MINERALOGICAL CHARACTERIZATION AND METALLURGICAL PROCESSING OF SEAFLOOR MASSIVE SULPHIDES FROM THE GERMAN LICENSE AREA IN THE INDIAN OCEAN

*M. Sommerfeld, D. Friedmann, and B. Friedrich
Institute of Process Metallurgy and Metal Recycling (IME), RWTH Aachen University
Intzestraße 3,D-52056 Aachen, Germany
(*Corresponding author: m sommerfeld@ime-aachen.de)

U. Schwarz-Schampera
Federal Institute for Geosciences and Natural Resources (BGR)
Stilleweg 2, D-30655 Hanover, Germany

ABSTRACT

The steadily growing demand for metals and their price increase at metal exchanges make the mining and utilization of marine mineral resources like polymetallic nodules, manganese crusts or sulfide deposits in the near future a viable option to potentially increase the supply of base and precious metals. For a country with low potential to mine land-based resources like Germany, the industrial recovery of metals from marine mineral resources could lead to a decreased dependency on imports. In this study, seafloor massive sulfides from the German license area in the Indian Ocean (Kairei field, Southern Central Indian Ridge) are treated to recover copper and precious metals. The aim of the project is to demonstrate the transferability of existing metallurgical techniques to the raw material of deep-sea massive sulfides. As a starting point to process this unconventional resource, samples from the Indian Ocean are chemically analyzed and mineralogical characterized. A comparison is carried out between the samples and land-based copper resources, to highlight the potential which lies in mining the deep-sea floor. This paper will show the general possibility of applying a two-stage pyrometallurgical process, based on a concentrate smelting operation, followed by a converting operation in lab-scale to the provided samples of massive sulfides. Generated slag from the concentrate smelting and the converting operation are investigated by X-ray diffraction to determine the mineralogical composition. The two-stage pyrometallurgical process is investigated by the thermochemical modelling tool FactSage™ 7.2 to evaluate the phase distribution of relevant elements between the metal, matte, slag and gas phase. The thermochemical boundaries of the pyrometallurgical process are therefore set and the results of the thermochemical study can be used as an indicator for the efficiency of an up-scaled process and the generated amount of side-streams, which need to be further treated or circulated back into the process.

KEYWORDS

Concentrate smelting, Converting, Marine mineral resources, Thermochemical modelling, Seafloor massive sulfide

INTRODUCTION

Seafloor massive sulfides (SMS) are the third kind of discovered deep-sea minerals besides ferromanganese nodules and cobalt-rich ferromanganese crusts (Sharma, 2017). They occur in water depths around 250–4,000 m (Koschinsky et al., 2018). SMS are characterized by a high base metal and sulfide content. They were created by fluid circulation and hydrothermal convection over time (Han et al., 2018).
Commonly, areas rich in SMS are associated with hydrothermal vent fields on the seafloor (Keith et al., 2018).

The samples provided by the Federal Institute for Geosciences and Natural Resources (BGR) are from the Kairei sulfide site in the Indian Ocean, approximately 2,400 km east of the southern tip of Madagascar (coordinates: 70°02'E, 25°19'S). The field lies in the area of the Central Indian Ridge, and the deposit can be assigned to the Cyprus-type. The investigated sample is a large block of massive copper sulfides taken by the research vessel SONNE during cruise INDEX2011. The chemical composition of the sample is listed in Table 1 and compared to copper concentrates from terrestrial ore bodies. In addition to the listed composition, 0.86 ppm of gold, 22.4 ppm of silver and 8 ppb of platinum are detected in the SMS-sample.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Zn</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMS-sample</td>
<td>39.4</td>
<td>21.6</td>
<td>27.4</td>
<td>0.90</td>
<td>2.60</td>
<td>1.74</td>
<td>0.99</td>
<td>0.25</td>
<td>0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>Yunnan Province (Hua, Cai, &amp; Cui, 2006)</td>
<td>23.0</td>
<td>31.0</td>
<td>30.0</td>
<td>*</td>
<td>1.8</td>
<td>5.2</td>
<td>0.7</td>
<td>*</td>
<td>*</td>
<td>2.7</td>
</tr>
<tr>
<td>Gibraltar (Lundström, Liipo, Taskinen, &amp; Aromaa, 2016)</td>
<td>26.5</td>
<td>28.3</td>
<td>32.9</td>
<td>0.06</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Erdenet (Lundström et al., 2016)</td>
<td>21.1</td>
<td>23.8</td>
<td>32.3</td>
<td>0.31</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Salobo (Lundström et al., 2016)</td>
<td>29.2</td>
<td>24.7</td>
<td>29.7</td>
<td>0.37</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* Composition not given in the reference

Compared to the listed concentrates, the SMS-sample contains highly elevated copper concentrations and lower iron contents. Combined with the estimated potential reserves of SMS, this could represent a valuable resource for base metals like copper. Precious metals can be also found as a trace component in SMS, but in some deposits they are highly enriched up to several tens of g/t for gold and several hundreds of g/t for silver (Petersen et al., 2016). Solely in easily accessible neovolcanic zones, the estimated SMS-reserves are in the order of 6·10⁸ tons (Hannington, Jamieson, Monecke, Petersen, & Beaulieu, 2011). Furthermore, SMS can contain significant amounts of sphalerite and galena, and generally are potentially valuable sources for zinc (Sharma, 2017) and lead (Hoagland et al., 2010).

Currently, the International Seabed Authority lists seven contractors, who got licenses for investigating massive sulfides in the Atlantic or Indian ocean (International Seabed Authority, 2019). However, up to 40% of the known hydrothermal vent fields or SMS-deposits are actually in shallower depths in national exclusive economic zones (EEZ) of coastal states (Hoagland et al., 2010). Current actions include investigation of those deposits for example in the EEZ of Japan, Papua New Guinea, New Zealand, Norway and Micronesia (Schrope, 2007; Hoagland et al., 2010; Snook, Drivenes, Rollinson, & Aasly, 2018). Although the potential of SMS for metal extraction is large, only little research was carried out with respect to mineral processing (Nakajima, Sato, Thornton, Dodiba, & Fujita, 2016; Hahn, Lennartz, Kleiv, Wotруба, & Kowalczik, 2018) or to metallurgical extraction (Kowalczik et al., 2018; Kowalczik, Snook, Kleiv, & Aasly, 2018), therefore, this paper explores the possibility of transferring pyrometallurgical extraction routes already used for terrestrial ore bodies to seafloor massive sulfides.

**MINERALOGICAL CHARACTERISATION**

An SMS-sample from the German license area was analyzed by reflected light microscopy to demonstrate the mineral phases present in the material. Table 2 lists the phases and abbreviations used in the SMS-mapping shown in Figure 1.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Mineral</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>bn</td>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
</tr>
<tr>
<td>cct</td>
<td>Chalcocite</td>
<td>Cu₂S</td>
</tr>
<tr>
<td>cp</td>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td>cv</td>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td>mc</td>
<td>Marcasite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>py</td>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>sl</td>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
</tbody>
</table>

Figure 1. Photomicrographs of Kairei SMS-samples to demonstrate sulfide mineralogical composition

The photomicrograph in Figure 1 a) shows a dense texture with major chalcopyrite, which is partly replaced by chalcocite along rims and fractures. In Figure 1 b) massive chalcopyrite is accompanied by aggregates of very fine-grained chalcocite, bornite, and sphalerite. In Figure 1 c) sphalerite is visible next to chalcopyrite, with secondary covellite along fractures. In Figure 1 d) chalcopyrite is surrounded by marcasite as a result of oxidation processes. In Figure 1 e) sphalerite lies next to chalcopyrite with secondary covellite along fractures. In Figure 1 f) euhedral pyrite grains in interstices accompany massive chalcopyrite.
EXPERIMENTAL DETAILS

To process the SMS, a two-step pyrometallurgical operation was considered, concentrate smelting producing a copper matte with an iron content below 5 wt%, followed by matte converting. In a larger scale, it is planned to integrate the SMS into the Outokumpu process and to use an autogenous flash smelting furnace, which is a well-known furnace already in commercial operation since 1949 in Harjavalta, Finland (Bryk, Ryselin, Honkasalo, & Malmstrom, 1958). Converting can be carried out for example by batch converting in a Peirce Smith converter, Hoboken converter or Top Submerged Lance (TSL) furnace or continuously by flash converting or also in a TSL-furnace (Habashi, 1997). Figure 2 shows a simplified process scheme of the applied process in laboratory scale.

![Diagram of the pyrometallurgical process for Kairei SMS](image)

**Concentrate smelting**

The SMS with the composition presented in Table 1 was mixed with fluxes before the experiment. The mixture for the first melting operation is composed of 4 kg SMS with 720 g of quartz and 160 g of lime. The purity of the quartz is 99.5 wt% and the purity of lime is 97 wt%. The addition of fluxes was determined by previous experiments in a smaller scale. Regarding the formation of fayalite, the quartz addition is 1.7 times higher, than the stochiometric required addition of quartz under the assumption, that all iron is transferred into the slag and quartz only reacts with wüstite in the slag.

The experiments were carried out in a resistance-heated furnace. A crucible was inserted into the furnace and the furnace was heated up to 1350°C. The mixture was charged in small amounts of around 200 g into a clay graphite crucible lined with a chromium corundum ramming mass. During the charging operation, oxygen was blown onto the charge with an alumina lance to promote oxidative smelting reactions. The flow rate in this period was 10 L/min, a higher flow rate would lead to a significant emission of flue dust. The oxygen results in the partial melting of the material where the oxygen stream contacts and reacts under heavy SO₂-emittance. The duration of the charging period was 69 minutes. Therefore, the oxygen supply was 172.5 L/kg of SMS during the charging period.

Figure 3 shows a schematic side view of the inside of the testing furnace during material charging and blowing. Charging the whole material at the same time proved to be not possible, since this led to incomplete melting at the bottom of the crucible where the oxygen could not interact with the charge. In that case, a liquid phase was only formed on the upper layer of the charge and the unreacted charge in the bottom was only slowly penetrated by the downflowing melt, leading to long reaction times. After all the material was charged and completely molten, the lance was inserted into the matte and oxygen was blown into the
liquid with a maximum of 12 L/min for 30 minutes. Therefore, the oxygen supply was 90 L/kg of SMS during the blowing period. Including the oxygen supply from the charging period, a total of 262.5 L of oxygen was consumed per kg of charged SMS. Under the assumption, that all iron sulfide is converted to FeO, the stochiometric requirement would be 130.0 L per kg of SMS, therefore double the amount of oxygen was consumed during the experiment, however especially during the charging period, only a fraction of the oxygen reacted and the efficiency of converting compared to the blowing period after charging is rather small. The oxygen consumption was also determined by trials in a smaller scale beforehand. Afterward, the melt was held at 1200°C to allow a good phase separation between matte and slag by gravity for 30 minutes. This way, 12 kg of SMS are processed in three batches to produce 6.1 kg of matte and 5.8 kg of slag. The resulting matte and slag are cooled in the crucible and separated for further treatment.

![Figure 3. Schematic concept of the experimental build-up for Kairei SMS-treatment](image)

**Matte converting**

The converting step was carried out in a very similar fashion. The temperature of the furnace was again 1350°C and the matte is fully molten. However, since in this step the lance has to be constantly inserted into the liquid matte, only smaller batches of the matte could be processed due to splashing of the liquid. For converting trials, 3 kg of matte are used per trial. Two trials were carried out and therefore, 6 kg of matte were converted in total. As a flux 200 g of slag from the smelting step was used per trial to cover the matte during converting, this was done, because the quartz addition in the concentrate smelting was higher than the stochiometric requirement and therefore it was assumed, that unreacted quartz has the capacity for further uptake of iron oxide. Furthermore the matte was charged and the lance was inserted into the molten matte with an oxygen flow of 15 L/min for 50 minutes. A total of 250 L of oxygen was consumed per kg of charged matte. The stochiometric requirements for oxidizing sulfur and iron are 145.5 L of oxygen per kg of charged matte, the higher oxygen supply was chosen, because of pre-trials, which showed an incomplete reaction of oxygen with the melt. Generally, conditions in the crucible and the melt are extremely turbulent. For good phase separation, the crucible is held at 1300°C for 60 minutes under regular atmosphere after the blowing phase. A higher temperature and retention time compared to the first step is used to allow better settling after this turbulent process. The copper losses are still quite high and would be somewhat mitigated when used on an industrial scale. However, even in the industrial operation, high copper contents in the converter slag occur. Those losses can be minimized by keeping the slag in the furnace for the following batch, so that this copper is not removed from the process. In lab-scale this was not possible to carry out, due to the small amount of material for experiments.
THERMOCHEMICAL MODELLING

Thermochemical modelling was carried out to investigate the concentrate smelting and matte converting unit operations. FactSage 7.2™ was used as a tool and all simulations are based on the databases FactPS, FToxid, FTmisc and FScopp (Bale et al., 2016).

Simulation of concentrate smelting

The basis for the simulation of concentrate smelting was the composition of the SMS as listed in Table 1 and the parameters from the experiments. Therefore, an equilibrium temperature of 1350°C and a pressure of one atm were assumed. However, a few adjustments were made for this simulation:

- The addition of 180 g quartz and 40 g lime per 1 kg of SMS is considered to be pure SiO₂ and CaO
- Instead of pure oxygen, oxygen-enriched air with 35 vol% oxygen and 65 vol% nitrogen is used as an oxidizing agent – to represent possible operating conditions
- The supplied process air is varied during the simulation and correlated to the results of the experimental trial, based on analyzed generated products, since the reaction of oxygen during the trials is probably not complete

Figure 4 shows the simulated composition of the matte and the copper loss while varying the oxygen supply per kg of charged SMS. Oxygen is expressed under Normal conditions (temperature of 273.15 K and a pressure of one atm).

![Figure 4. Simulation of concentrate smelting operation with varying oxygen supply](image)

According to Figure 4, the sulfur content in the matte is decreasing nearly linear, while oxygen is supplied to the system, however, the decrease is rather small compared to the decrease of iron in the matte, which is removed after supplying 180 L of oxygen completely. The copper losses are quite small at the beginning of the blowing period, but they increase more rapidly when the iron content in the matte drops below 2 wt%. While sulfur and iron are constantly removed from the matte, the copper content is increasing from 45.6 wt% in the initially formed matte up to 80.3 wt% in the investigated area.

Simulation of matte converting

The basis for the simulation of matte converting are the parameters from the experiments and the composition of the matte and slag according to the simulation. Therefore, an equilibrium temperature of 1350°C and a pressure of one atm are assumed. However, a few adjustments were made in the simulation similar to the concentrate smelting modelling:

- It is assumed, that 150.5 L of oxygen reacted per kg of charged SMS during the concentrate smelting, which is the necessary amount of oxygen for the targeted iron content of under 5 wt% in the matte
• Per 1 kg of matte, 66.7 g of slag from the concentrate smelting is added to the converter
• Instead of pure oxygen, oxygen-enriched air with 35 vol% oxygen and 65 vol% nitrogen is used as an oxidizing agent
• The supplied process air is varied during the simulation and correlated to the results of the experimental trial, based on analyzed generated products, since the reaction of oxygen during the trials is probably not complete

Figure 5 shows the simulated copper content of matte and metal, while varying the oxygen supply per kg of charged matte. Furthermore, the removal of iron and sulfur and the copper loss are displayed. Oxygen is expressed under Normal conditions (temperature of 273.15 K and a pressure of one atm).

![Graph showing the impact of oxygen supply on copper content, iron removal, sulfur removal, and copper loss.](image)

Figure 5. Simulation of matte converting operation with varying oxygen supply

According to Figure 5, first iron is removed, while only a little sulfur is removed from the matte and the copper losses are still small. After 95 % of iron is removed from the matte (i.e. the slag blow), the copper losses are nearly constant in the area of matte and metal equilibrium and are around 1.5 %. The copper content of the metal in this area of matte/metal-equilibrium is 97.3 wt%, while the matte has a copper content of 80.5 wt%. An increase in copper content in the metal occurs only after the matte is completely converted (i.e. the copper blow) to metal. However, the conversion is also accompanied by a large increase in copper losses to the slag.

RESULTS

In this section, the results of the experiments are presented and compared to the thermochemical model. A mineralogical analysis of the generated slag is carried out and the phase composition will be presented. Furthermore, detailed information about the input and output of mass are shown at the end of this section.

Results of concentrate smelting

Figure 6 shows the comparison of the matte and slag analysis of the trials with the thermochemical simulation for major compounds in the material.
Figure 6. Comparison of concentrate smelting simulation and experimental trial: (a) Matte analysis; (b) Slag analysis

The values for the thermochemical models for an oxygen supply of 150.5 L match the results of the trials fairly well. Compared to the 262.5 L of oxygen actually blown onto the charge and melt, this would lead to an efficiency of 57.3 % for the blowing operation. The matte has an elevated copper content of 74 wt%, part of the sulfur was oxidized and left the matte with the off-gas, while iron mostly reacted to iron oxide and is part of the slag. The composition of the slag from the trials meets the prediction by the models quite well, except for lime, which is significantly lower in the trial compared to the model. An explanation could be, that the finely grained lime was entrained by the off-gas system.

Results of converting matte

Figure 7 shows the comparison of the blister copper and slag analysis of the trials and the thermochemical simulation for major compounds in the material. However, the oxygen analysis in the material is not carried out and therefore only the simulated value for oxygen in the metal is displayed.

Figure 7. Comparison of converting matte simulation and experimental trial: (a) Metal analysis; (b) Slag analysis

The values for the thermochemical models for an oxygen supply of 159.25 L match the results of the trials fairly well. Compared to the 250 L of oxygen actually blown into the melt, this would lead to an efficiency of 63.7 % for the blowing operation. The produced metal has an elevated copper content of 98.9 wt%. Therefore, the copper content lies in the typical composition for blister copper and can be further processed by fire refining in an anode furnace (Habashi, 1997). The Cu₂O-content in the slag is elevated with 14 wt% in the trial and 16 wt% according to the model. The copper losses according to the model, however,
are quite low in this process step with 2.9% and the slag can be recirculated into the process to recover copper or into an electric arc furnace for slag cleaning.

**Mineralogical analysis of generated slag**

X-ray diffraction analysis is used to identify the mineral composition of the generated slag. Table 3 shows the results of the analysis for a slag sample from the concentrate smelting step and the matte converting step.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Concentrate Smelting</th>
<th>Matte Converting</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Cristobalite</td>
<td>SiO₂</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td>Fayalite</td>
<td>Fe₂SiO₄</td>
<td>46</td>
<td>-</td>
</tr>
<tr>
<td>Spinels</td>
<td>(Cu,Mg,Fe,Zn)₂O₄</td>
<td>18</td>
<td>52</td>
</tr>
<tr>
<td>Pyroxenes</td>
<td>(Ca,Fe,Mg,Ba,Zn)₂(Al,Si)₂O₆</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>α-Quartz</td>
<td>SiO₂</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cuprit/Tenorite</td>
<td>Cu₂O / CuO</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

The analysis reveals, that the concentrate smelting slag mostly contains fayalite, pyroxenes, spinels and cristobalite, while the matte converting slag mostly contains spinels and cristobalite. In comparison to the measured mineralogical composition, a Scheil-Gulliver cooling calculation is carried out with FactSage, based on the slag composition from the trials given in Figures 6 and 7. However, the copper content is neglected in this simulation, since the simulation would only predict the precipitation of pure Cu₂O and there would be no solid solution phase containing copper present. The results of this simulation are shown in Table 4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Concentrate Smelting</th>
<th>Matte Converting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>(Fe,Ca)(Fe,Ca)SiO₄</td>
<td>60.7</td>
<td>60.8</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>(Ca,Fe)(Fe)Si₂O₆</td>
<td>12.9</td>
<td>17.4</td>
</tr>
<tr>
<td>Tridymite</td>
<td>SiO₂</td>
<td>13.4</td>
<td>21.8</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>(Ca,Fe)SiO₃</td>
<td>12.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Compared to the results from the measurements, the high content of olivine, which is mostly Fe₂SiO₄, in the matte converting step is conspicuous, also instead of cristobalite FactSage predicts the present of tridymite as the stable SiO₂-phase. The presence of SiO₂ according to FactSage and in the slag samples is an indication, that a smaller addition of quartzite in the concentrate smelting step would be sufficient for slagging of iron as fayalite.

**Modelling of the entire process chain**

Figure 8 shows all mass streams including copper contents of the proposed process for the processing of 1000 kg SMS according to the simulation. It is noted, that the analysis of the SMS from Table 1 is not normalized up to 100 wt%, therefore the Sankey diagram only has an input of 950.7 kg. Other minor components not mentioned in Table 1 are neglected.
The simulation predicts the production of 382.5 kg blister copper with a purity of 98.8 wt%. The total recovery efficiency is therefore 95.9 % and could be increased further by slag cleaning operations, for example in a submerged arc furnace or in direct current electric arc furnace coupled with a magnetic stirring reactor (Friedrich et al., 2018). The main consumable in the process is oxygenated air, with a consumption of 669.6 Nm$^3$/t. Furthermore, 180 kg/t quartzite and 40 kg/t lime are used. The main output-stream is off-gas with 622.8 Nm$^3$/t in both process steps. The amount of generated slag is 587.19 kg/t. However, this amount could be reduced further by slag cleaning or circulation of the copper-rich slag into the process.

CONCLUSIONS

The provided seafloor massive sulfide sample was successfully processed by a two-stage pyrometallurgical process, based on concentrate smelting and matte converting. The composition of generated matte, slag and metal match the results of the thermochemical simulation with FactSage$^\text{TM}$ 7.2 well. The copper content in the produced blister copper is 98.9 wt% and 98.8 wt% according to the simulation and a further fire refining operation should be able to produce copper suitable for anode casting. The combined copper recovery rate based on both smelting steps is 95.9 % according to the simulation.

ACKNOWLEDGMENTS

The German Federal Institute for Geosciences and Natural Resources (BGR) is acknowledged for the supply of massive sulfide samples, financial and additional support. Furthermore, the authors would like to thank Klaus Hahn and Jutta Lennartz from the AMR at RWTH Aachen University for support within the project. The anonymous reviewer is acknowledged for helpful comments.

This research was funded by internal BGR funding under the grant number 212-10083362.
REFERENCES


