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Reduction of Anode Furnace Slag from Secondary Copper Production with different Metallic Reducing Agents

Lars Felkl, Michael Stelter, Alexandros Charitos

Anode furnace slags contain significant amounts of valuable elements such as copper, nickel, tin, lead and zinc. To avoid losses during processing, the slag is typically recycled to upstream processing stages, such as the Peirce-Smith converter. However, the material typically used in the converter contains higher levels of copper. Hence, slag recirculation limits processing capacity and efficiency, and leads to the accumulation of impurities. This research focuses on the separate treatment of slags within an independent furnace. Carbon based reductants are commonly used in current processes due to their known reduction efficiency. However, there is a growing need for carbon-free reductants to reduce the CO_2 footprint. Therefore, this study will investigate the feasibility and reduction efficiency of metallic reductants such as iron, aluminium and magnesium. These metals often are found as scrap in automotive and construction materials industries and are sometimes used in combination with plastics, which can aid the reduction process.

Keywords:

Slag reduction – Anode furnace slag – Metallothermic reduction – Slag valorisation

Reduktion von Anodenofenschlacke aus der Sekundärkupfererzeugung mit verschiedenen metallischen Reduktionsmitteln

Anodenofenschlacken enthalten erhebliche Mengen an wertvollen Elementen wie Kupfer, Nickel, Zinn, Blei und Zink. Um Verluste bei der Verarbeitung zu vermeiden, wird die Schlacke in der Regel in vorherige Verarbeitungsschritte, wie den Peirce-Smith-Konverter, zurückgeführt. Das üblicherweise im Konverter verwendete Material enthält jedoch einen höheren Kupferanteil. Infolgedessen begrenzt die Schlackenrückführung die Verarbeitungskapazität und die Effizienz des Konverters und führt zur Anhäufung von Verunreinigungen. Diese Untersuchung konzentriert sich auf die getrennte Behandlung von Schlacken in separaten Aggregaten. Kohlenstoffhaltige Reduktionsmittel werden aufgrund ihrer bekannten Reduktionseffizienz in den derzeitigen Verfahren häufig eingesetzt. Es besteht jedoch ein wachsender Bedarf an kohlenstofffreien Reduktionsmitteln, um den CO_2-Fußabdruck zu verringern. Daher werden in dieser Studie die Möglichkeiten und die Reduktionseffizienz von metallischen Reduktionsmitteln wie Eisen, Aluminium und Magnesium untersucht. Diese Metalle fallen häufig als Schrott in der Automobil- und Baustoffindustrie an und werden manchmal in Kombination mit Kunststoffen verwendet, die den Reduktionsprozess unterstützen können.

Schlüsselwörter:

Schlackenreduktion – Anodenofenschlacke – Metallothermie – Schlackenverwertung

Réduction des scories de four d'anode provenant de la production secondaire de cuivre à l'aide de différents agents réducteurs métalliques

Reducción de escorias de horno anódico procedentes de la producción secundaria de cobre con diferentes agentes reductores metálicos

1 Introduction

In metallurgical processes, slags play an important role. They protect the metallic or matte phase from undesired contact with oxygen from the atmosphere, while also acting as collectors for impurities. These impurities could lead to contaminations of the metal phase and therefore influence the required properties of the produced metals. When working with copper, it is essential to minimise impurities as even small amounts of other elements can disrupt the lattice structure and reduce electrical conductivity. Furthermore, slags tend to dissolve or trap metallic droplets, leading to losses during metal production [1]. These mechanical losses are often associated with viscosity, which is

strongly influenced by the slag liquidus temperature and composition. Modifying the slag composition can decrease chemical losses as different compositions dissolve varying amounts of metals as their oxides. However, direct contact and mixing of slag and metallic phases, potentially accompanied with induced turbulence from injected gases like natural gas or hydrogen, make some metal loss inevitable, whether in metallic or oxidic form. Efficient recovery of valuable elements from slags is necessary, considering that converter slags from copper production contain up to 15 wt.-% [2] and anode furnace slags contain up to 28 wt. % [3]. In secondary black copper melting operations, the slag can contain up to 30 wt.-% of copper [4]. Therefore, these slags are suitable for processing in dedicated unit operations.

According to standard practice, these materials are already recycled in previous process steps to reduce the loss of valuable materials through recirculation [2]. However, this approach results in two challenges: processing recycled slags in the converter or anode furnace with feed materials of higher concentrations of valuable elements, such as matte (45 to 75 wt.-% Cu) [5], blister copper for primary production or black copper (up to 70 wt.-% Cu), and raw copper for secondary production, reduces the respective aggregate's production capacity. Furthermore, impurities are recycled back to the previous process steps, which may cause them to concentrate in the process phases and alter the properties of both the slags and metal phases. For instance, chromium is derived from PGM-rich ores in primary copper smelting and from chromium-containing steel scrap and certain copper-chromium alloys (i.e. CuCr1Zr) in secondary copper smelting. This leads to the formation of spinel phases of the type $(Mg, Fe)(Al, Cr, Fe)_2O_4$, as well as olivine $(Fe, Mg, Cr)_2SiO_4$ and pyroxene $(Fe, Mg, Cr)SiO_3$ structures. These chromium-containing structures are formed below 1450 °C [6]. The presence of solid particles in a molten phase can increase its viscosity at a given temperature, which is commonly referred to as the slurry effect [1, 7]. As a result, slags may become less effective as collectors for impurities as their viscosity increases and thus the phase separation between metallic phase and slag is getting more difficult. Through that the amount of mechanical entrapped metallic droplets in the slag is increased.

Separate treatment of converter and anode furnace slags from copper processing can meet all requirements. However, it requires higher capital costs for equipment installation and the addition of a reduction agent stream. Thus, slags have the potential to collect impurities effectively. By treating the used slags appropriately, it is possible to minimize the loss of valuable elements such as copper. Impurities, such as chromium, can be excluded from the main process since slag recirculation is avoided. This allows the aggregates associated with the main process chain to handle more feed that is richer in valuable elements.

Many research groups have studied the separate treatment of slags from copper production for various purposes and using different methods. One such study, conducted

by [7], focused on the recovery of copper from copper converter slag through a melting and settling process in primary production. A recent area of study involves extracting iron from copper process slag. This aim has been the production of pig iron and an oxidic phase for the glass fibre or cement industry through a reductive carbothermic treatment [8-10]. Other studies have pursued similar goals through an aluminothermic reduction treatment of low copper-bearing slags [11, 12]. Despite the wide range of studies, there is little data available for reductive carbon-free slag treatment via a metallothermic reduction of high copper-bearing slags to produce a copper-rich alloy. The aim of this study is to provide respective information.

2 Methodology: Sample characterisation, modelling and experimental procedure

The anode furnace slag analysed in this study was obtained from a secondary copper production plant. A sample was ground into a fine powder for XRF (X-ray fluorescence) analysis. The chemical analysis results are presented in Table 1. These results are used to calculate the stoichiometric mass of the reduction agent required to theoretically reduce all valuable metal oxides, including copper-, nickel-, lead-, tin-, and zinc oxides. This value serves as the basis for thermodynamic modelling and experiments.

Table 1: Composition of studied anode furnace slag, contents from XRF-analysis [wt.-%]

Cu_2O	NiO	SnO_2	PbO	ZnO	FeO	SiO_2	CaO	Al_2O_3	BaO	Cr_2O_3
38.6	3.2	5.8	3.4	9.7	7.4	18.7	1.1	7.8	1.1	1.2

The copper detected via XRF analysis is assumed as cuprous oxide (Cu_2O) due to the environment in the anode furnace, which is however not oxidizing enough to form cupric oxide (CuO) in the slag. In reality, the copper present in the slag is chemically dissolved cuprous oxide, as well as mechanically entrapped metallic copper droplets. However, the XRF is only capable of detecting elements and reports specific oxides according to user definition. The same difficulties are encountered for the analysis of iron oxide: As the XRF can only detect elements, the output is defined as ferrous oxide (FeO), while in the slag sample a mixture of ferrous oxide and ferric oxide (Fe_2O_3) will be present. The oxides of valuable metals constitute approximately 60 wt.-%, while typical slag formers such as FeO, SiO_2, and Al_2O_3 only sum up to 33.9 wt.-%. This makes predicting slag behaviour challenging.

2.1 Prediction via thermodynamical modelling

This study utilises FactSage™ version 8.1 [13] (Figure 1) with the FactPS and FToxid databases, while the FScopp database is version 7.3. The composition of the input slag is defined in the mixture-module and used in the equilib-module as a stream of reactants with a mass of 100 g. The stoichiometric mass of a given reducing agent, previously calculated, is used as the reaction partner. Calculations using FactSage™ were performed with 100 % of the required mass of reducing agent, as well as with fractions (25 % and 50 %) and multiples (125 %, 150 %, and 200 %) of that
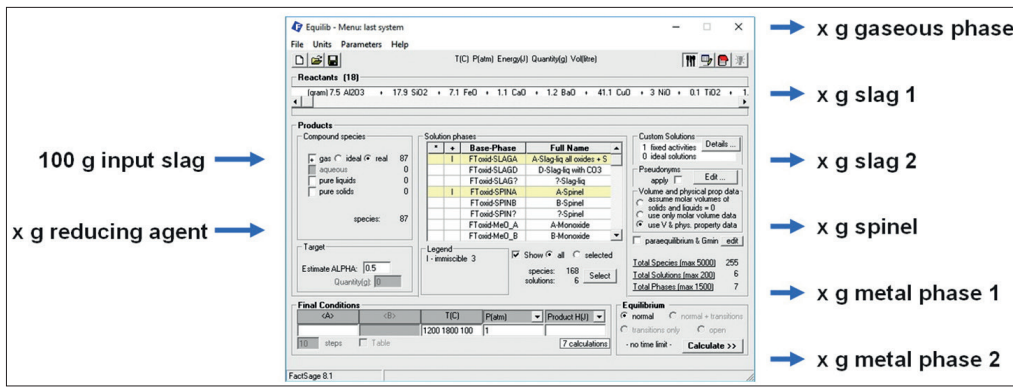
Fig. 1:
Illustration of the program interface and schematic representation of thermodynamic modeling with FactSage

value. The model output was calculated based on the most likely phases to form, including a gaseous phase (FactPS), a slag phase (FToxid-SLAGA), a phase for spinels (FToxid-SPINA), and a molten metal phase that is copper-based (FScopp-Liqu).

2.2 Experimental procedure

The experiments utilised a system, with the key components displayed in Figure 2. The anode furnace slag was fragmented into pieces smaller than 1 cm and then weighed into small, high-wall crucibles made of corundum (Al_2O_3) with a height of 150 mm and an inner diameter of 37 mm. For each experiment, 150 g of anode furnace slag was mixed with a fraction (25 % to 200 %) of the calculated mass of a reducing agent to ensure good blending and a large reaction surface. The experiments were conducted using an induction furnace, which requires an outer carbide crucible for inductive coupling. Up to three alumina crucibles can be placed in a carbide crucible simultaneously, allowing for three parallel reduction experiments to take place. To keep the corundum crucibles in place, a lid made of refractory material with three 44 mm-wide drillings is used. The three inner alumina crucibles are placed in a bed of loose high-grade corundum to ensure heat transfer between them and the outer carbide crucible. A fourth drilling hole is located in the centre, which is used by a type B thermocouple. The thermocouple's tip is placed in the high-grade corundum to measure the temperature.

The experiments were conducted at a temperature of 1300 °C. The experimental temperature was reached within 3 hours and held for 2 hours. The setup was then cooled down through simple heat transfer with the atmosphere. After cooling, the alumina crucibles are removed, weighed, and then broken to extract the metallic nugget and separate the secondary slag from the remaining parts of the crucible. The weight of the nugget is measured, and the mass of the secondary slag, as well as the mass loss of the entire system, is calculated through mass balancing. The crushed and milled secondary slag is transformed into powder tablets for XRF analysis (Bruker S2 Puma). The composition of the metal phases is determined through ICP-OES (Varian 725-ES) after dilution.

3 Results

This chapter presents the results of the thermodynamic calculations using FactSage™ and the experiments conducted to reduce the anode furnace slag using iron fillings. The focus is on the recoverable and recovered metal phase, as well as the theoretical and measured content of copper and the remaining reducing agents (iron, aluminium, and magnesium) in the metallic phase. Furthermore, it is important to keep the (residual) copper content in the remaining secondary slag as low as possible to minimize copper losses. In the experiments when iron is used as a reduction agent, a brief look on the secondary slag attained is given.

3.1 Simulation results

3.1.1 Utilization of iron as a reduction agent

Figure 3 illustrates the achievable mass of metallic phase in g per 100 g of input slag as a function of the added mass of iron as a reducing agent in g per 100 g input slag. The mass
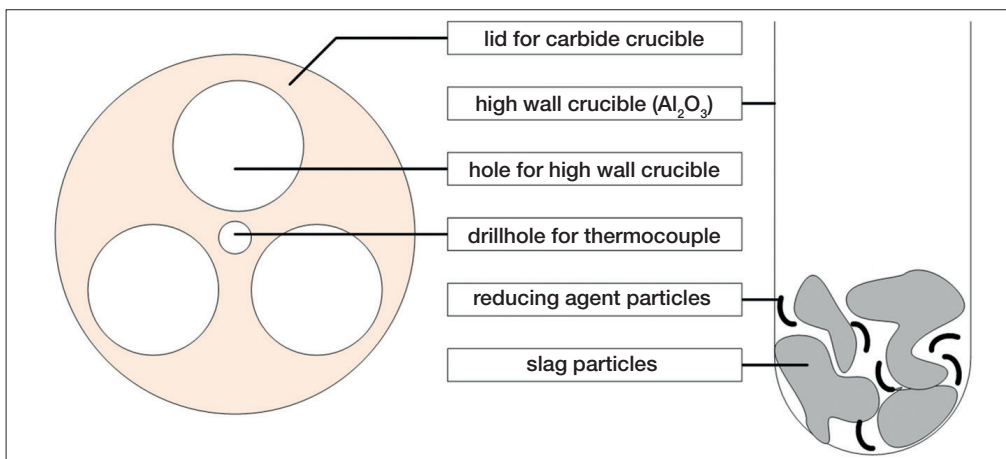

Fig. 2:
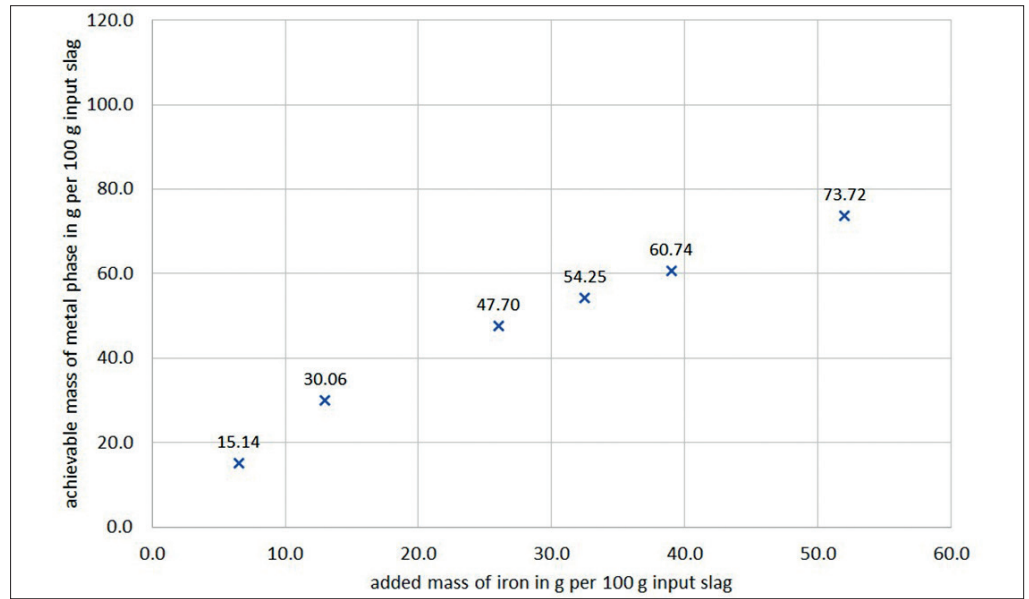Illustration of the most important components of the experimental setup

Fig. 3:
Dependency of the theoretical metal yield and the specified mass of reducing agent (iron) at 1300 °C (values from thermodynamic modelling with FactSage™)

of metallic phase is rising with increasing addition of iron as reducing agent. It is evident that adding 25 % of the stoichiometrically required mass of iron (6.5 g Fe/100 g slag) results in a metal phase with a mass of 15.14 g per 100 g of anode furnace slag. In this case, the copper content in the slag phase can be reduced from 34.28 wt.-% to 22.63 wt.-%. The resulting metal phase contains 97.27 wt.-% copper (refer to Figure 4), with the remaining portion being a mixture of other metals, primarily nickel and tin. When increasing the addition of iron up to 50 % of the stoichiometric amount (13.0 g Fe/100 g slag), the amount of achievable metal phase increases to 30.06 g per 100 g anode furnace slag while the copper content in the slag can be reduced to 8.04 wt.-%. The copper content in the metal phase slightly decreases to 93.44 wt.-%, but the iron content remains at 0 wt.-% (see Figure 4).

Increasing the iron addition to 100 % of the stoichiometric amount (26.0 g Fe/100 g slag) results in an achievable metallic phase with a mass of 47.70 g. The copper loss in the

slag can be reduced to 0.30 wt.-% in the remaining 73.20 g of secondary slag while its ferrous oxide content rises to 50.44 wt.-%. In the corresponding metal phase, the copper content falls to 70.16 wt.-% while for the first time in this simulation an iron content of 3.22 wt.-% is predicted. Further iron addition results in a further increase in the predicted metallic phase mass, up to 73.72 g when 200 % of the calculated stoichiometric mass of iron per 100 g input slag is added. However, the copper content of the slag cannot significantly be further reduced and remains at 0.21 wt.-%.

The mass of the secondary slag (73.2 g) and the spinel phases (~4.4 g) formed remain constant for additions of 100 % (26.0 g Fe/100 g slag) and 200 % (52.0 g Fe/100 g slag) of the stoichiometrically required mass of iron. On the other hand, the copper content in the metal phase decreases steadily from 97.27 wt.-% to 45.48 wt.-% as the iron addition increases, as shown in Figure 4. The iron content in the metal phase rises up to 36.13 wt.-% when adding 200 % of the needed mass of iron for a stoichiometric reduction.
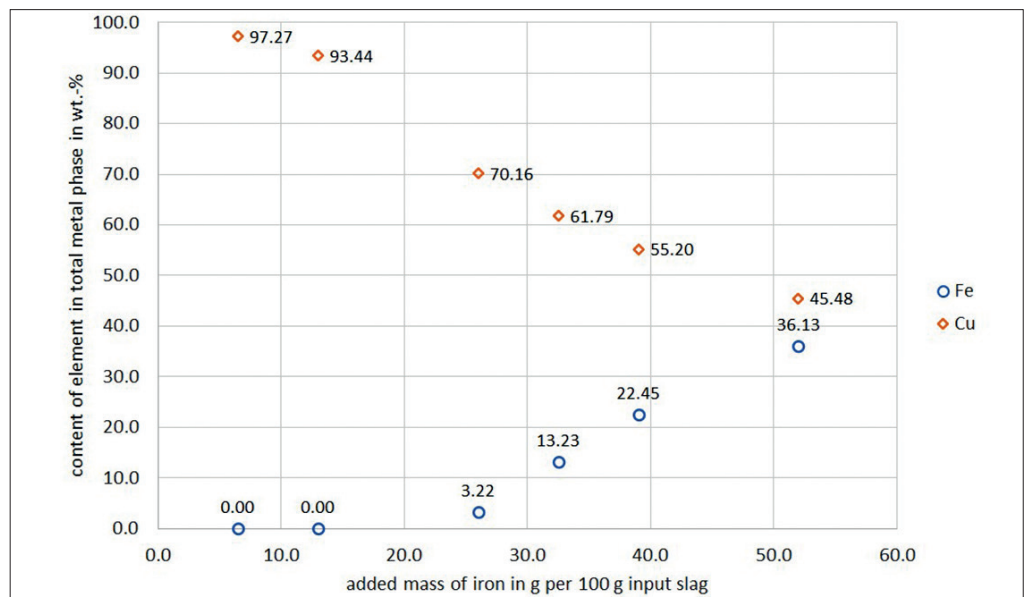

Fig. 4:
Dependency of theoretical metal contents in the metallic phase and the specified mass of reducing agent (iron) at 1300 °C (values from thermodynamic modelling with FactSage™)
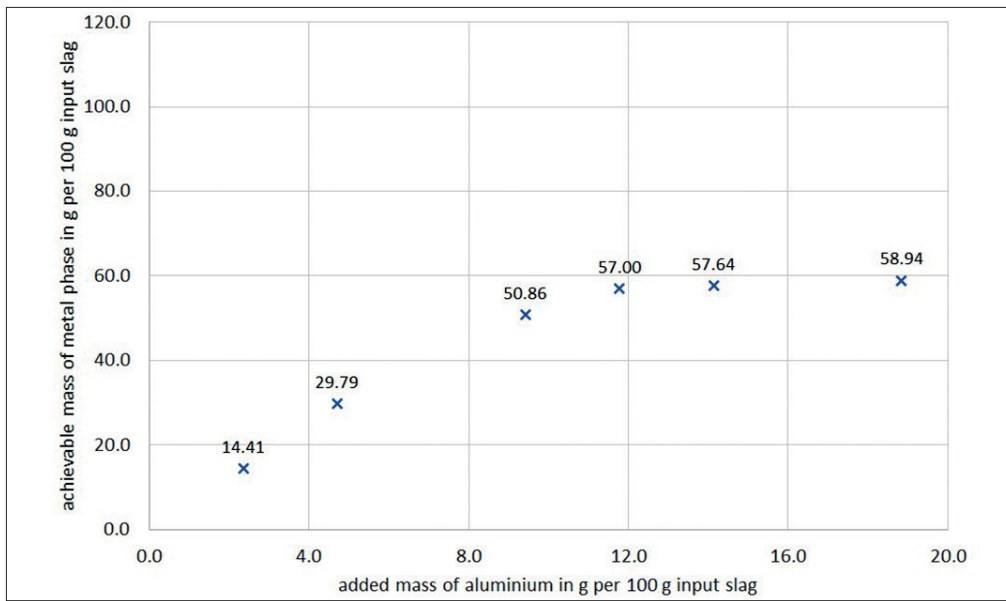
Fig. 5:
Dependency of theoretically metal yield on the specified mass of reducing agent (aluminium) at 1300 °C (values from thermodynamic modelling with FactSage™)

3.1.2 Utilization of aluminium as a reduction agent

Figure 5 shows the achievable mass of metal phase in g per 100 g input slag as a function of the mass of aluminium added as reducing agent in g per 100 g of input slag. The expected mass of the metallic phase is increasing with an increasing addition of aluminium as a reducing agent but seems to reach a plateau between 57 wt.-% and 59 wt.-% when adding between 125 % (11.8 g Al/100 g slag) and 200 % (18.8.0 g Al/100 g slag) of the stoichiometrically required reductant mass. The expected mass of the secondary slag decreases from 75.31 g at 25 % (2.4 g Al/100 g slag) to 37.14 g at 100 % (9.4 g Al/100 g slag) of the stoichiometric mass of reducing agent.

By adding 25 % (2.4 g Fe/100 g slag) of the needed stoichiometric mass of aluminium, the copper content in the slag can be reduced to 26.10 wt.-%. When increasing the aluminium addition up to 100 % (9.4 g Al/100 g slag) the copper content can be lowered down to 0.04 wt.-%.

Further addition of aluminium has the potential to reduce the copper content insignificantly to 0.00 wt.-%. With the rising addition of aluminium as reducing agent the mass of secondary slag is decreasing but the mass of spinel phases is increasing. Their mass is rising from 11.54 g at 25 % (2.4 g Al/100 g slag) up to 39.11 g at 200 % (18.8 g Al/100 g slag) of the stoichiometrically required aluminium addition. Not only the mass but also the type of spinel changes with increasing aluminium addition. At lower aluminium additions (25 % and 50 %), spinel phases containing zinc and nickel dominate ($ZnAl_2O_4$ and $ZnNi_2O_4^{2-}$), while the aluminium-containing species (mostly $Al_3O_4^-$) are quite low (13.36 wt.-% of spinel phases). However, their content rises to 88.67 wt.-% of the spinel phases with AlO_4^{5-} (11.07 wt.-%) as their bonding partner. The impact of spinel phases on metal/ slag phase separation cannot be assessed through thermodynamic simulation. The expected content of iron, copper and aluminium as a function of the mass of aluminium added as reducing
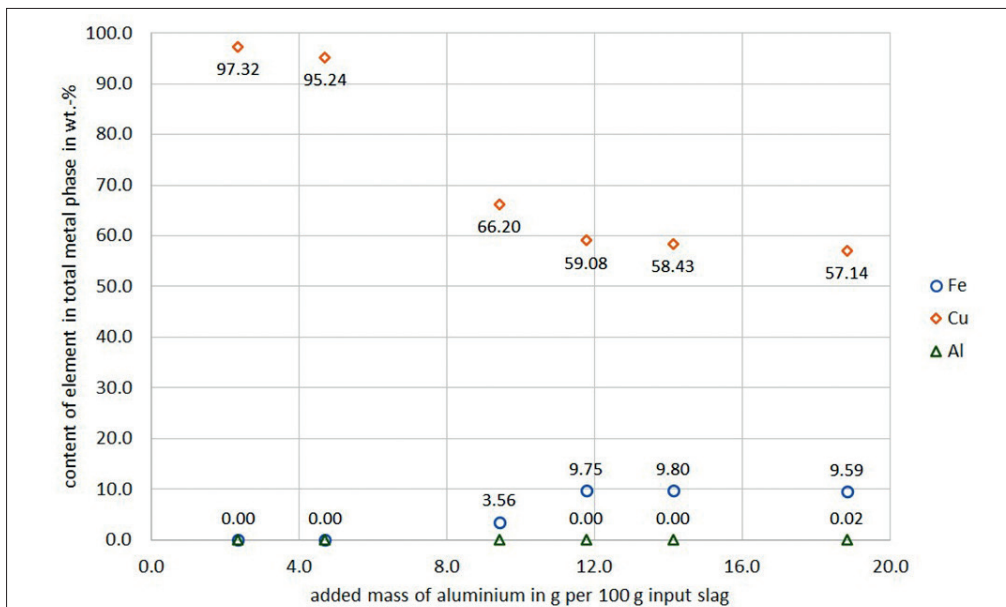

Fig. 6:
Dependency of theoretical metal contents in the metallic phase and the specified mass of reducing agent (aluminium) at 1300 °C (values from thermodynamic modelling with FactSage™)

agent is plotted in Figure 6. It can be seen that the copper content is at 97.32 wt.-% at 25 % (2.4 g Al/100 g slag) of the stoichiometric mass of aluminium added, while the iron and aluminium contents are also 0 wt.-%. The first time iron is predicted in the metallic phase is at the addition of 100 % (9.4 g Al/100 g slag) stoichiometric mass of aluminium. At this point 3.56 wt.-% of the metallic phase should consist of iron while the copper content drops to 66.20 wt.-%. The aluminium content still remains at 0 wt.-%. When further increasing the aluminium addition, the copper content in the metallic phase can be reduced to 57.14 wt.-%. The iron content in the metallic phase is only slightly altered between the addition of 125 % (11.8 g Al/100 g slag) and 200 % (18.8 g Al/100 g slag) of aluminium and remains at about 9.7 wt.-%. A single simulation result predicting aluminium in the metallic phase is for the addition of 200 % (18.8 g Al/100 g slag) stoichiometric mass of aluminium and is quite low at 0.02 wt.-%.

3.1.3 Utilization of magnesium as a reduction agent

The achievable mass of the metallic phase in relation to the mass of magnesium added as a reducing agent is plotted in Figure 7, while Figure 8 shows the copper, iron and magnesium contents in the metallic phase. From Figure 7, it can be seen that the mass of metallic phase achievable from 100 g of input slag increases with increasing addition of magnesium. By adding 25 % (2.9 g Mg/100 g slag) of the calculated stoichiometric mass of magnesium, 12.63 g of metallic phase can be obtained per 100 g of input slag. In this case, the copper content in the secondary slag can be reduced to 26.11 wt.-%. Increasing the magnesium addition to 100 % (11.8 g Mg/100 g slag) of the stoichiometric requirement increases the mass of the reduced metallic phase by a factor of four to 48.78 g. The copper content in the secondary slag is predicted to decrease to 0.44 wt.-%.

A further increase in the addition of magnesium results in a slight increase in the mass of the metallic phase obtained to

Fig. 7:
Dependency of theoretically metal yield on the specified mass of reducing agent (magnesium) at 1300 °C (values from thermodynamic modelling with FactSage™)
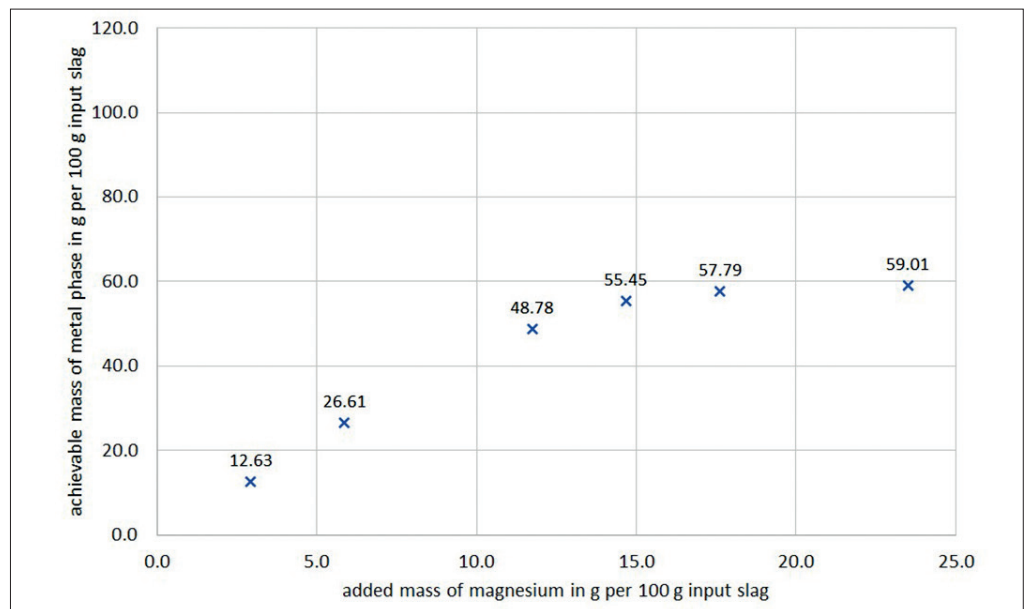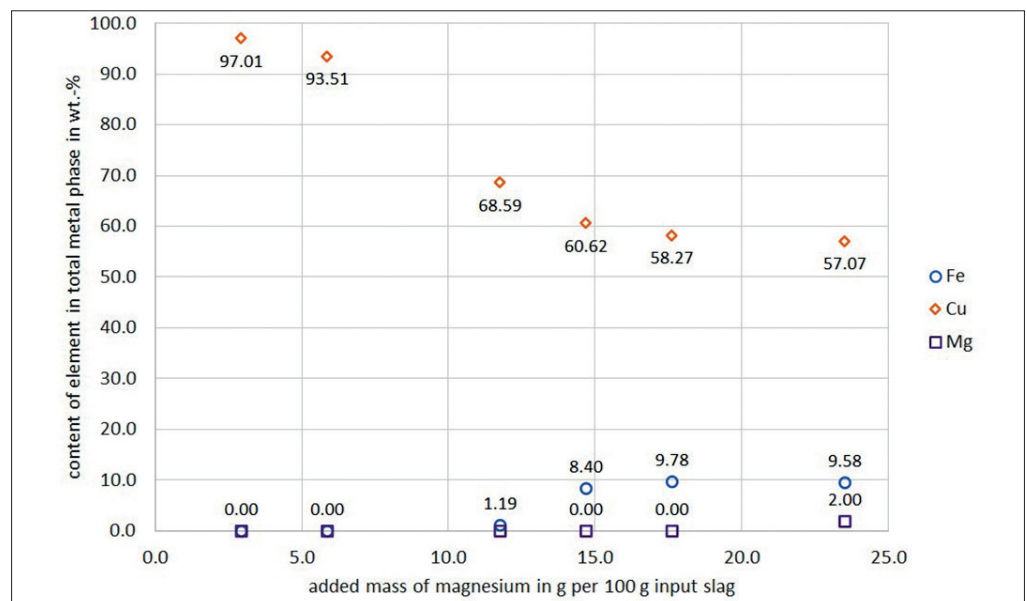
Fig. 8:
Dependency of theoretical metal contents in metallic phase on the specified mass of reducing agent (magnesium) at 1300 °C (values from thermodynamic modelling with FactSage™)

59.01 g, while the copper content in the secondary slag can be reduced down to 0.00 wt.-%. The mass of the secondary slag decreases from 82.05 g at 25 % (2.9 g Mg/100 g slag) stoichiometric magnesium addition to 51.56 g at 100 % (11.8 g Mg/100 g slag) addition and to 46.63 g at 125 % (14.7 g Mg/100 g slag) addition. With a higher amount of magnesium added, the mass of the secondary slag increases again up to 50.12 g. The mass of the spinel phase behaves in the opposite way to the slag: The spinel mass increases from 7.21 g to 11.44 g when the magnesium addition is increased from 25 % (2.9 g Mg/100 g slag) to 125 % (14.7 g Mg/100 g slag) and decreases to 9.37 g when the addition of magnesium as reducing agent is increased to 200 % (23.5 g Mg/100 g slag) of the stoichiometric amount. Over the whole range of the magnesium addition (25 % to 200 %), the content of the spinel phases $Al_3O_4^+$ and $MgAl_2O_4$ increases, while the content of $ZnAl_2O_4$ decreases. Similarly, to the case of aluminium use as a reduction agent, the topic metal/slag phase separation in the presence of spinel phases cannot be assessed through thermodynamic simulation.

The copper content in the metallic phase decreases as the magnesium addition increases, while the iron content is increasing. At a magnesium addition of 25 % (2.9 g Mg/100 g slag) of the stoichiometric required mass, the metallic phase consists almost entirely of copper (97.01 wt.-%), while the iron is absent. Increasing the magnesium addition up to 100 % (11.8 g Mg/100 g slag) of the stoichiometric mass results in a significant reduction of the copper content in the metallic phase to 68.59 wt.-%, while the iron content is predicted to be 1.19 wt.-%. A further increase in the magnesium addition predicts a metal phase containing 57.07 wt.-% copper, 9.58 wt.-% iron and 2.00 wt.-% magnesium at 200 % (23.5 g Mg/100 g slag) magnesium addition relative to the stoichiometric required amount.

3.1.4 Example mass balance of slag cleaning furnace using iron as the reduction agent

An example mass balance is shown in Figure 9. For a 100 % stoichiometric addition of iron at 1300 °C, the distribution of masses to the individual target phases and the contents of some selected elements and compounds in the individual phases are shown. The secondary slag represents the combination of all remaining and resulting oxidic phases (molten or solid). It should be noted that the mass balance is valid in thermodynamic terms, i.e. phenomena like metal/slag phase separation and metal droplet entrainment cannot be predicted here. In addition to the secondary slag, one or two metal phases are produced, which are also combined here to form a total metal phase, and the gas phase, which contains the fuming components. For the metal phase, the yield of the individual target metals and the iron, some of which is transferred to the metal phase, is also calculated.

The reaction releases just over half a gram of waste gas and fumes per 100 g of input slag, which are mainly composed of zinc and other volatile components. Under the present conditions, the volatilisation of lead and tin is low. Therefore it can be assumed that these elements are almost completely distributed between the metal phase and the secondary slag phase. By adding 26.0 g of iron per 100 g of input slag, the contents of the valuable elements in the oxidic phase can be greatly reduced: The content of cuprous oxide decreases from 38.6 wt.-% to 0.32 wt.-%, which corresponds to a copper loss to the slag phase of 0.29 wt.-%. A similar behaviour can be observed with lead and the other valuable metals - nickel and tin (see Figure 9). These metal oxides can almost be completely reduced and transferred to the metal phase. The corresponding metal phase is predicted to have a mass of 47.70 g, with the majority (>70 wt.-%) consisting of copper. The remaining 30 wt.-% is made up of a mixture of the other valuable elements (Ni, Sn, Pb and Zn), as well as a certain proportion of iron equal to 3.22 wt.-%.

When calculating and analysing the metal yield, it is noticeable that a full yield (>97.5 %) can be assumed for the metals copper and lead. For nickel and tin the yield is minimally reduced, but still exceeds 90 %. Only in the case of zinc the metal yield in the metallic phase is found to be less than 33 %. There are two reasons for this: First, some of the zinc is volatilised into the gas phase, which is not counted as metal yield here. Second, and more important under these condi-
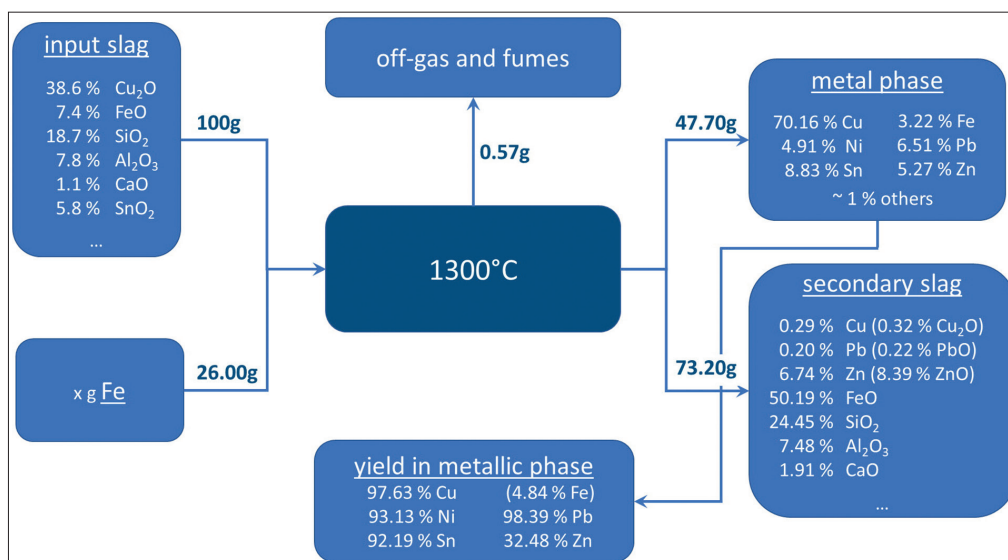

Fig. 9:
Mass balance for iron-based reduction with addition of 26 g iron per 100 g input slag at 1300 °C with contents of selected elements/compounds and calculated metal yield

tions, the reduction potential of the available iron is not sufficient to sufficiently disrupt the affinity of the zinc to oxygen so that more zinc could be converted into its metallic state.

3.2 Experimental results: Metallothermic reduction of anode furnace slag with iron

The results of the experiments for the reduction of the anode furnace slag with iron as reducing agent are plotted in Figure 10 and Figure 11. The mean mass of metallic phase obtained is plotted in Figure 10 as a function of the mass of iron added as reductant. Both axes are normalised to 100 g to make the graph comparable with the simulation results. It can be seen that the range of error between individual experiments is very small between replicates (two reps). In some cases, the error bars are not visible behind the mean markers. The data points resemble quite well a linear function (y = 1.8307 x + 2.8254) with a coefficient of determination of 0.9791.

For comparison, the result for a nil test, where the copper refining slag is simply melted without the addition of any reducing agent, is shown in Figure 10. By melting the anode furnace slag and allowing the metal droplets to settle, the mass of metallic regulus obtained is 6.27 wt.-%. If 25 % (6.5 g Fe/100 g slag) of the calculated mass of iron is added, the mass of regulus obtained is 14.67 g ± 1.00 g while the corresponding secondary slag retains its reddish

colour but in a weakened form. The reddish colour is due to the relatively high copper content in the secondary slag which is at 17.89 wt.-%. This reddish hue changes to a blackish hue when the iron addition is increased to 50 % (13.0 g Mg/100 g slag) of the required iron mass and changes to a greyish hue when 100 % (26.0 g Fe/100 g slag) of the stoichiometric mass of iron as reducing agent is added, see Figure 11. This greyish colour remains also when iron is added in excess of the stoichiometric amount. If the iron addition is increased to 200 % (52.0 g Fe/100 g slag) of the stoichiometric mass required, the mass of the metallic regulus reaches 99.90 g ± 0.90 g.

The mass of the secondary slag produced is about 50 g per 100 g of input slag, so the mass of the slag is halved, when adding 13 g Fe per 100 g input slag while the content of ferrous oxide content in the secondary slag is increased to 39.65 wt.-% while the copper content is reduced to 1.52 wt.-%.

With 100 % (26.0 g Fe/100 g slag) stoichiometric mass of iron as reducing agent a metallic regulus with a weight of 58.10 g ± 1.03 g is obtained, while the copper content in the secondary slag is lowered down to 1.43 wt.-%. The corresponding secondary slag reaches a mass of just under 80 g per 100 g input slag. At 150 % (39.0 g Fe/100 g slag) iron addition, the lowest copper content in the slag was observed at 0.68 wt.-%.

Fig. 10:
Dependency of experimental metal yield on the specified mass of reducing agent (iron) at 1300 °C (values from experiments; average values and spread width from repeated experiments above; resulting function and coefficient of determination is given)
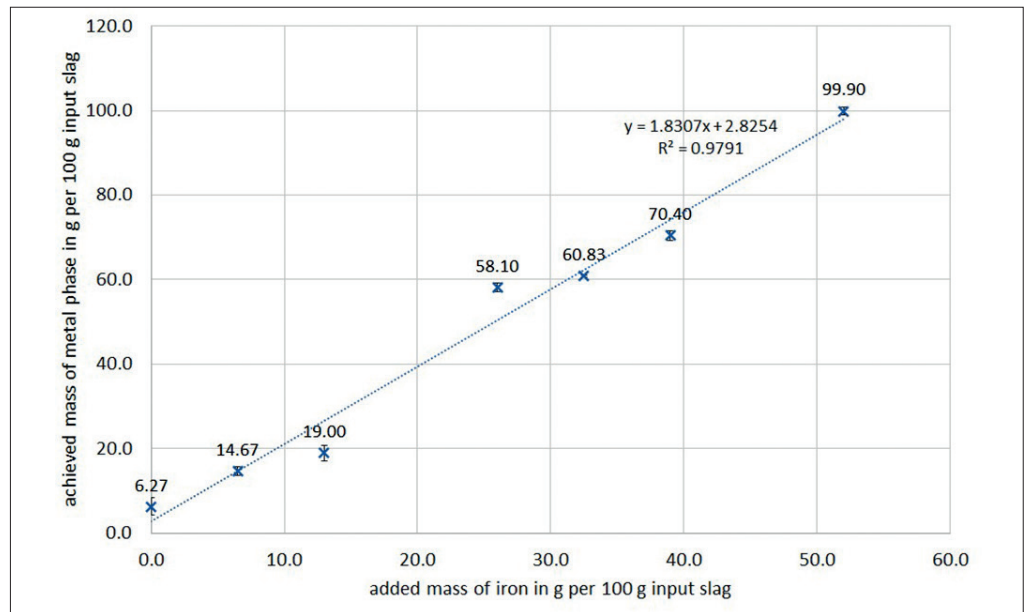

Fig. 11:
Prepared samples of secondary slags with rising iron addition (from left to right)
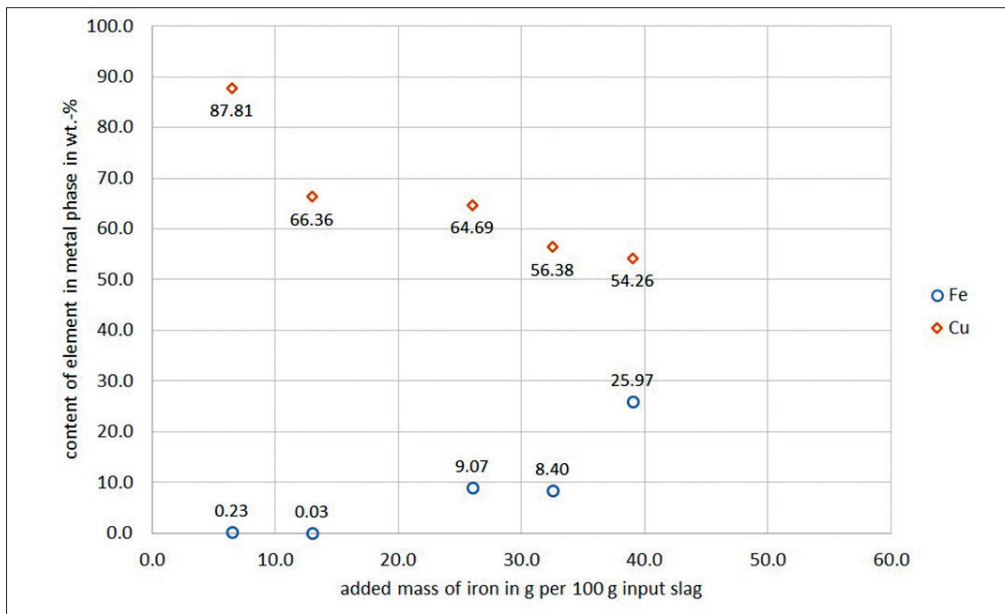
Fig. 12:
Dependency of experimental metal contents in metallic phase on the specified mass of reducing agent (iron) at 1300 °C

Figure 12 shows the copper and iron contents in the resulting metallic phase as a function of the mass of iron added per 100 g of starting slag. The iron content in the metallic phase starts at 0.00 wt.-% and rises up to 25.97 wt.-% when an iron addition of 150 % (39.0 g Fe/100 g slag) of the stoichiometric needed mass is applied. The copper content decreases from 87.81 wt.-% at 25 % (6.5 g Fe/100 g slag) of the stoichiometric iron addition to 54.26 wt.-% at 150 % iron addition. The difference between the sum of the iron and the copper contents and 100 % represents the content of other metals such as nickel, tin, lead and zinc in the metallic phase.

4   Discussion

Comparing Figure 3 and Figure 10, both showing the mass of metallic phase as a function of the mass of iron added as a reducing agent, it can be seen that the trends are similar. The mass of metallic phase appears to be linearly dependent on the mass of iron added as a reducing agent. A closer comparison of the two plots shows that the metallic phase masses obtained in the experiments are generally higher than those derived from the simulation. Contrary to the apparent linear dependency of the metallic phase mass on the addition of iron as a reducing agent, the plots in Figure 5 (considering the addition of aluminium) and Figure 7 (considering the addition of magnesium) show a different behaviour. The mass of metallic phase seems to follow a saturation function which has an upper limit at about 59 g.

A possible explanation can be found in the chemical activity of the metals used as reducing agents. While aluminium and magnesium have an ignoble character, the nobility of iron is high enough to remain in the metallic state under these conditions. Iron added in excess (more than 100 % of the calculated stoichiometric mass) dissolves directly in the metallic phase. This is shown by the iron content of the metallic phases, which increases steadily as more iron is added, while the copper content decreases linearly (see Figure 4). The iron content in the metallic phases when aluminium and magnesium are used as reducing agents is limited to 9.8 wt.-% in this study (compare Figure 6 and Figure 8).

Further evidence for direct dilution of the excess iron into the metallic phase is provided by the compositions of the secondary slags and spinel phases. Their masses and compositions remain almost unchanged above the addition of 100 % (26.0 g Fe/100 g slag) of the required iron mass. The FeO content of the secondary slags varies between 50.4 wt.-% and 52.09 wt.-% with an unchanged silica content of 25.9 wt.-%, indicating that the addition of iron does not lead to further reduction of addition metal oxides within the slag. The mass of the secondary slag can be predicted to be 73 g. This behaviour was only partially demonstrated in the actual experiments: When iron is added in an amount less than 100 % (26.0 g Fe/100 g slag) of the stoichiometric requirement, the secondary slag mass obtained exceeds the prediction, whereas when iron is added in large excess (200 % – 52.0 g Fe/100 g slag), the secondary slag mass obtained is well below the prediction.

If 100 % of the calculated mass is added to reduce all the valuable metal oxides (Cu_2O, NiO, PbO and SnO_2), it might be assumed that no iron should be diluted into the metallic phase. However, Figure 4 and Figure 12 show that this is not the case in the simulation and also in the practical experiments. The simulation predicts an iron content of 3.22 wt.-% in the metallic phase, while in the experiments an iron content of 9.07 wt.-% is obtained. A possible explanation could be that in the experiments more iron is brought directly into the metallic phase because some of the starting material (copper in the anode furnace slag) is already in its metallic state and therefore does not require reduction but only a molten environment and time to settle into the metallic phase. Therefore, the calculated amount of iron required for stoichiometric reduction is likely to exceed the actual amount, with the excess iron being transferred to the metallic phase, explaining the discrepancy noted above.

Another point to consider is the miscibility gap in the copper-iron thermodynamic system. Iron and copper are only
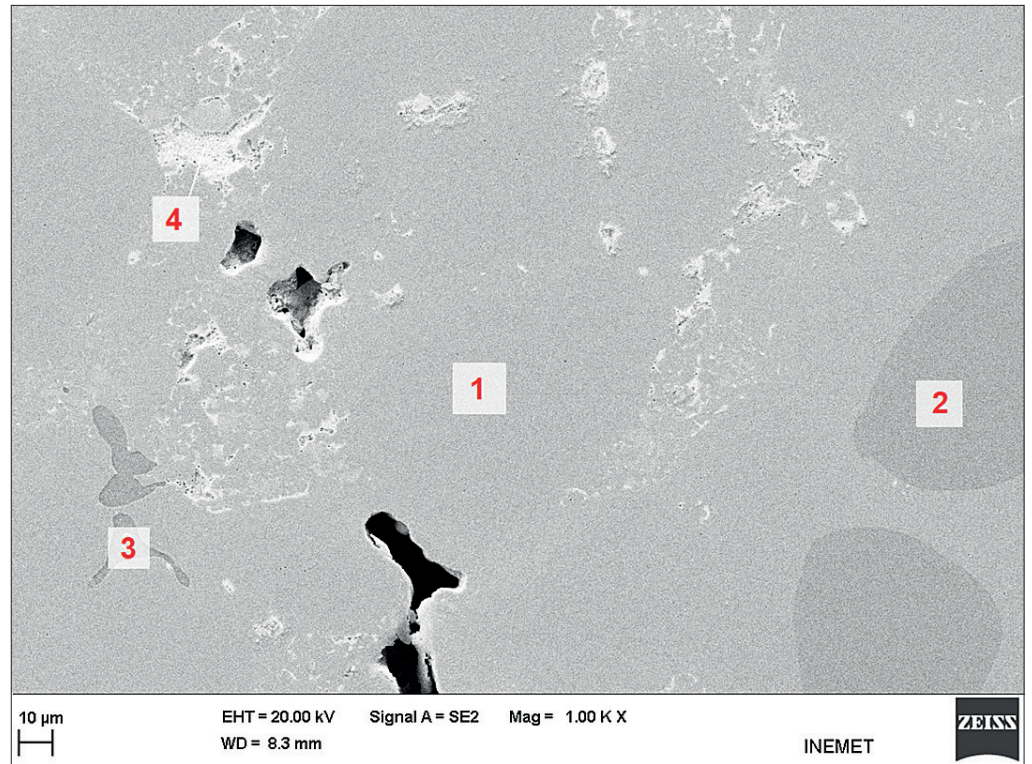
Fig. 13:
Section from a black copper sample, recorded and analyzed using SEM-EDX (Zeiss Ultra55), phase components numbered

partially soluble in each other in the liquid state. The limit of iron solubility in solid copper is about 3 wt.-%, while copper solubility in solid iron is limited to 13 wt.-%. In the liquid state, the homogeneous molten phase separates into a copper-rich and an iron-rich melt at temperatures below 1397 °C [14]. This behaviour has also been demonstrated in [15] by SEM-EDX analysis of solidified black copper phases with high iron content, (see also Figure 13). However, this separation of the two liquid metal phases cannot be observed with the naked eye, but only at microscopic resolution, because the observed iron-rich parts in the copper-rich matrix are smaller than 80 μm in diameter [15]. This type of metal phase separation is predicted by thermodynamic modelling using FactSage™. For a better understanding of the whole phase composition Table 2 is given. Four different phase components can be identified. While copper and iron are present in every phase in changing amount other elements like nickel, tin and lead are only present in a limited number of the phase components. The "copper-rich matrix" and the "iron-rich grains" resemble the maximum solubility of the elements copper and iron in each other quite well [14]. The other two components have their origin in the combination of copper and lead, which form together another miscibility gap.

When 100 % of the stoichiometric required mass of iron is added as a reducing agent, a second metallic phase is predicted with a mass of 0.23 g. As the addition of iron is increased, the formation of the secondary metallic phase also increases at the expense of the first metallic phase, whose formation decreases. In Figures 3, 5 and 7 the total mass of the two metallic phases is plotted as a function of the mass of each reducing agent added (as the total metallic phase), since in the actual experiments the two metallic phases (see

Table 2: Composition of the found for different phases [wt.-%]

	Cu	Fe	Ni	Sn	Pb
1 "copper-rich matrix"	91.3	2.7	3.9	2.1	–
2 "iron-rich grains"	13.3	75.5	11.2	–	–
3 "copper and lead rich inclusions"	43.3	11.7	–	–	45.0
4 "lead-rich inclusions"	2.1	4.3	–	0.2	93.4

also Figure 10) cannot be distinguished. The formation of a second metallic phase when aluminium and magnesium are added as reducing agents starts at 125 % of the required reducing agent mass.

The addition of aluminium and magnesium should also result in the separation of a second metallic phase, as predicted by the simulation, when 125 % (11.8 g Al or 14.7 g Mg/100 g slag) of the calculated stoichiometric mass of the respective reductant is added. The segregation is caused by the reduction of ferrous oxide to its metallic state, leading to the formation of a second metallic phase when the iron content in the first metallic phase exceeds 3 wt.-%. Aluminium and magnesium themselves are unlikely to be dissolved in the metallic phase, as shown in Figure 6 and Figure 8. Only when aluminium and magnesium are added in large excess are low levels of aluminium (0.02 wt.-%) and magnesium (2.00 wt.-%) predicted. Most of the mass of aluminium and magnesium added as reducing agents is slagged and found in the secondary slag or bound in spinel formation. The crucibles used are another source of aluminium or aluminium oxide. During the tests, some adhesion between the slag and the crucible was observed, which influenced the separation after the end of the test. However, the integrity of the crucibles was not reduced during the tests carried out here and no loss of wall thickness was observed.

In the secondary slag, aluminium and magnesium increase the liquidus temperature [16]. Increasing melting points result in increasing viscosity at the lower end of the melting range. Both elements also lead to increasing spinel formation as the addition of each element increases [17]. Spinel formation also leads to increasing viscosity at a given temperature, as spinels have high melting points above 1300 °C [1] and the resulting solid particles increase viscosity [7]. This has to be raised as a major concern when considering aluminium or magnesium for the metallothermic reduction of the anode furnace slag, as the high spinel content estimated could make the secondary slag unworkable.

This behaviour is more pronounced for aluminium than for magnesium, which is intermediate between iron and aluminium in its slagging and spinel formation behaviour. Therefore, aluminium and magnesium need to be studied in more detail to fully understand their behaviour in the real process.

5   Conclusions

This study has shown that slag from an anode furnace can be used to produce a copper-rich metallic phase by separate ferro-thermic reduction. Separate treatment of this type of slag can be used to break the cycle of concentration of unwanted and interfering elements and compounds (e.g., of chromium) in the secondary copper process. The chromium content achieved in the metallic phases is quite low and therefore no chromium is returned to the secondary copper process where these metallic phases are used in earlier aggregates of the copper production unit chain such as the Peirce-Smith converter. Experiments have shown that the copper content in the secondary slag can be reduced to 1.12 wt.-% by increasing the mass of iron as a reducing agent up to 150 % (39.0 g Fe/100 g slag) of the stoichiometric requirement. On the other hand, this increases the iron content in the metallic phase produced to 25.97 wt.-%, which is undesirable and the iron must be slagged in further treatment. If 100 % (26.0 g Fe/100 g slag) of the stochiometric mass of iron is added, a metallic phase with a mass of 58.10 g can be obtained with an iron content of 9.07 wt.-%. The copper content in the secondary slag can be reduced to 1.43 wt.-%. The trends in the simulation and experiments are quite similar, while the exact values in the experiments for the mass of metallic phase obtained exceed respective predictions, especially at higher iron additions.

6   Outlook

The secondary slag obtained is lower in mass, copper content and other valuable elements such as nickel, tin, lead and zinc, but its composition needs to be studied in terms of use and suitability. This is because most countries in the world have strict regulations on the permitted composition of construction materials and additives. The secondary slag must therefore meet these requirements in order to be used in this way. An adjustment of the composition of the secondary slag produced is being investigated. Taking into account the iron and silica values obtained in the slag during modelling and experiments (see for example Figure 9, where FeO:50.19 wt.-% and SiO$_2$:24.45 wt.-%), it is possible to obtain a fayalitic type of slag, which is well known in the primary copper industry and has more established routes of utilisation. A further aspect to consider here is the further removal of zinc (see Figure 9, where ZnO: 8.49 wt.-%), potentially through a zinc fuming operation.

The simulation of aluminothermic and magnesiothermic reduction is promising for a good output of metallic phase, while the iron content can be limited to less than 10 wt.-%, which cannot be easily achieved by using iron as a reducing agent. However, the high addition of aluminium and magnesium would lead to high spinel formation, which has a negative impact on the process. Therefore, the possibility of using high levels of aluminium and magnesium as reducing agents should be carefully investigated, with particular emphasis on the slag composition. For this further research, the slag composition should be adjusted from the outset, as the viscosity of the slag increases with increasing alumina and magnesia content. This is true since the latter oxides lead to the formation of solid spinel phases, with high melting points. The alumina and magnesia content also has a direct effect on the basicity of the slag. Alumina lowers the basicity mainly because the addition of aluminium as a reducing agent can also reduce ferrous oxide to metallic iron, which reduces the slag to basic oxides. Magnesium as a reducing agent has the same effect as ferrous oxide, but acts as a basic oxide itself. Basicity plays an important role in the chemical durability of the refractory lining.

Another possible reducing agent for the reduction of slags is hydrogen, as other studies have shown [18, 19]. Hydrogen has been shown to be effective in reducing the oxides of valuable metals even in slags with lower levels of oxides. It has been shown that reduction to very low copper contents in a submerged arc furnace (SAF) can reduce the cuprous oxide content by up to 25 % and also appears to be effective in removing ZnO and PbO [18]. Further investigation of the use of hydrogen as a reducing agent for slags containing large amounts of valuable metal oxides, such as those used in this study, is an alternative that should be investigated in the future. This could potentially be realized also in conjunction with ferrothermic reduction in an effort to minimize overall slag production.

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