THE SUBMERGED ARC FURNACE (SAF) STATE OF ART IN METAL RECOVERY FROM NON-FERROUS SLAGS

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Introduction

In metallurgical production, the traditional aim is to increase recovery of metal to the maximum. It becomes apparent that the application of the submerged arc furnace (SAF) in non-ferrous metallurgy processes is increasing, in particular for the extraction of zinc, lead, copper and nickel, but also for the processing of residues and stripping of slag. SMS group has been developing this technology for 100 years, and has supplied a diverse market with about 700 furnaces and major furnace component [2]. During this time numerous applications were constantly developed serving various user [3]. Especially slag cleaning furnaces have supplied more than 20 in the last 40 years. Slag cleaning furnaces are commonly connected to smelting units such as Teniente and Noranda converter, Outokumpu flash smelter, reverbertory furnaces. The main function of the furnace is the reduction of the matte and metal level in the slag. Depending on the upstream process, the slag is either liquid-charged via launders into the furnace or is cold-charged in solid form via conventional feeding systems.

Principle of SAF

The SAF works with electrical energy which is converted into heat, mainly using the electrical resistance of the burden or molten slag. The electrodes are immersed in the melt which provides the required energy exchange area between electrode and melt. The melt is the heat exchange medium which supplies the energy required for melting and chemical reactions of the charge [1]. The submerged arc furnace comprises the following major equipment parts as seen in Figure 1.
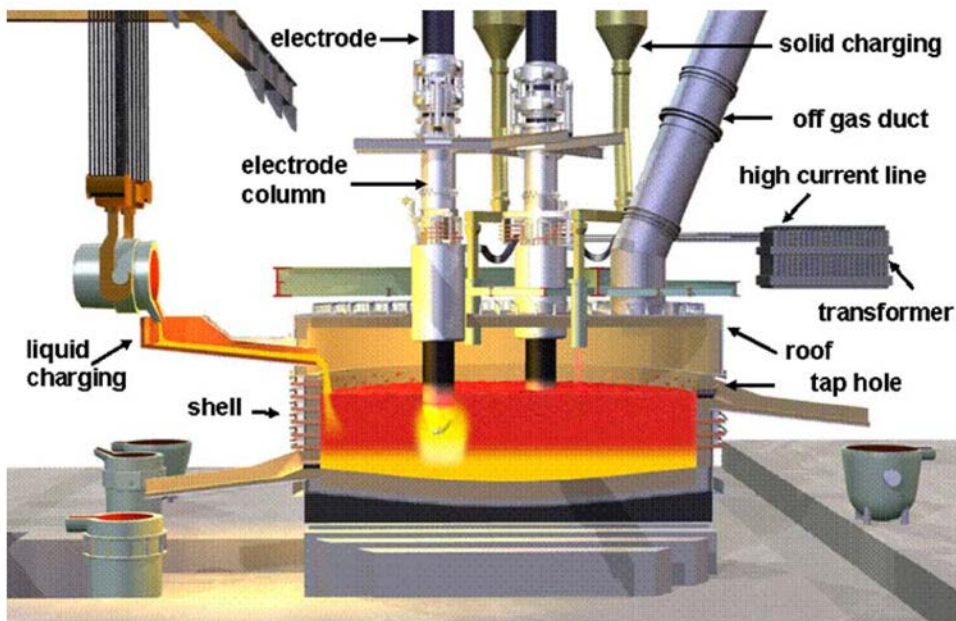
Figure 1: Main components of a submerged arc furnace [1]

A typical furnace with slag operation comprises a round or rectangular furnace shell with tap holes for slag, matte or metal. The furnace shell is refractory lined and – if additional shell cooling is required by the process – water-cooled. Various sidewall cooling systems are available depending on the specification of the process: rinse cooling, spray cooling, chamber cooling, channel cooling or Cu-strip cooling (see Figure 2). For safety reasons the cooling channels remain outside the furnace shell. In certain applications such as PGM (Platinum Group Metals), pig iron and several ferroalloys and non ferrous processes, a sufficient heat removal rate will create a layer of frozen slag, the so-called "freez line", which protects the remaining sidewall lining. In this case a high thermal conductivity of the lining is of capital importance.
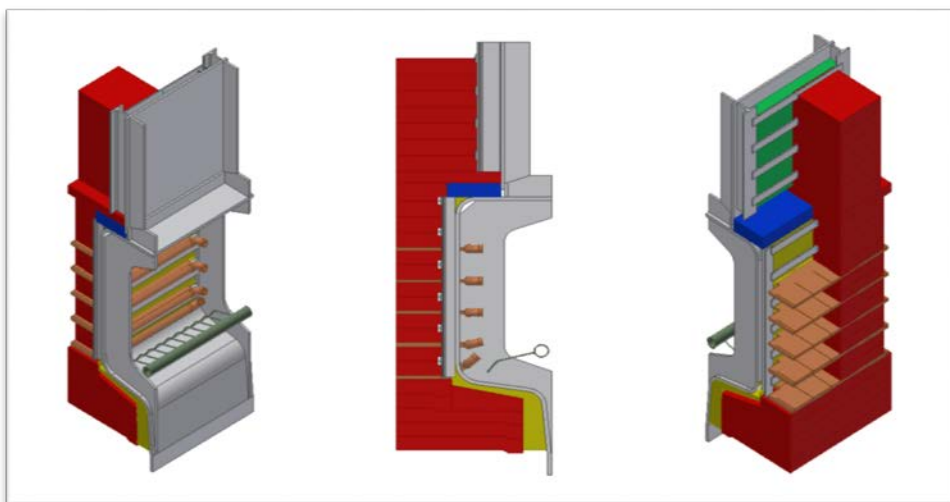

Figure 2: Side wall copper stripe cooling [5]

The shell bottom is cooled, if cooling is necessary, by forced air ventilation. In special applications water cooling may be required. Furnace roofs, either brick type or water cooled type, comprises all required glands, openings and sealings for the electrode columns, charging pipes and off-gas ducts.

The electrical energy is transferred into the furnace via self-backing carbon electrodes or pre-baked graphite electrodes. The electrode arrangements are depending on the process and the installed power. They are arranged either centrally (single electrode) or as triangle (three electrodes); in case of a rectangular furnace, they are arranged either as 3 or 6 electrodes along the centerline as 2 lines with 3 electrodes each. Therefore one of the key components of the furnace is the electrode column (see Figure 3).
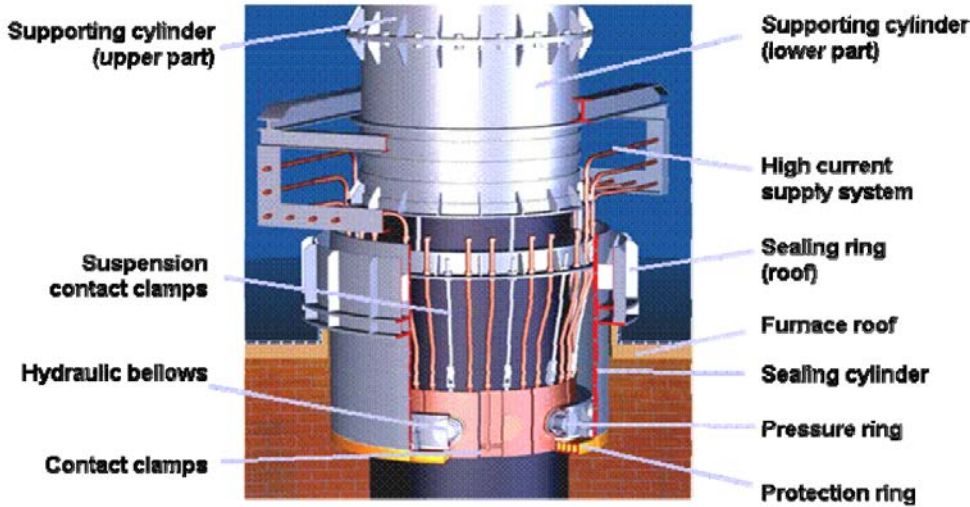

Figure 3: Electrode column [6]

The electrode is semi-automatically slipped into the bath, carried out under full electrical furnace load with no interruptions to furnace operation. The electrode column assemblies contain all facilities to hold, slip, backslip and regulate the penetration into the bath. All operations on the electrodes are executed hydraulically. The electrical power is normally transferred from the furnace transformers via high current lines, water-cooled flexibles, bus tubes at the electrodes and the contact clamps into the electrodes. Today the control and supervision is effected by a PLC (Programmable Logic Controller) and visualisation system. A back-up for manual operation is foreseen and is located in the control room [6].

Metal, slag or matte are tapped periodically by means of a drilling machine and closed either with a manually placed plug or a mud gun. Metal is tapped in ladles, slag/matte is either tapped into slag pots, dry pits or granulation systems (see Figure 4).

Figure 4: 3D illustration of a rectangular slag cleaning furnace [5]

The process gas created from the chemical reactions is provided at the gas stack connection at the furnace roof. Depending on the plant design, the process gas is combusted either inside of the furnace or outside the furnace by balanced addition of combustion and cooling air and sent to the filter system. If the process generates off-gas which contains a certain amount of CO in the process gas or other hazardous substances, the furnace is designed as a closed furnace type.

The above described furnace type is considered to be a typical design. Various other layout/design options meet the individual requirements of specific processes. Successful operation is always based on the right choice of furnace design and furnace dimensions. The choice of the raw material according to the customer's aspects has the biggest impact on the process. On the one hand it affects the slag composition and on the other hand the smelting pattern inside the furnace based on the physical properties and the amount of energy input.

Fundamentals of slag cleaning

Smelting slags can contain valuable metals in dissolved form and as mechanically entrained matte or metallic inclusions in the size range from 2 to 1000 µm. Conditions that encourage suspended matte droplet to settle to a matte layer are low viscosity slag, low turbulence settling, a long residence time, and a thin slag layer. These conditions are often difficult to obtain in a smelting vessel, particularly the necessary residence time.

Pyrometallurgical slag cleaning usually consists of heating the slag, reduction of oxides and settling of matte/metal droplets. Heating the slag decreases viscosity and accelerates reactions. Reduction of magnetite liberates inclusions and facilitates co-reduction of dissolved metal oxides. A significant amount of the matte and metal is present as very fine metallic inclusions, too small for settling. The coalescence of these matte or metal inclusions is required to remove them from the slag.

Chemical slag cleaning process

The Metals in smelting and converting slags are present either dissolved, present mostly as ions (e.g. for copper slag as Cu^+ ions) or as entrained droplets of matte. The dissolved metals is associated either with O^{X-} ions (i.e. Cu_2O) or with S^{X-} ions (e.g. Cu_2S). Electric furnace slag cleaning uses coke as a reductant. So, coke bed is floating on the slag surface and reacting with oxides. At the initial moment of the contact of carbon and slag the direct reduction reaction takes place, forming a gas film separating solid carbon and liquid slag phases as it is illustrated in Figure 5.
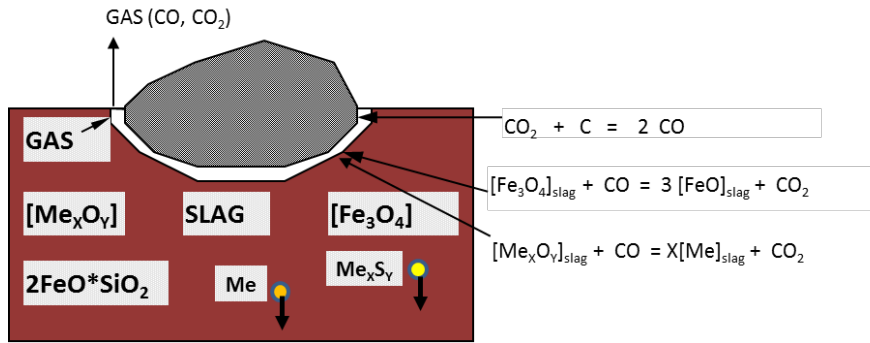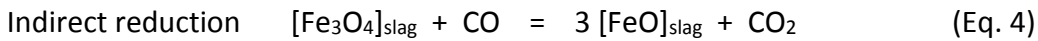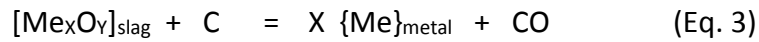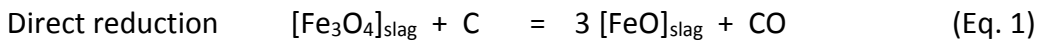

Figure 5: Slag reduction with coke floating on its surface [9]

At the coke/slag interface indirect magnetite (Fe_3O_4) reduction and Boudouard's reaction (CO/CO_2) take place, together with the reduction of metal oxide (Me_XO_Y).

Direct reduction

$$[Fe_3O_4]_{slag} + C = 3[FeO]_{slag} + CO \qquad \text{(Eq. 1)}$$

$$[FeO]_{slag} + C = \{Fe\}_{metal} + CO \qquad \text{(Eq. 2)}$$

$$[Me_XO_Y]_{slag} + C = X\{Me\}_{metal} + CO \qquad \text{(Eq. 3)}$$

Indirect reduction

$$[Fe_3O_4]_{slag} + CO = 3[FeO]_{slag} + CO_2 \qquad \text{(Eq. 4)}$$

$$[FeO]_{slag} + CO = \{Fe\}_{metal} + CO_2 \qquad \text{(Eq. 5)}$$

$$[Me_XO_Y]_{slag} + CO = X\{Me\}_{metal} + CO_2 \qquad \text{(Eq. 6)}$$

Boudouard reaction $\quad CO_2 + C = 2CO \qquad\qquad\qquad\qquad\qquad\qquad$ (Eq. 7)

Reducing viscosity can be achieved by increasing the slag temperature, and changing slag chemistry. The main focus of changing slag chemistry is to reduce the magnetite that is present within the slag, mainly according to Equations 1 and 4. Other reactions to reduce the magnetite content involve pig iron and sulfides [9].

Physical slag cleaning process

Settling rate of spherical body in a liquid defines Stokes' law:

$$u = \frac{2 \left(\rho_M - \rho_S \right) g\, r^2}{9 \eta_S} \qquad \text{(Eq. 8)}$$

Matte and metallic inclusions are present in a molten slag in the form of liquid droplets. The rate of settling of a liquid, spherical drop in a liquid is given by Hadamard-Rybczynski formula:

$$u = \frac{\left(\rho_M - \rho_S \right) g\, r^2}{3 \eta_S} \; \frac{3\eta_S + 2\eta_M}{3 \left(\eta_S + \eta_M \right)} \qquad \text{(Eq. 9)}$$

Because slag viscosity is much more greater than matte or metal viscosity (η_S >> η_M) the settling rate of matte and metallic inclusions in the slag can be calculated using modified Hadamard-Rybcznski formula for slag/matte system:

$$u = \frac{\left(\rho_M - \rho_S \right) g\, r^2}{3 \eta_S} \qquad \text{(Eq.10)}$$

The wide range of sizes of inclusions, varying from 2 to 1000 μm, and differences in the settling rates of different sized droplets cause the droplets to collide and coalescence, called gravitational coalescence. The bigger droplets "wash out" the smaller ones by absorbing them as the big droplets fall faster through the slag than small ones do [14]. It requires precise information about size distribution of matte and metallic inclusions. E.g. based on the microscopic examination of the slag of 3.5 % copper content from Teniente Converter a typical size distribution of copper matte inclusions and metallic copper inclusions are shown in Figure 6 and Figure 7.
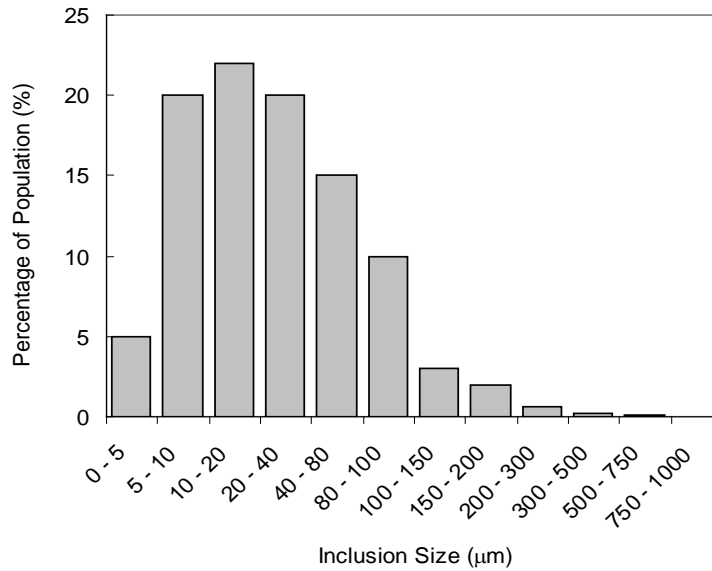

Figure 6: Size distribution of copper matte inclusions in slag form Teniente Converter [7]
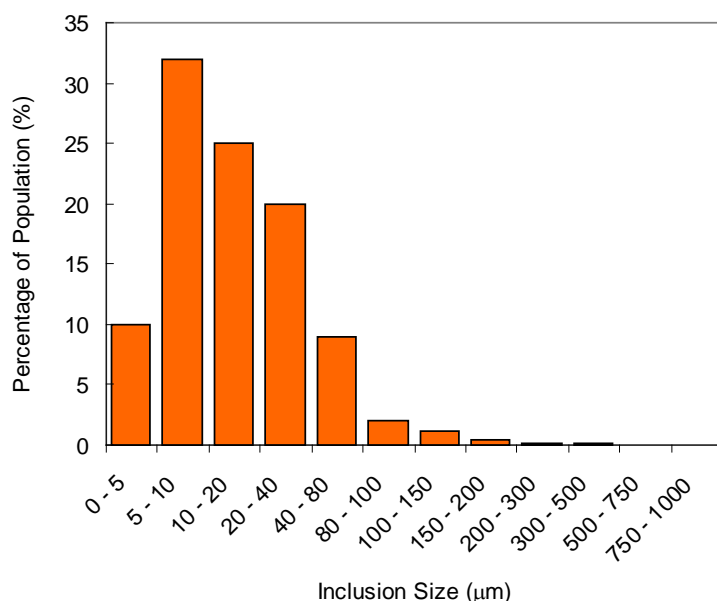
Figure 7: Size distribution of metallic copper inclusions in slag form Teniente Converter [7]

In Figure 8 the curve for calculation of the copper content with only gravitational settling (Eq. 10) is given. After two hours the copper content is close to 2%. Also, the copper content was calculated using the gravitational coalescence model (Figure 8 – Curve 2).

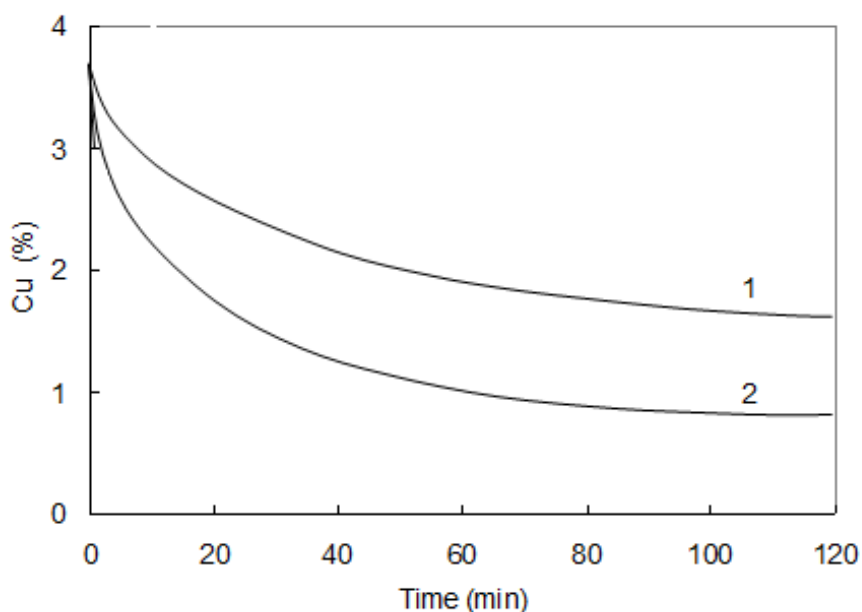**Figure 8: Calculated copper content in the form of matte inclusions versus time 1.) Gravitational settling 2.) Gravitational coalescence**

If the droplets are too small, then settling takes a lot of time. This can be countered by allowing a long settling time, and by reducing the viscosity of the slag. A longer settling time is achieved by properly designing the furnace, but there are limits to the practical

size of a furnace. If the droplets are too small, then settling takes a lot of time. This can be countered by allowing a long settling time, and by reducing the viscosity of the slag. A longer settling time is achieved by properly designing the furnace, but there are limits to the practical size of a furnace. The principle of the model of gravitational coalescence is schematically shown in Figure 9. Every settling droplet creates an "attraction volume" in the period of time Δt. The attraction volume is a function of inclusion diameter, settling rate and time. Assuming homogeneous distribution of inclusions in the slag, the average, maximal settling distance is equal to half of the slag height.
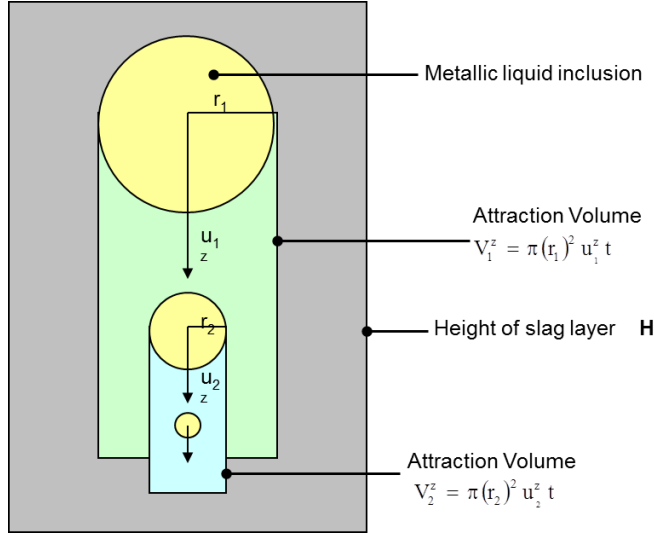

Figure 9: Gravitational settling and coalescence of matte inclusions in the slag [7]

$$V_i = \pi \, r_i^2 \, u_i \, \Delta t \qquad \text{(Eq. 11)}$$

The moment the bigger and smaller droplet collide, the bigger droplet "absorbs" the smaller one and the size of bigger droplet increases.

$$r_i^{k+1} = \sqrt[3]{\left(r_i^k\right)^3 + \beta \, V_i \sum_{j=1}^{i-1} n_j^k \left(r_j^k\right)^3} \qquad \text{(Eq. 12)}$$

The effectiveness of coalescence depends on the number of collisions and interfacial tension. The empirical coefficient β represents the coalescence effectiveness on a scale of $0 - 1$.

The passing of inclusions from slag to the matte layer and the coalescence results in the change of inclusions number in all size fractions. In the iteration step **Δt** (number **k**) the number of inclusions size **i** is defined by formula:

$$n_i^{k+1} = n_i^k \left[\left(e^{-\frac{u_i}{H} \Delta t} \right) + \left(1 - \beta \sum_{j=1}^{i-1} n_j^k \left(r_j^k\right)^3 \right) \right] \qquad \text{(Eq. 13)}$$

Finally, the metal content (in the form of matte inclusions) in the slag at time **t,** corresponding to iteration number **k** , is calculated by summarization of all matte inclusions in the unitary volume of slag, assuming that the metal content in the matte inclusions is equal to metal content in produced matte [14].

$$Me_M^k = \frac{4}{3} 10^4 \ \pi \ \frac{1}{Me_{CM}} \ \frac{\rho_M}{\rho_S} \sum_{i=1}^m n_i^k \left(r_i^k\right)^3 \tag{Eq. 14}$$

Similarly the gravitational coalescence of metallic inclusions has been calculated, their size distribution have to be based on microscopic examination. The total metal (Me_T) content at iteration step **k** is equal to the sum of contents of metal in the form of matte (Me_M), metallic (Me_{CM}) and metal oxide (Me_O):

$$Me_T^k \ = \ Me_M^k \ + \ Me_{CM}^k \ + \ Me_O^k \tag{Eq. 15}$$

Exemplary results and industrial applications

Copper Slag Cleaning First Quantum at Kansanshi Copper Smelter

Copper Slag cleaning in (electrical) furnaces has been increasingly popular over the last decades. METIX, part of the SMS group, has recently constructed an electric furnace for the First quantum project at Kanshansi, Zambia. The plant was commissioned successfully in February 2015.

- **1,200,000 t/y smelting capacity**
- **1,000,000 t/y acid production**
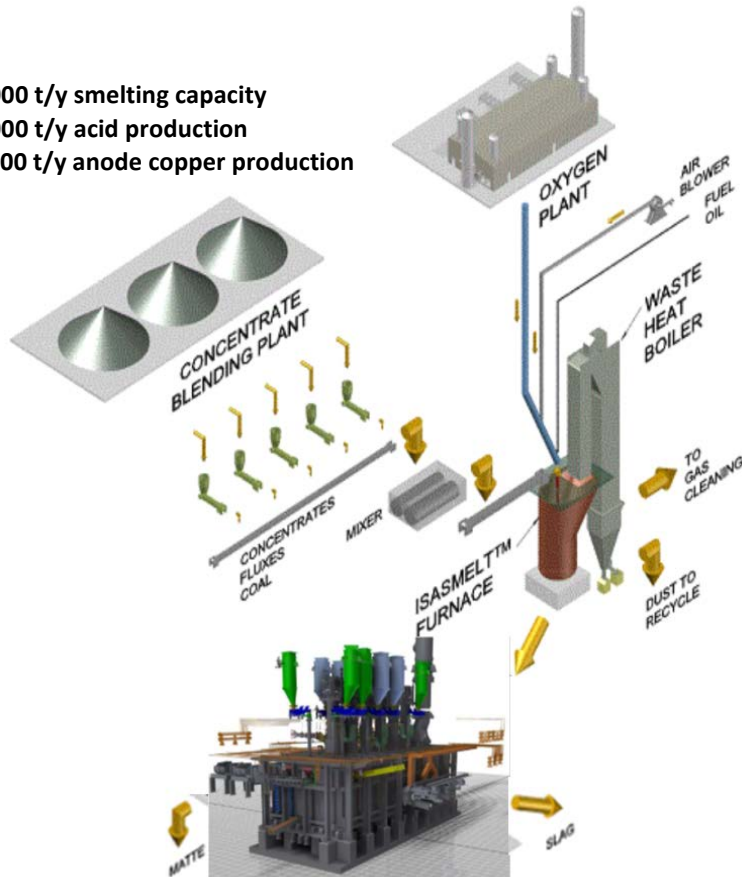- **> 300,000 t/y anode copper production**

Figure 10: 3D illustration of Kansanshi Copper Smelter

First Quantum Minerals Limited, was already a major producer of SX-EW (Solvent extraction and electrowinning) copper at their operation in Kansanshi, Zambia when they chose to expand their operation by installing a copper smelter. An ISASMELT was chosen for the smelting furnace application. The new smelter concept with an downstream Matte Settling Electric Furnace promises to provide a major benefit. The Kansanshi Smelter is producing 300,000 tonnes per annum of blister copper from a concentrate blend based on feed from the Kansanshi and Sentinel mines by treating up to 1.2 million dry t/y copper concentrates.

There is a trend towards to semi-continuous operating practice of the primary smelters (such as ISASMELT or Ausmelt) as well as of the slag cleaning furnaces. The rectangular SAF is more suitable for this task due to better geometrical conditions. It is expect that for continuous operation, the recovery rate of a rectangular furnace can be (depending on the specific parameters) 0.1 – 0.4 % higher in comparison to the conventional round type SAF's. This fact persuaded First Quantum at Kansanshi copper smelter in Zambia to install a six-in-line rectangular slag cleaning furnace of 12.5 MW downstream a continuously operating ISASMELT furnace [3].

The Matte Settling Electric Furnace (MSEF) is capable of processing copper matte, various converter slags, reverts from different sources and coke to produce a slag with a maximum copper content of 0.7 %. The MSEF at Kansanshi is continuously charged via two launders with matte and slag coming from the ISASMELT. The launders enters the furnace shell in the gas area through the side wall and are positioned to convey the slag directly into the reaction area to prevent the precipitation of a major quantity of magnetite. Molten slag from the PSC is charged by ladle at regular intervals into the furnace by means of two dedicated cast iron launders in the eastern end wall from the converter aisle side. A mixture of reverts, coke and limestone is fed through the feed chutes into the furnace on top of the molten slag layer in the furnace. The coke and limestone act as modifiers to the slag to improve conductivity and viscosity to assist with the copper matte settling in the furnace, while reverts are fed back to ensure recovery of contained copper. Ultimate analysis of the input raw materials carried out by SNC LAVALIN, is shown in the Table I. Based on the raw material and product analysis the following mass balance (Table II) has been made.

Table I: Input (design base) Kansanshi raw materials and quantities [approx.] based on SNC LAVALIN

Material		ISA- matte	ISA- slag	PSC-slag	Reverts	Lime	Coke
Qty	tph	86	112	28	6.3	3.6	1.4
Temp.	°C	1,160	1,160	1,200	25	25	25
C-fix	%						78
VM	%						
Al_2O_3	%		2	< 0.5	1	1	2.6

CaO	%		3	< 0.5	1	53	0.5
Cu	%				5		
Cu$_2$O	%		0.4	2	2		
Cu$_2$S	%	75	0.4	7	45		
FeO	%		43	43	13		1.3
FeS	%	22	< 0.5		2		
Fe$_3$O$_4$	%	3	12	22	11		
MgO	%		1	0.6	< 0.5	1	< 0.5
SiO$_2$	%		35	25	14	3	8

Table II: Output (design calculation) products and quantities [approx.] based on SMS mass balance

Material		Matte	Slag	Off gas	Dust
Qty	tph	**72**	**115**	**28**	**0.24**
Temp.	°C	1,180	1,180	1,000	1,000
Free C	%				7
Al$_2$O$_3$	%		2		1
CaO	%		4		8
MgO	%		1		1
FeO	%		52		22
SiO$_2$	%		33		18
Fe$_3$O$_4$	%	4	4		9
FeS	%	20			6
Cu$_2$S	%	74			27
Cu	%	< 2	< 0.7		< 0.5
CO$_2$	%			11	
SOx	%			< 0.5	

As mention above, the settling will be achieved by temperature increase and reduction of copper oxides and magnetite in the slag with carbon and maximizing of the settling rate of the metallic or matte droplets by improving the viscosity of the slag. It is common agreement that reduction of oxides from a liquid slag with carbon:

$$[Fe_3O_4]_{slag} + C \quad = \quad 3\,[FeO]_{slag} + CO \qquad \text{(Eq. 16)}$$
$$[Cu_2O]_{slag} + C \quad = \quad 2\,\{Cu\}_{metal} + CO \qquad \text{(Eq. 17)}$$
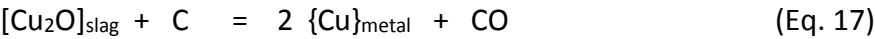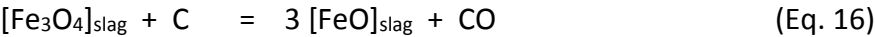
is the first order reaction with respect to the oxide concentration, so the rate of magnetite reduction is represented by equation:

$$\frac{dC_{Fe_3O_4}}{dt} = k\,\frac{A_R\,\rho_S}{m_S}\,C_{Fe_3O_4} \qquad \text{(Eq. 18)}$$

where A_R represents reaction surface area and m_S/ρ_S ratio slag volume. Value of reaction constant **k** as the function of temperature has been determined experimentally by reduction of slag with coke.

When reaching the fayalite point with approx. 29 % of SiO_2 the viscosity of the slag shows a maximum regarding the viscosity. A slag with 30 to 33 % SiO_2 will lead to poor slag cleaning results as it is very difficult for Cu and Cu matte droplets to settle. This is one of the reasons to keep the magnetite content in the range of 4 to 6%. Figure 11 shows representative discard slag results with the correlation between magnetite and total Cu content in MSEF slag.
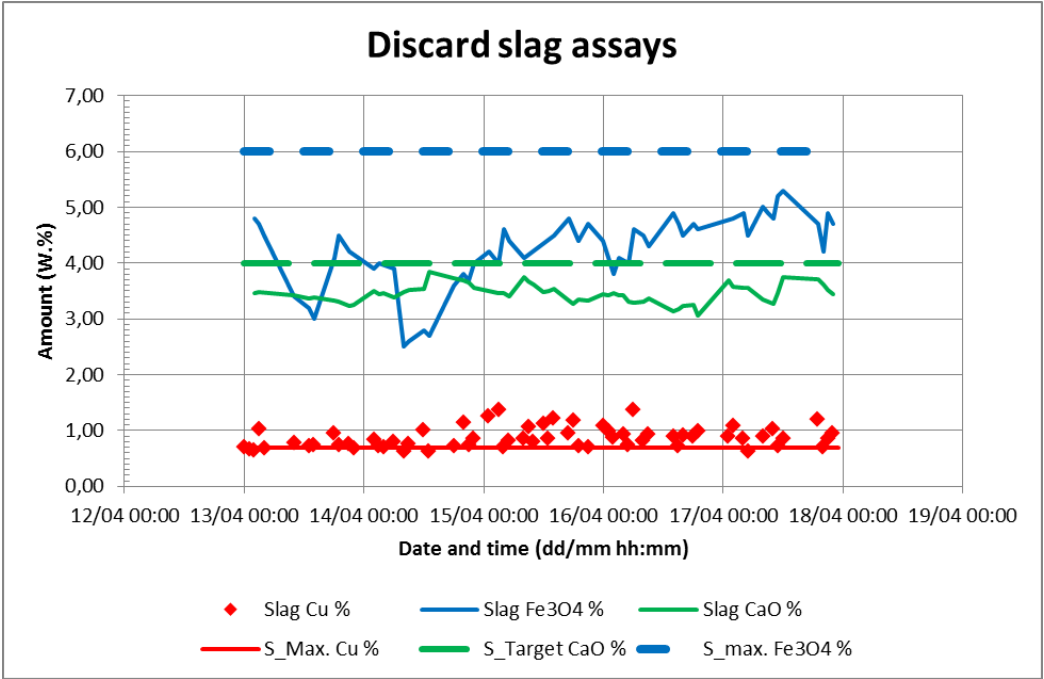

Figure 11: Kansanshi MSEF discard slag assays CW16 2015

Tapping of the furnace is done through eight matte tap holes all situated on the same level and on both the north and south sides. The matte tap holes are equipped with a rail mounted mud gun and drill on each side of the furnace to assist with opening and closing of the tap holes. The tapped MSEF matte is ladled to Peirce-Smith converters and the MSEF slag will be granulated and discarded.

Latest Results from Pilot-Scale Operation – Highly Efficient Slag Cleaning

Conventional pyrometallurgical slag cleaning by submerged arc furnaces comprises slag heating, reduction of oxides and settling of matte/metal droplets. Slag overheating decreases its viscosity and accelerates reduction reactions. By applying a magnetic field crossing a DC field to a slag, stirring can be improved and the settling of entrained copper droplets is thereby fostered. Based on this theoretical background and on the results of an intensive parameter study by CFD simulation, the results were subsequently verified in a 2-4 t/h pilot plant [13]

The background is that the given process conditions only allow copper particles to settle if they are above a certain minimum size. As a result, the smaller copper sulfide droplets included in the iron-silicate product (the real constituent of the slag) remain, which means that the economic use of the valuable metal content becomes impossible. The new process combination is intended to separate the remaining metal phase from the slag. This combination envisages that a stirring reactor with induced magnetic, activated "washing" (stirring) will be installed downstream of the already established submerged arc furnace [10].
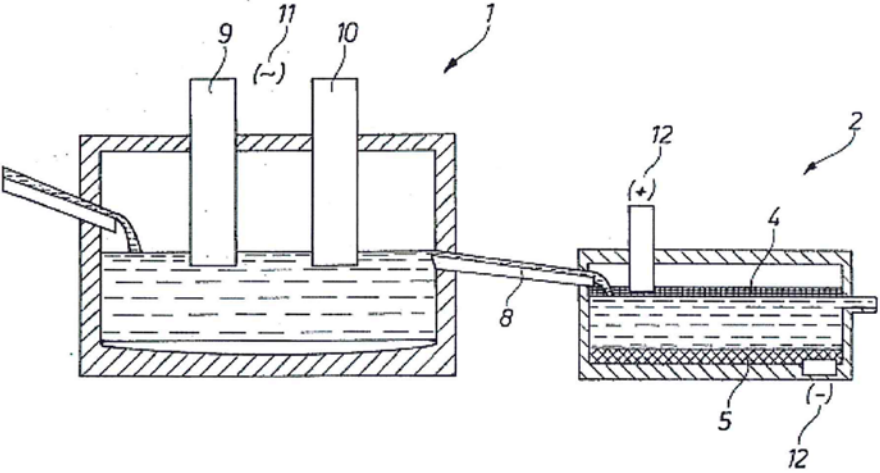

Figure 12: Patent drawing SMS group [10]

Physically the Lorenz force is used. This works on metal particles if they are in a DC electric field which is crossed at right angles by a magnetic field. The copper particles are put into a rotary motion, which leads to impact and agglomeration due to different velocities of the particles, and then after acquiring greater mass they can settle [8].

The new process and furnace concept has been tested extensively. Two pilot plants were built for smaller and larger laboratory trials at the University of Chile and a small test facility in Charges in Chile. After these promising but short-term campaigns, a small plant was installed at the Institute of Metallurgy, Recycling and Process Engineering (IME) at the RWTH University of Aachen, primarily for scientific purposes served by the university. And finally a large pilot plant was erected, fully integrated into an industrial company involved in copper production at Aurubis Hamburg. The pilot plant in Hamburg was operated in campaigns. The duration of each campaign was 8 to 10 days, including the heat-up phase for 2-3 days and the operating period. During the operating period, the furnace was fed with slag from the industrial slag cleaning furnace semicontinuously. Figure 13 shows some illustrations of the pilot scale operation [8].

Figure 13: Pilot plant at Aurubis Hamburg [8]

Each test campaign, except the last one, includes a time period for slag treatment in the stirring reactor without magnetic stirring in order to obtain the reference value of copper separation. In terms of the application of the magnetic stirring device, the position of the magnetic poles, the operating mode and magnetic force were investigated.

All samples form the pilot plant at Aurubis Hamburg were taken directly from the overflow mass-flow at a certain time after the first overflow of slag phase and were granulated in water. To evaluate the relative efficiency of copper separation, a comparison to a reference status without any enhanced magnetic stirring is required. As there are also certain minor effects like slag temperature of the feed and overflow as well as retention time and several others, the presented results are illustrated in the form of histograms [8].
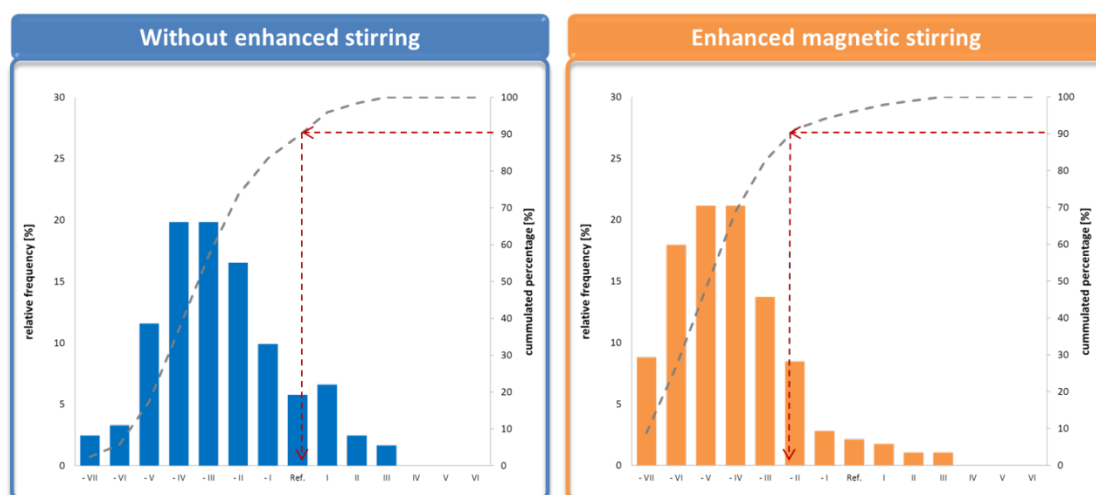
Figure 14: Comparison of results obtained without enhanced stirring and with applied enhanced stirring [12]

Figure 14 shows the histogram for the results obtained without enhanced stirring and with applied enhanced stirring. Since the copper separation depends on the copper concentration of the feed material, it is necessary to compare both measurement series with respect to average and standard deviation before determining the differences in the achieved results. The comparison of these two parameters showed no significant deviation between the two investigated states [12].

The graph for the enhanced magnetic stirring shows an accumulation of values in the classes V and below. The relative frequency of copper concentration in the iron silicate product is nearly tripled compared to the status without enhanced stirring to 47.9 % of the investigated charges. In general, the results obtained during the application of the magnetic field show a smaller variety of the achieved Cu concentration in the overflow. The red dotted line illustrates the difference between the cumulative percentages for both measurement series. Assuming that the reliability of the gained copper concentration of 90 % would be sufficient for industrial operation, it is evident that without enhanced stirring the results are comparable to the reference state and it would need the enhanced stirring to achieve even better results. Summarizing these results, it can be stated that the application of a magnetic field led to a significantly lower copper concentration in the remaining iron silicate product [12].

To demonstrate the effect of copper feed content on the remaining copper content in the final iron-silicate product, Figure 15 illustrates the average copper separation. For the histogram the copper feed content was classified according to the above-mentioned procedure and the average copper separation was determined for each process mode on the one hand and for each histogram class on the other hand [8].
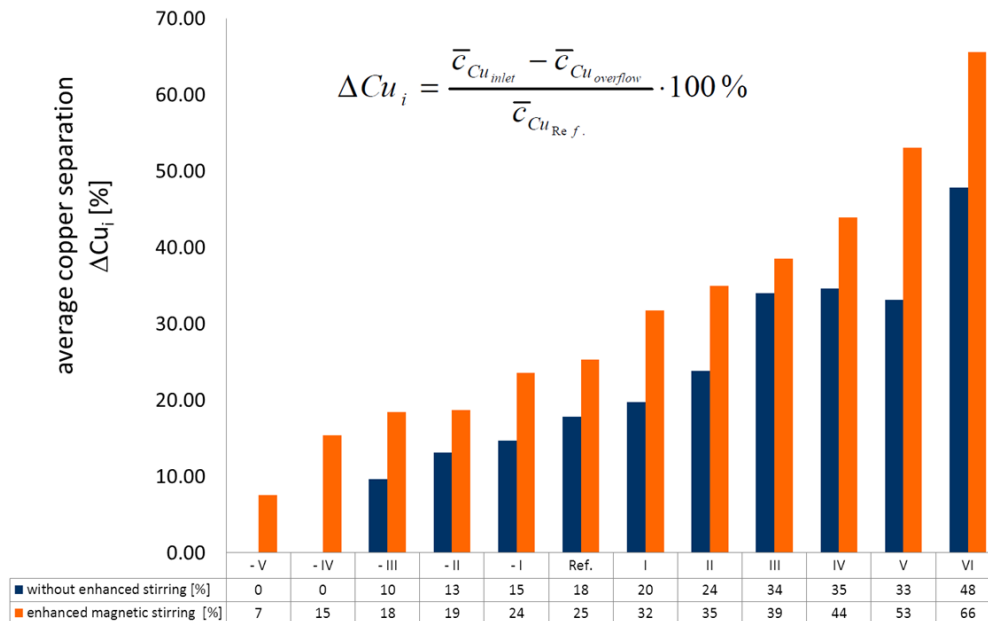
The chart shows:

$$\Delta Cu_i = \frac{\overline{c}_{Cu_{inlet}} - \overline{c}_{Cu_{overflow}}}{\overline{c}_{Cu_{Ref.}}} \cdot 100\,\%$$

Y-axis: average copper separation ΔCu_i [%]

	- V	- IV	- III	- II	- I	Ref.	I	II	III	IV	V	VI
without enhanced stirring [%]	0	0	10	13	15	18	20	24	34	35	33	48
enhanced magnetic stirring [%]	7	15	18	19	24	25	32	35	39	44	53	66

Figure 15: Comparison of results obtained without enhanced stirring and with applied enhanced stirring [8]

The driving force of separating copper from the feed material increases with a rising copper concentration. This means that even at high copper concentrations in the feed, sufficient separation to low copper concentrations in the overflow iron silicate product is feasible. On determining the copper separation ratio between the enhanced stirring status and the status without stirring, the value is > 1 for every histogram class. This means that independently of the copper concentration of the feed material, the application of the magnetic field leads to a better copper separation than the reference status without enhanced stirring. Even at low copper concentrations (IV, V) in the feed, copper can be separated by applying the magnetic field, while this was not observed without the additional stirring [8].

Reduction Smelting of Redmud [19]

Red mud is the so-called bauxite residue after the solid-liquid separation from alkaline high pressure leaching of aluminum bearing bauxite ore. Depending on the composition of the primary mineral deposit, 4-7 tons of bauxite are necessary to gain 2 tons of alumina in order to produce 1 ton of aluminum. The leaching process is very selective on the extraction of aluminum and gallium and the undissolved minerals remain in the residue. Due to its high hematite content, the bauxite residue has a reddish color and is therefore called red mud. With each ton of primary produced aluminum, 1-2.5 tons of red mud are generated. The composition of red mud varies strongly dependent on the composition of the original bauxite and the employed process parameters (digestion temperature, caustic concentration, digestion time, etc.). Table III shows the average ranges in composition of commonly produced red

muds. It can be seen that the predominant phases are iron compounds like hematite or goethite which can be easily recovered by carbothermic reduction.

Table III: Composition of different red muds and composition of the raw material used in the experiments

Component in wt.-%	Average red mud	Red Mud Lünen (Germany)	After re-leaching	After re-leaching with CaO (CaO/SiO$_2$ ~ 0.5)
Fe$_2$O$_3$	30-50	29.5	35.5	34.7
Al$_2$O$_3$	10-20	27	18.3	17.7
SiO$_2$	5-20	13.1	14.9	15
TiO$_2$	3-15	8	9.3	9
Na$_2$O	3-7	7	9.3	9.1
CaO	1-8	3.8	4.7	7.7
Cr$_2$O$_3$	-	0.35	0.41	0.4
P$_2$O$_5$	-	0.22	0.25	0.27
SO$_3$	-	0.47	0.5	0.58

The examined red mud comes from the landfill of the former "Vereinigte Aluminiumwerke" near Lünen, Germany. The original composition is shown in table 1 and indicates high amounts of remaining alumina. In former times high through-puts and cheap but poorly digestible bauxites as raw material refused a high alumina recovery. Therefore X-ray diffraction patterns show, the predominant phases are hematite and still aluminum hydroxides (gibbsite and boehmite). The exact aluminum content is measured by x-ray fluorescence and the aluminum values in Table III are converted into alumina as quite common in literature. Therefore the sum of all components does not reach 100 %. This original red mud from landfill is one material for the following test trials.

Moreover the entire research project includes a recovery of the main parts of the remaining alumina content. Thereby the red mud from the landfill is leached a second time employing the Bayer-process with optimized parameters. From this second leaching originates a red mud with the composition called after "re-leaching" (see table 1) which is also examined for iron recovery.

The third examined raw material for carbothermic iron recovery experiments is presented in the last column of table 1. In this case small amounts of lime are added during the second leaching of the initial red mud in order to increase the recovery of alumina in the leaching step. Experiments confirmed an increased alumina yield of

about 10 % since the molar ratio CaO/SiO$_2$ increased from 0.31 in the initial red mud to 0.5 by the addition of lime. Thus the remaining leaching residue is increased in its lime content, while the other constituents are slightly diluted.

Theoretical considerations

It can be seen from Figure 16 that firstly the hematite is reduced to FeO. At about 15 grams carbon addition the co-reduction of titania to Ti$_2$O$_3$ starts but stagnates on a low level. Only 15-35 % of the titania is reduced to Ti$_2$O$_3$. By adding 26 g carbon per kg re-leached red mud, the hematite is almost completely (remaining Fe$_2$O$_3$ content <0.9 wt.-%) converted into FeO. If the addition of the reducing agent is further increased, a phase of metallic iron will be produced and the FeO-content of the slag declines. At about 80 g carbon addition to the FeO activity descends rapidly and the titania activity increases dramatically which leads to a significant titania reduction. At 87.5 grams carbon addition the iron oxide content in slag is below 1 wt.-% so the reduction is completed. The metal phase firstly forms after the addition of 26 g carbon and at about 80 grams addition, carbon is even dissolved in the metal phase. At about 90 grams carbon addition the silica reduction to metallic silicon which is collected in the metal phase starts and at about 96 grams carbon, the reduction to titanium slightly begins (threshold 0.1 wt.%).
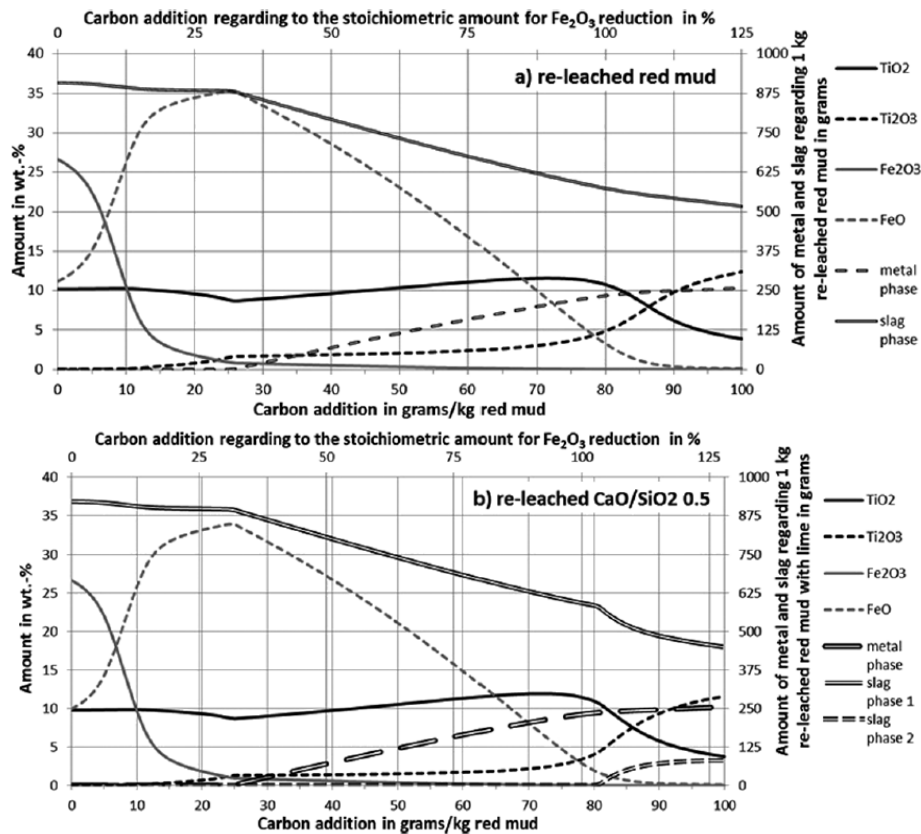

Figure 16: Component distribution of oxides and sub-oxides during the reduction of a) re-leached red mud and b) re-leached red mud with lime addition calculated at 1650 °C

The slag must not be contaminated by the used refractory and the aim of all experiments was a complete reduction of iron-oxide. Therefore the raw material was smelted in a graphite crucible with the dimensions of 150/120 mm outer/inner diameter and 200 mm depth. To minimize the graphite consumption of the crucible due to the carbon absorption by the slag and to cover the melt from reoxidizing at the surface, approximately 200 g (depending on the hematite content of the raw material) of lignite coke with a grain size below 1 mm have been fed together with 3 200 g pre-dried and lumpy raw material of a particle size 10-30 mm. All experiments were conducted in a tiltable AC electric arc furnace, which is presented in Figure 17. Although the set up with one top electrode made of graphite in combination with a water-sprayed copper bottom electrode is typical for DC mode, the furnace was driven without a rectifier. In order to establish a good electrical contact, a thin layer of graphite powder was put between the bottom electrode and the graphite crucible. The electrical power during the smelting process was 12-15 kW. A process temperature of 1600 °C was aspired and controlled discontinuously by a pyrometer. Actually the temperatures varied from 1600 °C to 1700 °C. The feed rate of the input material was continuously 2 500 g/h. After 90 min the whole material has been fed and the melt was hold for additional 10 min to complete the hematite reduction. Afterwards the entire melt was tapped into a steel mold, in which metal and slag phase were separated due to the settling behavior of the higher density metal droplets.
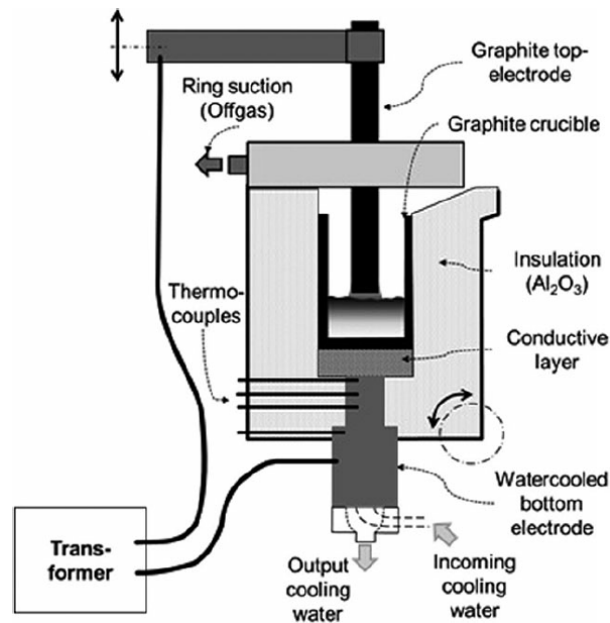

Figure 17: Sketch of the laboratory electric arc furnace

After the carbothermic reduction of red mud, the hazardous residue from the Bayer-process, a salable pig iron with about 4 wt.-% carbon and less than 0.5 wt.-% silicon and 0.2 wt.-% titanium can be obtained. The slag is by the addition of lime adjustable in its viscosity and the sodium content can be varied by the length of the reduction

time. An important role during the reduction process plays the slag viscosity, since many reduction products like CO, Na and SiO are gaseous species and have to pass through the melt. At high viscosities, the ascend of gas bubbles is hindered and leads to a foaming slag. The addition of lime during the prior leaching step affects the process handling in the smelting step positively by decreasing the slag viscosity which was obvious during the experiments. Unfortunately the calculation of the viscosity is not that easy because the high content of titania in trivalent and tetravalent state is not exactly defined in any known model for slag viscosities. But FactSage® states the viscosities of all slags in the range of 0.27-0.36 Pa*s with positive effect on lowering the viscosity by the addition of lime even though lime increases the liquidus temperature by 100 °C to 1500 °C.

Cobalt-Recovery from Copper-Smelter-Slags [15]

In January 2001, Chambishi Metals commissioned a 40MW DC arc furnace using selective carbothermic reduction for processing reverberatory furnace slag stockpile of 20 million tons containing 0.34 to 4.5 % cobalt, and an average of 1.1 % copper. Cobalt occurs as fayalite whereas copper occurs as oxide and sulphide. An atomizer unit to atomize furnace product, molten Co/Cu/Fe alloy, and a pressure oxidation leach process to leach cobalt and copper and separate iron as goethite was also commissioned. Cobalt and copper containing solution is processed in the refinery for production of metals. Commercial application of the DC arc furnace on smelting of copper smelter slag was unique and therefore required extensive literature search to broaden the knowledge of the theory and the practice.

Mineralogical analysis of the slag carried out by MINTEK, RSA, is shown in the Table IV, indicate that the cobalt is present as fayalite (Iron Silicate Matrix) whereas copper is present as oxide, sulphide and metal. Presence of significant level of sulphide and metallic copper are due to entrained losses.

Table IV: Mineralogical composition of the Rokana Reverberatory Slag

Group Total Co	Mineral Phases	% of Total Cu	% of Total Co
Slag	Fe, Ca, Al (Mg, K, Co, Cu) - Silicates	46.6	94.6
Spinel	Fe(Al, Cr, Ti, Ca, Co, Cu) - Oxides	1.1	5.2
Sulphide	Cu(Co, Fe) - Sulphide	39.3	0.2
Metal	Cu(Co, Fe) - Metal	13.0	< 0.1
	Total	100.0	100.0

Following commissioning of the 40 MW DC Arc furnace in the year 2001, the Chambishi operation's flow sheet is shown in Figure 18. The slag excavated from the dump, crushed and screened to +6, -16mm particle size, beneficiated to high grade the furnace feed by 15 – 20 %, dried to reduce moisture to < 1 %, is fed to the furnace. Furnace product is an alloy of cobalt, copper and iron. Molten alloy is tapped and atomized to < 150 micron particle size which is pumped to the pressure/oxidation leach plant for leaching cobalt and separating iron as goethite. The leach solution containing cobalt, copper and other trace impurity elements is processed in cobalt refinery for cobalt and copper metal production.
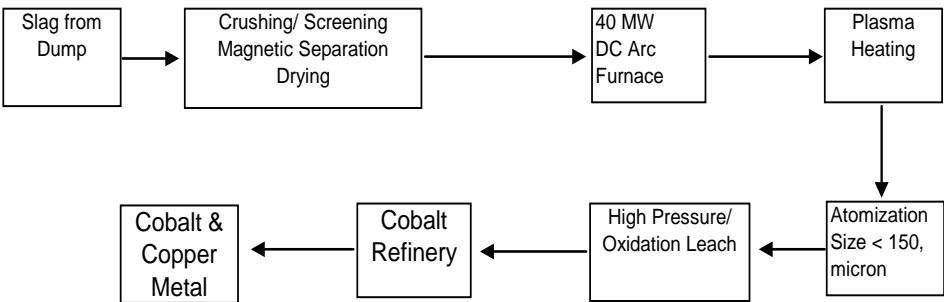

Figure 18: Simplified Flow Chart of Chambishi Operation after 2001

Furnace was experiencing severe power fluctuations which caused erratic feed rates. This resulted in difficulties in controlling slag bath temperature to 1500 – 1550 °C. Overfeeding was causing cooling of the bath whereas underfeeding causing high temperature, both changing the resistance. This frequent swing in the bath resistance triggered the electrode movement to maintain power set point, causing power fluctuations. Figure 19 gives the circuit control diagram originally built in PLC. The power fluctuations were experienced due to a sudden drop in resistance causing the power to begin to drop. The controller would try to compensate by increasing the current, thus maintaining the power at the set point, until it eventually reached a maximum limit for the tap position. Once the current reached the maximum limit then the power would fall in line with the resistance. Under these circumstances the tap changer should tap down, thus increasing the allowable current. The ABB controller prevented the transformer from tapping down below tap 10. This was designed to limit the maximum current such that the current density remained under 300 A/m², specified by the supplier. The ABB was convinced to remove the tap changer control from their custom PLC. Chambishi then engineered this functionality into the Plant Scape control system.
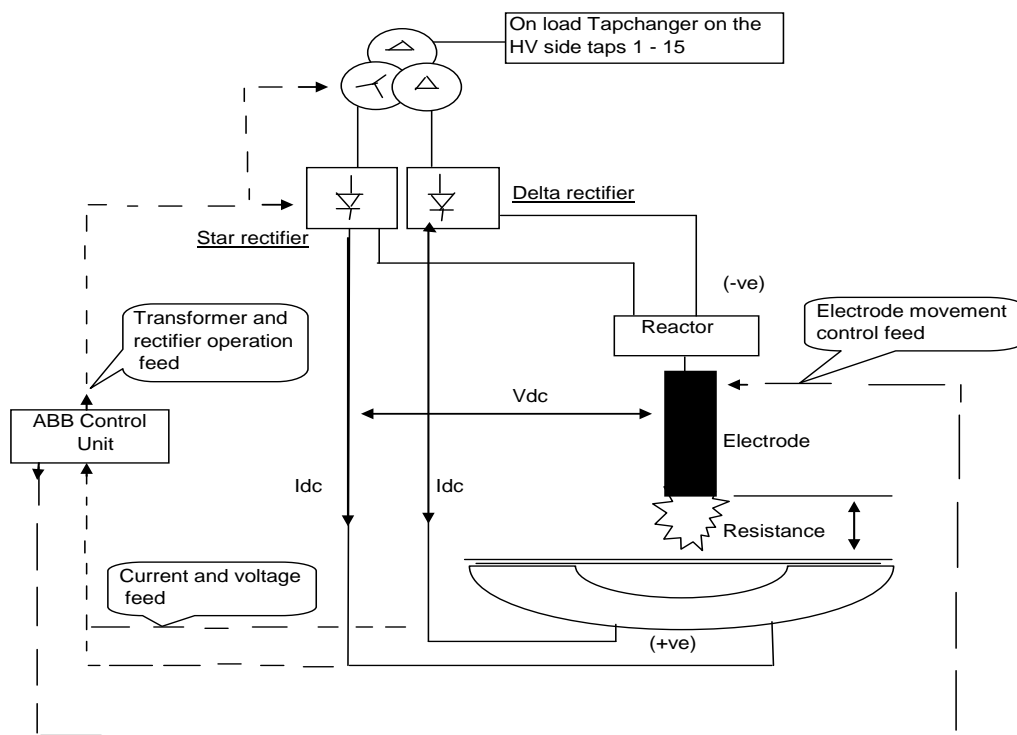
Figure 19: Schematic electrical/control diagram for electrode movement for power control

The advantage of this change was that Chambishi had the flexibility to alter the philosophy whilst retaining the integrity of the safety features built into the ABB control system. The Plant Scape system requests a tap change from the ABB system, which executes it if it is safe to do so. The maximum limit for current was set at 70 kA (250 A/m^2). This meant that the tap setting could safely go down to position 3 (Figure 20) with no safety risks to electrical equipment.
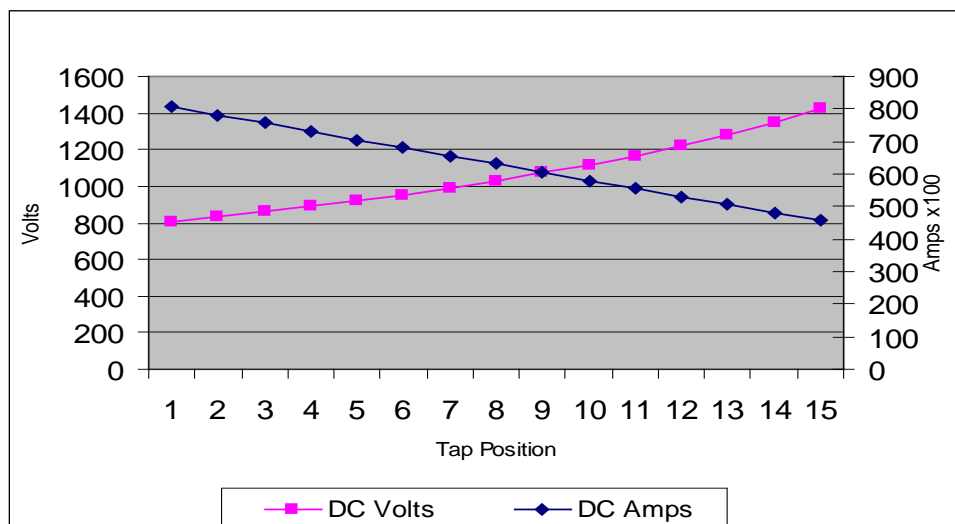

Figure 20: Voltage and Current limits for Tap Positions, 1 – 15

After this change was made to stabilize the power, the standard deviation improved to 0.84 from 1.6 in the year 2005, indicating a significant improvement as shown in figure 16. The standard deviation improved from 1.6 to 0.847 by the end of the year 2006. The standard deviations are calculated for 6 monthly averages at 40 MW power only.
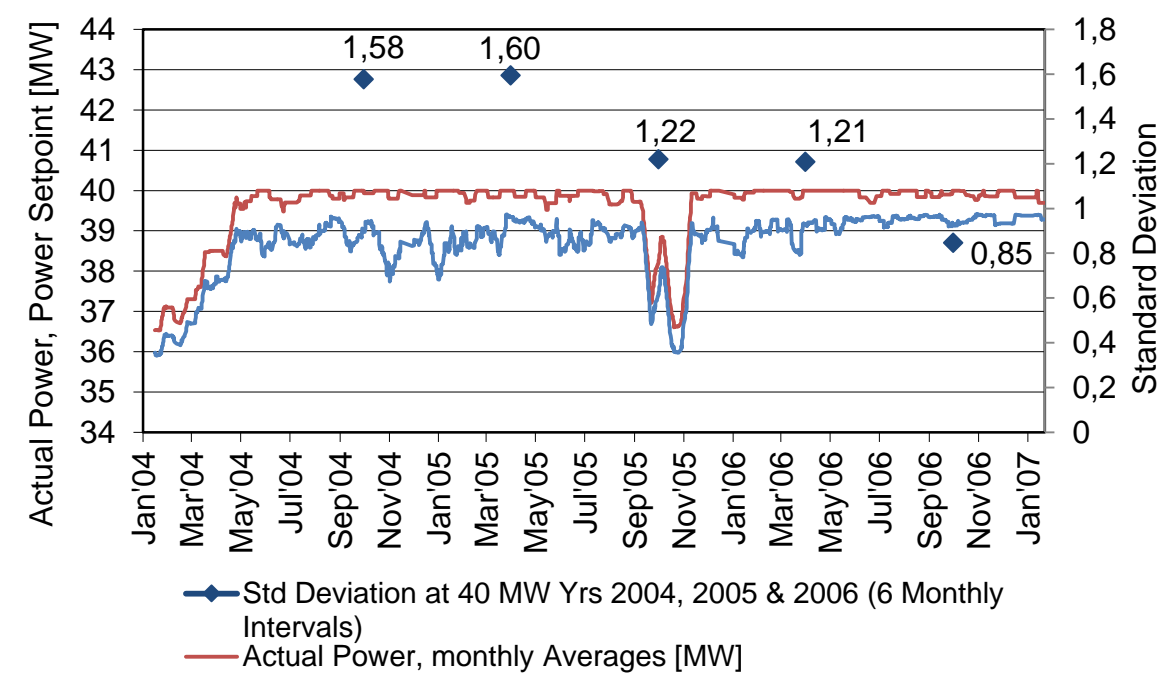

Figure 21: Furnace power set point vs. Actual power (Jan'04 – Jan'07)

Valorization of Pb containing Slags [16]

The lead and zinc contents of slags from lead production vary depending on the type of the production process and the process parameters. A slag from an oxidation step of crude lead production has a lead content of 50 % or more, whereas a slag from a reduction step usually lies below 6 % lead and 18 % zinc. Therefore one motivation for a subsequent treatment of the slag is to increase the metal yield of the production line and by doing so to increase the profitability of the process. If the metals contained in the otherwise discarded slag are regained and transferred into a product this can decrease the use of primary resources and thus increase the sustainability of lead production. This in turn can achieve or add to a positive company's perception of the public.

	conventional		direct wining			
crude lead winning / oxidation	SM		QSL	ISA / Ausmelt 50 % 6 - 10 %	SKS OBBF 46 % 10 %	Kivcet (FS + EF)
reduction	BF 1.5 % 11 %	ISF 2.5 % 16 %	QSL 3 - 6 % 8 - 16 %		SKS OSBF 2 % 16 %	6 % 18 %
slag cleaning / reduction	FF 0.1 % 3 %		ISA / Ausmelt 1 % 6 - 8 %		FF 0.5 – 1.5 % 2.5 - 4 %	FF 0.1 % 2 %

Legend:
- X — process / furnace
- X — not employed in all installations
- y % — Pb-content of slag
- z % — Zn-content of slag

- SM: sinter machine
- BF: blast furnace
- ISF: Imperial smelting furnace
- OBBF: Oxygen-Rich Bottom-Blowing Furnace
- OSBF: Oxygen-Rich Side-Blowing Furnace
- EF: electric furnace
- FS: flash smelter
- FF: fuming furnace

Figure 22: Comparison of relevant lead winning processes with lead and zinc contens of the produced slags

Facts about lead winning processes are published only fragmentary and intermittent. On the basis of the 2012 minerals yearbook for lead by the USGS [18] and the 2010 lead smelter survey [17], it is possible to estimate the amount of slags that have been produced in 2008 after the reduction step of crude lead winning by smelters that treat only primary feed material or a mixture of primary and secondary feed materials. On the basis that 2008 the world lead production from primary sources is 3.9 million tons which represents a share of 75 % in the primary and primary/ secondary smelter's lead production, and that 3 % of the lead input of these smelters is lost in the slag, it can be calculated that the amount of slag is 5.3 million tons for 2008. If it is assumed that these slags contain in average 3 % lead and 10 % zinc, the lead amount in the slag is 160 000 tons, zinc amounts to 530 000 tons. Together, the metal value equals 982 million Euros. If all of these slags would have been treated towards a final slag with 0.1 % lead and 1 % zinc, more than 150 000 tons of lead and 370 000 tons of zinc could have been recovered, which represents a metal value of 751 million tons. In 2013, the lead production was 20 % higher than in 2008, so that lead and zinc entrained in the slags will be considerably higher as well.

The slag fuming process and, to a minor extent, the ISA/Ausmelt-process are the standard processes for the treatment of lead slags from crude lead production. Slag fuming takes place in a rectangular water-cooled furnace and is usually carried out batchwise with durations from 30 minutes up to three hours per batch. By injection of pulverized carbon and air an active gas-slag-interface is established that can be twenty

times the size of the furnace surface. At temperatures between 1150 °C and 1300 °C lead and zinc are reduced and volatilized from the slag and subsequently oxidized with additional air over the melt, so that they can be recovered in the flue dust as oxides. The slag produced by fuming typically contains 0.5 % to 1.5 % lead and 2 % to 4 % zinc. The main disadvantages of the process are that lower zinc contents are not possible due to the risk of iron reduction and that it produces large amounts of off gas and waste heat that have to be treated.

There are some publications about the possibility of using an electric arc furnace or plasma furnace for the treatment of slags, but its main use still is as holding or settling furnace. Nevertheless, electric arc furnaces offer multiple advantages for a slag treatment:

- high versatility in terms of feed material (e.g. solid / liquid), processing mode (e.g EAF / SAF / SRF etc.) and parameters (e.g. temperature; continuous / batchwise)
- small off gas volume
- little space required
- high energy density and high space-time-efficiency

On the opposite, the disadvantages are low turbulences in the bath and a high demand of electrical energy which can require an expensive electrical infrastructure. In this work it has been investigated if the electric arc furnace is a viable alternative for the treatment of lead slags. It can be added into an existing process line with only little demand for space and off gas treatment. It certainly makes most sense to process the liquid slag inline of the main process, but there still is the option to feed solidified slag and to melt it before treatment, too. In any case the electric arc furnace is able to adjust the slag temperature as needed. It is possible to generate stronger reducing conditions than in the slag fuming process, because if iron is reduced to metallic state it can be molten and consumed as reducing agent. This should enable the electric arc furnace to produce slags which are low both in lead and zinc.

Experimental

On the basis of the results of the preparatory work several test series in a 500 kW pilot-scale DC electric arc furnace have been conducted. In total more than six tons of six different industrial lead slags have been treated in 25 tests. The aim was to reduce the lead content below 0.1 % and the zinc content below 1 % and thereby to confirm and if possible extend the findings of the previous work, so that a scale-up into commercial scale is possible. A schematic of the furnace is depicted in Figure 23.
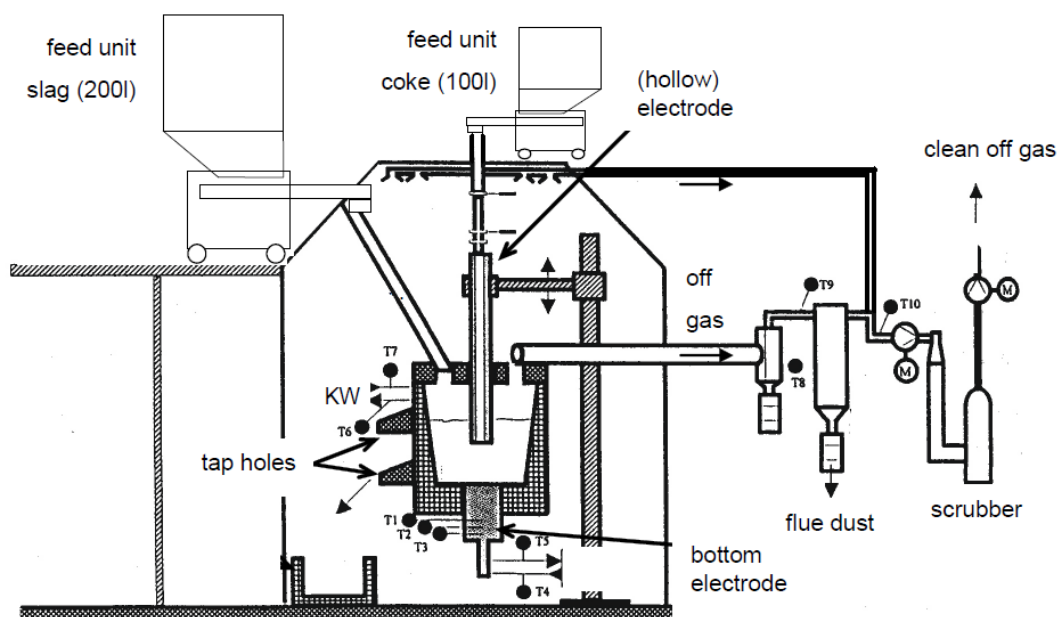
Figure 23: Schematic of the „old"pilot scale EAF at IME

Table V gives the initial chemical composition of the slags treated at pilot-scale at IME. Additionally, the average trial results are given in terms of final Pb and Zn concentration in the slags. The methods of coke additions to the melt are furthermore mentioned.

Table V: Composition of treated slags and average final experimental results from 25 trials
* "h.el."-hollow electrode, "pre"-premixed (slag & coke), "p.i."-pneumatic coke injection

slag type	Pb [%]	Zn [%]	Fe [%]	S [%]	SiO$_2$ [%]	CaO [%]	MgO [%]	Al$_2$O$_3$ [%]
I	8.9	11.7	28.2	0.1	25.1	9.8	1.3	2.3
II	1.1	5.1	25.5	2.6	24.6	16.4	4.4	7.9
III	55.3	5.9	10.3	0.1	7.1	3.4	0.4	0.7
IV	54.4	7.7	9.5	0.4	7.4	3.1	--	1
V	6.8	12.4	23.4	0.3	23.5	9.9	2.2	2.4
VI	5.8	11.4	24.5	0.4	23	10.8	1.5	2.8

slag type	method of coke feeding*	number of test runs	final slag			
			Pb [%]		Zn [%]	
			average	best	average	best
I	h. el.	6	0.80	0.08	3.50	0.10
II	h. el.	7	0.12	0.02	0.24	0.10
III	h. el.	3	16.6	0.29	0.09	0.05
IV	pre.	2	5.85	3.30	1.44	1.36
V	h. el.	1	0.39	0.39	2.98	2.98
V	p. i.	4	0.78	0.38	6.09	3.89
VI	p. i.	2	0.49	0.32	2.94	2.49

Despite of the partly insufficient results (in terms of the final lead and zinc contents) important correlations can be derived from the test runs. At first, all test runs show a comparable interdependence of the zinc content upon the lead content throughout the duration of the test runs. Figure 24 shows exemplary a test run with slag type I. The lead content in the slag decreases faster than the zinc content (left). This could be expected, but more interesting is that the decline of the zinc content shows a logarithmic dependency on the lead content of the slag (right).
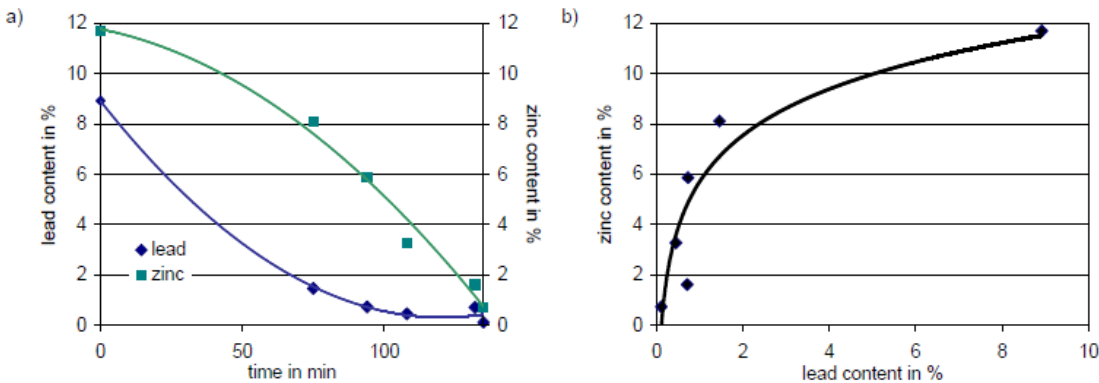

Figure 24: Slag type I: lead and zinc content vs. duration of a test run (left) and zinc content vs. lead content (right)

In consideration of the empirical variation in the samples, this dependency can be found in all test runs. For each slag type the logarithmic correlation between lead and zinc is unique, so that by averaging the logarithmic functions of the slag types one mean function for each slag type can be obtained. Generally speaking all of these trends can be expressed by an equation of the form

$$Zn_t = f(Pb_t) = A \cdot \ln(Pb_t) + B \tag{Eq. 16}$$

Zn_t: Zn content in % at time t; Pb_t: Pb content in % at time t; A: Factor; B: Constant

Altogether by calculating the factors A and B the time-dependent Zn concentration in relation to the Pb content may be expressed as:

$$Zn_t = Zn_0 - (-0.01953 \cdot Pb_0 + 4.455 - 0.0063 \cdot Pb_0^2 + 0.5552 \cdot Pb_0 - 3.436) \cdot \ln(Pb_t/Pb_0)$$

Summarizing Remarks

The first SAF was commissioned 100 years ago in Germany. Since then a tremendous development of this smelting tool was recognized all over the world and submerged arc furnaces (SAF) are now operating in at least 20 different main industrial fields. In metallurgical production, the traditional aim of the SAF is to increase recovery of metals form slags to the maximum. SMS group has supplied numerous furnaces for this application. Especially in the field of rectangular furnace technology, the SAF could enhance its market position for slag cleaning.

The last order in rectangular furnace for the First quantum project at Kanshansi, Zambia demonstrates convincing results and confirms the intelligent solution (such as side wall cooling system, furnace integrity). The stirring reactor as a new unit in the

line in copper production enables new dimensions in the industrial improvement of the iron silicate product, commonly only named slag. With the copper content in the by-product slag being able to be reduced by 30-50%, depending on the starting raw materials, the raw material copper is better exploited. Furthermore, additional byproducts, which are unwanted for reuse of the iron silicate product, are to some extent even more significantly reduced than copper.

Furthermore, over the last decades the SAF has taken an enormous position in non-ferrous metallurgy research. Numerous dissertations have been published and underline the versatility on this type of furnaces in many different industrial and scientific applications. Some examples of recent scientific results have been demonstrated. The applications for SAFs range from the reuse of previously landfilled Redmud, Cobalt-recovery operations and the reduction and removal of Pb and Zn from slags to future applications for example in the pyrometallurgical treatment of deep-sea minerals such as polymetallic Mn-nodules.

The close cooperation of University researchers and experienced industry engineers is fundamental to the advancement and optimization of industrial processes. The cooperation between SMS and IME shows that the entire size spectrum from lab- and technical-scale up to pilot- and industry-size research may be realized and leads to important process improvements. Generally, it was shown that the application of the submerged arc furnace technology to the valorization of slags enables the production of low-level heavy metal contamination of the slags while simultaneously allowing the recovery of valuable metals from the slags.

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