

HydroCopper™—a new technology producing copper directly from concentrate

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Abstract

The direct leaching of copper concentrate instead of smelting will be beneficial and gain ground in the future. This paper presents the HydroCopper™ Technology, which is comprised of a chloride-leaching method for copper sulphide concentrates and the copper production up to semi-products. The technology is developed and registered by Outokumpu.

The advantages of the brine solutions, compared with the generally used sulphate solutions, are the aggressiveness and stability of the copper(I) ion and, consequently, lower energy consumption in leaching and recovery. Copper(II) ions and oxygen are used as oxidants. Iron reports to the leaching residue as oxide and sulphur as elemental sulphur. Precious metals, Au and Ag, are also dissolved and recovered. Copper(I) oxide is precipitated from the purified pregnant leach solution as an intermediate, which is further reduced with hydrogen before melting and casting into the final copper product. A unique feature of the HydroCopper™ process is the regeneration of the lixiviant, i.e., sodium chloride, using a chlor-alkali electrolyzer. The sodium hydroxide generated is used to precipitate copper(I) oxide, the chlorine gas in leaching, and hydrogen gas to reduce the copper(I) oxide. The reduced copper powder is melted and cast into copper semi-products.

The HydroCopper™ process is capable of treating different kinds of copper concentrates and it is currently in the stage of commercialization.

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1. Introduction

About 83% of the worldwide annual primary copper production, 15 million tonnes, is produced by smelting,

and a half of that by flash smelting, a method developed and marketed by Outokumpu. Heap leaching of oxidized copper ores with weak sulphuric acid together with copper solvent extraction and electrowinning has gained popularity during recent decades, so that its share in primary copper production is close to 20%. Limited resources of oxidized copper ores inhibit this growth, but bacteria-aided bioleaching in heaps may be economically viable in some cases. Secondary copper

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sulphide minerals are amenable to bacterial leaching, but the primary copper sulphide, chalcopyrite, requires a prohibitively long leaching time. The success of heap leaching is based on its lower costs compared with that of smelting and refining, thanks to the omission of energy-intensive ore grinding and flotation. In a hydrometallurgical process, the concentrate is dissolved oxidatively in an agitated reactor. However, chalcopyrite, the most common copper mineral, dissolves with some difficulty in sulphate conditions, which are 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 (Hoepfner, 1893). Recently, Flett has reviewed chloride hydro-metallurgy (Flett, 2002). Chalcopyrite dissolves below the boiling point of water with divalent copper as oxidant. An additional benefit of chloride solutions is the stability of monovalent copper and also that the sulphur in the sulphide minerals dissolved reports to the leaching residue in elemental form. In both cases, it results in energy savings compared with sulphuric acid leaching, where copper and sulphur are oxidized to higher oxidation states.

The recovery of copper after chloride leaching by electrowinning seems a natural option, particularly when cuprous ions are oxidized to cupric ions at the anodes of the EW cells to be used as an oxidant in leaching. But copper is deposited on the cathodes from chloride solutions as dendritic 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.

Outokumpu chose the method based on chlor-alkali electrolysis for development when batch and pilot tests had shown that, the precipitated copper oxide was pure enough for the production of high-quality copper by reduction and smelting. The new method has been patented (Hyvärinen and Hämäläinen, 1999) and registered as HydroCopper™. The method can be divided into three main stages (Fig. 1): (1) leaching of copper concentrate, (2) regeneration of chemicals and (3) production of copper semi-products (Hyvärinen et al., 2002; Hietala and Hyvärinen, 2003).

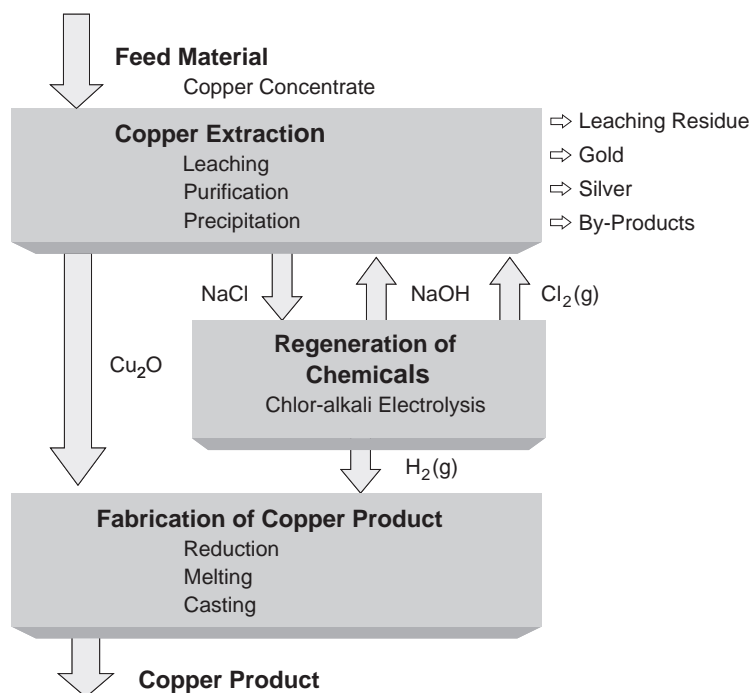


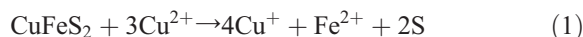
Fig. 1. Block diagram of the HydroCopper™ method.

2. Characteristics of the developed procedure

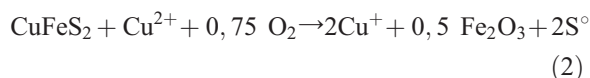
2.1. Leaching of copper concentrate

Copper concentrate is leached into a strong (250–300 g/dm³) sodium chloride solution containing CuCl₂, oxidized by cupric ions in agitated reactors at a temperature of 85–95 °C. Leaching is done in a three-stage counter-current system. Air or oxygen is blown into the leaching reactors in order to oxidize iron and to precipitate it as hydroxide or oxide at a pH of 1.5–2.5. Almost all sulphide minerals are dissolved and elements such as Zn, Pb, Ni, Ag etc. end up in the leach solution. When all sulphides are leached in the last stage of counter-current leaching, the redox potential of the solution increases to such high values that gold is dissolved as a chloro-complex. Gold is recovered either with activated carbon or by chemical precipitation.

Chalcopyrite, the most important but slowly dissolving copper mineral, is leached in the chloride solution with the help of Cu²⁺ according to the basic reaction:

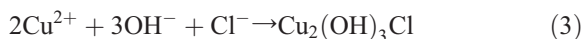


Ferrous iron is further oxidized by air to ferric which precipitates as goethite or hematite, resulting in the following overall reaction:



The blowing of air or oxygen and monitoring the pH control leaching. If the oxidation is too intense, the

pH tends to rise and at about a pH of 2.5 a copper hydroxyl chloride 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 sulphur. In addition it contains silicates of the concentrate and some gypsum. During leaching, 5–10% of the sulphur in the sulphides is oxidized to sulphate, which is removed as gypsum by adding limestone.

2.2. Solution purification

The pregnant leach solution typically contains 60 g/dm³ Cu⁺ and 10 g/dm³ Cu²⁺. Depending on the concentrate leached there are some grams per litre of other metals in the solution (Hämäläinen et al., 2003). All other metals except monovalent copper have to be removed during the solution purification step. In the first phase, divalent copper is precipitated as hydroxylchloride by increasing the pH of the solution to 4–5 with sodium hydroxide (Fig. 2). In the next phase, silver is recovered by cementation with copper powder. In order to bring the reaction to completion a small amount of mercury chloride is added, which forms an amalgam with silver. This amalgam is separated and leached into weak acid, so that silver is recovered as solid silver chloride and soluble mercury is re-circulated back to silver recovery.

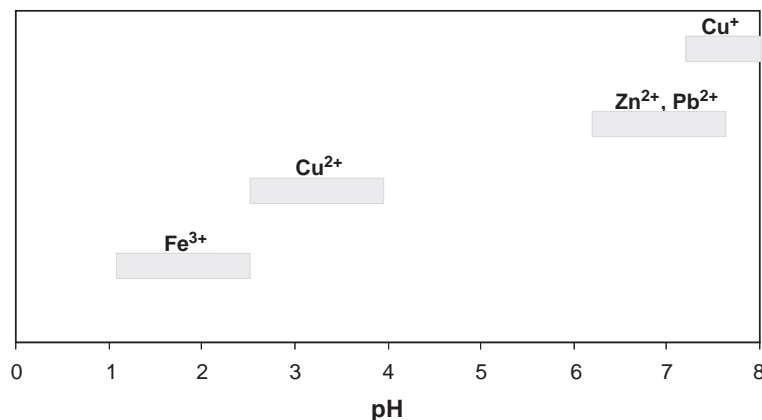
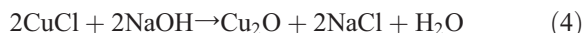


Fig. 2. Precipitation of different ions as a function of pH.

Subsequently sodium carbonate is added to the silver-free solution to increase the pH to 6–7, then the majority of the remaining metals, such as Zn, Pb, Ni etc., precipitate as carbonates (Fig. 2) and are filtered off. It is not possible solely by chemical precipitation to attain sufficiently low impurity levels without copper losses due to the co-precipitation of copper. Therefore, the final purification is accomplished with chelating ion exchange resins, which remove impurities to trace levels.

2.3. Copper extraction

After solution purification copper(I)oxide is precipitated with sodium hydroxide at pH 9:



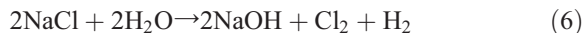
Oxide is separated by filtration and the filtrate, NaCl solution, is routed to the regeneration of chemicals. The very pure copper(I)oxide is reduced, melted and cast into a copper product. Reduction of the oxide is carried out with hydrogen in a rotary kiln at a temperature of about 400 °C:



The product of the continuously operating rotary kiln is copper powder, which is melted in an induction furnace.

2.4. Regeneration of chemicals

A specific feature of the HydroCopper™ method is the use of chlor-alkali electrolysis in the regeneration of chemicals. The pure sodium chloride solution formed in the precipitation of copper(I) oxide is routed to chlor-alkali electrolysis, where the salt is decomposed by electricity into sodium hydroxide, chlorine and hydrogen:



The sodium hydroxide solution is re-circulated to the precipitation of copper(I) oxide and the hydrogen gas is used in the reduction of copper(I)oxide. The chlorine gas is used for the oxidation of copper(I) to copper(II) in the solution during leaching:



3. Special features of the HydroCopper™ technology

Low investment costs are the main benefit of the HydroCopper™ process. In general, the capital costs of hydrometallurgical plants are between about \$ 1000 and \$ 2500 per annual tonne of copper production. The heap leach operations are at the lower end, the pressure leach at the higher. HydroCopper™ is somewhere in the middle of this range, depending on the mineralogy of the copper deposit, the local infrastructure, etc. Therefore, the capacity of a HydroCopper™ plant can be much lower, say 20,000–150,000 t/a, than the capacity of a new pyrometallurgical green field plant, whose capital costs are typically \$ 3000–4000/a-t Cu.

Operating costs are favourable, about 20–30 US\$/kg, depending mainly on the composition and mineralogy of the feed and the price of energy. In addition, high recoveries for copper, silver and gold, 96–98%, warrant the economy of the process. In particular, the dissolution of gold after the leaching of copper sulphides is advantageous, because no extra leaching steps are needed. Gold is recovered from the pregnant leach solution with activated carbon or by precipitation.

Low quality concentrates, i.e., low copper or high impurity concentrations, can be utilised. Arsenic, a common impurity, which otherwise could cause environmental penalties, is manageable, because it precipitates during leaching as a relatively stable ferriarsenate.

Premium prices of copper are to be expected, because copper semi-products are produced instead of cathodes. The HydroCopper™ plant does not produce sulphuric acid, which can be a benefit in a tight market situation.

Notable additional advantages are achieved by processing the concentrate at the mine site taking into account the whole production chain from mine to concentrator and the HydroCopper™ plant. Copper recovery in ore dressing can be optimized. Usually this means a decrease in the copper concentration of the concentrate, but an increase in total copper recovery. In addition, exploitable ore resources are increased if the cut-off grade of copper ore can be lowered. Leach residue, which otherwise needs a special dumping pond, can be disposed of with the tailings to the existing dump area of the mine.

Certain freight and storage costs of concentrate are avoided, if the plant is on the mine site. Freight costs for secondary material such as gangue disappears and only the valuable metals: copper, gold, silver and other products, need to be transported. The payback time of metals is quicker due to the shorter processing time. It takes only a few days to enrich the concentrate to copper. Consequently, working capital and cost of interest are considerably smaller.

4. Ongoing development of the HydroCopper™ technology

Outokumpu aim is to develop the HydroCopper™ method for technology sales. In addition, participation in production activities with a partner from the mining industry is possible and Outokumpu is actively searching for partners to implement a co-operative endeavour. The expertise of Outokumpu in the production and marketing of copper products can be utilized, and also the launching of products is possible.

In order to confirm the operability of the new process and to dimension equipment, Outokumpu Technology Oy has designed and implemented a demonstration plant in connection with the hydrometallurgical pilot facilities of Outokumpu Research Oy, in Pori, Finland. The demonstration plant includes all the process steps of HydroCopper™. The capacity of the plant is 1 tonne of copper per day, corresponding to about 4 tonnes of concentrate per day. This production rate is optimal for the testing of the process equipment. Many proprietary products of Outokumpu Technology Oy have been used, such as: leaching reactors with agitators, thickeners, press filters and belt filters, ion exchange systems, melting and casting equipment and automatic analyzing and process control systems. The installation, testing and calibration of the process equipment of the demonstration plant as well as the first campaign of the operation

were carried out during 2003 (Leimala et al., 2003). Based on the results of the demonstration plant operations, a reference plant of the HydroCopper™ process with a capacity of 20,000–150,000 t/a will be designed.

The HydroCopper™ process has evolved from an on long-term process investigation, research and development at Outokumpu Research. This new process is based on the latest technological breakthroughs, high-quality products and proprietary equipment, culminating in a new concept, where the available, proven technologies and Outokumpu know-how are combined. The demonstration plant in Pori will ensure the suitability of different copper concentrates for the HydroCopper™ process, facilitating the design of the reference plant.

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