

HYDROCOPPER® - FOR TREATING VARIABLE COPPER CONCENTRATES

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ABSTRACT

The Outokumpu HydroCopper® process is a chloride based atmospheric leaching process alternative that can treat a variety of different concentrates. Chalcopyrite and other copper sulfides can effectively be leached under atmospheric pressure in strong, aggressive chloride solution using copper (II) ions as oxidant. Impurities are removed from the solution as carbonates and ion exchange. Copper is precipitated from the purified pregnant leach solution as copper (I) oxide, which is filtered and reduced by hydrogen gas to metallic copper powder, which is melted and cast into copper product. Sodium chloride solution from copper (I) oxide precipitation is decomposed in a chlor-alkali electrolyser, to products of which are circulated back to the process. The process has been designed for copper concentrates and is a fast and economical way to produce copper wire rod directly from concentrate. The process can efficiently handle impurities like arsenic and mercury, which can be harmful in the pyrometallurgical processes. The process has been tested in the laboratory and 1 ton/day demonstration plant scale and it has been proven to be commercially viable. The process has been designed to meet the strictest directives for emissions. Other environmental factors are carefully considered to obtain the highest possible eco-efficiency.

INTRODUCTION

Outokumpu Technology's HydroCopper[®] process has been designed to produce a copper product directly from concentrate. The process can treat a copper concentrate of a wide variability due to the in-built variation tolerance of copper content in concentrate and can handle a wide range of impurities. In the HydroCopper[®] process sulphidic concentrates with various mineralogy and copper grade can be treated to produce high-quality copper. Instead of copper cathodes the HydroCopper[®] products could be copper wire rod, bars or billets.

During the development of the HydroCopper[®] process, mineralogically different concentrates have been tested in the laboratory scale. Along with the copper and gold leaching also the leaching and purification behaviour of many different elements has been identified.

THE HYDROCOPPER[®] PROCESS

The HydroCopper[®] process is based on chloride hydrometallurgy. A number of other components are leached along with copper, mainly other metal sulfides and carbonates. The HydroCopper[®] process consists of six stages: leaching of copper concentrate, oxidation of leach solution, a four stage solution purification, precipitation of copper (I) oxide, regeneration of chemicals and fabrication of copper products (Figure 1) [1].

Copper and Gold Leaching

Chalcopyrite, other copper sulfides and oxides are leached effectively under atmospheric pressure in strong, chloride solution using copper (II) ions as oxidant. The leaching temperature is 85 - 95°C. Copper leaching circuit has normally three stages in a counter-current principle (Figure 2).

Depending on mineralogy of the concentrate, the first leaching stage leaches 15 – 30% of the copper. Second leaching stage is the most powerful one and is operated with air or oxygen oxidation and leaches most of the copper in concentrate. Third leaching stage handles the last 2 - 5%. A standard leaching extraction figure for copper in most of the concentrates is 98%.

Gold leaching is practiced in the same leaching circuit as copper leaching. Gold will be dissolved after all the copper in concentrate has been leached. If there is gold present in the concentrate, the redox-potential in the last leaching stage is raised to a level of 620 – 650 mV (Ag/AgCl).

Leach residue consists of iron, sulphur, and inert silicates. Iron reports as hematite or goethite, sulphur in elemental form.

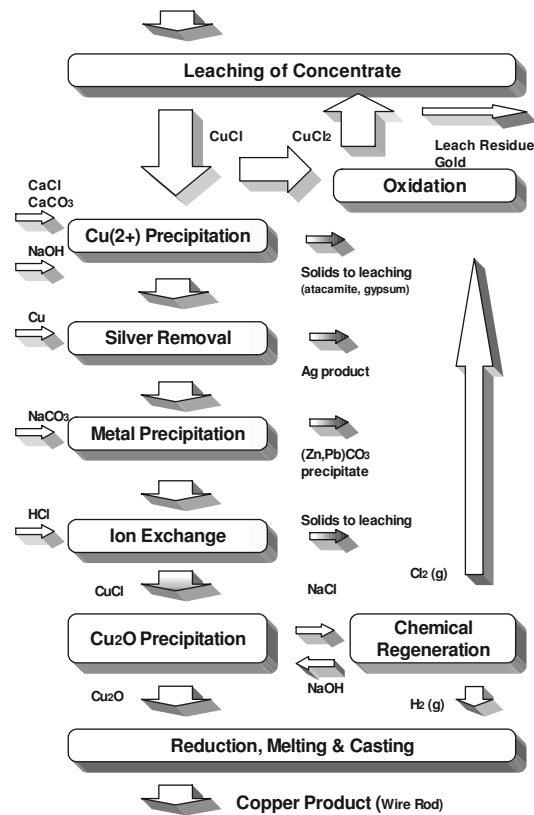


Figure 1 - Block diagram of the HydroCopper[®] process [1]

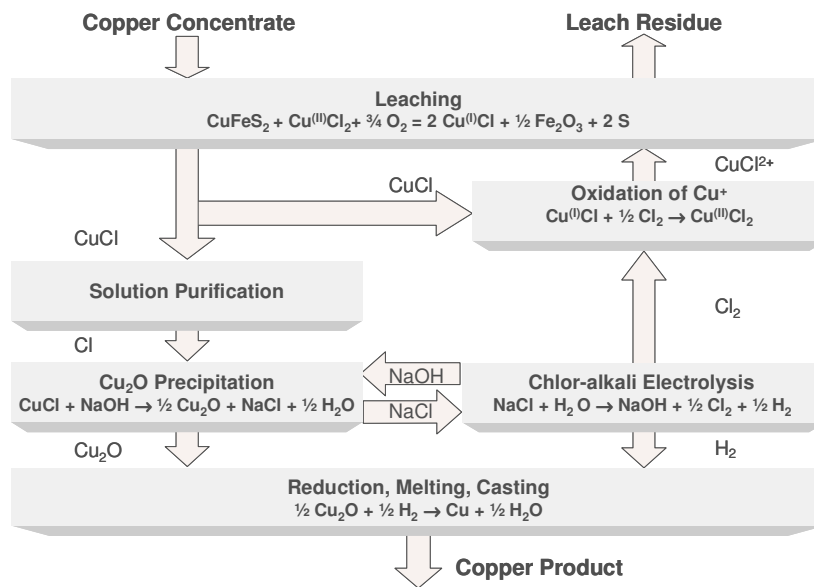


Figure 2 - A diagram of all the process stages in the HydroCopper[®] process [1]

Solution Purification

A four-step solution purification procedure is needed to polish the solution to ensure the quality of the copper product [2].

The first solution purification stage is precipitation of copper (II) as atacamite, cupric hydroxide chloride $\text{Cu}_2\text{Cl}(\text{OH})_3$, combined with sulfate removal. The precipitate is circulated back to leaching stage to re-leach the atacamite.

The second purification stage is silver and mercury removal. The silver in solution is recovered to less than 1 mg/L level, and mercury reports to the mercury chloride solution circulated within the silver removal stage. After precipitation, silver is recovered as silver chloride for further processing.

The third stage of the purification is a neutralization stage. Solubilized metals from the PLS are treated either by precipitation or, if there is a significant quantity of a valuable metal present, the flow sheet can be modified to include separation steps for metals. The precipitation pH for most of the metals is lower than the one of Cu^+ [2], which gives selectivity to the solution purification (Figure 3).

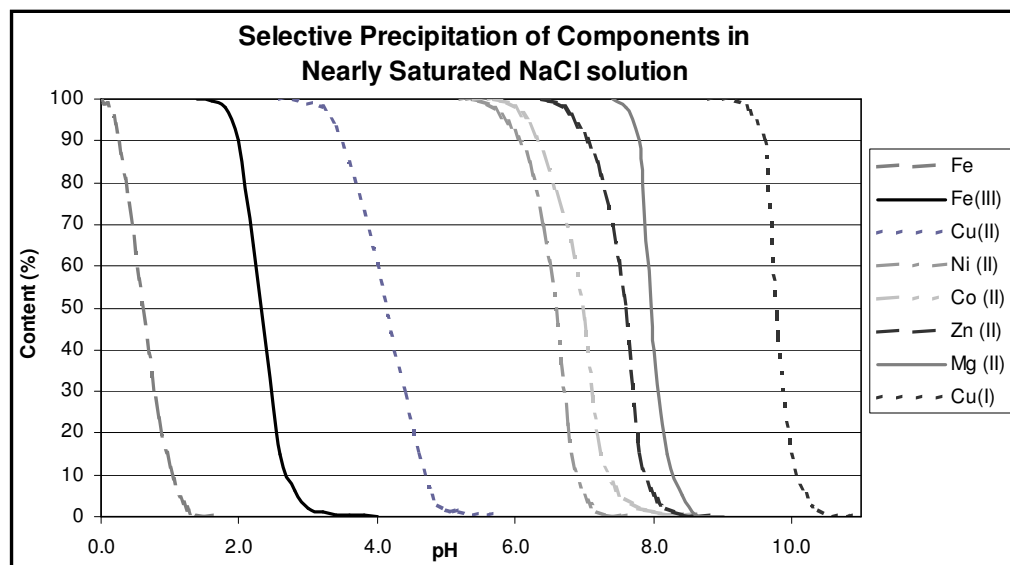


Figure 3 - Precipitation curves of soluble metallic components in PLS

The fourth and final solution purification stage is ion exchange. The step takes out the remaining metallic impurities as well as calcium and magnesium. The weak elution acids produced in the ion exchange unit are circulated back to leaching to recover metal values.

Oxide Precipitation

Copper is precipitated as copper (I) oxide in pH of 9-10 (1)



The copper (I) oxide is the intermediate product of the process. The purity requirements for metals in an LME-A grade copper product are met at this stage (Table 1).

Table 1 - Typical analysis of copper produced in the HydroCopper[®] process [1].

Element		
Selenium	ppm	<0.1
Tellurium	ppm	<0.01
Bismuth	ppm	<0.002
Chromium	ppm	<0.05
Manganese	ppm	<0.1
Antimony	ppm	0.07
Cadmium	ppm	<0.003
Arsenic	ppm	0.66
Phosphorus	ppm	<0.3
Lead	ppm	<0.02
Sulfur	ppm	<0.2
Tin	ppm	<0.007
Nickel	ppm	<0.2
Iron	ppm	2.3
Silica	ppm	<0.2
Zinc	ppm	0.4
Cobalt	ppm	0.12
Silver	ppm	21
Aluminum	ppm	0.19
Total		25

Reduction, Melting and Casting

Copper (I) oxide powder is reduced with hydrogen gas to metallic copper. Reduction takes place in a belt-type furnace at 600 - 800 °C. Resulting copper metal is sintered during the reduction and contains typically 200 - 300 ppm of oxygen.

Sintered copper sponge is fed to an induction furnace where residual oxygen is removed by graphite layer on top of the melt. Copper is cast, for instance, to 8 - 32 mm wire rod, which can be used to copper cable manufacturing.

Chlor-Alkali Electrolysis

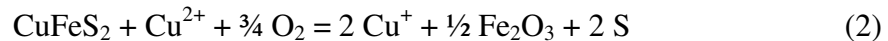
Sodium chloride solution from copper (I) oxide precipitation is pumped into a chlor-alkali electrolysis (CAE) unit. Sodium chloride concentration in the HydroCopper[®] process is at 270 g/L NaCl, suitable for the CAE process. In the chlor-alkali electrolysis the sodium chloride solution is decomposed into sodium hydroxide, chlorine gas and hydrogen, all used in different parts of the process.

BEHAVIOUR AND REMOVAL OF ELEMENTS

HydroCopper[®] process was originally developed for copper sulphide concentrates, especially chalcopyritic ones, being the most abundant and refractory mineral compared to other main copper minerals. The intensive chloride leaching circuit attacks other sulphide minerals as well, so there are a number of different elements from concentrates introduced to the process solution.

Iron

Iron in copper sulphide minerals is leached in the leaching circuit in both non-oxidative and oxidative stages, the major part being leached in the oxidative environment. With oxygen or airflows to the leaching reactors iron is oxidized and precipitated mainly as hematite and goethite, which report to the leaching residue [3].



Gangue minerals

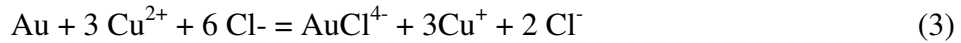
Quartz and most other silicates are inert and do not interfere leaching. The clay minerals might interfere with copper leaching and especially to the filtering of leach residue. Carbonates are dissolved having sometimes a significant effect to the acid balance of the process.

Arsenic

Arsenic is leached in the leaching circuit. In the oxidative conditions of the second leaching stage arsenic is oxidised and when iron is available, they are co-precipitated as ferric arsenate. Ferric arsenate is a stable form of arsenic, and it can be disposed with the leaching residue to the tailings area for permanent storage.

Gold

After the copper sulphides have leached, the redox potential will rise. Gold will start to leach at approximately 600 mV on the AgCl/Ag scale; although the form in which the gold occurs will impact the leaching rate. The most challenging forms are the refractory ones. Also large amounts of pyrite will have an effect on leaching.



Sulphur

Elemental sulphur formed in the leaching process reports to the leach residue. 5...10% of the sulphur in concentrate is oxidized to sulphate, which must be precipitated out of the PLS. The requirement for the sulphur level allowed in the PLS comes from the membranes within the chlor-alkali cell, which can tolerate up to 10 g/L of sulphate. The sulphate level is controlled in the first solution purification stage by adding calcium to the leaching solution. The gypsum precipitate is circulated back to leaching and is disposed with the leach residue.

Bismuth

Bismuth is leached in the leaching circuit. The first solution purification step is operated at pH 4, where bismuth also precipitates. Bismuth hydroxide can further be separately purified.

Silver and mercury

Silver and mercury are leached with copper. They are recovered in the second solution purification stage by cementation on copper powder, forming a silver-rich amalgam. The copper from the amalgam is leached into weak hydrochloric acid. Silver is precipitated as silver chloride, and can be post processed to metallic silver.

Other Metal Sulphides

Metal sulphides, such as zinc, lead, nickel and cobalt, dissolve readily in the leaching circuit. The metals will be taken out of the PLS before the copper (I) oxide precipitation stage either by precipitation or with the ion exchange process step. The amount of metal sulphides available in the concentrate determines the way of removal; if there is a significant, valuable metal component available, it can be recovered as a by-product.

Calcium (Ca)

Calcium is leached if present in the concentrate as carbonates. Calcium must also be added to the process for precipitating sulphate. The calcium balance is handled via the ion exchange, where the excess calcium in the PLS is removed. The calcium is returned back to leaching within the elution acids. It is re-used to precipitate the sulfates formed during leaching.

Magnesium (Mg)

Magnesium carbonates leach rapidly in the first leaching stage. Another source of magnesium is as impurity in the calcium compounds added to the process. Mg is

removed from the PLS in the ion exchange stage. Selective elution will produce a magnesium fraction, which is precipitated with caustic from the chlor-alkali cell.

Table 2 summarizes the fate of the main elements during the various stages of the HydroCopper process.

Table 2 – The behaviour of main elements in HydroCopper process

Metal/Mineral	PURIFICATION STAGE	OUTLET
Sulphur (S)	Elemental sulfur formed in leaching	Leach residue
Sulphate (SO₄²⁻)	Precipitated as gypsum (CaSO ₄)	Leach residue
Gold (Au)	Leaching	Gold concentrate
Gangue minerals		Leach residue
Arsenic (As)	As is precipitated with iron in leaching	Leach residue
Iron (Fe)	Iron mainly as hematite in leaching stage	Leach residue
Iron (II) ion	1. Stage, Solution purification	Leach residue
Bismuth (Bi)	1. Stage, Solution purification	Leach residue
Silver (Ag)	2. Stage, Solution purification, Silver removal	Ag metal
Mercury (Hg)	2. Stage, Solution purification, Silver removal	Hg metal
Zn, Pb, Co, Ni,....	3. Stage, Solution purification, Neutralization	MeCO ₃ precipitate
Magnesium (Mg)	4. Stage, Solution purification, IX	Mg precipitate
Calcium (Ca)	4. Stage, Solution purification, IX	Gypsum

CONCLUSIONS

The HydroCopper[®] process has a flexible modular flow sheet easy to tailor for requirements of different kinds of copper concentrates. The unit operations are proven hydrometallurgical steps that can be modified according to the variations in the concentrate feed.

HydroCopper[®] plant can be built for a specific concentrate or it can work as a custom refinery treating concentrates from various sources. The process features are ready to meet the variations in the feed material. This gives room for optimization in the whole, metallurgical process chain from mine to metal, and mine life can be extended to lower cut-off grades.

Outokumpu Technology's HydroCopper[®] process introduces an innovative alternative for small and medium sized as well as and complicated copper deposits. When smelter concentrate cannot be cost efficiently produced, HydroCopper[®] will come to picture as a cost competitive, feasible process for all kinds of copper concentrates and a wide range of other valuable metals, or impurities.

REFERENCES

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3. L. Haavanlammi, O. Hyvärinen and J. Karonen, "Iron behavior in the HydroCopper[™] –process", Iron Control in Hydrometallurgy, J.E. Dutrizac and P.A. Riveros, Eds., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, 2006, pp 221 – 229.