mass transfer [9]. Furthermore, the equilibrium restrain of solvent extraction is eliminated, which implies much lower diluent and extractant amounts for performing the same separation. Moreover, the large specific interfacial areas associated with ELMs result in higher permeation rates, which together with the reaction rather than equilibrium restrain, enable the achievement of higher metal concentrations in fewer separation stages, maintaining the high selectivity of solvent extraction [10–12]. In view of all these advantages, the separation of metals by the ELM technique has drawn considerable attention [13].

Liquid membranes are not only an important technique for concentration, separation and recovery, but also of fundamental importance from an environmental engineering point of view in understanding the mechanisms of ion transport. The transport of metal ions from wastewater solutions by liquid membranes has been the subject of many studies over recent years. Hundreds of cation separation systems have been published in the literature, but only a few examples are known for the separation of anions which concentrated on anion separation. The removal of toxic elements such as thiocyanate anions by liquid membranes has been of great interest in recent years [14].

In this study, separation and concentration of cobalt from acidic thiocyanate leach solutions containing cobalt–nickel by emulsion liquid membranes using tributyl phosphate (TBP) as extractant was presented. In order to have a better understanding of the dynamics of ELM process, the major parameters influencing the extraction extent of cobalt were experimentally studied and the optimum conditions were determined.

2. Experimental

2.1. Reagents

The liquid membrane phase is composed of a surfactant, an extractant and a diluent. The surfactant is sorbitan monooleate which is a product of Fluka and commercially known as SPAN 80. The mobile carrier is tributyl phosphate which is purchased from Merck, Germany. A commercial kerosene (density 830 kg/m^3 and viscosity 7.3 mPa s at 20 °C) was used as diluent. Commercial kerosene is a complex mixture of aliphatic origin and also contains aromatics about 15% (w/w). Hydrochloric acid, ammonia, ammonium thiocyanate, acetic acid, sodium acetate and all other chemicals were purchased from Fluka and were used directly as-received from the manufacturer.

2.2. Feed solution preparation

The zinc plant copper cake (CINKUR Co., Turkey) consists an average of 15% Zn, 10% Cu, 8% Fe, 2.5% Cd, 0.2% Co, and 0.6% Ni on mass basis was leached with a 2 M hydrchloric acid solution using a solid/liquid ratio of 1/4 at 85 °C for 240 min and was obtained acidic leach solution containing Zn, Cu, Fe, Cd, Co, and Ni ions. In order to obtain relatively rich cakes in this process, except for cadmium, cobalt, and nickel, the other metal ions in the acidic leach solution were gradually precipitated by adding various reagents and adjusting the pH of solution. The decrease of concentrations of Fe, Cu, Zn, ions in the feed solution was not studied. But, it was observed that the corresponding concentrations of Cd, Co and Ni in the feed solution scarcely changed.

After precipitation process, adjusting the pH of leach solution, cadmium was separated by solvent extraction. Final leach solution contained about 525 mg/L Co and 1080 mg/L Ni. Then, ammonium thiocyanate, cobalt, and nickel concentrations and the pH of final acidic leach solution were made as desired by adding ammonium thiocyanate, water and acetic acid–sodium acetate buffer solution. Ammonium thiocyanate was added into the feed mixture to increase the selectivity of cobalt against nickel. Acetic acid/sodium acetate buffer used was essential for cobalt–nickel separation to maintain the desired feed pH, which was very critical. In this work, unless otherwise statement, the pH of acidic thiocyanate leach solution used ELM process is adjusted to 3.75 with acetic acid/sodium acetate buffer. Thus, the acidic thiocyanate leach solutions prepared by dilution of final acidic leach solution were used as feed solution in ELM experiments. In this work, unless otherwise stated, pH and cobalt, nickel and thiocyanate concentrations of the acidic thiocyanate leach solutions used as feed solution in ELM experiments are 5/5, 50/250, 3.75, 100 mg/L Co, 200 mg/L Ni (approximately) and 0.5 M SCN$^-$, respectively.

2.3. Membrane preparation

In 250 mL beaker, a 25 mL portion of TBP and SPAN 80 in kerosene are emulsified at mixing speed of 1800 rpm by a variable speed mixer. 25 mL of 6 M ammonia solution was used as stripping solution. Stripping solution was added dropwise to the stirred membrane solution. The solution was stirred continuously for 20 min, so the mixture of the membrane and the stripping solutions was emulsified.

2.4. Experimental method

In 600 mL beaker, the ELM prepared was added to 250 mL of the feed solution. The contents were stirred by a variable speed mixer equipped with a turbine-type impeller at speed of 400 rpm for extraction time of 30 min. To determine the important variables governing the permeation and separation of cobalt (II) from the acidic thiocyanate leach solution containing cobalt (II) and nickel (II), cobalt (II) and thiocyanate concentrations of the acidic thiocyanate leach solution, pH of the acidic thiocyanate leach solution, mixing speed, base concentration of stripping solution, extractant and surfactant concentrations, phase and treatment ratios were varied to observe their effect on cobalt (II) extraction and separation. At the end of each run, the emulsion was recovered and subsequently broken into its constituents using a high voltage splitter with niobium electrodes.

2.5. Analytical method

The uptake of metal ions was monitored by removing samples of the feed solution periodically for analysis. Determinations of metals (Co and Ni) was made by atomic absorption spectrophotometry (Shimadzu AA-6701F model, Tokyo, Japan) at autosampler operating mode. All the extraction experiments were carried out batchwise at the ambient temperature of 20 ± 1 °C. All aqueous solutions were prepared using deionised water.

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