

CONCENTRATED CUPRIC CHLORIDE SOLUTIONS: POSSIBILITIES OFFERED IN COPPER PRODUCTION

Lundström M.¹, Aromaa J.¹, Forsén O.¹, Haavanlammi L.²

¹Helsinki University of Technology, Laboratory of Corrosion and Materials Chemistry,
P.O. Box 6200, 02015 HUT, Finland

²Outokumpu Technology, P.O. Box 86, 02201 Espoo, Finland
e-mail: Mari.Lundstrom@tkk.fi

KONCENTROVANÉ ROZTOKY CHLORIDU MEĎNATÉHO: MOŽNOSTI ICH VYUŽITIA PRI VÝROBE MEDI

Lundström M.¹, Aromaa J.¹, Forsén O.¹, Haavanlammi L.²

¹Helsinki University of Technology, Laboratory of Corrosion and Materials Chemistry,
P.O. Box 6200, 02015 HUT, Finland

²Outokumpu Technology, P.O. Box 86, 02201 Espoo, Finland
e-mail: Mari.Lundstrom@tkk.fi

Abstrakt

V tomto príspevku sú prezentované výhody použitia chloridového prostredia na lúhovanie sulfidických minerálov. Výhodou použitia chloridu meďnatého ako lúhovacieho činidla je jeho schopnosť tvoriť komplexy, čo značne zvyšuje redox potenciál a oxidačnú silu roztoku. Diskutované sú termodynamické vlastnosti a prevládajúce zložky roztoku. Jednomocný ión meď je prítomný prevažne ako $[\text{CuCl}_3]^{2-}$ a čiastočne vo forme $[\text{CuCl}_2]^-$. Komplexy dvojmocnej meď sú nestabilné, ale je možné predpokladať, že ióny dvojmocnej meď nie sú úplne vo forme komplexov. Pri nízkej koncentrácii chloridových iónov Cu^{2+} nemôžu tvoriť komplexy. V práci sú uvedené základné chloridové procesy, ich výhody a porovnanie. Najdôležitejšie procesy sú CLEAR, CYMET a HydroCopper[®], ktoré v súčasnosti dosiahli komerčného využitia. Jednou z výhod v procese HydroCopper[®] je, že 95% síry môže byť získané v elementárnej forme. Dobrým základom pre získanie meďi vysokej kvality je rafinácia roztoku v piatich stupňoch. Rafinácia pozostáva z odstraňovania Cu^{2+} a síranu, odstraňovania striebra, neutralizácie, iónovej výmeny a nakoniec z precipitácie Cu_2O . Technológia procesu v HydroCopper[®] nie je nová, ale inovácia v kombinácii so známou technológiou robí tento proces unikátnym.

Abstract

This study presents the advantages of chloride media as a leaching media for sulfide minerals. The advantage in using cupric chloride solution as a leaching media is its ability to form complexes, which increases the redox potential and thus the oxidative power of the solution remarkably. The thermodynamics of the solution are discussed and the prevailing species suggested. Cuprous ion can be suggested to be present mostly as $[\text{CuCl}_3]^{2-}$ but also partly as $[\text{CuCl}_2]^-$. The complexation of cupric ion is more inconsistent, but it can be suggested that cupric ion is not totally in a complex form. With lower chloride concentrations Cu^{2+} may not form complexes. At high Cl concentrations $[\text{CuCl}]^+$ or $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ may be present. Some chloride based processes are presented and the advantages of them are compared. The most important processes are CLEAR, CYMET and HydroCopper[®], of which the latter has

recently reached the commercial scale. One of the advantages in HydroCopper[®] is that 95 % of the sulfur can be turned into the elemental form. Also the five step solution purification starting from Cu^{2+} and sulfate removal, silver removal, neutralization, ion exchange and ending in Cu_2O precipitation is a good base for high quality copper production. The unit processes used in HydroCopper[®] are not new, but the innovative combination of known unit processes makes HydroCopper[®] unique.

Keywords: Chloride leaching processes, thermodynamics, cupric chloride, sodium chloride, chalcopyrite, HydroCopper[®].

1. Introduction

The development of the hydrometallurgical process options for sulphide minerals is of great importance specifically from an environmental viewpoint. As sulfur dioxide emissions from the pyrometallurgical industry are highly undesirable, there is a need to develop economically beneficial processes, which turn the sulfur coming from the sulphide minerals into elemental form. The possibility to use low-grade concentrates, low energy consumption and ability to regenerate leaching solutions increase the importance of the research of the hydrometallurgical process options. Hydrometallurgical processes can also operate profitable in small scale plants.

In the search for hydrometallurgical alternatives to copper smelting, leaching of chalcopyrite with sulfuric acid, in combination with various oxidizing agents, has received most of the attention. Processes like Activox, Nenatech, Dynatec, AAC/UBC, Placer Dome process, Biocop, Bactech/Mintek and Geocoat are nowadays the main sulfate processes for chalcopyrite leaching. Many of them use pressure leaching at high temperatures (150-225 °C). Sulfate-based process have advantages due to it's generally simpler and better understood chemistry. However, chloride based processes are of increasing interest. Faster kinetics in chloride solution makes it possible to use atmospheric leaching and high dissolution rates of metals makes it possible to use smaller solution volumes in subsequent steps. One major advantage is that almost all sulfur can be oxidized into elemental form. Lately, a cupric chloride based process, HydroCopper[®] has reached the commercial scale [1-4].

2. Copper Chloride solution

Copper can be present in three forms in the stability area of water; in the oxidation state two as cupric (Cu^{2+}), in oxidation state one as cuprous (Cu^+) or as solid copper. In aqueous solutions cupric ions are usually stable, since cuprous ions are not very soluble in cold water [5]. The redox couple $\text{Cu}^{2+}/\text{Cu}^+$ has a standard electrode potential of -0.044 V vs. Ag/AgCl ($E^0 = 0.153$ V vs. SHE) [6], which is not related to a very oxidative leaching environment. Thus it could be considered that Cu^{2+} cannot be used as an oxidant in order to leach sulfide minerals. However, it is known that in chloride solutions Cu^+ is eager to form complexes, such as $[\text{CuCl}]^0$, $[\text{CuCl}_2]^-$, $[\text{CuCl}_3]^{2-}$, $[\text{CuCl}_4]^{3-}$ and that Cu^+ in the complex form is very stable [7-14]. This is advantageous to the redox potential of the solution, which increases significantly due to the complex formation. The redox potential cupric/cuprous in concentrated chloride solution is in the range 0.73 – 0.90 V vs. SHE (0.53-0.70 V vs. Ag/AgCl) [15], which is remarkably higher than the standard electrode potential. This behaviour makes concentrated copper chloride solutions highly oxidizing and effective leaching media for sulfide minerals and interesting topics for research.

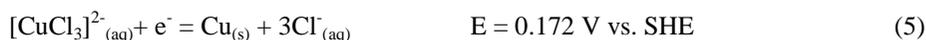
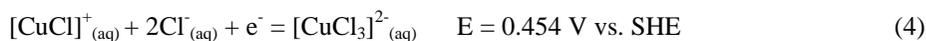
2.1 Thermodynamics

The electrode potentials, E, for copper ions and copper are as follows at 90 ° C (1)-(3). The values of E were calculated with the HSC 5.11 thermodynamic calculation software.



The electrode potentials for copper species suggest that it is more likely that Cu^{2+} would reduce straight to solid copper, instead of going first to the cuprous form Cu^{+} . However, these thermodynamic values can not be applied to concentrated copper chloride solutions due to complex formation and incomplete activity coefficient information.

One very strong characteristic of a chloride solution is that it can form complexes with copper cations and thus make even cuprous ions stable in the form of various cuprous complexes instead of cuprous ions. Thus for example reactions (4)-(5) are possible in cupric chloride solutions. The values of E in reactions (4)-(5) are calculated at $T = 90 \text{ }^{\circ}\text{C}$. The Gibb's energy for all the reactions (1)-(5) is below 0.



As it is assumed that cupric and cuprous ions form complexes as described in the equations (4) and (5), it is suggested that the cupric complex reduction proceeds in two steps: first the cupric complex reduces to a cuprous complex and after that the cuprous complex reduces to solid copper with decreasing potential. That differs from the behaviour of cupric ion reduction in an ideal dilute water solution (1)-(3).

2.2 Cuprous and cupric complexation

There are a number of studies in the field of cuprous ion complexation in chloride solutions [7-14]. It is generally agreed that complexes such as $[\text{CuCl}]^0$, $[\text{CuCl}_2]^{-}$, $[\text{CuCl}_3]^{2-}$, $[\text{CuCl}_4]^{3-}$ and even the dimer and trimer $[\text{Cu}_2\text{Cl}_4]^{2-}$, $[\text{Cu}_3\text{Cl}_6]^{3-}$ can be present in chloride solutions. It has also been proposed that complexes with charges greater than three are highly unlikely, even at very high Cl^{-} concentrations [8].

Table 1 summarizes the prevailing complexes in cuprous chloride solution near the boiling point of the solution. In dilute solutions $[\text{CuCl}]^0$ is shown to be predominant, where as at more concentrated solutions $[\text{CuCl}_2]^{-}$ and $[\text{CuCl}_3]^{2-}$ dominate. Generally near the boiling point of the solution $[\text{CuCl}_2]^{-}$ is dominant when $[\text{Cl}^{-}] > 0.1 \text{ M}$, but the importance of $[\text{CuCl}_3]^{2-}$ increases with increasing chloride concentrations and temperature [7-14].

It seems clear that cuprous ion can be present only in a complex form in concentrated chloride solutions. However, the complexation of cupric ion is still disputed. Berger *et al.* [7] reviewed in their article that at low Cl^{-} concentrations the hexaqua complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is dominant and in more concentrated solutions $[\text{CuCl}]^{+}$ and $[\text{CuCl}_2]^0$ dominate. As the Cl^{-} concentration reaches 2.5 M, $[\text{CuCl}_3]^{-}$ is formed and with 5 to 10 M $[\text{CuCl}_4]^{2-}$. Opposite to that, Collings *et al.* [16] concluded that no complexation of Cu^{2+} with Cl^{-} ions occurs at $<75 \text{ }^{\circ}\text{C}$ with

0.2 and 2.2 M Cl. However, with higher chloride concentrations (5 M NaCl) $[\text{CuCl}]^+$ was observed to be the dominant species at 25-75 °C, becoming $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ at 125 °C. Generally Collings [16] summarizes that the stability of CuCl^+ complex appears to be overestimated.

Table 1 Significant complexes formed in cuprous chloride solutions near the boiling point of the solution with increasing chloride concentration. Reaction conditions vary by studies

Complex	[Cl] / M	Conditions	Source
$[\text{CuCl}]^0$	0.01-0.1 m	50 °C, 0.2 m NaAc	[13]
$[\text{CuCl}]^0$	0.01-0.1 m	150 °C, 0.2 m NaAc	[13]
$[\text{CuCl}]^0$	0.001-0.1 m	100 °C, Saturated water vapour pressure	[10]
$[\text{CuCl}_2]^-$	0.1-0.5	50 °C, 0.2 m NaAc	[13]
$[\text{CuCl}_2]^-$	>0.1	150 °C, 0.2 m NaAc	[13]
$[\text{CuCl}_2]^-$	>0.1	100 °C, Saturated water vapour pressure	[10]
$[\text{CuCl}_2]^-$	<2	100 °C, Chloride added as LiCl	[12]
$[\text{CuCl}_3]^{2-}$	>0.5	50 °C, 0.2 m NaAc	[13]
$[\text{CuCl}_3]^{2-}$	>1.0	200 °C, Saturated water vapour pressure	[10]
$[\text{CuCl}_3]^{2-}$	2-7	100 °C, Chloride added as LiCl	[12]
$[\text{CuCl}_4]^{3-}$	>7	100 °C, Chloride added as LiCl	[12]

Based on the earlier studies done in this field, the cuprous ion can be suggested to be present mostly as complex $[\text{CuCl}_3]^{2-}$ but also partly as $[\text{CuCl}_2]^-$, in solutions similar to HydroCopper® ($[\text{NaCl}] = 280 \text{ g/l}$, $\text{Cu}^{2+} = 40 \text{ g/l}$, $T = 90 \text{ °C}$). The complexation of cupric ion is more inconsistent, but it can be suggested that with lower chloride concentrations Cu^{2+} does not form complexes. At high Cl concentrations, such as $[\text{NaCl}] = 5 \text{ M}$, $[\text{CuCl}]^+$ or $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ may be present.

2.3 Pourbaix diagrams in concentrated chloride solutions

The effect of cupric ion concentration (0.0014 M with dashed line and 0.41 M with solid line) on the stability areas of copper species in cupric chloride solution can be observed with the help of Pourbaix-diagrams shown in Fig.1. The diagrams was made with HSC 5.11 program having similar parameters to those in the HydroCopper® process ($[\text{NaCl}] = 250 \text{ g/l}$). Diagrams show the ions, complexes and solids that are thermodynamically likely to prevail on certain potential-pH area. In Fig.1 the increase in copper concentration decreases the stability area of Cu^{2+} and $[\text{CuCl}]^+$ to lower pH values. The increase in copper concentration increases also the redox potential of $[\text{CuCl}_3]^{2-}/\text{Cu}$.

Pourbaix diagram in Fig.1 suggests that with high Cl^- concentration Cu^{2+} would form complex $[\text{CuCl}]^+$ in the potential area 0.55 V – 1.35 V vs. SHE at pH 2. Cu^+ would be mainly present as $[\text{CuCl}_3]^{2-}$. The calculated redox potential at pH is ca. 0.55 V vs. SHE (0.35 V vs. Ag/AgCl), increasing slightly with increasing cupric ion concentration. Fig.1 has been calculated by taking into account all the species that can be present in cupric chloride solutions.

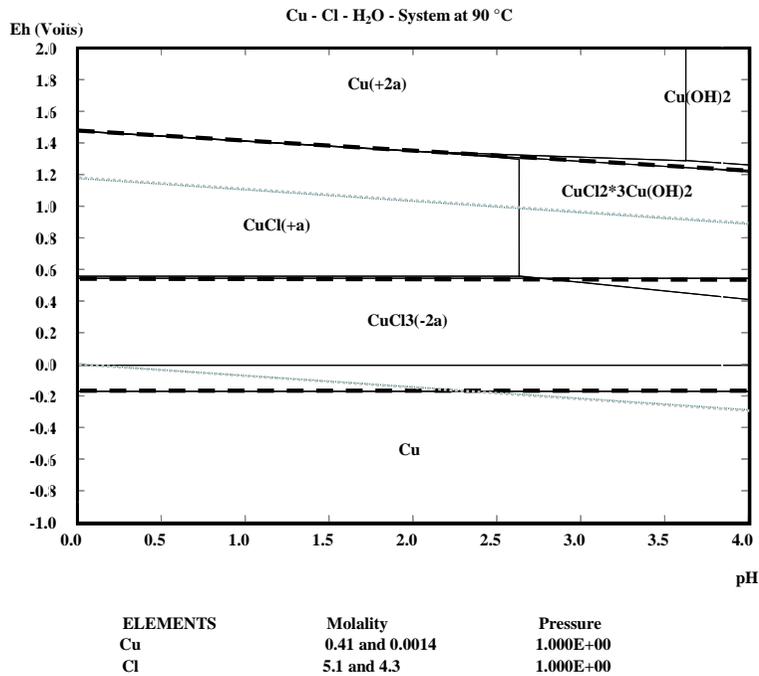


Fig.1 E-pH diagram of aqueous copper chloride system. The effect of copper concentration (solid line = 0.41 M and dashed line = 0.0014 M, being equal to 26.6 g/l and 0.09 g/l, respectively) to the stability areas at 90 °C. Also 4.3 M sodium chloride is added to solution making the final chloride concentrations 5.1 M and 4.3 M respectively

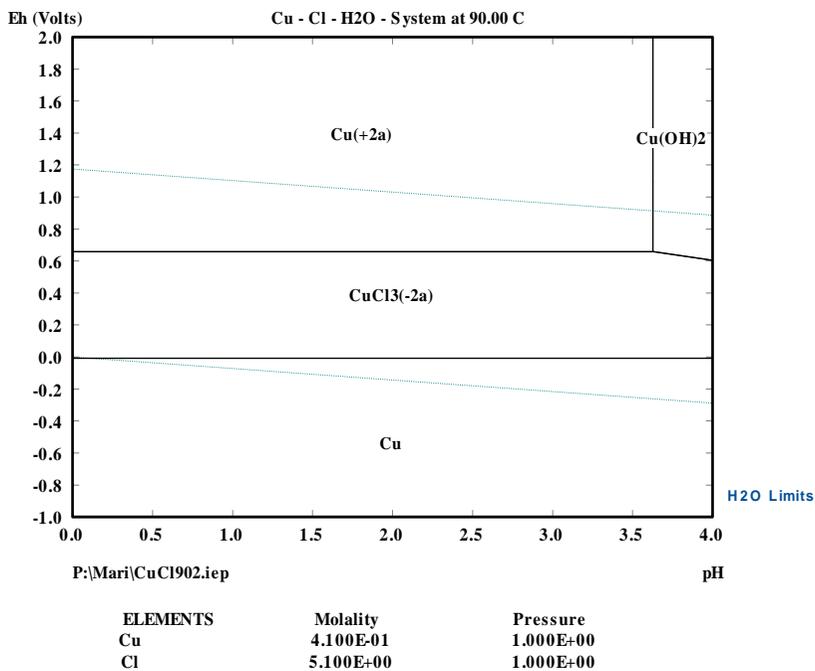


Fig.2 E-pH diagram of aqueous copper chloride system at 90 °C with $[Cu^{2+}] = 0.41$ M and $[Cl] = 5.1$. Cupric complexes are ignored

Collings [16] suggested that there might be some misestimating of the stability of some complexes. The complexation of Cu^{2+} is controversial. Fig.2 was calculated in a similar environment to that of Fig.1, assuming that cupric ions stay in ionic form and do not form complexes.

According to the Figure 2, the redox potential of $\text{Cu}^{2+}/[\text{CuCl}_3]^{2-}$ is ca. 0.45 V vs. Ag/AgCl (0.65 V vs. SHE). The redox potential of $[\text{CuCl}]^+ / [\text{CuCl}_3]^{2-}$ in Figure 1 is ca. 0.35 V vs. Ag/AgCl (0.55 V vs. SHE). This shows that thermodynamically the redox potential of concentrated cupric chloride solution is higher, if Cu^{2+} is not forming complexes. The suggestion, that Cu^{2+} would not form complexes is supported by the experimental redox measurements, which showed redox potential values from 0.73 V to 0.90 V vs. SHE [15]. It must be noted that cupric ion can also be partly complexed.

3. Chloride based processes

Chloride leaching has advantages compared to sulfate leaching of copper sulfides. Faster dissolution kinetics in chloride solution makes it possible to use atmospheric leaching and high solubility of metals makes it possible to use smaller solution volumes in subsequent steps. One major advantage is that almost all sulfur can be oxidized into elemental form [17]. The major difficulties are need of special construction materials due to corrosivity of chloride solutions leading to a relative high capital and maintenance costs for the plant. The most favoured lixiviant in chloride based processes is FeCl_3 but also CuCl_2 and BrCl and some combination of these are of the interest. The main chloride processes have been CLEAR, CYMET, Cuprex, Intec and HydroCopper[®], from which CLEAR, CYMET and HydroCopper[®] use cupric chloride as the leaching agent. Also several laboratory studies for copper sulfide leaching have been carried out using cupric chloride solutions [1].

Also mixtures, like sulfate-chloride lixiviants have been studied. Chloride addition to sulfate based processes has been shown to improve leaching kinetics and to allow leaching at lower temperatures. The main sulfate/chloride leaching processes are Antler Noranda, BHAS process and CESL process, which all oxidize sulfur into elemental form. Copper is recovered in these processes by solvent extraction / electrowinning. Chloride, nitrate and ammine based lixiviants have been used as well and specifically chloride leaching of copper sulfides has received a lot of attention in the past decades [1-4].

Most of the chloride based processes can be grouped into three main classes:

- 1) Processes that use chloride leaching, solvent extraction to sulfate solution and electrowinning from sulfate solution.
- 2) Processes that use ferric chloride or cupric chloride to produce cuprous chloride solution. Copper is recovered by chemical precipitation.
- 3) Processes that use ferric chloride or cupric chloride to produce cuprous chloride solution. Copper is recovered by electrowinning in diaphragm cells and leachant is regenerated at the anodes.

The electrowinning directly from chloride solutions usually does not produce solid cathode copper. The exchange current density of Cu^+/Cu equilibrium in pure chloride solution is very high, 240 mA/cm^2 [18]. According to the theories of Fischer [19] and Winand [20] on electrodeposition, the reaction inhibition is low and so the deposit morphology becomes easily powdered. The electrowinning of copper from chloride solutions often results in impure deposits. In a cuprous chloride solution, the discharged copper ions are monovalent, so the

electrochemical equivalent is half of that of divalent copper in sulfate solutions. The anodic overpotential of chloride evolution is 0.5-0.6 V lower than that of oxygen overpotential with lead anodes in sulfate solutions. The lower electrochemical equivalent of cuprous ion and lower anode overvoltage would significantly decrease the energy consumption. However, the current efficiency in cuprous chloride electrolytes is low if the electrolyte contains even small amounts of cupric ion. The cupric ion is a powerful oxidant and it will leach again the cathode deposit.

3.1 CLEAR

Many chloride leaching processes were developed in the 1970's, but only a few reached commercial scale like the chloride based CLEAR (Copper Leaching Electrowinning and Recycle) process. The CLEAR process was used commercially from 1976 to 1982 in Arizona, USA. The principles of the CLEAR process were reviewed by Dutrizac [21]. In the CLEAR process a two-stage counter current leach was used to achieve high copper extractions. The first stage used cupric chloride at atmospheric pressure at 105 °C with 20 g/l CuCl_2 , 4 g/l FeCl_3 , 80 g/l NaCl and 44 g/l KCl . The solution from the first stage leach was treated with metallic copper to ensure that all the copper was present as Cu^+ [22]. After yielding a cuprous chloride solution the leaching solution was sent to copper electrowinning. The copper was electrowon from nearly saturated chloride solution. The electrowinning cell was of unique construction. Metal cathodes were suspended in the solution above a continuous conveyor belt within the tank. Non metallic anodes were suspended in diaphragm bags [23]. At the second leaching stage the residue from the first stage leach was re-leached at 150 °C under 330 kPa O_2 pressure using ferric ion as the leaching agent. Some sulfur was also oxidized to sulfate in that stage and it was removed by precipitation as gypsum (CaSO_4) [1, 24].

The copper that was produced in CLEAR process by electrowinning contained Ag and other impurities that necessitated its treatment as blister copper, i.e. it had to be melted, cast into anodes and refined electrolytically [22]. The commercial operation had several major problems including gypsum fouling in the tankhouse, silver contamination of the final product and washing of the final product. Due to the problems with the gypsum fouling, the final product could not meet London Metal Exchange (LME) specifications. Silver contamination of the final product and washing of the final product led finally to the situation that the process was not economically beneficial [1].

3.2 Cuprex

In the Cuprex process, the copper sulfide concentrates were leached with a sodium chloride and ferric chloride solution in two stages to produce a cupric chloride solution. Copper was extracted by solvent extraction and recovered as powder by electrowinning. The process used Metclor cells with DSA-type anodes, hollow titanium cathodes and cation selective membranes. Copper was deposited on the cathode and chlorine is evolved on the anode. Sodium ions transport through the membrane to the catholyte. The operating principle of the Metclor cell was quite close to that of the chlor-alkali diaphragm cell. Copper was deposited at current density of 1500 A/m^2 . The spent catholyte contained cupric, cuprous and sodium ions. Chlorine generated at the anode was recovered and used to reoxidize the cuprous chloride generated in catholyte during electrowinning. Recovered anolyte was depleted from copper and used again as anolyte [25].

3.3 *Intec Copper Process*

The Intec Copper Process is a chloride based method of converting copper sulfides to high purity copper and elemental sulfur. The main components of leaching solution are sodium chloride and bromide. The lixiviant, BrCl_2^- also known as "HalexTM", is produced anodically in the electrowinning cell. The leaching is carried out at atmospheric pressure using air as the oxidant. The process utilises a three-stage countercurrent leaching at 80-85 °C. Copper is leached in stages 1 and 2 and gold is leached in stage 3. The pregnant solution is purified in several stages. First all copper is converted to cuprous by contact with copper powder. Then silver is removed by an amalgam process using mercury and aluminium additions. The final step is neutralization with limestone to pH 4.0-4.5 to precipitate the residual impurities. The purified cuprous chloride - sodium halide solution contains 80 g/l Cu^+ , 250 g/l NaCl, 30 g/l CaCl, and 30 g/l NaBr at 75 °C. The solution is fed to an diaphragm cell where Cu dendrites are deposited on corrugated titanium cathode. The depleted catholyte permeates through membrane to anode, where lixiviant is formed and remaining copper is oxidized to Cu^{2+} . At current densities of 1000 A/m^2 the cell voltage is 3.2 V. The current efficiency is 98%. Power consumption is approximately 1.4 kWh/kg. The dendritic copper produced from electrowinning is collected by a belt conveyor, washed and dried under inert atmosphere [26].

3.4 *CYMET*

CYMET was one of the first processes, which used chloride based leaching solution. The chalcopyrite concentrate was subjected to a two-stage countercurrent leach in FeCl_3 - CuCl_2 -NaCl solution. Copper was precipitated as CuCl by vacuum crystallization and iron was rejected from solution as jarosites and various hydrous oxides during the second leaching stage. Cuprous chloride was washed free of the mother liquor, dried and reduced by hydrogen reduction in a fluidized bed reactor. Silica was used as a substrate for reduction. Finally the copper-silica product was smelted and cast to wire as bar-grade copper. Also in this process there was partial oxidation of sulfur to SO_4^{2-} . The exact process data, such as process temperatures and solution concentrations are unfortunately very difficult to find [1, 22].

The CYMET process is reputed to have achieved the production level of 22.75 tonnes of copper concentrates per day. It was claimed that electrolytic-grade copper would be achieved, but that was not always the case. Also the operation of a fluid bed using hydrogen gas and cuprous chloride and generating hydrogen chloride gas posed some engineering problems. Additionally some corrosion problems were present. Substantial energy costs in the crystallization and the reheating of the mother liquor were problematic. This all together with the slump in the copper industry led to the shut down in 1982 [22].

3.5 *HydroCopper[®]*

HydroCopper[®] is based on the good leaching properties of chalcopyrite in cupric chloride solution. The advantage of using chloride solution is its aggressivity as well as the stability of cuprous ion in the process solution. HydroCopper[®] is driven at normal pressure and at a temperature of 80-100 °C using stirred tank reactors and thickeners. The raw material used is chalcopyrite concentrate, which is leached in a chloride solution with the help of Cu^{2+} , which is a very good oxidizer in a chloride environment. The pH is kept in between 1.5 and 2.5 with the help of oxygen purging. The typical total retention time for the concentrate is 10-20 hours. If

the oxygen purging rate is too high, the pH increases causing the precipitation of copper hydroxychloride. The process scheme and the chemical reactions of the HydroCopper[®] process are illustrated in Fig.3 [27].

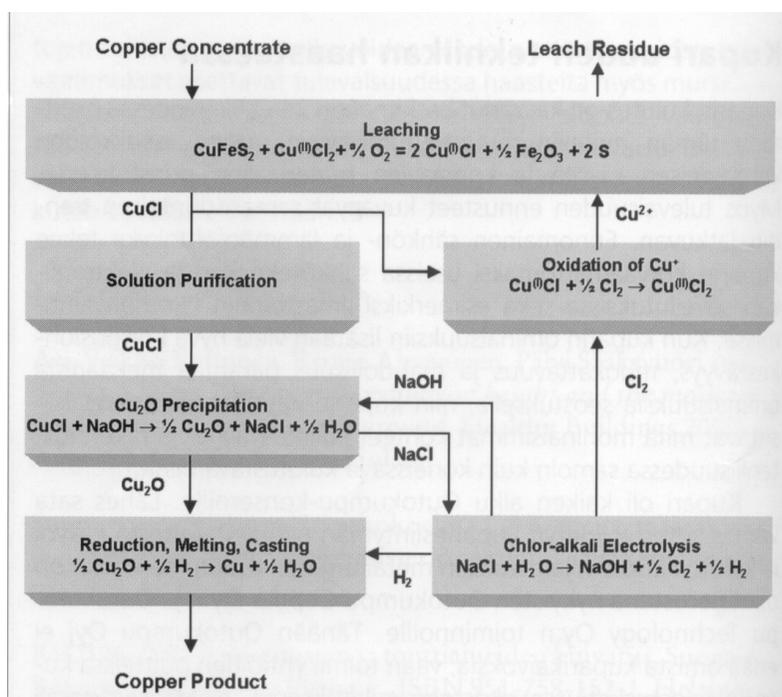
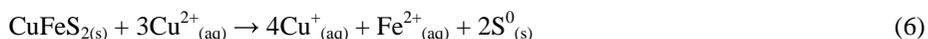
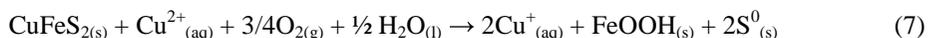


Fig.3 The chemical reactions of the HydroCopper[®] process [28]

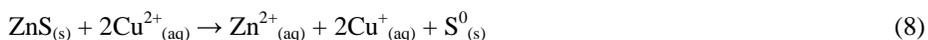
Chalcopyrite can be oxidized in a chloride solution with the help of Cu²⁺ ions according to the reaction (6):



Ferrous ions are further oxidized by air to ferric, which precipitate as goethite (FeOOH) or hematite (Fe₂O₃). This results in the overall reaction (7).



The other sulfides (Zn, Pb, Ni, Ag) are dissolved out of the concentrate into the solution e.g. by the reaction (8).



In equations (6) – (8) Cu⁺ and Cu²⁺ represent the general oxidation state of the copper species and not the exact form of compound, since the copper ions may be present also in complex form. After the sulfides are dissolved, the oxygen purging increases the redox potential in the solution causing the leaching of gold as chloro-complexes [29]. Gold can be leached at potentials > 600 mV vs. Ag/AgCl [30]. Gold can be recovered by precipitating it on activated carbon or copper concentrate.

The solution from the leaching stage of the HydroCopper[®] process contains about 70 g/l copper of which 60 g/l is Cu⁺ and 10 g/l is Cu²⁺. The solution can also contain some amounts of other metal ions, which have to be taken out from the solution in the solution purification stage. The solution purification stage consists of five stages: cupric and sulfate removal, silver removal by cementation, neutralization in which zinc, lead etc. are removed, ion exchange with impurity removal and Cu₂O precipitation. At the Cu₂O precipitation stage the precipitation is made with the help of sodium hydroxide, which is received from the chlor-alkali electrolytic cell (9). The solution purification procedure is shown in Fig.4.

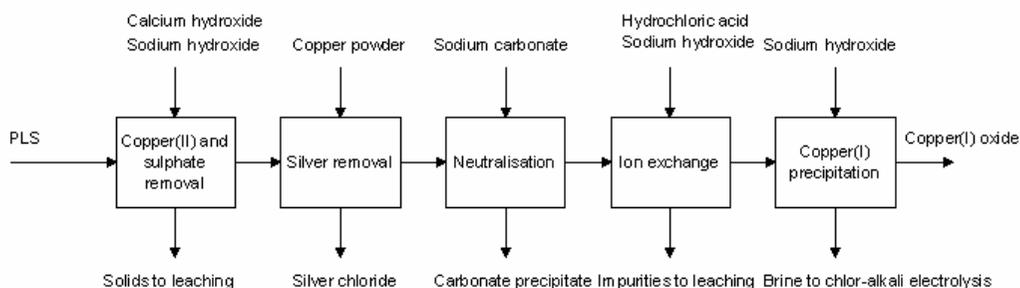
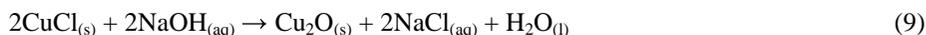


Fig.4 HydroCopper[®] process – Solution Purification [31]

The product from the precipitation stage, cuprous oxide, is precipitated in two parallel reactors, producing octahedral crystals with particle size of 20-50 micrometers (p80). The slurry is washed and filtered on a vacuum belt filter. The filtrate is recycled to the chlor-alkali electrolysis, where the regeneration of chemicals occurs. The filter cake is fed into a belt furnace, which dries and reduces cuprous oxide to metallic copper at a temperature in the range of 650-850 °C with hydrogen-nitrogen flow (10).



The reduced copper plates formed are then discharged into the melting furnace, where molten copper is covered with a protective graphite cover and deoxidised. The copper quality is good and it can be cast in any form. [27, 28, 31-33]

4. Discussions and Conclusions

The complexation in cupric chloride solution is advantageous, since the redox potential is sufficient for leaching sulfide minerals. According to the thermodynamic considerations and earlier studies, it is clear that cuprous ions form complexes in concentrated chloride solutions. Cuprous ion can be suggested to be present mostly as $[\text{CuCl}_3]^{2-}$ but also partly as $[\text{CuCl}_2]$, in the environment similar to that of HydroCopper[®]. The complexation of cupric ion is more inconsistent, but it can be suggested that cupric ion is not totally in a complex form. With lower chloride concentrations Cu²⁺ may not form complexes. At high Cl concentrations $[\text{CuCl}]^+$ or $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ may be present.

HydroCopper[®] is the only cupric chloride based process, which has reached the commercial scale for a long time. It reached the commercial scale on November 2006, when Outokumpu Technology Oyj and Erdenet Mining Corporation of Mongolia signed the design agreement of the first HydroCopper[®] plant [34]. CLEAR was operating in commercial scale on 1976-1982, but the problems with the gypsum fouling in the tankhouse, silver contamination of the final product and washing of the final product led finally to the situation that the process was not economically beneficial and that the final product could not meet LME specifications. Also the operation of CYMET was shut down in 1982 as well, ostensibly because of the slump in the copper industry [1, 22].

As HydroCopper[®] is compared to the CLEAR and CYMET, some improvements can be seen. The corrosion problems have been overcome in HydroCopper[®] by new materials like plastics, polymers, ceramics and composites, which allows HydroCopper[®] to use more concentrated chloride solutions than for example in CLEAR. The ability to use more concentrated solutions improves the dissolution rate and the cuprous complexation. More concentrated solutions allow also the decrease of the process temperature, which brings economical benefits in HydroCopper[®].

Many of the hydrometallurgical processes, as CYMET and CLEAR, have had difficulties to keep sulfur in the elemental form. The proportion of S⁰ in both has been reported to be ca. 75 % [35]. HydroCopper[®] has been successful also in this area, since at least 95 % of sulfur can be remained in elemental form.

Both HydroCopper[®] and CYMET use hydrogen reduction for cuprous chloride to reduce copper: in HydroCopper[®] Cu₂O is reduced in a rotary kiln to metallic copper whereas in CYMET CuCl was reduced in a fluidized bed reactor to metallic copper. The reduction operation in the rotary kiln in HydroCopper[®] is advantageous, since it produces only copper and water whereas fluidized bed in CYMET was generating hydrogen chloride gas, which is highly toxic and corrosive.

In HydroCopper[®] the effective 5 step solution purification starting from Cu²⁺ and sulfate removal, silver removal, neutralization, ion exchange and ending in Cu₂O precipitation is a good base for high quality copper production. The quality of copper is higher than that achieved with CuCl crystallization and hydrogen reduction in CYMET or by electrowinning in CLEAR. CLEAR process was not meeting the LME specifications since the loss of silver to the final copper product was too high and washing of the final product was too difficult. CYMET did not reach always the electrolytic grade expected, which was due to the problems in the washing the cuprous chloride crystals.

One more economical benefit in HydroCopper[®] is that it does not need any re-leaching stage at high pressure like in CLEAR. This is due to the effective three-step counter current leaching. It can be concluded that after the 1980's a lot of development in the field of cupric chloride leaching has been carried out and that HydroCopper[®] seems to be a very promising hydrometallurgical technology for copper production. The unit processes used in HydroCopper[®] are not new, but the innovative combination of known unit processes makes HydroCopper[®] unique.

Literature

- [1] Peacey J., Guo X.J. & Robles E. (2004): Copper Hydrometallurgy - Current Status, Preliminary Economics, Future Direction and Positioning versus Smelting - Transactions of the Nonferrous Metals Society of China, 14(3): pp. 560-568.

- [2] Hackl R.P., Dreisinger D.P., Peters E. & King J.A. (1995): Passivation of Chalcopyrite During Oxidative Leaching in Sulfate Media - *Hydrometallurgy*, 39(1): pp. 25-48.
- [3] Roman R.J. & Benner B.R. (1973): The Dissolution of Copper Concentrates - *Minerals Science and Engineering*, 5(1): pp. 3-24.
- [4] Padilla R., Zambrano P. & Ruiz M.C. (2003): Leaching of Sulfidized Chalcopyrite with H_2SO_4 -NaCl- O_2 - *Metallurgical and Materials Transactions B*, 34B: pp. 153-158.
- [5] Winand R. (1991): Chloride Hydrometallurgy - *Hydrometallurgy*, 27: pp. 285-316.
- [6] Pourbaix (1966): Atlas of Electrochemical Equilibria in Aqueous solutions - First English edition, J. W. Arrowsmith LTD, Oxford, Great Britain, pp. 385-386.
- [7] Berger J.M. & Winand R. (1984): Solubilities, densities and electrical conductivities of aqueous copper(I) and copper(II) chlorides in solutions containing other chlorides such as iron, zinc, sodium and hydrogen chlorides - *Hydrometallurgy*, 12: pp. 61-81.
- [8] Fritz J.J. (1980): Chloride Complexes of CuCl in Aqueous Solution - *Journal of Physical Chemistry*, 84(18): pp. 2241-2246.
- [9] Fritz J.J. (1982): Solubility of Cuprous Chloride in Various Soluble Aqueous Chlorides - *Journal of Chemical and Engineering Data*, 27: pp. 188-193.
- [10] Xiao Z., Gammons C.H. & Williams-Jones A.E. (1998): Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300°C and saturated water vapor pressure - *Geochimica et Cosmochimica Acta*, 62(17): pp. 2949-2946.
- [11] Fontana A., Van Muylder J. & Winand R. (1983): Etude spectrophotométrique de solutions aqueuses chlorurées de chlorure cuivreux, à concentrations élevées - *Hydrometallurgy*, 11: pp. 287-314.
- [12] Liu W., Brugger J., Mcphail D.C. & Spiccia, L. (2002): A Spectrophotometric Study of Aqueous Copper(I)-Chloride Complexes in LiCl Solutions Between 100 °C and 250 °C - *Geochimica et Cosmochimica Acta*, 66(20): pp. 3615-3633.
- [13] Liu W., Mcphail D.C. & Brugger J. (2001): An Experimental Study of Copper(I)-Chloride and Copper(I)-Acetate Complexing in Hydrothermal Solutions Between 50 °C and 250 °C and Vapor-Saturated Pressure - *Geochimica et Cosmochimica Acta*, 65(17): pp. 2937-2948.
- [14] Archibald S.M., Migdisov A.A. & Williams-Jones A.E. (2002): An experimental study of the stability of copper chloride complexes in water vapor at elevated temperatures and pressures - *Geochimica et Cosmochimica Acta*, 66(9): pp. 1611-1619.
- [15] von Bonsdorff R., Järvenpää N., Aromaa J., Forsén O., Hyvärinen O. & Barker M.H. (2005): Electrochemical Sensors for the HydroCopper™ Process Solution - *Hydrometallurgy*, 77: pp. 155-161.
- [16] Collins M.D., Sherman D.M. & Ragnarsdóttir K.V. (2000): Complexation of Cu^{2+} in oxidized NaCl brines from 25 °C to 175 °C: results from in situ EXAFS spectroscopy - *Chemical Geology*, 167: pp. 65-73.
- [17] Flett D.S. (2002): Chloride hydrometallurgy for complex sulphide: A review. - *CIM Bulletin*, 95(1065): pp. 95-103.
- [18] Lin H.K., Wu X.J. & Rao P.D. (1991): The electrowinning of copper from a cupric chloride solution - *Journal of Metals*, 43(8): pp. 60-65.
- [19] Fischer H. (1954): *Elektrolytische Abscheidung und Elektrokristallisation von Metallen* -, Berlin: Springer. 729.
- [20] Winand R. (1992): Electrocrystallization - theory and applications - *Hydrometallurgy*, 29(1-3): pp. 567-598.

- [21] Dutrizac J.E. (1992): The Leaching of Sulphide Minerals in Chloride Media - Hydrometallurgy, 29(1-3): pp. 1-45.
- [22] Hoffmann J.E. (1991): Winning Copper via Chloride Chemistry - An Elusive Technology - JOM, 43(8): pp. 48-49.
- [23] Atwood G.E. & Livingston R.W. (1980): The CLEAR Process, a Duval Corporation development - Erzmetall, 33: pp. 251-255.
- [24] Anon.(2002): Acid Pressure Leaching of Copper Sulfides Part 1 - Pincock Perspectives, (26): pp. 1-4.
- [25] Dalton R.F., Diaz G., Price R. & Zunkel A.D. (1991): The Cuprex metal extraction process: recovering copper from sulfide ores - Journal of Metals, 43(8): pp. 51-56.
- [26] Moves J., Lam J., Santos V. & Gabb P. (2003): The Intec Copper Process: development of a new electrowinning cell - in Copper 2003 - Cobre 2003. Santiago, Chile: Canadian Institute of Mining Metallurgy and Petroleum. pp. 487-508.
- [27] Hietala K. & Hyvärinen O. (2003): HydroCopper™ - A New Technology for Copper Production - in Alta 2003 Copper Conference. Perth, Australia. pp. 1-10.
- [28] Hyvärinen O. (2003): HydroCopper™ - Outokumpun käänteentekevä uusi kuparinvalmistusmenetelmä - Vuoriteollisuus - Bergshanteringen, 3 / 2003: pp. 49 - 52.
- [29] von Bonsdorff R. (2004): Dissolution of gold in cupric chloride solution, M.Sc. Thesis Helsinki University of Technology: Espoo. pp. 69.
- [30] Hyvärinen O., Hämäläinen M., Lamberg P. & Liipo J. (2004): Recovering Gold from Copper Concentrate via the HydroCopper™ Process - JOM, 56(8): pp. 57-59.
- [31] Karonen J. (2006): HydroCopper™ Process - in Thermodynamic and Kinetic Phenomena in Hydrometallurgical Processes. Espoo: Helsinki University of Technology, TKK-MT-182
- [32] Haavanlammi L., Karonen J. & Rodriguez C. (2006): HydroCopper(R) - Moving up in the copper production chain - in I International Workshop on Process Hydrometallurgy, 11 - 13th October. Iquique, Chile
- [33] Hyvärinen O., Hämäläinen M. & Leimala R. (2002): Outokumpu HydroCopper™ Process A Novel Concept in Copper Production - in Chloride Metallurgy 2002, 32nd Annual Hydrometallurgy Meeting. Montreal, Quebec, Canada: MetSoc. pp. 609-612.
- [34] [TTP://WWW.KAUPPALEHTI.FI/4/0X13001907AC/PORSSI/HEX/PORSSITIEDOTE.JSP?ID=200611160074&REQUEST_AHAA_INFO=TRUE](http://WWW.KAUPPALEHTI.FI/4/0X13001907AC/PORSSI/HEX/PORSSITIEDOTE.JSP?ID=200611160074&REQUEST_AHAA_INFO=TRUE) (2006): Pörssitiedote, Outokumpu technology Oyj. Kauppalehti.
- [35] Havlik T. (2006): Elemental Sulfur Creation and Nowadays Used Leaching methods - in Thermodynamic and Kinetic Phenomena in Hydrometallurgical Processes. Espoo: Helsinki University of Technology, TKK-MT-182