



Ammonia Leaching: A New Approach of Copper Industry in Hydrometallurgical Processes

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Abstract Ammonia and ammonium salts have been recognized as effective leaching agents in hydrometallurgical processes due to low toxicity and cost, easy recovery and high selective recovery of metals. New research findings on considerable advantages of leaching by these agents and elimination of problems associated with acid leaching have resulted in a new approach in the world to this method. The investigations in this field indicate more frequent use of this method for extracting copper from ore and concentrate relative to other basic metals. In this paper, an attempt was made to describe the basis and different ammonia leaching methods and present the major research activities in this field for copper. Also latest findings and related novel processes have been presented. Comparisons including assessment of advantages and disadvantages of this method relative to acid leaching method, kinetic study of copper ammonia leaching and evaluation of Eh–pH diagrams in a system containing water and ammonia are other parts of this study. Finally, by describing the studies on copper extraction from the resulting pregnant solutions, the applicable extraction agents have been reviewed.

Keywords Leaching · Extraction · Ammonia · Copper

Introduction

The use of sulfuric acid in an acid leaching process is a conventional method for recovery of copper, but in some cases it is necessary to use other reactants such as ammonia. Ammonia has been known as an effective leaching agent in hydrometallurgical procedures, although it has been less studied than the chemical agents used in leaching.

Ammonia leaching was first used for recovery of non-ferrous metals such as copper from oxide ores or ores containing pure copper, but gradually the use of this technology was developed from more traditional elements of copper, nickel and cobalt to the extractive metallurgy of zinc, cadmium, silver and gold [1].

The aim of this paper was to review studies in various fields of ammonia leaching of copper and extraction of copper from the resulting pregnant solution by solvent extraction process.

History

The first industrial application of this process related to hydrometallurgical recovery of copper was put into operation in 1916, and the two factories of Kennecott in Alaska (Fig. 1) and Calumet in northern Michigan were separately established for copper recovery.

Although copper oxide and pure copper were first used to recover copper due to high solubility in ammonia, later on ammonia leaching of sulfide ores was also considered. The common method was the use of oxide roasting at high

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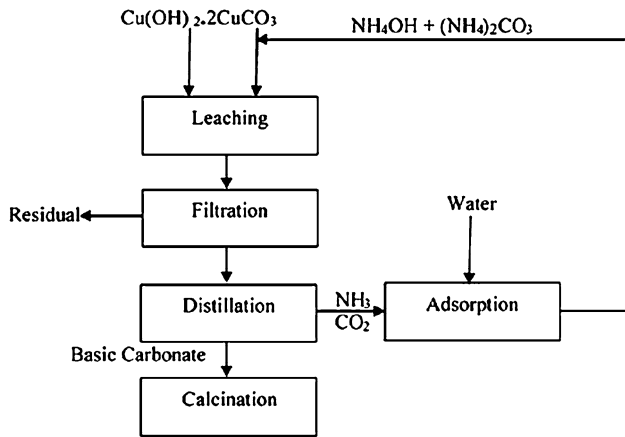
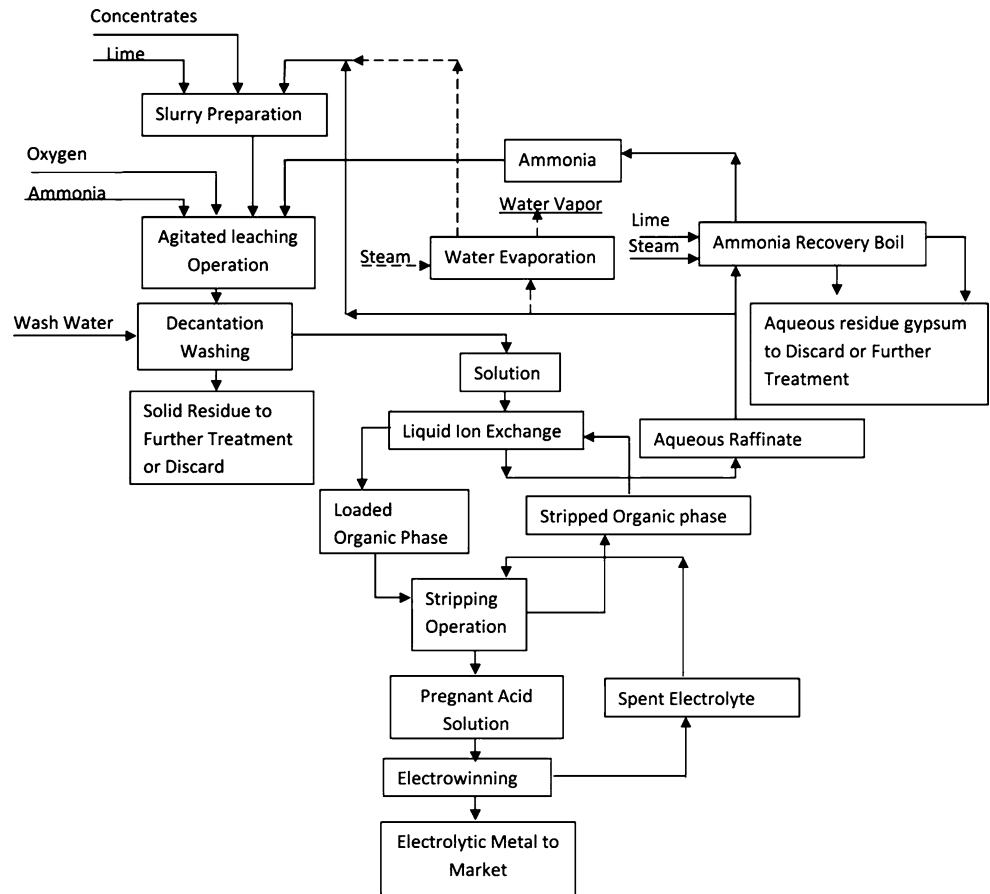


Fig. 1 Flow sheet of Kennecott plant

temperatures to convert sulfides to oxides in order to facilitate dissolution in ammonia solutions [1].

In 1947, a process (Fig. 2) in this regard was invented by Sherritt Gordon. In this process, ammonia leaching of sulfide minerals of copper, nickel, cobalt and iron was conducted at a temperature of about 105 °C and air pressure of 0.8 MPa. Under these conditions, copper, nickel and cobalt were dissolved but iron was precipitated in hydroxide form. By separating the unsolved solids, the

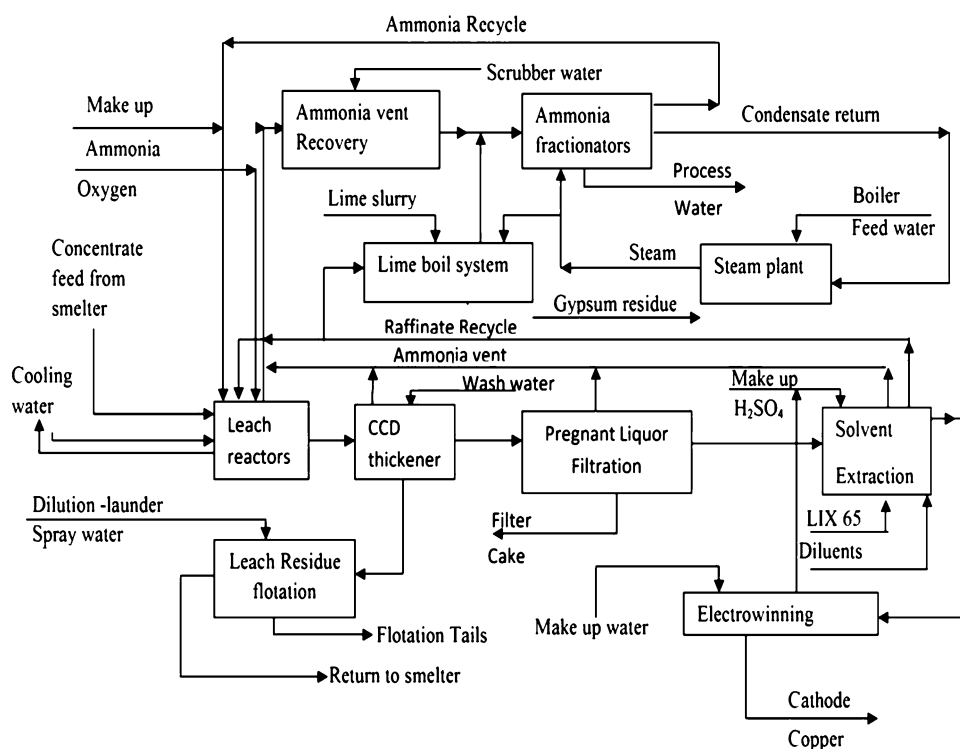
Fig. 2 Flow sheet of Gordon process [2]



pregnant solution was heated to evaporate excess ammonia. After that, first the solution was allowed to react with air to oxidize all its thiosulfates, and was then reduced using hydrogen. Thus, metal nickel was obtained through reduction of amine nickel ion. It was necessary to add some metallic nickel powder to the solution as budder to start the reaction, or add an appropriate catalyzer to the solution to accelerate the reaction. Reduction operations continued up to precipitation of nickel without affecting the cobalt ions in the solution [3]. The good results of this innovative process led to the construction of a factory in Canada in 1954 [4].

Another innovative process in this field is the Arbiter process. This process was introduced in 1970 in a pilot plant in Arizona under the supervision of Arbiter Company. A few months later, a plant with 91 t of daily copper production capacity was commercially set up in Anaconda. In this leaching factory, ten reservoirs were used equipped with powerful mixers connected to five thickeners as opposite flow, each with a volume of 14 m³, of which the first overflow was filtered for the pregnant solution. The basis of this process was ammonia leaching of chalcopyrite concentrates in presence of oxygen at 70–80 °C temperature to form amine copper sulfate and iron hydroxide.

Fig. 3 Arbiter process in Anaconda mine [4]



The charged output solution from the filter was extracted using LIX65N, and stripped by sulfuric acid. The resulting concentrated solution was subject to the electrolysis to produce metal copper. Finally, lime was added to the output raffinate and the pulp was distilled to recover ammonia and precipitate gypsum for use.

Flow sheet of Arbiter process is shown in Fig. 3. This process was not welcomed by the industry due to technical and economic problems in the final stage, the recovery of ammonia and due to weak elimination of sulfate ions from the solution at the investigated temperature [4].

Another process to extract nickel, cobalt and copper from pyrite flotation concentrate was developed by INCO of Copper Cliff, Ontario, Canada with satisfactory results. This process involves oxide roasting of sulfide concentrate followed by rapid quenching of the calcine under reducing conditions and eventual leaching in an ammonia–ammonium carbonate solution [5].

Although most studies in the past, focused on the dissolution of sulfide concentrates in reactors and many of them led to low process kinetics and high temperatures and pressures being needed, most recent studies have been directed towards the dissolution of oxide ores including malachite.

Table 1 lists the titles of studies conducted in recent decades, along with chemical agents, parameters under study and the resulting recoveries.

In new research work [12], suitable parameters of ammoniacal column leaching for Meskani Mine copper ore

in Iran were determined. Taguchi method was used to design experiments and evaluate the behavior of the parameters like ammonia concentration, acid flow rate, size of ore and leaching time. By investigating the effect of above parameters on copper oxide recovery rate, the optimum condition for concentration, acid flow rate, size of ore and leaching time were found to be 40 g/l, 60 cm³/h, 1–4.75 mm and 10 days, respectively. Studies showed that the ammonia concentration and size of ore were more important parameters. The final experiment was conducted to confirm the optimal conditions obtained from the Taguchi method in which the copper recovery was 80.6.

Methods

In general, ammonia leaching methods include:

Neutral method: In this method, the metals are dissolved without any oxidizing or reducing agents. Leaching of copper, zinc or molybdenum oxides are of this type.

Oxide method: In this method, leaching requires the use of an oxidizer to oxidize solids such as metals or sulfide minerals.

Reduction method: In contrast to the oxide leaching method, a reducing agent is used in this method. It is mainly used for dissolving metals from highly oxidized ores such as ocean floor manganese nodules and lateritic ores [1].

Table 1 Activities performed in the past decade

Topic	Lixivent	Parameters	Recovery in optimum condition	Reference
Dissolution kinetics of an oxidized copper ore in Ammonium chloride solution	Ammonium chloride	Ammonium chloride concentration, particle size, solid/liquid ratio, stirring speed and reaction temperature	–	[6]
Leaching of malachite ore in NH ₃ -saturated water	Ammonia	Ammonia concentration, particle size, temperature, stirring speed, and solid-to-liquid ratio	–	[7]
Dissolution kinetics of malachite in ammonia–ammonium carbonate leaching	Ammonia–ammonium carbonate leaching	Leaching time, ammonium hydroxide, and ammonium carbonate concentration, pH, stirring speed, solid/liquid ratio, particle size and temperature	98	[8]
A study on the oxidative ammonia–ammonium sulphate leaching of a complex (Cu–Ni–Co–Fe) matte	Ammonia–ammonium sulphate	–	93.8	[9]
Ammonia pressure leaching for LUBIN SHALE MIDDLEINGS	Ammonia and ammonium sulfate	Temperature, oxygen partial pressure, ammonia and ammonium sulfate concentration and stirring rate	95	[10]
Leaching of copper from tailings using ammonia–ammonium chloride solution and its dynamics	Ammonia–ammonium chloride	Leaching time, the concentration of ammonia, solid/liquid ratio and temperature	75	[11]
Dissolution kinetics of low grade complex copper ore in ammonia–ammonium chloride solution	Ammonia–ammonium chloride	Concentration of ammonia and ammonium chloride, ore particle size, solid-to-liquid ratio and temperature	–	–

Advantage

Ammonia leaching has many advantages over acidic leaching. The main advantages are as follows:

- a. Marked difference of the two methods. Operations in the alkaline solution enable the use of ores with high carbonation, which cannot be used in acidic leaching due to high consumption of acid.
- b. The problems associated with equipment corrosion are eliminated due to acid replacement.
- c. This type of process is more appropriate for mass leaching of low-grade ores and reservoir leaching of high grade ores, although this choice also depends on the grade and the amount deposited.
- d. Since metals such as iron and manganese are not soluble in ammonia or their complexing capacity with ammonia is low, ammonia leaching has a suitable selective capacity for the desired metal relative to the mentioned metals, while the high solubility of these elements in acidic factors leads to high consumption of these agents and a non-economic leaching process.
- e. In the leaching solution, ammonia prevents calcium solubility in the presence of carbonate and small amounts of sulfate. This results in reduced permeability in heap due to jarosite or gypsum precipitation, and high acid consumption in acid leaching is also avoided.
- f. Another element causing problem in permeability and drainage of the heap is silica. Unlike acid types, ammonia does not react with different compounds of this element such as alumina silicates and ferrosilicates.
- g. Elimination of the problems associated with formation of non-filterable precipitates during pH adjustment at acid leaching factory and non-requirement of viscosity solutions are other advantages of ammonia leaching.
- h. After completion of ammonia leaching, problems associated with heap washing, neutralization and long-term monitoring to prevent acid runoff are minimized. Moreover, the residual ammonia in the soil can act as fertilizer for growing plants.

In addition to the above advantages, characteristics such as low toxicity, low cost, easy recyclability and economic gain are the main factor for increased use of ammonia in hydrometallurgical processes particularly leaching [1, 13].

Disadvantages

- a. Lower capacity of leaching of acidic compounds, although not significantly.
- b. The use of ammonia due to its high evaporation capacity is more difficult than acidic compounds,

although through hydrolysis of urea, the risk of its transport can be minimized [13].

c. Extractors so far used for copper recovery from ammonia medium do not have high efficiency.

Kinetics

The kinetics of copper dissolution in ammoniacal solution has been comprehensively studied. Lu and Graydon [14] showed that the total concentration of ammonia and oxygen play an important role in determining the overall rate. They defined the overall expression of rate as follows:

$$\text{Rate} = \frac{2AD_{O_2}[O_2](K_{NH_4^+}[NH_4^+] + K_{NH_3}[NH_3])}{8D_{O_2}[O_2] + \delta K_{NH_4^+}[NH_4^+] + \delta K_{NH_3}[NH_3]} \quad (1)$$

In this regard, K_{NH_3} and $K_{NH_4^+}$ are the rate constants and δ is the diffusion layer thickness that can be determined based on the continuity equation. According to their studies, whenever the overall reaction was of the limited diffusion type, penetration layer thickness was found to be 0.6×10^{-3} cm. They also showed that the dissolution mechanism is such that due to the formation of a kind of copper oxide during leaching process, the dissolution of copper is inhibited. However, the cupric ion had a catalytic effect on the dissolution of metal copper known as the self-catalytic phenomenon.

Meng et al. [15] evaluated the effect of oxygen on copper dissolution kinetics in ammoniacal solution. Figures 4 and 5 show the results of their studies. It can be clearly seen that under low oxygen pressure, the dissolution of copper is a linear function of leaching time. In fact, the dissolution process is electrochemical in nature. When air or oxygen was used as an oxidizer, in low pressure, the reaction was controlled with diffusion phenomenon, and in high pressure, it was controlled by surface reaction.

Similar results were obtained in studies by other researchers such as Habashi [17] and Luo et al. [18]. Some researchers also studied the dissolution of copper minerals in different ammonia solutions. In a study on malachite leaching in ammonium chloride solution [6], it was determined that the dissolution rate is controlled by a compound kinetics. Their mathematical model for the reaction kinetics is as follows:

$$K_t = 1 - 2(1 - X)^{1/3} + (1 - X)^{2/3} \quad (2)$$

According to their calculations, the activation energy for malachite dissolution reaction was found to be 71 kJ/mol.

In another study [8] on malachite leaching in ammonium carbonate solution, it was established that there are two steps for the dissolution reaction. Firstly, the malachite was rapidly dissolved, but after completion of 10 % of reaction,

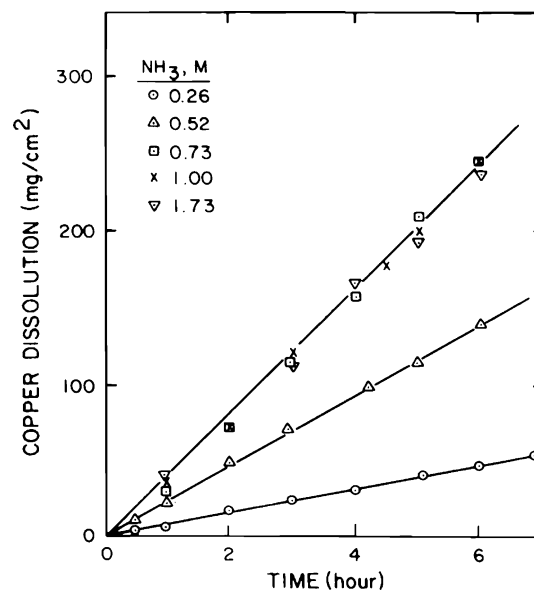


Fig. 4 The dissolution of copper in ammonia solution as a function of time at various concentrations of ammonia (Stirring speed of 600 rpm and oxygen pressure of 304 kPa) [16]

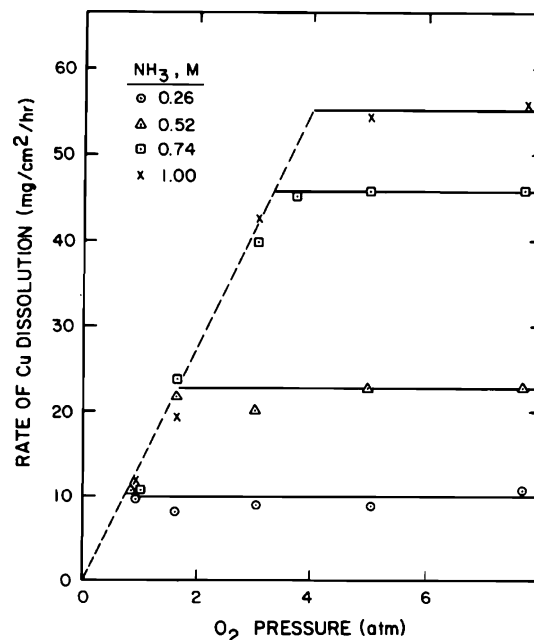


Fig. 5 Effect of oxygen pressure on the dissolution rate of copper in ammonia solution (Various concentrations of NH₃ and 26 °C temperature) [16]

leaching rate was reduced with the formation of needle-structured middle phase causing surface blockage. This phase was mainly Cu(OH)₂. This stage continue to exist with the concurrent dissolution of malachite and the middle phase. In the second stage of the reaction and after reaching

90 % of the reaction, essentially all of malachite was dissolved and only the remaining middle phase was subject to dissolution. Equations 3 and 4 show the reaction kinetics for the first and second stages:

$$K_1 t = 1 - (1 - X)^{1/3} \quad (3)$$

$$K_2 t = 1 - (1 - X)^{1/2} \quad (4)$$

where X represents the solid reactant part, K_1 and K_2 rate constants at the leaching time. According to their calculations, the activation energy for the first and second stages were 64 and 75 kJ/mole, respectively.

Eh–pH Diagram for the Copper–Ammonia–Water System

In Cu–NH₃–H₂O system, several soluble species are present such as NH₃, NH₄⁺, H⁺, Cu²⁺, Cu⁺, Cu(OH)³⁻, Cu(OH)₄²⁻, Cu₂(OH)₂²⁺, Cu(NH₃)₂²⁺, Cu(NH₃)₃²⁺, Cu(NH₃)₂⁺, Cu(NH₃)₃⁺ and Cu(NH₃)₄²⁺. There are therefore many equilibrium equations in the solution relating these components in the solution to each other. To use these equations to understand the different reaction mechanisms in ammonia solutions, the Eh–pH diagram is used. Eh–pH diagram shown in Fig. 6 has been determined for 25 °C temperature, Cu activity of 0.5 and total ammonia (NH₃ and NH₄⁺) concentration of 7 kmol/m³.

The broken lines indicate the following reactions:

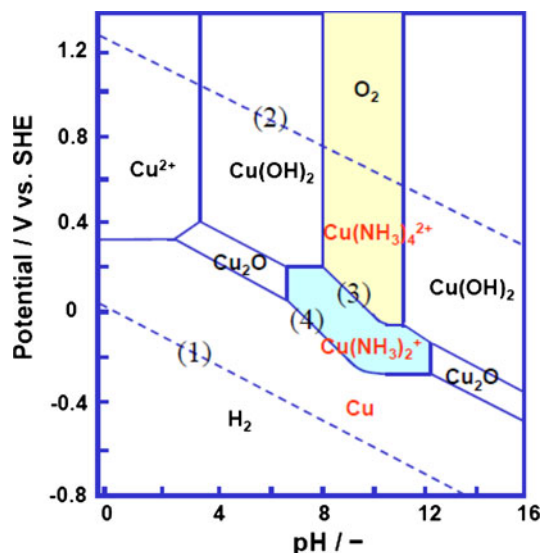
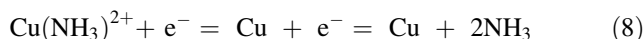
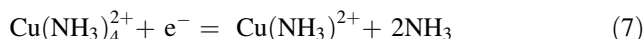


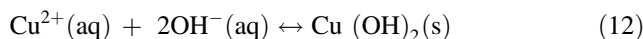
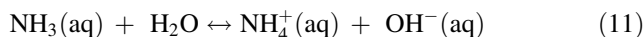
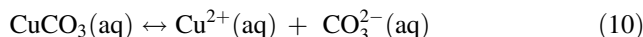
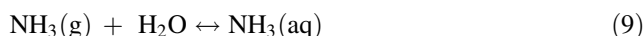
Fig. 6 Eh–pH diagram for Cu–NH₃–H₂O system (25 °C temperature, Cu activity of 0.5 and total ammonia concentration of 7 kmol/m³) [19]

According to this diagram, Cu (I) and Cu (II) complexes with NH₃ are stable ionic species in neutral and alkaline solutions. In the presence of excess ammonia, Cu(I) and Cu(II) are also stable as Cu(NH₃)₂ and Cu(NH₃)₄²⁺. The following equations show oxidation–reduction reactions of Cu (II)/Cu (I) and Cu (I)/Cu:



The oxidation–reduction potential of Cu (NH₃)₄²⁺/Cu (NH₃)₂⁺ is more positive than that of Cu (NH₃)₂⁺/Cu. This indicates that Cu (NH₃)₄²⁺ can oxidize metallic copper in an ammoniacal alkaline solution. Moreover, the oxidation–reduction potential of Cu (I)/Cu is more positive than that of hydrogen evolution (Eq. 5), indicating that Cu(I) can be preferentially reduced to metallic copper [17]. Figure 7 shows the schematic presentation of the process of electrochemical dissolution of copper in ammonia solution.

There are limited electrochemical studies about ammonia leaching of copper. Arzutug et al. [7] were among the few people who used the chemical equilibrium in solution to evaluate the general reactions in this process. Based on their studies, during the process of ammonia leaching of copper ore (malachite) to Cu(OH)₂.CuCO₃, first CuCO₃ was dissolved and was then converted to Cu(OH)₂ based on the following reactions:



The formation of Cu(OH)₂ is succeeded by the following reactions:

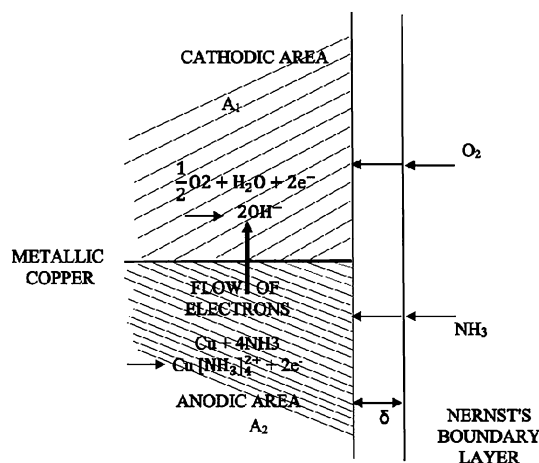
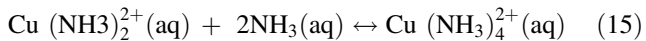
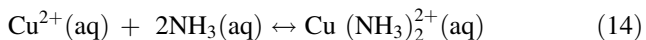
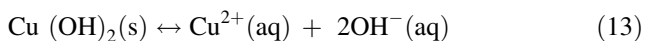
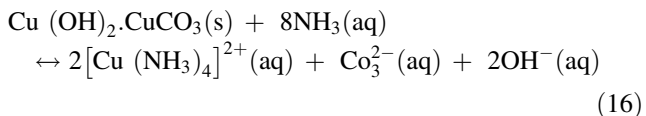


Fig. 7 Schematic presentation of the process of electrochemical dissolution of copper in ammonia solution [17]



Firstly, the intermediate compound $\text{Cu(NH}_3)_4^{2+}$ and finally the $\text{Cu(NH}_3)_4^{2+}$ complex was formed. These researchers [7] proposed the following general reaction for ammonia leaching of copper:



Copper Extraction from Ammoniacal Solutions

Case Studies

Copper leaching from ore using ammonia should be followed by selective extraction of copper using the extraction agent in the solvent extraction process. LIX63 was the first extraction agent used in this field. The low extraction capacity of this extractor for copper transfer from the acidic solution led to studying its extraction capability from the ammonia solution. Although this extractor had a high efficiency in the extraction of copper from ammoniacal solutions, due to difficult stripping process, it was not considered by the industry. Other extractor under study was LIX64N. This extractor which is cheaper and more practical than LIX63, was commercially only used for the recovery of copper from an ammoniacal solution in Arbiter Process and in melting process. However, the low extraction ability of copper (12 g/l) and high ammonia loading of it led to further studies of new extraction agents from the ammoniacal solutions [20].

These efforts led to synthesis of P204 (D-2-ethyl hexyl phosphate), which is an organophosphorous acid extractor. It is reported that under 25 °C temperature, the two phase contact time of 10 min and phase ratio of 1:1, an ammonia solution with pH 10 and 20 % P204 concentration (volume fraction), the copper extraction rate was found to be 93.9 % [21]. However, P204 is highly soluble in alkaline solution, and its commercial use in ammoniacal solution (9 < pH) is impossible.

Subsequently, a beta-D-ketone extractor called LIX54 was used. This extractor had a high extraction potential for copper and a low loading capacity for ammonia, and copper strip from it needed low concentrations of the acid [22]. In 1995, ESCONDIDA in Chile used this extractor for extracting copper from an ammoniacal solution on a pilot scale. However, due to a reaction between a keto group of LIX54 and ammonia and production of ketamine, the

extraction agent disappeared. Therefore, copper strip from the charged organic phase was difficult, and finally the pilot plant was closed [23]. So, the choice of LIX54 was considered inappropriate for copper extraction in ammoniacal solution.

In addition to beta-D ketones, ketoximes and hydroximes were also used for the extraction of copper from ammoniacal solution. The results of studying some of these compounds such as LIX84 indicate a very high extraction capacity of copper (more than 50 g/l) from ammoniacal solutions [24–28]. However, a hydroxime like LIX84 had serious problems of ammonia extraction in the ammoniacal solution [29, 30]. The ammonia present in the charged organic phase must be eliminated by the electrolyte used before attempting to strip copper. Otherwise, ammonia in the charged organic phase is transferred to the pregnant electrolyte after the stripping process, resulting in the accumulation and precipitation of $(\text{NH}_4)_2\text{SO}_4$ in the charged electrolyte [29]. Recently, in another research, to decrease ammonia extraction in the charged organic phase, stearically hindered beta-D ketone was used. In this study, under the temperature 25 °C, 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 % (volume fraction), ammonia in the water phase was far less extracted by the organic phase (only 14.5 mg/l), while the copper extraction rate was 95.09 %. Table 2 show the general characteristics of the chelate type extractors used in the extraction of copper from an ammoniacal solution [20].

Extraction Mechanism

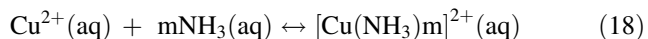
In general, extraction equilibrium between Cu^{2+} and a chelation extractor is as follows:



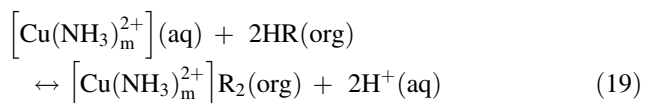
Table 2 Characteristics of copper extractors from ammoniacal solutions [20]

Beta-D-ketone	Hydroxime	Property
Moderate	Strong	Extractive strength
Excellent	Good	Ease of stripping
Low	Moderate	Viscosity
Very low	Low	Ammonia loading
Very good	Very good	Selectivity of copper
Fast	Fast	Kinetics
Good	Good	Stability
Very good	Good	Phase separation
Very high	Very high	Copper complex solubility

If the aqueous solution contains copper and aluminum ions, in sufficiently high pH levels where free ammonia is released, amine complexes will be formed in aqueous phase as follows:



When the phases contact, ammonia in aqueous phase may be extracted in the form of $[\text{Cu}(\text{NH}_3)_m]\text{R}_2(\text{org})$ expressed as follows:



in which $\text{HR}(\text{org})$ represents extractor in the organic phase, $\text{CuR}_2(\text{org})$ extractor-copper complex in organic phase, $[\text{Cu}(\text{NH}_3)_m]^{2+}(\text{aq})$ amine-copper ion complex in aqueous phase and $[\text{Cu}(\text{NH}_3)_m]^{2+}\text{R}_2(\text{org})$ extraction compound of $\text{Cu}(\text{NH}_3)_m^{2+}$ and extractor in the organic phase [31].

Ammoniacal Leaching of Other Elements

In addition to studies on copper, ammonia leaching has been used to recover some other basic elements.

Manganese nodules are in fact Ferromanganese oxide ores containing copper, nickel and cobalt. These metal oxides have been reported mainly in lateritic iron and manganese minerals. Crushing these laterites using pyrometallurgy reduction or hydrometallurgical reductive dissolution is an important step for proper recovery of

precious metal. Therefore, the recovery process of manganese nodules has been studied in two ways:

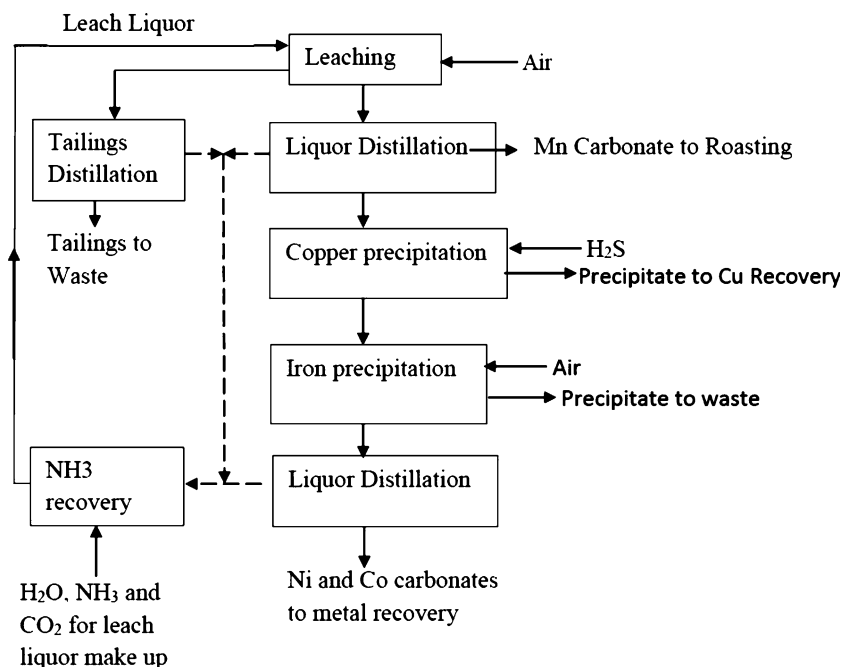
- Initial pyrometallurgical preparation and then performing the metallurgical process.
- Performing the hydrometallurgical process alone.

Initial pyrometallurgical preparation operations often involve melting, reduction-roasting, sulfidation and chlorination. Reductive dissolution takes place by Hydrochloric acid, sulfuric acid, ammonia, etc. in the presence or absence of reducing reactants such as sulfur dioxide, pyrite, sodium sulfide, charcoal, alcohol, etc. [32–34].

In research conducted for processing of manganese nodules by ammonia leaching [35–37], after reductive roasting of the sample for releasing precious metal oxides from manganese and iron oxide phase, reduction operations were done to form copper, nickel and cobalt metals and facilitate their ammonia leaching. During the ammonia leaching process, in addition to dissolution of precious metals such as copper, nickel and cobalt as stable amine complexes, the dissolution of unwanted metals such as iron and manganese was also prevented. Overall flowsheet of this process is shown in Fig. 8.

Ammonia leaching has also been used for recovery of nickel and cobalt from oxide, sulfide and complex ores. For example, the so-called Caron process was developed to recover nickel and cobalt from low-grade ores such as lateritic ores with an ammonia–ammonium carbonate solution. This process involves reductive roasting of nickel ore followed by leaching using ammonia–ammonium

Fig. 8 Flowsheet of precious metals' recovery from manganese nodules of the ocean floor [35]



carbonate compound, commercially adopted in Nicaro in Cuba, Marinduque in the Philippines and Queensland in Australia [38].

Cadmium, gold and silver are other precious metals of which ammonia leaching has been studied, although none of the innovative processes used for their recovery has found industrial application [39–43].

Summary

In this review, various topics related to ammonia leaching of copper have been studied. The history of this process, different methods involved in it, the advantages and disadvantages, kinetics, Purbeh diagram, the way to extract copper from the pregnant solution obtained and extraction agents used are different issues described in this paper. Evaluation of the studies shows that, despite a long history of using this process, easy use of acidic leaching agents and their higher leaching capacity have prevented ammonia leaching from being accepted as an acid leaching process. In recent years, however, due to decrease in proper reserves for acid leaching and considerable advantages of this method such as lower toxicity, easier recovery and economic gain, ammonia leaching has again been looked upon as a possible option by researchers and industrialists.

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