

Technology Section

Pakistan J. Sci. Ind. Res., Vol. 24, No. 4, August 1981

RECOVERY OF METALLIC COPPER FROM LEACH SOLUTIONS. PART II

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(Received August 23, 1980)

First part of this review dealt with the salient features of the application of cementation and solvent extraction in the recovery of copper from its leach solutions. In this Part we shall try to present the case of gaseous reduction and ion exchange with solid resins.

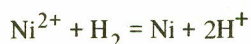
INTRODUCTION

The solutions resulting from leaching of copper ores are generally dilute (30–50 kg m⁻³ from vat and agitation leaching; 1–5 kg m⁻³ from situ, heap, and dump leaching) and contain impurities, such as iron, calcium, aluminium, silica, etc. The pH of these solutions lies between 1 and 2 in case of acid leaching and above seven in case of ammonia leaching. In the case of ammonia leaching, the impurities such as iron and aluminium are precipitated and eliminated whereas in the case of acid leaching they have to be taken care of.

As we have indicated in the first part of this review the methods used most extensively for the extraction of copper from acid leach solutions are the cementation and solvent extraction. However, methods such as gaseous reduction and ion exchange on resins, have also been studied on a limited scale.

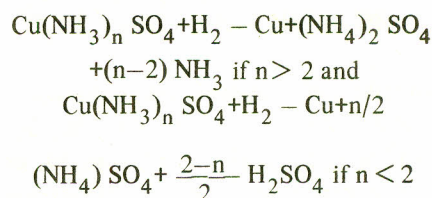
GASEOUS REDUCTION

Reduction with Hydrogen. The chemistry of the reduction of metals in solutions with hydrogen to produce metal powders has been known for quite some time. During the period 1946–1955, a group of research chemists and engineers, working with the Chemical Construction Corporation of U.S.A., developed a method of producing metals from aqueous solutions using hydrogen gas under pressure as the reductant. Nickel, for example, was obtained in the form of a powder from the following reaction:



At about the same time, i.e., between 1948–1954, Sherritt

Gorden Mines Ltd. of Canada developed a process [1] for the recovery of Ni, Co, and Cu from sulfide ores and nickel concentrates. The sulfides were solubilised by ammonia in the presence of oxygen under pressure and at elevated temperatures. The process was tested on a pilot plant scale in Ottawa and the commercial production started at Fort Saskatchewan plant in 1954. In 1967 it was producing 30X10⁶ pounds/annum of Ni and 1x10⁶ pounds/annum of cobalt [2]. The reduction reaction for copper may be written as follows:



This process has basically been used for the treatment of nickel ores and concentrates containing smaller amounts of cobalt and copper. Cobalt and copper are recovered as by-products along with (NH₄)₂SO₄ as fertilizer.

Copper may be obtained in the form of powder from either acid or alkaline solutions by reaction with hydrogen. However, severe corrosion problems may be encountered in acid conditions. Ammoniacal ammonium carbonate and ammoniacal ammonium sulphate have been used as the alkaline medium. The addition of polyacrylic acid or its ammonium salt prevents the adhesion of copper powder to the walls of the autoclave during reduction.

The reduction of copper in solution has been studied by numerous workers. Thus, Nakazawa [3] studied the reduction of a copper sulfate solution containing 50 g Cu/l, in an autoclave at 150^o under a hydrogen partial pressure of 20–30 kg/cm². He observed that the addition of a dis-

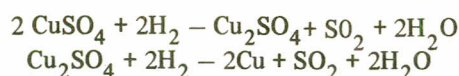
persing agent like an acrylic compound 0.19 g/l, and $(\text{NH}_4)_2\text{SO}_4$ were necessary to obtain a granular copper powder and an increasing rate of reduction respectively.

Burkin and Richardson [4] examined the effect of pH, nucleating and surface active agents on the hydrogen reduction of Ni, Co and Cu from solutions containing their ammonia complexes. It was found that no nucleating agents were necessary for copper precipitation.

Yaroslavtsev and Saprygin [5] reduced a sulfate solution containing Cu 12, Zn 120 and Mn 2g/l, with hydrogen under a hydrogen partial pressure of 15–20 atmospheres at 150–160°. The copper obtained had a dendritic structure and contained Cu 99.7–99.9%.

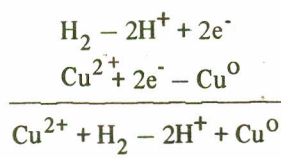
Niemiee and coworkers [6] obtained copper and nickel metal powders from a solution containing Cu 32, Ni 24.3, Fe 3.9, H_2SO_4 198, and Zn, As, Sn about 1 g/l. The reduction was conducted in an autoclave at 175–200° under a hydrogen partial pressure of 10–30 atmospheres. The powders obtained were 99.32 and 99.27% pure copper and nickel.

Habashi and Dugdale [7] suggested the crystallisation of CuSO_4 from the leach solutions followed by its reduction with hydrogen at 300°. The reduction of CuSO_4 has been shown to follow the following reaction sequence.



Rumianowski [8] studied the reduction of leach liquors containing Cu 42–55, Fe 90–100, and H_2SO_4 85–95 kg/cm³ with hydrogen at 438–463°K in an autoclave at 45–50 atmospheres. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was first removed from solution by crystallisation. The bulk density of the copper powder produced was 730–4200 kg/m³. After pressing, the density of pellets was 7100–7900 kg/m³. The product was dried in argon, and its purity was 99.65–99–95%.

The general reaction of the reduction of copper in solution by hydrogen may be represented as follows:



It is apparent from the studies referred to above, that the production of copper metal from its solution involves the use of autoclaves working under pressures ranging from about 28–65 kg/cm² and temperatures of 130–210°. Moreover, the quantities of leach solutions to be treated are enormous which would involve large capital investments.

The ready availability of hydrogen would be another factor affecting the cost of copper powder produced. In acid solutions, the problem of corrosion also exists. It is probably for these reasons that hydrogen reduction of copper solutions has not been practised on larger scale. However, materials such as sulfide ores and concentrates [9] matters from various sources, sulfides precipitated from nickel winning operations, cement copper, copper scrap, and other secondary sources [10] may be treated by this technique using ammonia leaching. Thus, a plant producing 2,070,000 kg/year of copper powder from scrap has been operating in the U.S.A., since 1954 [11].

REDUCTION WITH SO_2

Sulphur dioxide may also be used for the reduction of copper ions in solutions. When SO_2 is added to copper sulfate leach solution and heated to about 170° under pressure, metallic copper precipitates according to the following reaction: [12–13].

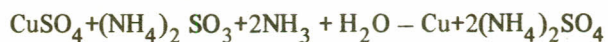


The metallic copper is separated and the acid produced may be used for leaching purposes. However, the process has some drawbacks which may be enumerated as follows: low yield of copper [14], problems of corrosion due to acidic environment under pressure and temperature, and the presence of small amounts of sulfur in the copper produced. The presence of sulfur may be due to the partial decomposition of sulfurous acid to sulfuric acid and elemental sulfur at the reaction temperature.

This method was in use in early nineteenth century. Thus Potter [15] got a patent for the production of copper from sulfate leach solution. The solution was charged with SO_2 and heated to 127° under a pressure of 100 lb sq. in to precipitate metallic copper.

Another publication [16] describes the treatment of a copper leach solution with SO_2 in lead lined copper or iron digestors. The solution is then heated until all the copper is precipitated.

Sulfur dioxide may be used in the form of sulfites as well for the reduction of copper sulfate leach solution. Thus ammoniacal ammonium sulfate has been used for the reduction of a copper leach solution resulting from the leaching of a roasted sulfide ore [17].



The reaction takes place at 170° under pressure. The copper recoveries are higher, and the reaction takes place under nearly neutral conditions, the problems of corrosion

are minimised. The by product ammonium sulfate may be marketed as fertilizer.

ION EXCHANGE

Ion exchange resins have been used extensively for the purification of uranium leach solutions from early fifties.

During sixties solvent extraction with amines started replacing them in the uranium hydrometallurgy. But with the depletion of high grade uranium ore deposits and the energy crisis of the seventies, attention was again diverted to the use of ion exchange resins. This was because the resins are cheaper than the organic extractants and they have the proven capability of treating low tenor leach solutions very effectively. They have the added advantage of accepting turbid leach solutions up to a certain extent whereas the liquid exchangers are used with clarified liquors. Recently a number of articles have appeared dealing with the extraction of uranium from low-grade ores by ion exchange resins [18–24]. In the meantime efforts were made to devise a system where-in resins could be used more profitably. Thus, Himsley and his co-workers [25–27] published a number of articles which described in detail the Himsley continuous fluid–solid contactor. At about the same time, the National Institute for Metallurgy in South Africa, developed a continuous fluidized bed ion exchange system which has been described fully in the literature [28–30]. This contactor was named NIMCIX after the name of the Institute, CIX standing for Continuous Ion Exchange. The Chemical Separations Corporation also produced the “Chem-seps” continuous counter-current Ion Exchange Contactor (C.C.I.C) [31] and Porter [32] patented another contactor. Lermigeaux and Roques [33] have prepared an inventory of the ion exchange systems used prior to mid-seventies giving details of the apparatuses and the methods of their operation.

There are instances of operating plants where Continuous Ion Exchange (CIX) is used in combination with Solvent Extraction (SX). Such a system is called Eluex in South Africa and Bufflex in the U.S.A. and Canada. In this system the dilute leach solution is concentrated and purified by a CIX system followed by further purification by the SX part of the plant. The resulting pure concentrated solution is treated for precipitation of the yellow cake.

The use of ion exchange resins for the recovery of base metals, such as copper, has not been made on commercial scale. However, attempts have been made from time to time to recover copper from its leach liquors by resin ion exchangers. The system used was either static or continuous. In the continuous operations the resin and liquor are

contacted either in counter current or in fluidized beds of the resin.

In the acid copper leach solutions, as encountered in the heap or dump leaching operations or in *in-situ* leaching the most important impurity is the ferrous and ferric iron. It is useful to remove this iron from the solution before it finally goes to the electrowinning plant where it reduces the current efficiency of the electrolytic operation. The removal of iron from the pregnant solution may be effected by treating it with lime prior to its transfer to the ion exchange columns. Thus, Jacobi [34] has described the treatment of mine waters containing copper on pilot plant scale using lime for the removal of iron before the ion exchange recovery of copper. The recoveries reported were of the order of 95 % with a copper to iron concentration factor of 37 to 1. In another study Sopkova *et al.* [35] eliminated iron from the mine drainage water using a 25 % solution of ammonia. After removal of the hydroxides of iron, aluminium, etc., the solution containing the copper amine complexes, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ was passed over a weak acid resin Ostion KM (Na⁺). Elution with 10 % H_2SO_4 gave copper recoveries of the order of 92 %.

In the case of fixed bed ion exchange, the exchange is not continuous and the bed has to pass through fixation, elution and washing cycle. To overcome this inconvenience a number of workers proposed different continuous systems for the recovery of copper from its leach solutions. Selke and Bliss [36] developed a continuous system for the exchange of copper ions in solution with the hydrogen ions in Amberlite resin IR-120. The recovery of copper was reported to be 99 %. Shulman *et al.* [37] used a spiral mounted on a horizontal axes to obtain a counter current contact between a copper solution and an Amberlite resin IR-120 in the Mg form. They determined the mass transfer coefficients as a function of various operating parameters of the equipment. They showed that the rate of transfer is controlled by the mass transfer between Cu^{2+} and Mg^{2+} in the liquid phase. Miles [38] got patented another helical system for the treatment of a copper solution (0.25 M) with Zeocarb 225 H^+ . In this system the rate of movement of the resin varies with the rotation of the horizontal axes. The solution is injected in the middle of the spiral. The resin and the solution move in opposite directions and are recovered at the two extremities of the spiral. Slater [39] used a column comprising of seven sections, each section 60 cm long and 5 cm in dia. Polythene blocks with 1.25 cm central holes were placed between the sections, and served as solution distributors. The solution was pumped from the bottom upwards through the resin, thus fluidising the resin, for a predetermined time in a

closed circuit. The resin was recovered at the bottom of the column.

In another publication, Slater [40] discussed the factors favourable in the utilisation of continuous counter-current ion exchange methods for the recovery of metals from leach solutions, effluents, and pulps, etc. Slater and his coworkers [41, 42] also developed a system wherein the ratio of the length of adsorption column to its dia was large. Fluidization of the resin was obtained in the column by the passage of the solution from bottom upwards. Lucas [43] has reported the use of such a deep fluidized bed continuous ion - exchange system on a pilot plant scale for the treatment of base metal mine water (containing copper), cyanide-waste water, uranium leach liquor and uranium mine water.

The continuous operation of an ion exchange system has been variously applied by numerous workers to study the concentration and purification of copper solutions originating from different sources. Thus Abrams *et al.* [44] studied the extraction of copper from mine drainage water containing 0.634 g/l of copper using the Duolite A (H^+) resin in a continuous counter current ion exchange system. From seven samples treated the copper recoveries were 95, 92, 82, 95, 96, 87, and 93 % respectively. Laskorin and coworkers [45] used a modified aminocarboxylic resin (ANKB-7) for the treatment of 20 tons of a discard pulp coming from the flotation of copper minerals. The pulp contained 1.5 to 1.6 g/l of copper at a pH of 3.5. The pulp-resin counter current contact was brought about in a pilot plant. The elution of the loaded resin was done with 20 % H_2SO_4 with an efficiency 99.7 %. The copper recovery was 82.5 % and the concentrated eluates contained 15.6 - 26.4 g/l of copper. Salter [46] studied the fixation of copper on four types of resin in fluidized beds. Roland [47] discussed the advantage of continuous ion exchange systems as applied to Chemical Industry and hydrometallurgy. Slater and Lucas [48] proposed a mathematical model for the frontal analysis curves in the case of fluidized bed ion exchange. Pimenov and Startsev [49] developed a method for the calculation of isochrones in the case of an exchange between copper and a weak acid resin ANKB-1.

The strong acid resins adsorb all cations completely unselectively. The higher valency cations are adsorbed in preference to lower valence cations at all pH values of the solution. Thus iron in solution will be adsorbed more easily than copper and the resulting eluate will contain the iron, the presence of which is not acceptable beyond a certain limit. On the other hand weak acid resins show some selectivity for copper over the iron ions. At the same time

chelating resins like the aminodiacetic acid Lewatit TP207 and Zerolit S1006 show the properties of selectivity of weak acid resins and pH insensitivity of strong acid resins. Naden and Evans [50] studied the resin Lewatit TP 207 with respect to its loading and stripping characteristics and its selectivity for copper in the presence of iron. They showed that the resin offered attractive possibilities for use in CIX units, combining some selectivity for copper with useful rates and levels of copper loading and rapid strip kinetics. Riče and Nedved [51] studied Zerolit S-1208 chelating resin for the recovery of copper and nickel from ammoniacal leach solutions.

The introduction of solvent extraction in the recovery of copper from its leach solutions during early sixties brought in a new era of copper hydrometallurgy. However, with the passage of time and accumulation of experience with the new technology it became known that the solvents and diluents used were lost in the effluent stream due to their solubility or entrainment with the aqueous phase. Typical losses have been reported by Ashbrook [52] and such losses can contribute to the costs of operation of the process. Ritcey and coworkers [53] reported on the toxicity of some of the new reagents. This aspect of solvent extraction was probably the reason behind the awakening of interest in the fabrication of chelating and solvent impregnated resins for the recovery of copper and other metals. Difficulties were, however encountered in the beginning as to what substrate should be used for impregnation so that the impregnated material would have the requisite hydrophilicity, tight bonding of the chelating reagent with the substrate, minimum leakage and acceptable rates of uptake of the ions of interest. The situation improved with the introduction of macroporous polymeric substrates and the development of techniques of impregnation. Flett [54] has reviewed the various resin impregnates showing their uses for the recovery of different elements. XAD-2 and oleogon etc. have been used as substrates for impregnation with LIX64 N, LIX 65 N and Kelex 100. XAD-2 was used by Warshawsky [55] and Vernon and Eccles [56] for impregnation with LIX 64 N, LIX 65 N and Kelex 100 respectively while oleogon was employed by Hughes and Purdey [57] for impregnation with LIX 64 N. The variables studied by different authors on the resin impregnates have been the rate of uptake of copper ions, selectivity of the resin for copper ion, loss of solvent from the impregnate, loading, and stripping kinetics, etc.

At the end it may be pointed out that the present state of the art of utilising impregnated resins is not fully grown and as such it cannot be used for the treatment of leach liquors to produce solutions for direct electrowinning.

However, they may profitably be used for scavenging the solvent extraction raffinate, mine waters and the process rinse waters.

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