EFFECT OF SULPHUR AT REDUCING ATMOSPHERE ON THE CHROMITE PELLET PROPERTIES

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ABSTRACT

Chromite pellets, coke, upgraded lumpy ore and quartz are used as raw materials when producing ferrochrome in submerged arc furnace (SAF). Coke contains typically approximately 0.7 mass-% of sulphur and there are indications that traces of sulphur are present in SAF. In this paper the influence of sulphur on chromite pellet's electrical behavior, reduction degree and structure are studied. Experiments with chromite pellets were conducted at 1100°C using two different atmospheres – CO/CO2 and CO/CO2/S2. Pellets' structure, reduction degree and electrical conductivity were analyzed. According to measurements, the occurrence of sulphur has an effect on the structure of reduced chromite pellet and its electrical conductivity, but not on reduction degree.

Keywords: *chromite pellet, SAF, electrical behavior, sulphur*

1 INTRODUCTION

Submerged arc furnace (SAF) is a part of ferrochrome production process. The electrical behavior of the charge is important due to the effects on the productivity of furnace. The feeding material includes coke, chromite pellets, upgraded lumpy ore and quartzite as slag modifier.

One important aspect of the operation of SAF is electrical behavior of feed material. Electrical conductivity of SAF's burden should be small at the upper part of furnace and high near the electrode tips. This is to ensure that the current path is via metal baths by arcing, not by ohmic conduction through the solid feed material of less reactive zone where the heat energy would be mostly wasted. A way to affect the electrical conductivity and electric current distribution is to change the fraction sizes and proportions of different feed materials [1, 2].

Sulphur, alkalis, zinc and silicon are the most common of circulating elements in blast furnace. The effect of sulphur to olivine and acid iron ore pellets has been studied by Iljana et al.[3]. Metallurgical coke and hydrocarbon fuels are ways for sulphur to enter the blast furnace. Most of the sulphur burns in the oxidizing zone and sulphur containing gases are formed. The sulphur ascends to upper parts and is absorbed in the charge materials and reduced iron affecting the reduction behavior of olivine and acid ore pellets. [4]

There are some indicators that the mechanism described above can happen also inside SAF [5]. Sulphur enters the SAF via charge materials, especially coke. Sulphur containing gases are formed and these gases ascend to upper part of SAF reacting with the charge. If the hypothesis of circulating behavior of sulphur exists in SAF, then research of the effect of sulphur on chromite pellets is important.This paper concentrates on the effect of sulphur on chromite pellets' structure, reduction degree and electrical conductivity.

2 EXPERIMENTS

2.1 Sulphur Tests

Main composition of industrial chromite pellets used in experiments is MgO 11%, Al_2O_3 13%, SiO_2 4%, CaO 0.5%, Cr_2O_3 44% and Fe 19%. The experiments with different sulphur contents at atmosphere were made with a BFS-device presented in Figure 1. Sulphur is generated into the atmosphere using reaction $2SO_2(g) + 2C(s) = S_2(g) + 2CO_2(g)$.

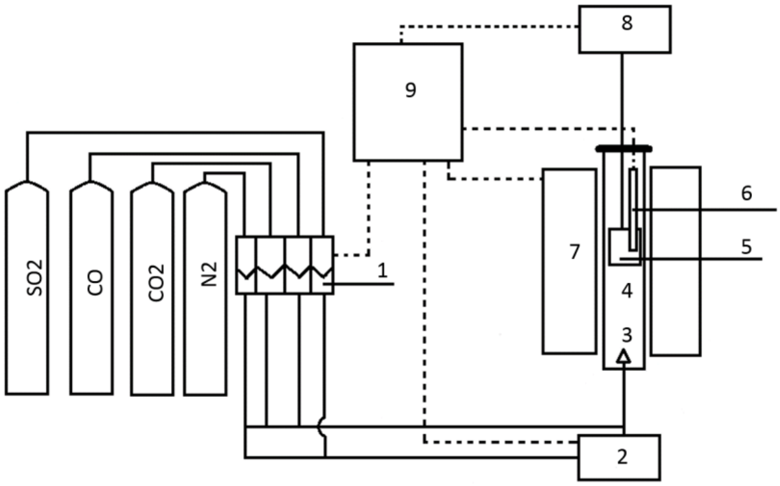

Figure 1. A sketch of BFS-device used in experiments.(1) Mass flow controller, (2) Sulphur generator, (3) Gas inlet, (4) Reduction tube, (5) Sample basket, (6) Thermocouple, (7) Electrically heated furnace, (8) Scale for TGA and (9) Computer system. (Modified from [3])

Industrial chromite pellets were used in the experiments. One experiment consisted of 26 chromite pellets which were placed in the sample basket and heated to 1100 degree Celsius. More precise temperature profile used in experiments is presented in figure 2.

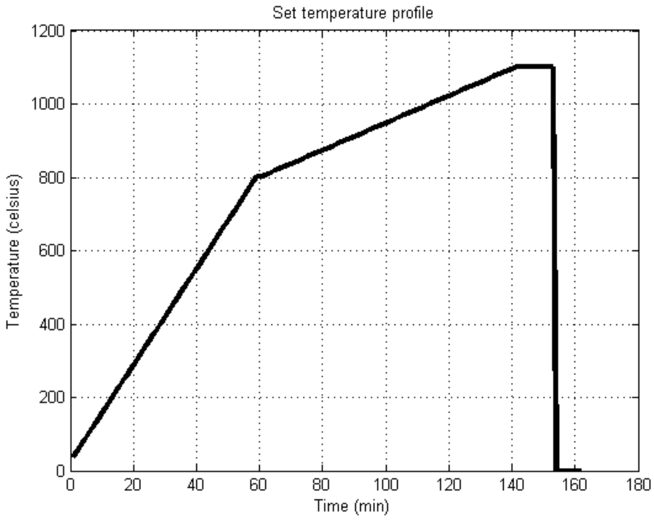

Figure 2. Temperature profile used in experiments.

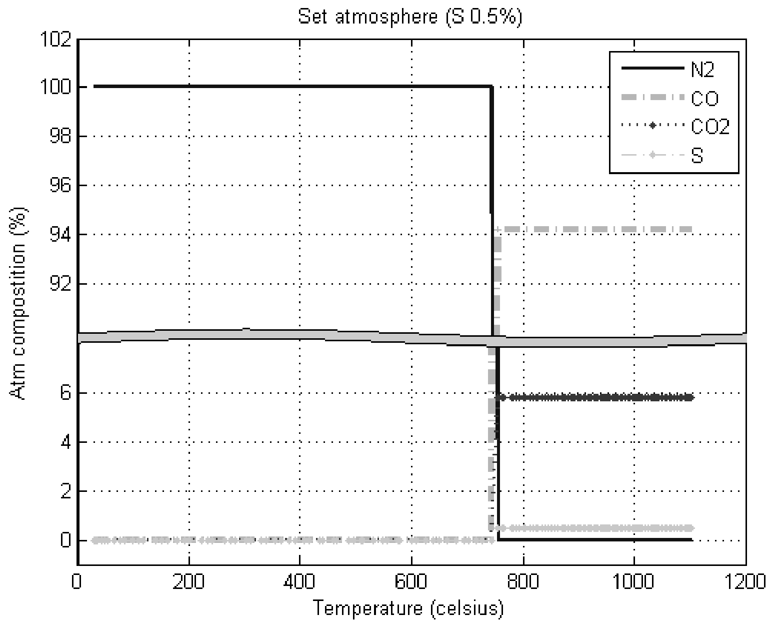

Figure 3. Set atmosphere conditions for experiment where sulphur content is 0.5%.

Nitrogen was used during the heating up to around 750 degree Celsius (figure 3). Then carbon monoxide, carbon dioxide and sulphur were switched on and nitrogen was set to 0%. Sulphur content was either 0 % (experiment 1) or 0.5 % (experiment 2) and CO/CO~16. At the cooling down period atmosphere consisted of 100 % nitrogen again.

Total of five pellets were analyzed from both experiments. One chromite pellet was used in optical microscope and field emission scanning electron microscope (FESEM) analysis and four were used in electrical measurements.

2.2 Electrical Conductivity

Permittivity is a way to describe how a medium affects the electric field. In this paper we use relative permittivity which is the relation between permittivity of the medium and vacuum permittivity. Here pellet slices are handled as a plate capacitor and its relative permittivity is defined using equation 1

$$\varepsilon_r = \frac{cd}{\varepsilon_0 A}, \quad (1)$$

where ε_r is the relative permittivity, c is the capacitance, d is the thickness of the dielectric, ε_0 is the vacuum permittivity and A is the area of the plate. Here ε_0=8.854 187 817... $*10^{-12}$F/m.

Electrical measurements were made with measurement device presented in figure 4.

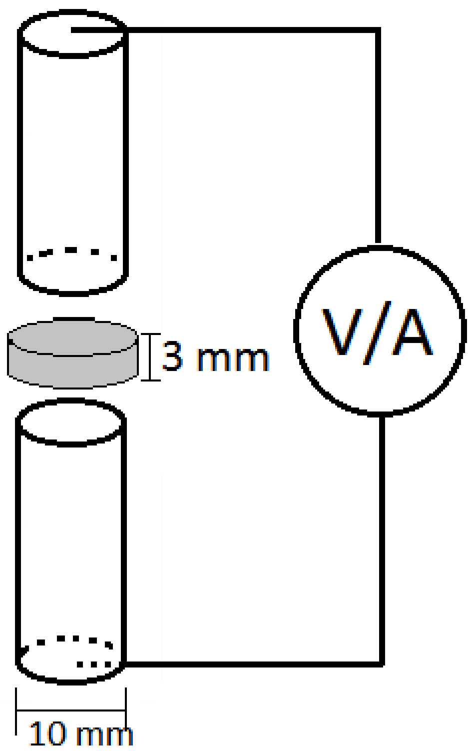

Figure 4. A rough sketch of measurement device (GW Instek LCR-817) and measurement setup for the electrical conductivity.

A 3 mm slice was severed from the centre of the pellet. Probes were made from copper with diameter of 10 mm. The pellet slice was placed between probes, and electrical measurements were made.

Based on the previous study, [6] the electrical conductivity measurements were performed using voltage of 1.275 V and frequency of 0.5 kHz. A series circuit was used in capacitance measurements.

3 RESULTS AND DISCUSSION

3.1 Reduction Degree

Varied reduction degrees in SAF are achieved when the charge descends and faces hot reducing gases. These gases, which are mainly CO, are formed at the high temperature area beneath the electrode tip. When pellet faces these hot gases it heats up and the most easily reducible oxides – iron oxides – are reduced. The reduction degree is defined in equation (2) and it is the percentage of oxygen removed from the total removable oxygen in chromite [7].

$$R(t) = \frac{w_0 - w_t - w_{volatiles}}{w_0^{reducible}}, \quad (2)$$

where R(t) is the degree of reduction [%], w_0 is weight of the dried sample in the beginning of the reduction [g], w_t is the weight of the sample at time t during the reduction [g], $w_{volatiles}$ are 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. Reduction happens also with solid carbon [8], but in this work we concentrate only on the reduction by CO gas.

Reduction degrees calculated using equation 2 are available in table 1. Xiao et al. [8] suggests that Fe^{2+}/Fe^{3+} = 24/76 for this kind of chromite, and this ratio is used in these calculations.

Table 1. Calculated reduction degrees.

Experiment	Reduction degree (%)
Sulphur 0 %	5.1
Sulphur 0.5 %	4.6

According to Table 1, the difference in reduction degree between the experiments is not great. One reason for this could be holding time in 1100 degree Celsius, which was only 10 minutes. The holding time could be too short for the reduction degree to saturate.

3.2 Optical and FESEM analysis

One pellet from both experiments was analyzed first with optical microscope and then with field emission scanning electron microscope, FESEM. Optical microscope pictures are presented in figure 5.

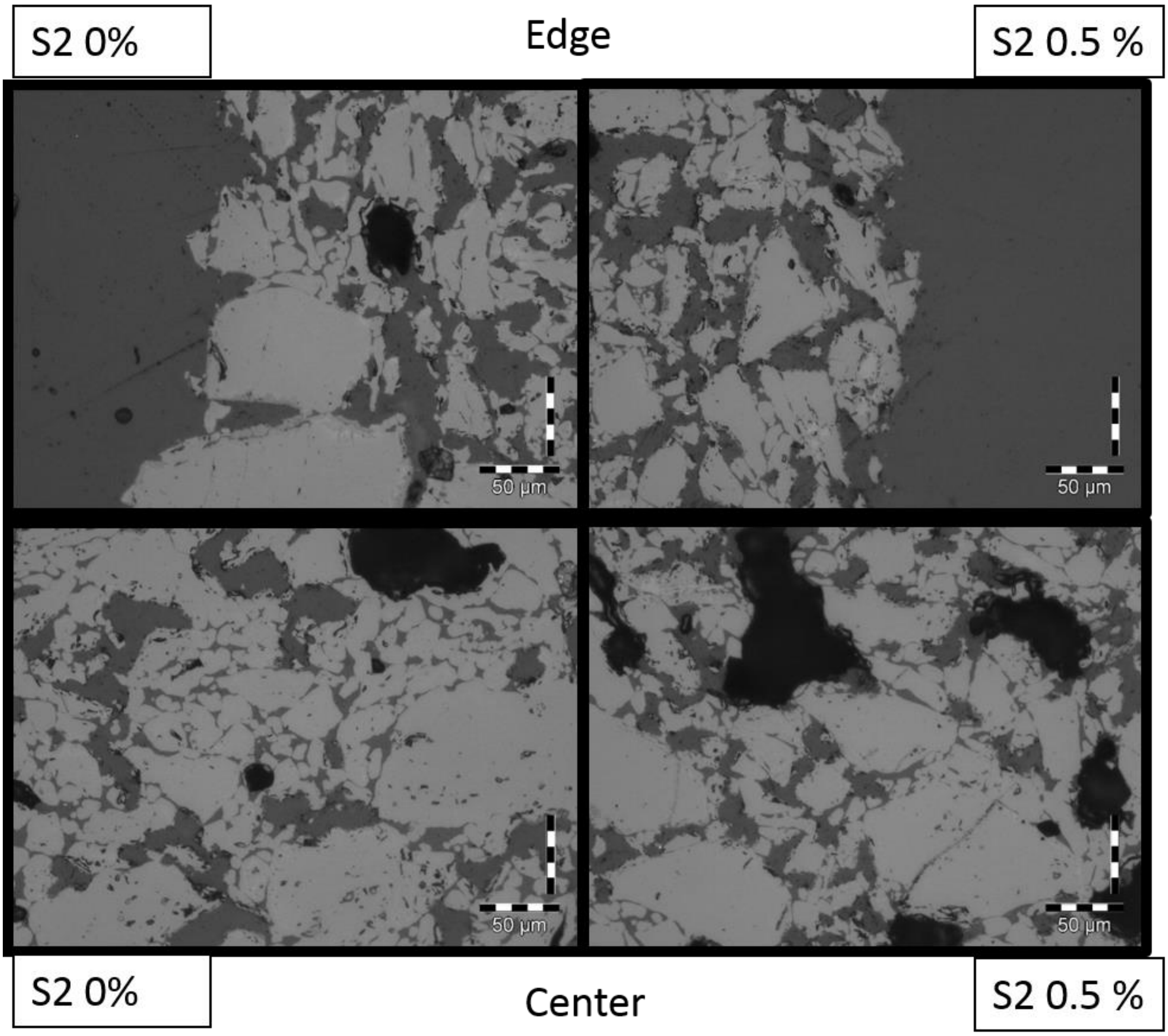

Figure 5. Optical microscope pictures for two experiments (sulphur 0% and 0.5%) from centre and edge of pellets.

Optical microscope did not show great difference between the experiments (sulphur 0% and 0.5%). This is one of the reasons why FESEM analysis was reasonable. The analysis positions are presented in figure 6 and analysis results are presented in table 2.

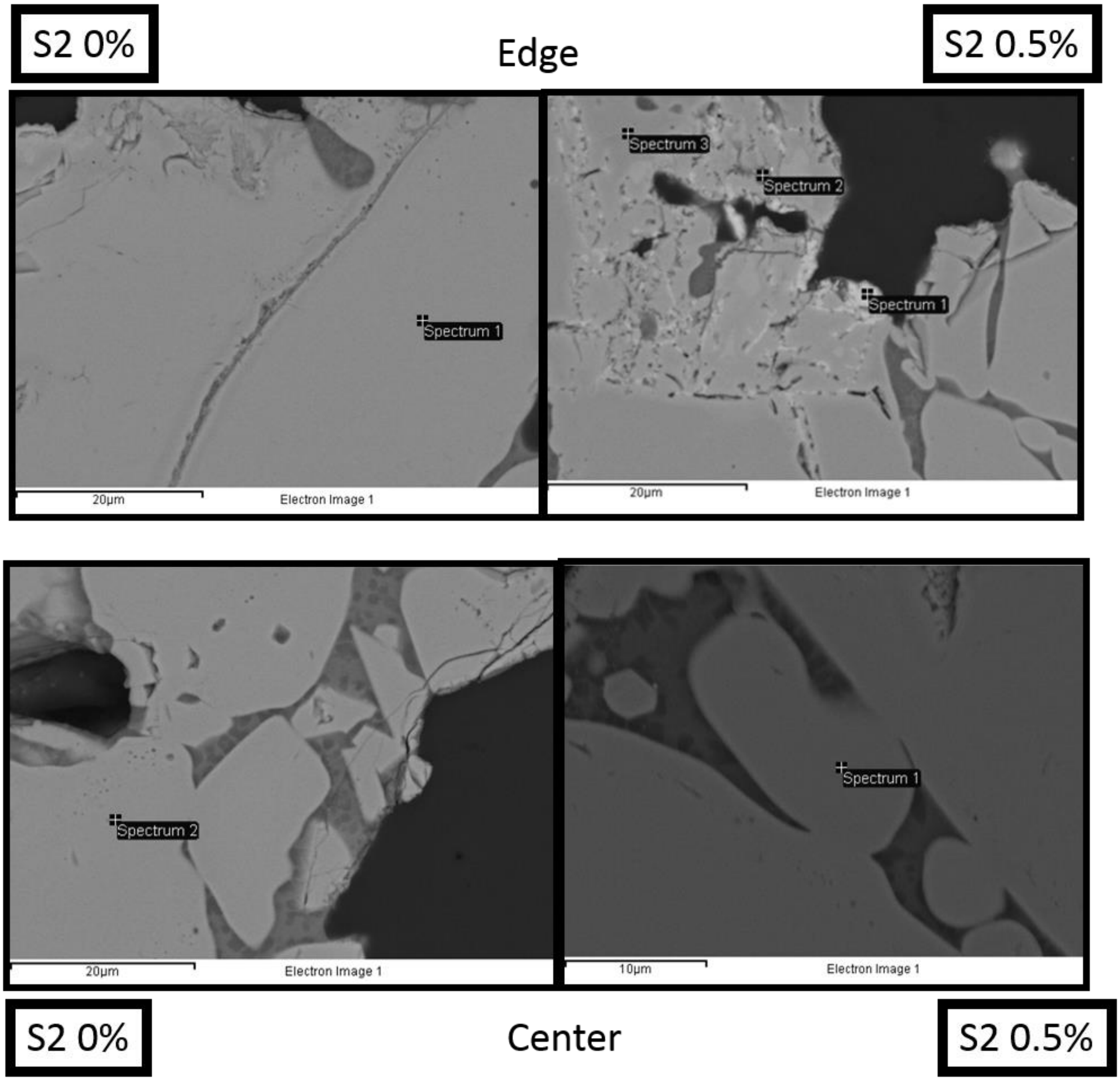

Figure 6. Positions of FESEM analysis pictures for two experiments (sulphur 0% and 0.5%) from centre and edge of pellets.

Table 2. Results of FESEM analysis.

Element	**Sulphur 0 %**(weight %)		**Sulphur 0.5 %** (weight %)			
	Edge	**Centre**	**Edge**			**Centre**
			Sepctrum1	Spectrum2	Spectrum3	
O K	31.57	31.57		34.20	32.98	32.33
Mg K	7.64	7.11		1.46	9.94	7.85
Al K	5.61	6.48		5.80	6.65	7.17
Si K				13.03		
Ca K				2.12		
S K			38.72			
Cr K	34.34	33.97	4.91	21.60	34.85	32.22
Fe K	19.52	18.89	54.37	11.09	14.75	19.97
Totals	98.68	98.02	98	89.3	99.17	99.54

FESEM showed differences between the experiments. Similar compositions can be found at the centre of both pellets as well as from the edge of pellet from experiment with 0% sulphur. Divergence was found from samples taken from the edge of pellet in experiment with 0.5% sulphur. An area has been formed which consists of sulphur, chrome and iron (Spectrum 1). This shows that sulphur does form compounds in the pellet and thus affects its properties.

These measurements show that sulphur affects the structure of reduced chromite pellet. How much or does it affect the operation of SAF cannot be concluded based on these measurements only.

3.3 Electrical Measurements

Conductivity measurements were made for four pellet slices in two different experiments (0% sulphur and 0.5% sulphur). Calculated relative permittivity using equation 1 for pellet slices is presented in Figure 7.

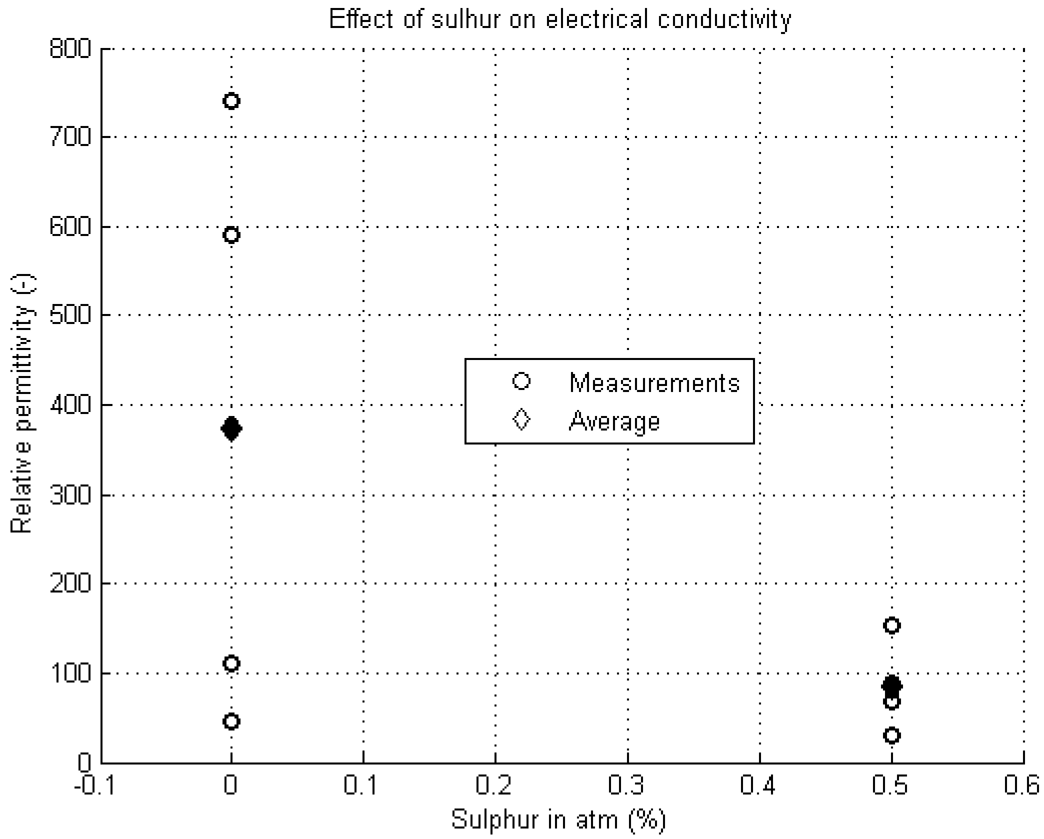

Figure 7. Effect of sulphur on electrical conductivity.

According to the test made at room temperature, higher sulphur content yields lower electrical conductivity as well as lesser deviation. At this point it is good to remember that experiments with chromite pellets reduction degree showed results where higher reduction degree yielded lower electrical conductivity when measurements were made at room temperature [6].

In conclusion, sulphur does affect the relative permittivity and thus electrical behaviour of reduced chromite pellets. How sulphur affects the electrical conductivity at high temperature is an interesting research problem.

These tests alone cannot answer the question whether sulphur content in atmosphere has great influence on how SAF operates. Nevertheless, it gives an interesting starting point for further experiments and discussion. If negative effects of sulphur on SAF performance can be reliably identified with high temperature experimenting, the quality requirements of raw materials might have to be reconsidered from the point of view of overall process efficiency and profitability.

4 CONCLUSIONS

In this work, the effect of sulphur at reducing atmosphere to chromite pellet’s properties was studied. Sulphur did not seem to have great influence on the reduction degree. Yet, had the holding time at 1100°C been longer, a larger difference in reduction degree might have been seen.

The structure of pellets from both experiments (sulphur 0% and sulphur 0.5%) was also studied. Especially FESEM analysis revealed that sulphur does form compounds in pellet and has an effect on the pellet’s structure and composition.

Chromite pellet's electrical conductivity was also measured. It was found out that pellets with 0% sulphur in atmosphere during experiment had higher electrical conductivity at room temperature than pellets with 0.5 % sulphur, thus giving indication that sulphur does affect the electrical behaviour of a single pellet.

5 ACKNOWLEDGEMENTS

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