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# ELECTRICAL BEHAVIOUR OF SUBMERGED ARC FURNACE'S CHARGE MATERIALS

UNIVERSITY OF OULU GRADUATE SCHOOL; UNIVERSITY OF OULU, FACULTY OF TECHNOLOGY



### ACTA UNIVERSITATIS OULUENSIS C Technica 662

**ANNE HIETAVA** 

### ELECTRICAL BEHAVIOUR OF SUBMERGED ARC FURNACE'S CHARGE MATERIALS

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#### Abstract

When producing ferrochrome, a submerged arc furnace (SAF) is used. The charge of an SAF consists of chromite pellets, coke, lumpy ore and quartzite as a slag modifier. The charge is preheated before it descends into the SAF where the charge eventually reduces and melts. The electrical conductivity of the charge is important because, among other things, it affects the productivity of the furnace. The electrical conductivity of the charge should ideally be low on the higher parts of the furnace and high near the electrode tip. This is to ensure that the electric current path travels through the metal bath via arcing, which provides the most effective heat transfer. Another option for the current path would be through the solid feed material via ohmic conduction, but since this zone is less reactive, the heat energy would be mostly wasted.

This work brings forth new information about the electrical behaviour of coke and chromite pellet is produced. The electrical conductivity was measured at room temperature for different simulated process conditions (different coke textures, different reduction degrees of chromite pellets, sulphur in atmosphere and replacing the coke used in chromite pellet production with charcoal). It was found out that unlike gasification with a  $CO/CO_2$  mixture, heat treatment at 950°C increased the degree of graphitization and changed the electrical behaviour of coke. Furthermore, it was observed that increasing the chromite pellets' reduction degree reduced the electrical conductivity measured at room temperature. In the case of chromite pellets and sulphur in the atmosphere it was found that sulphur has an effect on the pellets' electrical behavior and structure during reduction, which - in turn - has an effect on the SAF performance when raw materials with varying sulphur contents are used. Lastly, it was found that substituting coke with charcoal when producing chromite pellets affects the sintering behaviour, cold compression strength, and electrical conductivity of the chromite pellets.

*Keywords:* charcoal, chromite pellet, coke, cold compression strength, electrical conductivity, graphitization, relative permittivity, SAF, sintering, sulphur

#### Hietava, Anne, Uppokaariuunin panoksen sähkönjohtavuus.

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#### Tiivistelmä

Uppokaariuuni on osa ferrokromin valmistusprosessia. Uppokaariuuniin panostetaan kromiittipellejä, koksia, palarikastetta ja kvartsiittia. Etukuumennusuunista panos laskeutuu uppokaariuuniin, jossa se pelkistyy ja lopulta sulaa. Uppokaariuunin panoksen sähkönjohtavuus on tärkeää uunin toiminnan kannalta, koska se vaikuttaa suoraan esimerkiksi tuottavuuteen. Jotta virran kulku tapahtuisi optimaalisesti sulan metallin kautta, panoksen sähkönjohtavuuden tulee olla pieni uunin yläosissa ja suuri alaosassa lähellä elektrodien päitä. Mikäli virran kulku tapahtuu uunin yläosassa, hukataan lämpöenergiaa ja uunin toiminta hankaloituu. Tässä työssä on selvitetty koksin ja kromiittipellettien sähköisiä ominaisuuksia. Sähkönjohtavuutta on tutkittu useilla simuloiduilla prosessiolosuhteilla (koksin eri tekstuurit, kromiittipellettien eri pelkistysasteet, rikin pitoisuus atmosfäärissä ja kromiittipellettien valmistuksessa on korvattu koksi puuhiilellä). Nämä mittaukset on tehty huonelämpötilassa.

Huomattiin, että toisin kuin koksin kaasutus, koksin lämpökäsittely (950°C) nosti grafitoitumisastetta ja vaikutti sähköisiin ominaisuuksiin. Kromiittipelletin pelkistymisasteen noustessa huonelämpötilassa mitattu sähkönjohtavuus laski. Kun kromiittipelletit altistetaan atmosfäärille, jossa on rikkiä, pellettien sähköiset ominaisuudet muuttuvat samoin kuin rakenne pelkistyksen aikana. Tämä vaikuttaa uppokaariuunin toimintaan, kun käytetään raaka-aineita, joissa rikkipitoisuus vaihtelee. Kun kromiittipellettien valmistuksessa käytettävä koksi korvataan puuhiilellä, tämä vaikuttaa sintrausprosessiin, kylmälujuuteen ja sähköisiin ominaisuuksiin.

Asiasanat: grafitointi, koksi, kromiittipelletit, kylmälujuus, puuhiili, rikki, sintraus, suhteellinen permittiivisyys, sähkönjohtavuus, uppokaariuuni

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### Abbreviations

### Abbreviations

А	Constant given by the reflection plane
А	Area of the plate
A <sub>ad</sub>	Coke ash content
В	Half-value width
BFS	Blast furnace simulator
c	Conductance
ccs	Cold compression strength
d	Thickness of the dielectric
DTA	Differential thermal analysis
Fesem	Field emission scanning electron microscope
L <sub>a</sub>	Width of the graphite crystallite
L <sub>c</sub>	Height of the graphite crystallite
m <sub>0</sub>	Coke mass in the beginning
m <sub>t</sub>	Coke mass at the time t
R(t)	Reduction degree
SAF	Submerged arc furnace
TG	Thermogravimetric / thermal gravimetric
w <sub>0</sub>	Weight of the dried sample in the beginning of the reduction
$\mathbf{w}_{0}^{reducible}$	Total initial reducible oxygen calculated theoretically from oxygen in
	iron and chromium oxides based on chromite composition
W <sub>t</sub>	Weight of the sample at time t during reduction
Wvolatiles	Weight loss due to volatiles
x(t)	Gasification degree
XRD	X-Ray diffraction
XRF	X-Ray fluorescence

Greek symbols

$\varepsilon_0$	Vacuum permittivity, 8.854187817 $*10^{-12} Fm^{-1}$
$\mathcal{E}_r$	Relative permittivity
λ	X-ray wavelength
θ	Reflection angle of peak

### Chemical formulas

$Al_2O_3$	Aluminium oxide
С	Carbon
CaO	Calcium oxide
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
Cr	Chromium
Fe	Iron
FeO	Iron(II)oxide / ferrous oxide
Fe <sub>2</sub> O <sub>3</sub>	Iron(III)oxide / ferric oxide
K <sub>2</sub> O	Potassium oxide
MgO	Magnesium oxide
Na <sub>2</sub> O	Sodium oxide
$S_2$	Disulphur
SiO <sub>2</sub>	Silicon dioxide
$SO_X$	Sulphur oxides i.e. $SO_2$ and $SO_3$

### List of original publications

This work is based on the following articles, which are referred to in the text by their Roman numerals (I–V):

- I Heikkilä A, Pussinen J, Mattila O & Fabritius T (2013) Effect of coke's texture on electrical behavior. The Thirteenth International Ferroalloys Congress (INFACON XIII), Almaty, Kazakhstan.
- II Heikkilä A, Pussinen J, Mattila O & Fabritius T (2015) About electrical properties of chromite pellets - effect of reduction degree. Steel research int. 86 (2): 121-128.
- III Heikkilä A, Raiskio J & Fabritius T (2015) Effect of sulphur at reducing atmosphere on the chromite pellet properties. The Fourteenth International Ferroalloys Congress (INFACON XIV), Kiev, Ukraine.
- IV Heikkilä A, Sakaranaho M, Raiskio J, Heikkinen E-P & Fabritius T (2017) Sulfur containing atmosphere's effect on chromite pellets' structure and conductivity during reduction in SAF. Steel research int. 88 (7): 1600369.
- V Sakaranaho M, Heikkilä A, Suopajärvi H, Päätalo M & Fabritius T (2018) Charcoal use in chromite pellets - effect on sintering process, pellet properties, and electrical conductivity. Steel research int. 89 (2): 1700260.

The contribution of the author Anne Hietava (neé Heikkilä) is the following:

**Papers I and II:** The author carried out the analysis of the experimental results and wrote the paper. **Paper III:** The author defined the research problem, carried out a literature review, conducted the experimental work and the analysis of the experimental work and wrote the paper. **Paper IV:** The author defined the research problem, carried out the literature review, conducted the experimental work and the analysis of experimental work (except for the phase diagram calculated by other author) and was responsible for writing the paper. **Paper V:** The author did the major part of the writing, defined the electrical conductivity problem, and carried out the experimental and analytical work concerning electrical conductivity.

### Contents

Ał	ostrac	et		
Tii	iviste	lmä		
Ac	knov	vledger	nents	7
Ał	obrev	iations		9
Li	st of (	origina	l publications	11
Co	onten	ts		13
1	Intr	oductio	on to sintering process and submerged arc furnace	15
	1.1	Sinteri	ng process	15
	1.2	Subme	erged arc furnace	15
	1.3	Object	tive of the current work	17
2	Exp	erimen	tal	19
	2.1	Measu	rement, experimental and analytical devices	19
		2.1.1	BFS-device	19
		2.1.2	TG-device	
		2.1.3	Electrical conductivity measurements	21
		2.1.4	Light optical microscope, LOM	23
		2.1.5	Field emission scanning microscope, FESEM	23
		2.1.6	X-Ray Diffraction, XRD	23
	2.2	Sampl	e preparation	23
		2.2.1	Coke	23
		2.2.2	Chromite pellets	27
3	Res	ults and	1 discussion	43
	3.1	The el	ectrical conductivity of coke	43
		3.1.1	XRD measurements	43
		3.1.2	Electrical measurements	43
	3.2	About	the electrical properties of chromite pellets - the effect of	
		reduct	ion degree	
		3.2.1	Electrical measurements	46
	3.3	A sulp	hur containing atmosphere's effect on chromite pellets'	
		structu	re and conductivity during reduction in SAF	53
		3.3.1	Fesem analysis and phase diagram	53

		3.3.2	Electrical measurements	.57
	3.4	oal use in chromite pellets	. 58	
		3.4.1	Electrical conductivity	. 59
4	Con	clusion	and future work	63
Re	ferer	ices		65
Oı	rigina	ıl publi	cations	67

### 1 Introduction to sintering process and submerged arc furnace

When ferrochrome is produced, sintering process and submerged arc furnace are part of the production process.

### 1.1 Sintering process

The main composition of the chromite pellets used in this work is MgO 11%,  $Al_2O_3$  13%,  $SiO_2$  4%, CaO 0.5%, Cr<sub>2</sub>O<sub>3</sub> 44% and Fe 19%. Here the Fe is analyzed as elemental.

Chromite pellets are typically produced in a sintering process. Green pellets consist of chromite ore, coke fines and bentonite, which is typically used as a binder.

Green pellets are put through a belt sintering process in Outokumpu Tornio, Finland. One layer of pellets that have been sintered once are placed on top of a continuous perforated steel belt. Still wet (containing about 9-10% water) green pellets are fed into the sintering furnace on top of the already sintered pellet layer. Speed of the sintering belt is about 0.6m/min giving an approximate time of 48 minutes for the pellet to go through the sintering process. [1]

The sintering furnace can be divided into seven different sections. The sections are: the drying zone (390°C), the heating zone (1190°C), the sintering zone (1350°C), the leveling zone, and three cooling zones (1250°C, 1180°C, 520°C). The first three sections have a gas outlet at the bottom and the last three sections have gas blown in from the bottom of the perforated belt. Hot gas from the cooling zone can be used by the drying zone. This has a positive effect on the energy efficiency of the sintering process.

### 1.2 Submerged arc furnace

A submerged arc furnace (SAF) is used in ferrochrome production. The SAF is charged with chromite pellets, coke, upgraded lumpy ore, and quartzite as a slag modifier.

In Finland ferrochrome is produced by using a closed submerged arc furnace, see Figure 1. One advantage of a closed furnace is the ability to use the forming CO-gas to heat the burden batch before it descends into the actual furnace and other unit processes in an integrated steel plant. Preheating happens in a preheating furnace above the submerged arc furnace and the feed material is heated to about 500-800°C. Feeding pipes connect the preheating furnace to the SAF. These feeding pipes are always full so they act as the dispenser for the submerged arc furnace. [2]



Fig. 1. Closed SAF and preheating system, modified from Teräskirja [3].

Because the atmosphere inside the furnace is a reducing atmosphere, the charge also reduces when it descends. Material movements and a schematic temperature profile can be seen in Figure 2. The charge is heated with electrical energy via three Søderberg electrodes which are submerged in the feed material. The reduced metal droplets sink to the bottom of the furnace through the formed slag layer situated on top of liquid metal. The liquid ferrochrome and slag are tapped out from the furnace several times a day.

In order for an SAF to work efficiently the electrical behaviour of the charge needs to follow certain guidelines. The charge should have low electrical conductivity at the top of the furnace and sufficiently high conductivity near the electrode tips. This is because the current does not shortcut between electrodes in the upper part of the furnace



Fig. 2. A sketch of reaction zones in a smelting furnace. Here the highest temperature area near the electrode tip is a cavity dug by the electrode. (Paper II, modified and published by permission of Steel research international.)

and that of the current path is via the metal bath. If the current travels in the upper part of the furnace it reduces the amount of energy used in the correct place during heating, reduction and melting processes. This increases heat loss and reduces the energy efficiency and productivity. Usually the electrical performance requirement is achieved by changing the volume fractions of lump ore, pellets, coke and fluxes. [4, 5]

### 1.3 Objective of the current work

The aim of this study was to produce new information about the electrical behaviour of a submerged arc furnace's charge material, more precisely about coke and chromite pellets. The approach in this study was to measure the electrical conductivity at room temperature after experiment which simulated different process conditions for coke and chromite pellets. When looking at different charge materials, chromite pellets form the main part of research done in this work. Where coke is studied from the perspective of different textures (paper I), chromite pellets are seen from points of different reduction degrees (paper II), used sulphur in atmosphere (papers III and IV) and change in chromite pellet production where coke is replaced with charcoal in pellet production (paper V).

### 2 Experimental

This chapter presents the experiments carried out in this work, as well as briefly introducing the measurement, experimental and analysis devices used. The used measurement, experimental and analytical devices can be seen in Table 1.

I	П	III	IV	V
х			х	
	х	х	х	
	х	х	х	х
х	х	х	х	х
х		х	х	
	х			х
				х
•	I x x x	I II x x x x x x x x x x	I II III x	I   II   III   IV     x   x   x   x     x   x   x     x   x   x     x   x   x     x   x   x     x   x   x     x   x   x     x   x   x     x   x   x

Table 1. Analytical and measurement devices used in papers I-V.

#### 2.1 Measurement, experimental and analytical devices

This section presents measurement, analytical and experimental devices used in this work. All analyses are made at room temperature.

### 2.1.1 BFS-device

The blast furnace simulator (BFS) presented in Figure 3 is a device used in this work. The BFS device allows the temperature and atmospherice composition to change as a function of time. The electrically heated furnace uses different atmospheres with adjustable partial pressures of N<sub>2</sub>, CO, CO<sub>2</sub> and S<sub>2</sub>. Sulphur is generated in the atmosphere in an individual furnace according to the reaction equation  $2SO_2(g) + 2C(s) \rightarrow S_2(g) + 2CO_2(g)$ . The diameter of the furnace tube is 95 mm and both the tube and sample basket are made of heat-resistant steel. The maximum operating temperature for the BFS with the mentioned construction is around  $1100^{\circ}C$ .



Fig. 3. A sketch of the BFS-device. (1) Mass flow controller, (2) sulphur generator, (3) gas inlet, (4) reduction tube, (5) sample basket, (6) thermocouple, (7) electrically heated furnace, (8) scale for TGA and (9) computer system (Paper III, modified and published by permission of INFACON XIV).

### 2.1.2 TG-device

The TG-device presented in Figure 4 was used to reduce chromite pellets in this work. The furnace allows using different atmospheres such as  $N_2$ , CO and CO<sub>2</sub>. The furnace tube is made of Al<sub>2</sub>O<sub>3</sub> and allows the operation temperature to be around 1500°C. The samples are placed in a crate which can be made from different materials such as platinum or molybdenum. The furnace allows for the atmosphere and temperature to change with time.



Fig. 4. A sketch of the TG-device. (1) Flow indicator, (2) flow controller, (3) temperature controller, (4) scale, (5) computer, (6) gas, (7) Mo-wire, (8) crate, (9) thermocouple, (10) furnace insulator, (11) resistor tube SiC and (12) furnace tube  $AI_2O_3$  (Paper II, modified and published by permission of Steel research international).

### 2.1.3 Electrical conductivity measurements

Electrical conductivity measurements were made with the device presented in Figure 5. A sample is placed between two probes made from Cu and electrical measurements were made with a GW Instek LCR-817 device. There are two different probes with different diameters of: 5 mm and 10 mm.

The relative permittivity can be measured with the device presented in Figure 5. Permittivity describes how a medium affects the electrical field. Furthermore, relative permittivity is the relation between permittivity of the said medium and the vacuum permittivity. In this setup sample slices are treated as a plate capacitor. Relative permittivity is defined in this work as seen in equation (1).



Fig. 5. A sketch of the electrical conductivity measurements device (GW Instek LCR-817). (Paper I, modified and published by permission of INFACON XIII.)

$$\varepsilon_r = \frac{cd}{\varepsilon_0 A},\tag{1}$$

where  $\varepsilon_r$  is the relative permittivity, *c* is the conductance, *d* is the thickness of the dielectric,  $\varepsilon_0$  is the vacuum permittivity, and *A* is the area of the plate. Here  $\varepsilon_0 = 8.854187817... \cdot 10^{-12} \text{Fm}^{-1}$ .

Two reference measurements were made for this device with  $Al_2O_3$  and MgO. Measured values of relative permittivity were calculated with equation 1 for  $Al_2O_3$  and MgO were 10.5 and 8.6 respectively. When comparing these values with values given by suppliers and presented in the previous research [6] (7.8-11.1 for  $Al_2O_3$  and 9.0-10.1 for MgO) it is noted that the device can be used to measure directional relative permittivity.

### 2.1.4 Light optical microscope, LOM

In order to visually observe the polished sample sections an Olympus BX51 light optical microscope (LOM) was used. Different magnifications were available (40, 100. 200 and 500X).

### 2.1.5 Field emission scanning microscope, FESEM

The phase composition of polished samples was measured with a field emission scanning electron microscope (FESEM). The FESEM used was a Zeiss Ultra Plus fitted with an energy-dispersive X-ray spectroscopy (EDS) detector. Chemical analysis was made using an energy-dispersive x-ray spectroscopy analyzer attached to the FESEM. Polished sections were coated with a thin layer of carbon to ensure the electrical conductivity necessary for this analysis.

### 2.1.6 X-Ray Diffraction, XRD

X-Ray Diffraction (XRD) analysis was used for defining the chemical composition of the samples. The XRD measurement device used was a Rigaku SmartLab 9 kW general purpose XRD system with a cobolt lamp, tube voltage 40 kV and tube current 135 mA were used. Samples are ground into a fine powder for this analysis method.

### 2.2 Sample preparation

In this section the sample preparation for the coke and chromite pellet experiments is discussed.

### 2.2.1 Coke

Coke is made from coal that has many variables to be taken into account such as moisture, grain size, volatiles, ash concentration and different mineral concentrations. The coking process itself takes place in a coking battery which consists of several coking ovens that are separated by walls. The coke battery is heated by gas running inside the walls.

The coking process starts from the outer edge of the coke bed, proceeds to the centre and ends when the centre of the coke bed has been coked [7]. Variables that effect the coking time include, but are not limited to, the width of the oven, the coking temperature and heat loss features of the coal[8].

The changes coal goes through during the coking process are volatiles leave the coal [9], coal softens, melts, shrinks, extends and re-solidifies. The maximum temperatures the coal and coke are exposed to during the coking process are between 1000 and 1300°C.

#### Coke structure and electrical conductivity

The structure of graphite is very organized making the electrical conductivity depend on the orientation of the atomic layers in the graphite. Parallel to these layers the electrical conductivity is similar to metal, and on the other side perpendicular to the layers, electrical conductivity is more like a semiconductor [10].

The electrical conductivity of coke is not as good as graphite because coke is not as structured as graphite is[11]. The microtexture of coke has an effect on the resistivity (a lower resistivity means greater local molecular orientation, i. e. a more organized micro texture) and reactivity (reactivity increases when resistivity increases) [12].

In an industrial furnace the electrical conductivity of coke depends on the quality of the coke. If the coke originates from the edge of the coking furnace it is more likely to be more organized than if the coke comes from the centre of the coking bed [4]. This makes the coke selection important in an industrial scale SAF. Reorganization happens in the coke bed when coke particles descend inside the furnace [13], which may cause a decrease in the electrical conductivity of the charge. In laboratory scale experiments a minimum in electrical conductivity has been reported [14] but this has not been confirmed in an industrial scale SAF. It is expected that an increase in the coke particle structure as well as in electrical conductivity will be seen when coke particles descend inside an SAF experiencing temperatures which the coke has not been exposed to previously.

In order to study the effect of the coke's texture on electrical behaviour coke samples were divided into three different groups. One group was used as a reference, i. e. no treatments were made for it (raw), and two groups were treated in two different ways, using a) heat treatment at 950°C (graph) and b) gasification in a  $CO/CO_2$  gas mixture

(gas). Electrical measurements as well as XRD measurements were made for samples in all three groups.

**Selective gasification.** A carbon solution loss reaction (gasification) for coke happens at high temperatures in an oxidized atmosphere. A simple sketch of the gasification process can be seen in Figure 6. Crystalline carbon and non-crystalline carbon gasify at different rates. Non-crystalline carbon gasifies faster when compared to crystalline carbon. When gasification happens, graphitization occurs of non-crystalline carbon at the same time. This graphitization rate increases as the temperature rises. Thus, the reactivity of coke decreases as the coking temperature and organization of structure increases [15].



Fig. 6. Gasification and crystallization of carbon (Paper I, modified and published by permission of INFACON XII).

In this study coke was gasified using the BFS-device presented earlier in Figure 3. First, 108.65 g of coke was dried for over 24 hours. The experiment started by raising the temperature to 950°C in 90 minutes using nitrogen atmosphere. Next, the coke was held at  $CO_2$  atmosphere at 950°C for 240 minutes and then cooled in a nitrogen atmosphere. The flow rate for the gases was 10 l/min.

The coke gasification degree was calculated using equation 2 and was found to be 10.8%.

$$x(t) = \frac{m_0 - m_t}{m_0 - m_t A_{ad}} \cdot 100\%,$$
(2)

where x(t) is the degree of gasification,  $m_0$  is coke mass at the beginning,  $m_t$  is coke mass at time t and  $A_{ad}$  is the coke's ash content. The change in mass during coke

gasification can be seen in Figure 7. The total mass decrease was 10.32g, or about 9.5%. The 0.5% change in mass in the inert atmosphere at the beginning of the experiment is probably due to volatives in the coke.



Fig. 7. Mass change as a function of time in the coke gasification experiment (Paper I, modified and published by permission of INFACON XII).

**Graphitization of coke.** 93.24 g of coke was heat treated. The coke was placed in a graphite crucible which was placed inside a corundum crucible and the space between the spinel and graphite lids was filled with crushed graphite. This was done to make sure that only the temperature would affect the coke's texture. The samples were placed in an experimental furnace at room temperature and heated at the rate of  $10^{\circ}$ C/min to  $1600^{\circ}$ C. The samples were kept for 24 hours at  $1600^{\circ}$ C and then cooled to room temperature using a cooling rate of  $10^{\circ}$ C/min. After the experiment the mass of the sample was 83.90g.

The graphitization degree is defined by the height of graphite crystallite ( $L_c$ ), see Figure 8. When looking at the coke structure, similar types of organized crystallites can be found. In order to provide a numerical value for the degree of graphitization, the height of the crystallites ( $L_c$ ) is defined using a Scherrer equation (Equation 3). Note that the width of the graphite crystallites is defined in the same way.

$$L_{a/c} = \frac{A\lambda}{B\cos\theta},\tag{3}$$

where  $L_c$  is the height of the graphite crystallite,  $L_a$  is the width of the graphite crystallite, A is a constant given by the reflection plane (note that  $L_{002} = 0.9$  and  $L_{10} = 1.84$ ),  $\lambda$  is the x-ray wavelength [Å], B is the half-value width [rad] and  $\theta$  is the reflection angle of the peak. The height as well as the width of the graphite crystallites are compared to the coke particle's electrical conductivity, see Figures 20 and 21.



## Fig. 8. Structure of graphite crystallite (Paper I, modified and published by permission of INFACON XII).

Graphitization itself happens via four different stages and transformation from one stage to another is rapid. The first stage is where the material consists of parallel centers which are situated arbitrarily. In the next stage these parallel centers form pillar like structures at around 800-1500°C. The height of the pillar-like structures increases while the width remains the same. This is the most typical level of organization for metallurgical cokes. During the third stage at around 1500°C, the layers begin to merge and the height of the crystallites ( $L_c$ ) increases. The graphitization is completed during the fourth stage when the layers straightens. [11]

### 2.2.2 Chromite pellets

### Electrical properties of chromite pellets - the effect of the reduction degree

Even though the electrical conductivity of chromite pellets is less than that of coke [5], the pellets have an impact on the electrical conductivity of an SAF charge.

When the pellets desced inside the SAF they do so in rising hot reducing gases which consist mainly of CO originating from the high temperature area near the electrode tip. Reaction equations producing CO can be sorted by temperature as:

$$800^{\circ}\text{C} : \text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2,$$
  
 $1200^{\circ}\text{C} : \text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO},$   
 $1400^{\circ}\text{C} : \text{Cr}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Cr} + 3\text{CO} \text{ and}$   
 $1600^{\circ}\text{C} : \text{SiO}_2 + \text{C} \rightarrow \text{Si} + \text{CO}.$ 

When the pellets descend the most easily reducible oxides - iron oxides - reduce. This work concentrates only on the reduction by CO gas, not the reduction with solid carbon which has been discussed before [16].

**Reduction degree.** The reduction degree for chromite pellets reduced with CO gas is the amount of oxygen removed compared to the total amount of removable oxygen [17]. The reduction degree is defined the following way:

$$R(t) = \frac{w_0 - w_t - w_{volatiles}}{w_0^{reducible}},$$
(4)

where R(t) is the degree of reduction,  $w_0$  is the weight of the dried sample at the start of the reduction,  $w_t$  is the weight of the sample at time t during the reduction,  $w_{volatiles}$  is the weight loss due to volatiles and  $w_0^{reducible}$  is the total initial reducible oxygen calculated theoretically from oxygen in iron and chromium oxides based on the chromite composition.

In this study chromite pellets were reduced using the TG-device presented in Figure 4. Six experiments were carried out where three pellets were first placed in a nitrogen atmosphere for 10 minutes and then in a CO atmosphere for 15 - 180 minutes, see Table 2.

Table 2. Holding times for experiments 1-6.

Experiment number	1	2	3	4	5	6	
Holding time	180 min	120 min	75 min	45 min	30 min	15 min	

As mentioned before, the main composition of chromite pellets is MgO 11%, Al<sub>2</sub>O<sub>3</sub> 13%, SiO<sub>2</sub> 4%, CaO 0.5%, Cr<sub>2</sub>O<sub>3</sub> 44% and Fe 19%. Here the Fe is analyzed as elemental.

The reduction degree for the pellets in experiments 1-6 was calculated using Equation 4 and can be seen in Figure 9.



Fig. 9. Reduction degrees for pellets in experiments 1-6. Paper II, modified and published by permission of Steel research international.

Light optical microscope pictures from the edge and centre of the tested pellets can be seen in Figure 10. Here white droplets are metal droplets. The number and size of these metal droplets can be calculated using the very robust Image J-program.





Fig. 10. Light optical microscope pictures from experiments 1-6. The reduction degree is shown in parenthesis. Paper II, modified and published by permission of Steel research international.

In the light optical microscope pictures, the total number of metal droplets is compared to the total area of the pellet. The percentage of metal droplets is calculated for the centre of the pellet as well as the border of the pellet. The results can be seen in Figure 11. It can be seen that there are more metal droplets on the surface than at the centre of the pellet.



Fig. 11. Percentage of metal droplets at the centre and border of the pellets. Paper II, modified and published by permission of Steel research international.

When examining the relative droplet size seen in Figure 12, there does not seem to be any systematical difference in droplet size between the surface and the inside. This suggests that the reduction happens through the whole porous pellet and occurs faster on the surface of the pellet.



Fig. 12. Average size of metal droplets at the centre and border of the pellets. Paper II, modified and published by permission of Steel research international.

# The effect of a sulphur containing atmosphere on chromite pellet structure and conductivity during reduction in an SAF

Thus far there is no reported data on sulphur behaviour in SAF, but there are some indicators of circulating behaviour similar to the one in a blast furnace [13]. Similarly to what occurs in a blast furnace the sulphur enters the SAF via charge materials such as coke.

It may be concluded that since sulphur is a part of the feed material, sulphur gases are formed inside the SAF. Circulating sulphuric behaviour occurs when sulphur containing gases rises to the upper part of the SAF and reacts with the charge.

**Sulphur experiments.** When studying the effect sulphur has on the behaviour of chromite pellets, four different test sets were conducted with the BFS-device presented in Figure 3. In each experiment a total of 26 pellets were placed in a sample basket and different amounts of sulphur were added in the atmosphere (0%, 0.1%, 0.3% and 0.5%). In other respects the atmospheric composition remained the same: nitrogen was used during heating up to about 800°C, then nitrogen was set to 0% and carbon monoxide, carbon dioxide and sulphur were introduced. Nitrogen was used during the cooling down period. An example of the atmospheric composition can be seen in Figure 13. The temperature profile for the experiments can be seen in Figure 14.



Fig. 13. An example of the atmospheric composition during experiments from an experiment with a sulphur content of 0.5%. Paper III, modified and published by permission of INFACON XIV.



Fig. 14. The temperature profile during sulphur experiments. Paper III, modified and published by permission of Steel research international.
#### Charcoal use in chromite pellets

As mentioned earlier, chromite pellets are formed using chromite ore, coke fines and bentonite. The burning of coke releases both  $CO_2$  and  $SO_X$  into the atmosphere since coke contains carbon and sulphur as well as ash. One way to reduce the amount of these emissions is to replace the coke in chromite pellets with charcoal which is almost sulphur free. [18]

Biomass utilization in chromite pellet sintering has not been studied before. Still it is possible to find studies on utilizing biomass - such as charcoal - in iron ore sintering. [19–23] These studies indicate that if the tumble strength and reduction disintegration of the agglomerate are at acceptable levels, half of the coke can be replaced by charcoal. These studies provide a basis for investigating the impact of substituting coke with charcoal in chromite pellet sintering. This effect is studied here by looking at the changes in cold compression strength (ccs), sintering process and electrical behaviour.

In order to study the effect of replacing coke with charcoal, chromite pellets with different charcoal/coke amount must be made. The main grain size of chromite ore used in these experiments is 70% below 74  $\mu$ m and the chemical composition is 45.2% Cr<sub>2</sub>O<sub>3</sub>, 18.9% Fe, 13.3% Al<sub>2</sub>O<sub>3</sub>, 0.4% CaO, 9.8% MgO, 3.3% SiO<sub>2</sub> and the Cr/Fe-rate is 1.6. Here Fe is analyzed as elemental. The coke used is a mixture of coke dust from off-gas filters from a sintering plant and ground metallurgical coke. When examining an industrial sintering plant, the coke used to make chromite pellets is mainly fine coke (0-4mm) from coke screening. This fine coke is then fed into grinding mills alongside chromite concentrates. Before pelletizing, coke from the off-gas filters is needed to balance the carbon content.

The charcoal used in this research was made from chips of silver birch (*Betula pendula*) and downy birch (*Betula pubescens*) in a process of slow pyrolysis. The birch chips were placed in an SiC-reactor and the furnace was heated to 900°C, at a rate of 4°C/min. The pyrolysis was carried out in an oxygen-free atmosphere which was ensured by feeding nitrogen gas at a rate of 2 l/min. The formed charcoal was ground into four different particle size ranges (< 90µm, 90 – 250µm, 250 – 500µm and 500 - 1000µm).

Carbon and sulphur contents were analyzed using an LECO CS200 -analyzer and the results can be seen in Table 3. Furthermore, the ash composition in both fuels was analyzed by XRF (PANalytical Axios max 4 kW) and the compositions can be seen in Table 4. The amount of ash in the charcoal and coke was 3.0% and 14.0%, respectively.

Fuel	Carbon	Sulphur
Charcoal	96.18%	0.006%
Coke	85.21%	0.741%

#### Table 3. Carbon and sulphur contents for coke and charcoal.

Table 4. Ash composition of coke and charcoal.

Fuel	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	CaO	FeO
Charcoal	0.30%	22.62%	13.50%	1.25%	7.06%	38.38%	16.98%
Coke	1.28%	1.56%	3.32%	26.20%	47.53%	5.85%	14.25%

The pelletizing batches consisted of approximately 550g of fine concentrate mixed with 5.5g of bentonite and different amounts, proportions and types of fuels. The compositions of the different batches can be seen in Table 5. The reference pellet represents the industrial pellet. In batches 1-4 the amount of coke replaced by charcoal varies (25, 50, 75 and 100 w-%). The particle size of charcoal was varied in batches 6-8 and excess charcoal was added to concentrate the mix in batches 9-11. The moisture content was raised to 10% by mixing water with the pelletizing batch.

Pellets were then made using a laboratory-scale pelletizing disc with a diameter of 40 cm and a wall height of 9 cm. The rotation of the disc was 30 rpm and the disc was inclined at an angle of  $45^{\circ}$ . A chromite-fuel-bentonite-water mixture was added to the disc and rotated for 5 minutes. The formed pellets were screened and those of the correct size (10-14 mm of diameter) were set aside. Oversized pellets were crushed and put back into the disc as were undersized pellets. This procedure was repeated until the whole pelletizing batch consisted of pellets with a diameter size between 10-14 mm.

About 130 green pellets were sintered in a laboratory scale sintering furnace, see Figure 15. The sample basket diameter was 70 mm and the height was 160 mm and the pellet sample itself was in the form of a cylinder with a diameter of 55 mm and a height of 125 mm. A thermocouple on the top was situated inside the pellet layer, more precisely 25 mm from the bottom of the said layer. The thermocouple underneath was placed 5 mm from the bottom of the sample basket. The green pellets were placed in the sample basket which was perforated from the bottom in order for the air to flow through the pellet bed. The air flow rate from the bottom of the furnace was 4 l/min which ensured that all of the fuel was burned. The tubular furnace was heated to about 1380°C while the temperature in sample basket reached 1300°C. The sintering furnace had two thermocouples which created a differential thermal analysis (DTA) type setup

Batch no.	C <sub>fix</sub> (%)	Coke/Charcoal	Particle size range of used			
			fuels			
Reference	2	100/0	100% < 250μm, 50% < 90μm			
1	2	0/100	100% < 250μm, 50% < 90μm			
2	2	25/75	100% < 250μm, 50% < 90μm			
3	2	50/50	100% < 250μm, 50% < 90μm			
4	2	75/25	100% < 250μm, 50% < 90μm			
5	2	0/100	100% < 90μm			
6	2	0/100	100% 90 - 250μm			
7	2	0/100	100% 250 - 500μm			
8	2	0/100	100% 500 - 1000μm			
9	2.5	0/100	100% < 250μm, 50% < 90μm			
10	3	0/100	100% < 250μm, 50% < 90μm			
11	3.5	0/100	100% < 250µm, 50% < 90µm			

Table 5. Fixed carbon, coke/charcoal-rate, and particle size range of used fuels in different pelletizing batches.

and this was used to determine the temperature at which the fuel started to burn and to determine the maximum temperature that the mixture can create.

The sintering process presented here differs from the industrial sintering process. In the laboratory sintering process, the material bed is static whereas in the industrial process the material bed is continuously moving. Furthermore, in an industrial process the airflow is downwards and is at a much greater volume than in a laboratory setting where the air flow is from the bottom of the furnace. These differences are the reason why a reference batch was created.

The cold compression strength (ccs) of the pellets was measured using a Zwick/Reoll Z100 testing machine which provides data about the force needed to break the pellet. The ccs was measured for 30 pellets from each sintering batch. Pellets measured were selected to be roughly the same size in order to eliminate the size factor from the results.

Polished sections were prepared from each batch and examined with a light optical microscope (LOM). The purpose of this was to visually evaluate the difference between the textures of pellets from different batches.

A 3 mm slice was severed from ten pellets from each of yhe batches 1-4 as well as the reference batch. Also, electrical conductivity measurements were made and the relative permittivity was calculated using Equation 1 presented previously. Furthermore, nine pellets from each of the batches mentioned were reduced at 1500°C for 10 minutes in a nitrogen atmosphere and then for 120 minutes in a CO atmosphere using the



Fig. 15. Schematic presentation of the sintering furnace used. (1) Furnace tube with sample basket holder, (2) sample basket with green pellets, (3) heating elements, (4) thermocouples and (5) air inlet with mass flow controller. Paper V, modified and published by permission of Steel research international.

custom-built TG-furnace presented earlier in Figure 4. Then the pellets were cooled in a nitrogen atmosphere.

**Sintering process.** In order to study the sintering process, temperature profiles between the different batches were studied and compared to reference batch. As an example, the temperature profile of batch 6 (100% charcoal, particle size 90-250µm) is presented in Figure 16. The temperature profiles were found to be similar and consisted of five different phases described in Table 6. The lower thermocouple (Furnace) was situated below the hotspot of the furnace and thus its temperature is lower than the actual temperature of the furnace which could not be logged. The temperature difference at the end of the sintering between the lower thermocouple and the furnace was about  $150^{\circ}$ C. The sample was cooled by lifting it to the higher part of the furnace and leaving the airflow on.

Phase number	Phase description	Temperatures at the end of Temperatures at the end of				
		phase (°C), Sample	phase (°C), Furnace			
1	Evaporation of final	100	pprox 250			
	moisture					
2	Heating of the sample	$\approx$ 600	≈520			
	alongside the furnace					
3	Burning of the fuel in the	$\approx 1000$	pprox850			
	pellets					
4	Heating of the sample and	1200	≈1200			
	furnace					
5	Cooling	20	≈950			





Fig. 16. Temperature curves of sintered batch 6 (100% charcoal, particle size 90-250 $\mu$ m) Paper V, modified and published by permission of Steel research international.

The final temperature of Phase 3 is the temperature when the rapid increase in temperature caused by the burning of carbon has decreased. This Phase 3 temperature is the maximum temperature each fuel mix can generate. This maximum temperature from different batches is compared to the reference batch enabling comparison of the fuel mixture performance. This temperature should be as high as possible in order for the chromite pellet to achieve adequate strength.

Since the precise time that each Phase 3 ended was difficult to define precisely, the average temperatures from the temperature range in which Phase 3 changed to Phase 4 were used. The final temperatures of Phase 3 varied between 909°C and 1077°C. The times needed to reach the final temperature of Phase 3 were between 150 and 222 minutes.

Figure 17 represents the effect the charcoal substitution rate had on the final temperature of Phase 3 and the Phase 3 end time. For the reference batch, the final temperature and end time of Phase 3 were  $1056^{\circ}$ C and 222 minutes respectively. When examining a charcoal substitution rate of 25% the final temperature is slightly increased ( $1077^{\circ}$ C) and the end of Phase 3 was reached 38 minutes earlier compared to the reference case. When the charcoal substitution rate was increased to 50% and above, the final temperature of Phase 3 dropped drastically - and was only 909° with a 100% substitution rate. Furthermore, the time needed to reach the end of Phase 3 was only 150 minutes with the 100% charcoal rate.

The slightly higher temperature with a 25% substitution rate compared to the reference pellet was probably due to the beneficial burning behaviour of small amounts of charcoal mixed with coke. Charcoal burns more rapidly than coke [23] enhancing the burning of coke and generating higher temperatures in less time than in other batches. Higher charcoal substitution rates leads to the charcoal burning too early and/or quickly thus lowering the final temperatures of Phase 3 and making the end time occur earlier than in the reference batch. This is in accordance with the results obtained for iron ore sintering [23]. They suggested that with a 25% substitution rate the sintering speed and thus also productivity increased. Therefore, small amounts of charcoal with coke could also be beneficial to the productivity of chromite pellet sintering.



Fig. 17. The effect of the charcoal substitution rate on the final temperature of Phase 3 and the Phase 3 end time. The presented sintered batches are the reference batch and batches 1-4. Paper V, modified and published by permission of Steel research international.

A detailed evaluation of the effect of particle size and excess charcoal amounts on the sintering process can be found in original article (Paper V).

The airflow rate could also have an effect on the final temperature of Phase 3. It has been suggested that increasing the air flow rate, for example, would increase the available oxygen and thus prevent the gasification of C with  $CO_2$ . When the CO levels are returned close to zero, fuel utilization would be improved and sintering process heat would be increased. [24]

**Cold compression strength, ccs.** The cold compression strength is used for evaluating chromite pellets' mechanical durance during handling and charging in the SAF. If pellets' strength is too weak, they will more easily be crushed, negatively affecting the furnace performance in the smelting process. Depending on the process and raw materials used, the strength of industrial chromite pellets is between 1000-2000N [25]. In this study the force needed to break the sintered pellets varied between 878.1 and 495.3 N. Laboratory-made chromite pellets have lower strength than industrially made pellets. This is due to the lower sintering temperature on a laboratory scale, differences in production conditions and the fuel mixtures used. The difference between laboratory made pellets and industrially made pellets is the reason the reference batch is made to simulate the industrially made pellets.

The effect of the charcoal substitution rate on the cold compression strength is presented in Figure 18. It can be seen that the coke/charcoal ratio has a significant effect on the ccs of the pellets. When the charcoal substitution rate exceeds 50% the ccs of the pellets drops notably. The difference between the reference pellets and pellets with 75% charcoal in the fuel mixture is 40.7% or 357.4N. With a 50% substitution rate the difference between reference pellets is only 67.9N (7.7%). These results indicate that about a 50% charcoal fuel mixture is possible without a significant degradation in ccs. The cold compression strength of the pellets falls below acceptable levels with higher substitution levels. Large standard deviations result from the heterogeneous nature of the pellets, even though the pellets should be as homogeneous as possible.



Fig. 18. The effect of the charcoal substitution rate on the ccs. The presented sintered batches are the reference and batches 1-4. Paper V, modified and published by permission of Steel research international.

A detailed evaluation of the effect of particle size and excess charcoal amounts on the cold compression strength can be seen in original article (Paper V).

## 3 Results and discussion

### 3.1 The electrical conductivity of coke

In order to research the effect of the texture of coke on electrical behaviour coke samples were divided into three groups: those with no extra treatment (raw), those gasified in a  $CO/CO_2$  gas mixture (gas) and those undergoing heat treatment at 950°C (graph).

### 3.1.1 XRD measurements

XRD measurements were made for coke particles (gasification, graphitization, raw), see Figure 19. It can be seen that the graphitization and gasification XRD differ from each other and especially the graphitization XRD differs from the one for untreated (raw) coke.

#### 3.1.2 Electrical measurements

Electrical measurements were made with the device presented in Figure 5. The coke samples were cut into hexahedron shape to form a cube. The cube made from coke was put between 20mm x 20mm copper plates for good contact and measurements were made from all three directions. The electrical measurement results can be seen in Table 7. It can be seen that coke with graphitization process has the highest electrical conductivity and displays an increase of 97% when compared to the raw coke.

Table 7. Electrical measurements for coke particles.

Samples	Average electrical conductivity (1/Ohm)	Max. deviation (1/Ohm)	Standard deviation (1/Ohm)
Raw coke	0.437	0.239	0.109
Graphitization	0.837	0.434	0.216
Gasification	0.382	0.184	0.100



Fig. 19. XRD spectra (gasification, graphitization, raw). Paper I, modified and published by permission of INFACON XIII.

When looking at Figures 20 and 21 the heat treatment increases the height of the graphite crystallites. The graphitization of the coke also yields the highest electrical conductivity of the compared samples. This is probably due to the higher graphite crystallites of the samples. The heat-treated coke samples also had a greater graphite crystallite width, but this most likely does not greatly affect the electrical conductivity. The gasification of the coke does not increase the height of the graphite crystallites compared to raw coke, thus making electrical conductivity similar in these two groups. The width of the graphite crystallites has less impact on electrical conductivity than the height of the crystallites.



Fig. 20. The height of graphite crystallites  $L_c$  as a function of electrical conductivity. Paper I, modified and published by permission of INFACON XIII.



Fig. 21. Width of graphite crystallites  $L_a$  as a function of electrical conductivity. Paper I, modified and published by permission of INFACON XIII.

The structure of pure graphite is organized. During the graphitization process the graphite crystallites' size increases. When treating coke in two different ways it was found that heat treatment led to a more organized structure. Graphitization also increased the electrical conductivity and size of graphite crystallite, whereas the gasification of coke did not seem to have the same effect.

# 3.2 About the electrical properties of chromite pellets - the effect of reduction degree

Chromite pellets were reduced to different reduction degrees in order to study the effect the reduction degree has on the electrical behaviour.

#### 3.2.1 Electrical measurements

A 3 mm slice was taken from the pellet and electrical conductivity measurements were made with the measurement device presented previously in Figure 5. Measurements were made with two different probes with diameters of 10 mm and 5 mm. The voltage used was 1 V and the frequencies were 0.03 kHz, 1 kHz and 10 kHz. The relative

permittivity as a function of the reduction degree can be seen in Figures 22 and 23. The error bars represent the difference between the minimum and maximum values.

It can be seen that the convergence is greater with smaller reduction degrees. Even when looking at the error bars this tendency remains. As seems to be normal there are large differences between the sintered pellets. This is probably due to the different places the chromite pellets can have in the sintering process. It can be observed that when the reduction degree increases the relative permittivity decreases.





Fig. 22. The average relative permittivity with probe 1 (diameter 10 mm) as a function of the reduction degree for frequencies (a) 0.03kHz, (b) 1kHz, (c) 10kHz and for all frequencies (0.03 kHz, 1 kHz and 10 kHz) with error bars. Paper II, modified and published by permission of Steel research international.

Electrical measurements were made with probe 1 with a diameter of 10 mm (Figure 22) and 5 mm with probe 2 (Figure 23). It can be seen from the measurements made with both probes that a higher reduction degree yields lower relative permittivity. Looking at the measurements made at different frequencies it can be said that the lowest frequency yields slightly higher relative permittivity values, but the shape is similar between all frequencies.

When comparing the relative permittivity of the centre of the pellet (Probe 2, diameter 5 mm) to the whole pellet (Probe 1, diameter 10 mm) it would seem that the relative permittivity is slightly higher at the centre of the pellet. This is something to be expected in the light of the fact that the centre has fewer metal droplets.





Fig. 23. The average relative permittivity with probe 2 (diameter 5 mm) as a function of the reduction degree for frequencies (a) 0.03kHz, (b) 1kHz, (c) 10kHz and for all frequencies (0.03 kHz, 1 kHz and 10 kHz) with error bars. Paper II, modified and published by permission of Steel research international.

A more organized structure indicates a better conductor. [26] It is assumed that when the pellets reduce, the structure of the pellet changes to more structured one as a consequence of chemical reactions. When looking at the conductivity measurements made at room temperature, the relative permittivity decreases as the reduction degree increases. One reason for this could be that changes have occurred in the microstructure of the pellet. Furthermore, the number of metal droplets increases as the reduction degree increases and this is one reason for changes in the micro texture when samples are cooled to room temperature. In order to highlight the effect of the reduction degree in itself, the effect of temperature was eliminated. It is good to remember that measurements made at room temperature do not correlate directly to high temperature settings.

This correlation between the reduction degree and relative permittivity allows samples to be taken from an industrial SAF as presented in previous study [13] to obtain a rough estimate of the reduction degree.

### 3.3 A sulphur containing atmosphere's effect on chromite pellets' structure and conductivity during reduction in SAF

In order to study the effect of sulphur in the atmosphere on chromite pellet behaviour, four test sets were made (with 0%, 0.1%, 0.3% and 0.5% sulphur in the atmosphere).

#### 3.3.1 Fesem analysis and phase diagram

Electrical conductivity was once again calculated using equation 1 and treating the pellet slices as plate capacitors. Conductivity measurements were made with the measurement device presented in Figure 5. A probe with a diameter of 10 mm was used. The FESEM pictures and analysis point results can be seen in Figure 24 and Table 8. From Table 8 it can be seen that the sulphur formed compounds - a phase which consists of sulphur, chrome and iron (Spectrum 1) - in the experiment where the sulphur content in atmosphere was 0.5%. Similarities are found in the centre of all the presented pellets. Areas which consisted of chrome and iron were found in the pellets which had 0.1% and 0.3% of sulphur in the atmosphere.



Fig. 24. FESEM pictures for chromite pellets which were exposed to different sulphur contents (0%, 0.1%, 0.3% and 0.5%) in atmosphere. Paper III, modified and published by permission of Steel research international.

Element	Element Sulphur 0% (weight%)		Sulphur 0.1% (weight%)		Sulphur 0.3% (weight%)			Sulphur 0.5% (weight%)		
	Centre	Edge	Centre	Edge	Centre	Edge	Edge	Centre	Edge	Edge
						Sp1	Sp2		Sp1	Sp2
ОК	31.57	31.14	31.28		31.22		32.30	32.60		32.98
Mg K	7.11	7.64	8.68		8.20		9.75	7.62		9.94
Al K	6.48	5.61	6.41		6.21		6.78	8.03		6.65
SK									38.72	
Cr K	33.97	34.34	34.17	3.64	34.27	1.69	37.99	31.30	4.91	34.85
Fe K	18.89	19.52	16.41	97.64	17.70	98.69	10.14	19.51	54.37	14.75
Totals	98.01	98.26	96.95	101.2	97.60	100.38	96.96	99.16	98.00	99.18

Table 8. The results of an FESEM analysis for chromite pellet experiments with different sulphur contents (0%, 0.1%, 0.3%, 0.5%) in the atmosphere.

These results would suggest that it is possible for sulphur to have an effect on the chromite pellet structure during reduction. The FESEM analysis would suggest that FeS is formed and it is important to remember that the phase diagram of iron-saturated melts in the system, FeO-FeS [27] liquids are formed at temperatures as low as 910°C. If partially liquid phases are formed, it can increase the likelihood of forming accumulations based on fine chromite particles. When considering an industrial scale SAF, this accumulating behaviour may have an even larger effect since the volume of sulphur containing gas compared to chromite pellets is remarkably higher than in these presented experiments. This could be problematic since the charge needs to be solid in the upper parts of the SAF. To clarify how this affects the operation of the SAF more in depth experiments are required.

An isothermal phase diagram for a  $Cr_2O_3$ - $Fe_2O_3$ - $O_2$ - $S_2$ -system was computed using the thermodynamic software FactSage (version 6.4) and its databases (FactPS, FToxid, FSstel). This is presented in Figure 25. To illustrate the conditions of the experiment the temperature was set to 1100°C and the pressure was set to 1 atm. In order to illustrate the material composition based on previous study [17] the  $Cr_2O_3/(Cr_2O_3+Fe_2O_3)$ -ratio was chosen to be 0.6206.



Fig. 25. A phase diagram of a  $Cr_2O_3$ - $Fe_2O_3$ - $O_2$ - $S_2$  system at 1100°C under 1 atm with logarithmic partial pressures of  $O_2$  and  $S_2$  as variables. The square represents the range of the sulphur content during the experiments. Paper III, modified and published by permission of Steel research international.

The phase diagram presented in Figure 25 suggests that the formation of a molten sulphide phase containing both iron and chromium is possible. The area in which molten sulphide is stable increases with the increasing sulphur content. The logarithm of the partial pressure of sulphur gas is located between [-3,0[ in these experiments. This area also corresponds to the excess sulphur amount in an industrial SAF. Thus, the formation of sulphides is possible during the experiments. The reason for the range in the oxygen content is that the oxygen content changes in the SAF. In the experiments the oxygen content is fixed to be around -15.

#### 3.3.2 Electrical measurements

Four pellets from each experiment were used for electrical conductivity measurements with device presented in Figure 5. Relative permittivity is then calculated using Equation 1 and results can be seen in Figure 26. The results of the average relative permittivity as a function of sulphur in atmosphere would suggest that sulphur has an impact on chromite pellets' electrical behaviour.



Fig. 26. The effect of sulphur in the atmosphere on the relative permittivity of chromite pellets. Paper III, modified and published by permission of Steel research international.

It is known (see Figures 22, 23) that reduction degree does have an impact on the relative permittivity of chromite pellets. Thus, the relative permittivity was calculated using equation 4 and the reduction degree varied between 4.6-5.1%.

Since the reduction degree varies between 4.6% - 5.1% the reduction degree is not the reason for changes in the relative permittivity in sulphur in the atmospheric experiments. This would suggest that the reason for changes in relative permittivity is the different amount of sulphur in the atmosphere. The measurements would also suggest that when increasing the amount of sulphur in the atmosphere the variance in the relative permittivity decreases.

According to these experiments, the amount of sulphur in the atmosphere has an effect on the chromite pellets' electrical behaviour and structure. When the atmospheric sulphur content increases it enables compounds with a lower melting point to form. When considering industrial SAFs this sulphur could have an impact on the behaviour of the furnace. More precisely partial melting could cause agglomeration of the burden material and thus create solid blocks in the upper part of the furnace disturbing the material flow affecting the way SAF operates. Thus, it is important to control the amount of sulphur in the SAF and a means to do this is to control the amount in the charge, especially coke. Since it is known that coke quality can differ it is important to determine the the parameters that have an effect on the behaviour of the SAF. As this research suggests, the sulphur amount could be one element to optimize in the sense that the agglomeration of charge material into larger agglomerates is not a desired occurrence in the upper part of the SAF disturbing the material flow and has a negative impact on the performance of the furnace.

This research is the starting point for examining the effect of atmospheric sulphur on chromite pellets. In order to define this effect on an industrial scale SAF, industrial data from furnaces charged with different burden materials should be examined.

#### 3.4 Charcoal use in chromite pellets

Coke was substituted with charcoal in chromite pellets. The effect this substitution has on the sintering process and ccs is discussed previously. Sintered batches and their final Phase 3 temperatures and cold compression strength values ( $F_{max}$ ) can be seen in Figure 27. It can be seen that when a fuel mixture containing more than 50% charcoal is used the cold compression strength is significantly lower than the batches where less than 50% coal is replaced with charcoal. It can also be seen that even if the final Phase 3 temperature is high (over 1020°C) it does not guarantee high ccs values. One reason for this kind of behaviour could be that the CO-gas formed in the pellets is burned outside of the pellets. This raises the temperature of the thermocouple, which is measured, but the temperature inside pellets remains lower. A lower temperature inside the chromite pellet yields less formed melts and therefore the strength of the pellets remains lower.



Fig. 27. Speciments plotted for the  $F_{max}$ -final temperature of the Phase 3 -diagram. Paper V, modified and published by permission of Steel research international.

The cold compression strength of the pellets can also be affected by the chemical composition and amount of ash in different fuels. The chemical composition of ash in coke is quite similar to that found in bentonite (mostly alumina and silica) so it may have beneficial effects on the melt formation during sintering. According to thermodynamic calculations the ash in coke is almost (>90%) fully melted at a temperature of  $1300^{\circ}$ C, whereas the ash in charcoal is only partially melted (<40%). The amount of ash in coke is almost five times higher than that of charcoal. The amount of melt from the ash is over ten times higher in a 100% coke fuel mix at a temperature of  $1300^{\circ}$ C.

#### 3.4.1 Electrical conductivity

In order to see wether charcoal in the fuel mix would have an effect on the electrical properties of chromite pellets, electrical measurements were made for batches 1-4 and a reference batch. Ten pellets were taken from each batch for measurements. Furthermore, nine pellets were also taken from the studied batches and were reduced in a carbon monoxide atmosphere. The reduction was made with the TG-furnace presented previously in Figure 4. The chromite pellets were kept in a carbon monoxide atmosphere

for 120 minutes at a temperature of 1500°C. Nitrogen was used during the heating and cooling periods. The reduction degree was calculated using Equation 4.

A 3mm slice was taken from each pellet and electrical conductivity measurements were made for all 19 pellets from each batch. The relative permittivity was calculated using Equation 1.

The reduction degree of the sintered pellets was found to be between 32% and 37%. Thus, there was no great difference between the batches.

The relative permittivity of the sintered chromite pellets as well as the reduced pellets can be seen in Figure 28. The relative permittivity seems to be lower with those pellets which had charcoal in the fuel mix. The reference pellet has the highest relative permittivity, which is approximately 34.6% higher than that of pellets with 100% charcoal. When the relative permittivity is compared to the reference pellet, batch 1 had a 25.7% lower relative permittivity, while batch 2 was 18.3% lower, batch 3 was 15.7% lower and batch 4 was 25.2% lower. The reason for this lower relative permittivity with charcoal in the fuel mix could be that coke has a different structure compared to the fibrous charcoal, and that the main oxide components differ so that charcoal has 38.38% CaO as the largest share while coke has 47.53% SiO<sub>2</sub>. Laboratory made pellets have a considerably lower relative permittivity compared to industrially made pellets (for ten pellets the average is 572.7). This is mainly due to differences in the production processes.

The relative permittivity would seem to be affected by substituting coke with charcoal. Electrical conductivity measurements made at room temperature would suggest that replacing coke with charcoal reduces the relative permittivity.

The reduction degree lowers the relative permittivity, see Figure 28. As seen before in Figure 23 relative permittivity decreases in industrially made chromite pellets as the reduction degree increases. The relative permittivity of reduced pellets is closer (between pellets) compared to the relative permittivity of unreduced pellets. When the relative permittivity is compared to the reference pellets, batch 1 had a 7.42% lower relative permittivity, while batch 2 was 10.28% lower, batch 3 was 2.47% lower and batch 4 was 4.85% lower.



Fig. 28. The relative permittivity values for ten chromite pellets as well as for nine reduced chromite pellets from batches 1-4 and the reference. Paper V, modified and published by permission of Steel research international.

In industrial SAF the electrical conductivity of the charge needs to be low enough in the upper part of the furnace and high enough near the electrode tip. Coke substitution with charcoal reduced the electrical conductivity in laboratory made pellets. On the

other hand, the difference in relative permittivity values decreases when the pellets were reduced. This would suggest that from the perspective of electrical conductivity, the amount of charcoal in the pellets is mostly relevant in the upper part of the SAF where the lower degrees of reduction take place. This would suggest that it is more likely that any possible problems would occur in the upper parts of SAF because the pellets' reduction degree increases as the pellets descend.

## 4 Conclusions and future work

In this work electrical measurements were made for cooled coke and chromite pellet samples at room temperature.

Graphitization and gasification of coke yield different electrical conductivity results. The highest electrical conductivity was found with heat treated coke. Untreated coke and gasified coke did not display different electrical conductivity values.

When chromite pellets were treated to different reduction degrees and electrical measurements were made, it was seen that the reduction degree did have an effect on electrical conductivity. This can be useful in the case where samples can be taken from a submerged arc furnace and the reduction degree could be established via electrical measurements.

Chromite pellets were also treated in different atmospheres with varying sulphur amounts. It was found that atmospheric sulphur has an effect on electrical conductivity. This could imply that sulphur might be one of the elements to take into account and possibly to optimize in an SAF charge.

Chromite pellets are produced using chromite ore, coke fines and bentonite via a sintering process. In this study coke was replaced by charcoal in differing amounts and electrical measurements were made. Furthermore, some of the pellets were reduced, and electrical measurements were made for both reduced and non-reduced pellets. It was found out that charcoal in chromite pellets has an effect on electrical conductivity and that the effect is smaller when pellets are reduced. This would suggest that if problems arise and originate from electrical behaviour they occur in the upper parts of the SAF where smaller degrees of reduction take place.

These measurements are a good starting point when examining the possible effect of the electrical behavior of coke and chromite pellets. Different treatments and compositions appear to have an effect on electrical conductivity.

As for future work, the study of electrical conductivity needs to be continued since electrical behaviour is an important part of how industrial SAF works. One extremely interesting step would be to take electrical measurements at high temperatures instead of at room temperature. It would be interesting to create a link between room temperature measurements and high temperature measurements.

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# **Original publications**

- I Heikkilä A, Pussinen J, Mattila O & Fabritius T (2013) Effect of coke's texture on electrical behavior. The Thirteenth International Ferroalloys Congress (INFACON XIII), Almaty, Kazakhstan.
- II Heikkilä A, Pussinen J, Mattila O & Fabritius T (2015) About electrical properties of chromite pellets - effect of reduction degree. Steel research int. 86 (2): 121-128.
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- V Sakaranaho M, Heikkilä A, Suopajärvi H, Päätalo & Fabritius T (2018) Charcoal use in chromite pellets - effect on sintering process, pellet properties, and electrical conductivity. Steel research int. 89 (2): 1700260.

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