

PRELIMINARY CHARACTERIZATION OF THE SAMPLES TAKEN FROM A SUBMERGED ARC FERROCHROME FURNACE DURING OPERATION

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ABSTRACT

The chemical and physical phenomena in a Submerged Arc Ferrochrome Furnace are broadly studied in the laboratory and pilot scales. Profound research in the production scale has been limited by the challenging process conditions.

The goal of the Experimental Research of the Submerged Arc Ferrochrome Furnace was to have samples from the operational furnace burden. Specially developed drilling equipment was used to take samples from the closed 75 MVA submerged arc ferrochrome furnace during a short maintenance break when the furnace was in normal operation condition.

The drill samples (pellets, lump ores, cokes, dust) were subjected to chemical and microscopic analysis. Large amounts of fines were found in the top burden samples. The pellets were partly reduced but lump ore reduction was not detected. The contents of Zn, S, alkalis and the reactivity of cokes were found to increase towards the top of the burden. The experiment result will give a better understanding of the furnace burden condition in different sections of the ferrochrome furnace. Information on the experimental research will be used to optimize the smelting charge materials and furnace operation, and future modeling and dimensioning of the SAF furnace.

1 INTRODUCTION

High carbon (HC) ferrochrome is mostly produced in submerged arc furnaces (SAF). They can be open, semi-closed or closed. Researching charge material reactions in any furnace during production is challenging, but it is the most difficult with closed furnaces. The closed SAF represents BAT technology in HC ferrochrome production.

Reduction of different chromium concentrates in a solid and in a smelted state has been extensively studied in laboratory tests. Various other reactions have also been studied, such as moisture evaporation and decomposition reactions of gangue minerals related to ferrochrome production.

In addition to the laboratory tests, samples from real furnaces have been collected. In those cases, samples have been taken after the final tapping of the furnace, and after the furnace has cooled down. Samples from a shutdown and cooled furnace are not equivalent to conditions during operation and do not represent the phenomena in the operating state of the SAF.

In ferrochrome production, gas samples from a closed submerged arc furnace have been taken in an operating state. Gas samples have been used for studying the formation of nitrogen/carbon compounds and chromates in submerged arc furnace smelting. The conditions in a closed furnace are reducing for the formation of nitrogen oxides and hexavalent chromium compounds [1]. Samples from the gas space represent overall gas reaction products from the furnace, but they do not clarify the reactions in different positions inside the SAF. Figure 1 shows chromium concentrates reduction reactions depending on the temperature [2].

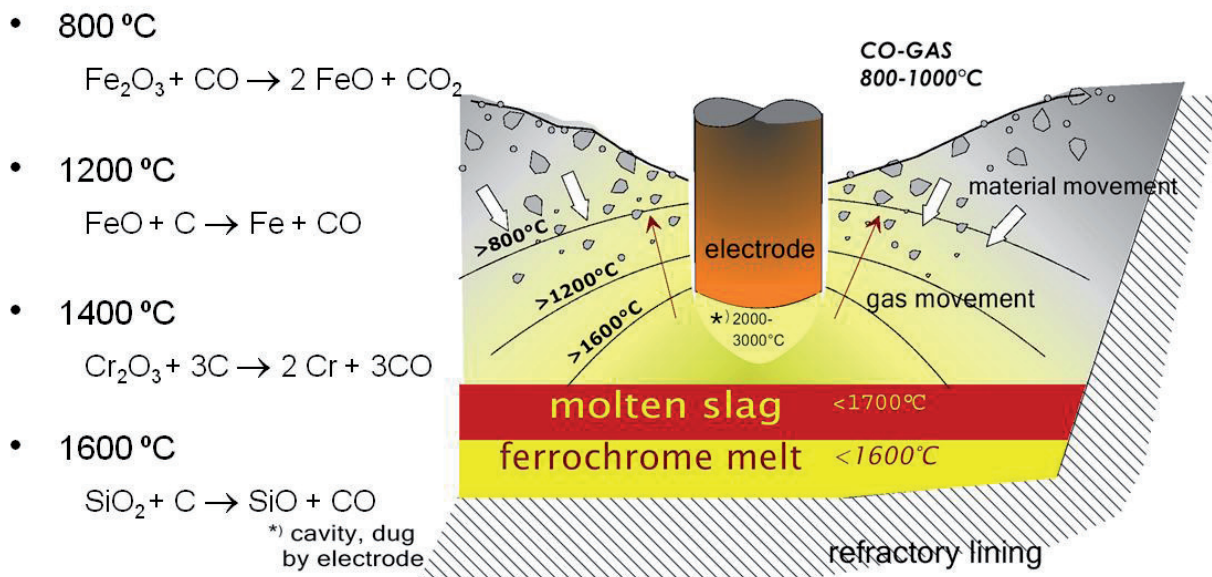


Figure 1: Reaction zones in a smelting furnace.

In the closed SAF, various conditions exist depending on furnace dimensioning, preheating, variable electrical conductivities and the smelting characteristics of charge materials, furnace active power, timing and success of tapping and scull formation. Current conducting routes change continuously during operation, and conditions near electrodes and on furnace walls differ significantly from each other.

Inspection hatches of the closed SAF and other possible access holes in the wall are directed into the gas space above the burden. Due to this, the collection of solid and smelted materials from a furnace during operation requires sampling downwards, which is technically very challenging. It is possible to analyze only final smelted reaction products through a tap hole.

The active power of a closed ferrochrome furnace is in the range of 65-70 MW and the main voltage 450 V. They, together with furnace gas, place safety requirements on on-power sampling during operation. In this study, sampling equipment has been designed, which enabled sampling in a closed SAF from the surface of charge materials towards electrodes during a short maintenance break. Samples have been used for analyzing the thermal decomposition and grindability of charge materials, decomposition and reduction reactions and structure changes in charge materials. In this paper, results for reduction degree and easily gasified compounds (Zn, S, K) together with the developed sampling equipment are presented.

2 DESCRIPTION OF THE SAMPLING EQUIPMENT AND SAMPLING

2.1 Sampling Equipment

Drill core sampling has been performed in blast furnaces for a long time. In blast furnaces the samples are taken from the tuyere level in a horizontal direction. These samplers are specially manufactured and generally enable drilling only in a horizontal direction.

In a closed ferrochrome furnace, horizontal sampling is not possible. Samples must be taken with a tilted drill tube, which makes sampling even more difficult. For this, project sampling equipment for a closed submerged arc furnace had to be designed. The equipment was modified from a diesel-driven earth drill with rubber rollers. Drilling equipment is small- to medium-size, 1800 kg by weight and is equipped with rotation, thrust and stroke capabilities.

Technical characteristics:

Drill effective stroke

- Effective stroke	5100 mm
- Thrust force	40 kN
- Extraction force	70 kN
- Tilt	10° – 80°

Drill rotation

- Torque Nm/RPM	80/2000
- Adjustable rotation speed RPM	0-2200

The following modifications were made on the standard earth drill

- special long boom $L = 5700$ mm, which enables a 5100 mm effective stroke for a drill core tube, (standard size $L = 2000$ mm with a 1400 mm effective stroke)
- special large drill core tube $L_{\max} = 6000$ mm, $\varnothing 127$ mm; (standard size $L = 3000$, $\varnothing 32$ -50 mm)
- drilling tube equipped with a material lock
- water cooling for drilling tube
- inert gas (nitrogen) flushing inside the drill tube



Figure 2: Drill sampling equipment

2.2 Drill Sampling of the Ferrochrome Furnace

Electric furnace drillings were performed at Outokumpu Tornio Ferrochrome Works. Samples were drilled from electric furnace no. 2 with a transformer power of 75 MVA.

A separate access door ($H=500$ mm, $L=400$ mm) was made in the gas space of an electric furnace shell. The access door was located next to the electrode, which enabled the shortest pathway to reach the most extreme environment in the SAF. Figure 3 shows a schematic drill sampling set up.

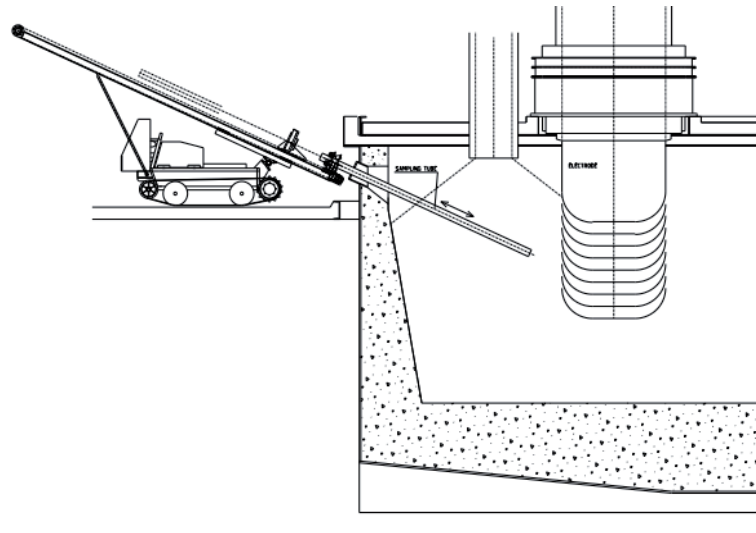


Figure 3: Schematic presentation of drill core sampling

Sampling was performed about 1 hour after the electric furnace tapping. The furnace power was switched off during the sampling. Drilling was done at an angle of 25° until the drill tube faced hard scull material. During the drilling, nitrogen was conducted into the drill tube, which cooled the tube and formed an inert gas atmosphere inside it. The head of the extracted drill core tube was blocked with tap hole clay in order to prevent the outflow of the sample and to maintain the inert gas atmosphere in the tube. Electric furnace drilling was performed twice.

The diameter of the drill tube opening, about 12 cm, is the same size as the largest particles in charge material. This prevented the tube from filling completely as large particles were repelled from the tube opening. Despite this, particles from different depths could be collected, but the amount of particles representing different depths in SAF varies and creates some uncertainty in the sample processing. In these first drillings, the drill core was divided into 20 cm sections.

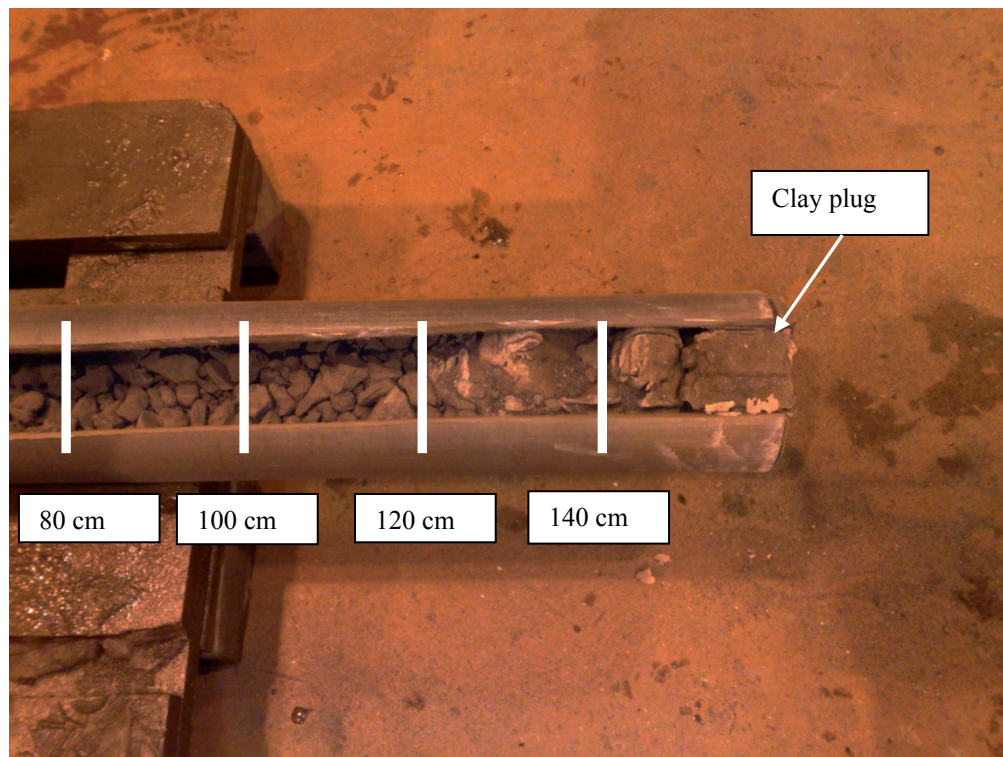


Figure 4: Opened drilling core

The samples from the divided sections were transferred into a sample vessel. Total length of the drill core sample was 140 cm, which gave seven sample entities per drilling. Visually the drilling samples consisted mostly of charge particles and dust. In the second drilling, the head of the sampling tube also contained partly melted material. At the end of the drilling the distance between the drill tube and electrode was close to 50 cm and the drill tube penetration in the charge material was close to 200 cm. Figure 4 shows the opened drill core tube.

3 RESULTS

3.1 Microscopic Analysis of the Obtained Results

From each separate sample entity, pieces of pellets, lump ore, coke and quartz were selected and split for SEM analysis. The partly smelted samples from Drilling 2 were also prepared for the SEM analysis. With some exceptions, the drill core samples were mostly unchanged without any noticeable chromium/iron reduction or smelting. Among the samples taken from Drilling 1 at the depth of 100-120 cm, the microscopic studies showed a thick grey ZnS layer on the surface of two quartz particles and one lump ore, but the particles themselves were unaltered (Figures 5 and 6).

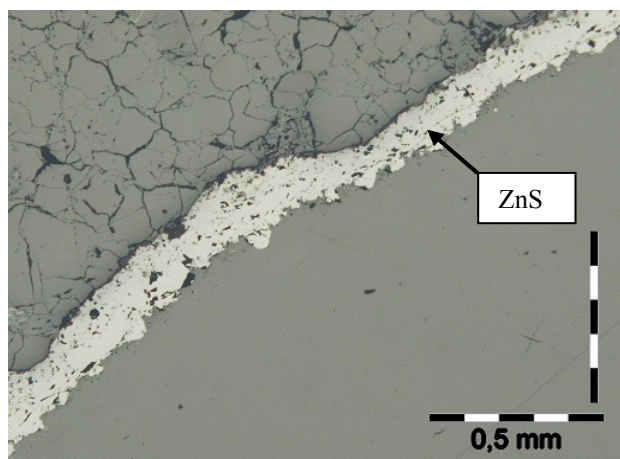


Figure 5: ZnS layer on quartz surface

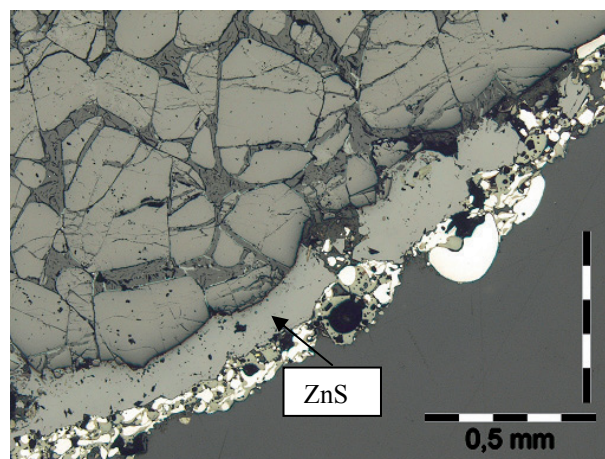


Figure 6: ZnS layer and metal drops on lump ore surface

According to the electron probe microanalysis (EPMA), the composition of the ZnS layer in both figures was (33 wt-% S, 5 wt-% Fe, 61 wt-% Zn). In Figure 6, distinctive metal phases have formed on the top of the zinc sulphide layer on the surface of a lump ore. Composition of the metal phases was 98 wt-% Fe.

A quartz sample taken from Drilling 2 (Figure 7) at a depth of 100-120 cm had a big metal drop on its surface enveloped by a layer of chromium sulphide (40 wt-% S, 60 wt-% Cr). Two different phases were found in the metal phase, one high with iron (4% Cr, 96% Fe), and the other with higher chrome content (58 wt-% Cr, 34 wt-% Fe, +C). All the samples were carbon-coated for electron microscope study, thus making the definition of reliable carbon content of carbides impossible. Figure 7 shows that some concentrate has been smelted on quartz surface.

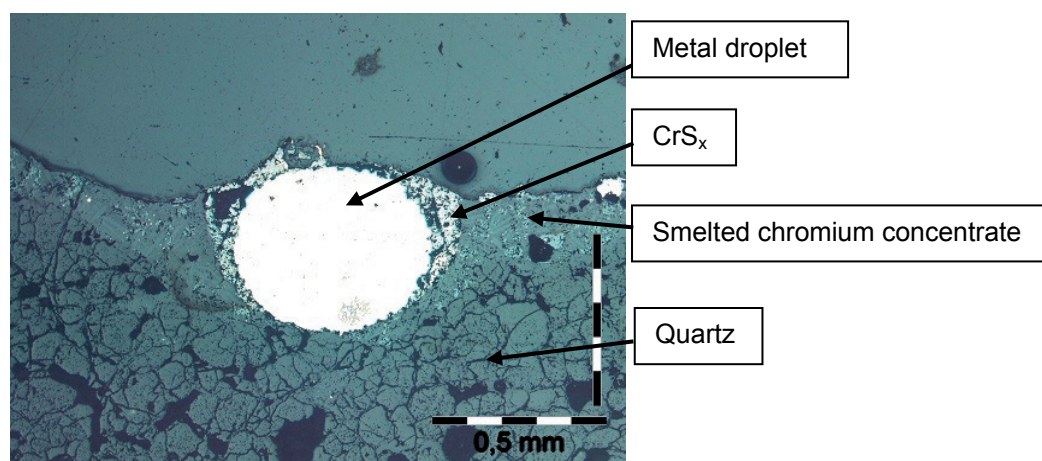


Figure 7: Metal drop formed on quartz surface

Figures 8 and 9 represent SEM pictures of partly smelted material from Drilling 2, which showed distinctive smelting and a large metal phase inside the pellet (Figure 4). Large metal phases have formed especially at the boundaries of coke and pellets (Figure 9) and of quartz and pellet. Here the large metal droplet inside the pellet (Figure 8) consisted of darker (63 % Cr, 24 % Fe, + C) and lighter (15 % Cr, 77 % Fe, +C) metal phases, which could be formed after cooling. Preliminary thermodynamic calculations made with HSC for chromium and iron reduction and for carbide formation indicated that the temperature had been over 1100 °C.

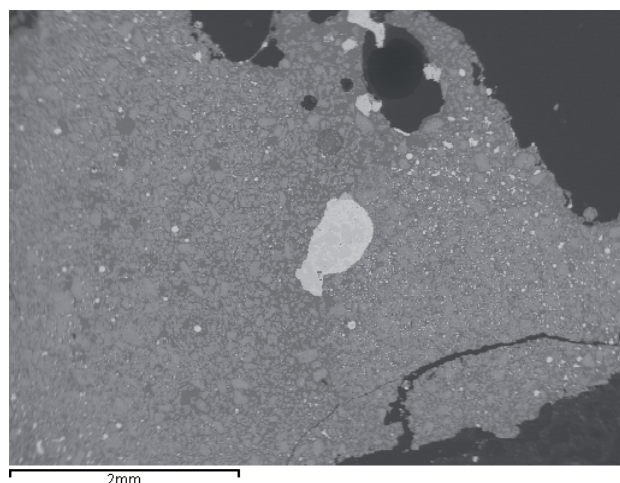


Figure 8: Center of pellet

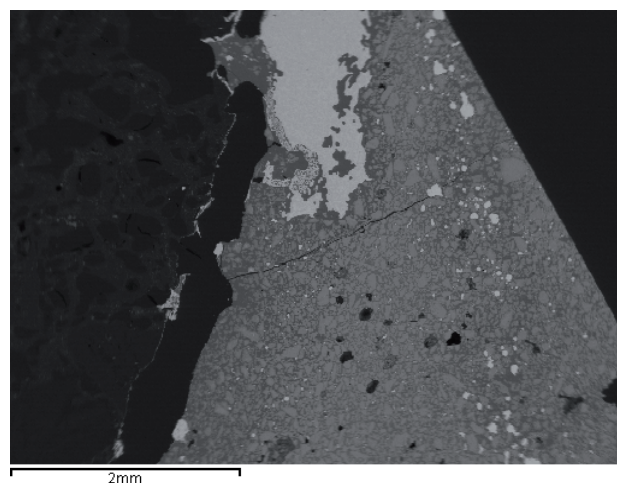


Figure 9: Boundary of coke and pellet

3.2 Overall Chemical Analyses for the Charge Materials

Among the samples from the submerged arc furnace, of each layer (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm, 80-100 cm, 100-120 cm, 120-140 cm) one piece of each material (pellet, lump ore, coke) and dust were selected for chemical composition analysis. In some cases, certain material was missing at a certain depth and thus the analysis could not be done for the whole range of drilling. The focus of chemical analysis was on observing the alkali contents and Fe^{2+} quantity. Compositions of coke, quartz, pellets and lump ore before charging into SAF are presented in table 1 and 2. Sulphur inside the furnace originates from coke and approximately 95 % of zinc from pellets and lump ore. Potassium is originally found in quartz.

Table 1: Composition of coke and quartz before charging into furnace

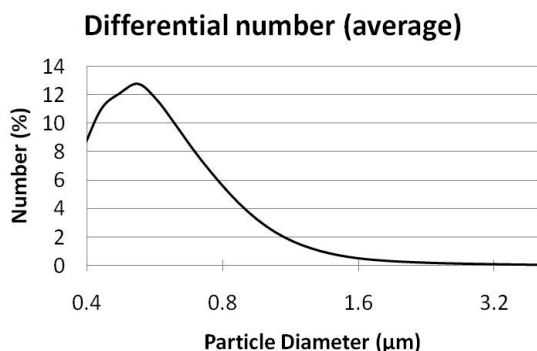
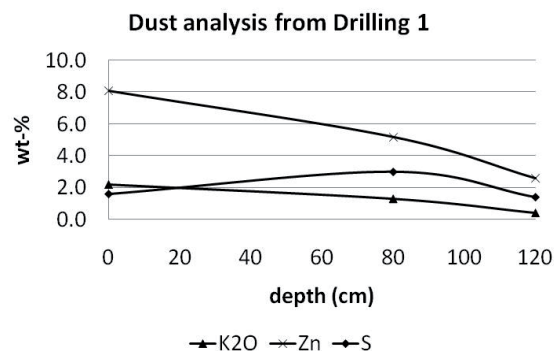
Wt-%	C (fix)	S	P	Fe_2O_3	SiO_2	Al_2O_3	MgO	CaO	TiO_2	Cr_2O_3	K_2O
Coke	88.5	0.58	0.028	0.99	6.6	2.7	0.18	0.3	0.17	0.2	-
quartz	-	0.007	0.03	0.7	95.3	1.1	0.4	0.4	-	-	0.2

Table 2: Composition of pellets and lump ore before charging into furnace

Wt-%	Cr	SiO ₂	Al ₂ O ₃	MgO	CaO	Cr/Fe
Pellets	30.2	4.5	13.0	11.5	0.5	1.68
Lump ore	25.5	10.1	11.9	16.2	1	1.89

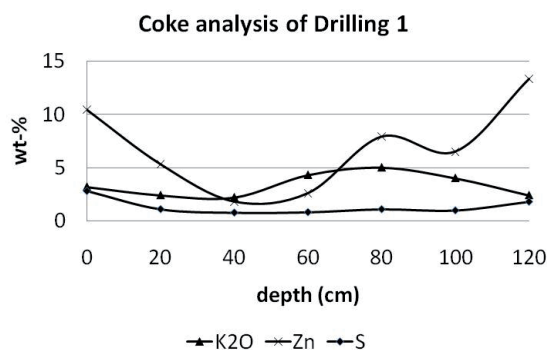
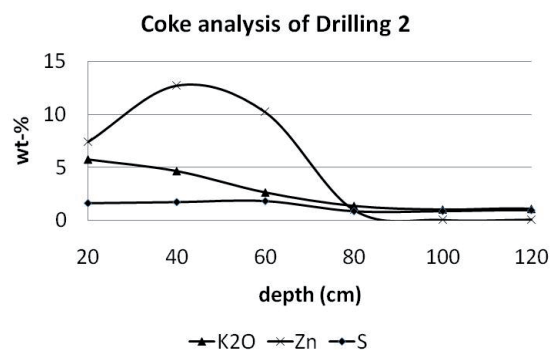
3.3 Dust Analysis

Dust samples were taken from both drillings. Large amounts of dust were found at a depth of 0-40 cm from both drillings, and the samples were subjected to particle size distribution measurement. The results in Figure 10 show that the largest quantity of particles were in the size range of 0.4 – 1 µm. Dust from depths of 0 cm, 80 cm and 140 cm were analysed to average chemical composition. Figure 11 shows the zinc, sulphur and potassium oxide contents of three dust samples taken from various depths in Drilling 1. It can be seen from the results that the contents of K₂O, Zn and S increase towards the top of the burden.


Figure 10: Dust analysis from Drilling 1

Figure 11: Dust particle size distribution

3.4 Coke Analysis

Contents of K₂O, Zn and S in coke ash collected in different sections are shown in Figures 12 and 13. It can also be seen that with cokes the K₂O, Zn and S contents increase towards the top of the burden. The measured reactivity of coke samples seems to decrease deeper in the burden (Figure 14).


Figure 12: Coke analysis of Drilling 1

Figure 13: Coke analysis of Drilling 2

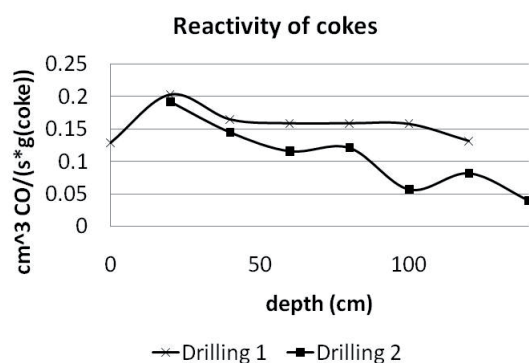


Figure 14: Measured reactivity of cokes

3.5 Chemical Composition of Lump Ores and Pellets

Change of K_2O , Zn and S contents in lump ores and pellets taken from separated sections are presented as a function of depth in Fig. 15-18. Potassium, zinc and sulphur contents seem to grow in the case of pellets towards the surface of the burden, but not in case of lump ores. The reason for this is most probably the pellets' more porous structure and larger surface area, which is essential if Zn-, K- and S-bearing compounds are transferred via the gas phase.

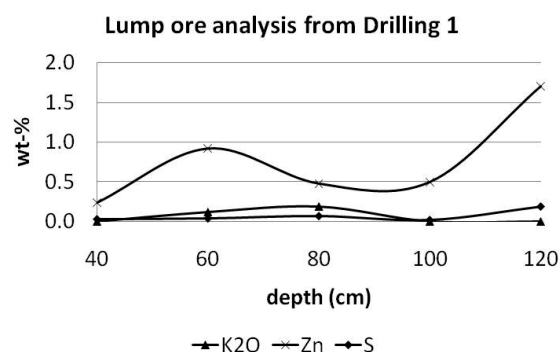


Figure 15: Chemical analysis of lump ore from Drilling 1

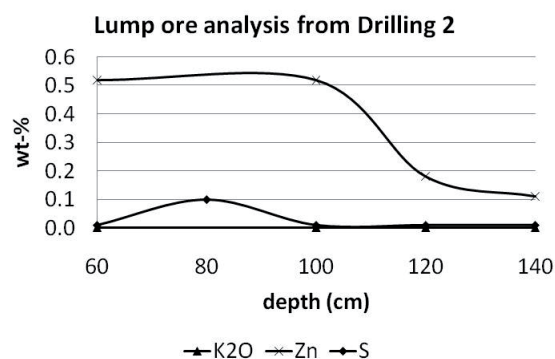


Figure 17: Chemical analysis of lump ore from Drilling 2

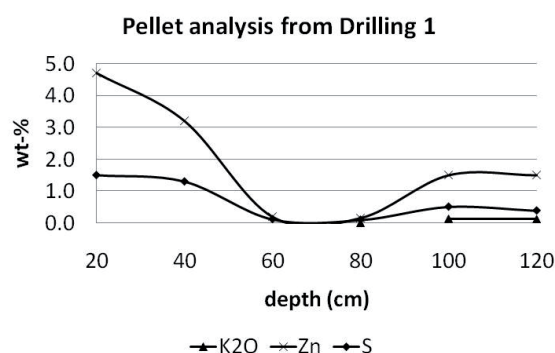


Figure 16: Chemical analysis of pellets from Drilling 1

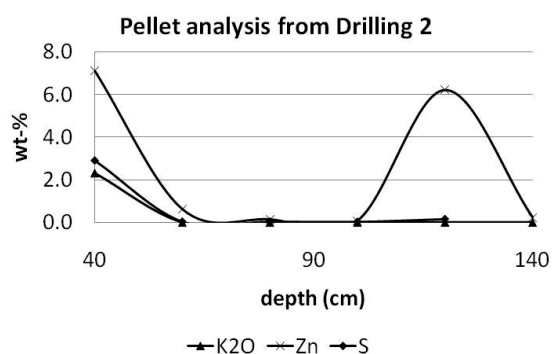


Figure 18: Chemical analysis of pellets from Drilling 2

3.6 Strength of Pellets and Reduction Degree of Chromium Concentrates

The strength of pellets remained close to the original values. The average strength of pellets from drillings was 111-128 kg. The average compression strength from the sintering furnace was 140-150 kg/pellet. Reduction degree of pellets and lump ore samples from Drilling 2 are presented in figure 19. Typically the $\text{Fe}^{2+}/\text{Fe}_{(\text{tot})}$ value for sintered pellets is 0.20-0.25 and for lump ore 0.8. It can be seen from the figure that the values for pellets are higher than after sintering, indicating that the sample pellets are partly reduced. The reduction level seems to increase deeper in the burden in the case of pellets. However, the length of the drill sample was not long enough for the detection of lump ore reduction.

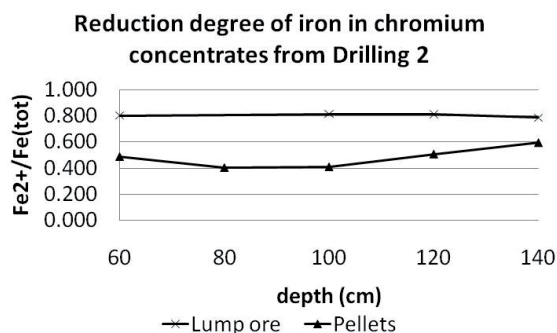


Figure 19: Reduction degree of iron in chromium concentrates

4 DISCUSSION

The reduction reactions

The pellets were partly reduced and the reduction degree increased deeper in the burden. Lump ore reduction was not detected from the samples, indicating that reduction of the pellets starts at an earlier state than the lump ore.

Earlier studies concerning chromium concentrates reduction with CO [3] showed similar dual-phase formations inside a metal droplet at a high temperature as in this study, with the exception of carbide formation. CO gas can transfer through a pellet and reduce chromite particles forming large metal phases, but the carbon content in CO gas is not high enough for carbide formation. In the SAF, as shown in this paper, the pellets and lump ores are in direct contact with cokes making the supplement of carbon adequate for carbide formations. Moreover, the difference between experimental and process conditions is in the thermal profile. The tendency of process gas in lower temperature is to shift towards CO_2 diverge carbon in higher parts of the burden, which also eases carbide formation.

The behavior of Zn, S and alkalis

The thermal profile and basic operation (solid material flows downwards and gases rising upwards) is analogous to the blast furnace process. The measured amount of Zn-, K- and S-bearing compounds significantly exceeds the value of feed material. Also the ZnS layers found in the top of quartz and lump ore indicate the existence of gas phase transfer of these compounds. In this way, the behavior of Zn- and K-bearing compounds is quite similar to BF. These results indicate that temporary circulation is possible.

Reactivity of cokes

As mentioned earlier, the downward motion of the burden takes coke to a higher temperature area. Temperature has an effect on the characteristics of cokes by gasifying isotropic components or increasing carbon layer ordering. Cokes decreasing reactivity deeper in the burden indicate that isotropic areas selectively gasify in a similar manner to BF [4].

The applicability of the developed drilling machine to assess SAF internal state

The drilling machine allows monitoring of process dynamics in a way which has never been possible before. Drilling done at different points of time and furnace conditions enables metallurgy development and optimization of the furnace in a more detailed way. The sampling method itself requires only small modifications in the drilling practices and tube-opening design, including a material lock to prevent samples from rolling out of the drilling tube. Further development is needed for the identification procedure regarding the specific locations each collected sample represents.

The results show different trends in Drilling 1 and 2. This could indicate differing internal states in the SAF. Differences in internal states can originate from different current paths in the furnace hearth, leading to a different thermal profile in the SAF. As a consequence, depending on the internal thermal profile, the phenomena can show differences in measured values. It is also possible that the drilled core does not represent the full range of drilling depth.

5 CONCLUSIONS

The operating efficiency of the submerged arc furnace is not high with fine charge materials. Feed materials are required to be strong. The right pretreatment methods are important in order to avoid fines.

Reduction reactions proceed quite near electrodes in the submerged arc furnace. Reduction in solid state is quite insignificant in the top and wall burden layers, except for the iron in chromite pellets.

The developed sampling method provides cutting-edge knowledge of the phenomena in the SAF, and can be used as a tool to further develop and optimize the SAF process. Based on the first drillings, new information could be obtained on the behavior of burden materials.

6 REFERENCES

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