

Recovering Gold from Copper Concentrate via the HydroCopper™ Process

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HydroCopper™ technology comprises a chloride-leaching method for copper sulfide concentrates and copper production up to semi-products. As compared with the commonly used sulfate solutions, brine solutions offer aggressiveness and stability of the copper(I) ion and, consequently, a lower energy consumption in leaching. Copper(II) ions and oxygen are used as oxidants. Iron reports to the leaching residue as oxide and sulfur as elemental sulfur. Gold is dissolved and recovered in the third stage of the counter-current leaching when the redox potential reaches higher levels.

INTRODUCTION

The most widespread method of producing copper is the smelting of copper sulfide concentrates. An alternate method that is growing in popularity is heap leaching of oxidized copper ores with weak sulfuric acid together with copper solvent extraction and electrowinning (EW). Now approaching a 20% share of primary copper production, heap leaching offers reduced costs compared with the costs of smelting and refining. Those savings result from the omission of energy-intensive ore grinding and flotation. Limited resources of oxidized copper ores, the long leaching time of chalcopyrite, and an inability to recover gold inhibit growth of this method.

In the treatment of copper concentrates, hydrometallurgical leaching methods have long been studied as alternatives to smelting. In a hydrometallurgical process, the concentrate is dissolved oxidatively in agitated reactors. However, chalcopyrite, the most common copper mineral, dissolves with some difficulty in sulfate media, which is normally used. Consequently,

high temperatures and high-pressure autoclaves are required.

The excellent leaching power of chloride solutions has been well known for over 100 years.¹ Flett recently reviewed chloride hydrometallurgy,² a process in which chalcopyrite dissolves below the boiling point of water with divalent copper as an oxidant. Chloride solutions offer the stability of monovalent copper. In addition, the sulfur in the dissolved sulfide minerals reports to the leaching residue in elemental form. In both cases, energy savings result compared with sulfuric acid leaching, where copper and sulfur are oxidized to higher oxidation stages—copper to valence +2 and sulfur to valence +6.

The recovery of copper after chloride leaching by EW seems a natural option, particularly when cuprous ions are

oxidized to cupric ions on the anodes of the EW cells and these ions can be used as an oxidant in leaching. But copper is deposited on the cathodes from chloride solutions as dendroid copper grains, which are difficult to harvest from an electrowinning cell provided with a diaphragm. An alternative to electrowinning is the chemical precipitation of copper as an oxide with sodium hydroxide. Chlor-alkali electrolysis can be used to produce the sodium hydroxide required. Energy consumption per kilogram of copper is about the same in both cases. See the sidebar for HydroCopper process details.

RECOVERY OF GOLD

The recovery of gold in the HydroCopper process has been studied with two different feed materials. Pyhäsalmi copper concentrate was used in a

Table I. Conditions and Results in the HydroCopper™ Three-Stage Bench-Scale Pilot Test

Reactor	Reactor 1	Reactor 2	Reactor 3
pH	—	1.5	1.4
Redox potential $E_{AgCl/Ag}$ /mV	470	650	700
Cu g/L of solution (total)	—	55	55
Cu % of solids	6.8	2.1	0.7
Au ppm of solids	4.3	1.1	0.7
Leaching yield of Cu (%)	—	—	97.5
Leaching yield of Au (%)	—	—	86.9

Table II. Conditions and Results of the HydroCopper™ Two-Stage Batch Test

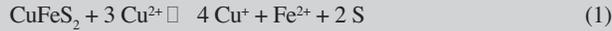
Stage	Time (h)	pH	Measures Redox Potential ($E_{AgCl/Ag}$ /mV)	In Solids				Recoveries (%)		
				Cu ²⁺ (g/L)	Cu (%)	Au (g/t)	Cu	Fe	Ag	Au
1	0.0	2.75	440	40.9	23.5	4.3	0.0	0.0	0.0	0.0
	2.0	2.21	420	14.5	—	—	62.8	3.1	—	—
	4.0	2.13	420	12.6	—	—	62.6	4.0	—	—
	6.0	2.11	420	11.0	11.0	—	66.0	4.7	89	—
2	0.0	1.93	450	—	—	—	—	—	—	—
	2.0	1.87	450	21.1	—	—	88.9	8.2	—	—
	4.0	1.70	530	49.7	—	3.6	99.2	9.7	—	44.2
	5.5	1.56	650	55.5	—	—	—	—	—	—
	6.0	1.61	650	—	0.23	0.7	99.4	10.0	>91	94.2

HYDROCOPPER PROCESS

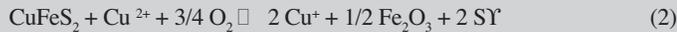
The HydroCopper™ process³ can be divided into three main stages (Figure A): the leaching of copper concentrate, the regeneration of chemicals, and the production of copper semi-products.^{4,5}

Copper concentrate is leached into a CuCl_2 -containing strong sodium chloride solution (250–300 g/L) by oxidation of cupric ions in agitated reactors at a temperature of 85–95°C. Leaching is done in a three-stage countercurrent system. Air or oxygen is blown into the leaching reactors in order to oxidize the iron and to precipitate it as hydroxide or oxide at a pH of 1.5–2.5. Sulfide minerals are dissolved and elements such as Zn, Pb, Ni, and Ag end up in the leach solution.

Chalcopyrite, the most important but slowly soluble copper mineral, is leached in the chloride media with the help of Cu^{2+} according to the basic reaction:



Ferrous iron is further oxidized by air to ferric which precipitates as goethite or hematite, resulting in the following sum reaction:

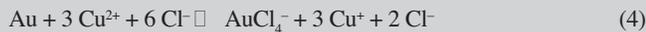


Leaching is controlled by the blowing of air or oxygen and monitoring of the pH. If the rate of oxidation is too intense, the pH tends to rise. At a pH of about 2.5 the copper hydroxychloride starts to precipitate, which has to be avoided because it means copper losses in the leach residue:



The main components of the leach residue are iron oxides and elemental sulfur. It also contains silicates of the concentrate and some gypsum. During leaching, 5–10% of the sulfur in the sulfides is oxidized to sulfate, which is removed as gypsum by adding limestone.

When all the chalcopyrite is leached, which is seen as an increase in the redox potential, gold along with pyrite starts to dissolve in the last stage of countercurrent leaching as a chloro-complex according to the reaction:



The gold-bearing solution from the third leaching stage is pumped through columns where gold is adsorbed on activated carbon. Another possibility is chemical precipitation.

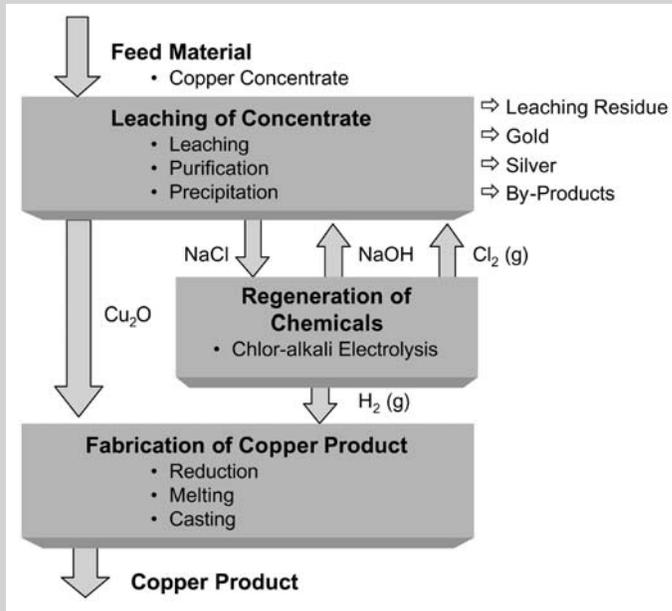


Figure A. Block diagram of the HydroCopper™ process.

continuous three-stage bench-scale leaching pilot test. The concentrate contains 25.7% copper, 28.1% iron, 2.1% zinc, and 32.2% sulfur, which equates with the occurrence of 73.7%

chalcopyrite, 9.3% pyrite, and 3.5% sphalerite. The accessory minerals are pyrrhotite, galena, and barite. The concentrate contains 6.3 ppm gold.

In the pilot test, the size of the

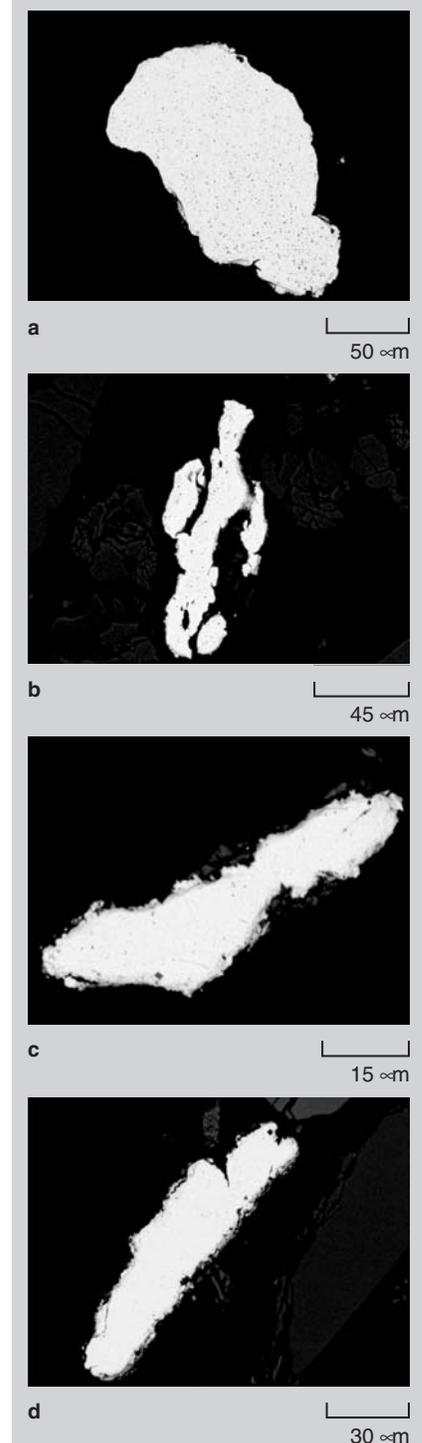


Figure 1. (a–d) Rolled gold grains from the heavy fraction of the Pyhäsalmi copper concentrate.

leaching reactors was 5 L each and the solids feed rate was 160 g/h. The solution feed was about 1 L/h and it contained about 40 g Cu^{2+} /L as CuCl_2 and 280 g NaCl /L. The gold was leached

in the third stage that consisted of a series of three reactors, in which chloride gas was used to adjust the redox potential to a sufficiently high level, >600 mV AgCl/Ag vs. Pt. The temperature was 95°C and the solution residence time in this stage was 10 h. The other conditions and results are given in Table 1. The gold content of the feed of the gold leaching stage was 4.3 ppm (Reactor 1 in Table I) and the final leaching residue contained 0.7 ppm gold and 0.7% copper. This equals the recovery of 87% gold and 98% copper, respectively. The gold-containing solution was pumped through small carbon columns that removed gold down to a level less than 0.02 mg/L.

Another commercial chalcopiritic copper concentrate containing 23.5% copper and 4.3 ppm gold was studied in a series of batch tests with a 5 L reactor. About half of the concentrate was leached in the first stage that lasted 6 h and was operated at 90°C. The leaching solution contained 40 g Cu²⁺/L as CuCl₂ and 280 g NaCl/L. After the first stage, the solids were settled in the reactor, solution was removed, and half of it was diluted with a solution containing 280 g NaCl/L. The diluted solution was fed back to the reactor. This operation was done to keep the copper concentration of the solution within reasonable limits. In the second stage, which lasted 6 h and was operated at 90°C, the redox potential was raised with the help of chlorine gas. The main conditions and results of the two stages

are given in Table II. The total gold recovery in the test was 94%, with a major portion of gold recovered during the last 2 h with higher redox potential.

The leaching of gold in the Pyhäsalmi copper concentrate was significantly slower than in the other concentrate; therefore, the mode of occurrence of gold in the Pyhäsalmi concentrate was studied in more detail. About 20% of the gold in the copper concentrate is gravitative recoverable, as shown by Knelson preconcentration tests resulting in a heavy fraction with 92 ppm gold. According to mineralogical studies, gold occurs in the heavy fraction mainly as gold-silver alloy. The silver content of these alloys ranges from 4.8 wt.% to 93.8 wt.%; the average silver content is 31 wt.%. The gold reports to a heavy fraction as liberated and rolled grains and the grain size ranges from 2.9 μm to 159 μm (Figure 1). The average grain size of gold is 40 μm, though 75.4 vol.% of detected gold particles were coarser than 100 μm in size.

CONCLUSIONS

Hydrometallurgical production of copper offers lower investment costs and treatment of complex copper ores from which profitable copper concentrates cannot be floated due to the excess of harmful elements such as arsenic. The HydroCopper process also enables efficient recovery of silver and gold, which is important because gold is often a valuable element in chalcopiritic

copper concentrates.

The essential prerequisite for good gold recovery is a sufficiently high leaching yield of soluble sulfides that hinder the dissolution of gold. The difference in the gold leaching kinetics in the two concentrates studied is probably due to the presence of coarse-grained gold in the Pyhäsalmi copper concentrate.

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