# Carbon Materials for Silicomanganese reduction

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## ABSTRACT

*Silicomanganese and Ferromanganese are mainly produced by carbothermic reduction in electric submerged arc furnaces [1]. The aim of this project is to develop a method to investigate the various carbon materials of different sizing. The method simulates the coke bed zone, the reduction and melting of charge materials into the coke bed zone. It has been shown that the main part of the reduction and the metal producing reactions will occur mainly at the top of the coke bed. If the reduction rate is slow, or the slag flow into the coke bed at a slow rate, the temperature in the slag will increase, hence giving a higher Si content in the metal and a lower MnO in the slag. The experimental work is carried out in an open induction furnace by using a crucible of 40 cm long with inner diameter of 11 cm, where one can use close to industrial-sized particles that are up to maximum of 20 mm. For this study, five different carbon materials of varying sizes with a fixed ore type were used. The main results are:*

*(i)* *Larger carbon particles show slower reduction at a given temperature compared to smaller particles which shows that the reduction rate is more important than flow parameters.*

*(ii)* *Though quite small, it was observed a difference between the reduction rates with different carbon materials, were the most rapid was anthracite followed by coke 3, with coke 2 and coke 4 as the slowest. It must, however, be mentioned that anthracite showed an untypical behaviour. The high reduction and flow rate of coke3 could be due to an enhanced wetting behaviour.*

## 1. INTRODUCTION

Carbon materials such as coke, charcoal, anthracite etc. serve as the primary source of reducing agent during the smelting of manganese ferroalloys. Carbonaceous materials are very complex systems with a wide variety of chemical and physical properties. The most important properties of coke as a reductant during the furnace operation are;

(i) Reactivity towards reaction with $CO_2$ gas. Low reactivity of ore and high $CO_2$ reactivity of coke will result in high energy consumption. Therefore the relative reactivity of ore and coke are the main factors affecting the degree of pre-reduction during the manganese process.

(ii) Reactivity of the solid carbon with liquid slag components [1].

(iii) Electrical resistivity of the carbon material. The electrical resistivity of the carbon materials will determine the electrode tip position, and hence with the resistance set point, it affects the stability of the operation. Monsen 2004 reported that the high resistivity of charcoal result in more efficient operation with respect to energy and electrode consumption in the silicomanganese process [3]

The reaction between slag and carbon material is dependent on thermodynamic variables like slag composition and temperature. However, the kinetics is also of importance since most of the reduction occurs on the interface between the liquid slag and the carbon. Osterovski *et al.* studied the ore melting and reduction in silicomanganese production. They found that the amount of carbon in the charge is the main factor affecting the silicon content of silicomanganese [2]. Monsen et al. (2004) also observed that the rate of MnO reduction from the slag by charcoal is higher than coke. Further, MnO reduction rate was higher for industrial cokes than the cokes produced from the single coals [4]. It was shown that the major part of the reduction occur on the top of the cokebed [Olsen et al. 2007]. Especially in ferromanganese production it was shown how the viscosity will prevent the slag from flowing into the cokebed, before it was reduced. Hence, if the reduction is slow or if the flow into the cokebed is prevented, the temperature in the slag will be higher and hence the Si content will be higher as well. This work will look at the reduction of a silicomanganese charge on top of a cokebed with various types of carbon materials and with different sizing.

The objective of the experiments was to investigate how various carbon materials of different sizing affecting reduction temperature and reduction behaviour of MnO containing slags. An open induction furnace (IF75) has been used to study the reduction and melting. Comilog ore, commercial sinters, high carbon ferromanganese slag, quartz and differently sized industrial carbonaceous materials have been chosen for the investigation. The aim of this project is to develop a technique to find the melting temperatures of ores and how much slag and molten materials pass through the coke bed during the manganese process. By this technique, on the one hand, one may reproduce operating conditions in the furnace and on the other hand, it allows us to use materials that are charged to the industrial furnace. This technique is called stationary charge in controlled environment (SCICE) [5]. The apparatus uses a representative portion of furnace charge in the form of a coke bed and also showing the change in the height of the charge mix at different temperatures. The method simulates the cokebed zone, the reduction and melting of charge materials into the cokebed zone. As previously mentioned, it has been shown that the main part of the reduction and the metal producing reactions will occur mainly at the top of the cokebed.

## 2. INDUCTION FURNACE EXPERIMENT

To investigate the melting and reduction of manganese ores an induction furnace was used. The furnace has a maximum power supply of 75 kW, but the maximum power used in these experiments was 10-30 kW. A graphite crucible of 40 cm long with inner diameter of about 11.5 cm was used, where one can use close to industrial-sized particles that is up to maximum of 20 mm. Initially the crucible was filled by coke of desired size similar to the coke bed found in the industrial furnaces. Then a graphite tube of 50 cm long was placed just on the top of the coke bed for keeping the thermocouple to measure the temperature. On top of the coke bed, the charge mix of desired quantity is added, which is weighed out based on the chemical analyses of the ore. For the charge mix a mixture of commercial sinters, high carbon FeMn slag, quartz, and cokes were used. Then a coke layer is added on the top of the charge mix. These coke layers acts as an insulator which ensures that the charge is not re-oxidized. For each experiment 10 cm of coke bed, 7-9 cm of charge mix and 10 cm of top layer coke over the charge mix was used. A graphite block of 20 cm long and 10 cm in diameter is kept on the top of the crucible for measuring the change in height of the charge level at different temperatures. The complete set up for the experiment is shown in Figure 1 below.

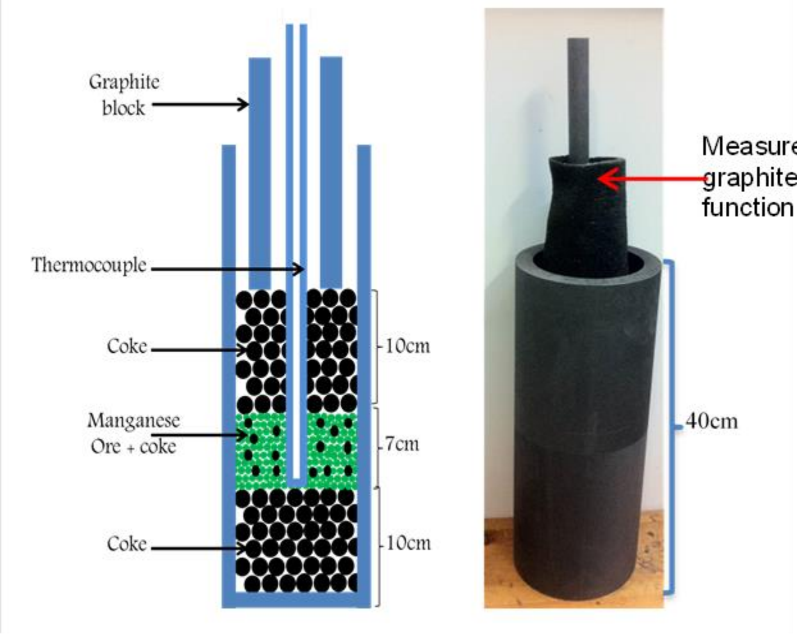


**Figure 1:** Experimental set up in an open induction furnace

The power was set initially to about 10-20 kW. The crucible was heated up to $1200^0$C to prereduce all the raw materials. The power was then reduced manually to 5kW to hold the temperature steady at $1200^0$C for 10-15 minutes. This was done to make sure that the ore was completely prereduced before the next set of heating. After the prereduction step the crucible temperature was increased until the target temperature of $1600^0$C was reached. During this process the prereduced ore will sinter, soften and melt with increasing temperature. As the melting and reduction occurs, the graphite block starts to move down. This shows that the reduced charge mix will start to drain into the coke bed. The change in the height of the charge level has been measured by a normal ruler. The maximum power used was 10-30 kW. A 10% decrease in the length of the graphite block is defined as the reduction in the height of the charge level and that particular temperature was the initial melting point. By increasing the temperature, the graphite block slumps down to 70% which means that the charge is defined as fully molten. When the power to the furnace stops, the melting and reduction reaction stops instantly due to the endothermic nature of the reaction. The experiments were repeated for several sets of samples in order to investigate the effect of carbon materials during the melting and reduction of manganese ores. When the crucibles were cooled, they were filled by epoxy and kept overnight for hardening. After that the crucibles were vertically cut through the middle.

### 2.1 MATERIALS

In this study five different carbonaceous materials of various sizes are used to investigate how different sizing affect the reduction temperature and reduction behaviour of MnO-containing slags. The types investigated are coke 1, coke 2, coke 3, coke 4 and Anthracite used in the production of ferroalloys. It is expected that the flow of slag into the cokebed is affected by the void fraction of the carbon materials, and hence this was measured for all the materials used.

The void fraction α is determined by the bulk density of the cokebed and the particle density of the coke. If we know the bulk density and the particle density we can easily calculate the void fraction which was calculated using the following equation;

$$\alpha = 1 - \frac{\delta_{bulk}}{\delta_{particle}} \qquad (1)$$

The bulk density, particle density and void fraction of each carbon material are shown in Table 1. While the cokes are quite similar, the void fraction of anthracite is lower than the void fraction when it is compared with the other three.

**Table 1:** Calculated void fraction of carbon materials that used in this study.

| Carbon Material | Bulk density (kg/dl$^3$) | Particle density coke (g/cm$^3$) | Void fraction (α) |
|---|---|---|---|
| Coke2 3-6mm | 0,749 | 1,82 | 0,59 |
| Coke3 5-10mm | 0,623 | 1,71 | 0,64 |
| Coke3 +10mm | 0,630 | 1,78 | 0,65 |
| Coke4 3-6mm | 0,642 | 1,78 | 0,64 |
| Coke4 5-10mm | 0,745 | 1,78 | 0,58 |
| Anthracite 5-10mm | 0,970 | 1,68 | 0,47 |
| Anthracite +10mm | 1,007 | 1,91 | 0,42 |

Industrial raw materials such as sinters, HC FeMn slag, quartz and coke are used as manganese sources for the production of silicomanganese. The calculated equilibrium relations of the slag composition with 52.8% MnO, 30.6% $SiO_2$, 7.5%CaO and 7%$Al_2O_3$ were analyzed using FACT Sage software which is shown in Figure 2. The phases changed significantly upon heating according to the diagram. A major phase in the HC ferromanganese slag is olivine and Al-spinel at equilibrium. Liquid slag becomes the only phase as observed between 1300$^0$C to 1600$^0$C according to the diagram.

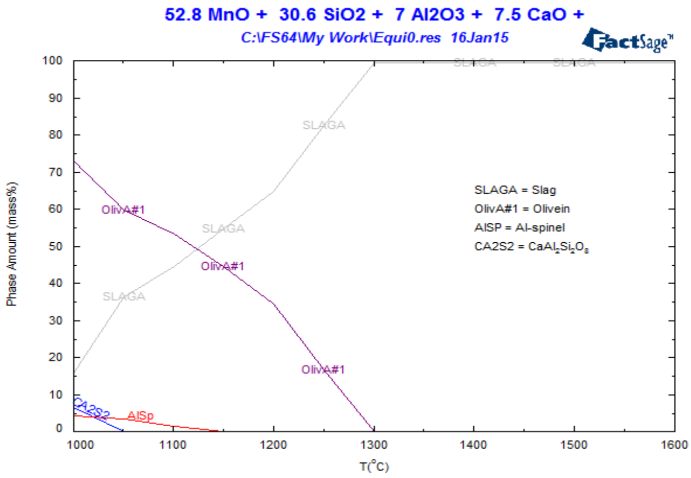


**Figure 2:** Equilibrium phases of manganese raw material by FACT Sage for a slag with 52.8 wt% MnO, 30.6 wt% $SiO_2$, 7.5 wt%CaO and 7 wt%$Al_2O_3$.

## 3. Results and discussion

### 3.1 Slumping results from open induction furnace experiments

Before carrying out slumping experiments of industrial raw materials with various carbon materials of different sizes, the melting behaviour of manganese ore (Comilog) with and without quartz and industrial manganese raw materials with quartz is verified. This is done in order to validate the SCICE method as well as to confirm the melting temperature of manganese ore with and without quartz which are in quite good agreement with the previously conducted studies [Brynjulfsen, 2013], Figure 3.1a. When an acid oxide is added to a basic oxide the liquidus temperature will decrease. The MnO-$SiO_2$ phase diagram tells that pure $SiO_2$ and MnO has very high liquidus point, when mixed together the liquidus temperature is decreased which can be seen in Figure 3.1b [1]. The Comilog ore without quartz gives a low reduction rate and high reduction temperature compared to the other two with quartz. Adding quartz decreased the temperature where the melting started to 1245°C from the original 1340°C [6]. When a manganese source is mixed with right amount of quartz for the production of silicomanganese the temperature needed for melting is lower compared to a manganese source without quartz. In order to get a liquid slag at low temperature the quartz must be in contact with the manganese source and the slag becomes less viscous so it can drain into the coke bed.

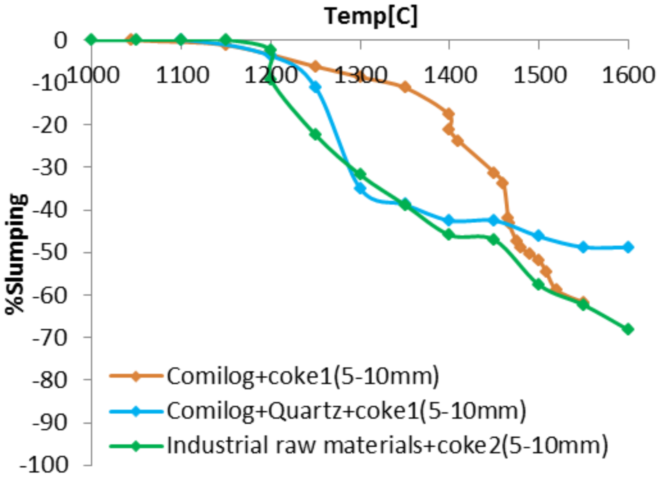


Figure 3.1a-Reduction behaviour of manganese ore with and without quartz.

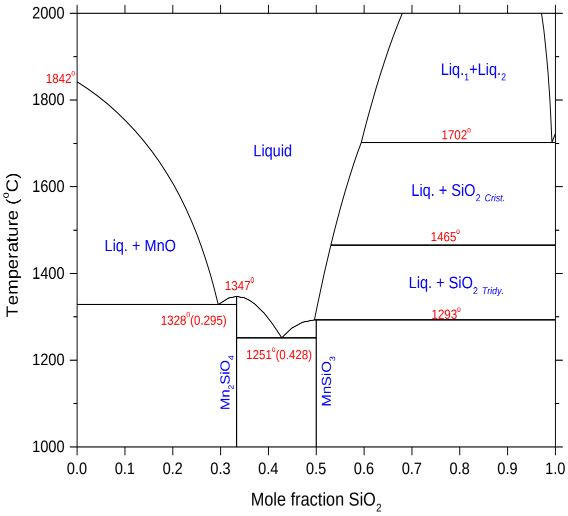
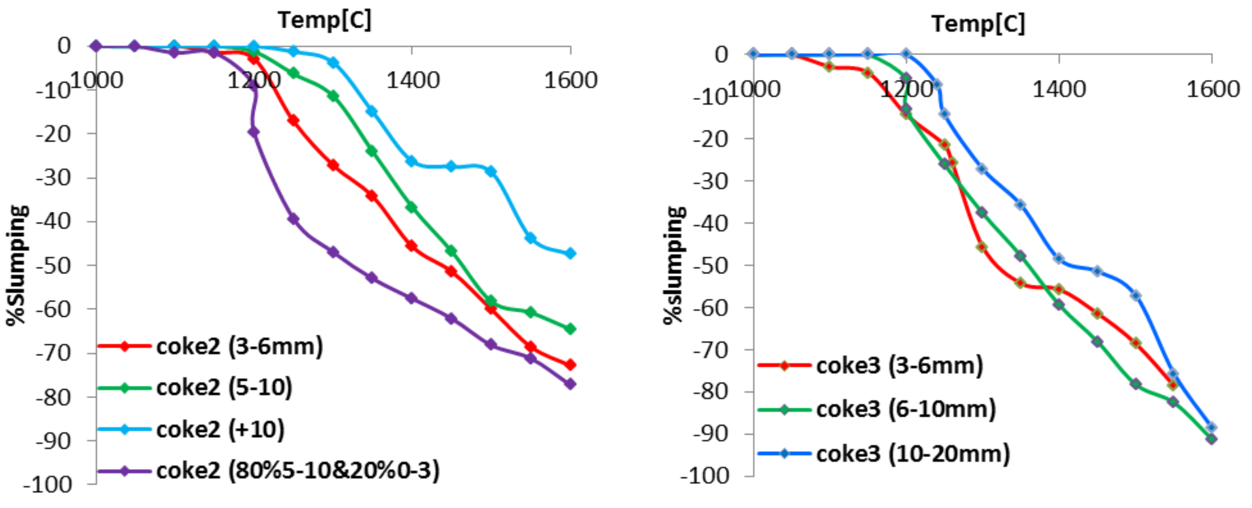


**Figure 3.1b:** Calculated phase diagram for the MnO-$SiO_2$ system [1].

The effect of using various sizes on the carbon material is shown in Figure 3.2 (a) and (b), Figure 3.3 (a) and (b).

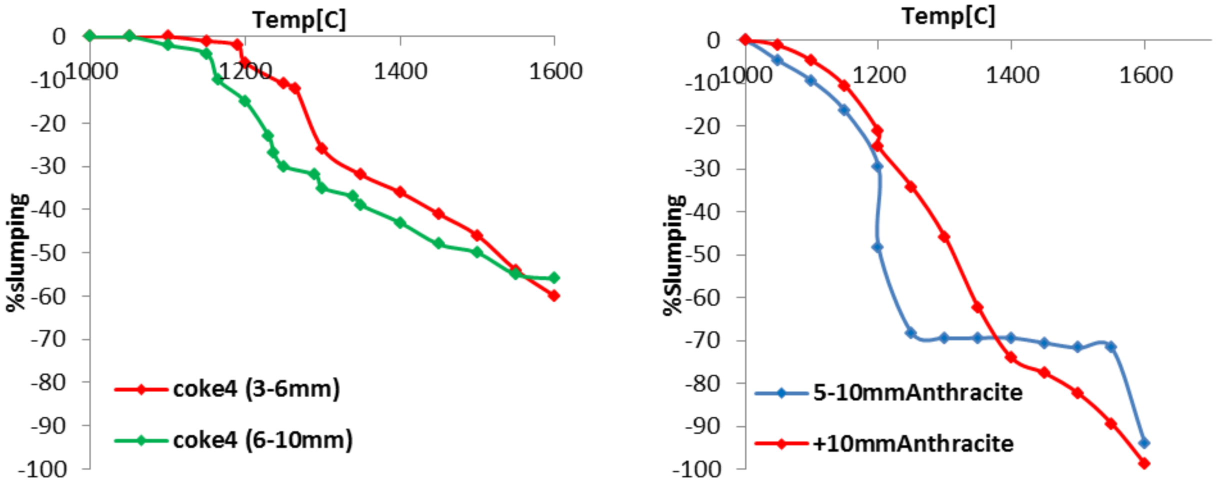


a) Coke2 b) Coke3

**Figure 3.2(a) and 3.2(b):** Reduction behaviour of manganese raw materials with coke 2 and coke 3 of various sizes.

From the graph 3.2 (a) it can be seen that typically the smaller coke gives a higher flow into the cokebed or actually the same flow at lower temperatures. This is believed to be due to the higher reduction rate of the smaller coke. To confirm this result, the addition of 20% smaller sized coke2 (0-3mm) with charge mix gives even faster reduction. The rate of reduction is lower for larger size coke which can be seen in experiments with larger sized coke (+10mm). Since coke is the common source of carbon for ore reduction, the addition of smaller sized coke in the charge mix will react more during the reduction of MnO containing slags which gives lower reduction. From the graph it can be seen that the melting behaviour and reduction rate is dependent on the size of carbon materials, however the difference between the different sizes may sometimes overlap.

The slumping results from coke3 demonstrated in Figure 3.2 (b) shows the same trend of reduction behaviour as seen in Figure 3.2 (a) that the smaller-sized coke gives higher reduction and lower reduction temperature. The experiments with smaller-sized coke (3-6mm) the reduction is started at between $1000^0$C-$1100^0$C. The reduction behaviour in experiments with larger-sized coke (6-10mm and 10-20mm) is quite similar and reduction starts when the temperature reaches $1200^0$C.



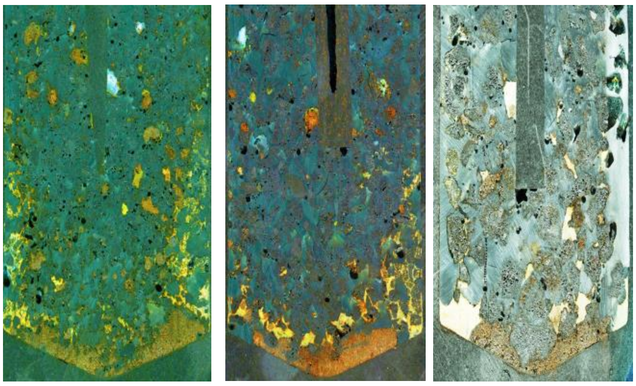
b) Coke4 a) Anthracite

**Figure 3.3(a) and 3.3(b)** - Reduction behaviour of manganese raw materials with coke4 and Anthracite of various sizes.

From figure 3.3 (a) the experiments with coke4 show that the larger coke size gives faster reduction rate and lower reduction temperature compared with the coke sized 3-6mm. We cannot confirm our results by these two experiments, more experiments will be needed to conclude the preliminary results with coke4.

In figure 3.3 (b) using anthracite, it was observed that the reduction rate of MnO containing slags was higher and reduction temperature was lower with smaller-sized anthracite (5-10mm). Compared with different cokes anthracite shows even lower reduction temperature than coke (<1100$^{o}$C). The bulk density, particle density and the void fraction value of the anthracite are different than the coke. The difference in the void fraction is at a range of 0.42-0.47 when compared with the void fraction of the coke of 0.60. Further experiments will be needed to conclude the preliminary results with anthracite**.** In general, from all the slumping experiments with different carbon sizes it has been observed that the smaller sized carbon material gives higher reduction and lower reduction temperature. One of the main reasons for this phenomenon is that the ore reactivity may be very high when a manganese source is mixed with carbon materials of smaller size, and is hence more important than the reduced flow into a smaller-sized cokebed.

The amount of metal and slag settled in the bottom of the crucible is higher in experiments with larger-sized coke when compared with the smaller size which can be seen from the crucible cross-sectional pictures (Figure 3.4). This is in accordance with the slumping results. The slag and metal are almost settled down at the bottom part of cokes with larger size, but for cokes with smaller size the slag is not completely drained towards the bottom and is settled near the sides of the crucible.



3-6mm 5-10mm 10-20mm

**Figure 3.4:** Cross-sections of the crucibles from experiments with three differently sized cokes

Different types of carbonaceous materials behave differently during the reduction of manganese raw materials. Comparing three different coke types, the rate of reduction behaviour of MnO-containing slags is higher with type coke 3 than the other two. Interestingly, the rate of reduction of MnO-containing slags is even higher with anthracite. From the overall experiments, though quite small, it was observed a difference between different coke types in manganese reduction experiments which are shown in Figure 3.5 (a) and (b).

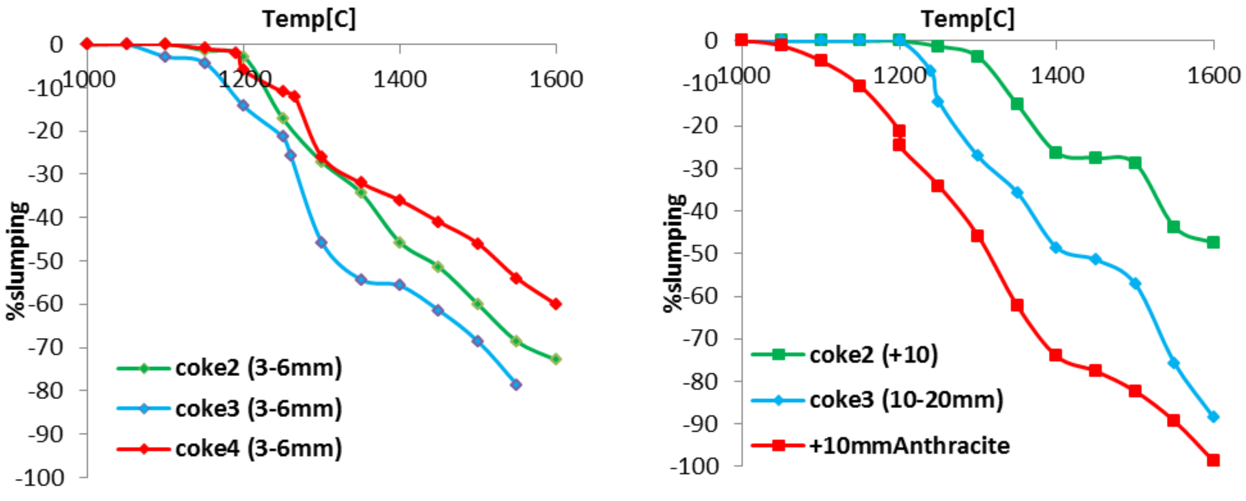


**Figure 3.5(a) and 3.5(b):** Difference between different coke types during manganese reduction experiments.

The wettability of the various carbon materials was studied. The contact angle θ, for reduction by different carbon materials were measured at different reduction temperatures as shown in figure 3.6.

It was seen that coke3 has better wetting compared to the other three. This can also be seen in figure 3.6 where the slag is placed at the carbon materials at increasing temperature. The contact angle at the starting point for coke 3 is 134$^{o}$, when the reduction temperature increases the contact angle reduces gradually and reaches below 100$^{0}$. The increased wetting of coke 3 may explain the increased reaction rate and flow compared to coke 2 and coke 4. The melting behaviour of fixed manganese charge with four different carbon substrates from the sessile drop experiments is shown in Figure 3.7.

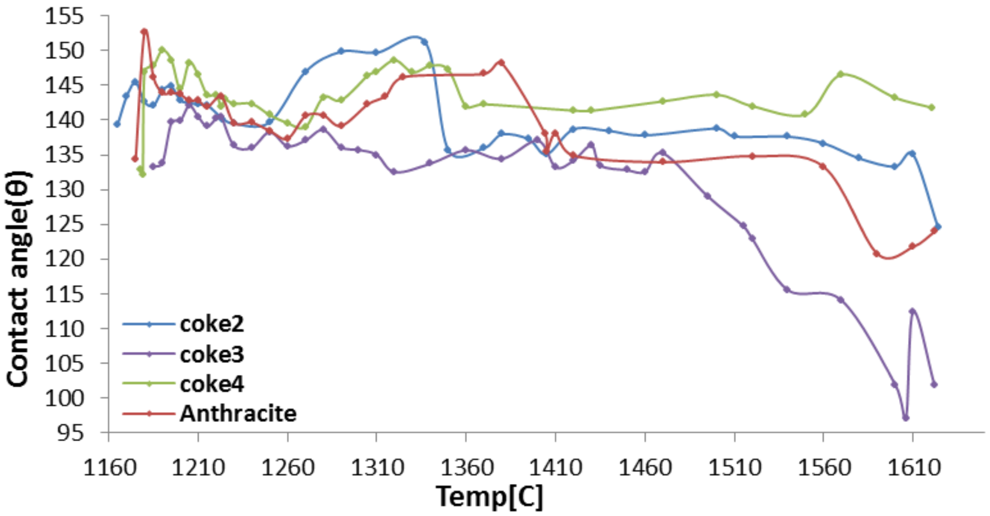


**Figure 3.6:** Contact angle during the reduction of MnO containing slags on different carbon materials at different temperatures.

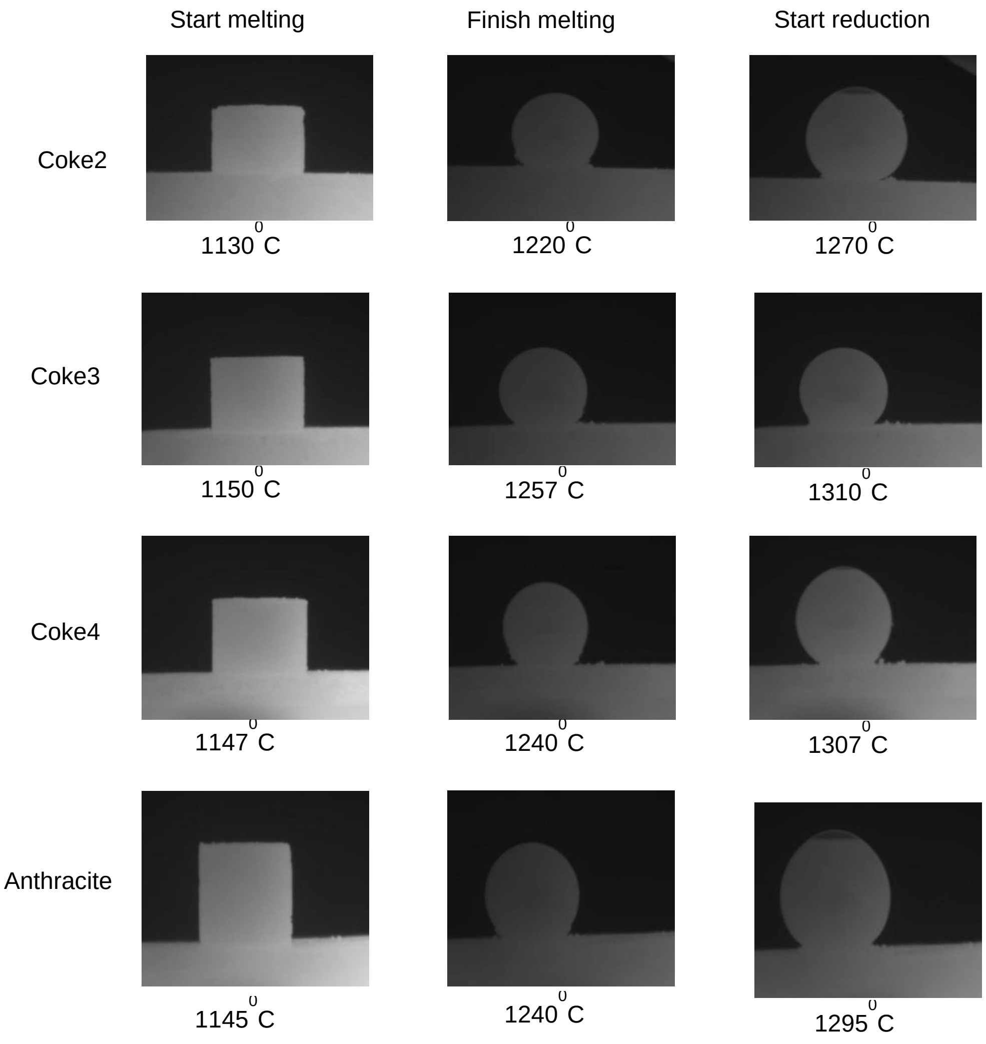


**Figure 3.7:** The melting behaviour with four different carbon substrates with a fixed charge from the sessile drop experiments.

## Conclusion

In order to investigate the reduction behaviour of MnO-containing slags with various carbon materials of different sizes, an open induction furnace and sessile drop furnace were used. Three different types of cokes and anthracite of various sizes were used in this study. To simulate the behaviour of the ore in a submerged arc furnace, a mixture of ore and various carbon materials of different sizes was placed on a coke bed. From the slumping results it was observed that experiments with larger-sized coke (+10mm) have lower flow of slag, which means lower reduction rate than the one with small-sized coke. A charge mix of coke sized 0-3mm shows even faster reduction than a charge mix of coke sized 3-6mm. Though quite slight, it was observed a difference between different coke types in manganese reduction experiments. Anthracite showed the highest reduction rate followed by coke3, coke2 and coke4. From the sessile drop furnace experiment coke3 shows higher wettability than the other three carbon materials, which may explain the higher flow into the cokebed of coke 3.

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