A LABORATORY INVESTIGATION OF THE INFLUENCE OF ELECTRIC CURRENT ON THE BURDEN REACTIONS IN A SUBMERGED ARC FURNACE

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ABSTRACT

A submerged arc furnace (SAF) is generally used in the production of ferrochromium. Typical raw materials used in the production are pellets, lump ore, quartz and coke. These materials are mixed together before being charged in the furnace.

In this paper the influence of electric current on the mixed burden materials used in ferrochromium production in SAF was investigated in a laboratory scale apparatus. The temperature range was 1300 – 1600 °C and the atmosphere gas phase consisted of either argon or CO. Experiments were done with and without the electric current. After the experiment a scanning electron microscope (SEM) was used to study the structure of particles. The electric current was found to enhance reduction and increase temperature on its path. Particles on the current's path reduced extensively and melted, forming large clusters. The particles, which were not located on electric current's path were reduced mostly by CO gas.

1 INTRODUCTION

Production of high carbon ferrochromium is commonly done in a submerged arc furnace (SAF). Typical feed materials consist of chromium comprising pellets and lump ore, reducing agent coke and fluxing component quartz. Charging of the furnace is done by mixing all the materials together and feeding them from the top of the furnace. The mixed burden then descends inside the furnace towards electrode tips. While descending the burden encounters different kinds of reducing conditions.

The reduction of chromite has been studied by many authors in the past [1-4]. Typically the experiments have been reduction experiments for pellets and lump ore with 1) coke, 2) CO or 3) coal. General findings clarify the reduction with solid reductant or with CO gas. In solid state reduction chromium concentrate was found to reduce mainly with CO gas, especially in case of fine ores and pellets. However, lump ore with less porosity was found to reduce better with direct contact to solid coke. It has been concluded that the reduction in the surface of lump ore is controlled by chemical reaction, while with fine ore, diffusion in gas phase is the rate controlling factor. Solid reductant is also found to regenerate CO_2 to CO after reduction and is therefore necessary for reduction continuity.

The formation of slag and its ability to dissolve spinel components from the chromite grain keeps the reductants and chromium containing components in a close contact with each other assisting the reduction process [5]. Flux addition has been found to mainly affect chromium oxide reduction in areas with high temperature [6]. The silicate slag formation enhances the diffusive flux of the different species within the chromite grains, thus increasing the importance of the chemical reaction on the surface. It has been shown that the main reduction of chromium takes place in the softening zone and not in the slag layer in SAF. However, early formation of slag may hinder or even stop the reduction if this early formed slag originates from porous cementing gangue. Cementing gangue can accumulate on the surface of the chromite grains thus preventing the reduction of chromites [7].

The direct effect of electric current on the burden components and reduction reactions in SAF requires more investigation. Large electric currents are transferred into the SAF without a complete understanding of the effects of the current on the various phenomena inside the furnace. Generally current is considered nothing else but a source of heat in the process. However electric current led through the partially ionic melt containing chromium oxides causes electrolytic reactions [8]. In this paper the effect of electric current on burden materials of SAF is studied with a laboratory made apparatus. Burden materials were exposed to strong electric current and the changes in structure and reduction were studied by using scanning electron microscope (SEM).

2 EXPERIMENTAL

An apparatus was built to study the influence of electric current on the burden materials at high temperature (Figure 1). The shell of the apparatus was a ceramic tube made of Al_2O_3 and graphite plates were placed on the both ends. The bottom graphite performed as a bottom electrode and its counterpart was a movable graphite electrode, with a support rod attached to it. The rod went through the cover and a 500 g weight was placed on top of it to reach a good contact pressure for the burden. Fluke- 125 industrial Scopemeter was used for voltage and current measurements and it was connected to the electrodes. In addition the Pt/PtRh10 thermocouple was installed inside the equipment and gas input was arranged through the bottom electrode. Finally the whole apparatus was placed inside a chamber furnace. The inner space of the apparatus was well isolated and thus it was possible to do the experiments with Ar and CO gases.

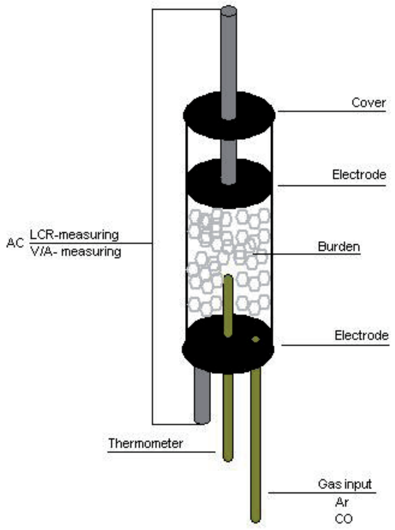

Figure 1: Experimental apparatus

2.1 The test with argon

In the first experiment argon gas was used. The selected burden materials and their amounts in the first experiment are presented in table 1.

Table 1: Materials selected for experiment with argon

	Particle size (mm)	Weight (g)	wt-%
Quartz	6.74-4.76	46	6.1
Lump ore	6.74-4.76	130	17.3
Pellets	6.74-4.76	210	28.1
Coke A	6.74-4.76	320	42.9
Coke B	6.74-4.76	42	5.6
Total		748	100

Coke A and B present two different kinds of commercial cokes. In SAF the burden is in constant downward motion thus continuously generating and disrupting connections between coke particles. Moreover the softening of burden components brings core particles closer to each other and joins the coke particles to a more or less continuous matrix. The softening of burden materials is also affected by the amount of alkalis in the particles. Samples taken out of the SAF [9] indicate the amount of alkalis, zinc and sulphur to be highest in the top part of the burden inside the SAF. In the experimental setup the burden being static and not in motion a larger amount of coke was used to simulate the possible connections of particles formed in the real furnace.

Argon, in the amount of 3 l/min, was used to simulate the gas flow of the real SAF process. The chamber furnace was used to heat the burden to 1300 °C. At 1300 °C the power supply was turned on and set to 100 V. The current rose rapidly to 40 A and it was necessary to lower the voltage to 60 V to avoid exceeding the limits of the transformer. This indicated the existence of negative resistance caused by arcing. Though lowering the voltage by 40 V the current only decreased to 34 A. High current increased the temperature in the burden to 1600 °C, although the main furnace temperature was set to 1450 °C. After 30 minutes the power was turned off and the furnace was left to cool down in inert gas atmosphere. The burden was removed from the furnace after 10 hours when it was fully cooled.

2.2 The test with CO

In the second experiment the following burden recipe was used (Table 2).

Table 2: Materials selected for experiment with CO

	Particle size (mm)	Weight (g)	wt-%
Quartz	6.74-4.76	46	6.6
Lump ore	6.74-4.76	130	18.6
Pellets	6.74-4.76	210	30.1
Coke A	9.52-6.74	150	21.5
Coke A	6.74-4.76	120	17.2
Coke B	6.74-4.76	42	6.0
Total		698	100

Heating was done in the similar way as in the experiment with argon. When the temperature of the burden had reached 1300 °C argon was replaced with CO, and the gas flow was kept at 3 l/min. At the same time the power supply was turned on. The voltage was set to 105 V, but was quickly lowered to 50 V due to an even faster increase in current than with argon. The current was more stable than with argon and 51 V was enough to sustain 38-40 A current. Reason for the more rapid rise in current after turning the power on in this test was more likely due to the different packing of burden particles. The different atmosphere was not considered to effect on the current transfer in these tests, because the CO gas was turned on at the same instant as the power supply. This time the burden temperature increased to 1550 °C and not to 1600 °C, which can also be due to a different current conduction path. After 30 minutes the power was turned off and the furnace was left to cool down in an inert gas atmosphere. The burden was removed from the furnace after 10 hours when it was fully cooled.

2.3 The test without electric current

For comparison the third burden patch was prepared for an experiment with the same apparatus but this time without the use of electric current. The burden was heated with argon to 1300 °C, where it was switched to CO. The flows of the gases were 3 l/min. After 30 minutes the temperature had reached 1496 °C and CO was switched back to argon for cooling down the furnace. After 10 hours the burden was removed from the apparatus.

Table 3: Materials selected for experiment without electric current

	Particle size (mm)	Weight (g)	wt-%
Quartz	6.74-4.76	46	6.6
Lump ore	6.74-4.76	130	18.6
Pellets	6.74-4.76	150	21.5
Pellets	11.3-9.52	60	8.6
Coke A	9.52-6.74	290	41.5
Coke B	9.52-6.74	23	3.3
Total		699	100

3 RESULTS

After the tests with argon and CO the burden samples were taken out from the apparatus. It was quickly discovered that some of the particles in the burden had experienced rough conditions. Clearly visible metal formations on the surface of the particles and particle fusions could be observed with the naked eye. The location of these clusters in the test burden pointed out the current transfer paths. Single –not fused- particles surrounding the clusters were apart from the current path and had reduced only by the influence of CO. Samples were selected from both experiments for further study with a scanning electron microscope (SEM). Pictures taken with SEM are presented in figures 2-7. Figures 2,4,6 and 7 present samples from the experiment with electric current and argon. Pictures 3 and 5 present samples from the experiment with electric current and CO. Lots of formed metal can be seen from the pictures. In some cases these reduced oxides formed “metallic bridges”, connecting them with cokes. Typically these large metallic phases had grown in contact with coke and on the surface of pellets and lump ores.

A closer look on those phases showed them to consist of darker and lighter phases. According to SEM analysis the dark phases consisted of (54 % Cr, 36 % Fe + C) and lighter phases of (7 % Cr, 88 % Fe + C) and (7 % Cr, 83 % Fe, 2 % Si + C). An image editing procedure allowed measurement of the fractions of lighter and darker phases, estimating the average composition of the metal droplet in figure 2 to be (42 % Cr, 48 Fe). The samples used in SEM analysis were coated with carbon, and therefore measuring the accurate carbon amount of the carbides was impossible. In figure 6 a small dark spot can be seen inside a metal droplet. This spot was found to consist of sulfur and chromium, while the metal surrounding it consisted mainly of iron. In general the spherical metal droplets were found to consist mostly of iron with a little amount of chromium. Chromium was found only in the large clusters.

In some cases like in figure 4 a large slag phase with partly reduced chromite had formed between the metal phase and unreduced pellet. In figure 5 lump ore behaves in practically the same way. The content of silicon inside metallic phases was found to increase if there was a particular large slag phase nearby (fig. 7). Lighter phases inside “metallic bridges” consisted of (6 % Cr, 81 % Fe, 6 % Si + C).

The results of the experiment done without electric current showed less reduction of particles. Pellets and lump ore samples were not reduced as much as in the experiments done with electric current. The number of clusters formed was also smaller and the few, which had formed were mostly caused by partial melting of chromium comprising particles. Pellets and lump ores worked here as combining reagent. The binding material of pellet and gangue of lump ore had melted and attached the particles to each other (Figure 8.). Thin metallic lines were formed between chromite particles and cokes (Figures 9 and 10) but their size was far less compared to the “metallic bridges” and large droplets formed in the experiments involving electric current. In figure 11 a small sulfur rich phase (3 % Cr, 60 % Fe, 36 % S) surrounds an iron droplet.

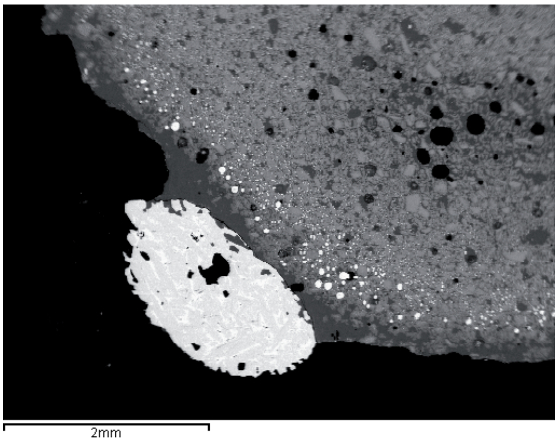

Figure 2: Large metallic droplet on surface of pellet (Test with CO)

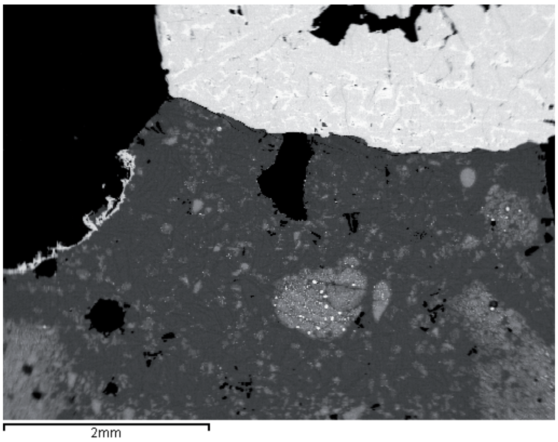

Figure 3: Strongly reduced pellet with large metal droplet (Test with CO)

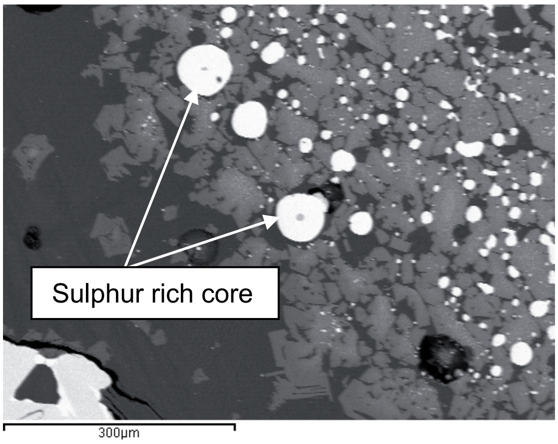

Figure 4: Metal droplets with sulphur core (Test with CO).

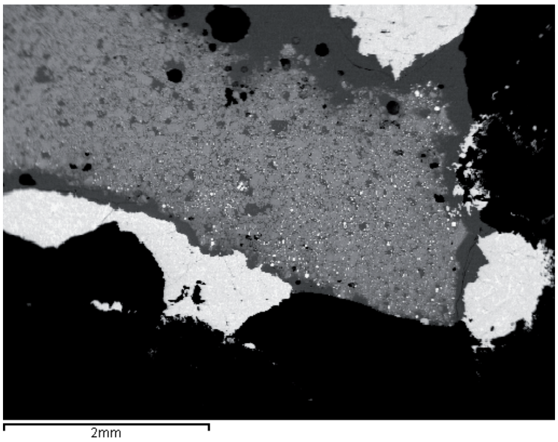

Figure 5: Metallic bridges formed between pellet and cokes (Test with Ar)

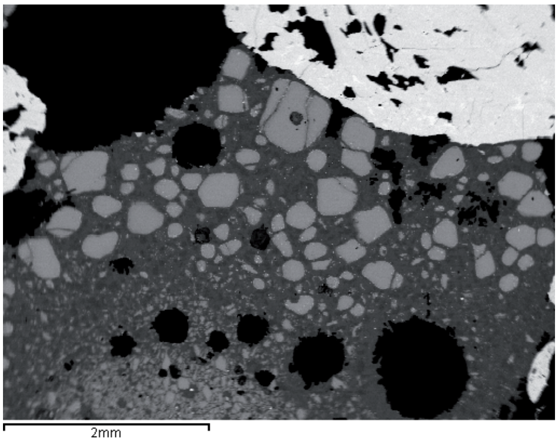

Figure 6: Lump ore attached to a pellet (below) and metal droplet (above) (Test with Ar).

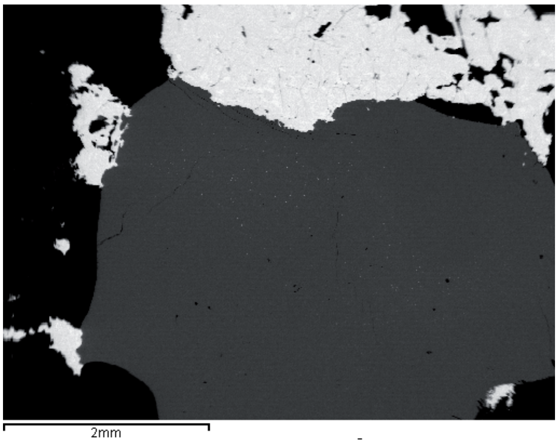

Figure 7: Glassy slag phase surrounded by large metallic phases and cokes (Test with CO)

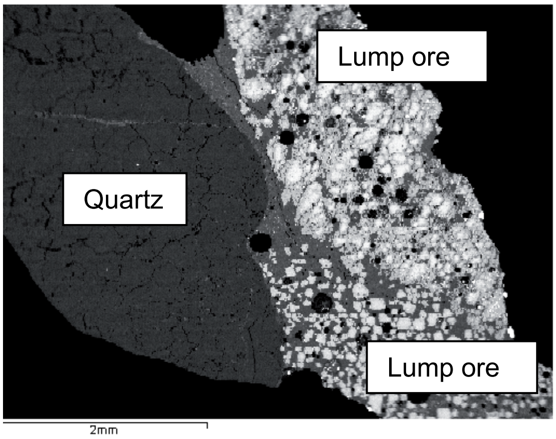

Figure 8: Two lump ores joined with quarz in (Test without electric current)

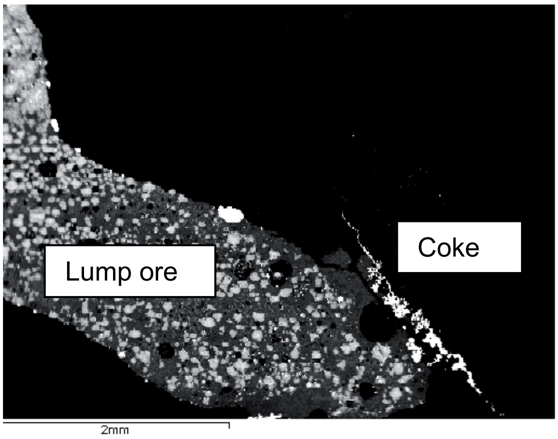

Figure 9: Thin metallic line between lump ore and coke (Test without electric current)

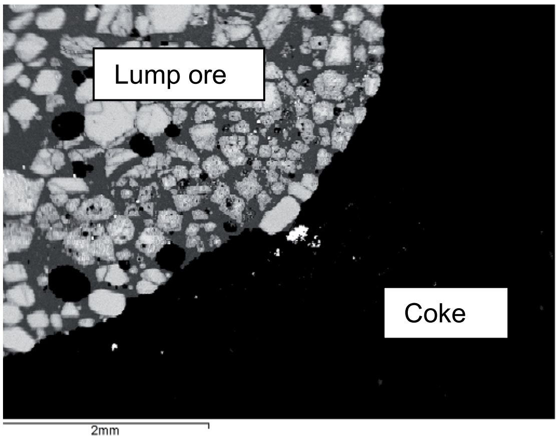

Figure 10: Small metallic bridge between lump ore and coke (Test without electric current)

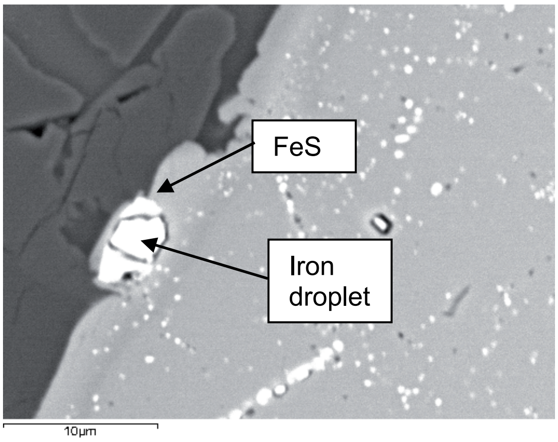

Figure 11: Sulfur rich metal phase around an iron droplet (Test without electric current)

4 DISCUSSION

In this research it was found that pellets and lump ores were significantly reduced when operating in a high temperature environment using electric current. Lots of metal droplets and metallization had formed throughout the particles. Two experiments, where electric current was used, were found to cause substantial reduction in pellets and lump ores and large cluster formation. Clusters were concluded to be formed by electric current running through the particles smelting, reducing and fusing them together.

Particle sizes used in the experiments varied only a small amount, and the effect on clustering and reduction is considered negligible. Earlier studies by Dawson et al. [1] with different sizes of reductant materials showed the rate of reduction to be depended on the size of the reductant. According to their experiments, coarse reductant decreased reduction considerably, when operating without CO gas input. Dawson et al. showed the direct contact of chromites and reductants to be necessary for reduction. The results presented in this paper showed extensive reduction occurring at the interface of cokes and chromite grains. Reduction taken place in these locations has resulted in formation of large “metallic bridges” between cokes and chromite grains.

The formation of “metallic bridges” (Figure 3.) in the experiments using electric current indicates current transfer through these bridges. Located between coke and chromite ore these bridges could have performed as contact points, hot spots, where ohmic current transfer or arcing has occurred. Formation of large metal phases indicates that electrolysis reactions are not prohibited by alternating current. Current heading one way reduces metal components and releases oxygen, which exits the area of reduction as soon as formed. Thus the change of direction in current caused by AC power supply cannot make reaction reversible in the absence of oxygen.

It can be seen from the results (Figure. 4) that the morphology of chromite around the large metallic phase, located next to coke, has changed dramatically, forming a liquid phase consisting of the remaining unreduced components without solid spinels. All the reduced chromium and iron of the chromite grains were transferred to large metallic phase. This finding agrees with Dawson et al. [1] who suggested that spinel dissolves only when it is in close proximity to a reducing agent.

It can be discussed if the temperature was the real cause for the formation of large metallic phases. It was certainly higher in the experiments with electric current than without it. Higher temperature will result in higher reduction, however, it was the electric current that increased the temperature as was mentioned in the results. What is unclear is which played the more important role, the rise in temperature in contact points due to current transfer or the transportation of free electrons into the same area. The experiments without electric current showed less metallization and localization of metal phases than did the experiments with electric current. Therefore electric current seems to effect reduction of chromite ores by enhancing the reduction in the areas where current transfer is taking place.

When comparing the reaction time of our experiments to earlier studies it can be seen that an interval of only 30 minutes to achieve large metallic phases is quite exceptional. Xiao et al. [3] used CO-gas in reduction of chromites at temperature range of 1450 – 1550 °C from 2-4 hours. In their case CO gas diffused in to chromite pellet resulting reduction of chromite grains first at the surface of the pellet followed by the reduction deeper in the pellet. High temperature with long heating time formed larger metallic phases on the surface of the pellet. These larger phases were found to consist of darker and lighter phases. Neuschütz [5] also found same “two-phase” formation in his studies. He studied chromite ore reduction with coal at 1200 to 1550 °C by using mixtures of 4 g of grinded chromite ore, 4 g of coal and 0,24 g of silica. Temperature used for reduction was 1550 °C with a hold up time of 150 minutes. With gas input (Ar 90 %, CO 10%) his results showed metal droplets formed at 1480 °C and higher to consist of three phases Fe-Cr-Si, Fe-Cr-C and Fe-Cr-Si-C. According to him these metallic phases were probably liquid at the reduction temperature and separated into three different phases after cooling. Similar findings occurred in this research, although only in the case of large metallic formations. According to the two earlier studies, a longer heating time seems to lead to this kind of “two-phase” formation after cooling. In our investigations electric current seemed to enhance formation of these metallic phases, moreover the size of the metallic phases found on the surface of particles reached over 2 mm in diameter.

Small metal droplets consisted mainly of iron. However, as presented in figure 6 there is a metal droplet with a darker core. This core consisted of (48 % Cr, 6 % Fe, 43 % S + C) while the surrounding lighter phase was (4 % Cr, 91 % Fe + C). This high chromium and high sulphur bearing droplet was formed in an experiment with electric current. On the other hand the small iron droplet in figure 11 with a surrounding layer of (3 % Cr, 60 % Fe, 36 % S) had formed in the experiment without electric current. Electric current involved results showed more advanced reduction than the one without electric current. Obviously chromium tends to replace iron in the sulphide as reduction continues.

In these experiments it was found that potassium travelled inside a quartz particle forming a different phase within the quartz structure. Even a small amount of potassium can effectively lower the melting point of quartz, making the particle partly melt and attach to other particles. This kind of melting and softening of particles brings cokes, unaltered by softening, closer to each other to form a more or less continuous matrix and making the current transfer easier to occur. This can also happen in real SAF, where the alkali amounts has been measured higher in the top section of the burden inside the SAF. If this kind of current transfer occurs it affects the whole furnace operation by increasing temperature and reduction locally in the “wrong” parts of the furnace. In addition, even though the current transfer may appear only for a short time, it may be enough to partly melt large amounts of particles and cause bridging inside the burden.

The two experiments with electric current did not show remarkable differences in particles when operating with argon instead of CO, although the initiation of arcing should be considerably easier in an argon atmosphere. Both results from these two experiments showed extensive reduction of chromites and formation of metallic phases. The experiment, where reducing gas was used without electric current, showed less reduction than the ones with electric current. From these results it can be concluded that used gases had much less influence on reduction of chromite particles than the electric current.

5 CONCLUSIONS

Following points were found out in this study:

1) Electric current travelling through the burden materials used in SAF enhances the reduction reactions. Reduction is strong on the surface of lump ore or pellet in direct contact with coke.

2) Electric current can increase temperature locally leading further melting and softening of particles, excluding coke particles. This is followed by the clustering of particles that brings cokes closer to each other forming a coke matrix. These matrixes can perform as current conducting paths, increasing conductivity in that particular area.

3) Electric current running through the burden causes significant differences in reduction rate and reduction degree. It can increase reduction locally, while the reduction apart from current path is limited by CO gas transfer.

6 ACKNOWLEDGEMENTS

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