Thermal decomposition of copper sulfides under concentrated irradiation

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THERMAL DECOMPOSITION OF COPPER SULFIDES
UNDER CONCENTRATED IRRADIATION

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
Doctor of Sciences

presented by
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2006
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nämlich die direkte thermische Zersetzung von Sulfide in Kupfer, Eisensulfid und elementaren Schwefel.


Thermische Zersetzungsstudien wurden mit thermogravimetrischen Experimenten unterhalb 1800 K eingeführt. Im Rahmen dieser Studien sind drei synthetischen Kupfersulfide (Chalkocit (\( \text{Cu}_2\text{S} \)), Chalkopyrit (\( \text{CuFeS}_2 \)), und Enargit (\( \text{Cu}_3\text{AsS}_4 \))) und zwei kommerzielle Kupferkonzentrate untersucht worden. Es wurde gezeigt, dass die Abwesenheit von Sauerstoff in Kombination mit hohen Zersetzungstemperaturen die Entfernung von Schwermetallen durch Verflüchtigung fördert. Elementaranalysen an behandelten Konzentraten zeigten, dass die Entfernung von flüchtigen Verunreinigungen bei drei verschiedenen Temperaturabschnitten eintritt: bei \( T < 1173 \text{ K} \), werden Arsen und Bismut entfernt. Die Verflüchtigung von Cadmium und Zinn verlangt eine Temperatur unterhalb 1673 K, während Blei und Zink erst bei Temperaturen zwischen 1673 and 1773 K verflüchtigen. Die Entfernung dieser beiden Elemente bei 1773 K beträgt jedoch mindestens 95 %. Selbst die Entwicklung einer schlackenartigen Phase ist für die effiziente Entfernung der Verunreinigungen nicht hinderlich.

In einem am PSI konstruierten Strahlungsofen wurden Zersetzungsexperimente bei höheren Temperaturen durchgeführt. In diesem Ofen
erreichen die Kupferkonzentrate eine Oberflächentemperatur von \( \approx 1920 \) K. Durch kontinuierliche Bestrahlung über 330 s unter Argon konnten bis zu 40 % des anfänglichen Schwefelgehaltes entfernt und elementares Kupfer gebildet werden. Wiederholtes Zerkleinern und erneutes Bestrahlen (5 bis 10 s) beschleunigte die Verflüchtigung von Schwermetallen deutlich, so dass zwischen 90 and 99 % des anfänglichen Gehaltes von Arsen, Zink, und Blei durch eine totale Bestrahlsungszeit von 90 s entfernt werden konnten. Der positive Effekt des Zerkleinerns zeigt, dass die Entfernung der flüchtigen Elemente durch langsamen Massentransport aus dem Inneren der Schmelze in die Gasphase limitiert ist. Für eine großtechnische Umsetzung muss die thermische Zersetzung von Kupferkonzentraten deshalb mit sub-millimeter Partikeln durchgeführt werden.


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Abstract

The main goal of this work was to gain fundamental scientific knowledge required for the development of a solar-thermal process for the extraction of copper. About 80% of copper in the world is found as sulfide ores, which are mainly treated by pyrometallurgical processes. In today’s smelting processes, the oxygen partial pressure in the furnace is used to minimize the amount of copper in the slag. Unfortunately, the oxygen partial pressure is also an important parameter in controlling the distribution of impurities between gas and condensed phases. Consequently, modern smelting processes have restricted abilities of impurity removal. Another inherent disadvantage of conventional copper extraction is the generation of sulfur dioxide (SO₂).

Three different approaches for a SO₂-free copper extraction have been evaluated: (1) the conversion of copper-iron sulfides to oxides with oxygen and steam, (2) with steam alone, and (3) directly (i.e. without oxygen or steam) into copper and iron sulfide. Chemical equilibrium calculations have shown that the proposed reaction scheme with oxygen and steam is limited to reactors with plug-flow behaviour, and hence not generally applicable. Similar calculations showed that the reaction of chalcopyrite with steam can theoretically fulfill the requirement for a SO₂-free process. However, excessive amounts of steam would be required and chalcopyrite conversion with steam would thus be very energy intensive. We therefore propose a more rigorous approach, namely the direct thermal decomposition of sulfides into the copper, iron sulfide and elemental sulfur.

The direct decomposition of sulfides offers three benefits. Firstly, the generation of SO₂ is avoided and consequently the need for processing SO₂ to sulfuric acid will be eliminated. Secondly, working at low oxygen partial pressures prevents the oxidation of heavy metal impurities and their
subsequent incorporation into slag. In combination with high operating temperatures, this provides a path for an efficient removal of impurities by volatilization. Thirdly, the absence of an iron silicate slag will substantially decrease the amount of waste.

Concentrated solar radiation represents a powerful energy source to effect the direct decomposition of copper concentrates. It is a clean and essentially inexhaustible energy source whose supply and use is free of CO₂-emissions. Solar furnaces have already been successfully applied for the conversion of solar energy into chemical fuels. Furthermore, many areas close to the growing Asian market receive sufficient sun light that recommends its use for processing traded copper concentrates.

Thermal decomposition studies were initiated with thermogravimetric measurements below 1800 K on three synthetic copper sulfides (chalcocite (Cu₂S), chalcopyrite (CuFeS₂), and enargite (Cu₃AsS₄)) and two commercial copper concentrates. It was demonstrated that the absence of oxygen, in combination with high decomposition temperatures, furthers the removal of heavy metal impurities by volatilization. Elemental analyses of residues of treated concentrates showed that removal of volatile impurities occurs in three distinct temperature ranges. At T < 1173 K, arsenic and bismuth are removed. Evaporation of cadmium and tin requires temperatures below 1673 K, whereas the onset of Pb and Zn evaporation commences at temperatures between 1673 and 1773 K. At 1773 K, the removal of these two elements exceeds 95 %. Even the generation of a slag-like phase does not hinder an efficient removal of the impurities.

Decomposition studies at higher temperatures were conducted in an in-house built imaging furnace. The copper concentrates were exposed to surface temperatures up to ≈ 1920 K in the imaging furnace. Continuous irradiation during 330 s in an argon flow resulted in the removal of 40 % of initial sulfur content and the formation of elemental copper. Repeated grinding clearly accelerated the evaporation such that between 90 and 99 % of the initial amounts of arsenic, zinc, and lead were removed within 90 s. The strong effect of grinding indicates that the elimination of volatile elements is hindered by a slow mass-transfer from the interior of the melt to the gas phase. The thermal decomposition of copper concentrates on a technical scale will therefore best be conducted with sub-millimeter particles.
Elemental distribution (SEM) and elemental analysis (EMPA) revealed that irradiated samples are subject to a temperature gradient. Consequently, elemental copper preferably compacts at the lower surface close to the cold sample support. Exposure of decomposed samples to moderate temperatures around 1400 K showed that tempering of liquid samples will facilitate the separation of metallic copper from residual iron copper sulfides.

To conclude, this work provides encouraging results to further pursue the solar thermal extraction of copper from copper concentrates. Expectations regarding impurity removal were largely fulfilled and the formation of copper was demonstrated. The results support a next step with experiments in a solar chemical reactor that ensures efficient mass-transfer of volatiles from the molten concentrate into the gas phase.
Chapter 1

Introduction

1.1. Introduction

Metals are fundamental to our contemporary society and essential for the development of modern economies. As the world population increases and new markets develop, the demand for metals grows. The ongoing development of expanding economies in China and India will be accompanied by an aspiration to achieve a standard-of-living as is now already present in western countries. At the same time, metal production industries face the challenge of improving economic performance to remain viable, but on the other hand, to act socially and environmentally responsible. To meet these challenges, innovative research and the development of sustainable technologies are required. To lessen the adverse environmental impact of today’s energy-intensive metal production industries, the application of renewable energy sources can play an important role. The world’s largest renewable energy source is solar power, which is also a promising energy source for metallurgical processes. An attractive route of implementing solar energy in large scale industrial processes is offered by using concentrated solar power (Wieckert et al., 2004). Recently, a novel route for the extraction of metals using the sun as energy source has been presented (Winkel et al., 2003). The main goal of the present work is to gain fundamental scientific knowledge required for the development of such a process. The outcome will pave the way for the development of specific process technology.

This first chapter is subdivided in four sections. In the next section, conventional extraction techniques of base metals are briefly analyzed. It will be shown that copper is the best candidate for solar thermal metal extraction.
Table 1.1: Summary of the analysis of Strengths, Opportunities, Faults and Threats (SOFT).

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Opportunities</th>
<th>Faults</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>• autothermal process</td>
<td>• monopolized market for nickel</td>
<td>• generation of SO₂</td>
<td>• impure ores</td>
</tr>
<tr>
<td>• well-established smelting technologies</td>
<td>• sulfuric acid production</td>
<td>• non-inert slags (often hazardous waste)</td>
<td>• governmental regulations regarding emissions</td>
</tr>
<tr>
<td>Copper/Nickel</td>
<td></td>
<td></td>
<td>• competitive market</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• saturated sulfuric acid market</td>
</tr>
<tr>
<td>• mixed raw materials can be processed</td>
<td>• new methods (pressure leaching, plasma process)</td>
<td>• generation of SO₂</td>
<td>• impure ores</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td></td>
<td>• saturated sulfuric acid market</td>
</tr>
<tr>
<td></td>
<td>• sulfuric acid production</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• high energy costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• CO₂-emission from electricity generation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• electrolytic residues</td>
<td></td>
</tr>
<tr>
<td>• mixed raw materials can be processed</td>
<td>• new methods (Kivcet, QSL)</td>
<td>• generation of SO₂</td>
<td>• decreasing demand</td>
</tr>
<tr>
<td>Lead</td>
<td>• sulfuric acid production</td>
<td>• Flue dust</td>
<td>• governmental regulations regarding uses of lead</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• saturated sulfuric acid market</td>
</tr>
</tbody>
</table>
1.3 Analysis of conventional metal extraction processes

Section 1.3 will discuss fundamentals of conventional copper extraction and its associated drawbacks.

1.2. Analysis of conventional metal extraction processes

With the aim of developing a solar thermal process for the extraction of metals, the following base metals have been considered: iron, copper, nickel, lead and zinc. Iron is by far the most used of all metals. It is hardly ever found as the free metal and can only be obtained by reduction of its oxide ores. In practice, iron is mainly extracted in blast furnaces by the carbothermic reduction of hematite (Fe₂O₃):

\[ Fe₂O₃ + 3 CO \rightarrow 3 CO₂ + 2 Fe, \Delta H < 0 \] (1.1)

About 80% of the high-grade nickel occurrences are in the form of oxides, namely as laterite ore bodies. The other base metals (copper, zinc and lead) are more chalcophile in character and are thus predominately present as sulfide ores. Nickel is also present in sulfide ore bodies, from which it is produced together with copper such as at Sudbury (Canada) and Norilsk (Russia). The first step that extraction processes of metals from sulfides all have in common is the removal of sulfur by roasting. To achieve this goal, the ore is oxidized and sulfur is released as sulfur dioxide (SO₂). In the extraction of zinc and lead, the roasting step is followed by a highly energy-intensive reduction step to free the metal.

The process of copper extraction (as well as nickel associated with copper sulfide) is more complex and will be described in section 1.3. For the base metals predominantly available as sulfides, the strengths, opportunities, faults and threats of conventional extraction processes were evaluated from the viewpoint of a plant owner (Table 1.1).

Key issues faced by the conventional extractive metallurgy are the generation of vast amounts of SO₂ and the steady increase of the impurity concentration in the ore (see Table 1.1). Even though most modern plants now convert SO₂ to sulfuric acid on-site, the problem is not definitively solved (for details see section 1.3.2). It can be seen in Table 1.1 that the problem of SO₂ generation and the threat of increasing impurities are both inherent in
extraction processes of copper and zinc, both of which are potential candidates for the development of a solar thermal extraction process. Guesdon et al. (2002) and Morianz (2000) conducted preliminary studies on the direct decomposition of zinc sulfide (ZnS) into zinc and sulfur and showed that although the direct decomposition of zinc sulfide is feasible, the back-reaction of gaseous zinc with gaseous sulfur needs to be prevented thus making the implementation of such a process very challenging. The extraction of copper and nickel by direct decomposition of sulfides is feasible since gaseous sulfur naturally separates from the liquid metal. However, it should be noted that the implementation of a nickel process would be hindered by its monopolized market (see Table 1.1). Although a novel approach for copper extraction is challenged by a competitive market, we have decided to focus further activities on the development of a solar thermal extraction process for copper.

1.3. Fundamentals of copper extraction

Due to its excellent workability and corrosion resistance, copper has been one of the first metals used by mankind in antiquity. Its outstanding physical and chemical properties made copper today the most consumed metal, besides iron and aluminium. Copper has a wide range of applications in the electronic, building and transportation industry and has a good recycling potential. About 80% of the exploited global resources are sulfide ores, which are mainly treated by pyrometallurgical processes (Biswa and Davenport, 1994). The main minerals present in these sulfide ores are chalcopyrite (CuFeS2), pyrite (FeS2), which are often accompanied by smaller amounts of bornite (Cu5FeS4) and chalcocite (Cu2S). Typical copper ores contain from 0.5% Cu (open pit mines) to 1 or 2% Cu (underground mines). After grinding and flotation, the Cu content is increased to about 30%. Unfortunately, copper concentrates can also contain substantial amounts of impurities, notably heavy metals such as Zn, Pb, As and Sb. After the initial ore beneficiation step, copper concentrates are either subjected to roasting or enter immediately the pyrometallurgical extraction stages of smelting and converting. These stages are common to all conventional smelting processes and mainly involve the oxidation of the charge. The step-wise extraction process is required to separate iron from copper. When oxygen is introduced in the system, the sulfides are oxidized but since iron has a higher affinity for oxygen than copper at smelting
1.2 Fundamentals of copper extraction

temperatures, iron is preferentially oxidized. The resulting iron oxides are subsequently reacted with a flux (SiO$_2$) to an iron silicate slag phase. Smelting results in two main phases, one comprising a heavier sulfide phase containing most of the copper (i.e. the matte) and the other, a slag phase floating on top of it. The slag is tapped and the matte is sent to the converting stage where it is further reduced to crude copper (blister copper 98-99 wt-%).

1.3.1. Flash smelting

The unavoidable byproduct of oxidation of the concentrates is the corrosive and toxic sulfur dioxide (SO$_2$). In the 1960’s, concerns arose about the polluting impact of SO$_2$ emissions on the local environment. At that time, the main type of furnace used in the smelting operation was the energy-intensive reverberatory furnace (Cocquerel and Holmes, 1988). During the 1970’s, energy prices rose steeply (Hilson, 2000) and increasingly stringent air quality standards were imposed, challenging the smelting industry to find energetically more efficient ways of copper production and to deal with the polluting SO$_2$ emissions. This marked the beginning of the large-scale implementation of the flash smelting technology, which was developed already in the early 1950’s by Outokumpu in Finland and INCO in Canada. In the 1970’s, flash smelting furnaces began to replace the older generation reverberatory furnaces and today flash smelting is fully established as a state-of-the-art copper smelting technology. Flash smelting is energetically efficient because it uses the heat released by the oxidation reaction of iron sulfides to bring the charge to smelting temperatures of between 1473 and 1573 K. A necessary condition for the implementation of an autothermal operation is the use of oxygen-enriched air or pure oxygen (INCO process). Less nitrogen (i.e. air) needs to be heated and a continuous off-gas stream with sufficiently high SO$_2$ concentrations enables the conversion to H$_2$SO$_4$.

1.3.2. Drawbacks of flash smelting

Even though flash smelting deals with the problem of sulfur fixation, sulfuric acid production is hardly the ultimate solution. Relative proximity of the smelter to the acid market is a necessary requirement to maintain economic viability, which in turn can only be fulfilled when local needs for sulfuric acid can keep pace with its production. Another negative aspect of working with high SO$_2$ contents is the release of fugative gas emissions, which have serious
health effects in the production plant and form a heavy burden on the local environment. Although up to 95% of the produced SO₂ can be captured (Warhurst and Bridge, 1996), the step-wise nature of the copper extraction process increases the risk of fugative gas emissions into the workplace.

With the introduction of the flash smelting, many aspects of the copper production process have been improved. The demand for energy savings and CO₂ abatement became a relatively unimportant issue and extensive progress has been made in handling SO₂ emissions. Nevertheless, regarding the implemented SO₂ abatement strategies, problems have been mainly solved by end-of-pipe technologies (Hilson, 2000) and have not been tackled in a more fundamental and effective way.

Another challenge that needs to be tackled in future smelting operations is the ability to deal with ores of increasingly low grades and ever increasing amounts of, often toxic, impurities. In today’s practice, the oxygen partial pressure in the furnace is used to minimize the amount of copper in the slag. Unfortunately, the oxygen partial pressure is also an important parameter in controlling the distribution of impurities between gas and condensed phases (matte and slag). Consequently, matte and slag phases accumulate unwanted impurities present in the charge. Resulting slag requires extensive cleaning operations before it can be safely disposed of.

Modern smelting processes have restricted abilities of impurity removal and rely heavily on further refinement operations. An alternative for the removal of unwanted impurities is provided by volatilizing them in the form of oxides, as studied by Sohn at al. (2004). This will however increase the amount of copper in the slag and expensive Cu recovery from the slag will be needed, if the working temperature is not increased. Other authors proposed the evaporation of volatile impurities under vacuum prior to smelting. Laboratory-scale experiments showed that many impurities and a part of the sulfur can be efficiently removed and individually collected in a condenser by step-wise condensation (Villaroel, 1999). A conceptual disadvantage is that cleaning under vacuum is most likely an additional pre-treatment that cannot substitute for the smelting process. In addition, the technical feasibility to conduct a process of such a size under vacuum is questionable.
1.4. Chapter outline

Chapter 2 focuses on alternative copper production technologies which circumvent the formation of SO₂, and reviews literature on this topic. A report which suggests the conversion of copper iron sulfide with steam as a SO₂-free process was chosen for further investigation. Chemical equilibrium calculations on a mixture of chalcopyrite in the presence of oxygen and steam will demonstrate that the reported products can only be achieved in a plug flow reactor. This implies that the process is not generally applicable. The direct conversion of metal sulfides into the metal and sulfur, under concentrated solar irradiated, is proposed as an interesting alternative.

Chapter 3 describes the advantages of a solar thermal copper extraction process in detail. Characteristics of high temperature solar technology and possible consequences for the extraction of copper are discussed. It will be shown why solar energy is a viable energy source for the extraction of copper.

Chapter 4 presents thermal decomposition studies on chalcopyrite (CuFeS₂), enargite (Cu₃AsS₄) and two different copper concentrates. Thermodynamic equilibrium calculations and thermal analyses on single-phase compounds will show that during decomposition, sulfur partly volatilizes and that arsenic is completely removed below 1000 K. Similar experiments on multi-phase copper concentrates will demonstrate that an almost complete removal of volatile impurities can be achieved below 1773 K. Phase analyses on cooled products will give insight into the decomposition reactions and intermediate phases.

Chapter 5 describes high-temperature (T ~ 1994 K) decomposition studies on copper concentrates under concentrated irradiation. It presents the imaging furnace as a useful experimental tool for decomposition studies at high temperatures and in inert atmospheres. Results of phase and elemental analyses on heated samples will show that up to 99 % of initial amounts of heavy metals can be removed by this method. The results of tempering experiments will give insight into Cu-Fe-S phase relations and mass-transport mechanisms in the hot material. Based on those results, treatment conditions will be suggested which aim at a facilitated separation of elemental copper from residual sulfides.
1.5. References


1.5 References


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Chapter 2

New Paths for a SO$_2$-free Copper Production

Abstract Sulfur dioxide (SO$_2$) generation is an inherent disadvantage of conventional copper extraction from sulfides. This chapter evaluates three different approaches for a SO$_2$-free copper production: (1) the conversion of copper-iron sulfides to oxides with oxygen and steam, (2) with steam alone, and (3) directly into copper and iron sulfide. Chemical equilibrium calculations have shown that the proposed reaction scheme with oxygen and steam is limited to reactors with plug flow behaviour and hence, not generally applicable. Similar calculations showed that the reaction of chalcopyrite with steam can theoretically fulfill the requirement for a SO$_2$-free process. However, large excesses of steam would be required and chalcopyrite conversion with steam would thus be very energy-intensive. We propose a more rigorous approach, namely the direct decomposition of sulfides into the copper, iron sulfide and elemental sulfur. A promising path to effect a direct conversion is the use of concentrated solar irradiation.
2.1. Introduction

The formation of toxic and corrosive sulfur dioxide (SO$_2$) and its release to the environment is a longstanding problem of conventional copper extraction from sulfide concentrates. Challenged by increasingly stringent air quality standards imposed in the 1970's, the smelting industry was forced to deal with the polluting SO$_2$ emissions. At the same time, the search for energetically more efficient ways of copper production was stimulated as the energy prices steeply rose (Warhurst and Bridge, 1996). The widespread implementation of autogenous flash smelting process lowered the need for fossil fuels. The use of oxygen-enriched air enabled the generation of an offgas with sufficiently high SO$_2$-concentrations to effect a continuous processing to sulfuric acid. Though on-site conversion of SO$_2$ to sulfuric acid promised to be the solution although this approach is currently threatened by saturation of the sulfuric acid market. Furthermore, the still widely used Pierce Smith converters release SO$_2$-bearing gas and dust into the workplace, which has a negative effect on workplace health.

The SO$_2$ abatement strategies implemented up to the present, are essentially end-of-pipe technologies (Hilson, 2000) and do not address the problem in a fundamental way. An interesting possibility to fundamentally solve the SO$_2$ problem is to generate elemental sulfur instead of SO$_2$. Liberated sulfur is condensed upon cooling and can be safely stored, e.g. in mine storage areas. As early as 1892, producing elemental sulfur by the reaction of “red-hot” iron sulfides with steam and oxygen was proposed (Stickney, 1892, 1894, 1897). In the 1970's, Norman picked up this idea and presented it as a solution to the problem of SO$_2$ pollution (Norman, 1973, 1975). He demonstrated that copper-iron sulfides can be converted in a plug flow reactor to its corresponding oxides. As reactive gas, a mixture of oxygen and steam was used, resulting in an offgas containing only S$_2$ and steam.

The experiments were carried out in a vertical batch-type stationary bed reactor. The shaft was preheated and subsequently charged to its full height (about 50 cm) with copper concentrate briquettes. A mixture of steam and oxygen (23 wt-%) was introduced at the lower end of the reactor. After the introduction of the gas mixture, the reaction started almost immediately and after about 3 hours maximum temperatures of 1173 K were obtained. The exit
gas was found to consist only of elemental sulfur and water vapour. Although steam is required, it is not consumed. The main phases found in the reaction products were hematite (Fe₂O₃) and copper oxide (CuO), together with minor amounts of magnetite (Fe₃O₄) and Cu₂O. Norman (1975) described the overall reaction by the following equation:

\[
2 \text{CuFeS}_2 + 2.5 \text{O}_2 + x \text{H}_2\text{O} = 2 \text{CuO} + \text{Fe}_2\text{O}_3 + 2 \text{S}_2 + x \text{H}_2\text{O} \quad (2.1)
\]

The absence of \( \text{SO}_2 \) was rationalized by the reaction of \( \text{SO}_2 \), formed in reaction 2.2, with hydrogen sulfide (\( \text{H}_2\text{S} \)), the gaseous product of reaction 2.3, in a Claus-type reaction (reaction 2.4):

\[
\text{MS} + 1.5\text{O}_2 = \text{MO} + \text{SO}_2 \quad (2.2)
\]

\[
\text{MS} + \text{H}_2\text{O} = \text{MO} + \text{H}_2\text{S} \quad (2.3)
\]

\[
\text{SO}_2 + 2 \text{H}_2\text{S} = 2 \text{H}_2\text{O} + 1.5 \text{S}_2 \quad (2.4)
\]

In this chapter, thermodynamic calculations are combined with kinetic considerations to evaluate the wide-spread applicability of the proposed process. Besides the conversion of chalcopyrite in a steam-oxygen mixture, a reaction scheme with steam alone is evaluated. However, the energetic inefficiency does not recommend this approach. As an alternative, the direct conversion of metal sulfides into copper, iron sulfide and sulfur in an inert atmosphere under solar radiation is proposed. The proposed direct conversion avoids the oxidation of the metals and thereby eliminates the additional reduction step. Elimination of \( \text{SO}_2 \) either as end or intermediate product ensures a safer workplace.

2.2. Methods

2.2.1. Equilibrium calculations

Equilibrium calculations were performed for two different scenarios. In scenario A, the experimental conditions used by Norman (1975) were simulated, whereas scenario B considers chalcopyrite in the presence of steam alone. The amount of steam and \( \text{O}_2 \) was normalized with respect to chalcopyrite. This normalization results in an input of 1 mole \( \text{CuFeS}_2(s) \), 6.179 moles \( \text{H}_2\text{O(g)} \), and 1.050 moles \( \text{O}_2(g) \). The equilibrium composition was first calculated for a temperature of 1173 K to match the maximum
2.3 Results and discussion

2.3.1. Conversion of chalcopyrite in the presence of steam-O₂

To shed some more light on the empirical results of Norman’s experiment, an equilibrium calculation was performed where the oxidation of chalcopyrite (CuFeS₂) in the presence of a steam-oxygen mixture (scenario A) was considered. The calculation was carried out for an input of 1 mole CuFeS₂(s), 6.179 moles of H₂O(g), and 1.050 moles of O₂(g) at a temperature of 1173 K. Table 2.1 presents the results of this calculation.

Table 2.1 clearly shows that the experimental observations by Norman (1975) disagree with the calculated equilibrium composition. While Norman (1975)
Table 2.1: Experimental Reaction products as observed by Norman (1975) and predicted by chemical equilibrium calculations at a temperature of 1173 K.

<table>
<thead>
<tr>
<th>Experimental observation [Norman (1975)]</th>
<th>Equilibrium calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase</strong></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>SO₂</td>
</tr>
<tr>
<td>S₂</td>
<td>H₂⁺</td>
</tr>
<tr>
<td></td>
<td>H₂S⁺</td>
</tr>
<tr>
<td></td>
<td>S₂⁺</td>
</tr>
<tr>
<td><strong>Solids</strong></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Fe₀.₈₇₇S</td>
</tr>
<tr>
<td>CuO</td>
<td>Cu₅FeS₄</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td><em>Species present in amounts less than 0.01 mol.</em></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Equilibrium compositions for 1 CuFeS₂ + 6 H₂O @ 1201 K

<table>
<thead>
<tr>
<th>Species</th>
<th>Input [mol]</th>
<th>Output [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFeS₂</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>6</td>
<td>5.73</td>
</tr>
<tr>
<td>Cu₂S</td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td>Fe₀.₈₇₇S</td>
<td></td>
<td>¹/₀.₈₇₇</td>
</tr>
<tr>
<td>SO₂(g)</td>
<td></td>
<td>1.38.10⁻¹¹</td>
</tr>
<tr>
<td>H₂(g)</td>
<td></td>
<td>1.13.10⁻⁰¹</td>
</tr>
<tr>
<td>H₂S(g)</td>
<td></td>
<td>1.62.10⁻⁰¹</td>
</tr>
<tr>
<td>S₂(g)</td>
<td></td>
<td>3.10⁻²²</td>
</tr>
</tbody>
</table>
Fig: 2.1: Chemical equilibrium composition for a mixture of 1 mole CuFeS$_2$(s), 6.179 moles H$_2$O(g), and 1.050 moles O$_2$(g) a) from 900 to 1200 K where all copper is bound up in bornite and b) beyond the stability of bornite.
reported a gas phase consisting of steam and S₂, the calculations show that under equilibrium conditions, the gas phase mainly consists of SO₂ accompanied by smaller amounts of H₂, H₂S and S₂. In addition, the solid products observed by Norman (1975) (i.e. hematite (Fe₂O₃) and CuO) are not present in the calculated equilibrium composition. Instead, iron is present as Fe₀₈₇₇S, bornite, as well as magnetite (Fe₃O₄).

Copper is solely present in the form of bornite (Cu₅FeS₄). The discrepancy between experimental observations and calculated data suggested that a broader examination of the system was required. The chemical equilibrium calculation with Norman’s (1975) input was thus extended to higher temperatures to check if copper and iron oxides will be present at higher temperatures.

Fig. 2.1 shows the results of the chemical equilibrium calculation for chalcopyrite and an oxygen-steam mixture (scenario A) in a temperature range of 900-1540 K. Compounds with concentrations less than 0.01 mole, as well as equilibrium amounts of steam are omitted for the sake of clarity. Between 900 and 1200 K (Fig. 2.1a), all copper is bound up in the ternary sulfide bornite. At temperatures higher than 1200 K, bornite is unstable and copper is solely present as chalcocite (Fig. 2.1b). This implies that under equilibrium conditions, Norman’s (1975) input of 1 mole CuFeS₂(s), 6.179 moles of H₂O(g), and 1.050 moles of O₂(g) does not allow for the existence of copper oxides. In Fig. 2.1b it is seen that at 1500 K Fe₀₈₇₇S(s) decomposes into FeS(l), producing SO₂(g) and magnetite (Fe₃O₄) due to the steam-oxygen atmosphere. Along with iron sulfide, magnetite is stable over the entire temperature range (900-1540 K). The amount of magnetite gradually increases at the expense of Fe₀₈₇₇S(s) with increasing temperature. Thus, in contrast to copper sulfides, iron sulfides are partly oxidized since oxygen preferentially reacts with iron sulfide rather than with copper sulfide. The concentrations of S₂(g), H₂S(g), and H₂(g) also gradually increase with temperature. Nevertheless SO₂ remains the most prominent gaseous species over the complete temperature range.

2.3.2. Conversion of SO₂ to elemental S?
According to the calculations described above, one would not expect an SO$_2$-free offgas from a steam-O$_2$ roasting process. Fig. 2.1 indicates that under equilibrium conditions, the majority of sulfur in the gas phase is present as SO$_2$. As pointed out by Norman (1975), elemental sulfur can be formed by a Claus-type reaction, where SO$_2$ reacts with H$_2$S (see Eq. 2.4) or likewise with H$_2$ (see Eq. 2.5) to produce elemental S; i.e.

$$SO_2 + 2H_2 = S + 2H_2O \quad (2.5)$$

However, under equilibrium conditions, H$_2$S and H$_2$ are not present in sufficient amounts to allow for the complete consumption of SO$_2$. Formation of metal oxides and an SO$_2$-free offgas, can however be explained by a sequential reaction of the gas feed in a reactor with a well-developed plug flow behavior: i.e. as long as the gas contains O$_2$, metal oxides and SO$_2$ are formed. However, once all O$_2$ has reacted, the metal sulfides start to react with H$_2$O producing H$_2$S and H$_2$. Thereafter, SO$_2$ reacts with H$_2$S or H$_2$ to form elemental S and H$_2$O. The requirement of a reactor with plug flow behavior limits the applicability of the process. Specifically, the application of a fluidized bed reactor, which would allow for higher conversion rates, is not possible.

The necessity of a sequential reaction for producing an SO$_2$-free offgas can be eliminated when pure steam is used to convert copper iron sulfides. We have already showed that the process temperature should be above 1200 K to allow for the oxidation of bornite by steam (see Fig. 2.1). Under these conditions, delafossite (CuFeO$_2$) is the least oxidized mixed metal oxide. Thus, at least 6 moles of steam are required, according to the reaction,

$$CuFeS_2 + 6H_2O = CuFeO_2 + 2SO_2 + 6H_2 \quad (2.6)$$

Full conversion of chalcopyrite according to Eq. 2.6 yields a gas phase with a H$_2$/SO$_2$ ratio of 3. Thus, enough H$_2$ is present to convert all SO$_2$ to S$_2$ according to the Claus-type reaction 2.5.

Combining reaction 2.6 and 2.5 yields the following net reaction:

$$CuFeS_2 + 2H_2O = CuFeO_2 + S_2 + 2H_2 \quad (2.7)$$

If instead of H$_2$, H$_2$S is formed, the amount of SO$_2$ will be smaller, thus, in general the following requirement has to be fulfilled, such that,
To test the fulfillment of this requirement under equilibrium conditions, further equilibriums calculations were performed. An input of one mole chalcopyrite and six moles of steam was chosen. The reaction products and their amounts are given in Table 2.2. The results demonstrate that at 1201 K, chalcopyrite dissociates into 0.5 mole chalcocite and \( \frac{1}{0.877} \) mole \( \text{Fe}_{0.877}\text{S} \). Only a part of the available sulfur is converted to \( \text{SO}_2(g) \) and \( \text{H}_2\text{S}(g) \). From the 6 moles of steam given as input, only 0.275 moles are consumed. The remaining part of the sulfur either reacts with \( \text{H}_2(g) \) to \( \text{H}_2\text{S}(g) \) or is present as \( \text{S}_2(g) \). Under these conditions, all iron and copper are present as sulfides and no metal oxides are formed. Therefore, relation 2.8 does not proceed spontaneously.

2.3.3. Conversion of chalcopyrite in the presence of excess steam

With the aim of shifting the equilibrium towards production of oxides, steam was added in excess. The equilibrium composition for these amounts of steam at 1201 K is presented in Fig. 2.2. For clarity, only condensed phases are shown while gaseous species are omitted. Chalcocite is present in a constant amount of 0.5 moles for the complete range of steam input values. Its stability even in the presence of excessive amounts of steam, prevents its oxidation. In contrast, oxidation of \( \text{Fe}_{0.877}\text{S} \) at 1201 K is feasible, even though more than 18 moles of steam are required to initiate conversion to magnetite, complete conversion requires at least 96 moles of steam (see Fig. 2.2).

Complete oxidization of \( \text{Fe}_{0.877}\text{S} \) by smaller amounts of steam can be achieved at higher temperatures as indicated by the minimum temperature \( (T_{\text{min}}) \) at which all iron is present as \( \text{Fe}_3\text{O}_4(s) \) (see Fig. 2.2). Table 2.3 lists the minimum temperature \( (T_{\text{min}}) \) for steam excess from 6 to 120 moles as is graphically represented in Fig. 2.2. The two columns on the right give the ratio as defined in 2.8 and the percentage of steam consumed, respectively. For all steam excesses, the ratio of \( \text{H}_2\text{S} \) and \( \text{H}_2 \) to \( \text{SO}_2 \) (ratio 2.8) is greater than 2, indicating that in principal, an \( \text{SO}_2 \)-free offgas can be produced. However, the right column in table 2.3 also shows that steam conversion is very low and highly inefficient. If large amounts of steam are to be avoided,
2.3 Results and discussion

Fig. 2.2: Chemical equilibrium composition for the reaction of 1 mole CuFeS$_2$ with excess amounts of steam at 1201 K. $T_{\text{min}}$ is the minimum temperature at which all iron is present as Fe$_3$O$_4$(s).

![Equilibrium composition diagram](image)

Fig. 2.3: Schematic representation of a solar-driven process for the direct decomposition of chalcopyrite.

![Schematic diagram](image)
Table 2.3: Conversion of 1 mole CuFeS$_2$ in the presence of steam. Input amounts of steam are given in the first column. $T_{\text{mm}}$ denotes the minimum temperature required to produce a mixture of Cu$_2$S and Fe$_3$O$_4$. To obtain a SO$_2$-free product gas, the ratio of H$_2$S and H$_2$ to SO$_2$ must be equal or greater than 2 according to equation 2.8.

<table>
<thead>
<tr>
<th>Steam excess [mol]</th>
<th>$T_{\text{mm}}$ [K]</th>
<th>$(\text{H}_2\text{S} + \text{H}_2)/\text{SO}_2$</th>
<th>Steam consumed [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>$&gt; 2000$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>$&gt; 2000$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>1851</td>
<td>3.50</td>
<td>17.3</td>
</tr>
<tr>
<td>24</td>
<td>1551</td>
<td>3.51</td>
<td>10.3</td>
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<td>42</td>
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<tr>
<td>60</td>
<td>1351</td>
<td>3.74</td>
<td>4.8</td>
</tr>
<tr>
<td>66</td>
<td>1301</td>
<td>3.89</td>
<td>4.2</td>
</tr>
<tr>
<td>72</td>
<td>1301</td>
<td>3.78</td>
<td>3.9</td>
</tr>
<tr>
<td>78</td>
<td>1301</td>
<td>3.69</td>
<td>3.7</td>
</tr>
<tr>
<td>84</td>
<td>1251</td>
<td>3.90</td>
<td>3.3</td>
</tr>
<tr>
<td>90</td>
<td>1251</td>
<td>3.81</td>
<td>3.1</td>
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<tr>
<td>96</td>
<td>1251</td>
<td>3.74</td>
<td>3.0</td>
</tr>
<tr>
<td>102</td>
<td>1201</td>
<td>3.99</td>
<td>2.6</td>
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<tr>
<td>108</td>
<td>1201</td>
<td>3.92</td>
<td>2.5</td>
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<tr>
<td>114</td>
<td>1201</td>
<td>3.86</td>
<td>2.4</td>
</tr>
<tr>
<td>120</td>
<td>1201</td>
<td>3.80</td>
<td>2.4</td>
</tr>
</tbody>
</table>
the minimum process temperature has to be increased to such an extent that energy requirements again become unacceptably high. Therefore, neither the production of copper oxides, nor that of iron oxides in the presence of steam seems technically feasible.

2.3.4. Solar thermal decomposition of chalcopyrite

A more elegant and versatile (and direct) conversion of copper iron sulfides into copper, FeS, and elemental sulfur employs concentrated solar radiation (Winkel et al., 2003). The direct decomposition in an O\textsubscript{2}-free atmosphere inherently avoids the generation of SO\textsubscript{2}. The solar thermal approach is schematically depicted in Fig. 2.3. During the decomposition of copper iron sulfides, gaseous sulfur naturally separates from the liquid metal and residual sulfide and can be collected by condensation. Imaging furnace experiments have confirmed the decomposition of copper sulfides under inert atmospheres at temperatures of approximately 1914 K (Guesdon et al., submitted). Such temperatures are also readily accessible in solar furnaces. High operating temperatures also promote the removal of undesired impurities such as arsenic and antimony by volatilization (Hilbrans et al., 1987). Besides impurity removal, solar extraction in the absence of oxygen also minimizes slag-forming reactions and thereby facilitates the evaporation of impurities.

2.4. Summary and conclusions

Three different approaches for a SO\textsubscript{2}-free copper production have been evaluated. The first approach dates back to a proposal by Norman (1975, 1982) who demonstrated that copper-iron sulfides can be converted to its corresponding oxides by reaction with a steam-oxygen mixture. However, thermodynamic calculations showed that in a well-stirred reactor, i.e. under equilibrium conditions, the gas phase mainly consists of SO\textsubscript{2}. The proposed concept only functions in a reactor with plug-flow behavior and is therefore not generally applicable. Furthermore, the resulting metal oxides (i.e. reaction products) need to be reduced in an additional, energy consuming reduction step. An assessment of the reaction of chalcopyrite with steam alone showed that a SO\textsubscript{2}-free offgas can theoretically be achieved, since the produced SO\textsubscript{2} subsequently reacts in a Claus-type reaction to S. The second requirement, being a complete conversion to metal oxides or ideally to the free metal, can
however not be fulfilled. Only high temperatures (T~2000 K) or large steam excesses result in the products, magnetite and chalcocite. A process where chalcopyrite is reacted with steam is thus energetically highly inefficient. To conclude, the production of copper and iron oxides from chalcopyrite in the presence of steam does not seem feasible. Therefore, a more rigorous approach is proposed in which copper iron sulfides are directly decomposed into copper, iron sulfide and elemental sulfur, without the formation of intermediate SO₂. A promising path to effect direct conversion is the use of concentrated solar irradiation.

2.5. References


2.5 References


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Chapter 3

Solar thermal extraction of copper: The approach

3.1. Introduction

Direct conversion of sulfides into the metal and elementary sulfur is a promising approach to extract copper in a sustainable manner with a key feature being the use of concentrated solar radiation to directly decompose metal sulfides under inert atmospheres (see Fig. 3.1). The direct solar thermal conversion offers three benefits:

1. The formation of SO$_2$, either as an end or intermediate product is avoided and consequently, the need for processing SO$_2$ to H$_2$SO$_4$ will be eliminated and fugitive gas emissions prevented. The inert gas, (e.g. nitrogen), can be recycled after condensation of sulfur and other volatile impurities. Sulfur will be produced in its elemental form and can be stored for later use.

2. Working under inert atmospheres, (i.e. at low oxygen partial pressures), changes the chemistry and volatility of the elements. The oxidation of heavy metals, impurities and their subsequent incorporation in slag is prevented. In combination with high operating temperatures, this provides a path for an efficient removal of impurities by volatilization (Sohn et al., 2004). The challenge will be to evaporate the volatile impurities prior to formation of copper to avoid dissolution of the impurities in the metal (Itagaki and Yazawa, 1983; Hino at al., 1985).

3. The absence of an iron silicate slag will decrease the amount of waste substantially (Winkel, et al., 2003; Winkel, in preparation). In addition, dust emission will be reduced by using closed reactors.
Fig. 3.1: Scheme for the extraction of copper from copper concentrates under concentrated solar radiation.

Fig. 3.2: Accumulated solar insolation in different regions of the world, taken from Krieth. Symbols denote important copper mining sites.
The absence of oxygen makes the solar process suitable for concentrates with a wide range of compositions. The role of selective oxidation of iron sulfides in the conventional process is nevertheless of crucial importance for the separation of copper from iron. Working under inert atmosphere will thus require other means to effect this separation. Of prime interest is firstly, the selective decomposition of copper sulfide into copper, which can be separated from the remaining iron sulfide. If the first option is not achievable, there is a second option of separating the thermodynamically stable copper-rich and iron-rich phases. The separation might be induced or accelerated by means of the magneto-hydrodynamic phenomenon (Shigeo et al., 2001; Warczok et al., 2003). A third possibility is the complete removal of sulfur followed by the selective oxidation of iron by steam to iron oxide and hydrogen. This approach benefits from the known slag technology.

3.2. Solar power versus plasma technology

The direct decomposition of copper concentrates requires temperatures of at least 2000 K. We foresee that only concentrated solar power or plasma technology have the potential to drive the reaction at this temperature level on a technical scale. Concentrated sunlight is a clean and essentially inexhaustible energy source whose supply and use is free of CO2-emissions. It was demonstrated that well-designed solar chemical reactors with a thermal input of 10 kW can use more than 30 % of the incoming solar radiation to drive the chemical reaction (Meier et al., 2004). Model calculations for these small scale reactors indicate that for larger solar reactors, efficiencies of between 50 and 60 % can be reached (Wieckert, 2005). In contrast, chemical processes in arc furnaces are often plagued by low energy efficiencies and thus give rise to high energy cost. Furthermore, electricity for running arc furnaces is largely produced from fossil fuels with an average efficiency of 35 %. The accompanying emission of large amounts of CO2 with its negative impact on the climate does not support the industry’s effort to advance environmentally benign technologies.

Solar driven processes encompass some specific features usually not found in conventionally heated reactors or furnaces. The next section will describe some of the characteristics of high-temperature solar technology and discuss possible consequences for the extraction of copper.
Fig. 3.3: Sketch of the SOLZINC solar chemical reactor for the carbothemic reduction of ZnO. It features two cavities in series with the upper one functioning as the solar absorber and the lower one as the reaction chamber (from Wieckert et al., submitted).

Fig. 3.3: The SOLZINC pilot plant at the Weizmann Institute (WIS) in Israel. A field of heliostats focuses the sun rays onto a hyperbolical reflector at the top of the tower to re-direct sunlight into the reactor (from Wieckert et al., submitted).
3.3. Characteristic features of high-temperature solar technology

3.3.1. Fundamentals

Concentrated solar radiation represents a powerful energy source to effect endothermic reactions, such as the direct decomposition of copper concentrates. Radiant heating allows for novel pathways of material processing under any atmosphere and in the absence of combustion products. Key components of the concentrated solar power technology for thermochemical applications are arrangements with many flat mirrors, so called heliostats, that reflect the incident solar radiation to a common point on top of a tower, where the concentrated radiation is used. The flux density is usually increased even more by non-imaging secondary optical concentrators (Welford and Winston, 1989). These arrangements supply flux density between 1 and 5 MW·m⁻² at the opening (aperture) of a solar reactor and give access to working temperatures up to 2500 K. The combination of high energy fluxes and fast high-temperature reactions results in compact reactors with a high throughput. The total power input depends on the application and varies from a few tens of kW to MW for research units and demonstration plants, respectively, while the installed thermal power of commercial plants is expected to be in the range of 500 to 1500 MW (Sargent and Lundy LLC Consulting Group, 2003).

Depending on the temperature range of the reaction two different types of solar reactors can be employed. For temperatures below 1600 to 1700 K, the decomposition in a cavity type solar reactor with indirect heating is a valid option. An example of a cavity type solar reactor is shown in Fig. 3.3. Fig. 3.4 shows the optical configuration of the solar tower concentrating system of this SOLZINC solar chemical reactor (Wieckert et al, submitted). Here a radiation absorber is located between the concentrated light and the feed. Preliminary experiments indicate that the decomposition of copper sulfides requires temperatures above 2000 K, which suggests that the feed itself must absorb the concentrated sunlight (direct heating). Reactor concepts for solid feeds with direct heating were demonstrated with self-lined reactors (Haueter et al., 1999) gas particle suspensions (Ganz et al., 1999; Kräupl et al., 2003) and fluidized beds (Flamant et al., 1987).
Since the energy is provided in the form of intense radiant energy, scaling up a solar chemical reactor is a non-trivial task. An efficient increase of the energy input cannot be achieved by enlarging the aperture as this would increase the re-radiation losses but with an increase of the flux density of the supplied radiation, preferably at a constant aperture. This in turn affects the surface temperature and all the other processes in a non-linear way. The development of solar chemical reactor therefore requires most often, models that include the interaction of radiation with matter. Because the thermophysical and kinetic parameters at these high temperatures are rarely found in the literature, the determination of these data is often an indispensable task in the early phase of reactor design. The complex interplay of the different processes is also the reason why many reactions need their own reactor design though their chemistry looks very similar at first glance.

3.3.2. Global Distribution of Solar Insolation

As with many other resources, solar energy is not evenly distributed on Earth and solar plants will be erected on the basis of perennial track records of the available solar energy. These kind of data are available for most of the globe based on ground or satellite observations. Fig. 3.2 displays a map with the accumulated solar insolation per year (a) and m². It shows that many important copper mining sites are located in areas with an annual insolation of more than 2000 kWh·a⁻¹·m⁻². 2000 kWh·a⁻¹·m⁻² are considered the minimum insolation to run economically viable solar plants. The map also shows that many areas close to the growing Asian market, receive sufficient sunlight that recommends its use for processing traded copper concentrates. Operation of a purely solar plant is obviously only possible during daylight hours; Six hours of full operation is a fair estimate [11] but it depends on specific parameters such as the characteristics of the solar reactor or reaction temperature. A solar reactor in a process chain will therefore be scaled such that it can serve a 24 h operation of the downstream refinement during its daily operation time.

3.4. References

3.4 References


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Chapter 4

Decomposition Studies on Copper Concentrates at Temperatures below 1800 K

Abstract The thermal decomposition of three synthetic copper sulfides, (chalcocite (Cu₂S), chalcopyrite (CuFeS₂), and enargite (Cu₃AsS₄)) and two commercial copper concentrates has been studied on a thermobalance in inert atmospheres. It was demonstrated that the absence of oxygen, in combination with high decomposition temperatures furthers the removal of heavy metal impurities by volatilization. Elemental analyses on residues of treated concentrates showed that removal of volatile impurities occurs in three distinct temperature ranges: At $T < 1173$ K, arsenic and bismuth are removed; at $T < 1673$ K, the evaporation of cadmium and tin occurs, while the evaporation of Pb and Zn only takes place at $T > 1673$ K. Between 1673 and 1773 K the removal exceeds 95%. The concentrate containing quartz produced a slag-like phase lying on top of the sulfide. Nevertheless, the additional phase does not hinder an efficient removal of the impurities.
4.1 Introduction

Copper concentrates contain the main elements copper, sulfur, and iron in addition to substantial amounts of impurities such as arsenic, antimony, bismuth, lead and zinc. Removal of these impurities is an essential task of the extraction process in order to obtain high purity copper. In the future, the ability to efficiently remove impurities will become even more important since copper ores have a decreasing ore grade and thus an increase in impurities. In conventional flash smelting, heavy metal impurities end up either in the slag phase or eventually in blister copper (Chaubal and Nagamori, 1988; Degterov and Pelton, 1999) from which they have to be eliminated by electrolysis. Copper slags containing heavy metals require either a controlled disposal in a landfill (Dutré and VandeCasteele, 1995), or a thorough clean-up before they can be safely disposed off.

Recently, we proposed a novel concept for a clean process to extract copper from copper concentrates in the absence of oxygen (Winkel et al., 2003). This new concept uses concentrated solar radiation as energy source to directly decompose copper concentrates into copper and valuable byproducts such as sulfur and heavy metals. Working under oxygen-free atmospheres has two major advantages. Firstly, the generation of sulfur dioxide (SO₂) as a byproduct or intermediate is avoided. Secondly, the oxidation of heavy metals and therefore their incorporation in a slag phase is prevented. In combination with high operating temperatures, this will result in an efficient removal of impurities by evaporation. The idea of impurity removal by evaporation has been previously described by Yazawa and Azakami (1969), who stated that at 1473 K, the elimination by volatilization may be expected for some sulfides, including those of Pb, Cd, Sb, Bi, As and Sn. Experimental work in this field has mainly focused on the pre-treatment of concentrates under vacuum (Villaroel, 1999; Jiang et al., 2003). Villaroel (1999) accomplished the complete removal of harmful impurities such as As, Sb, Bi, Pb, Zn under vacuum at 1223 K. However, the industrial application of a cleaning process under vacuum is questionable.

This chapter presents results of the thermal decomposition studies on synthetic chalcocite (Cu₂S), chalcopyrite (CuFeS₂) and enargite (Cu₃AsS₄), and two copper concentrates under inert atmospheres and thermodynamic
equilibrium conditions. Thermogravimetric (TG) analyses combined with chemical equilibrium calculations and inductively coupled plasma spectrometry (ICP) analyses will give insight into the conditions which allow for an efficient impurity removal by volatilization. In the TG experiments, small heating rates were selected as to eliminate kinetic effects. In the first part of the chapter the thermal decomposition of chalcocite and chalcopyrite and results of coupled TG-ICP studies on synthetic enargite will be discussed. Enargite, Cu\textsubscript{3}AsS\textsubscript{4}, is commonly found in Chilean copper and gold ores. In this study, it serves as a model substance for an arsenic-bearing phase. Arsenic was chosen because this impurity is very harmful in copper where it results in a sharp decrease in electrical conductivity. Its removal at an early stage of the process is of critical importance because it is very difficult to eliminate once elemental copper is present (Hino et al., 1985). The second part of the chapter presents thermal decomposition experiments of two different copper concentrates. These data demonstrate that thermal treatment is an efficient method to remove volatile impurities from multi-phase copper concentrates.

4.2. Experimental details

4.2.1. Materials

*Chalcocite* (-325 mesh) was obtained from Aldrich. It is specified as a non-stoichiometric compound with a slight excess of sulfur. X-ray powder diffractometry revealed that the material was in fact a mixture of Cu\textsubscript{9}S\textsubscript{5} (digenite) and Cu\textsubscript{7}S\textsubscript{4} (anilite) rather than chalcocite (Cu\textsubscript{2}S). By means of thermogravimetric analysis, the overall stoichiometry was determined to be Cu\textsubscript{2}S\textsubscript{1.26}. The amount of S is higher than one would expect for phases such as Cu\textsubscript{2n-1}S\textsubscript{n} (n=4, 5) and it suggests the presence of additional, probably X-ray amorphous phases. The material was used without further purification.

*Chalcopyrite* (CuFeS\textsubscript{2}) was synthesized from the elements under vacuum. The elements were fused in a sealed quartz tube at 1473 K during 30 minutes. The melt was quenched to room temperature. The resulting ingot was finally annealed at 773 K for 5 days and again quenched to room temperature (Woolley et al., 1996). Phase analysis of the yellowish crystals with blue and
4.2 Experimental details

purple iridescence by powder X-ray diffractometry confirmed the formation of single phase, tetragonal chalcopyrite.

*Enargite* was synthesized under vacuum from copper wire, As$_2$S$_3$ glass and native sulfur (Seal et al., 1996) at 1025 K, and subsequently annealed at $T = 773 \pm 10$ K for 14 days.

*Copper concentrate* contained 25 to 30 percent copper and is the product produced after crushing, milling and concentration of the sulfide ore (containing less than 1 percent copper). Two different copper concentrates were kindly provided by Outokumpu Oy (Finland). Their elemental contents are given in Table 4.1. Concentrate 1 is characterized by higher copper and zinc contents but lower iron and sulfur contents than concentrate 2. Concentrate 2 contains larger amounts of quartz (SiO$_2$) and arsenic.

Both concentrates were dried for 14 hours at 333 K in air and subsequently ball-milled for two periods of 5 minutes to improve homogeneity of the sample. Subsequently, their mineral phases were identified by X-ray powder diffractometry. The main minerals in the raw concentrates are chalcopyrite (CuFeS$_2$) and pyrite (FeS$_2$). Minor amounts of sphalerite (ZnS) are detected in both concentrates. Both concentrates contain some quartz (SiO$_2$) with concentrate 2 containing almost three times as much as concentrate 1. Traces of galena (PbS) were detected in concentrate 1.

4.2.2 Methods

*Chemical equilibrium calculations*

Thermal decomposition studies of enargite (Cu$_3$AsS$_4$) were preceded by chemical equilibrium calculations to provide the distribution of species with temperature over gas and condensed phases, assuming that substances behave ideally. Chemical equilibria were calculated, using Gibbs energy minimization approach with the Equitherm V5.03i software and thermodynamic database (Verlag Chemie Weinheim). Under the assumption that the phases are in equilibrium, the amounts of species containing Cu, Fe, As and S were calculated as a function of temperature for an input of 1 mole chalcopyrite and 0.5 moles enargite. The temperatures included in the calcula-
Table 4.1: Main and rock-forming elements content (a) and heavy metals content (b) of two copper concentrates. Concentrations were measured by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Elements in wt%</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>SiO₂</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate 1</td>
<td>29.0</td>
<td>28.2</td>
<td>33.4</td>
<td>0.6₃</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Concentrate 2</td>
<td>25.4</td>
<td>32.4</td>
<td>36.4₃</td>
<td>1.7₃</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*₃ provided by the supplier.

Table 4.2: Species included in chemical equilibrium calculations

<table>
<thead>
<tr>
<th>Solids</th>
<th>Liquids/Melts</th>
<th>Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂S₃</td>
<td>As₂S₃</td>
<td>As₂-As₄-As₄S₄-S₂-S₃</td>
</tr>
<tr>
<td>CuS</td>
<td>FeS-Cu₂S</td>
<td>S</td>
</tr>
<tr>
<td>Cu₂S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeS₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₉₈₇₇₃S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₅FeS₄</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Element-specific detection limits of the ICP measurements and relative uncertainties.

<table>
<thead>
<tr>
<th>Element [wt%]</th>
<th>As</th>
<th>Bi</th>
<th>Cd</th>
<th>Pb</th>
<th>Sb</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>0.05</td>
<td>0.01</td>
<td>1·10⁻³</td>
<td>0.10</td>
<td>0.03</td>
<td>0.02</td>
<td>3·10⁻³</td>
</tr>
<tr>
<td>Relative uncertainty</td>
<td>0.09</td>
<td>1·10⁻³</td>
<td>1·10⁻³</td>
<td>0.17</td>
<td>0.01</td>
<td>1·10⁻³</td>
<td>0.22</td>
</tr>
</tbody>
</table>
tions range from 300 to 2000 K and were calculated in steps of 20 K. Since
the evaporation of impurities in the absence of oxygen is of interest, oxygen
was excluded from the input file. Initial calculations that have resulted in the
stability of species with concentrations below 0.01 mol% were also removed
from the input file. The species included in the final input file are listed in
Table 4.2.

4.2.3. Thermal decomposition studies

Thermal decomposition of chalcocite and chalcopyrite was studied by
thermogravimetry (Netzsch STA 409) under inert atmospheres (N₂, 99.995%
or CO-CO₂ mixtures; gas flow 75-100 ml min⁻¹; sample weight 60-100 mg;
heating rates 10-20 K min⁻¹). Solid products were analyzed by X-ray powder
diffactometry (Philips Xpert) with FeKα irradiation.

The decomposition of enargite was studied using a thermobalance (Mettler
Toledo TG/SDTA 851) interfaced to an Inductively Coupled Plasma Optical
Emission Spectrometer (ICP-OES, Varian Liberty 110) which employed a Jet
Flow Condenser (JFC) (Ludwig et al., 2001). On the thermobalance (TG), 8
to 12 mg of ground enargite was heated up to 1233 K at a heating rate of 4
K min⁻¹ under 80 ml min⁻¹ argon (99.999%). The gases that are released during
the thermal treatment are simultaneously transformed into an aerosol by the
JFC device enabling online ICP spectrometry (Ludwig et al., 2001). Two runs
demonstrated a good reproducibility. The mineralogical content of solid
residues from the thermal treatment was analyzed by X-ray powder
diffactometry.

Preliminary results of coupled TG-ICP experiments on copper concentrates
have shown that experiments repeated under similar conditions revealed
evaporation pulses of heavy metals at different temperatures. At this point, a
successful application of this method on copper concentrates was therefore
not feasible. Therefore the decomposition of concentrates was studied by a set
of discontinuous TG experiments at higher temperatures.

The decomposition of the two copper concentrates was studied on a
thermobalance (Netzsch STA 409) under argon. Of both concentrates
amounts of approximately 1300 mg were accurately weighed into Al₂O₃
crucibles or glassy carbon crucibles and placed on the thermobalance. The
raw concentrate was heated under 100 ml·min⁻¹ argon (99.999%) with 4 K·min⁻¹ until a selected end temperature between 1173 and 1773 K (100 K interval). The seven runs performed for each concentrate were repeated once and showed no significant deviations. After thermal treatment of the concentrate and cooling to room temperature, the solid residue was visually inspected and then ground to a fine powder. The mineralogical content of the product was determined by X-ray powder diffractometry. A semi-quantitative analysis was obtained by using relative reference intensities (I/I₀), where corundum (α-Al₂O₃) serves as the reference material (Visser and de Wolff, 1964). The corrected intensities were subsequently normalized with respect to the corrected troilite (FeS) intensity. After dissolution under pressure in HCl (36 %) and HN₃ (65 %), the elemental content of the residue was determined by ICP spectrometry (ICP-OES, Varian Liberty 110). The element-specific limits of detection and relative uncertainties of minor elements are listed in Table 4.3.

4.3. Results and Discussion

4.3.1. Decomposition of synthetic copper sulfides under inert atmospheres

Fig. 4.1 shows the result of a thermogravimetric analysis for the binary copper sulfide. Single phase chalcocite is obtained by heating the sample to 1373 K. Further heating induces the decomposition of chalcocite directly into Cu and S. The observed weight loss of 22.9 wt% compares with the calculated value of 20.15 wt-% for the decomposition of Cu₂S into Cu according to:

\[ \text{Cu}_2\text{S} = 2 \text{Cu(l)} + 0.5 \text{S}_2(\text{g}) \]  (4.1)

The agreement between the two values is quite good given the fact that the inert gas flow induces evaporation of copper, as evidenced by the decreasing weight after completion of the decomposition and by control experiments with pure copper. The decomposition of chalcopyrite is more complex. Heating up to 1250 K induces a first weight loss that is attributed to the formation of bornite (Cu₅FeS₄), troilite (FeS) and gaseous S, according to:
Fig. 4.1: Thermogravimetric analysis of binary copper sulfide (ca. 100 mg sample in alumina crucible; 74 ml·min\(^{-1}\) \(\text{CO}_2\), 2.5 ml·min\(^{-1}\) \(\text{CO}\)) and \(\text{CuFeS}_2\) (ca. 60 mg sample in alumina crucible; 100 ml·min\(^{-1}\) \(\text{N}_2\)). Heating rates are 20 K·min\(^{-1}\).

Fig. 4.2: Schematic presentation of the chemical equilibrium composition for an input of 1 \(\text{CuFeS}_2\) + 0.5 \(\text{Cu}_3\text{AsS}_4\).
\[ \text{CuFeS}_2 = \frac{1}{5} \text{Cu}_5\text{FeS}_4 + \frac{4}{5} \text{FeS} + \frac{1}{5} \text{S}_2 \]  \hspace{1cm} (4.2)

The calculated weight loss of 7 wt\% agrees well with the measured value of 6.9 wt\%. Further heating causes evaporation of more sulfur, even though the reaction becomes sluggish.

A sample subjected to 1773 K for 225 min still contains 15% of the original amount of sulfur. Visual inspection of such a sample at room temperature revealed the formation of a grayish-black sphere (d \approx 2 mm) with metallic luster. It is decorated with smaller round particles (d \approx 0.3 mm) with metallic appearance and magnetic behavior. Perpendicular to the surface of the large sphere, reddish-brown copper fibers were observed. Phase analysis confirmed the formation of copper as well as troilite (FeS) and the presence of bornite (Cu$_2$FeS$_4$). The presence of small amounts of binary copper sulfides cannot be ruled out but they are certainly less prominent than troilite. The observed products qualitatively agree with the analysis of samples that were cooled to room temperature after decomposition under vacuum (Ugryumova et al., 1975).

Chalcocite and chalcopyrite have obviously very different decomposition rates (see Fig. 4.1). Chalcocite shows initially a rather slow decomposition as excess sulfur is evaporated and stoichiometric Cu$_2$S is formed. As the temperature of 1773 K is reached decomposition accelerates and metallic copper is formed. Chalcopyrite shows a fast decomposition during heating but after a temperature of 1742 K is reached, its decomposition attains a constant but smaller rate. Both decomposition produced samples comparable in size and shape. Therefore, the different decomposition rates seem to reflect the chemical properties of the phases involved rather than different surface to volume ratios. Ugryumova et al. (1975) and Isakova et al. (1976) conducted in situ high-temperature X-ray diffractometry experiments under vacuum and observed that the phase composition at elevated temperatures substantially differed from that of cooled samples. They concluded that the latter one is the result of secondary processes during cooling.

4.3.2. Thermal decomposition of enargite

Fig. 4.2 is a schematic presentation of the equilibrium composition for an initial input of 1 mole chalcopyrite (CuFeS$_2$) and 0.5 moles enargite
4.3 Results and discussion

(Cu₃AsS₄). The upper part of the diagram shows the presence of gaseous species with temperature and in the lower part, the condensed phases are presented. At lower temperatures, arsenic is bound up as the binary sulfide As₂S₃(s), copper and iron are present as binary sulfides and bornite (Cu₅FeS₄). At 995 K, incongruent evaporation of liquid As₂S₃ commences according to the following reaction:

\[ 2 \text{As}_2\text{S}_3(l) = \text{As}_4\text{S}_4(g) + \text{S}_2(g) \]  

At 1100 K, gaseous As₄S₄ decomposes into S₂(g) and As₄(g), which in turn decomposes at 1200 K into the lighter compound As₂(g). While at high temperatures elemental arsenic is present in the gas phase, copper and iron are present in the condensed phase as the binary compounds chalcocite (Cu₂S) and troilite (FeS). Elemental sulfur (i.e. S(l), S₂(g), S₃(g) and S₄(g)) is formed as a product of a number of decomposition reactions and is therefore present in increasing amounts towards higher temperatures.

4.3.3. Coupled TG-ICP experiments

Fig. 4.3 shows the weight change of enargite as well as the evaporation of arsenic and sulfur during the decomposition. Both elements show pronounced pulses, which suggest the formation of intermediates during decomposition. The ICP signal for sulfur shows that evaporation of sulfur starts at temperatures below 773 K. During the decomposition, four distinct pulses are observed. The largest pulses occur at 854 and 911 K. Arsenic mainly evaporates simultaneously with sulfur at 854 K. The first pulse (at 854 K) corresponds to the formation of tennantite (Cu₁₂As₄S₁₃) according to,

\[ 4 \text{Cu}_3\text{AsS}_4 = \text{Cu}_{12}\text{As}_4\text{S}_{13} + 1.5 \text{S}_2(g) \]  

Reaction 4.4 accounts for only 15.5% of the total weight loss. The second peak at 911 K qualitatively agrees with isothermal runs done by Padilla et al. (2001). Their experiment at 848 K produced chalcocite, which presence indicates that at least some arsenic must have evaporated as described by,

\[ \text{Cu}_{12}\text{As}_4\text{S}_{13} = 6 \text{Cu}_2\text{S}_{1+x} + \text{As}_4\text{S}_4(g) + (1.5-3x) \text{S}_2(g) \]
Fig. 4.3: Simultaneous TG-ICP analysis of enargite. The TG curve represents the weight change with time and the DTG curve is the derivative of the TG curve.

Fig. 4.4: Morphology of the thermally treated concentrate
The coincidence of the arsenic and sulfur peak is consistent with the evaporation of an arsenic sulfide, which in turn agrees well with chemical equilibrium calculations that predict the evaporation of arsenic as $\text{As}_4\text{S}_4$ at 995 K.

The solid product of enargite decomposition consists of chalcocite ($\text{Cu}_2\text{S}$), minor amounts of digenite ($\text{Cu}_9\text{S}_5$) and possibly traces of elemental copper. The absence of a mineralogical phase containing arsenic is consistent with the complete evaporation of arsenic. Stronger evidence that all arsenic was successfully evaporated below 1000 K is the absence of the ICP signal for arsenic above this temperature. Furthermore, chemical equilibrium calculations also indicated complete evaporation of arsenic at temperatures below 1000 K. Phase analysis is also consistent with the measured weight loss. Under the assumption that all arsenic evaporated and that the product only consists of chalcocite, a weight loss of 39.4 % is expected. The measured weight loss amounts to 38.4 %. The difference between the expected and observed value is explained by the formation of small amounts of digenite ($\text{Cu}_9\text{S}_5$). The results also show that simultaneous measurements of the weight loss and analysis of the gas phase can provide detailed insight into the decomposition reactions of single phase substances.

4.3.4. Thermal decomposition studies on copper concentrates

Characterization of the residues

Concentrate (1)

Both copper concentrates were subjected to thermal treatments with maximum temperatures between 1173 K and 1773 K. The residue of concentrate (1), treated at a maximum temperature of 1173 K, does not show evidence of large scale melting although the material has sintered slightly (see Fig. 4.4). The greenish-grey colour is similar to that of the raw concentrate and individual grains are still visible with the naked eye. The residues that were subjected to maximum temperatures between 1273 K and 1773 K are shiny greyish-black and appear to have been molten. The inside of the residues is highly porous with rounded bubbles that suggest the entrapment of gas in a viscous mass (see Fig. 4.4). Not only the morphology of concentrates has changed during treatment but new minerals were also formed (Fig. 4.5). In the concentrate treated at a maximum temperature of 1173 K, neither chalcopyrite ($\text{CuFeS}_2$) nor pyrite ($\text{FeS}_2$) were identified. Instead, the ternary
compound mooihoekite (Cu₉Fe₉S₁₆), the binary compound FeS and a second tetragonal phase was identified. Mooihoekite has a tetragonal structure similar to the low temperature chalcopyrite phase but a smaller sulfur content as can be seen from its normalized formula (Cu₁Fe₁S₁.₇₈). The structure is however known to accommodate a variable metal to sulfur ratio ranging from 1.12 to 1.135 for Cu ≡ Fe (atomic) and from 1.125 to 1.00 for Cu/Fe = 1.00 to 0.95 (all data for 373 K) (Cabri, 1973). The pattern for the second tetragonal phase is attributed to a compound structurally related to the stannite group. Minerals of the stannite group have a tetragonal structure with a general formula a₂bcx₄, where a = Ag, Cu, b = Cu, Ce, Fe, Hg, Zn, c = As, Ge, In, Sb, Se, Sn and x = S or Se. Substitution of Sn on the c site by Cu leads to a form of idaite, which has a chemical composition close to Cu₃FeS₄ (Hatert, 2003). Due to the relatively small amount of available Sn, As, and Sb, the second tetragonal phase is therefore interpreted as a solid solution between a stannite-type phase and idaite and it is thus referred to as stannite-like phase.

All samples treated at a maximum temperature of 1273 K and above contain bornite and the stannite-like phase, though in decreasing abundance relative to troilite. The two binary phases containing heavy metals, galena and sphalerite, show overall decreasing abundances and are absent in products that were treated at maximum temperatures higher than 1573 K. Small droplets of reddish brown copper were observed on the surface of residues treated at 1573-1773 K. The presence of elemental copper was confirmed by XRD analysis.

Concentrate (2)

After heating to 1173 K concentrate (2) has a similar morphology and mineralogy as the corresponding residue of concentrate (1), except that it additionally contains quartz. In contrast to concentrate (1), heating of concentrate 2 to maximum temperatures between 1273 and 1773 K produces two clearly distinguishable phases. The lower, predominant, phase has the shape of a flattened droplet with a greyish-black shiny appearance. On top of it lies a darker, more dull and porous phase, which comprises less than 10 % of the total mass. The upper phase shrinks with increasing temperatures, whereas the amount of the lower dense part increases. The two parts were individually analyzed after their separation. XRD analyses showed that the
mineral content in the two parts is identical, apart from the presence of quartz in the upper, porous, parts (Fig. 4.5). Residues of concentrate (2) also have identical mineral contents as their counterparts of concentrate (1). Again, bornite and the stannite-like phase are present between 1273 and 1773 K in decreasing amounts whereas FeS increases. Small copper droplets were observed at the surface of the residue that was treated at 1773 K.

The porous top of concentrate (2) is considered to be an early stage of a slag-like phase. The separation of concentrate (2) into the two distinct phases probably reflects a difference in melting behaviour between the sulfide phase and the high-melting quartz phase (m.p. 1983 K). The shrinking of the porous phase with increasing temperatures is explained by a more complete separation of quartz from the sulfide phase at higher temperatures. Decomposition experiments at about 1914 K on concentrate (2) in an imaging furnace resulted in the formation and segregation of an even more developed quartz phase, in the form of a greenish transparent glass bead.

Fig. 4.6 shows that concentrate (2) has an approximately two times larger weight loss than concentrate (1) over the whole temperature range. The weight loss (TG) and rate of weight loss (DTG) curves presented in this figure were obtained in experiments with a maximum temperature of 1773 K. The corresponding data of measurements stopped at lower temperatures do not show any significant difference and were therefore omitted from the figure. The two curves indicate that concentrate (2) clearly loses more weight than concentrate (1). Nevertheless, one recognizes that the mass-loss characteristics of both concentrates are very similar, suggesting that similar decomposition reactions occur. The weight loss of both samples is primarily due to the evaporation of sulfur (see Table 4.4).

Concentrate (1) shows that a sulfur decrease of around 4% occurs at temperatures between 1173 and 1773 K. This is in good agreement with the TG curve in Fig. 4.6. The larger evaporation of sulfur from concentrate (2) is not reflected by the ICP results. It is however seen that the pre-slag phase clearly contains less sulfur than the main sulfide phase.
### Fig. 4.5: Schematic semi-quantitative representation of mineralogical content of treatment products of concentrate (1) and concentrate (2), in temperature intervals of 100 degrees. The thickness of bars is a qualitative measure for mineral content.
4.3 Results and discussion

Fig. 4.6: Weight change (TG) and rate of weight change (DTG) during thermal decomposition of concentrate 1 and 2. Numbers 1 to 3 are discussed in the text.

Table 4.4: Sulfur concentrations in the residues of thermally treated concentrates, where n.a. denotes that a residue was not available. The relative uncertainty is 3.1 wt%.

<table>
<thead>
<tr>
<th>Maximum temperature of treatment [K]</th>
<th>1173</th>
<th>1273</th>
<th>1373</th>
<th>1473</th>
<th>1573</th>
<th>1673</th>
<th>1773</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>30.3</td>
<td>30.3</td>
<td>n.a.</td>
<td>28.6</td>
<td>n.a.</td>
<td>27.2</td>
<td>26.8</td>
</tr>
<tr>
<td>Conc 2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>23.4</td>
<td>n.a.</td>
<td>25.6</td>
<td>25.0</td>
<td>27.0</td>
<td>27.1</td>
<td>22.5</td>
</tr>
<tr>
<td>Conc 2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>20.8</td>
<td>22.2</td>
<td>20.9</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

<sup>a</sup>lower sulfide part.
<sup>b</sup>pre-slag phase obtained at maximum temperature above 1373 K.
Decomposition reactions and intermediate phases

The combination of thermal analyses with phase analyses of cooled samples provides insight in the sequence of decomposition reactions. For example, at $T < 1073 \text{ K}$, the weight loss is characterized by three large maxima at 776, 800, and 981 K. The first DTG peak at 776 K is attributed to the decomposition of pyrite to troilite. This reaction is known to take place at temperatures above 742 K (Landolt-Börnstein, 1971); i.e.

$$\text{FeS}_2 = \text{FeS} + 0.5 \text{ S}_2 \quad (4.6)$$

Indeed, pyrite is absent in the 1173 K residues and instead, the binary iron sulfide FeS was identified. Chalcopyrite, the other main constituent of raw concentrates transforms at 823 K into $\beta$-chalcopyrite, a member of the cubic disordered intermediate solid solution (iss) (Vorob’yev and Borisovskiy, 1981):

$$\text{CuFeS}_2 = \text{CuFeS}_{2-x} + x \text{ S}^\uparrow \quad (4.7)$$

This reaction and the accompanying evaporation of sulfur are attributed to the second DTG peak. According to Ugryumova et al. (1975) the S-poor chalcopyrite phase ($\beta$-chalcopyrite) may accommodate a sulfur-deficiency of up to 15 wt-%. Further evaporation of sulfur yields bornite and pyrrhotite ($\text{Fe}_{1-x}\text{S}$). In the TG and DTG signals (Fig. 4.6), a third acceleration of weight loss with a maximum at 981 K (3rd DTG peak) is observed, which is possibly explained by the decomposition of $\beta$-chalcopyrite according to the reaction,

$$\text{CuFeS}_{2-x}(s) = \frac{1}{5} \text{Cu}_5\text{FeS}_4(s) + \frac{4}{5} \text{FeS}(s) + \left(\frac{1}{5} - \frac{x}{2}\right) \text{S}_2(g), \text{ where } x \leq \frac{2}{5} \quad (4.8)$$

However, in the 1173 K residues, bornite was not found. Instead, the stannite-like phase [Cu$_2$Fe(Cu,Sn)S$_4$] and mooihoekite (Cu$_9$Fe$_9$S$_{16}$) were identified together with troilite. This suggests that $\beta$-chalcopyrite possibly decomposes to bornite via an intermediate that crystallizes with the tetragonal stannite structure upon cooling. In this interpretation, mooihoekite must be seen as a relict of unreacted $\beta$-chalcopyrite. The interpretation is supported by the fact that mooihoekite is no longer found in samples treated at higher temperatures. Such samples that were treated above 1173 K were at least partly molten. In those samples, no more iss-like phases are found. Instead, the ternary compound bornite was found together with troilite and the stannite-like phase,
as is expected from reported equilibrium studies (Chang et al., 1979; Villars et al., 1995). The appearance of bornite is attributed to the loss of more sulfur from β-chalcopyrite or an intermediate phase, which causes its instability and results in the formation of bornite akin to equation 4.8. It should be noted that bornite is most likely not present at high temperature in the molten state but appears only during cooling (see Uglyumova et al., 1975). At 1461 K, FeS melts and the whole sample is liquid. Solidified residues contain both bornite and the stannite-like mineral in decreasing amounts (see Fig. 4.5). Since there is no evidence for the loss of copper, another copper-bearing phase must have formed at higher temperatures. The observation of reddish brown copper droplets at the surface of residues treated at 1473 - 1773 K suggests the formation of elemental copper, which was confirmed by XRD analysis. In contrast to the presence of elemental copper, no elemental iron is detected. It is solely present as FeS above the decomposition temperature of bornite and at T< 1461 K, it becomes part of the Cu-Fe sulfide melt.

4.3.5. Evaporation characteristics of volatile impurities

**Concentrate (1)**

This section discusses the effect of the thermal treatment on the volatile impurities in copper concentrates. Concentrations of arsenic and bismuth in treated samples are below the detection limit (of 0.05 and 0.01 wt%) over the whole temperature range. These results are consistent with experiments conducted by Sohn et al. (2004) who demonstrated that arsenic and bismuth readily evaporate due to their high volatility when argon is bubbled through a copper matte at 1523 and 1673 K. Furthermore, arsenic and bismuth in copper concentrates are likely to be incorporated in complex copper sulfide compounds (e.g. as solid solutions with the main Cu-Fe sulfide minerals). Decomposition of such compounds into binary substances supports the release of volatile impurities. In contrast, heavy metals like zinc and lead are bound up primarily in binary compounds, i.e. sphalerite (ZnS) and galena (PbS). Decomposition of the copper-bearing phases is therefore not expected to facilitate the evaporation of substantial amounts of zinc and lead. Indeed, the amounts of these elements are relatively constant in the low and mid-temperature range up to 1673 K. Only at T > 1673 K are zinc and lead removed in substantial amounts (i.e. 60% of the content at 1173 K; see Fig.
Fig. 4.7: Amounts of heavy metals in thermally treated concentrate (1), normalized with respect to maximum concentrations in residues.

Fig. 4.8: Amounts of heavy metals in thermally treated concentrate (2), normalized with respect to maximum concentrations in residues.
Table 4.5: Concentrations of heavy metals in concentrates (1) and (2) after thermal treatment at different maximum treatment temperatures. Relative uncertainties are 1·10⁻³ wt% for Cd, 1·10⁻³ wt% for Sn, 0.17 wt% for Pb, 0.22 wt% for Zn and 0.01 wt% for Sb.

<table>
<thead>
<tr>
<th>Element</th>
<th>Maximal temperature of treatment [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1173</td>
</tr>
<tr>
<td>Concentrate (1)</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.01</td>
</tr>
<tr>
<td>Sn</td>
<td>0.05</td>
</tr>
<tr>
<td>Pb</td>
<td>0.61</td>
</tr>
<tr>
<td>Zn</td>
<td>2.47</td>
</tr>
<tr>
<td>Concentrate (2)</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.12</td>
</tr>
<tr>
<td>Pb</td>
<td>0.20</td>
</tr>
<tr>
<td>Zn</td>
<td>1.51</td>
</tr>
<tr>
<td>Sb</td>
<td>0.13</td>
</tr>
<tr>
<td>Sulfide phase</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.12</td>
</tr>
<tr>
<td>Pb</td>
<td>0.20</td>
</tr>
<tr>
<td>Zn</td>
<td>1.51</td>
</tr>
<tr>
<td>Sb</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pre-slag phase</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pb</td>
<td>n.a.</td>
</tr>
<tr>
<td>Zn</td>
<td>n.a.</td>
</tr>
<tr>
<td>Sb</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

- superscript a: residue is not available
- superscript b: value is below limit of detection of 1·10⁻³ Wt%
- superscript c: value is below limit of detection of 0.02 Wt%
- superscript d: value is below limit of detection of 0.10 Wt%
- superscript e: value is below limit of detection of 0.03 Wt%
4.7 and Table 4.5). Accordingly, sphalerite is found only in residues treated up to 1573 K (see Fig. 4.4). Cadmium and tin require less high temperatures to fall below the detection limit of $1 \times 10^{-3}$ and 0.02 wt%, respectively. In the residues treated at maximum temperatures of 1673 and 1773 K, these elements were no longer detected.

Concentrate (2)

Fig. 4.8 graphically depicts the depletion of heavy metals in the two phases of treated concentrate (2). The similarity of heavy metal concentrations in both phases is striking and shows that heavy metals are not retained in the pre-slag material. The absence of oxygen during thermal treatment prevents the formation of heavy metal oxides and thus their incorporation in a silicate slag component. This implies that an efficient removal of impurities is not hindered by the formation of a slag phase. As for concentrate (1), a maximum temperature of 1173 K is sufficient to lower the concentration of arsenic and bismuth in concentrate 2 below the detection limit of 0.05 and 0.01 wt%, respectively. Cadmium was detected neither in the raw concentrate nor in the residues. The values for antimony (see Table 4.5) indicate that this metal can hardly be removed by thermal treatment from neither the sulfide phase nor the pre-slag. Possibly, it has entered a new stable phase after decomposition of the main sulfide phase. For both concentrates, the evaporation of tin, lead and zinc shows similar trends. Tin is removed to a concentration below the detection limit at maximum temperatures up to 1673 K. At least 95% of zinc and lead is removed from samples treated at a maximum temperature of 1773 K. This implies that at least twice as much lead and zinc were removed from concentrate (2) than from concentrate (1). The acceleration of impurity removal above maximum treatment temperatures of 1573 K coincides with the melting of the samples (see also Fig. 4.4). This suggests that lead and zinc are more easily released from the melt than by congruent or incongruent evaporation of the binary phases ZnS and PbS.

There are two possible explanations for the observed trends. Firstly, the diffusion of zinc and lead from the interior of the melt into the gas phase could be hindered. From thermal decomposition experiments at even higher temperatures ($T \approx 1914$ K) (Winkel and Sturzenegger, in preparation) it is known that repetitive grinding has a positive effect in enhancing the removal of volatile impurities. This suggests that mass transport limitations play a role
even at these temperatures. However, the initial contents of lead and zinc in the two concentrates are too close to explain the differing degrees of depletion. A second explanation considers the difference in chemical properties between the two concentrates. Concentrate (2) has lost nearly two times more weight (i.e. sulfur) than concentrate (1). This indicates that sulfur removal positively correlates with that of lead and zinc. The fact that residues with the larger sulfur concentrations (concentrate (1)), also contain the larger amounts of lead and zinc is in agreement with kinetic studies on the removal of Pb from Cu-Bi-Pb-S alloys in vacuum induction melting at 1403 K as shown by Ohno (1991). They demonstrated that increasing sulfur concentrations in the alloy led to decreasing concentrations of lead and bismuth in the gas phase above the alloy. Thus, the different extent of zinc and lead removal is attributed to the specific chemical properties of the two molten concentrates.

4.4. Summary and conclusions

The absence of oxygen in combination with high operating temperatures stimulates the removal of heavy metal impurities by volatilization. The study of direct decomposition of metal sulfides was initiated by thermal analyses in an inert atmosphere and at maximum temperatures of 1773 K. The studied materials were single-phase compounds chalcocite (Cu$_2$S), chalcopyrite (CuFeS$_2$) and enargite (Cu$_3$AsS$_4$) as well as two multiphase copper concentrates. Thermal analyses on chalcocite and chalcopyrite showed that both substances lose sulfur upon heating although at very different rates. The different decomposition rates seem to reflect the chemical properties of the phases involved. Coupled TG-ICP studies on the decomposition of enargite demonstrated that complete evaporation of arsenic is feasible below 1000 K. The coincidence of evaporation peaks for sulfur and arsenic suggests that arsenic is released as an arsenic sulfide entity.

Thermal treatment of copper concentrates showed that their decomposition proceeds in a stepwise manner involving several decomposition reactions and the loss of volatile elements. Final products of the decomposition series as found in the cooled residues are bornite, troilite, elemental copper and a small amount of a stannite-like phase [Cu$_2$Fe(Cu$_3$Sn)S$_4$]. The small amount of quartz present in concentrate (2) was found to form a slag-like phase at T >
1573 K. It was demonstrated that the formation of a pre-slag does not hinder the efficient removal of volatile impurities. Elemental analyses on residues of treated concentrates showed that volatile impurities are removed in three distinct temperature ranges. A maximum treatment temperature of 1173 K is sufficient to lower the concentrations of arsenic and bismuth to a value below the detection limit (i.e. < 0.05 and 0.01 wt%, respectively). These elements are thus completely removed before elemental copper is formed. The removal of cadmium and tin requires higher temperatures; concentrations are below the detection limits (i.e. < \(1 \cdot 10^{-3}\) and 0.02 wt%, respectively) in residues treated at maximum temperatures above 1673 K. Removal of Pb and Zn poses the most severe requirements to the thermal treatment. Substantial evaporation occurs only at temperatures between 1673 and 1773 K. Nevertheless, a removal of at least 95% of initial contents of zinc and lead were achieved for concentrate 2.

4.5. Acknowledgements

We would like to thank Mr. R. Seal II from the U.S. Geological Survey at Reston (VA) for kindly providing single-phase enargite. The copper concentrates were made available by Outokumpu Oy in Finland. We also would like to thank Albert Schüler for elemental analyses and Alwin Frei for experimental support. Financial support from the Swiss Federal Office of Energy (BFE) and the Gebert Rüf Foundation as GRS-058/00 is gratefully acknowledged.

4.6. References


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Abstract The thermal decomposition of two copper concentrates has been studied in an imaging furnace while developing a solar driven process for the extraction of copper. Exposure (heating) of the concentrates in the imaging furnace produced surface temperatures of $\approx 1920$ K. Continuous irradiation during 330 s in an argon flow resulted in the removal of 40 % of initial sulfur content and the formation of elemental copper. Repeated grinding clearly accelerated the evaporation and increased its extent such that between 90 and 99 % of the initial amounts of arsenic, zinc, and lead are removed within 90 s. The strong effect of grinding indicates that the elimination of volatile elements is hindered by a slow mass transfer from the interior of the melt to the gas phase. The thermal decomposition of copper concentrates on a technical scale will therefore be most favorably conducted with sub-millimeter particles. Elemental distribution (SEM) and elemental analysis (EMPA) revealed that irradiated samples are subject to a temperature gradient. Consequently, elemental copper preferably compacts at the lower surface close to the cold sample support. Exposure of decomposed samples to moderate temperatures around 1400 K showed that tempering of liquid samples will facilitate the separation of metallic copper from residual iron copper sulfides.
5.1. Introduction

A knowledge of the behaviour of copper-iron sulfides and their accompanying volatile impurities at high temperatures is essential for the development of a novel approach for the extraction of copper (Winkel et al., 2003). Such an approach is the solar thermal decomposition of copper concentrates into elemental copper and sulfur, and iron sulfide at temperatures of at least 2000 K in the absence of oxygen. These working conditions offer two major benefits. Firstly, sulfur which is released upon decomposition of sulfide minerals, is not oxidized to the toxic and polluting sulfur dioxide (SO₂). Secondly, the chemistry under reduced oxygen partial pressures provides opportunities for an efficient separation of unwanted impurities, especially of volatile heavy metals. In modern practice, control of the oxygen partial pressure in the smelting furnace is used as the main method of minimizing the amount of copper in the slag. Unfortunately, the oxygen partial pressure also determines the distribution of impurities between the gas and the condensed phases and hence this methodology to efficiently remove impurities is restricted.

Regarding the oxidative smelting process, thermodynamic studies (Yazawa and Azakami, 1969) and modeling (Degterov et al., 2000; Kim and Sohn, 1997) have greatly contributed to the understanding of the impurity distribution between matte and slag. However, the behavior of impurities in copper concentrates in the absence of oxygen is less well known. Villaroel (1999) and Jiang et al. (2003) studied the volatilization of heavy metal impurities under vacuum prior to smelting. In laboratory scale experiments ($T_{\text{max}}=1223$ K), these authors showed that arsenic, antimony, lead, and zinc are efficiently removed and individually collected by step-wise condensation. A conceptual disadvantage of a cleaning process under vacuum is that it comprises an additional step to what is already a complex smelting process. In addition, the technical feasibility of conducting a process of such a size under vacuum is to say the least, difficult. Winkel et al. (in preparation) studied the volatilization behavior of impurities under atmospheric pressure and in a nitrogen stream. This study showed that the concentration of volatile impurities decreases with increasing treatment temperatures up to $T = 1773$ K.
It is expected that higher decomposition temperatures would increase the extent of their removal.

This chapter presents the results of a high temperature (T ≈ 1914 K) decomposition study on copper concentrates under concentrated radiation and in an inert atmosphere. The aim of this study was twofold. Firstly, it aimed to quantify the removal of volatile impurities at a high temperature and to give insight into the rates of volatilization. The second aim was to provide phase relations at high temperatures and clues as to the feasibility of a separation of metallic copper from the residual sulfide phases. Understanding the phase relations of the main components, in the Cu-Fe-S system at elevated temperatures, is of crucial importance for the development of a solar thermal extraction process. Earlier studies on the decomposition of copper iron sulfides have mainly been conducted by thermal analyses in vacuum (T_{max}=1273 K) as described by Ugryumova et al. (1975) and Isakova et al. (1976). To conduct high temperature decomposition experiments in an inert atmosphere, an in-house built imaging furnace was used. This experimental tool gives access to temperatures up to 2700 K and the sample can be rapidly quenched in order to obtain the high temperature composition of the sample. To study the separation of copper from other phases, tempering experiments have also been carried out in the imaging furnace. Decomposed products have been examined by electron microscopy (SEM), analyzed for phase assemblages (XRD), and elemental content (XRF). It will be shown that the treatment of copper concentrates under concentrated irradiation is a promising path for the removal of volatile impurities. It will also be shown that the prevailing mass transport mechanisms open up possibilities for the separation of metallic copper.

5.2. Experimental Methods

5.2.1. Materials

Two different copper concentrates were provided by courtesy of Outokumpu Oy (Finland). Their elemental composition is given in Table 5.1. Concentrate (1) (c1) has a higher copper and zinc content than concentrate (2) (c2), while the iron and sulfur content is lower. Concentrate (2), on the other hand, has higher contents of quartz (SiO₂) and arsenic. The concentrates were dried for
Table 5.1: Concentration of main and rock-forming elements (a) and heavy metals (b) of copper concentrates c1 and c2. Concentrations were measured by ICP spectroscopy.

a)

<table>
<thead>
<tr>
<th>Elements [wt-%]</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>SiO₂</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate 1</td>
<td>29.03</td>
<td>28.15</td>
<td>34.18</td>
<td>0.6³</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>Concentrate 2</td>
<td>25.40</td>
<td>32.40</td>
<td>36.40³</td>
<td>1.7³</td>
<td>0.06</td>
<td>0.08</td>
</tr>
</tbody>
</table>

b)

<table>
<thead>
<tr>
<th>Elements [wt-%]</th>
<th>As</th>
<th>Bi</th>
<th>Cd</th>
<th>Pb</th>
<th>Sb</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate 1</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.65</td>
<td>0.00</td>
<td>0.01</td>
<td>2.11</td>
</tr>
<tr>
<td>Concentrate 2</td>
<td>0.86</td>
<td>0.01</td>
<td>0.00</td>
<td>0.36</td>
<td>0.03</td>
<td>0.23</td>
<td>2.02</td>
</tr>
</tbody>
</table>

³measured by Outokumpu

Table 5.2: Semi-quantitative mineral content in the two concentrates, obtained by using relative reference intensities (I/I₀), where corundum (α-Al₂O₃) serves as the reference material (Visser and de Wolff, 1964).

<table>
<thead>
<tr>
<th>Mineral [wt-%]</th>
<th>Concentrate 1</th>
<th>Concentrate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFeS₂ (chalcopyrite)</td>
<td>87</td>
<td>58</td>
</tr>
<tr>
<td>FeS₂ (pyrite)</td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>SiO₂ (quartz)</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>ZnS (sphalerite)</td>
<td>7</td>
<td>5</td>
</tr>
</tbody>
</table>
14 hours at 333 K in air and subsequently ball-milled for two periods of 5 minutes in order to improve homogeneity of the sample. The mineral phases were determined by X-ray powder diffractometry and are presented in Table 5.2. For decomposition experiments in the imaging furnace, the homogenized concentrates were pressed into 2 mm thick pills and subsequently broken into pieces with a mass of, approximately 90 mg.

5.2.2. Decomposition experiments

Decomposition experiments were conducted in an in-house constructed imaging furnace (IF) (Guesdon et al., in press), the key features of which are schematically shown in Fig. 5.1. In the upper focal point of an ellipsoidal reflector, a 1 kW xenon short-arc lamp is located. Rays of light emitted by the lamp are reflected and focussed in the second focal point of the ellipsoidal reflector (see Fig. 5.2), where the sample is placed. A glass dome positioned above the sample allows for working under inert gases and with condensable gases. Condensation of gases such as sulfur is prevented by an inert gas flow ($\approx 10 \text{ l min}^{-1} \text{ Ar (99.999 \%)}$) fed through the ring slit between the sample stage and the inner wall of the glass dome. The sample is placed on a water-cooled sample support from copper, a configuration that is especially suited for working with melts, as it minimizes reactions and wetting of the surface (see Fig. 5.3). Despite these design precautions, a black sulfide layer was found to cover the sample holder after each IF experiment. No native copper was observed on this sulfide layer and the layer was maintained during subsequent measurement campaigns.

Pressed concentrate samples of about 90 mg were loaded onto the sample support and treated for different periods of time. In a first series, samples were continuously heated for multiples of 45 s. In a second series, the samples were first treated for 45 seconds. Then multiple periods of 5-second-treatment followed, after repeatedly grounding and pressing. We refer to the first treatment as series 1, while the latter is referred to as series 2. At the end of each run, the lamp was switched off. The cooled, solidified residues were ground and prepared for further heat treatments or analyses.
5.2 Experimental methods

Optical access to sample

1 kW Xenon short arc lamp

Diamond machined reflector

20 cm

Sample stage

Fig. 5.1: 2D-technical drawing of the imaging furnace (Guesdon et al., in press).
Fig. 5.2: Photograph of the imaging furnace in the lab. The computer on the left side of the reflector operates the stepping motor connected to the sample support. The rack on the right is only used for control measurements of the focus position.

Fig. 5.3: Close-up of the sample stage. The sample holder is positioned in the centre of the photograph.
5.2 Experimental methods

5.2.3. Tempering experiments

Tempering experiments were carried out in the imaging furnace to assess the possibility of separating metallic copper from residual sulfide phases. Two experimental conditions were chosen in order to study the separation from sulfides in the liquid and solid state (see Fig. 5.4). Number 1 represents the regular decomposition of the sample, which comprises heating in the focal plane during 330 s and subsequent quenching with the cold hammer. Number 2 refers to samples that were irradiated for 330 s, and then kept for 600 s at 6 mm above the focal plane (i.e. at about 1397 K) at a position where the bulk of the sample is still in the liquid state. Number 3 refers to samples where decomposition (330 s) was followed by tempering 8 mm above the focal plane where the bulk of the sample is expected to be solidified. All samples were rapidly quenched with the hammer after the thermal treatment. From each procedure, one sample was analyzed by SEM and microprobe analysis, the other two were ground and further analyzed for element and phase contents.

5.2.4. Analytical Methods

XRD

Phases in the solidified products were characterized by X-ray powder diffractometry using a X’Pert diffractometer (PANalytical, Almelo/ The Netherlands), with Fe Kα radiation. Diffraction patterns were recorded in a 2θ range of 10-110°. Lattice parameters were determined using LATCON (Schwarzenbach, 2000), a general program for the LS-refinement of lattice constants.

X-ray fluorescence analyses

The method was calibrated for the determination of minor levels (0.1-3 %) of As, Cd, Pb, Sb and Zn as well as major concentration levels (> 1 %) of Cu, Fe and S in raw and treated copper concentrates. Standards for Cu, Fe and S were prepared from commercially available copper sulfide (-325 mesh, Aldrich), iron sulfide (FeS₂) (99.9% -100 mesh, Alfa Aesar) as well as from CuFeS₂, which was synthesized from the elements. Standards for lower Cu (1-10 %) and higher Fe (> 40 %) concentrations were prepared from CuSO₄·5H₂O (> 99.0, Merck) and Fe₂O₃ (> 99.0, Merck). Standards for As, Cd, Pb, Sb and Zn
Fig. 5.4: Treatment scheme for tempering experiments in the imaging furnace. Procedure 1 represents the decomposition without subsequent tempering. Procedures 2 and 3 give the conditions for tempering in the all-liquid state (2) and partly solid state (3). Temperatures above the focal plane were experimentally determined (Guesdon et al., in press).

Table 5.3: Experimental conditions used in XRF measurements

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal/ detector</th>
<th>Spectral line</th>
<th>2θ</th>
<th>Measuring time [s]</th>
<th>Tube conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>LiF 200/SC</td>
<td>K_{α1,2}</td>
<td>45.03</td>
<td>30</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>44.37/45.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>LiF 200/FPC</td>
<td>K_{α1,2}</td>
<td>57.52</td>
<td>30</td>
<td>30 kV, 80 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>56.8/58.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Ge 111/FPC</td>
<td>K_{α1,2a}</td>
<td>110.69</td>
<td>30</td>
<td>30 kV, 80 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>109.8/111.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>LiF 200/SC</td>
<td>K_{α1,2}</td>
<td>34</td>
<td>50</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>33.5/34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>LiF 220/SC</td>
<td>K_{α1}</td>
<td>21.66</td>
<td>50</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>21.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>LiF 200/SC</td>
<td>L_{β1}</td>
<td>28.26</td>
<td>50</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>27.9/28.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>LiF 220/SC</td>
<td>K_{α1}</td>
<td>19.01</td>
<td>50</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>18.51/19.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>LiF 200/SC</td>
<td>K_{α1,2}</td>
<td>41.8</td>
<td>50</td>
<td>50 kV, 50 mA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bg</td>
<td>41.4/42.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2 Experimental methods

were prepared from a matrix of Cu$_2$S, FeS$_2$ or CuFeS$_2$, to which the appropriate volumes of commercially available 1000 mg/l stock solutions (Merck) were added and subsequently dried overnight at 383 K.

The weighed standards and samples were mixed with a di-lithiumtetraborate (Li$_2$B$_4$O$_7$) flux (HRT Labortechnik, Engstingen/ Germany) in a typical sample to flux ratio of 1:60. In order to retain the sulfur in the sample, sodium nitrate (> 99.5, Merck) was added in a “flux to oxidant” ratio of 3: 1. This low melting point substance oxidizes the sulfide to a sulfate and thereby prevents the loss of sulfur as SO$_2$. To obtain flat glass disks 15 drops of 25% LiBr (> 99.0, Merck) solution were added on top of the mixture, after which it was allowed to dry for at least 30 minutes at 383 K in air.

A fully automatized fluxer, Claisse Fluxy 10/M4 (HRT Labortechnik, Engstingen/ Germany), was used to cast the glass disks. The fusion program for sulfides was developed by Claisse (1999) and involves a low-temperature (573-1073 K) heating step, which oxidizes the sulfides, followed by fusion at a temperature of about 1273 K.

Instrumentation

The XRF analyses were carried out in a standard procedure with an ARL 8410 wavelength dispersive X-ray fluorescence spectrometer (Thermo ARL, Ecublens/ Switzerland) equipped with a Rh X-ray tube. The measured elements and operating conditions are given in table 5.3.

SEM and microprobe

In total, nine solid residues were prepared for SEM and EDX analyses. The residues were embedded in an epoxy resin, and then allowed to dry for at least 6 hours under vacuum. After drying, they were ground until a central cross section of the residue was exposed. The exposed surfaces were polished on 3 to 1 micron diamond grits until a flat and unscratched surface was obtained. The polished samples were examined using a binocular microscope under reflected light. For quantitative analyses the residues were ultrasonically cleaned in ethanol and carbon coated. The morphology of the treated residues was analyzed using a Zeiss DSM 962 scanning electron microscope (SEM), using a 30keV electron beam. Information on local chemical composition was obtained by semi-quantitative analyses using EDX with the Noran System.
Fig. 5.5: Typical residue of a concentrate treated in the imaging furnace ($T \approx 1914$ K). The larger phase is a copper iron sulfide decorated with small droplets of native copper. The glassy droplet on top is a silicate slag.

Table 5.4: Products of thermal decomposition in multiple periods of 45 seconds. After each thermal treatment the sample was ground, pressed and heated again.

<table>
<thead>
<tr>
<th>#</th>
<th>Educt</th>
<th>Total time [s]</th>
<th>Duration of volatile release [s]</th>
<th>Appearance of copper in focus</th>
<th>Appearance of copper in Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raw copper concentrate</td>
<td>45</td>
<td>15/30</td>
<td>faint copper shimmer</td>
<td>traces of copper</td>
</tr>
<tr>
<td>2</td>
<td>Ground products #1</td>
<td>90</td>
<td>15/30</td>
<td>copper shimmer</td>
<td>traces of copper</td>
</tr>
<tr>
<td>3</td>
<td>Ground products #2</td>
<td>135</td>
<td>5/40</td>
<td>Top: copper</td>
<td>no copper</td>
</tr>
<tr>
<td>4</td>
<td>Ground products #3</td>
<td>180</td>
<td>5/40</td>
<td>small copper droplets</td>
<td>no copper</td>
</tr>
<tr>
<td>5</td>
<td>Ground products #4</td>
<td>225</td>
<td>5/40</td>
<td>small copper droplets</td>
<td>no copper</td>
</tr>
<tr>
<td>6</td>
<td>Ground products #5</td>
<td>270</td>
<td>5/40</td>
<td>copper shimmer</td>
<td>traces of copper</td>
</tr>
<tr>
<td>7</td>
<td>Ground products #6</td>
<td>315</td>
<td>5/30</td>
<td>faint copper shimmer</td>
<td>few copper traces</td>
</tr>
<tr>
<td>8</td>
<td>Ground products #7</td>
<td>345</td>
<td>10/20</td>
<td>no visible copper</td>
<td>no visible copper</td>
</tr>
<tr>
<td>9</td>
<td>Ground products #8</td>
<td>375</td>
<td>10/20</td>
<td>no visible copper</td>
<td>no visible copper</td>
</tr>
</tbody>
</table>
5.3 Results

SIX for X-ray fluorescence analysis, with a relative accuracy of ± 2%. Quantitative analyses were obtained from electron microprobe analyses (JEOL JXA-8200, JEOL Ltd., Tokyo/ Japan) operated at an acceleration voltage of 15kV and a sample current of 20 nA. Chalcopyrite and pyrite were chosen as reference samples to determine copper, iron, and sulfur contents, respectively. The precision is estimated to be 1.5 wt%.

5.3. Results

5.3.1. Qualitative observations

Exposure of the samples to concentrated light immediately led to the formation of fog above the sample. As the decomposition proceeds, the intensity of fog formation decreases. We attribute its formation to the release of volatile species and their subsequent condensation in the cold inert gas. After about 15 seconds, release of volatiles decreases, as was seen from weaker, pulsed fog clouds. Typically after 45 seconds, fog formation ceased. In discontinuous decomposition experiments (series 2), it was observed that volatiles were formed again as soon as the samples were positioned in the focus again. The timing of volatilization as well as the descriptions of residues and sample support are presented in Table 5.4. It is observed that the duration of volatile release decreases as the sample exposure time and/or the frequency of grinding and re-exposure increases. The mode of release of volatiles gradually changes from continuous to pulsed. Exposed products generally consist of greyish black sulfide beads with a flattened droplet-like shape (about 2 mm height) with a smaller slag bead (0.5 to 1 mm diameter) on top (see Fig. 5.5). After exposure times between 45 and 135 s, a copper shimmer was seen on the surface of the sulfide matrix, as well as traces of copper at the bottom. After the samples were ground and heated again, the formation of small copper particles was observed but copper was no longer found at the bottom of the residues (#4, 5 and 6). Further exposure led to the apparent disappearance of metallic copper, both on the surface and at the bottom (#7, 8 and 9).
5.3.2. Volatilization of heavy metals and sulfur during decomposition

The effect of thermal treatment on the concentration of arsenic, lead, and zinc in concentrates c1 and c2, respectively, is shown in Fig. 5.6 a-c. In both concentrates, the three heavy metal concentrations decrease as the treatment time increases. Despite of the higher initial concentrations of zinc and lead in c1, the removal of impurities is slightly larger for c1 than for c2. For both concentrates, the extent of impurity removal is largest during the first 45 seconds of thermal treatment, which is consistent with the visual observation of fog formation. For continuously exposed samples, the rate of impurity removal strongly decreases after this period. For c1, almost constant concentrations of lead are seen after 90 seconds and removal of arsenic and zinc stagnates after 135 seconds. In concentrate (2), all three elements show almost constant concentrations after 180 seconds. This trend, however, is not observed when samples are repeatedly ground and re-exposed. Such discontinuous experiments (series 2) show an increased impurity removal between 90 and 99 wt-% of the initial concentrations.

Fig. 5.6 d displays the sulfur concentrations in both concentrates as a function of treatment time in the focus. Similarly for the heavy metal removal, the extent of sulfur removal is slightly higher for c1 than for c2 and the largest amount is evaporated during the first 45 seconds. Beyond this exposure time, the removal of sulfur takes place at lower rates. Again, grinding and re-exposure of samples resulted in a faster depletion of sulfur.

5.3.3. Tempering experiments

*Morphological features of decomposed products*

The top surface of non-tempered reference samples is decorated with small metallic copper droplets. The bottom surface is duller and darker and incorporates a few irregular copper patches. A vertical cross section of the residue is shown in Fig. 5.7. Two distinct regions are identified in the BSE image. The lower part, which will be referred to as region I, is dark-grey and porous, whereas the larger upper part (region II) is light-grey and less porous. The two areas are separated by a distinct boundary which is manifested in the cross section as a curved upwards line. At a higher magnification, it is observed that the apparent one-phase regions are actually a complex inter-
Fig. 5.6: Concentrations of arsenic (a), lead (b), zinc (c), and sulfur (d) in treated concentrates. Open symbols are for concentrate 1 and solid symbols for concentrate 2. Circles denote initial concentrations, triangles and squares represent series 1 and series 2, respectively. wt% refer to initial sample weights.
Fig. 5.7: Back-scattered electron image by SEM of the non-tempered residue.

Fig. 5.8: A closer look at the boundary between region I and II. Region I is dominated by dark iron sulfide patches and region II by Cu-Fe sulfides.

Fig. 5.9: Lower surface of a non-tempered residue. Lightly shaded features are metallic copper occurrences in a matrix, which is predominated by iron sulfides.
5.3 Results

Fig. 5.10: Optical micrograph (in reflected light) of a sample tempered in the solid state. The beginning of a layering is observed in region I.

Fig. 5.11: Optical micrograph showing a close-up of the boundary between the two sulfide regions I and II. Just above the boundary a native copper band is present.

Fig. 5.12: Back-scattered electron image showing different structures of iron sulfide in region II. Iron sulfide is present as irregular blobs and as lamellae oriented along preferred crystallographic directions of the cubic Cu-Fe-S phase.

Fig. 5.13: Back-scattered electron image taken in the lower part of a sample tempered in the all-liquid state. Native copper is present in three distinct morphologies: along grain boundaries (1), as compact features (2) and in a newly formed maze-like structure (3).
growth between dark-grey and light-grey patches (see Fig. 5.8). EDX and EMPA examination of these phases showed that the dark-grey patches are mainly composed of iron sulfide, and that the light-gray patches are copper iron sulfide phases. Magnification also revealed that the apparent boundary is a transition zone with elongated darker patches in a lighter matrix. The area just above the transition zone contains fewer dark patches as higher up towards the irradiated. Elemental copper is mainly observed at the upper and lower surfaces, as well as in pores and along fractures. On and near the lower surfaces native copper is typically present in larger amounts as quench textures like globules (up to 80 μm) and along grain boundaries (Fig. 5.9). In short, the non-tempered residues are characterized by two distinct sulfide regions and copper globules in the lower part (region I).

5.3.4. Morphological features of products tempered in the solid state

The residues that were tempered after decomposition appear initially to be very similar to the non-tempered residues. Again, two major sulfide parts are recognized with the naked eye and in the SEM overview images. However, within these two parts and in the surface area, the beginning of a fine layering of irregularly alternating lighter and darker patches is observed. From the edge towards the interior, the thickness of the layers increases in a wedge shape (see Fig. 5.10). Exsolution textures are observed, especially around phase boundaries in the interior of the residues. In the lighter grey phase, irregularly shaped and oriented lamellae of darker, a Fe-richer sulfide is seen. Areas around the larger native copper features are locally enriched in copper as is seen from the presence of neighbouring lighter shaded, patches. In the lower part (region I) native copper is present as irregular, at some places elongated features enclosing lighter shaded patches of Cu-Fe sulfides. One residue contained a copper layer with a thickness exceeding 200 μm in between region I and II (see Fig. 5.11). This layer is compact and liquid-free in contrast to the native copper in the lower part. In summary, these results, the samples that were tempered in the solid state are morphologically similar to the non-tempered residues. Also here, two distinct sulfide regions are recognized and metallic copper is present in the lowest part. However, in one residue a dense copper layer is found in region II, just above the transition zone between the two sulfide regions.
5.3.5. Morphological features of products tempered in the liquid state

SEM images show that the clear distinction between the two major sulfide parts is less evitable as in the residues that were subjected to the other treatments. The difference in grayscale between the darker, iron-enriched, area and the light, copper-enriched, area is obliterated by a large variety in unmixing textures resulting in areas of different shades of gray. Despite of the absence of a distinctive boundary, the predominantly dark shaded and mainly light shaded areas are still visible. In region II, various exsolution structures of different sizes are seen (see Fig. 5.12). Narrow, relatively regular, iron-enriched lamellae positioned at right angles are present in the interior of the residues, indicative for a longer cooling time (i.e. solid state reaction?) and a growth along preferred crystallographic directions of the orthogonal parent Cu-Fe-S phase. Near the upper surface an enrichment of smaller amounts of FeS is present as skeletal unmixing structures (Philpotts, 1990). Also, many microfractures are observed that are filled with native copper. At and near the lower surfaces, native copper is present along grain boundaries of iron sulfide patches and as compact copper features which are free of sulfide inclusions (see Fig. 5.13). In comparison to the earlier described samples, these samples show the presence of newly formed native copper with a fine network structure around the denser copper features. To briefly summarize our findings: tempering in the all-liquid state produces samples that display a less clear distinction between the two sulfide regions than the other residues. This observation, together with the large variety of exsolution structures, suggests that these liquids have been more developed at the time they were frozen in. The same is observed for metallic copper in the lower part, which occurs in more compact structures as well as in newly formed maze-like structures.

5.3.6. Mineral phases

The presence of the two sulfide phases in decomposed samples was confirmed by powder X-ray diffractometry. Diffraction intensities are indicative of bornite and Fe$_{0.985}$S, with minor amounts of sphalerite (ZnS). The cell dimensions of these three phases are listed in Table 5.5.
Table 5.5: Lattice parameters of main phases in decomposition products.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>System</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron sulfide (Fe$_{0.985}$S)</td>
<td>hexagonal</td>
<td>5.969 (0.00018)$^a$</td>
<td>11.74 (0.0010)</td>
</tr>
<tr>
<td>Bornite (Cu$_5$FeS$_4$)</td>
<td>cubic</td>
<td>10.90 (0.0036)</td>
<td>-</td>
</tr>
<tr>
<td>Zinc sulfide (ZnS)</td>
<td>cubic</td>
<td>5.42 (0.0015)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Standard deviation

Lattice parameters for iron sulfide are in good agreement with synthetic troilite (FeS), ($a=5.97$ Å, $c=11.75$ Å) (Yund and Hall, 1968; Fasiska, 1972) and as is found in iron meteorites (Okada, 1971). The bornite-like phase was indexed as a metastable bornite resulting from rapid cooling with $a=10.94$ Å, (Allais, 1968). However, a value of 10.94 Å is still significantly different from 10.90 Å, but the difference is explained by the lower copper content of our samples compared to stoichiometric bornite. If one moves in the Cu-Fe-S phase diagram to higher iron and slightly higher sulfur concentrations, the first phase is talnakhite (Cu$_{18}$Fe$_{16}$S$_{32}$). Talnakhite is cubic, has a lattice parameter of $a=10.593$ Å (Hall and Gabe, 1972; Townsend et al., 1972) and is also based on a cubic closed packed sulfur structure. It can form an extensive solid solution in which the cations are distributed over the tetrahedral interstices of a cubic close-packed sulfur structure (Putnis, 1978), which is smaller than the one of intermediate bornite ($a=10.94$ Å). It is likely that, between bornite and talnakhite, a relation exists between the ratio of copper to iron, which is reflected on the lattice parameter. In this view, the bornite-like phase has a slightly larger iron content than the metastable bornite described by Allais (1968). For cubic zinc sulfide ( sphalerite), the lattice constants strongly depend on the temperature of crystallization. The observed lattice constant of 5.42 Å is characteristic for ZnS formed between 473 and 676 K (Moss et al., 1980).

5.3.7. Chemical compositions

Local chemical compositions in the decomposed and tempered residues were determined by microprobe analyses. Since copper, iron and sulfur are the main elements in the studied samples the total of these three elements was approximated to be 100 %. The measured concentrations were accordingly
plotted in a ternary diagram (Fig. 5.14). The position of each point is determined by the concentration in wt% of two elements, either copper, iron or sulfur. Compositions best match the bornite-like solid solution and the extended stability field of troilite in the Cu-Fe-S phase diagram for a temperature of 1273 K. It shows that the bulk mass of residues was solidified around 1273 K. The purity of copper features, large enough to be analyzed (> 2 μm), is between 96 and 99 mol-%, with iron as the only impurity (up to 4 mol-%). This is in excellent agreement with the composition of a copper liquid at 1273 K, which can dissolve up to 5 mol-% iron. This supports the finding that the Cu-bearing phases were frozen at 1273 K. Dark grey patches have an average composition of Fe_{0.96}Cu_{0.07}S, which is close to the composition of troilite (FeS). Light grey patches have a larger compositional variability and plot on the copper-poor side of the bornite solid solution stability field. They have an average composition of Cu_{4.02}Fe_{1.59}S_{4}, which reflects the enrichment in iron and sulfur compared to stoichiometric bornite (Cu_{5}FeS_{3}). For the bornite-like phase, no relation could be established between position in the residue and its chemical composition. However, observing the sulfide phases as a whole, a gradient in copper concentration can be recognized (see Figure 5.15). In the lowermost parts of the residues the concentration of copper is high, due to the presence of larger copper features surrounded by bornite-like phases. The region above (region I) is dominated by iron sulfide and relatively depleted in copper. In region II, bornite-like phases form the majority, especially in the top layer of this region. To summarize, through region I and II a copper gradient is observed which peaks at the top layer of the residues.

5.4. Discussion

5.4.1. Decomposition

*Early phase of heating*

As seen in the triangular plot (Fig. 5.14), the composition of raw concentrates lies on the line that joins chalcopyrite and pyrite, which are the main mineral components. According to Lusk and Calder (2004) chalcopyrite or variants with slightly different compositions \([(\text{CuFeS}_{2}^{(ss_{a})})_{x}]\) decompose at 623 and 773 K to an intermediate solid solution (iss) (reaction 5.1) or to chalcopyrite with a slightly different composition \([\text{CuFeS}_{2}^{(ss_{b})}]\) plus iron sulfide (reaction
Global composition (XRF):
- Raw concentrate
- Product

Local composition (EMPA):
- Non-tempered
- Tempered in solid state
- Tempered in liquid state

Mineral phase
Stability field of the intermediate solid solution @ 623K

**Fig. 5.14:** Composition of copper concentrate and of constituent phases in thermally treated concentrates plotted in the phase diagram for the Cu-Fe-S system at 1273 K (after Chang et al., 1979). Mineral phases are: bn=bornite (Cu$_5$FeS$_4$), chc=chalcocite (Cu$_2$S), chp=chalcopyrite (CuFeS$_2$), cub=cubanite (CuFe$_2$S$_3$), ida=idaite (Cu$_3$FeS$_4$), py=pyrite (FeS$_2$), tnk=talnakhite (Cu$_{18}$Fe$_{16}$S$_{32}$), and tr=troilite (FeS).

**Fig. 5.15:** Schematic vertical cross section of a treated copper concentrate. The arrow indicates the copper gradient across the two sulfide regions.
5.4 Discussion

5.2).

\[ \text{CuFeS}_2(s) + \text{FeS}_2(s) = \text{iss} + \frac{1}{2} \text{S}_2(g) \]  \hspace{1cm} (5.1)

or

\[ \text{CuFeS}_2(ss_a) + (1-x) \text{FeS}_2(s) = \text{CuFeS}_2(ss_b) + \text{Fe}_1xS + (1-x) \text{S}_2(g) \]  \hspace{1cm} (5.2)

The observed formation of fog is attributed to the release of gaseous sulfur during decomposition. Phase analyses of samples that were treated for only 5 s in the imaging furnace revealed the presence of mooihoekite (Cu_9Fe_9Si_6) and a cubic Cu-Fe-S phase, which is structurally related to the intermediate solid solution. Only minor amounts of iron sulfide and bornite were detected. According to Cabri (1973), quenching of the intermediate solid solution produces a mixture of a phase with a primitive cubic cell plus either chalcopyrite or mooihoekite. The presence of mooihoekite and the cubic phase in our samples is thus indicative for a quenched copper-rich iss phase and hence for reaction 5.1. The presence of bornite and of minor amounts of iron sulfide, supports this conclusion.

5.4.2. The molten sample

As the samples are further heated, the iss phase melts. The samples appear shiny and droplet shaped, indicating that they were molten. This observation is supported by quench structures in the solidified residues. Phase diagrams by Chang et al. (1979) and Villars et al. (1995) show that above 1273 K, a single sulfide liquid is present. However, the two experimentally observed sulfide regions in the solidified residues indicate that the elements are not homogeneously distributed in the sample. These heterogeneities and other morphological features are indicative of processes taking place in the molten stage or during cooling. This section discusses processes that took place in the liquid state. At temperatures above 1273 K, the Cu-Fe-S system is dominated by the presence of one extensive field of sulfide liquid, which coexists with a sulfur-rich liquid and metallic copper (Vaughan and Craig, 1997). The formation of metallic copper from a copper iron sulfide requires the removal of sulfur to such an extent, that the overall composition plots between the sulfide and the copper liquid. The presence of elemental copper in the decomposed products shows that this goal is achieved in part. In residues
continuously exposed for 330 seconds, the sulfur content is reduced from 39.6 to 29.7 wt%. This translates to,

$$\text{FeCu}_{0.75}\text{S}_2 = \text{FeCu}_{0.73}\text{S}_{1.27}$$  \hspace{1cm} (5.3)

where $\text{FeCu}_{0.75}\text{S}_2$ and $\text{FeCu}_{0.73}\text{S}_{1.27}$ represent the global composition of the raw concentrate and the product, respectively. According to this schematic reaction, about 40% of sulfur has been removed during decomposition. The desired result of decomposition experiments is copper in the elemental form together with FeS according to the following overall reaction:

$$\text{FeCu}_{0.75}\text{S}_2 = \text{FeS} + 0.75 \text{Cu} + \frac{1}{2} \text{S}_2$$  \hspace{1cm} (5.4)

Phase analyses revealed that substantial amounts of copper are still bound up in the bornite-like phase. Other final products are FeS and elemental copper. Mass conservation for the three elements provides the stoichiometric coefficients for reaction 5.5. They show that 38% of total copper has been extracted from its sulfides, under the specific experimental conditions; i.e.

$$\text{FeCu}_{0.73}\text{S}_{1.27} = 0.91 \text{FeS} + 0.09 \text{Cu}_5\text{FeS}_4 + 0.28 \text{Cu}$$  \hspace{1cm} (5.5)

As mentioned above, the removal of sulfur is an important requirement for the formation of elemental copper. The XRF data showed that the rate at which sulfur is removed (about 8%) is largest within the first 45 seconds of the experiment. The removal continues at a much slower rate throughout the rest of the decomposition process until it finally stagnates. It has also been observed that after an initially extensive release of volatiles, the molten sample appears to be stable. In discontinuous experiments (series 2), with repeated grinding between heating, sulfur depletion is enhanced. A similar but more pronounced behaviour is observed for volatile heavy metals. This suggests that creating fresh surfaces by grinding promotes the removal of volatile impurities, which is consistent with the conclusion that mass transfer from the melt to the gas phase is the rate-limiting step.

The question arises as to which specific process hinders the removal of sulfur. Very little is known about the evaporation of sulfur from a sulfide melt. The evaporation of sulfur from solid phases, however, is better characterized. Tsuchiyama et al. (1997) studied the evaporation of sulfur from troilite (FeS) at 1 atm under H$_2$-rich conditions and observed a linear rate law for the
removal of sulfur and concluded that the evaporation reaction at the surface is the rate-limiting step. The evaporated gaseous sulfur can escape easily through the porous residual iron layer. Similarly, Tachibana and Tsuchiyama (1998) concluded that the evaporation rate of sulfur from troilite at 1073-1243 K is controlled by the surface chemical reaction. From our observations, it is evident that the introduction of fresh surfaces by grinding the sample has a positive effect on impurity evaporation. This is a strong argument which suggests that surface reactions control the evaporation rates. Nevertheless, as soon as the samples are brought in the focus, they melt and shortly after, sulfur removal decreases and stagnates. Therefore, a second hypothesis to account for stagnating sulfur removal is put forward. It is suggested that the rate of sulfur transfer in the melt is the limiting step for sulfur removal. To discuss this hypothesis, a more thorough insight into processes taking place in the molten sample is required. This insight is provided by the morphology of solid residues, which will be discussed in the next section.

5.4.3. Evolution of Soret separation

Microprobe and EDX analyses indicate the presence of a copper gradient in thermally treated samples. Features characteristic for the rapid cooling of the samples are observed, even close to the water-cooled sample support. This indicates that the Cu gradient has already been present in the liquid state. Majewski and Walker (1998) studied a Fe-Ni-S-P melt in a temperature gradient (about 75 K/mm, at 10 kbar) and obtained samples with a morphology that resembles the samples produced in this study. In their experiments they observed that iron compacts against the cold end of the sample and that, by fractional crystallization of Fe, the liquid just above the compact Fe layer is more S-rich than the bulk composition. Transport of elements in opposite directions driven by a thermal gradient is referred to as thermal diffusion or the Soret effect. The chemical compositions and morphology of the residues of this study suggest that a similar mechanism has played a role in our samples. The following thermal diffusion model was established. After melting of the sample and the loss of about 40 % sulfur, two liquids coexist: a sulfide and a copper-rich liquid. Then, in the stagnant binary system, a temperature gradient is induced, due to the temperature difference between the water-cooled sample support and the irradiated upper part. Since the composition and the solubility of the two liquids is temperature
dependent, their compositions change along the temperature gradient. The solubility of copper in the sulfide melt increases with temperature and the sulfide liquid is thus richer in copper in the upper part of the residue than in the part close to the elemental copper occurrence in the lower part of the sample. As copper exsolves from the melt, S-(and Fe)-rich liquid is expelled into the overlying sulfide liquid in order to retain the temperature induced Cu gradient across the sulfide regions. In spite of this, the lower part of the sulfide regions of solidified residues (region I) is locally enriched in iron sulfide and this indicates that the diffusion rates of S (and Fe) have been relatively small. This is in agreement with the observation that a stagnating removal of sulfur and heavy metals is only counteracted by a renewed homogenization of the sample by grinding and subsequent re-exposure.

Microprobe analyses revealed that, especially in the tempered samples, a top layer exists which has a composition different from the bulk composition of region II. It has a thickness of 50-80 micrometer and is characterized by the absence of the darker FeS conclusions. A similar boundary layer is also observed between region I and II. Whereas the boundary layer in the intermediate position can be explained by a crystallization front of FeS, the upper boundary is probably also an effect of slow mass transfer. The absence of iron sulfide indicates that iron and sulfur have partly evaporated at the surface, possibly as an iron sulfide compound. The observation of a black condensation at the cooled sample support is in agreement with the evaporation of an iron sulfide. This is a further indication that mass transfer in the melt has been too slow to replenish the surface area with sulfur. Therefore we favour the second hypothesis, which states that mass transfer of sulfur and also of other volatile elements in the melt is the rate-limiting step in their removal. This conclusion suggests that working with smaller particles increases the extent of volatile removal and the copper yield.

5.4.4. Solidification of the sample

The formation of two sulfide phases with compositions close to bornite and pyrrhotite must have taken place during cooling. Even though the samples were quenched with a hammer, cooling was apparently not fast enough to freeze in a single sulfide liquid as present at temperatures above 1373 K. From phase diagrams over 1273 K is seen that copper can dissolve up to 5
mol-% Fe. The chemical compositions of the larger copper features plot in this range hence they must originate from a temperature above 1273 K. As the sulfide liquid was still saturated in copper during fast cooling, metallic copper deposited in microfractures and pores.

The complex intergrowth between the light Cu-Fe-S and dark Fe-S patches suggests their simultaneous formation from a bulk composition close to the iss phase (see Fig. 5.14). From the ternary phase equilibrium diagrams, is known that decreasing temperatures rapidly reduce the liquid fields and expand the extensive solid solution fields (Tachibana and Tsuchiyama, 1998). One of the first phases to form from the sulfide liquid is the stable compound FeS. The angular pores in region I and irregular shapes of dark patches suggest that this was indeed the first phase that crystallized from the sulfide melt during cooling. In this respect, the border between region I and II is likely to present a front of pyrrhotite crystallization. To test this hypothesis, concentrates were decomposed during shorter times and subsequently analyzed by optical microscopy. Following this treatment, two distinct sulfide regions were also, observed, but the pyrrhotite rich region (region I) appeared to be substantially smaller, which supports our hypothesis.

5.4.5. Tempering

The tempered residues, in particular region II of samples tempered in the liquid state, exhibit various characteristic exsolution structures. Regular iron sulfide lamellae indicate that tempering in the liquid state provided sufficient time for iron sulfide patches to grow in ordered structures. As with to the non-tempered samples, copper patches are found predominantly at or near the lower surface.

The effect of tempering on the morphology of copper features is remarkable. In one of the residues which was tempered in the solid state, a dense copper layer is found just above the transition zone between region I and II. It indicates that the sample had not been completely in the solid state during tempering (i.e. some melt was present). Its formation is explained as follows. During decomposition, a binary liquid composition exists and metallic copper accumulates in the lower, colder part of the sample. As the sample is moved to the tempering position, a new temperature gradient develops such that the lower part is cold enough to induce crystallization of iron sulfide, while the
upper part (region II) remains liquid. Indications for an earlier solidification of the lower part are the irregular and at some places elongated native copper occurrences enclosing lighter shaded patches of Cu-Fe-S sulfides. A tempering period of 10 minutes was sufficient to separate copper from the sulfide layer, which resulted in a dense copper layer without any sulfide inclusions. Similarly, dense copper features, observed in the residues that were tempered in the all-liquid state also indicate a more advanced copper separation. Metallic copper present in the fine network structure supports the ongoing evolution of copper separation. In general, it can be concluded that tempering in the all-liquid state facilitates the separation of copper from residual sulfides.

5.5. Summary and conclusions

The study shows that in the absence of oxygen sulfur, arsenic, lead and zinc are readily volatilized from copper concentrates at high temperatures above 1900 K. The extent of volatilization was largest during the first 45 seconds of thermal treatment but increased at a much smaller rate throughout the rest of decomposition and then finally stopped. On average, about 40 % of sulfur was removed during decomposition. Repeated grinding and exposure of the samples increased the removal of volatile impurities to values between 90 and 99 wt-% of the initial concentrations within 90 s. Based on the experimental observations, we attributed the observed behaviour to a slow-transfer of volatile elements from the interior of the melt into the gas phase. To obtain higher copper yields and an increased release of volatile into the gas phase, the process would be preferably conducted with smaller (sub-mm) particles. These experiments will then show if a temperature of 1900 K is sufficient for a viable copper extraction. The decomposition of copper concentrates includes a number of reactions. During the first seconds of heating, chalcopyrite and pyrite form an intermediate solid solution (iss) accompanied by evaporation of S. As the temperature rises the iss melts and above 1273 K, a single sulfide liquid forms. Enough sulfur was evaporated to allow the formation of elemental copper. By thermal diffusion, copper moved to the cold end of the sample where it formed a separate copper liquid by exsolution. The upper 50-80 micrometer of solidified residues is depleted in FeS. The absence of FeS indicates, firstly, that iron and sulfur have partly evaporated at the surface, and secondly, that diffusion in the melt is limiting the removal of
sulfur. Upon cooling of the melt, the first phase that crystallized was FeS. Thereafter, the residual liquid quickly solidified, which resulted in a complex intergrowth of patches of bornite-like phases and iron sulfide. It was demonstrated that tempering in the all-liquid state facilitates the separation of metallic copper from residual sulfides.

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5.7. References


5.7 References


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