Heavy Metal Recovery from Slags of Copper Production via SAF Techniques

M. Zander; B. Friedrich; R. Degel

Abstract

Slags resulting from pyrometallurgical processes are an important by-product of the European copper industry. The need for a “waste to product” treatment becomes obvious due to the significantly larger volumes of slag compared to those of metal.

After matte smelting and standard slag cleaning the fayalitic slag still contains up to 1 % copper and other precious metals like nickel, cobalt or molybdenum. The EU and the German government are planning further restrictions on heavy metal contents in slags used for construction purposes. Furthermore, metal contents in ores in the available deposits are decreasing, considerably below the upper values of some of the discarded slags. Thus a sustainable slag management is necessary considering economical and environmental factors. At IME Process Metallurgy and Metal Recycling, different procedures are developed in order to improve metal recovery and to create a marketable mineral product from the original slag.

The first treatment improved slag cleaning directly in the submerged arc furnace (SAF) using coke injection. The benefit of this process in comparison to the traditional method is that it decreases process duration by accelerated kinetics and improves efficiency by an increased reduction potential. Furthermore, different fluxes/additives are investigated in order to decrease the viscosity and the melting point of the slag. By means of electrodynamic slag movement using a magnetic field, the settling behaviour of the metal droplets is positively influenced as a third option.

This paper summarizes the results attained up to now for the different slag treatment processes. An efficient, reasonable and interleaving combination of these procedures is aspired in near future.

Keywords: copper slag, recycling, slag cleaning, settling behaviour, arc furnaces

1 Introduction and Background

In the last decade environmental regulations and economical settings have put strong pressure on the primary copper industry. The following aspects will become more and more important for the European nonferrous industry which is exposed to intensive global competition:

- Higher throughput
- Cleaner operations
- Higher metallurgical recoveries
- Cleaner and higher quality of by-products. [1]

In this context, slag treatment becomes more and more important.

The following picture (Figure 1) depicts why the use of slag is required for the pyrometallurgical copper process route. In addition, the state of the art and desirable improvements by slag cleaning processes are explained in the flow chart:

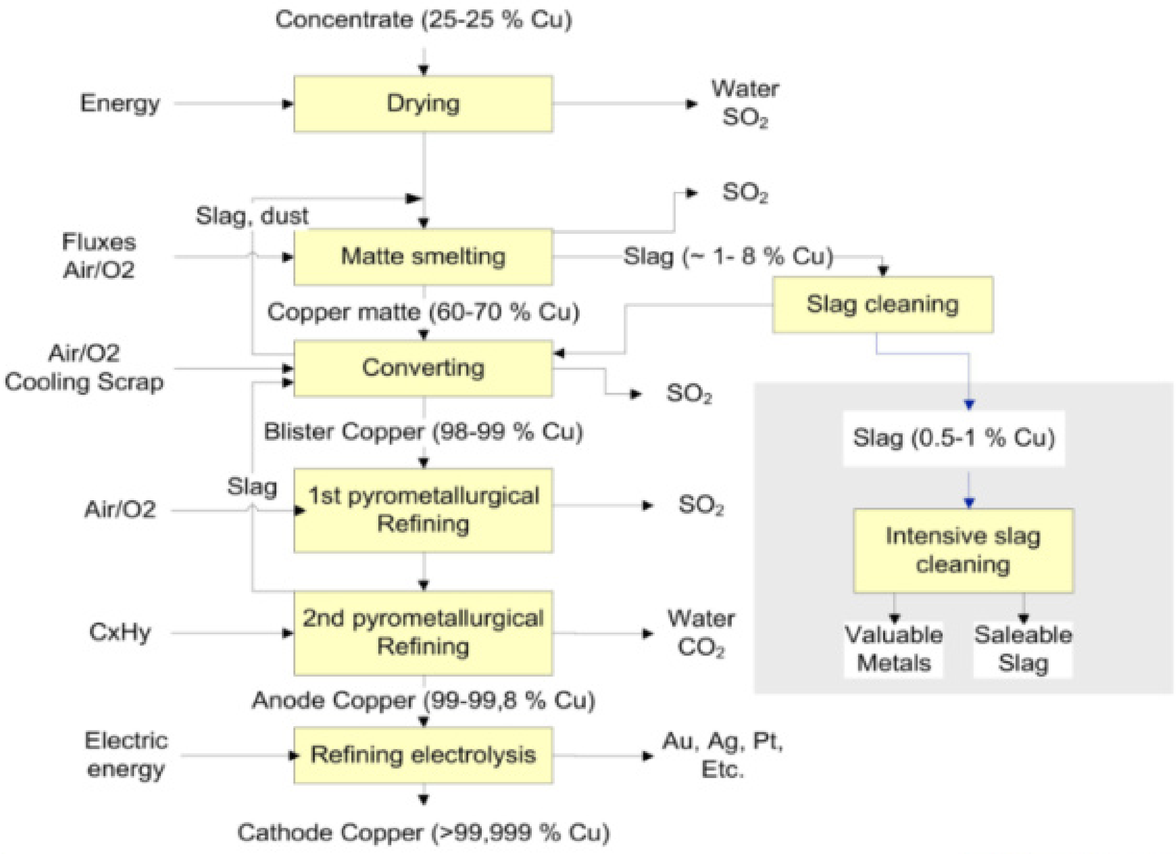


Figure 1: Flow chart of the pyrometallurgical copper process

After concentration and flotation, matte smelting is the first important pyrometallurgical process step. The aim of this procedure, which is nowadays mostly realized in flash smelters, is to yield a copper enriched phase, the so called copper matte, from which sulphur and iron are separated during the process. This matte contains ~60 wt.% of copper.

Another product of flash smelting is the slag. It serves in separating iron from the copper during matte smelting by enhancing the miscibility gap. The main components of the slag are iron oxides and silicon dioxide. After the process, the slag still contains a low percentage of copper matte, which cannot be removed completely. State of the art for the largest primary copper producer is the slag cleaning in submerged arc furnaces (SAF). These furnaces work with electrical energy, which is converted into heat by the electrical resistance of the slag. Electrodes are immersed in the melt to provide the required energy exchange area where the contact with the melt (Figure 2). This is the main difference in comparison to electric arc furnaces (EAF), which are used for secondary steelmaking and are partly operated in an open arc mode, i.e. the resistance is that of the air atmosphere. Another difference is that many of the SAF work semi-continuously, charged directly with liquid slag from the matte smelter.

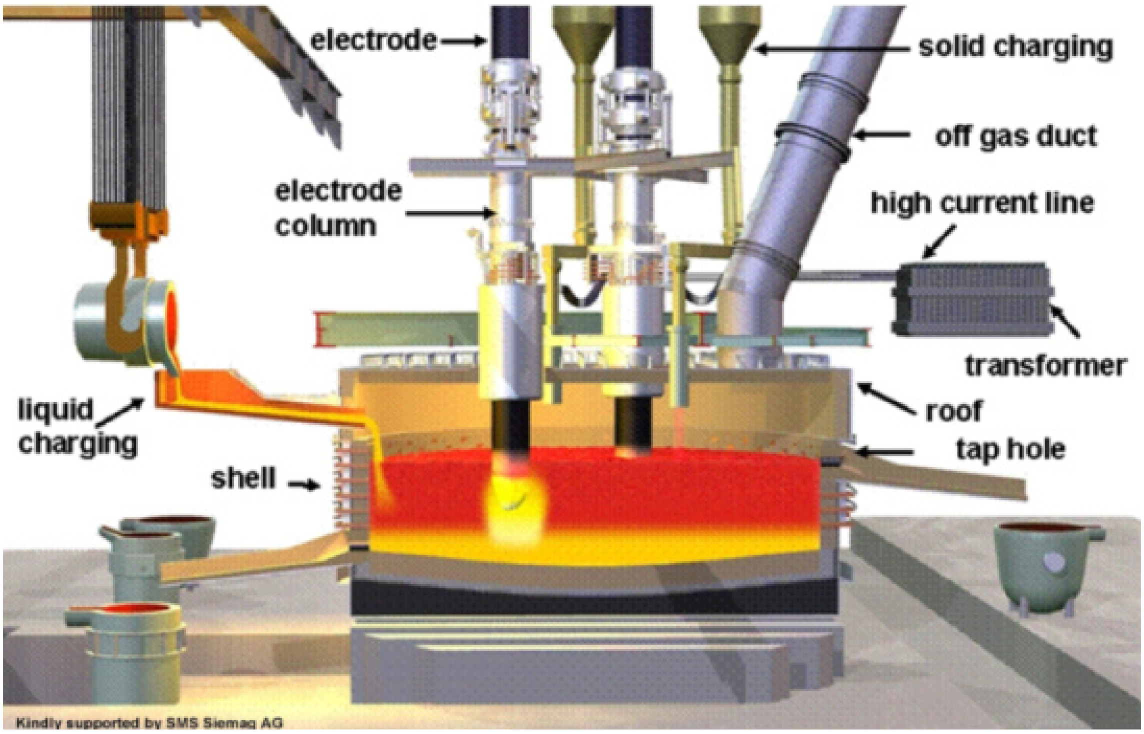


Figure 2: Layout of a submerged arc furnaces [2]

The major equipment consists of the furnace charging system, the carbon electrodes, a high current supply system and the tapping equipment. Copper is separated by sedimentation of the matte particles due to the higher density of the Cu_2S (ca. 5.2 g/cm^3) in contrast to the density of the fayalitic slag (ca. 3 g/cm^3).

Furthermore arc furnaces can be used for cleaning of copper slag, which are products of the Noranda or Teniente converters. In general the slag product still contains 0.5–1 wt.% of copper and is taken out by a separate tap hole (in Figure 2 at the right-side). The remaining copper content in the slag is determined by the portion of matte, which is not sedimented, because of the limited holding time, reduction- and flow conditions in the SAF. The settled copper-matte is taken out at a different tap hole and recirculated to the converter. The generated slag amount, which is normally bigger than the produced metal, can ideally be used as a saleable product.

Yet if this product contains one critical element exceeding the regulation limits, the dumping and disposal of these byproduct quantities cause logistical, environmental and economical problems for metallurgical plants.

The following aspects conclude why slag cleaning has become a growing concern and why the presented research work concerning different pyrometallurgical cleaning procedures is a matter of consequences:

- Copper content in the slag after the traditional cleaning and in the ore is comparable. Accordingly you can win a high amount of copper by an energy efficient slag cleaning process.
- The higher metal yield resulting from the slag cleaning leads to an improved process efficiency and higher overall metallic yield.
- It is possible to recuperate other metals like molybdenum, nickel, lead or precious metals such as Ag, Au. These elements are mostly accompanied in the copper ore.
- The EU and the German government are planning to further restrict heavy metal contents in slags which are used for road construction. The result is that the contents of heavy metals have to be reduced in future in order to treat slags as saleable products.

In this paper we will describe activities of slag cleaning based on SAF technology at IME in Aachen. After characterization of the applied fayalith slag, the improvement of slag cleaning by using coke injection is presented. Furthermore, the influence of some additives to improve metal recuperation is illustrated. As a third procedure, the influence of the settling behaviour by electrodynamic stirring is presented.

2 Characterization of the slag

The feed material is the product of the submerged arc furnace in the process chain of the biggest European copper producer. Due to the high bulk density water granulated slag is used. Figure 3 demonstrates the feed material of the trials. The table lists the main slag components, which are detected by X-Ray fraction analysis (XRF).

Element / Compound	**Content Weight %**
Fe	40,3
SiO_2	32,7
Al_2O_3	5,2
CaO	3,7
Cu	0,8
S	0,4

Figure 3: Granulated slag and composition of the feedstock

Electron probe micro analysis (EPMA) visualizes the bonds of copper and iron (Figure 4). It can be observed that the valuable metal copper is mainly bonded with sulphur in a separate phase and has an insignificantly low content in the main oxide composition. Iron and silicon are mainly bonded together with oxygen to fayalite (Fe_2SiO_4). A characteristic magnetite particle (Fe_3O_4) is visible on the right side of the Fe–O mappings. In consideration of non-representative samples, the calculation of this area verified the content of copper sampled with XRF analysis:

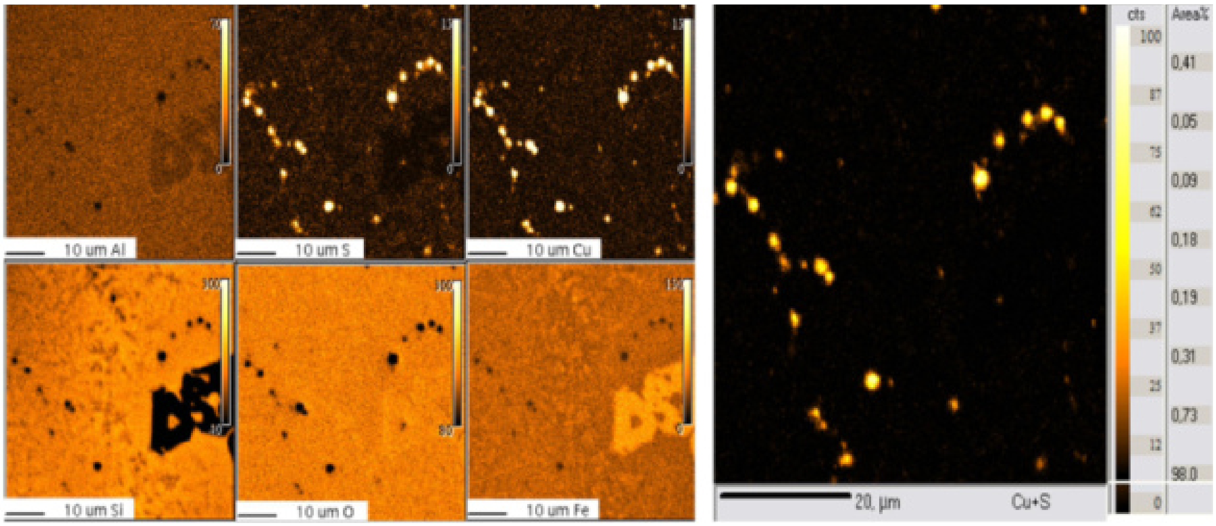


Figure 4: EPMA of the grained slag (left), area calculation of copper sulphur content (right)

To analyse the homogeneity of the slag, liquid slag was filtered through a porous ceramic filter. The experimental setup is comparable to the one described in section 4 below. During casting it was obvious to see that the melt was flowing through the filter. After a while, the slag froze on the top of the filter because of the cooling down of the filter system under atmosphere. XRF analysis of the filtercake and of the filtrate showed that the content of the elements was nearly the same. In summary, the composition of the slag can be regarded as homogeneous at a melt temperature of about 1300 °C.

3 Coke injection in electric arc furnaces

With injection technology for SAF also fine and reactive particles can be inserted into the melt, fine coke for example can be injected. Another advantage in comparison to the normal coke layer in SAF is that the injected gas produces a flow force, which yields in a better mixing of coke, carbon monoxide bubbles and the liquid slag. These conditions allow a decreased process time in comparison to the traditional slag cleaning in arc furnaces.

For the insertion of powdered material IME possesses special feeding equipment. With this tool coke can be injected in a pilot-scale electric arc furnace with the help of a lance. Fine materials can be connected to a pressure up to three bars. The injection facility is equipped with a pressure vessel of 45 l. Weight calculation is accurate to 0.1 kg.

A first test trial was conducted in a 380 kW pilot scale arc furnace with 300 kg of copper slag being remelted with an average content of 1.1 wt.% copper (higher copper content compared to Chapter 2 due to different another slag charge). Afterwards, 5 kg of coke were injected in different blow sequences within a time span of 8 minutes.

During these sequences, off-gas temperature raised due to exothermic reactions during the combustion of air from the top of the melt. Consequently the off-gas temperature decreased again immediately after the blowing sequences.

By using this procedure, a residual copper content of 0.4 % in the slag was achieved. Figure 5 visualizes the process. [3]

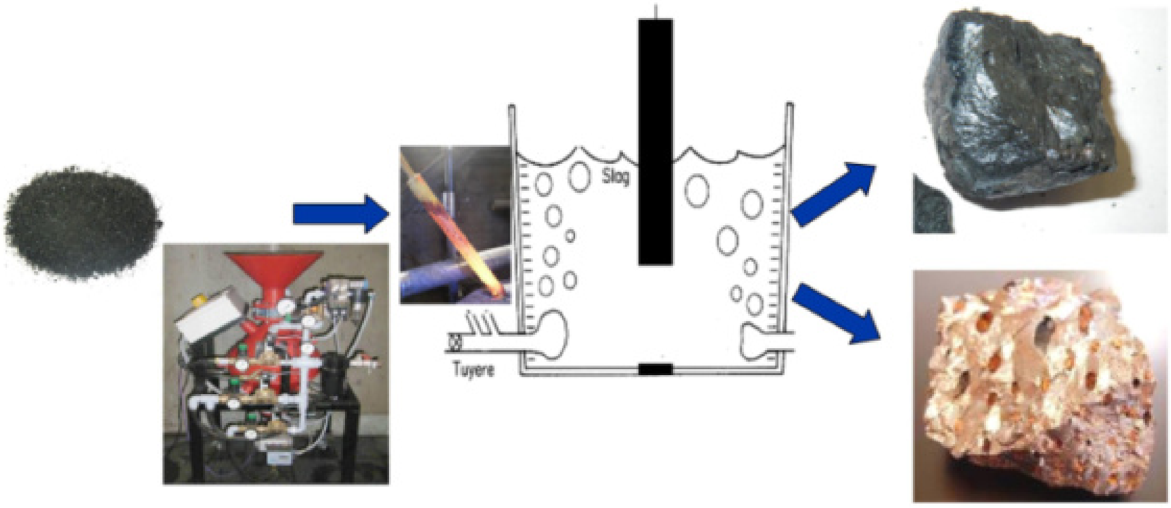


Figure 5: Procedure of the slag cleaning with coke injection [4]

Slag cleaning with coke injection is also proven for zinc and lead slags. For the same reasons as in the copper industry, by-product treatment is a growing concern in the lead and zinc industry. After a 1 hour treatment, zinc content in the slag could be reduced from 12.7 wt.% to less than 1 wt.% and Lead was reduced by the injection of coke from 9.6 wt.% to content less than 0.1 wt.% in the final slag. [5]

4 Slag cleaning by using additives

The copper recovery from slag during smelting is generally related to the settling behaviour of the matte. The settling velocity mainly depends on the size of the particles. Metallic/matte droplets with a big diameter settle very fast, smaller particles settle much slower to the ground of the bath. Thereby if no relative slag movement is considered, the metal yield depends on the residence time in the SAF and droplet settling is described in the Stokes equation (1). [6]

$$u = \frac{d_p{}^2 \bullet g \bullet (\delta_p - \delta)}{18 \bullet \eta} \tag{1}$$

Where: $d_p{}^2$ =particle size in mm, g =gravitation in m^2/s, δ_p = droplet density in kg/m^3, δ = slag density in g/cm^3, η = viscosity of the fluid in Ns/m^2, u= settling velocity m/s

It becomes obvious that decreasing the viscosity is a strong variable to improve the settling character of particles. During a test run the influence of fluxes was tested. To get an impression of the reducing character of the elements, the slag was also cleaned by using different types of reducing agents.

4.1 Experimental Work with fluxes

Equilibrium experiments were conducted in an induction furnace under standard atmosphere. The maximum power of the furnace is 40 kW at a frequency of 4 kHz. As an outer crucible graphite was used for better inductive coupling and an inner lining a fireclay based crucible contained the slag. Granulated graphite fills the space between the crucibles to support the heat transfer to the inner crucible and the slag (Figure 6). A small lignite-coal layer of 20 g in each trial is placed on the top of the feeded slag in order to achieve reducing conditions and to limit (re)oxidation.

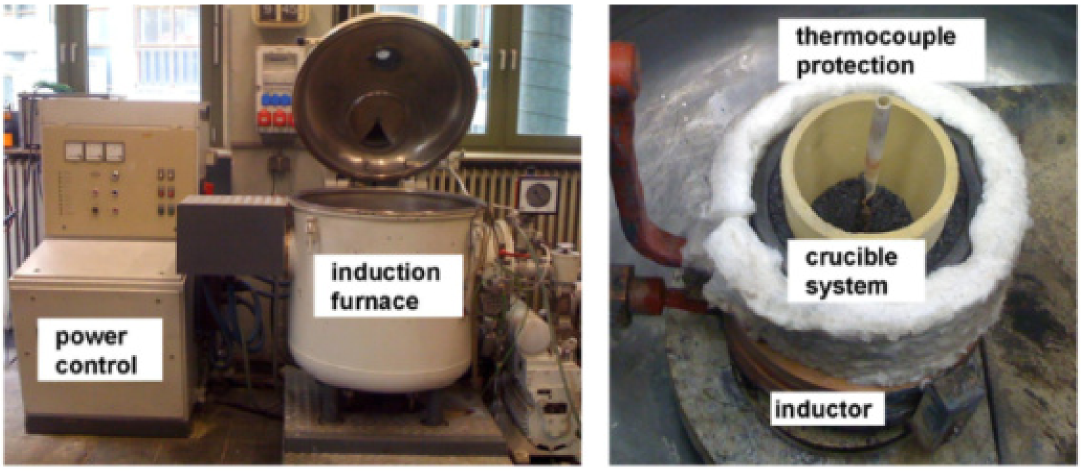


Figure 6: Induction furnace with control (left) and crucible set-up (right)

4.2 Influence of fluxes

In the experiments, the role of different fluxes was tested. In general, it is well known that the increase of basicity decreases the slag viscosity. Because of the good metal (especially copper) recovery results in a previous research work by Banda et al. [7] the addition of 5 wt.% of lime (CaO), fluorspar (CaF_2), rutile (TiO_2) and magnesia (MgO) were tested.

During the trial temperature was measured with a Ni-NrCr thermocouple enclosed in a protection tube and directly immersed in the melt. The melting point was optically observed as was the viscosity by stirring and optical observation at casting temperature. Upon achievement of a qualitatively satifactory viscosity the slag was cast through a ceramic filter.

Table 1 describes the influence of melting point and of the viscosity and thereby the influence of the settling behaviour by using different fluxes. The melting point of trials without additives with a heating rate of around 400 °C/h was observed to be at 1190 °C. The holding time of all trials was 30 minutes and the holding/casting temperature was set to be about 1280 °C.

Table 1: Results of the trials with different fluxes

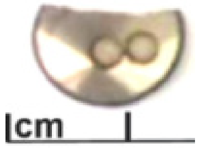
Flux	**wt.%**	**Melting point decrease** (compare to original slag)	**Influence of the viscosity** 0 = original slag -3 = strong viscosity decrease	**Influence of Cu settling behaviour** 0 = original slag -3 = strong influence of droplet settling
CaF_2	2% 5%	- 40/ - 55	-2 / -3	2/ 3
CaO	5%	- 40	-2	2
MgO	5%	- 15	-2	3
TiO_2	5%	+ 40	0	1

The influence of different additives on the settling behaviour was proven by the different Cu and S contents of the casted slags. The strongest viscosity decrease was observed with calcium fluoride. However, CaF_2 poses an additional effect that environmentally harmful slags are formed. In general, the fluxes CaO and MgO improved the settling behaviour in SAF-processes. The basicity improves by the dissolution of MgO/CaO and leads to viscosity decreases. To determine optimal parameters under economical and environmental slag composition settings, the optimal amount of CaO and MgO has to be investigated deeper.

4.3 Reducing experiments

Beside the influence of fluxes on the settinling behaviour, the influence of several reducing agents on the metal yield is tested. During the first trial, 5 wt.% of coke were added as a reducer in combination with magnesia as flux. In another trial, the reducing agent calcium carbide was used. In both trials, the temperature was constant at a level of 1330 °C and the holding time was about 1 hour. After the trials, the crucible including the slag is cooled down under atmosphere. In both cases a visible metal phase was detected on the bottom of the crucible. Table 2 lists the metal yields of both trials, which are analysed by ICP-OES.

Table 2: Metal yield and composition of the reducing experiments

Element	**Trial** **5% MgO + 5% C**	**Trial** **5% CaC_2**
Metal Yield **Composition [wt.%]**	**1.3 %** 	**2.3 %** 
Cu	16	76.5
Fe	76.6	12.2
Mo	2.2	2.1
As	2.1	2.2
Ni	0.41	1
Co	0.57	0.13
Pb	0	1.2

The reason for the higher rate of slag reduction with calcium carbide in comparison to the reduction with coke is the exothermic effect of the magnetite and cuprous oxide reduction. Furthermore the dissolution of CaO and $CaSiO_3$ is lowering the viscosity in the slag, which improves the reduction rate. [8]

Because of the lower reduction rate when using coke, mostly iron is reduced in the respective trial. Additionally the hyper-stoichiometric use of coke leads to the reduction of a semi-solid iron phase. A reason for the produced metallic iron is the high activity coefficient of iron due to the multiplex amount of iron in comparison to copper in the feedstock. Additionally, the effective amount of the reacted coke/calciumcarbide has to be investigated in further trials. The cross section of the crucible in figure 7 demonstrates the settled metal phase (marked is the sampled area). Copper content in the slag was reduced down to 0.3 wt.% on the ground and 0.4 wt.% in the middle of the crucible by the use of calcium carbide (compare to figure 4). The concentration of other harmful heavy metals, i.e. lead, zinc and nickel was also significantly decreased in, with similar reducing efficiencies for CaC_2 and the combination of magnesia and coke respectively.

By using a resistance heated furnace, only a few, really small metal particles are found on the crucible ground due reduced slag bath movement compared to the described induction furnace trials. One reason is the slag stirring in induction furnaces due to the electrical currents and resulting Lorentz forces. Further trials will analyse the influence of bath stirring on the settling behaviour of copper slags in a more detailed way.

Figure 7: Cross-section of the crucible after the trial with sampled areas marked by the filled rectangles

5 Slag cleaning by electromagnetic stirring

At the moment, IME is working together with SMS Siemag AG and Aurubis AG to construct a special reactor for metal recovery from slags. This pilot scale rectangular DC furnace is equipped with an electro-magnet on the outside in order to produce an intensive slag stirring due to magneto hydrodynamics. This slag rotation enhances the coalescences of the small matte or metallic inclusions, which have an inclusion size from 2–1000 µm. The second, calmer zone allows sedimentation of the inclusions after their coalescence.

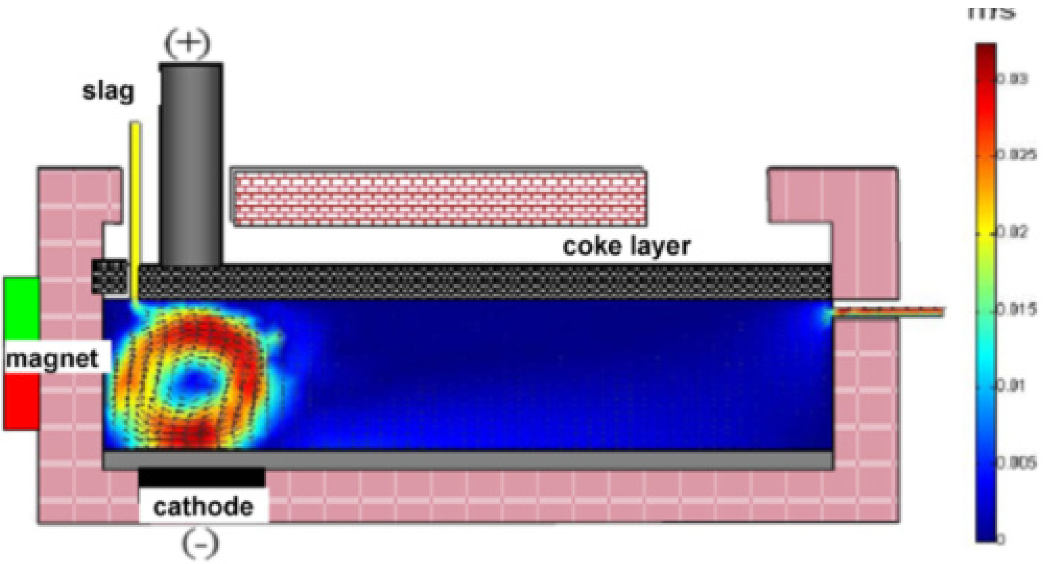


Figure 8: Principle of the stirring reactor [9]

The settling behaviour of the droplets in the stirring reactor (Figure 8) is enhanced by several effects.

- Joule´s heat liberation for additional temperature increase
- Cathodic and anodic reactions
- Injection of additives (reducers and fluxes)
- Enhancing of mass transfer to the reactant surface
- Forced migration of metal/matte droplets under the electric field
- Coalescence leads to faster settling of the droplets.

First small test trials in Chile confirmed that the copper content is reduced from 4.4 to 1 wt.% in a DC magnetic field. Also, the magnetite content decreases significantly, which is necessary for the reduction of copper. [9]

At IME, a lab-scale stirring reactor is currently set-up and will have a capacity volume of 350 l of copper slag, which is treatable within one hour. A possible exchange of refractory material and a varying number and position of the magnets and the electrode is planned. This flexible design enables the transfer of this process unit design to other applications. For example the unit might be suitable for by-products of the iron and steel metallurgy as well as for the platinum, palladium, nickel, cobalt and chromium producing industry. The positive effect of the stirring is already proven by the influence of the matte copper settling behaviour in different lab-scale furnaces. Droplet settling in induction furnaces, which enable electromagnetic stirring in the bath, is much better than in resistance heated furnaces, which have no bath agitation apart from minor buoyancy forces in case of thermal gradients. First trials in resistance heated furnaces illustrated only some small inclusions and no coagulated metal phase at the crucible bottom after cooling down under comparable trial conditions.

6 Conclusion and Outlook

The recent innovation presented by IME focuses on the recovery of valuable metals; especially copper out of slags which origin from the SAF cleaning process of the primary copper process route. This slag has an average copper content of 0.8 wt.%, which is mainly bonded to sulphur. The first procedure described the possibility to inject reducing agents in the SAF process, which leads to an improved copper reduction rate and shortened processing time. Lab-scale trials show the positive influence of fluxes, especially CaO and MgO. These oxides decrease the melting temperature and the viscosity and thereby improve the settling behaviour of the copper matte. In exemplary trials the use of different reducers was tested. The advanced selective reduction of copper with CaC_2 in comparison to carbon is determined. During the next months, optimal additive contents will be calculated by the thermo chemical Software FactSage™ and afterwards be proven by experiments to optimize the copper yield. The improvements of slag cleaning by electrodynamic stirring will be investigated by using lab-scale furnaces under varying stirring conditions.

In order to be close to an industrial slag cleaning plant, trials in the new IME recycling research centre (IRRC) are planned. The heart of this centre is the new 1 MW large-scale arc furnace, in which the slag can be melted by direct, alternating or rotary current (figure 9). The influence of additives, possibly charged through hollow electrodes, can be tested up to a melt volume of 1500 l.

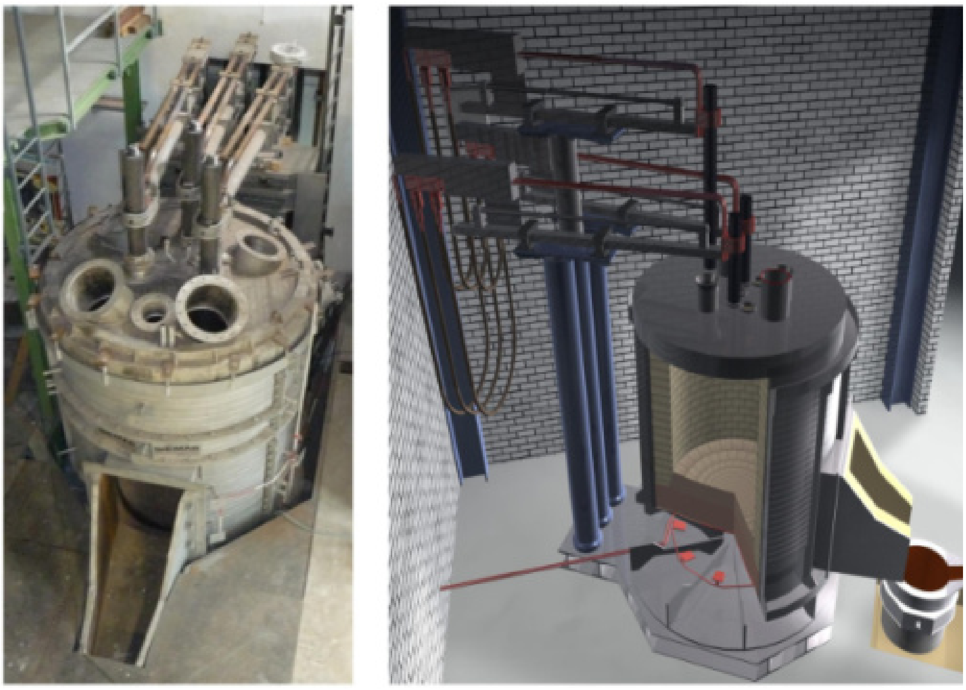


Figure 9: Large-scale SAF in the IME Recycling Research Centre (IRRC)

Afterwards, the liquid slag is transferred and charged by ladles into the IME stirring reactor. The goal is to optimize the slag composition to a saleable product and to maximize the metal yield. This will be realized by trials with the aim to find the perfect injection technology, economically and environmentally insert of additives in combination with optimal stirring conditions. Figure 10 illustrates a possible slag-cleaning process route at IME´s world unique recycling research centre (IRRC). In future slag cleaning experiments for different metal processes will be possible.

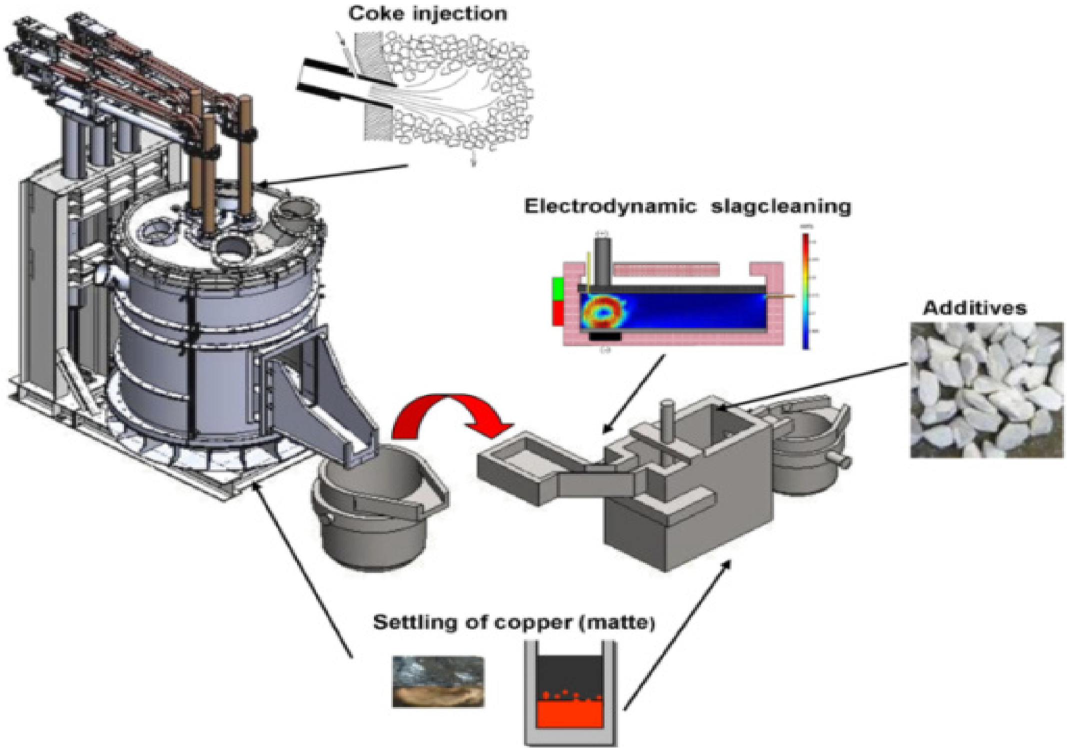


Figure 10: Large-scale slag cleaning in the IRRC

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