Journal scientific and applied research, vol. 11, 2017
Association Scientific and Applied Research
International Journal

Original Contribution ISSN 1314-6289

COPPER RECOVERY FROM LOW GRADE ORES, CONCENTRATES AND TECHNOGENIC WASTE BY AMMONIA LEACHING - AN OLD IDEA WITH PROMISING FUTURE

Marinela Panayotova, Vladko Panayotov

UNIVERSITY OF MINING AND GEOLOGY, SOFIA 1700," BOYAN KAMENOV" STR 1, E-MAIL:marichim@mgu.bg

Abstract: *Sustainable development of the society and our everyday life increasingly needs copper. To meet this demand impoverished ores, low-grade concentrates and technogenic waste have to be processed. For these raw materials the classical route "mineral processing - pyrometallurgy" is inapplicable and / or unprofitable. Leaching followed by recovery from the obtained solutions is increasing being applied worldwide. Ammonia leaching is progressively finding its use, especially when ores are carbonaceous and / or oxidized. The paper presents development of ammonia leaching and its nowadays application for copper recovery, including leaching technological conditions, leaching kinetics and means for copper recovery from pregnant leach solutions with an emphasis on solvent extraction and the latest development in the area.*

Keywords: *ammonia leaching of copper, copper hydrometallurgy, solvent extraction from ammonia PLS*

1. Introduction

Hydrometallurgy is a technology for "wet" extraction and recovery of valuable metal components from solid materials. Due to its flexibility (ability to be applied to different relatively small and with changing composition material streams, usability at low metal contents in complex mineralogy) hydrometallurgy takes a wide share of the extractive metallurgy. In addition, basic chemicals needed in hydrometallurgical leaching and extraction from pregnant leach solutions (PLSs) are produced in large tonnages at low prices, and suitable materials for the needed equipment construction, have been developed at reasonable prices. Furthermore, the problems with air pollution by smelters can be avoided.

Generally, different solutions are used in hydrometallurgy (solutions of acids, salts and alkaline reagents - alone, in mixtures, or aided by oxidizing or reducing reagents). Among them, ammonia-based leaching solutions have found their place in hydrometallurgy of nonferrous metals and especially - of copper. Despite of this, the number of publications discussing jointly the leaching conditions and means for copper recovery from PLSs is very scarce.

The present work is devoted to advances in ammonia leaching of copper and recovery from PLSs - applied to different types of ores and concentrates, and to technogenic (pre-consumer) waste. Each class of these raw materials possesses particularities: The gangue material represents the major part in ores, and even in low-grade concentrates. The copper concentration is low. The copper concentration in the technogenic waste is relatively high, however usually other metals in high concentrations are also available.

2. Leaching from ores and concentrates

Copper forms water soluble and very stable ammonia complexes - $[Cu(NH_3)_4]^{2+}$ and that is why it can be easily leached by ammonia water solution. Ammonia leaching was first applied and developed for recovery of copper from its metallic and oxide raw materials. Because very few metals form such complexes, all ammoniacal leaching processes have the advantage of being very selective. Ammoniacal processes are ideal when the gangue minerals are acid consuming (e.g., calcareous or dolomitic). Ammonia leaching was first used at the Kennecott Plant, Alaska, because copper ore contains carbonates in limestone–dolomite gangue which are acid soluble, consequently - increasing the acid consumption [1].

Sherritt Gordon Mines were pioneers in hydrometallurgy with their Ammonia Pressure-Leaching Process which they used for treating nickel concentrates [2]. In laboratory and pilot-plant tests on chalcopyrite, they achieved a 95 % extraction of copper. Most of the unleached copper was floated from the residue and recycled. The leaching was conducted at a temperature of about 105 °C and air pressure of 0.8 MPa. Unsolved solids were separated, the pregnant solution was heated to evaporate excess ammonia. Then the solution was allowed to react with air to oxidize all available thiosulfates (by-products), followed by hydrogen reduction. The flowsheet for the treatment of copper-zinc concentrates is shown in Fig. 1. The generalized stoichiometric equation for the copper dissolution reaction from chalcopyrite ($CuFeS_2$) - the main used ore - can be written as follows:

$$2CuFeS_2+8.5O_2+12NH_3+2H_2O \rightarrow 2Cu(NH_3)_4SO_4+2(NH_4)_2SO_4+Fe_2O_3 .$$

The Arbiter Process (Fig. 2), developed by Anaconda, uses ammoniacal processing at 70-80 °C but eliminates the use of high pressures [2]. In the leaching step, oxygen, instead of air, is used with special agitation techniques that result in good dispersion of the oxygen in the slurry. Use is made of the availability of the liquid-liquid-extraction reagents, such as LIX-group, to extract copper by liquid-liquid extraction followed by electrowinning.

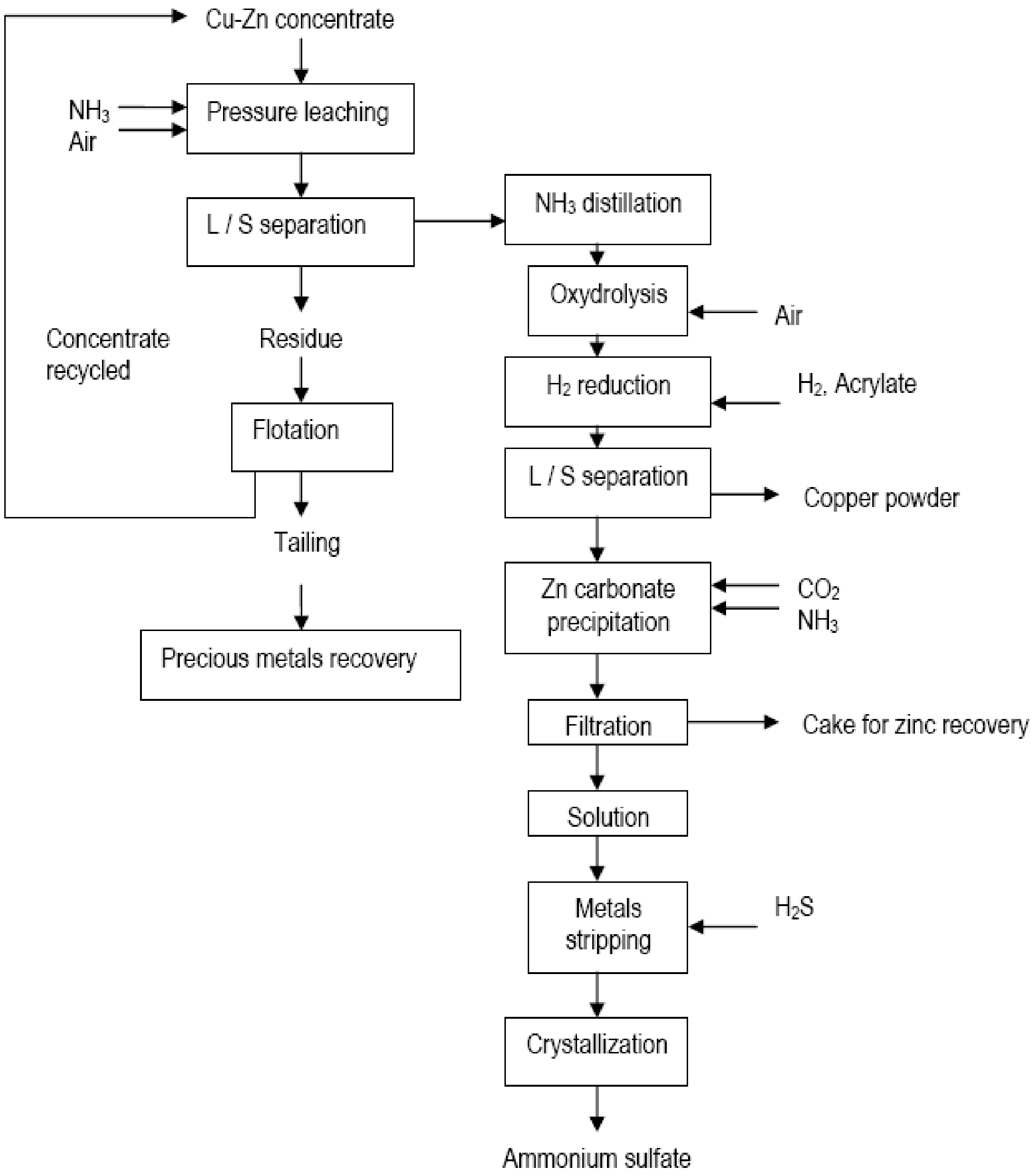


Fig. 1. Flow-sheet of the Sherritt Gordon Ammonia Pressure-Leaching Process

Copper recovery is not complete and unreacted copper has to be floated from the residue. Liquid-liquid extraction using LIX in ammoniacal systems has the advantage over acid systems that the solvent can take higher loadings of copper.

The disadvantage is that LIX is less selective for copper over nickel and zinc than in acid systems, but there are techniques for overcoming this problem. One further potential advantage of the ammoniacal system is that copper can exist in the cuprous form, which makes the possibility of direct electrowinning of the copper from the leach liquor rather attractive, since the power cost would probably only be about 50 % of that from cupric solutions and the cost of liquid-

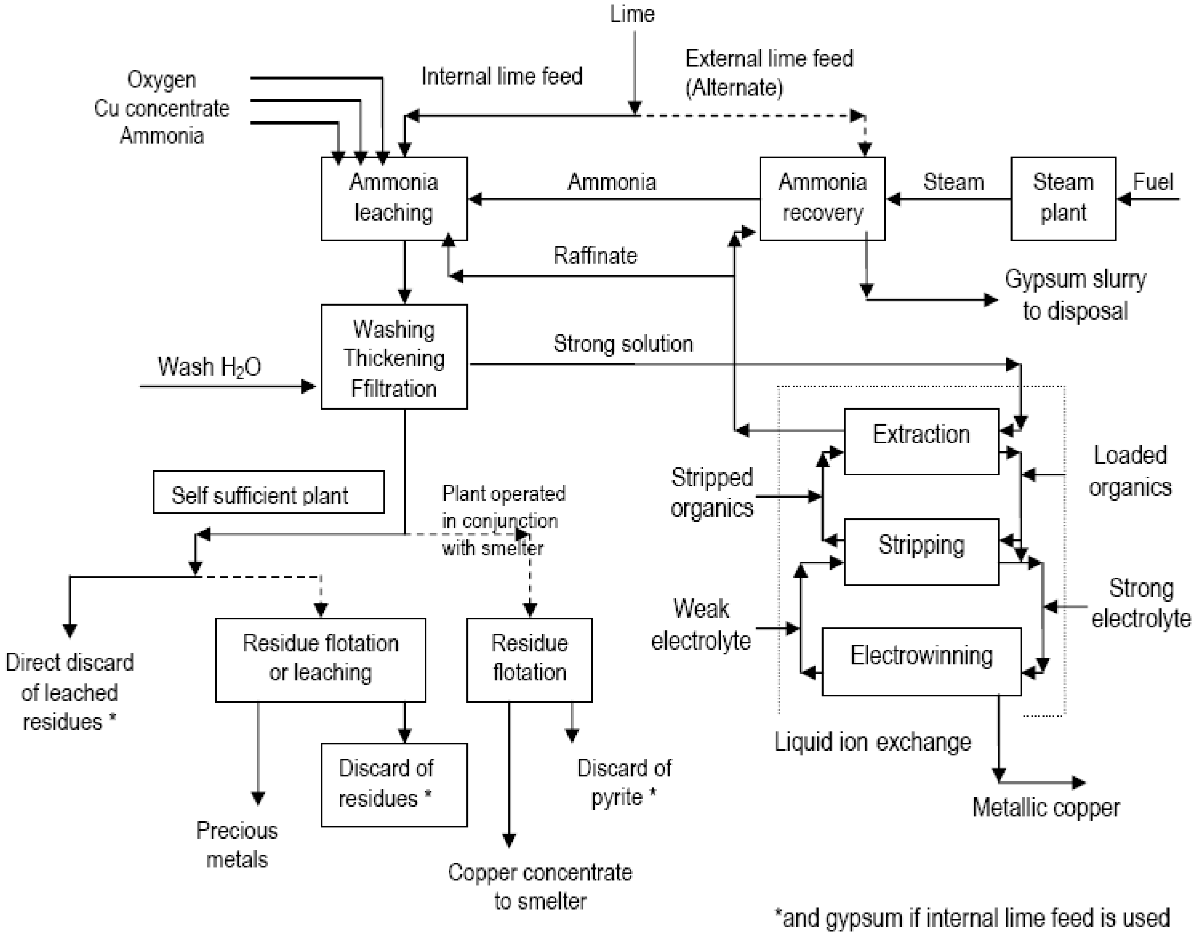


Fig. 2. Flow-sheet of the Arbiter Ammonia Leaching Process

liquid extraction would be eliminated. Electrochemical studies are going on in this direction.

The Arbiter process has been commercialized for copper, the Sherritt process - for nickel.

Together with the establishment of technological schemes, research efforts have been directed to investigate the leaching of copper from systems containing sulfides of other minerals. The oxidation behaviour and dissolution of copper, zinc and lead sulphide minerals and mixtures, and single concentrates has been studied under standard leaching conditions: temperature - from 25 to 135°C, agitation 1080 rpm, ammonia concentration - 3.34 mol/L, ammonium sulphate when added - 0.34 mol/L, and pH - 11.2 [3]. The found sequence of sulphide mineral dissolution from a quaternary mixture of CuS, ZnS, PbS and FeS_2 is the following: PbS > CuS > ZnS. FeS_2 does not react. The solid products formed during the leaching reaction, such as goethite (from oxidation of iron present in chalcopyrite) and oxidised lead compounds, such as $PbSO_4$ and $PbO.PbSO_4$ (due to galena oxidation) remain insoluble in the leach residue along with the unreacted pyrite (FeS_2). However, it has been pointed that the pyrite does become leached to some extent in the presence of Cu_2S. The proposed chemical equations describing the oxidation reactions of CuS, FeS_2 ZnS and $CuFeS_2$ during oxidative ammonia leaching are as follows:

$$CuS + 4NH_3 + 2O_2 \rightarrow Cu(NH_3)_4SO_4$$

$$2FeS_2 + 8NH_3 + 7.5O_2 + (4+n)H_2O \rightarrow Fe_2O_3.nH_2O + 4(NH_4)_2SO_4$$

$$ZnS + 4NH_3 + 2O_2 \rightarrow Zn(NH_3)_4SO_4$$

$$2CuFeS_2+12NH_3+8.5O_2+(2+n)H_2O\rightarrow2Cu(NH_3)_4^{2+}+4SO_4^{2-}+4NH_4^{+}+Fe_2O_3.nH_2O$$

Some authors are classifying the ammonia leaching methods applied to copper ores and concentrates as neutral (the metal is dissolved without aid of any oxidizing or reducing agents), oxidative (where leaching requires the use of an oxidizer to oxidize solids) and reduction (where a reducing agent is used) methods [4].

However, actually leaching without oxidizing reagent can be applied only to materials bearing copper under the form of copper hydroxide. In the case of copper leaching by ammonia (applied mainly to highly oxidized ores such as ocean floor manganese nodules), the reduction method actually represents initial reductive roasting of the material and / or preconditioning of the suspension of the reduction-roasted and grinded materials under reductive conditions. The actual copper leaching reaction is carried out by introducing O_2 / air in the system. In addition of the above described, below are presented some examples of the mentioned types of leaching of copper ores and concentrates by ammonia solution.

A process which can be described as "Leach-precipitation-decomposition - recovery" has been patented [5]. According to the author: (a) the patented process is suitable for recovery of a metals from sulfde ores, especially copper, from chalcopyrite and other copper sulfide ore, and (b) the leaching of chalcopyrite can be carried out under lower temperature and pressure, compared to the above-described processes, there is no water or material balance problem, and the ammonia can be completely recycled.

The process involves the recovery of mineral values from ore using ammonia oxidative leaching wherein the mineral values include at least one metal selected from a preferred group including nickel, copper, cobalt, manganese, molybdenum, tungsten and silver, platinum, palladium, gold, and uranium in the presence of other metals such as iron, aluminum, lead, bismuth, mercury, cadmium, zinc, arsnic, magnesium, beryllium, yttrium, cerium, germanium, antimony, zirconium, tellurium, vanadium, and tin because they precipitate or are not leached by ammonia oxidative leaching. Metals such as sodium, potassium, and lithium which remain in solution through the process can be present. The source material or leach solution must contain a nonhydroxide anion, such as a halide, carbonate, phosphate, or sulfate.

Especially for the case of recovery of copper mineral values from flotation concentrate, or a low grade ore, where iron is present, the preferred anion is sulfate. It can be supplied by sulfuric acid, by a sulfate salt, or by oxidizing sulfur in the source material. According to the author, the invention is applicable not only to ores and concentrates but also to scrap metal, or a combination of ore and scrap metal. In brief, the source material is mixed with an aqueous ammonia leach solution and an oxidizing agent (preferably oxygen, air, or an oxygen bearing gas). The ammonia solution can be fresh solution, solution recycled from subsequent steps, or a mixture of both. The copper is converted to a soluble ammine complex and iron available is oxidized to the insoluble oxide Fe_2O_3. All sulfur in the ore is oxidized to sulfate. Then the PLS is mixed with lime (or slaked lime) to precipitate the excess sulfate and simultaneously to facilitate the separation of iron oxide. After separation of calcium sulfate, iron oxide and unreacted material, mostly silica, the leach solution containing dissolved copper-ammonia-sulfate is next ammoniated, or pressurized with, ammonia or aqueous ammonia to precipitate an unsoluble copper complex ammine. The preferred temperature range was about 15°-40 °C, and the preferred pressure range - 0.12-0.35 MPa. Copper is generally precipitated (according to the inventor) as the copper ammine sulfate monohydrate [$Cu(NH_3)_4SO_4.H_2O$, $Cu(NH_3)_4(H_2O)_2SO_4.H_2O$], and possibly [$Cu(NH_3)_6SO_4.H_2O$]. After a separation step the precipitate passes to a decomposition step (heating to decompose the ammine complex to solid $CuSO_4$, NH_3 and some H_2O). The ammonia can be recycled to ammoniation, washing or reacting (i.e., leaching) steps of the process and the H_2O is-recycled. The decomposition process should be either a gradual heat process or a two-stage heat process to avoid some sulfate decomposition. Decomposition for 30 minutes at 340 °C in a rotary furnace followed by decomposition at 380 °C produces a solid material (anhydrous copper sulfate). Fluid bed decomposition reduces the decomposition time and temperature. Thus obtained solid copper sulfate can be reduced to elemental copper by either of two methods: (a) electrowinning of an aqueous solution of the salt (after dissolving in water) or (b) reduction with hydrogen (at temperatures of 450 °C or higher) to copper powder. The obtained byproduct - a concentrated stream of SO_2 can be converted to sulfuric acid. The overall chemical reaction is represented by the equation:

$$2\ CuFeS_2 + 11.5\ O_2 + 4\ CaO \rightarrow 2\ CuSO_4 + 4CaSO_4 + Fe_2O_3\ .$$

The reactions of the different steps are, as it follows:

$$2CuFeS_2+12NH_3+8.5O_2+2H_2O \rightarrow 2Cu(NH_3)_4^{2+}+4SO_4^{2-}+4NH_4^{+}+Fe_2O_3$$

$$Cu(NH_3)_4^{2+}+2SO_4^{2-}+2NH_4^{+}+CaO+H_2O \rightarrow Cu(NH_3)_4^{2+}+SO_4^{2-}+CaSO_4\downarrow+2NH_4OH$$

$$Cu(NH_3)_4^{2+}+SO_4^{2-}+NH_4OH+H_2O \xrightarrow{NH_3} Cu(NH_3)_4SO_4.H_2O\downarrow+NH_4OH$$

$$Cu(NH_3)_4SO_4.H_2O \rightarrow 4NH_3+CuSO_4+H_2O\uparrow .$$

Ammonia pressure leaching in oxygenated NH_3 + $(NH_4)_2SO_4$ solution has been pointed out as an effective process for leaching of shale middlings with high pyrrhotite (FeS) content, allowing the recovery (at optimum conditions: ammonia concentration > 1.5 M, ammonium sulfate concentration 50 g/L, oxygen pressure: 1.27 MPa, 120 – 160 ºC, 90–120 min) of Cu (> 95 %), Ag (60 %), Ni (70 %), Co (30 %) and Zn (95 %), while Fe and As remain in the solid [6]. Temperature, ammonia concentration, ammonium sulfate concentration, oxygen pressure and stirring rate have been found as the key leaching parameters. Proposed by the authors chemical equations describing the leaching are as follows:

$$2Cu_2S + 12NH_3 + 4NH_4^+ + 5O_2 \rightarrow 4[Cu(NH_3)_4]^{2+} + 2SO_4^{2-} + 2H_2O$$

$$CuS + 4NH_3 + 2O_2 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

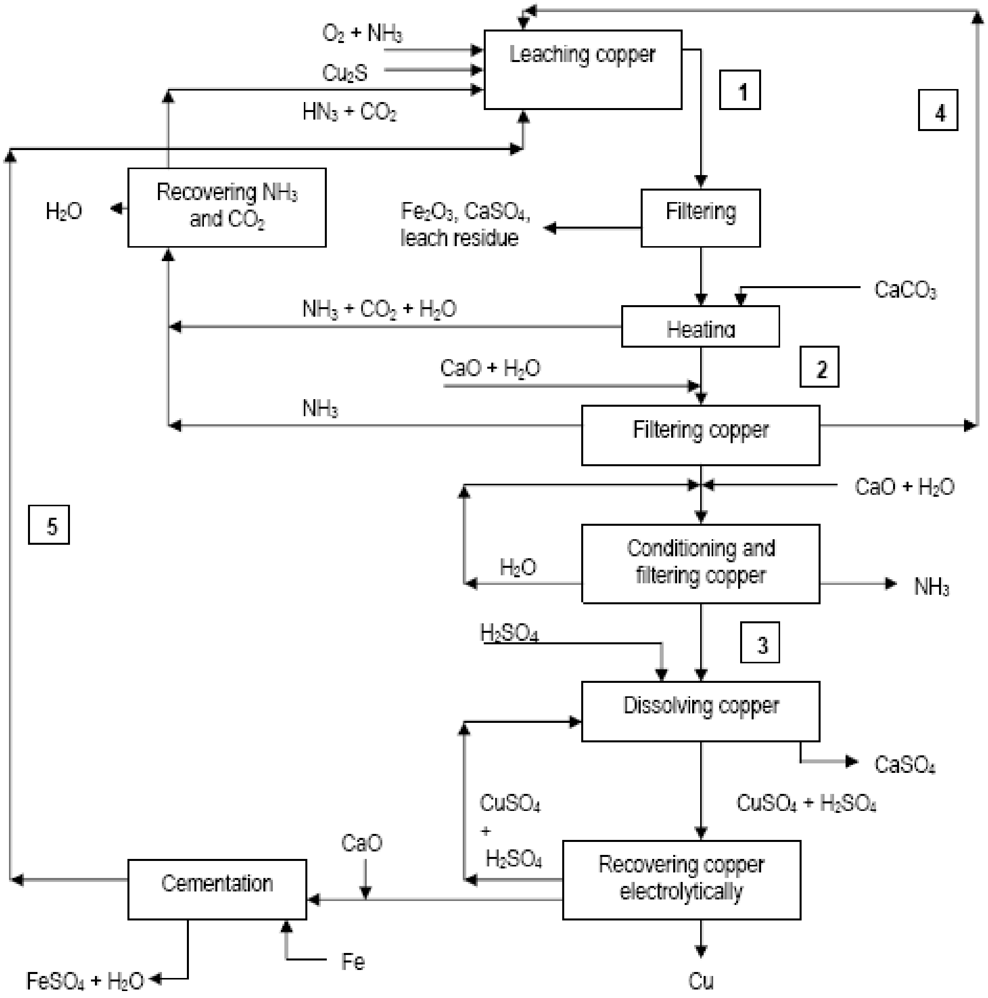
$$NiS + 6NH_3 + 2O_2 \rightarrow [Ni(NH_3)_6]^{2+} + SO_4^{2-}$$

$$2CoS + 10NH_3 + 2NH_4^+ + 4.5O_2 \rightarrow 2[Co(NH_3)_6]^{2+} + 2SO_4^{2-} + H_2O$$

$$4FeS + 6NH_3 + 9O_2 + 4H_2O \rightarrow 2Fe_2O_3\downarrow + 2HSO_4^- + 2SO_4^{2-} + 6NH_4^+.$$

An improved process for obtaining copper from copper sulfide has been proposed [7]. It comprises the following steps: (1) treating the copper sulfide with oxygen and an aqueous leaching solution of ammonium carbonate, to form a leach liquor containing ammonia complexes of copper sulfate $Cu(NH_3)_4SO_4$ and copper carbonate $Cu(NH_3)_4CO_3$; (2) heating the leach liquor, while adding calcium carbonate or calcium bicarbonate, to form gaseous ammonia and carbon dioxide (gases recovering and recycling these gases to the leaching step); (3) treating the leach liquor with a strongly alkaline material to precipitate sulfates and form additional gaseous ammonia; and (4) recovering copper by dissolving the ammonia complexes of copper sulfate and copper carbonate by H_2SO_4 addition, followed by electrowinning and cementation. In the leaching step, temperature and pressure are not critical, the proposed ranges are 60 to 94 ºC and 0.03 to 0.7 MPa, preferably about 77 °C and about 0.35 MPa. In the leaching step, any iron or iron sulfdes which are leached, such as the iron in chalcopyrite, are converted to insoluble iron oxides, such as ferric oxide (Fe_2O_3). The proposed technological scheme is presented in Fig. 3.

The leaching of refractory low grade complex copper ore has been studied in ammonia-ammonium chloride solution [8]. The results have shown that increase in temperature (until 70 ºC), in concentration of ammonia (until 2 mol/L) and in concentration of ammonium chloride (until 3 mol/L) have impacted favorably the leaching rate of copper oxide ores. But, leaching rate decreases with increasing particle size and solid-to-liquid ratio. Actually, following the above-mentioned classification, the leaching described in this



1 = $H_2O + NH_3 + [Cu(NH_3)_4]CO_3 + [Cu(NH_3)_4]SO_4 + (NH_4)_2CO_3 + (NH_4)_2SO_4 + Fe_2O_3 + CaSO_4$ + leach residue
2 = $CaSO_4 + CuO + NH_3 + [Cu(NH_3)_4]CO_3 + [Cu(NH_3)_4]SO_4 + [Cu_4(OH)_6]SO4 + (NH_4)_2SO_4 + H_2O$
3 = $H_2O + CuO + CaSO_4 + [Cu_4(OH)_6]SO_4$
4 = $H_2O + NH_3 + (NH_4)_2SO_4 + [Cu(NH_3)_4]CO_3 + [Cu(NH_3)_4]SO_4$
5 = $H_2O + Cu + CaSO_4 + Fe$

Fig. 3. Flowsheet of an improved process for obtaining copper from copper sulfide

work may be classified as "neutral", since being applied to oxide ores it does not need oxidizing reagent.

Another example of "neutral" leaching is the dissolution of oxide copper ore containing mainly malachite [9]. More than 98% of copper has been effectively recovered at optimum leaching conditions for 120 min by leaching with ammonia/ammonium carbonate solution (5 M NH_4OH+0.3 M $(NH_4)_2CO_3$) at solid / liquid ratio = 1:10 g/mL, 25 ºC, stirring with 300 rpm. During the leaching copper dissolves in the form of $Cu(NH3)_4^{2+}$ complex ion, whereas gangue minerals do not react with ammonia.

The proposed electrokinetic processes for copper leaching could be also classified as a "neutral" leaching [10]. Based on the electrokinetic processes used for soil remediation, the technique suggested consists in the copper dissolution by ammonia solution using an electric field. The ore is mixed with NH_4Cl / NH_3 solution and it is inserted in a five compartment cell between two ion exchange membranes. Then the system acts as an electrodialyser where the ore represents the solution which should be demineralised. Ammonium crosses the membrane from an adjacent compartment to increase the dissolution. An oxidizing reagent is not needed to enhance the copper dissolution. A copper extraction of 98 % was achieved in 400 h. However, the question with electricity source and price still remains.

The reduction-roast ammonia leach process has been developed to recover copper, nickel and cobalt from polymetallic sea nodules [11]. Sea nodules can be described as oxidised ferro-manganese ore containing the mentioned nonferrous metals in their oxide forms. These metal oxides are reported to occur in the lattices of iron and manganese minerals. Therefore, breaking up of these lattices by pyrometallurgical reduction is important. The sea nodules have been roast reduced in the presence of solid, liquid or gaseous reductant to liberate the valuable metal oxides from the phases of iron and manganese oxides. The reduction operation also performs the metallization of copper, nickel and cobalt from their oxides and facilitates subsequent ammoniacal leaching of these metals. The roasted material has been wet ground with dilute ammoniacal solution 50 g/L NH_3 in presence of 25 g/L CO_2. The obtained product has been preconditioned with ammoniacal solution containing 200 g/L NH_3 and 110 g/L CO_2 for 30 min in the absence of air in order to dissolve Fe–Ni and Fe–Co alloys formed during roasting. During the two-stage leaching operation, ammonia and carbon dioxide concentrations of 125 and 62.5 g/L, respectively, have been maintained and air has been sparged at the rate of 2 L/min. In the ammoniacal leaching, the undesired metals such as iron and manganese have been rejected in the residue and valuable metals such as copper, nickel and cobalt are solubilised as their stable ammine complexes. Monitoring of redox potential during first leaching stage can avoid cobalt losses with variation of grade of nodules. Recycle leaching has been carried out to generate leach liquor having suitable composition for the subsequent solvent extraction – electrowinning operation. The average recovery of metals in 16 cycles of leaching has been found to be 92% Cu, 90% Ni and 56% Co.

The further development of the nodules leaching process has been reported later [12]. The aim has been to increase the cobalt recovery. The modifications and developments have included (a) use of coal instead of fuel as the reductant, (b) wet grinding in preconditioning of reduced nodules in concentrated ammoniacal liquor in presence of surfactant, (c) precipitation of Fe and Mn from the preconditioned liquor by air purging, and (d) use of NH_3 – $(NH_4)_2CO_3$ as leaching system at room temperature and air presence. The average metal recoveries of 92.5 % Cu, 91.5 % Ni and 71.3 % Co have been achieved in seven cycles.

3. Leaching from technogenic waste

Feasibility study on the recovery of copper from an industrial petrochemical sludge has been conducted [13]. Sludge is formed in the wastewater treatment plant within the industrial park producing different petrochemical products in Taiwan. It is classified as hazardous waste. Sequential extraction has been used to determine the chemical forms of copper in the sludge. To leach copper from the sludge, aqueous ammonia solution has been used. It has been found that increasing the temperature and solid to liquid ratio increases significantly the leaching efficiency of Cu (from 34 % at 20 ºC and 10 g/L solid concentration to ca. 94 % at 25 ºC and the solid concentration of 20 g/L). The leaching reaction has been completed within 6 h. Copper has been mainly leached from both the organic-bound and residual fractions and to the less extent from Mn oxides-bound fractions. The carbonates bound fraction of Cu is stable. Results suggested that the ammonia-leaching technique possesses the potential to recover metal from industrial sludges.

A method for leaching copper values from copper dross obtained from pyro-metallurgical lead bullion by contacting finely-divided particles of the copper dross with an aqueous solution of ammonium carbonate and ammonium hydroxide has been patented [14]. Where copper is present in the furnace charge of lead smelting it will always be present in the lead bullion, usually in amounts of less than 3 weight % but possibly in amounts up to 15 weight %. Lead is purified in kettles and thus copper containing dross is formed. Dross can be smelted with iron and sulphur, for example in the form of pyrites, to form bullion containing some copper and an iron-copper matte containing some lead. This matte is then converted, the blister copper cast into anodes, and the anodes refined electrolytically, as in conventional copper refning practice. However, the setting up of a plant to operate such a process is scarcely economically. As a best available technique, it has been proposed the copper dross to be treated in an additional reverberatory furnace to form copper-rich matte and speiss and these materials to be sent to copper smelter [15]. This also requires additional spending for equipment and transport. The copper in copper dross appears to be elemental or combined copper, for example, as copper sulphides or arsenides, embedded in a matrix of de-copperized metallic lead. In the patented copper leaching method [14] the leaching solution besides ammonium carbonate and ammonium hydroxide contains sulphate ions. The mole ratio of carbonate to sulphate in the leaching solution should be from 1:3 to 3:1. The presence of the sulphate ions in the leaching solution is believed to give rise to the following advantages: (a) A reduction in the ratio of impurity elements, particularly lead and zinc, to copper in the leachate solution, (b) A reduction in the amount of copper lost in the filter cake after filtration of the residue and (c) A lower partial pressure of ammonia over the leaching solution. The preferred molar proportions of ammonia to ammonium salt are 0.5 ÷4.0 NH_3 to l÷0 $(NH_4)_2X$, where X is a carbonate and / or sulphate, but ratios of about 0.1 to 10:1 may be used. The leaching can be carried out at a temperature between 20° and 100 °C. The preferred pH value of the leaching solution is from 9.5 to 10.5. The copper dross has to be vigorously agitated during the leaching process. Preferably the leaching solution contains at least 5 grams of Cu^{2+} per liter, since it has been found that the reaction proceeds more rapidly in the presence of cupric ions. The leaching solution may be produced by carbonating ammoniacal liquor with carbon dioxide, for example from a smelting furnace. Recovery of the copper can be carried out by a solvent extraction process using hydroxy oxime reagents from LIX series, dissolved in kerosene. From organic phase copper is re-extracted back into an aqueous solution by contact with dilute sulphuric acid. The organic reagent is recycled to the process. The aqueous copper sulphate solution is utilized in the production of copper sulphate crystals by an evaporation / crystallization process or as an electrolyte for the production of cathode copper by electrowinning. Also copper powder can be recovered by treatment with a reducing agent.

4. Kinetics of copper dissolution in ammoniacal solution

The kinetics of copper dissolution in ammoniacal solution has been widely studied. Only several examples will be mentioned here. According to some studies [8], the leaching of copper oxide ores in NH_3-H_2O-NH_4Cl solution can be described by the shrinking core model. According to this model, the reaction takes place on the outer surface of the solid and this surface shrinks toward the center of the solid as the reaction proceeds, leaving behind an inert solid layer, named “ash layer”, around the unreacted shrinking core. The leaching process is controlled by the diffusion of the lixiviant through the ash layer around the shrinking unreacted core. The authors derived a mathematical equation, describing the process kinetics, which equation involves the fractional conversion of malachite, the lixiviant concentration (ammonia and ammonium chloride), the solid-to-liquid ratio, the temperature, and the leaching time. Ekmekyapar et al. [16] studied the dissolution kinetics of malachite ore in ammonium chloride solutions and suggested that the dissolution rate is determined by a mixed control (with both diffusion and kinetic limiting stages). They have proposed a mathematical model to represent the reaction kinetics, which model includes the reacted fraction of the solid, the ammonium chloride concentration, the particle diameter, the solid to liquid ratio, the stirring speed, the reaction temperature and the reaction time. Bingöl and coauthors [9] found that the interface transfer and diffusion across the product layer control the leaching of malachite in ammonia/ ammonium carbonate solution.

We would join the understanding that in fact, the dissolution process is electrochemical in nature, which was proposed in the 1960s by Habasi [17] and reconfirmed recently [18, 19].

The leaching of a mineral can be explained as electrochemical, i.e. oxidation-reduction reaction. When a metal or a semi-conductor comes into contact with an aqueous phase, containing a reagent (such as oxygen) with high oxidation-reduction potential, this reagent acts as depolarizer (i.e. takes up electrons, released by other reaction). The reaction releasing electrons is actually the dissolution (oxidation) of the targeted metal (from virtually clean metal or from ore, or concentrate). Both reactions can not proceed in practice without each other. Whether anodic (dissolution) and cathodic (reduction) reactions will proceed on separated micro-zones or on the same zone on the surface of the dissolving solid material will depend on the mineral surface micro-heterogeneity. The oxidized (dissolved) species (copper ions in our case) may further participate in chemical reactions on the surface of the leached material, mainly with the complex-forming reagents, but some equilibrium reactions can also take place, as in the case with copper leaching:

$$[Cu(NH_3)_4]^{2+} + Cu \leftrightarrow 2[Cu(NH_3)_4]^{+}$$

Concerning the theoretical equations derived to describe the electrochemical nature of the dissolution processes at leaching, different proposals are available due to different understanding of the meaning of the term "mechanism" [18]. Joining the more common definition of mechanism of reactions as the pathway by which the reaction occurs, we would accept as more general and comprehensively considering different factors, the theoretically derived equation [19] that describes sulfides leaching processes, and actually takes into account the possibility of diffusion and chemical control of the total leaching reaction. The former could be understood also as availability of the oxidizing agent (which will be reduced) and the latter as availability of the reagent, which facilitates the oxidation of the component which is being leached (in the case of leaching with complexes forming, this is the complexing agent). In this line, the rate of dissolution can be expressed by the equation:

$$\text{Rate of dissolution} = (k_1\, k_2\, A\, C_{Ox}\, C_{Co}) / [k_1\, C_{Ox} + k_2\, C_{Co}]\ ,$$

where A is the surface area of the solid in contact with the liquid phase, C_{Ox} is the concentration of the oxidizing reagent (depolarizer), C_{Co} is the concentration of the complexing agent, k_1 and k_2 are rate constants of the reduction and the complexation reactions, respectively. There are two borderline cases:

When the concentration of C_{Co} is low the second term in the denominator may be neglected in comparison with the first, and the rate equation simplifies to

$$\text{Rate of dissolution} = k_2AC_{Co}$$

i.e., the rate of dissolution in this case is only a function of the complexing agent concentration.

When the concentration of C_{Co} is high, the first term in the denominator may be neglected in comparison with the second, and the rate equation simplifies to:

$$\text{Rate} = k_1 A C_{Ox}$$

i.e., the rate of dissolution under these conditions depends only on the concentration of the depolarizer.

Since the speciation of ammonia in aqueous solution is determined by pH, it is expected that in general, the leaching efficiency is dependent on pH. Acknowledging that the acidity constant of the (conjugate acid) $NH_4^+{}_{(aq)}$ equals to $10^{-9.25}$, the major species in solution is $NH_4^+{}_{(aq)}$ when pH is lower than 9.3 [20]. The complexation reaction of $Cu^{2+}{}_{(aq)}$ can occur only with $NH_{3(aq)}$, not with $NH_4^+{}_{(aq)}$ [21].

5. Copper recovery from leachate - emphasis on solvent extraction

Generally, from PLS copper is recovered by one of the following processes:

- Precipitation of Cu bearing compounds followed by their dissolution and electrowinning;
- Chemical reduction with hydrogen, or with less noble metal;
- Direct electrowinning;
- Ion exchange with resins / elution, followed by electrowinining;
- Extraction / re-extraction, followed by electrowinining.

Examples for the first mentioned recovery route are presented in some above-mentioned works [5, 7], and for the second - in [2, 5, 14].

The last technique (extraction / re-extraction / electrowinining) is mainly applied nowadays in the practice. The technique was introduced in 1960s - initially to extract copper from acidic PLSs.

5.1. Classical solvent extraction

The beta-diketones are preferred extraction reagents for copper from ammoniacal solutions because of their low ammonia loading properties. Different water-immiscible liquid hydrocarbon solvents can be used in the copper recovery process to form the organic phase in which the extractant is dissolved. These include aliphatic and aromatic hydrocarbons such as kerosenes, benzene, toluene, xylene and the like. The choice of essentially water-immiscible hydrocarbon solvents or mixtures for commercial operations depends on a number of factors, including the plant design of the solvent extraction plant, (mixer-settler units, extractors) and the like.

In the case of multicomponent solutions, extraction of metals can be carried out in two ways. The first one is selective sequential extraction –

stripping, while the second one is co-extraction – selective stripping. Very often it appears that the second method is more cost-effective, because it requires less stages comparing to the first way of separation. The concept of co-extraction (selective stripping) has been used in ammonia systems for Cu-Ni separation.

In general, extraction equilibrium between Cu^{2+} and a chelation extractor can be presented as follows:

$$[Cu(NH_3)_4^{2+}]_{(aq)} + 2HR_{(org)} \leftrightarrow CuR_{2(org)} + 2NH_4^+{}_{(aq)} + 2NH_{3(aq)}$$

in which $HR_{(org)}$ represents extractor in the organic phase, $CuR_{2(org)}$ extractor-copper complex in organic phase, $[Cu(NH_3)_4^{2+}]_{(aq)}$ amine-copper ion complex in aqueous phase. Considering that extraction reaction is reversible, it can be expected that the increase of ammonia or ammonium ion concentration in the aqueous phase will deteriorate extraction.

LIX63 (a water insoluble 5,8-diethyl-7-hydroxy-dodecan-6-oxime in a high flash point hydrocarbon diluent) was the first extraction agent used in ammonia solution. It showed a high efficiency in the extraction of copper from ammoniacal solutions, however, due to difficult stripping process, it was not considered by the industry. Other extractor under study was the LIX64N (cheaper than LIX63), which was commercially only used for the recovery of copper from an ammoniacal solution in the Arbiter Process.

An organophosphorous acid extractor D-2-ethyl hexyl phosphate (P204) has been synthesized and studied, however, due to its high solubility in alkaline solution its commercial use in ammoniacal solution is impossible [4].

A beta-D-ketone extractor named LIX54 was developed later. It possess high extraction potential for copper and a low loading capacity for ammonia, and copper strip from it needes low concentrations of the acid. In 1995, Escondida in Chile used this extractor for extracting copper from an ammoniacal solution on a pilot scale. However, due to LIX54 deterioration (which might be a result from the reaction between a keto-group of LIX54 and ammonia to generate ketimine), the copper in loaded organic phase was difficult to back extract. LIX54 was considered inappropriate for copper extraction from ammoniacal solution under the pilot plant conditions and the plant was closed [22].

LIX973N that is a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime, the salicylaldoxime being in excess with respect to the former component, diluted in Iberfluid - a kerosene type reagent has been studied for copper recovery from diluted ammoniacal-ammonium carbonate media [23]. The loaded organic phase has been found to pick up some ammonia, which can be selectively stripped at controlled pH.

Some studies have shown that LIX84 (2-hydroxy-5-nonyl-acetophenone oxime) possesses higher loading capacity for copper and nickel than LIX64 (under identical conditions) accompanied by less ammonia extraction [24]. Moreover, since the extraction of copper does not vary considerably with pH, while nickel extraction in 10 % LIX84 shows significant variation with pH, it is possible to extract copper in preference to nickel from their mixed solutions, leaving Co(III) in raffinate.

LIX84 – 40 vol.% diluted with kerosene, mainly aliphatic, has been applied to ammoniacal–sulphate leach liquors obtained from a copper–nickel–iron concentrate [25]. The leach liquor contained (in g/L) 13.8 Cu, 10.7 Ni, 90 NH_4OH and 45 $(NH_4)_2SO_4$. Two counter-current stages have been used at an aqueous to organic phase ratio of 1 : 2. Copper and nickel have been co-extracted quantitatively. Some ammonia has passed to organic phase and has been removed (at 99 %) prior to nickel stripping in a single stage scrubbing step using 6.6 kg/m^3 H_2SO_4 solution. From the NH_3-depleted organic, nickel was selectively stripped in four counter-current stages at an A:O phase ratio of 2:1. From the ammonia depleted and Ni-free loaded organic phase, copper has been stripped in three counter-current stages at equal phase ratio using the spent copper electrolyte containing 30 kg/m^3 Cu and 180 kg/m^3 H_2SO_4.

Studies have shown that by using 10% v/v (diluted with deodourised kerosene) of the reagent LIX 984N, which is a 1:1 mixture of LIX 84 and LIX 860N (mixture of 5-dodecylsalicylaldoxime and 2-hydroxy 5-nonyl-acetophenone oxime) both copper and nickel can be extracted from ammoniacal / ammonium carbonate medium [26]. Extraction of nickel is very sensitive to the extractant concentration. By using an appropriate concentration of the extractant, both metals are quantitatively extracted. Since some ammonia passed to the organic phase, it is removed by a single stage pH-controlled scrubbing with no loss of either metal. Selective nickel stripping from the ammonia free organic phase has been achieved in three stages with nearly 10 g/L sulfuric acid. The organic phase free from nickel has been subjected to stripping using 180 g/L of sulfuric acid in order to remove copper quantitatively. Thus, the separation of the two metals has been accomplished.

The chemical equation in the case when ammonia from aqueous phase may be extracted in the form of $[Cu(NH_3)_4^{2+}]R_{2(org)}$ can be written as follows:

$$[Cu(NH_3)_4^{2+}]_{(aq)} + 2HR_{(org)} \leftrightarrow [Cu(NH_3)_4^{2+}]R_{2(org)} + 2H^+_{(aq)}$$

in which $HR_{(org)}$ represents extractor in the organic phase, $[Cu(NH_3)_4^{2+}]_{(aq)}$ is the amine-copper ion complex in aqueous phase and $[Cu(NH_3)_4^{2+}]R_{2(org)}$ is the extraction compound of $[Cu(NH_3)_4^{2+}]$ and extractor in the organic phase [4].

It has been found that the increase of pH of the aqueous phase or extractant concentration in the organic phase is not necessarily beneficial for extraction [27]. The reason for this is that both parameters favour ammonia transfer to the organic phase. The type of hydroxyoxime extractant and diluent and content of metal in the organic phase can also significantly contribute to ammonia extraction. The observed phenomenon should be avoided. Otherwise, at a contact of loaded organic phase containing ammonia with a spent electrolyte used for re-extraction, ammonium sulfate (or carbonate, or chloride) can be formed in liquors directed to electrowinning section.

Ammonia transfer to the organic phase represents the main disadvantage of metals extraction from ammonia solutions. Scrubbing of the loaded organic phase before stripping with spent electrolyte is usually applied to significantly reduce ammonia concentration in strip liquors. To decrease ammonia extraction in the organic phase compared to LIX84, stearically hindered beta-D ketone has been synthesized and used [28]. In this study, under the temperature 25 ºC, 30 min contact time of two phases, phase ratio of 1:1, Cu concentration of 3 g/L, 3 mmol/L total ammonia concentration, water pH of 8.43 and beta-D ketone concentration in organic phase of 20 vol %, ammonia from the water phase has been far less extracted by the organic phase (only 14.5 mg/L, while the copper extraction rate was 95.09 % (a slightly less than with LIX 84).

An improvement in the process of recovery of copper from aqueous ammoniacal solutions has been patented [29], where the copper values are extracted from the aqueous ammoniacal solution by an organic phase comprised of a diketone copper extractant dissolved in a water-immiscible organic hydrocarbon solvent with addition (0.5 mole % with respect to the diketone) of a catalytic amount of an hydroxy-aryl-oxime. Improved stripping results were achieved by applying aqueous acidic stripping solution. The preferred solvents are the aliphatic or aromatic hydrocarbons having flash points of at least 66 ºC, and solubilities in water of less than 0.1 weight % . The solvents are essentially chemically inert. Representative commercial available solvents are ChevronTM ion exchange solvent, EscaidTM 100 and 110, NorparTM 12; ConocoTM C1214, Aromatic 150, etc.

Extraction of copper(II) from ammonia leach solutions generated in pressure ammonia leaching of commercial flotation concentrate has been studied [30]. The PLS (with pH 9.7) contained 8 g/L Cu(II), 0.58 g/L Zn(II), 15 mg/L Ni(II) and 45 mg/L Co(II). The commercial extractants LIX84-I, LIX®984N and LIX 54-100 have been tested. The active substance of LIX84-I is 2-hydroxy-5-nonylacetophenone oxime. LIX®984N is a mixture of oximes: 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime. The active substance of diketone type extractant LIX 54-100 is 1-phenyldecane-1,3-dion. Escaid®100, Exxsol D80 and toluene (POCh Gliwice) have been used as diluents. Significant differences in extraction performance have been observed for examined extractants. This applies particularly to the organic phase loading, concentration of copper(II) in raffinates and number of theorethical stages required to reach target extraction. The results clearly have indicated that in the case of systems using hydroxyoximes extraction efficiency is much better than for β-diketone reagent. The results have proved that extraction efficiency of Cu(II) is also dependent on the type of diluent and is less favorable for the systems with non-aliphatic diluents. It has been observed that transfer of ammonia increases with the increase in aromatic compounds content in the diluent. The ammonia extraction to the organic phase has been found to be inversely proportional to extractant concentration in organic phase. The presence of ammonia in the organic phase requires its elimination before stripping. It has been found that the effectiveness of washing depends on acidity of scrubbing solution and the number of washings.

Often copper leached from its dross as tetra-amino-copper(II)-carbonate complex in the solution is further processed through a solvent extraction process, using LIX-54 as a solvent and sulphuric acids as stripping agent to generate copper sulfate solution of the desired grade. Due to limited availability of LIX-54, performances of other solvents based on commercial cinnamate and β-diketone groups have been evaluated [31]. Both solvents and LIX-54 have been compared in fields of effective organic concentration, effective loading, extraction kinetics, extraction isotherms, stripping activity. Arol-light has been used as hydrocarbon diluent, studies have been conducted at ambient temperature. The optimized lab-scale values are 20 % organics' concentration, 20 g/L Cu, 35 s, one theoretical stage for extraction and stripper acidity of 120 g/L respectively. Under these conditions, >98 % of copper has been extracted. The performance of the new solvents has been tested at bench scale level in a mixer-settler with parameters optimized at lab-scale experiments. Feed copper concentration in PLS has been 10.7 g/L. Both the solvents have been found to work effectively with extraction and stripping efficiencies being > 98 %. Based on the results, β-iketone based solvent has been selected as a substitute for LIX 54-100. The changeover has shown a 33% increase in production volumes of copper sulfate.

5.2. Liquid membrane extraction

Solvent extraction is the preferred technique for copper recovery from PLSs since it offers many advantages such as absence of sludge formation, greater ease and flexibility of operations, ability to handle wide range of feed concentrations, choice of solvents to control selectivity of separation, etc.

With the depletion of high-grade ores along with a growing demand for metals, the utilization of low-grade ore has gained interest in recent years. Their leaching produces solutions with relatively low concentrations of valuable metals. Despite state-of-the-art processes for metals separation, solvent extraction for processing low-concentration solutions is no longer economical due to the large amounts of solvent, extractant and strippant required and sizeable equipment needed. For example, it has been found that the effectiveness of solvent extraction significantly depends on the copper concentration in PLS. A high copper extraction has been achieved by Alguacil and Alonso [32] from an ammoniacal / ammonium sulphate medium, using the LIX54 as extractant in two-extraction stages at an aqueous : ganic phase ratio of 2:1 and the copper content has been reduced from 1 to 0.01 g/L. However, if the concentration of copper in leach solution is lower (0.29–0.77 g/L), the use of two stages of extraction and one stage of stripping only allows a 40–50% recovery of copper.

Coupled with this are the possibilities of solvent carry over, solvent losses, inefficient stripping, etc. that lead to poor performance.

Compared to conventional solvent extraction, the liquid membrane technology offers advantages such as the relatively small volume of organic phase consumption, higher extraction efficiency of target metal ions from dilute solutions, more effective separation of elements with similar properties, simultaneous extraction and stripping within a single step, simple operation, and ease of scale-up.

The liquid membrane (LM) system involves a liquid which is an immiscible with the source (feed) and receiving (product) solutions and serves as a semipermeable barrier between these two liquid and gas phases. Liquid membrane separation is a rate-dependant process and the separation occurs due to a chemical potential gradient, not by equilibrium between phases [33].

The bulk liquid membrane (BLM) consists of a bulk aqueous feed and receiving phases separated by a bulk organic, water-immiscible liquid phase. The feed and receiving phases may be separated by microporous supports or the module configuration may be without microporous supports. Many BLM technologies have been developed and tested in the last decade grounded on membrane-based nondispersive (as the means for blocking the organic reagent from mixing with the aqueous feed and strip solutions) selective extraction coupled to permselective diffusion of solute-extractant complexes and selective stripping of the solute in one continuous dynamic process. The systems presented by the term membrane-based (or nondispersive) solvent extraction describe, as a rule, dynamic LM processes in which the equilibrium-based solvent extraction (forward and back) are only local processes taking place on the interfaces of the immiscible phases (on the surface of membrane support).

Membranes in a contactor act as a passive (not selective) barrier and as a means of bringing two immiscible fluid phases (such as an aqueous liquid and an organic liquid) in contact with each other without dispersion. The phase interface is immobilized at the membrane pore surface, with the pore volume occupied by one of the two fluid phases that are in contact.

Liquid impregnated (or immobilized) in the pores of a thin microporous solid support is defined as a supported liquid membrane (SLM). In the liquid are the carriers that perform the required separation. The SLM takes a chemical species from one side of the rigid membrane (the source phase) and carries it to the other side (the receiving phase) through this liquid phase. The SLM may be fabricated in different geometries. Instability in SLM is caused by the removal of carrier or organic liquid from the pores of that membrane. There are two possible ways for this to occur: carrier or solvent evaporation and a large pressure difference across the membrane that effectively pushes the fluid out. The hollow fiber and spiral wound modules are the mainly used SLM.

An emulsion liquid membrane (ELM) can be visualized as consisting of a "bubble within a bubble". The inner most bubble is the receiving phase, and the outer bubble is the separation "skin" containing the carriers. Anything outside the bubble is the source phase. In an ELM set-up there would be huge numbers of these bubbles. Initially, a water-in-oil emulsion is prepared by mixing a solvent phase (diluent, extractant and surfactant) with a stripping aqueous phase. The emulsion is then dispersed in the aqueous feed phase containing the solute to be removed. During this contact the solute is transported through the membrane towards the internal droplets of stripping phase. After permeation, the emulsion is separated from the raffinate phase and the splitting of the emulsion is usually performed by applying high voltage. The disadvantages of ELM are related to the formation and stability of the emulsion: (a) Everything effecting emulsion stability must be controlled, i.e. ionic strengths, pH, etc. (b) If, for any reason, the membrane does not remain intact during operation, the separation achieved to that point is destroyed, and (c) In order to recover the receiving phase, and in order to replenish the carrier phase, the emulsion has to be broken down easily. This is a difficult task, since in order to be used for the extraction the emulsion has to be stable and measures have to be taken for its stabilization. These two contradicting factors must be carefully balanced.

A non-dispersive solvent extraction (NDSX) processing using LIX 973N in Iberfluid as copper extractant phase has been pointed as a technological alternative for copper extraction from dilute copper ammoniacal / ammonium carbonate medium [34]. In the NDSX processing, hollow fiber modules are used as separation contactors in which a microporous hydrophobic membrane separates two liquid phases. Metal extraction is performed in one module, in which the aqueous feed phase flows through the tube side of the fibers and the organic phase through the shell side, without phase dispersion, thus avoiding emulsion formation and phase entrainment. A second module is used to perform metal stripping from the loaded organic solution. Copper stripping is accomplished using sulphuric acid solution. It has been found that aqueous pH, ammonium carbonate concentration, copper concentration, extractant concentration, organic phase volume barely impact the extraction, whereas the module configuration (counter- or co-current) has a significant impact.

The recovery of copper from ammoniacal medium using NDSX with hollow fibres as contactors and emulsion liquid membranes (ELM) has been studied [35]. The β-diketone LIX54 has been used as an extractant. It has been found that when the concentration of LIX54 was 0.2 mol/L and the initial concentration of copper in the feed phase was 0.3 g/L the extraction process was controlled by diffusion in the aqueous boundary layer. When the concentration of LIX54 was in the range of 0.015–0.10 mol/L, the extraction process was controlled by chemical reaction and diffusion in the aqueous boundary layer. The results, obtained by an integrated extraction-stripping process using two hollow fibre contactors, have shown that practically all the copper content can be removed from the ammoniacal feed solutions with low copper concentration (1 g/L). Raffinates with marginal concentration of copper have been obtained. The recovery of copper as high as 96–100% and concentration ratios of about 40-fold can be achieved. At this concentration range the application of "classical" solvent extraction process requires a large amount of solvent. The removal and the recovery of solute by applying the emulsion liquid membranes have been slightly lower compared to the NDSX.

Yang and Kocherginsky [36, 37] have studied the removal and recovery of copper from copper-containing ammoniacal solutions by developing a hollow fibre SLM system. Kerosene has been used as the diluent and LIX54 has been used as the carrier for copper. The optimum stripping phase concentration has been found to be 2 MH_2SO_4. In this arrangement, the solute has been transferred from the aqueous feed phase (lumen side) to the stripping phase (shell side) through the fibre membrane impregnated with LIX54. The experimental results have shown the possibility to reduce the concentration of copper of the aqueous feed phase from several hundred mg/L to values lower than 5 mg/L. The transport of the Cu-carrier complex through the hollow-fiber SLM has been determined as the rate-limiting step of copper permeation through the hollow-fiber SLM. The stoichiometry of the interfacial reaction taking place at the feed phase / SLM interface can be described by the equation

$$Cu(NH_3)_4Cl_2 + 2LIX \rightarrow Cu(LIX)_2 + 2NH_4Cl + 2NH_3 .$$

The interfacial reaction taking place at the SLM / stripping phase interface can be described by the equation

$$Cu(LIX)_2 + H_2SO_4 \rightarrow CuSO_4 + 2LIX .$$

The authors used the same membrane module almost for one month. In the first two weeks the mass transfer coefficient decreased by an half. But, in the next two weeks, it had remained constant. This fact, together with the high area of contact of the hollow fibre contactors led the authors to suggest the use of the hollow fibre SLM system for industrial application.

A SLM system for the simultaneous and selective separation of copper, cobalt, and nickel from ammonia / ammonium chloride solutions, using a two-membrane-three-compartment cell (sandwich SLM) has been proposed [38]. The model uses two polyvinylidene difluoride (PVDF) membranes both loaded with 20 vol.% Acorga M5640 in kerosene. Acorga M5640 (a hydroxyoxime) is one of the most widely-used salicylaldoxime derivatives applied as an extractant on commercial levels because of its excellent extraction ability of copper in both acidic and alkaline (ammoniacal) media. Experimental results have indicated that from PLSs copper and nickel have been transported through the first membrane into the central compartment (containing 5.0 g/L H_2SO_4), while cobalt has remained in the first (feed) compartment. Then copper has continued to penetrate through the second membrane into the third compartment (containing 50.0 g/L H_2SO_4), while nickel has remained in the second compartment. More than 99.5% of cobalt, 98.0% of nickel, and 98.9% of copper have been separated into the three different compartments from a mixed feed solution containing 100 mg/L of each of these three species with a transport time of 36 h, thus showing that copper, nickel, and cobalt in ammonia solution can be efficiently separated.

Extraction of copper from ammoniacal medium into ELM using LIX54 and LIX84-I as extractants has been studied [39]. The membrane phase consisted of a paraffinic solvent (Shellsol T, Shell Chemical Ltd.), 2 wt.% of a non-ionic surfactant (polyamine ECA 4360J, Essochem Europe Inc. or Span 80 - sorbitan monooleate, ICI, Spain) and the extractant. The results obtained have demonstrated the effectiveness of LIX54 and LIX84-I as extractants for copper recovery from ammoniacal medium using ELM, however some problems (associated with emulsion breakage) have been encountered with LIX84-I as carrier.

Since LIX84-I (2-hydroxy-5-nonyl-acetophenone oxime) is a popular copper extractant and is a stronger copper extractant than LIX54, experiments have been carried out to develop a processes where LIX84-I could be effectively used as carrier in ELMs for extraction of copper from ammoniacal /ammonium sulfate solutions, with the aim to avoid the above-mentioned problems. Kerosene, having boiling temperature range 152 °C – 271 °C, density of 821.3 kg/m^3 and containing n-paraffins (27.1%), naphthenes (55.9%), aromatics (16%) and olefins (1%), has been used as the membrane material and Span 80 (Sorbitan monooleate) - as the emulsifier [40]. The extraction process has been very fast and almost quantitative extraction has been observed in most cases in just two minutes contact between the feed and the emulsion phases. The optimal pH for extraction has been found to be pH 8.1, which limited the free ammonia transport through the membrane. It has been found that the loading capacity of the membrane governed the extraction rates. High carrier concentration and treat ratio (the ratio of continuous phase to emulsion) led to faster recoveries. Even when copper concentration in feed solutions was >3000 mg/L, extraction with ELMs containing 10% (v/v) LIX84-I in the oil phase and a treat ratio of 1:6 have resulted in almost 88% copper recovery in just three minutes of contact. Other physico-chemical factors like stripping, diffusion of the oxime complex, globule size and drop size distributions were of secondary importance in the overall extraction process. These parameters become important only when membrane loading approaches saturation. Attempts to enhance extraction capacity of emulsions by increasing the stripping phase volume fraction have not yield positive result. It has been found that the increase in carrier concentration and emulsion hold up was always favorable for copper extraction.

6. Conclusion

Ammonia leaching of low grade copper-bearing ores, concentrates and technogenic waste is becoming more important with the ores impoverishment, requirements to deal with the technogenic waste and the increasing need of metals.

The advantags of ammonia leaching over acidic leaching can be summarized as follows:

- Leaching in the alkaline solution enables the use of ores with high carbonation, which cannot be used in acidic leaching due to high consumption of acid.
- Selective capacity for ores bearing iron and manganese in high amounts, since these metals do not dissolve and do not form complexes in this medium. The high solubility of iron and manganese in acidic media leads to high consumption of reagents and a non-economic leaching process. In addition, jarosite may be formed which could reduce the heap permeability in heap leaching.
- Significant decrease, even practically elimination of problems associated with equipment corrosion.
- Problems, associated with formation of non-filterable precipitates during pH adjustment at acid leaching factory are avoided.
- Ammonia leaching is generally more appropriate for heap leaching of low-grade ores and reservoir leaching of high grade ores, although this choice also depends on the grade and the amount deposited, partially due to the following:

- In ammonia leaching calcium carbonate is not dissolved, like it is the case in acidic leaching, thus preventing additional use of acid and gypsum precipitation, the latter eventually leading to reduction in the heap permeability.

- Ammonia does not react with different soluble ferrosilicates and / or alumosilicates, thus formation of secondary compounds that could decrease the heap permeability is avoided.

- Problems associated with heap washing, neutralization and long-term monitoring to prevent acid runoff are minimized. Additionally, the residual ammonia in the soil can act as fertilizer for growing plants.

Ammonia high evaporation ability posing more handling difficulties during transportation and use and still lower capacity of market-available reagents to extract copper from ammonia medium, compared to acidic one, can be pointed as the major disadvantages of this leaching medium.

The above-presented and discussed examples of application of different ammonia-based leaching solutions to various raw materials, under different technological conditions, can be used as a basis for further studies and applications of ammonia leaching to other copper-bearing raw materials, as well as to other raw materials containing non-ferrous metals able to form stable ammonia complexes. The presentation and discussions on the different liquid-liquid extraction reagents and different techniques, applied to extract copper from ammonia PLSs, may be useful basis and starting point in studies aimed at finding the optimum way for recovery of non-ferrous metals from various liquid phases.

7. References:

[1]. Habashi F., Principles of Extractive Metallurgy, vol. 1, New York, Gordon and Breach Science Publishers, 1983.

[2]. Paynter J. C. A review of copper hydrometallurgy. J. of the South African Institute of Mining and Metallurgy, 1973, November, 158-170.

[3]. Rao K. S., Ray H. S. A new look at characterization and oxidative ammonia leaching behaviour of multimetal sulfides. Minerals Engineering, 1998, vol. 11, No. 11, 1011-1024.

[4]. Radmehr V., Javad Koleini S. M., Khalesi M. R, Mohammadi, M. R. T.J. Ammonia Leaching: A New Approach of Copper Industry in Hydrometallurgical Processes. Inst. Eng. India Ser. D, 2014, vol. 94, No 2, 95–104.

[5]. Fonseca A. G., Aqueous ammonia oxidative leach and recovery of metal values, US Patent 3,967,957, July 6, 1976.

[6]. Chmielewski T., Wodka J., Iwachow Ł. Ammonia pressure leaching for Lubin shale middlings. Physicochemical Problems of Mineral Processing, 2009, vol. 43, 5–20.

[7]. Satchell Jr., Ammonia leaching, US patent 4,165,264, Aug. 21, 1979.

[8]. Liu W., Tang M.-t., Tang C.-b., He J., Yang S.-h.,Yang J.-g. Dissolution kinetics of low grade complex copper ore in ammonia-ammonium chloride solution. Trans. Nonferrous Met. Soc. China, 2010, vol. 20, 910-917.

[9]. Bingöl D., Canbazoğlu M., Aydoğan S. Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching. Hydrometallurgy, 2005, vol. 76 55–62.

[10]. Sabba N., Akretche D. E. Selective leaching of a copper ore by an electromembrane process using ammonia solutions. Minerals Engineering, 2006, vol. 19, 123–129.

[11]. Jana R. K., Premchand B. D. P. Ammoniacal leaching of roast reduced deep-sea manganese nodules. Hydrometallurgy, 1999, vol. 53, 45–56.

[12]. Mishra D., Srivastava R. R., Sahu K. K., Singh T. B., Jana R. K. Leaching of roast-reduced manganese nodules in NH_3–$(NH_4)_2CO_3$ medium. Hydrometallurgy, 2011, vol.109, 215–220.

[13]. Chang C. J., Liu J. C. Feasibility of copper leaching from an industrial sludge using ammonia solutions. Journal of Hazardous Materials, 1998, vol. 58, 121–132.

[14]. Bryson J. L., Ammoniacal extraction of copper from metallic materials, US patent 3,971,652, July 27, 1976.

[15]. European Commission, JRC, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, Best Available Techniques (BAT) Reference Document for the Non-Ferrous Metals Industries, Chapter 2 - General processes and techniques, MR/GC/EIPPCB/ NFM_Draft_3 July 2014 63 2, Seville, European IPPC Bureau, 2014.

[16]. Ekmekyapar A., Oya R., Kunkul A., Dissolution kinetics of an oxidized copper ore in ammonium chloride solution. Chem. Biochem. Eng. Q., 2003, vol.17, No.4, 261–266.

[17]. Habashi F. Kinetics and mechanism of copper dissolution in aqueous ammonia. Ber. Bunsenges. Phys. Chem., 1963, vol. 67, No. 4, 402–406.

[18]. Crundwell F. K. The dissolution and leaching of minerals. Mechanisms, myths, and misunderstandings. Hydrometallurgy, 2013, vol.139, 132–148.

[19]. Habashi F., Bas A. D. Electrochemistry and mineral dissolution, XXVIII International Mineral Processing Congress Proceedings - ISBN: 978-1-926872-29-2, Quebec, IMPC, 2016.

[20]. Burrows A., Holman J., Parsons A., Pilling G., Gareth Price, Chemistry^3: Introducing Inorganic, Organic and Physical Chemistry, Oxford, OUP, 2013.

[21]. Morel M. M. F., Hering J.G., Principles and Applications of Aquatic Chemistry, New York, Wiley, 1993.

[22]. Hui-ping H., Chun-xuan L., Xue-tao H., Qi-wen L., Qi-yuan C. Solvent extraction of copper and ammonia from ammoniacal solutions using sterically hindered [beta]-diketone. Trans Nonferrous Met. Soc. China, 2010, vol. 20, No.10, 2026–2031.

[23]. Alguacil F.J. Recovery of copper from ammoniacal-ammonium carbonate medium by LIX 973N. Hydrometallurgy, 1999, vol. 52, 55–61.

[24]. Kumar V., Pandey B. D., Bagchi D. Application of LIX 84 for separation of copper, nickel and cobalt in ammoniacal leaching of Ocean nodules. Materials Transactions, JIM, 1991, vol. 32, No. 2, 157-163.

[25]. Parija C., Sarma P.V. R. B. Separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX84 as the extractant. Hydrometallurgy, 2000, vol. 54,195–204.

[26]. Sridhar V., Verma J. K., Kumar S. A. Selective separation of copper and nickel by solvent extraction using LIX 984N. Hydrometallurgy, 2009, vol. 99, 124–126.

[27]. Jergensen G.V., Copper Leaching, Solvent Extraction, and Electrowinning Technology, Littleton - USA, SME Inc., 1999.

[28]. Hu H.-p., Liu C.-x., Han X.-t., Liang Q.-w., Chen Q.-y. Solvent extraction of copper and ammonia from ammoniacal solutions using sterically hindered *β*-diketone. Trans. Nonferrous Met. Soc. China, 2010, vol. 20, 2026-2031.

[29]. Virnig M. J., Sudderth R. B., Copper recovery process, US Patent 5,908,605, June 1, 1999.

[30]. Ochromowicz K., Jeziorek M., Wejman K. Copper (II) extraction from ammonia leach solution. Physicochem. Probl. Miner. Process., 2014, vol. 50, No.1, 327−335.

[31]. Sombhatla S. S., Kumar A., Mashruwala S., Rokkam K. Kr., Akhilesh Shukla A. Comparative study of organic solvents for extraction of copper from ammoniacal carbonate solution. Hydrometallurgy, 2016, vol.166, 94–97.

[32]. Alguacil F. J., Alonso M., Recovery of copper from ammoniacal / ammonium sulfate medium by LIX 54. J. Chem. Technol. Biotechnol, 1999, vol. 74, No. 12, 1171–1175.

[33]. Kislik V. S., Liquid Membranes Principles and Applications in Chemical Separations and Wastewater Treatment, Ed., First edition, Amsterdam, Elsevier, 2010.

[34]. Alguacil F. J., Navarro P. Non-dispersive solvent extraction of Cu(II) by LIX 973N from ammoniacal/ammonium carbonate aqueous solutions. Hydrometallurgy, 2002, vol. 65, 77–82.

[35]. Gameiro L. F., Ismael M. R .C., M. Reis M. T. A., Carvalho J. M. R. Recovery of copper from ammoniacal medium using liquid membranes with LIX 54. Separation and Purification Technology, 2008, vol. 63, 287–296.

[36]. Yang Q., Kocherginsky N. M. Copper recovery and spent ammoniacal etchant regeneration based on hollow fiber supported liquid membrane technology: from bench-scale to pilot-scale tests. J. Membr. Sci., 2006, vol. 286, 301–309.

[37]. Yang Q., Kocherginsky N. M., Copper removal from ammoniacal wastewater through a hollow fiber supported liquid membrane system: Modeling and experimental verification. Journal of Membrane Science, 2007, vol. 297, 121-129.

[38]. Duan H., Wang Z., Yuan X., Wang S., Guo H., Yang X. A novel sandwich supported liquid membrane system for simultaneous separation of copper, nickel and cobalt in ammoniacal solution. Separation and Purification Technology, 2017, vol. 173, 323–329.

[39]. Gameiro L. F., Bento P., Ismael M. R. C., Reis M. T. A., Jorge M. R., Carvalho J. M. R. Extraction of copper from ammoniacal medium by emulsion liquid membranes using LIX 54. Journal of Membrane Science, 2007, vol. 293, 151–160.

[40]. Sengupta B., Bhakhar M. S., Sengupta R. Extraction of copper from ammoniacal solutions into emulsion liquid membranes using LIX 84 I®, Hydrometallurgy, 2007, vol. 89, 311–318.