Determining critical parameters of hydrogen reduction treatment of low copper-containing primary slags

Gunnar Hovestadt, [Marvin Coldewe, Bernd Friedrich]

Institute of Process Metallurgy and Metal Recycling (IME) RWTH Aachen
Intzestraße 3
Aachen, Germany

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Abstract

Due to European Union's aim to be climate-neutral by 2050, fossil reduction processes will no longer be state of the art in several years. One option to decrease fossil CO_2 emissions is the replacement of coal with hydrogen as a reductant agent. To understand the influences of the reducing reaction, it is necessary to simulate and model these. In this paper, the reaction of slag reduction below 4 wt.% copper is to be determined. FactSage^{TM} simulation and experimental trials deliver data to fill the models and figure out important parameters for injected hydrogen reduction in the molten phase.

1 Introduction

Within a circular economy no waste stream could be neglected. Therefore, the recovery of metals from waste streams is a huge metallurgical challenge. As copper slags are part of the primary winning and also recycling of E-scraps it constitutes important technology metals for the digital and electrical transforming of our economy. The reduction commonly takes place with carbon containing sources producing CO_2-emissions. To cut of those emissions and investigate a selective copper reduction process hydrogen was injected into primary based copper slags.

For a primary production process RÖBEN et al. [1] found out, that the common reduction process of slags produces around 20 % of the total emission of the production, seen in figure 1. The total amount of CO_2 produced per ton of copper varies between 1 and 9 t CO_{2e}/t Cu [2]. The impact could be large, when multiplying the value by 25 mio. t refined copper produced per year [3].

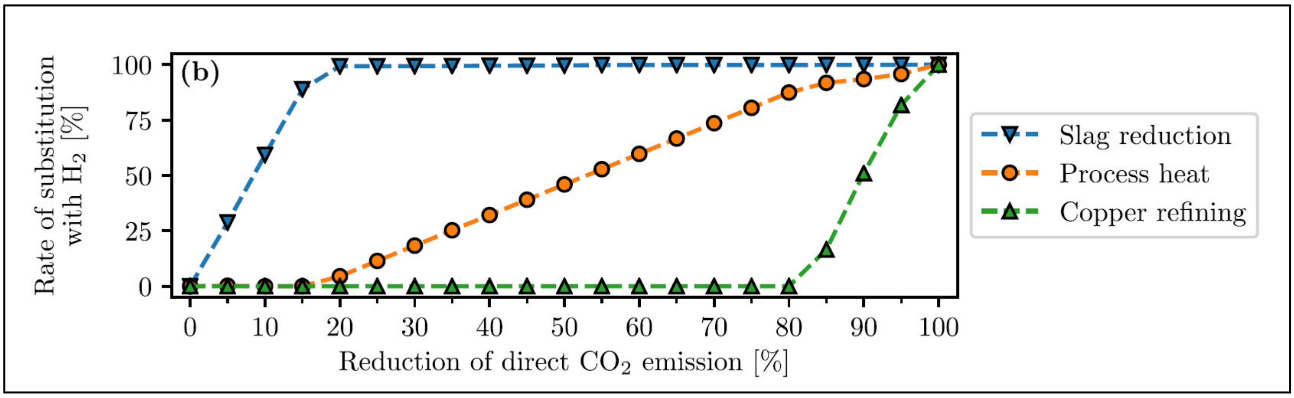

Figure 1: Experimental setup for small scale experiments at IME Aachen [1]

The second point of the metal recovery shows potential for the industry. Increasing demand and decreasing mining capacities are one of the challenges for the next decades [3]. Primary copper slag is produced by around 2-3 t per ton of copper, with concentrations around 1 wt.% Cu left inside after cleaning common processes [2, 3]. This copper left should be recovered and could provide around 350 kt/year copper (70 % copper recovery rate), which is the capacity of a 19th biggest smelter.

Several investigations could be found in literature to recover metals from copper slags. One approach is to reduce the slag to an iron with high copper contents [4, 5] or do a selective prereduction for copper winning [6]. Most of the studies were performed with carbon carriers like coal or carbon fibres. They show, that copper recoveries of more or less 100 % were possible, but within a selective winning the left copper content is around 0.3 wt.% producing a alloy with 50:50 Cu:Fe. The final iron alloy varies in copper content between 0.8 to 4 wt.%. Zhang [7] tries to recover the metals environmental friendly with hydrogen in a solid state process using hydrogen and lime. They found out, that high amounts of lime have to be used to free the iron out of the fayalitic phase to reduce free iron oxides to metal. They show higher reduction rates with an increasing hydrogen concentration. Reduction of iron oxides are performed by [8] show faster reduction when using hydrogen instead of carbon monoxide. A trend of a first order reaction could be seen, when the silica content in melt was below 20 wt.%.

Kinetics for first order reactions say, that the reduction rate will be doubled, if one of the educts will double. Therefore, one could double the concentration of hydrogen to show the impact on the reduction. In a time, based diagram an exponential curve could be easily plotted to detect the rate constant as the exponent. To understand different, evaluate the time determining step of the reduction, it could be split into 3 major steps. The diffusion and transport in the gas phase, a diffusion through the interface of gas and slag with the reaction and the mass transport of the molten phase.

This work aimed for the determination of the slowest process step of the reduction of copper from primary copper slags. The authors investigate the influence of hydrogen concentration and the turbulence by different flow rates injected using two different slags with 1 and 2 wt.% copper.

2 Experimental

A refractory-lined crucible was used for the experimental investigation. For the lining Al_2O_3-Cr_2O_3-based refractory was mixed with water, cast and burned inside the crucible. An amount of 1.5 kg of slag was processed in this setup. Above the melt, a lid made of the same refractory material was placed inside a protection refractory wall. The lance, made of sintered Al_2O_3, was inserted slightly above the bottom of the melt. The gas mixture was adjusted by a computer-controlled, mass flow controller (Bürkert GmbH, Ingelfingen, Germany), gas mixing station. Gases used have a purity of above 99.9 vol.%. The schematic setup could be seen in Figure 2. The slag was charged into a pre-heated crucible and molten under an inert nitrogen atmosphere.

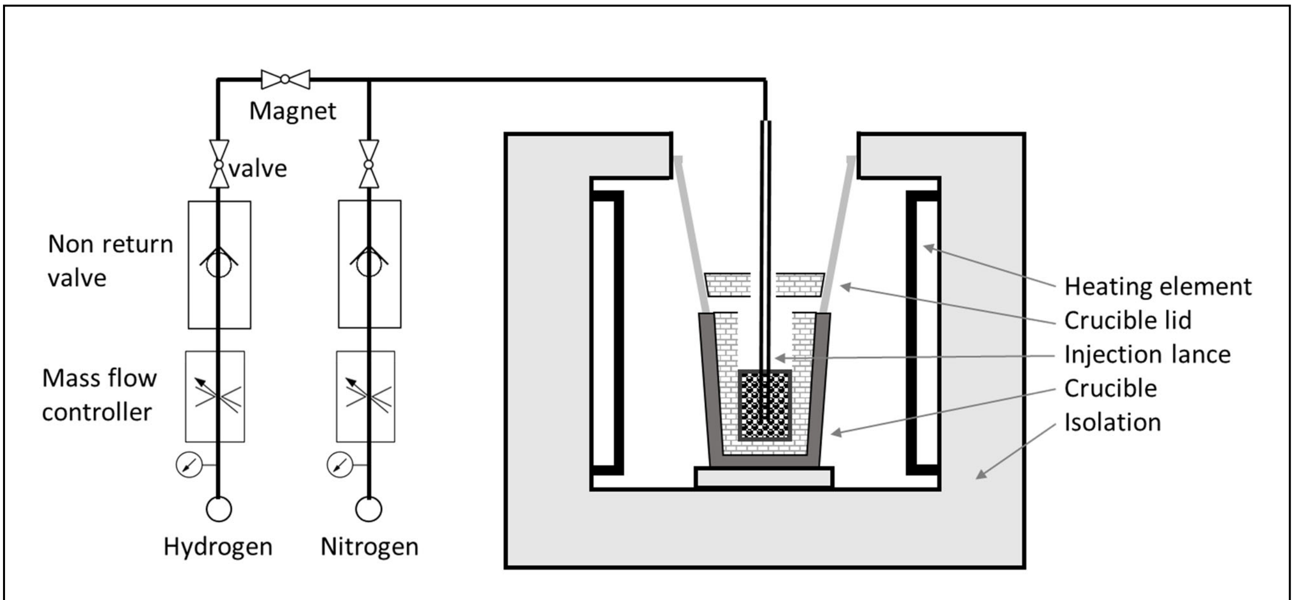

Figure 2: Experimental setup for small-scale experiments at IME Aachen

Two types of slag were processed within the study. A reduced primary slag from a submerged arc furnace and a second slag mixture with higher copper content should show different limitations within the reaction. Both slags have high contents of fayalite phase as well as small contents of impurities. The iron in hematite content is low with ratios of 100:3 (FeO to Fe_2O_3). The complete composition could be seen in table 1.

Table 1: Composition of used primary copper slag

	Fe	Si	Cu	Pb	Zn	Ca	Al	Ni & Sn	Rest
Slag 1	38.8	15.3	0.9	0.3	1.2	1.7	2.4	< 0.1	39.4
Slag 2	37.6	15.8	2.0	0.7	1.0	1.8	2.2	< 0.2	38.7

3 Thermochemical simulation

Calculations were performed using FactSage™ 8.0 software [9]. Linked databases were FactPS, FToxid and FScopp to calculate the reduction simulation of copper slags. To evaluate the reduction progress within a hydrogen injection the Equilib tool was used in open calculation mode. With the start of injection remaining hematite will be further reduced. The copper content stays constant for half a liter hydrogen per kg slag and decreases to 0.54 wt.% Cu_2O (0.49 Cu). After the low copper content is achieved the iron reduction starts. This results from high volume fractions of water vapor from hematite and copper oxide reduction. It drops below 50 vol.% for the first time at 1.44 (l H_2)/(kg slag), whereas the hydrogen fractions exceed 10 vol.%. The other oxides shown in figure 4 behave like copper and start decreasing after initial hematite reduction. The lead oxide content at 1.44 l/kg is 0.2 wt.% and 1.38 wt.% for zinc oxide. The recovery of copper is 50.7 % on this point and the removal rate of lead and zinc are 41.2 and 10.6 %. Last mentioned oxides will be fumed of to flue dust. Zinc could reach up to 30 vol.% of the off-gas stream. Injecting more hydrogen than 1.44 l/kg will reduce iron and form a solid-state metal phase and a slag phase. The copper relative content will not further decrease in the simulation. The content of zinc and lead will be fumed off to 0.07 wt.% lead and 0.88 Zinc at 4.8 l/kg hydrogen. Experimental results for the fuming behavior with hydrogen are published in the proceedings of the slag valorization symposium 2023. [10]

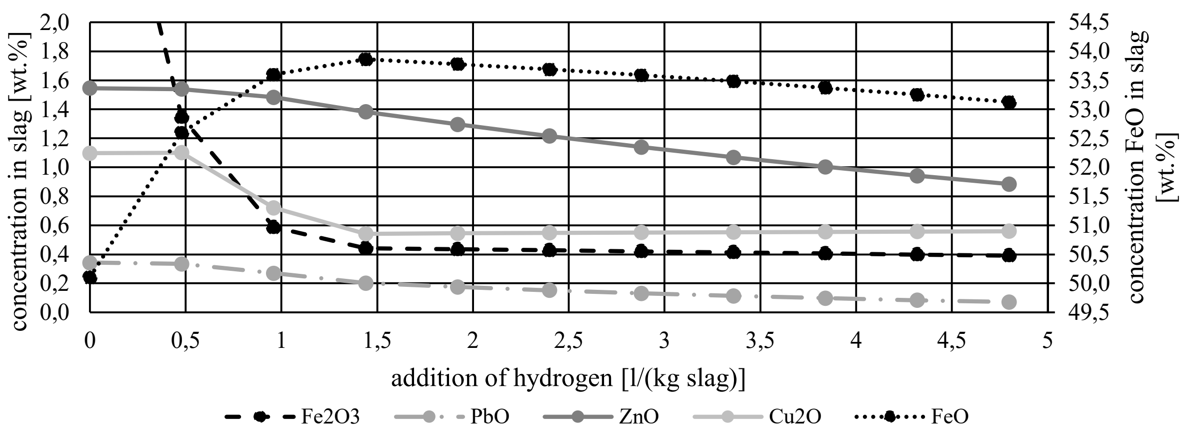

Figure 3: Simulation of used parameters at 1300 °C using FactSage™ 8.0 Equilib [9]

As a result, from simulation the most important point in the selective copper reduction by hydrogen treatment is the exact amount of introduced hydrogen. Theoretically a recovery of 50 % and a metal phase with 88 wt.% Cu could be achieved. The fuming of zinc and lead is thermochemically possible, but requires high amounts of hydrogen. In more detailed simulation the influence of the hydrogen concentration could not be significantly shown. Therefore, the result is not shown in a separate figure. To determine limiting kinetic factors 14 trials were performed. They aim for different concentrations of hydrogen gas injected (trials 1 to 8) and different copper concentrations. Also, the influence of the turbulence of the melt was determined with different flow rates (trials 7-14). The concentration range of hydrogen was chosen to be 15 to 90 vol.% for low copper content and 100 % for higher copper concentration. Table 2 shows the table of performed tests and parameters adjusted. In the trials the flow rate was set with hydrogen and nitrogen. The amount of hydrogen added was figured out in non-published trials to be around 36 l/kg for low copper contents and 60 l/kg with high copper.

Table 2: Table of performed experiments

Trial	Temperature [°C]	Hydrogen conc. [vol.%]	Flow rate [l/min]	Copper conc. [wt.%]
1 / 2	1300	15	2	0.94
3 / 4		30		
5 / 6		45		
7 / 8		90		
9 / 10		90	1	
11 / 12		100	1	2.0
13 / 14			2	

4 Experimental results

The analytical results from trials 1 to 8 could be seen in figure 5 in dependence of the injection time. The analytics were done with pressed tablet with XRF (Bruker, USA and Malvern Panalytics, UK). For every concentration two trials were performed and summed up in the graph. A function was plotted in exponential shape to point out the rate constant easily. Copper content is decreasing directly which was not expected from thermochemical simulation. Also, the percentage of copper is dropping below the limit of 0.49 wt.% from simulation within all concentrations. The reduction speed is increasing with the concentration injected, due to higher amounts of hydrogen injected per time. The lowest amounts of copper were determined to be 0.31 wt:% Cu.

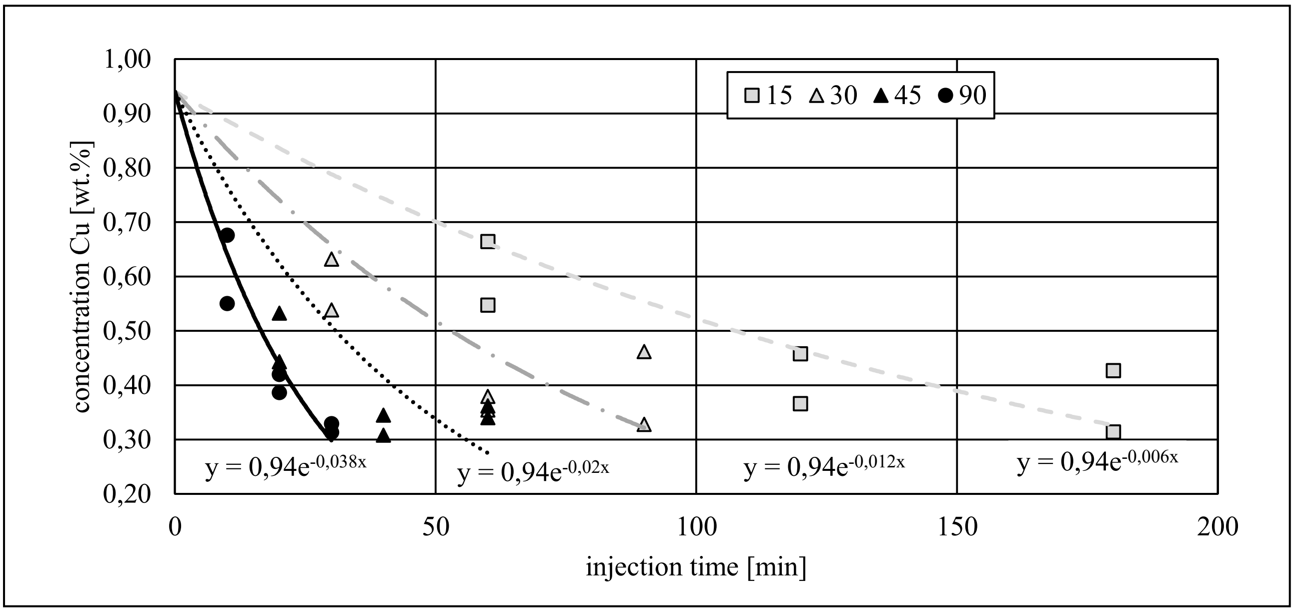

Figure 5: Influence of hydrogen concentration on reduction speed with primary copper slag with 36 l/kg hydrogen addition at 1300 °C

5 Discussion and outlook

In this paper the reduction of copper from primary, fayalitic slags was investigated. The initial copper content was 0.9 and 2.0 wt.% and the hydrogen concentration was set between 15 and 90 wt.%. It could be seen, that with sufficient turbulence in the melt the rate constant could be set as a linear function of hydrogen concentration. The reduction of low concentration slags reacts in first order, meaning the doubling of hydrogen concentration doubles the rate constant. Final achieved copper contents are lowest 0.3 wt.% by hydrogen treatment with sufficient reductant amount. The turbulence could enhance the reaction rate by up to 40 %. Therefore, the liquid transport is set to be the time determining step in the process. In further investigations other concentrations of hydrogen will be tested and also pilot scale tests are foreseen. The influence of the scale and melt column height will be tested for efficiency and rate constants.

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