Improving Copper Recovery from Production Slags by Advanced Stirring Methods

M. Zander, B. Friedrich
RWTH Aachen University
Chair and Dept. of IME Process Metallurgy and Metal Recycling
Intzstraße 3
52066 Aachen, Germany

M. Hoppe, J. Schmidl
Aurubis AG
Hovestraße 50
20539 Hamburg, Germany

R. Degel, G. Kleinschmidt
SMS Siemag AG
Eduard-Schloemann-Straße 4
40237 Düsseldorf, Germany

Keywords: slag cleaning, stirring mode, copper slag, submerged arc furnace, stirring reactor

Abstract

Slags resulting from pyrometallurgical copper processes are important by-products to be controlled in structure and composition. Due to the significant volumes of slag compared with those of the target metal it is mandatory – as already practiced today – to use the slag as a product e.g. for river embankments.

After matte smelting and standard slag cleaning in submerged arc furnaces (SAF), the fayalitic slag still contains up to 1% of copper and other valuable metals like nickel, cobalt or molybdenum. In addition future regulations may restrict the heavy metal contents both in the solid and eluate in slags used for construction purposes in the future. Furthermore, the metal contents in ores are decreasing in the available deposits, much below the upper value of discarded slags. Sustainable slag management is necessary from the economical and environmental point of view.

In the frame of a current collaborative BMBF funded research project lab-scale experiments are realized at the IME in order to improve the metal recovery and to create mineral product from the original slag with expanded market potential. Results will show the influence of different stirring conditions on the settling behaviour of metallic / matte droplets. Furthermore, the charging of various additives is investigated in order to decrease the viscosity leading to an improved settling velocity of metallic / matte inclusions as the paper will present.
In cooperation with SMS Siemag the previously announced new intensive slag cleaning reactor will be installed and commissioned in technical-scale at the IME and in a demonstration-scale plant at Aurubis AG, Hamburg. The actual status will be presented. A reasonable and interleaving combination of intensive slag cleaning processes by submerged arc furnace and stirring reactor is aspired in the future.

1 Introduction und Background

In the last decade the treatment and a following re-use of by-products has become more and more important for the industry. This paper highlights possibilities of intensive pyrometallurgical slag cleaning processes. “Traditional” slag cleaning processes in submerged arc furnaces are based on gravitational settling. The copper matte droplet settling is described by the Stokes equation under laminar flow conditions [1]:

\[
V = \frac{2}{9} \frac{r^2 (\rho_d - \rho_s) g}{\eta}
\]  

(1)

where: \( V \) = settling velocity [m\( \cdot \)s\(^{-1} \)], \( r \) = droplet radius [m], \( \rho_d \) = density of the metal [kg\( \cdot \)m\(^{-3} \)], \( \rho_s \) = density of the slag [kg\( \cdot \)m\(^{-3} \)], \( g \) = gravitational acceleration [m\( \cdot \)s\(^{-2} \)], \( \eta \) = viscosity [kg\( \cdot \)m\(^{-1} \cdot \)s\(^{-1} \)].

Therefore, decreasing viscosity has a strong influence on the settling behaviour of the particles. By using fluxes a resulting decrease of the viscosity leads to a faster settling velocity.

In this paper, the influence on different stirring conditions to the settling behaviour of heavy metals is tested in lab-scale trials. Feedstock is a slag resulting from the SAF process of the Aurubis AG. Furthermore, the principle of the new SMS Siemag stirring reactor for intensive slag cleaning and the construction of a technical-scale reactor in Aachen and a demonstration-scale reactor in Hamburg will be presented.

1.1 Why is slag cleaning a growing concern

The demand on base metals is still high and will further grow with increasing industrialization of especially Asian, South American and former CIS countries. Therefore it is necessary and also reasonable to improve and optimize existing processes of extractive metallurgy. As primary resources become more and more complex in their chemical composition or rather poor in their content of valuable metals in the ore secondary sources like slag phases from the production processes get in the focus of the metal industry.

With the existing process route in the pyrometallurgy of copper the recovery of valuable metals from the slag phase is not sufficient. The selective separation or enrichment of these metals into a metallic or matte phase would lead to an improved exploitation of the available potential. Beside economic reasons also ecological benefits would be given. While the metallic or matte phase can be
treated in the existing copper extraction route or separately in a subsequent reactor the slag phase can be used as construction material for example.

1.2 Conventional pyrometallurgical copper slag route

The following Figure 1 depicts how slag is produced during the pyrometallurgical copper process route. In addition, the conventional slag cleaning and desirable improvements in slag cleaning processes are visualized in the flow chart.

![Flow chart of the pyrometallurgical copper process](image)

**Figure 1:** Flow chart of the pyrometallurgical copper process

1.3 Characterisation of the slag

The slag type used in copper industry is normally a fayalitic based slag [2]. After processing the slag in the submerged arc furnace the slag still contains valuable metals. A typical slag composition including the main metal contents is given in Table 1.
Table 1: Typical slag composition

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃ [wt. %]</th>
<th>CaO [wt. %]</th>
<th>SiO₂ [wt. %]</th>
<th>Cu [wt. %]</th>
<th>Fe [wt. %]</th>
<th>Ni [wt. %]</th>
<th>Mo [wt. %]</th>
<th>Pb [wt. %]</th>
<th>Zn [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
<td>3 to 5</td>
<td>31 to 34</td>
<td>0.8</td>
<td>40 to 43</td>
<td>0.05</td>
<td>0.3</td>
<td>0.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The solidification of the slag in ladles follows a crushing and classification procedure. The product is called iron-silicate rocks. This material is used in the construction industry for hydraulic or road construction. It is comparable with magmatic rocks, such as basalt, diabas or gabbro [3].

The electron probe micro analysis (EPMA) of a granulated slag sample visualizes the localization of copper and iron, see Figure 2. Valuable metallic copper occurs mainly in the same place as sulphur in a separated phase and it has an insignificant low content in the oxide composition. Therefore most of the inclusions are copper sulphide droplets. Iron and silicon occur mainly bonded together with oxygen to fayalite (Fe₂SiO₄). A characteristic magnetite particle (Fe₃O₄) is visible on the right side of the Fe, O mappings. Via the analysis of one piece of copper slag with XRD, a magnetite content of approximately 9 wt. % was detected. In consideration of non-representative samples, the calculation of this area verified the content of copper sampled with XRF analysis (see Table 1).

![Figure 2: EPMA of the granulated slag (left), image analysis of copper sulphur content (right)](image-url)

2 Lab-Scale experimental section

2.1 Experimental Set-up

Equilibrium experiments were conducted in an indirectly heated inductive crucible furnace under atmospheric conditions. The maximum power of the furnace is 40 kW with a frequency of 4 kHz. The material of the outer crucible is clay-graphite. The inner crucible, in which the slag is charged, consists of alumina. The Al₂O₃ is chemically resistant against the slag. A permanent temperature...
control of the trials was maintained with the aid of a Ni-CrNi thermocouple, which is protected by an alumina protection tube.

Graphite granulate was used to fill the space between the crucibles in order to improve the heat transfer into the inner crucible and the slag. A small layer of 20 g of coal-pieces in each trial was placed on the top of the charged slag in order to attain reducing conditions and to limit back oxidation, especially to prevent the formation of magnetite (Fe₃O₄). Figure 3 shows the trial’s setup.

Figure 3: Induction furnace with control (left) and crucible set-up (right)

To investigate turbulent stirring conditions an inert gas injection by a lance was installed inside the crucible. The qualitative liquid slag movement by using purging gas and in an induction field (assumption: inductively coupling of the slag) is shown in Figure 4.
In addition, trials in a resistance heated furnace and a submerged arc furnace were carried out in order to test the influence of different parameters on the slag cleaning. The main intention behind all these trials was to test the influence on different stirring modes on the settling behaviour of the copper sulphide droplets and to investigate how other heavy metals like molybdenum, nickel and lead will behave under different stirring conditions.

Figure 4: Slag stirring in lab-scale crucible induction furnace with and without injection lance [4]

Figure 5: Lab-scale SAF and lab-scale resistance heated furnace
For the experiments, the following parameters were applied:

- Holding temperature: 1300 °C;
- Feedstock: Slag from traditional slag cleaning in SAF / adding 5 wt. % CaC₂;
- Holding time 1300 °C: 60 min;
- Heating rate: approx. 400 °C/h;
- Crucible is cooled down under atmosphere (no casting).

Exceptions are the trials in the lab-scale SAF (see chapter 2.2.1). In each lab-scale furnace melting experiments are carried out by feeding the slag without additives and trials by feeding the slag mixed with 5 wt. % calcium carbide. The idea of adding additives is to investigate the influence of reduction on the degree of slag cleaning. CaC₂ was selected because of its excellent reducing behaviour for copper slags in literature [5]. The reason for the five times higher rate of reduction in comparison to the use of coke is the exothermic effect of magnetite and copper reduction. Furthermore, the dissolution of CaO (fluxes) decreases the slag viscosity and improves the settling velocity of the copper sulphide droplets [5]. After the trials, the slag was sampled in three layers. Figure 6 visualizes the principle of the sampling. The percentages given in this figure are the proportion of each location in relation to the total mass of the slag.

![Sampling areas of the solidified slag after the trials](image)

Figure 6: Sampling areas of the solidified slag after the trials

The three layers were representatively sampled and analysed by XRF. For the trials, the contents of the main heavy metals of the feed slag are: Cu 0.68 wt. %, Pb 0.21 wt. %, Mo 0.19 wt. %. In order to compare all the results an index for the slag reduction is defined, the **degree of slag cleaning:**

\[
A_{Me} = \frac{m_{Slag,Me,P}}{m_{Slag,Me,R}} \times 100\% = \frac{m_{Slag,R} \times X_{Slag,Me,P}}{m_{Slag,E} \times X_{Slag,Me,R}} \times 100\%
\]

(2)
where: $A_{Me} = \text{percentage metal yield}$, $m_{\text{Slag,Me}} = \text{mass of each metal in slag phase}$, index $R = \text{Reactant}$; index $P = \text{Product}$,

$$A_{Me,\text{cleaning}} = 1 - A_{Me} \quad (3)$$

where: $A_{Me,\text{cleaning}} = \text{percentage of metal compared to the metal content in the feed slag}$.

### 2.2 Influence of different stirring conditions on the slag-cleaning level

The following part of the paper will summarize the results of the trials under different stirring conditions.

#### 2.2.1 Mode of stirring: moderate

Six trials in IME’s lab-scale SAF were carried out. In contrast to the trials mentioned above, by using a minimum current of 2 kV a constant holding temperature of 1300 °C cannot be controlled due to the nature of the furnace. After 20 min of holding time temperatures > 1500 °C are measured.

In order to get a stable arc, minimum feedstock for the trials is 2 kg. In three trials, 5 wt. % CaC$_2$ were mixed with the feedstock. In order to prevent further temperature increase, holding time is 20 min. Due to the furnace construction the melt must be cast after the end of holding time. It gets obvious that the trial conditions were not comparable to the general parameters (see chapter 2.1).

Nevertheless, the results are published as a “benchmark” for ideal settling conditions. Background is the temperature dependence of the viscosity, which is described by the Arrhenius equation [6]:

$$\ln \eta = A_\eta - \frac{E_\eta}{R \cdot T} \quad (4)$$

$\eta = \text{viscosity} \ [\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}]$, $A_\eta = \text{constant}$; $E_\eta = \text{activation energy}$, $R = \text{Gas constant} \ [\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]$, $T = \text{Temperature} \ [\text{K}]$

The formula shows that a higher melt temperature leads to a viscosity decrease. A faster settling velocity of the metallic inclusions is the result (see Equation 1)

A visible separation of metal and slag phase is attained. The analysis of the metal phases showed that especially in the trial using the reducing agent the removed copper from the slag is reduced, settled and coagulated on the furnace bottom. Due to the process temperatures, Fe and Mo are reduced and settled down to the regulus, too. The following table lists the degree of cleaning of copper, lead, molybdenum and nickel as average values from the top and middle layers. Zinc was not considered due to the volatile character of metallic Zn and ZnO at the operational temperature of 1300 °C.

Table 2: Results of the lab-scale SAF trials
Improving Copper Recovery from Production Slags by Advances Stirring Methods

<table>
<thead>
<tr>
<th></th>
<th>Cu [wt. %]</th>
<th>Pb [wt. %]</th>
<th>Mo [wt. %]</th>
<th>Ni [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-content in slag feedstock</td>
<td>0.68</td>
<td>0.21</td>
<td>0.19</td>
<td>340</td>
</tr>
</tbody>
</table>

**Degree of slag cleaning after the trials:**

<table>
<thead>
<tr>
<th></th>
<th>Without additive</th>
<th>With adding 5 % of CaC₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>54 %</td>
<td>52 %</td>
</tr>
<tr>
<td>Pb [wt. %]</td>
<td>94.5 %</td>
<td>96.5 %</td>
</tr>
<tr>
<td>Mo [wt. %]</td>
<td>86 %</td>
<td>92.5 %</td>
</tr>
<tr>
<td>Ni [ppm]</td>
<td>83.5 %</td>
<td>92 %</td>
</tr>
</tbody>
</table>

The corresponding values for trials with and without using additives were quite similar to each other. A possible explanation is the reducing atmosphere by the use of a coal electrode during all trials.

### 2.2.2 Mode of stirring: marginal and intensive

For all subsequent trials, the parameters are comparable (see 2.1). Due to the increasing conductivity of iron(II) oxide by rising temperatures and the high conductivity of copper matte and especially copper, which are components of the slag, a little stirring of the melt is expected. This bath movement can be theoretically described by the following equations [7]:

\[ p = \frac{1}{2} P_i A^* \sqrt{\mu^* \kappa / (\pi^* f)} \]

\[ H = \frac{I^* n}{\sqrt{l^2 + D^2}} \]

where: \( p \) = pressure on the melt [N·m⁻²], \( P_i \) = induced power [N·m·s⁻¹], \( A \) = feedstock surface [m²], \( \mu \) = permeability of the feedstock [N·A⁻²], \( \kappa \) = electrical conductivity [A·V⁻¹·m⁻¹], \( \pi \) = number pi, \( f \) = frequency [s⁻¹], \( H \) = magnetic field strength [A·m⁻¹], \( I \) = current [A], \( n \) = number of turns, \( l \) = length [m], \( D \) = diameter [m].

On the assumptions of a shielding effect on the magnetic field strength because of the graphite-layer between the two crucibles (compare to Figure 3) and different possible electrical conductivities and permeabilities (not directly determinable for the feed slag composition) a low pressure of the melt as driving force for the melt movement of between 0.01 and 0.16 N·m⁻² was calculated.

During the trials, a small oscillating bath movement is observable. When using the purging gas lance, the minimum possible injection of 1 l/min Argon is adjusted. The lance is set between 2 and 3 cm over the inner crucible bottom. A strong turbulence in the melt is observed.

The following spider diagram (Figure 7) illustrated the degree of slag cleaning for the main heavy metals Cu and Pb. Their contents in the top and middle layers are similar in all trials. Therefore the average cleaning degree of the top and middle layer is shown.
The results determine that the maximum decrease of the copper content (0.4 wt. %) is obtained by using CaC₂. By using purging gas, no significant improvement of slag cleaning compare to the trials under marginal stirring conditions is conducted. The degree of lead cleaning is improved by using purging gas and/or CaC₂.

A significant increase of the heavy metals in the bottom part of the crucible was observed, especially in the trials without using purging gas. In trials by using the reducing agent CaC₂ a coagulated metal phase was created. Possible explanation is the higher density of the reduced copper particles compared to the copper matte leading to a faster settling velocity (see chapter 1) of the copper inclusions. These phases contain mainly iron, copper and a few percentage of molybdenum.

2.2.3 Trials without stirring conditions

The experiments in the resistance furnace were intended to investigate the effect of settling without stirring. The influence of heat convection is negligible. Compared to the induction furnace trial series, the trial parameters are similar. Table 3 depicts the achieved cleaning levels.
Table 3: Results under no stirring conditions

<table>
<thead>
<tr>
<th></th>
<th>Cu [wt. %]</th>
<th>Pb [wt. %]</th>
<th>Mo [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-content in slag feedstock</td>
<td>0.68</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>Degree of slag cleaning after the trials:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without additive</td>
<td>28 %</td>
<td>-16 %</td>
<td>9 %</td>
</tr>
<tr>
<td>With adding 5 % of CaC₂</td>
<td>27 %</td>
<td>-3 %</td>
<td>13 %</td>
</tr>
</tbody>
</table>

The results demonstrate a decrease of 28 % Cu in the top and the middle layer without using an additive. By using calcium carbide, the copper content was decreased to the same level in the top and the middle layer. For Pb and Mo no significant settling was visible. In all trials a corresponding increase in percentage of copper content was detected in the crucible bottom. The analysed lead values at the bottom part of the crucible are comparable with the top layers. No significant settling of the lead was detected in this trial series. The influence of the additives was in contrast to the stirring trials not significant. One explanation could be that without bath movement the reduction reactions of the CaC₂ with the slag take more time compared to the trials under stirring conditions.

2.3 Chemically enhanced cleaning by using additives

Additionally, different additives such as CaO, MgO, TiO₂, CaF₂ and FeS and their influence on slag cleaning/metal recovery were tested. The trials were carried out in the open induction furnace. The results show that especially CaO, MgO and CaF₂ decreased the viscosity significantly and thereby decreased the copper content in the top and middle part of the crucible. Considering the fact that by using calcium fluoride toxic residues like silicon tetra fluoride arises, a re-use of the slag may be difficult.

In another series the slag reduction with coke in combination with CaO and MgO was tested and compared to the results by using CaC₂. A visible metal phase is reduced and settled to the bottom of the crucible in some trials (see Figure 8).
Figure 8: Cross-section of the crucible after a trial with 5 wt. % calcium carbide

A maximum cleaning level of 68 % compared to the feedstock was achieved in these trials. The copper, molybdenum and nickel contents in the metal phase are volatile. Between 25 to 50 % of copper, molybdenum and nickel were reduced and transferred into the metal phase whereas lead is only reduced up to 6 %.

3 Discussion of the lab-scale investigations

Different lab-scale trials were carried out in order to determine the influence of different stirring modes on the settling behaviour of a fayalitic copper slag. Figure 9 summarizes the average degree of slag cleaning in the top and middle layer after the trials.
The following conclusions can be drawn:

- A pyrometallurgical slag treatment leads to a further reduction of the copper content in all trials.

- By heating up the slag to a level of > 1500 °C with moderate stirring a maximum decrease of the copper content of 50% was achieved. The slag is totally cleaned from lead due to evaporation.

- By testing different stirring conditions the following results can be summarized: No significant differences in the degree of cleaning by the trials with no bath movement compared to the trials with a marginal bath movement were observed.

- Strong turbulence in the melt by flushing gas injection hinders the copper particle settling. The reason is that the copper particles are probably dispersed and thus kept floating in the melt. Another possible explanation is the strong upward flow due to the argon injection. In contrast to that, gas injection has a positive influence one lead cleaning.

- Different fluxes were tested in order to decrease the viscosity. The highest cleaning rates were achieved by using MgO and CaO.

- By adding coal, after the induction furnace trials with marginal bath movement a metal phase is detected. A higher metal yield of copper, molybdenum and nickel is achieved by using calcium carbide.

The lab-scale results point out that an intensive slag cleaning is generally possible. To test the influence of the inclusion movement on the cleaning rate, SMS Siemag, Aurubis AG and IME are planning to investigate the intensive slag cleaning in technical and demonstration-scale trials.
4 Intensive Slag cleaning by using a stirring reactor

In this part of the paper, the principle of the stirring reactor and the construction of the demo-scale testing reactors are presented.

4.1 Process principles of intensive stirring reactor

Currently, SMS Siemag AG is constructing a reactor for metal recovery from slags. This rectangular DC furnace is equipped with an electromagnet on the outside in order to produce intensive slag stirring by the superimposed magnetic field. The resulting slag rotation enhances the coalescences of the small matte or metallic inclusions, which have an inclusion size of 2 to 1000 μm. The second quiet zone allows settling of the included droplets after their coalescence (Figure 10).

![Figure 10: Principle of the DC furnace with electromagnet and resulting stirring conditions [6]](image)

The settling behaviour of the droplets in the stirring reactor is influenced by several effects:

- Joule’s heat liberation by additional temperature increase;
- Cathodic and anodic reactions due to DC operation mode;
- Injection of additives (reducer and fluxes);
- Enhancing of mass transfer to the reactant surface by the magnetic field;
- Forced migration of metal/matte droplets under the electric field leads to coalescence;
- Coalescence leads to a settling of the droplets.

First small test trials confirmed that the copper content was reduced from 4.4 to 1 wt. % in a DC magnetic field [8].
4.2 Design of a technical-scale stirring reactor

In order to simulate an industrial slag cleaning plant, trials in the new IME recycling research centre (IRRC) are planned. The heart of this centre is a 1 MW large-scale electric smelter, in which the slag can be melted by direct or alternating current. The influence of additives, charged by injection lances or hollow electrodes, can be tested up to a melt volume of 1500 l.

Afterwards, liquid slag is transferred and charged by ladles into the technical-scale SMS Siemag reactor. The stirring reactor will have a capacity volume of 300 l copper slag, with a planned retention time of one hour. Tests of various refractory materials and a variable number and position of the magnets and the electrode are planned. This flexible design enables the transfer of this process concept to other applications. For example, the unit may be suitable for treatment of slags from the iron and steel metallurgy as well as for the platinum, palladium, nickel, cobalt and chromium producing industry.

The goal is to optimize the slag composition to a marketable product and maximize the metal yield. This will be realized by optimized injection technology, economical and non-polluting insertion of additives in combination with optimal stirring conditions. Figure 11 illustrates the slag-cleaning process route at IME’s recycling research centre (IRRC). In future slag cleaning of different metal processes will be possible.

![Diagram of slag cleaning flow](image)

Figure 11: Slag cleaning flow based on initial slag melting / settling and subsequent treatment by the stirring reactor
4.3 Initial start-up of a demo-scale stirring reactor in Hamburg

Parallel to the university set up a demonstration-scale stirring reactor was installed at Aurubis Hamburg in cooperation with SMS Siemag. The reactor is designed for a slag mass flow of 4 tonne per hour. After tapping the slag from the submerged arc furnace into a ladle it is transported to the demonstration furnace by a forklift. The charging of the slag is carried out by crane. The cleaned slag flows via an overflow into a ladle and is allowed to cool down. In the field of the first electrode, the magnetic field is applied to the slag. Each campaign takes eight days with three shifts a day. The start-up phase is complete and first results are expected in the second half of 2011.

5 Conclusion and Outlook

Preliminary lab-scale results show that an intensive pyrometallurgical slag treatment leads to a further cleaning rate of the heavy metals in copper slags resulting from SAF. By marginal stirring a cleaning rate of 18 % Cu compared to the feedstock was achieved, under turbulent stirring conditions a cleaning of 23 % Cu and without stirring a cleaning rate of 28 % Cu was obtained. By overheating the slag, the maximum cleaning rate of 51 % was reached. Turbulent stirring conditions improve the cleaning rate of lead due to partial evaporation. By using CaC$_2$ as reducing agent under similar stirring conditions a maximal cleaning rate of lead and copper was achieved. The bath movement improves the reduction character. By using different additives a further reduction is achieved. Future investigations to analyse the copper reduction potential in the presented stirring reactors in Aachen und Hamburg will be made at the end of this year.

Acknowledgement

We would like to thank the BMBF (Federal Ministry of Education and Research) for the financial support of the project “Vermeidung von Metallverlusten in metallurgischen Schlacken am Beispiel der Kupfergewinnung” (reference number 033R006, project duration 05/2009-04/2012). Also we would like to thank the students Ann-Sophie Fahrle, Richard Meier and Christian Schwotzer for their support during the lab-scale experimentation.
References


http://www.induga.de/images/03_verfahren/01_schmelzen/01_schmelz_feucht_spaene/MV_2_5d.pdf


