

# ORE PROPERTIES IN MELTING AND REDUCTION REACTIONS IN SILICOMANGANESE PRODUCTION

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## ABSTRACT

*The paper discusses properties of Assman, Gabonese and CVRD ores, CVRD sinter and HCFeMn slag, and their change during the production of silicomanganese. The melting and reduction temperatures of these Mn-sources were measured in a CO atmosphere using a sessile drop furnace and a DTA/TGA. Equilibrium phases were analysed using FactSage software.*

*Experimental investigations and analysis of equilibrium phases revealed significant differences in the melting behaviour and reduction of different manganese sources. The difference in smelting of CVRD ore and CVRD sinter was attributed to faster reduction of sinter by the graphite substrate.*

*Calculation of the equilibrium phases formed in the process of reduction of manganese ores using FactSage correctly reflected the trends in the production of manganese alloys.*

*The temperature at which the MnO concentration in the slag was reduced below 10 wt% can be assigned to the top of the coke bed in the silicomanganese furnace. This temperature was in the range 1550-1610°C.*

## 1 INTRODUCTION

Silicomanganese (SiMn) is an important alloying component in steel production. Standard SiMn contains 67-70 % Mn and 17-20 % Si. SiMn is primarily produced in submerged arc electric furnaces with a power consumption of 3,500 – 4,500 kWh/ton alloy. Optimisation of the charge mix and process conditions will decrease the energy consumption and CO<sub>2</sub> emissions. This requires a better understanding of melting and reduction reactions.

The interior of a silicomanganese furnace can be divided into two main zones according to observations from pilot scale and industrial excavations [1], [2],.

1. Preheating and pre-reduction zone
2. Cokebed zone

The interface between these two zones (at the top of the coke bed), and the reactions that take place at the interface, must also be considered when discussing the effect of different raw materials in the silicomanganese process [3].

Different mixes of raw materials are used in SiMn production. The main Mn sources are various lump Mn ores and agglomerated Mn fines, in addition to slag from the production of HCFeMn. The main Si sources are quartz, in addition to SiO<sub>2</sub> in the Mn ore and in the HCFeMn slag. Fluxes, primarily dolomite or calcite, are added to adjust the slag composition, with a focus on the slag fluidity and silica content. Coke is often used as a reductant. Metal may also be present in the feed materials either as entrapped droplets in ferromanganese slag, as scrap or as recycling materials. The process temperature is around 1650°C.

The different charge materials behave differently when heated and in the presence of carbon. This affects the consumption of coke and electrical power, the quantity and composition of slag and the

furnace productivity. Analysis of silicomanganese production should include the behaviour of manganese ores, ferromanganese slag, quartz and fluxes during smelting, reduction and slag formation. These processes can be divided into the following stages:

1. Heating and pre-reduction in the solid state

Up to 1100 -1200 °C when manganese oxides are reduced to MnO and iron oxides to metallic iron.

2. Formation of liquid slag and MnO reduction

This stage is completed at the top of the coke bed. The temperature is uncertain, but is estimated to 1550 -1600 °C. Slag samples taken from the top of the coke bed during excavation of industrial furnaces [2] contained around 10 wt % MnO. Such low MnO contents in the slag are expected at temperatures above 1550 °C[1]. In addition the liquid slag should have a low enough content of solids and effective viscosity to drain through the coke bed [3].

3. Reduction of silica from the slag and further reduction of MnO

This stage occurs between 1550 and 1650 °C. These temperatures are required to achieve the observed silicon contents in the alloy [1].

CO is the major component of the gas phase and reduction reactions above 1100 °C are considered to take place in CO. SiO gas and manganese vapour are present in the gas phase in small amounts.

The focus of this paper is the properties of charge materials in the production of silicomanganese in the SAF. This is discussed based on laboratory investigations of smelting/reduction behaviour of charge materials and analysis of equilibrium phases from different raw materials and charge mixtures using FactSage software.

## 2 CHARGE MATERIALS

Assman ore, Gabonese ore, CVRD ore, CVRD sinter and HCFeMn slag were studied in this work. Industrial manganese ores were provided by ERAMET Norway and Vale Norway. The chemical composition of the ores and HCFeMn slag are given in Table 1:.

**Table 1:** Chemical composition (wt%) of manganese sources after pre-reduction.

Element	Assman ore	Gabonese ore	CVRD ore	CVRD sinter	HC FeMn slag
MnO	73.9	82.5	75.1	75.6	39.3
FeO	14.4	4.4	10.0	8.4	0.2
SiO <sub>2</sub>	6.1	5.1	3.4	5.8	23.6
Al <sub>2</sub> O <sub>3</sub>	0.4	7.0	11.1	9.4	12.5
CaO	0.3	0.9	0.3	0.5	16.7
MgO	4.8	0.3	0.1	0.2	4.4

Gabonese ore had the highest MnO content, while it was lowest in the HCFeMn slag. The silica and alumina content varied considerably between the ores. The phase composition of Gabonese and CVRD ores and CVRD sinter as determined previously [4] is presented in Table 2. In both Gabonese and CVRD ores, complex Mn oxides and hydroxides were the main phases, although pyrolusite (MnO<sub>2</sub>) and quartz were found in both ores.

Sintering of the CVRD ore resulted in a change in its phase composition. The manganese oxidation state was reduced with the O/Mn ratio changing from 1.8 to 1.2. Quartz reacted with Mn oxides forming Mn silicate (tephroite).

**Table 2:** Phase composition of Gabonese and CVRD ores and CVRD sinter (from[4]).

Mineral	Formula	%Mn	Gabonese ore %	CVRD ore %	CVRD sinter %
Hausmannite	$(\text{Mn}^{2+})(\text{Mn}^{3+})_2\text{O}_4$	64			49.2
Pyrolusite	$\text{MnO}_2$	63.2	14.3	3.0	
Cryptomelane	$\text{K}_x\text{Mn}^{4+}_{8-x}\text{Mn}^{2+}_x\text{O}_{16}$	56	35.3	13.7	
Bixbyite	$(\text{Mn}, \text{Fe})_2\text{O}_3$	55			
Todorokite	$(\text{Mn}^{2+}, \text{Ca}, \text{Na}, \text{K})(\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mg})_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$	49-52		18.3	
Braunite II	$\text{Ca}(\text{Mn})_{14}\text{SiO}_{24}$	52			
Lithiophorite	$(\text{Al}, \text{Li})\text{Mn}^{4+}_2\text{O}_2(\text{OH})_2$		7.4	5.3	
Nsutite	$(\text{Mn}^{4+})_{1-x}(\text{Mn}^{2+})_x\text{O}_{2-2x}\text{OH}_{2x}$ , (x = 0.06-0.07)		32.6	35.5	
Manganosite	$(\text{Mn}, \text{Fe})\text{O}$				5.9
Bixbyite	$(\text{Mn}, \text{Fe})_2\text{O}_3$				<1
Tephroite	$(\text{Mn}, \text{Fe}, \text{Mg})_2\text{SiO}_4$				4.2
Galaxite	$(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$				8.5
Jacobsite	$(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al}^{3+})_2\text{O}_4$				22.8
Quartz	$\text{SiO}_2$		5.9	1.8	
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$			15.2	
Hematite	$\text{Fe}_2\text{O}_3$		1.5	5.8	
Not identified					6.8

### 3 EXPERIMENTAL

The effect of ore properties were investigated by three different methods:

1. Determination of the softening, melting and start of reduction temperature by direct observation in a sessile drop furnace.
2. Determination of the sample mass and variations in the sample temperature indicating phase changes, as measured by DTA/TGA.
3. Calculation by FactSage of equilibrium phases for Mn sources and SiMn charge mixtures under different conditions.

#### 3.1 Sessile drop furnace

The sessile drop installation is designed to measure the contact angle of a liquid drop on a 10 mm diameter substrate. In this work, it was used to observe the melting of manganese ores under reducing conditions. The materials were visually observed to determine when they softened and melted, and when the first gas bubbles were evolved, which was considered as the start of reduction.

A manganese ore sample of about 25 mg was placed in the centre of a graphite substrate, 10 mm diameter and 3 mm high, which was located on the sample holder. After inserting the sample, the furnace was sealed, evacuated and backfilled to atmospheric pressure with carbon monoxide. The furnace was then continuously purged with 0.5 Nl/min of gas while the sample was heated at 250°C/min to 950°C, then 30°C/min to 1100°C and finally at 5°C/min to 1600°C.

A firewire digital video camera with a telecentric lens was used to record images at a resolution of 1280 x 960 with a 1/2" CCD sensor. The telecentric lens is able to produce an image from 40 to 3.3 mm across the frame, which at maximum magnification is equivalent to 2.6 µm per pixel. Before testing in the sessile drop furnace, the manganese ore was pre-reduced by heating to 1100°C over 2 hours in 70% CO / 30% CO<sub>2</sub>, and then quenched in Ar.

#### 3.2 Differential Thermal Analyser and Thermal Gravimetric Analyser (DTA/TGA)

The high temperature DTA/TGA provided information on the change in the sample enthalpy and weight in the process of heating in a CO atmosphere. Gabonese and CVRD ores and CVRD sinter were studied. Prior to experiments, the manganese ore, ground to 100-300 µm, was pre-reduced at

1200°C in a CO atmosphere with a holding time of 4 hours. The composition of the pre-reduced ores is provided in Table 1.

A sample of approximately 35 mg of manganese ore was placed in a graphite crucible 5 mm in diameter and 8 mm high, and loaded onto the DTA rod. The furnace was then sealed, evacuated and backfilled with carbon monoxide. The sample was then heated at 20°C/min to 1600°C, held for 5 minutes and then cooled at 20°C/min. The furnace was flushed with 100 ml/min of carbon monoxide during the experiment. The change in the sample enthalpy was characterized by the difference in temperature (expressed in  $\mu\text{V}$ ) between the reference sample and the sample under investigation. The Differential Thermal Analyser and Thermal Gravimetric Analyser (DTA/TGA) used was a SetSys Evolution 2400, supplied by Setaram.

The substrates and crucibles, both for the sessile drop and the DTA/TGA, were made from ISO-88, a high density iso-statically pressed graphite supplied by TANSO.

### 3.3 Equilibrium calculations

Type and amount of the various equilibrium phases obtained from different manganese sources and SiMn charge mixtures in a CO atmosphere at different temperatures were analysed using FactSage software. The calculations were performed using the composition of the ores presented in Table 1: mixed with excess carbon.

## 4 EXPERIMENTAL RESULTS

### 4.1 Sessile Drop Furnace

The results obtained in the sessile drop experiments are summarized in Table 3. The melting of the manganese ore was assessed in three different ways.

- Start melting, the temperature at which liquid became visible on the surface of the manganese ore.
- Finish melting, when the manganese ore appeared to be completely liquid.
- Start reduction, when the first gas bubbles were evolved from the sample.

**Table 3:** Results from sessile drop experiments.

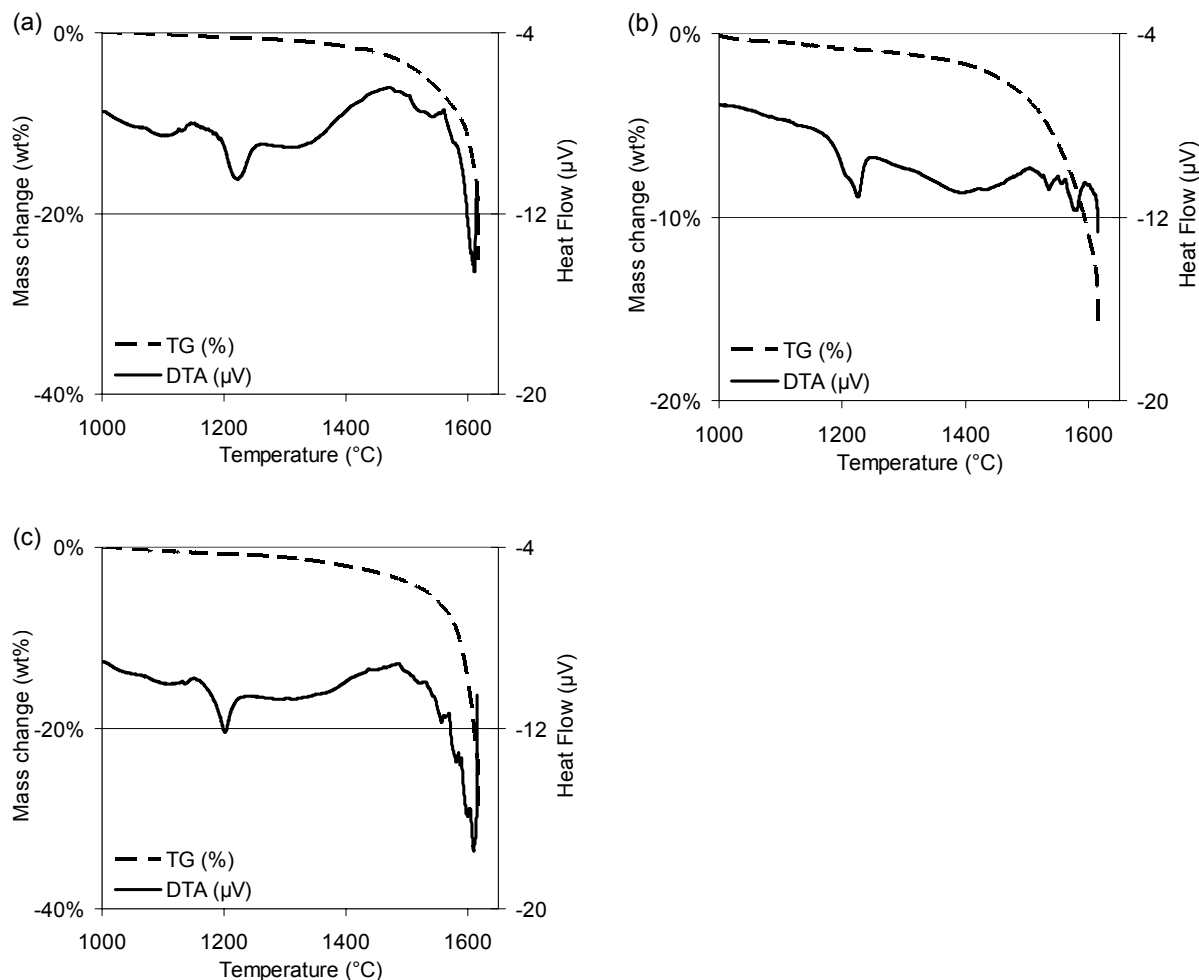
Exp. No.	Material	Final temperature	Start melting	Finish melting	Start reduction
1	Assman ore	1600°C	1545°C	1596°C	1590°C
2	Assman ore	1600°C	1444°C	1469°C	1445°C
3	Assman ore	1600°C	1404°C	1499°C	1441°C
4	Assman ore	1700°C	1390°C	1486°C	1420°C
<b>Average for Assman ore</b>			<b>1446±70°C</b>	<b>1513±57°C</b>	<b>1474±78°C</b>
6	Gabonese ore	1500°C	1471°C	-	-
7	Gabonese ore	1500°C	1479°C	-	-
8	Gabonese ore	1550°C	1478°C	1549°C	1484°C
9	Gabonese ore	1550°C	1500°C	1538°C	1511°C
10	Gabonese ore	1600°C	1485°C	1528°C	1493°C
11	Gabonese ore	1600°C	1496°C	1537°C	1496°C
<b>Average for Gabonese ore</b>			<b>1485±11°C</b>	<b>1538±9°C</b>	<b>1496±11°C</b>
14	CVRD ore	1550°C	1451°C	1479°C	1457°C
15	CVRD ore	1550°C	1455°C	1482°C	1452°C
16	CVRD ore	1600°C	1458°C	1488°C	1445°C
17	CVRD ore	1600°C	1479°C	1528°C	1502°C
<b>Average for CVRD ore</b>			<b>1461±13°C</b>	<b>1494±23°C</b>	<b>1464±26°C</b>
18	CVRD sinter	1400°C	1398°C	-	-
19	CVRD sinter	1500°C	1425°C	1497°C	1471°C
21	CVRD sinter	1600°C	1362°C	1481°C	1387°C
<b>Average for CVRD sinter</b>			<b>1395±85°C</b>	<b>1489±132°C</b>	<b>1411±52°C</b>

A significant scatter in the properties of manganese ores indicates that materials were inhomogeneous; which has been reported previously [3] for Assman ore which contains two distinct phases, one nearly pure MnO and the other containing significant quantities of iron.

#### 4.2 DTA/TGA

CVRD and Gabonese ores and CVRD sinter were analyzed with a DTA/TGA. The recorded changes in the sample enthalpy and mass are shown in Figure 1. The weight change for all samples exhibited the same trend; a slow decrease followed by quite a sharp change. Overall weight loss was significant: 25.1% for Gabonese ore, 16.3% for CVRD ore and 28.5% for CVRD sinter. Since no metal phase was observed after experiments, the observed weight loss was obviously caused by MnO reduction and vaporization of the reduced manganese. The measured weight losses correspond to 30.6% reduction for Gabonese ore, 21.7% for CVRD ore and 37.7% for CVRD sinter. The DTA response included enthalpies for the reduction reaction, ore melting and manganese vaporization. The start of the heat flow corresponded to the beginning of significant weight loss. This can be interpreted as the fact that melting and reduction started at about the same temperature, which is especially evident for Gabonese ore and CVRD sinter.

DTA curves for CVRD ore and sinter and Gabonese ore also included the endothermic dips at approximately 1200 °C, which can be attributed to a phase change.



**Figure 1:** The heat flow and weight change of (a) Gabonese ore, (b) CVRD ore and (c) CVRD sinter when heated in a CO atmosphere at 20°C/min to 1600°C. All samples were initially exposed to CO at 1200 °C for 4 hours.

## 5 EQUILIBRIUM PHASES

Two different cases were studied in the equilibrium calculations;

- 1 Reduction of manganese ores and HCFeMn slag were studied by calculating the equilibrium for the manganese sources mixed with excess carbon in a CO atmosphere at temperatures between 1100 °C and 1600 °C.
- 2 Equilibrium conditions during SiMn production were studied by calculating the equilibrium for products from the reduction of manganese ores mixed with dolomite (60 kg/t Mn source) silica (300 kg/t manganese source) and excess carbon in a CO-atmosphere at 1600°C, 1650°C and 1700°C. Composition and mass of phases found by the FactSage calculations at 1600°C in case 1 are used as starting points for the calculations of phases in SiMn production.

### 5.1 Reduction of Manganese Ores and HCFeMn Slag

Equilibrium phases for Assman, Gabonese and CVRD ore and HCFeMn slag with excess carbon are presented in Table 4. The chemical composition of liquid slag and metal formed during the smelting/reduction of different manganese sources in the temperature range 1100-1600°C were also calculated.

**Table 4:** Equilibrium phases in the process of reduction of manganese sources calculated using FactSage.

Mn source	Temperature, °C	Phases
<b>Assman ore</b>	1100	(Mn,Mg)O, (Mn,Mg,Ca) <sub>2</sub> SiO <sub>4</sub> , Iron (fcc) (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
	1200	(Mn,Mg,Ca) <sub>2</sub> SiO <sub>4</sub> , (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , (Mn,Mg)O, Liquid metal
	1300	(Mn,Mg,Ca) <sub>2</sub> SiO <sub>4</sub> , (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , Liquid metal, Liquid slag
	1400-1500	(Mn,Mg,Ca) <sub>2</sub> SiO <sub>4</sub> , Liquid slag Liquid metal,
	1600	Liquid metal, Liquid slag, MgO
<b>Gabonese ore</b>	1100	(Mn,Mg)O, MnAl <sub>2</sub> O <sub>4</sub> , Liquid slag, Fe (fcc)
	1200-1300	(Mn,Mg)O, Liquid slag, (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , Liquid metal
	1400-1600	Liquid metal, (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , Liquid slag
<b>CVRD ore</b>	1100	(Mn,Mg)O, MnAl <sub>2</sub> O <sub>4</sub> , Liquid slag, Fe (fcc), (Mn,Mg) <sub>2</sub> SiO <sub>4</sub>
	1200-1300	(Mn,Mg)O, MnAl <sub>2</sub> O <sub>4</sub> , Liquid slag, Liquid metal
	1400-1600	Liquid metal, (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , Liquid slag
<b>HC FeMn slag</b>	1100	(Mn,Mg,Ca) <sub>2</sub> SiO <sub>4</sub> , (Mn,Mg)Al <sub>2</sub> O <sub>4</sub> , Liquid slag, (Mn,Mg)O, Fe(fcc)
	1200	Liquid slag, (Mg,Mn)Al <sub>2</sub> O <sub>4</sub> , (Mn,Mg,Ca)O, Liquid metal
	1300-1600	Liquid slag, Liquid metal

## 5.2 Equilibrium conditions during SiMn production

Calculated equilibrium compositions of slags produced in the smelting/reduction of manganese ores and HCFeMn slag are given in Table 5. Solid phases at the various temperatures and the calculated mass of the metal phase are shown in Table 6.

**Table 5:** Equilibrium compositions of slag phase, wt%, from the reduction of different manganese sources mixed with quartz and dolomite.

Mn source	Temperature, °C	% MnO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% CaO	%MgO
<b>Assman ore</b>	1600	5.82	49.3	4.37	16.3	29.6
	1650	2.40	39.5	4.84	18.3	35.0
	1700	0.95	35.1	8.26	31.2	24.5
<b>Gabonese ore</b>	1600	16.1	33.3	30.8	14.2	5.52
	1650	7.05	25.7	40.6	20.3	6.33
	1700	2.76	15.6	54.1	21.2	6.31
<b>CVRD ore</b>	1600	15.3	33.4	31.5	14.4	4.79
	1650	6.82	25.0	42.9	20.8	4.36
	1700	2.53	11.7	62.8	18.5	4.37
<b>HCFeMn slag</b>	1600	10.7	40.7	16.8	24.6	7.18
	1650	4.81	34.9	21.0	30.7	8.62
	1700	1.93	30.0	24.1	35.3	8.52

**Table 6:** Equilibrium compositions, wt%, and mass of the metal and other phases in the reduction of different manganese sources mixed with quartz and dolomite.

Mn source	Temperature, °C	Mass, kg/t Mn source	% Mn	% Fe	% Si	% C	Other phases*
Assman ore	1600	795	68.0	14.1	15.2	2.76	SiC (Mg,Mn) <sub>2</sub> SiO <sub>4</sub> ,
	1650	801	67.6	14.0	15.5	2.93	SiC
	1700	800	67.0	14.0	15.9	3.09	SiC
Gabonese ore	1600	767	76.5	4.46	16.3	2.73	SiC (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
	1650	786	76.1	4.35	16.7	2.89	SiC (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
	1700	797	75.5	4.29	17.1	3.05	SiC
CVRD ore	1600	721	71.0	10.7	15.4	2.78	SiC (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
	1650	738	70.7	10.5	15.8	2.95	SiC (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
	1700	759	70.4	10.2	16.3	3.11	SiC (Mn,Mg)Al <sub>2</sub> O <sub>4</sub>
HC FeMn slag	1600	279	79.8	0.54	17.0	2.62	SiC
	1650	322	79.3	0.46	17.4	2.79	SiC
	1700	332	78.7	0.45	17.9	2.95	SiC

\*All reduction products included graphite

## 6 DISCUSSION

The melting temperature is defined as the temperature at which the sample contains no solid phases. During pre-reduction of the manganese sources studied in this paper, the higher manganese oxides were reduced to MnO and iron oxides to FeO and Fe<sub>2</sub>O<sub>3</sub>. When heated under reducing conditions in the sessile drop furnace and a DTA/TGA, the phase composition and chemistry changed as a result of the increasing temperature and due to the reduction of iron and manganese oxides from the ore. The melting temperature of pure MnO is 1842°C. The lower melting temperatures found in this investigation corresponds to the temperature at which all of the MnO phase was dissolved into the molten slag. Equilibrium analysis in this work showed that other solid phases can be present or formed during reduction of manganese and silicon oxide. The type and amount of these phases vary with ore type and with the added fluxes. Therefore the melting temperature, the temperature where all solid phases have disappeared, depends on the ore type and charge mixture.

The melting temperature of Assman, Gabonese and CVRD ores and CVRD sinter measured in a sessile drop furnace varied from 1489 to 1538°C. Melting of the CVRD ore started 65°C higher than the melting of CVRD sinter. The higher melting temperature for the ore than the sinter was confirmed by DTA/TGA, although the difference was 38°C. Pre-reduction before the experiments changed the phase compositions of the ores making the composition of CVRD ore and CVRD sinter similar, so no difference was expected. However their physical properties, particularly porosity and surface area were different. The observed difference in melting temperature can be attributed to different rates of MnO reduction caused by the difference in physical properties. The melting properties of manganese ore and sinter should therefore be analysed together with their reduction rate.

Under equilibrium conditions, carbothermal reduction in CO of MnO from ore to Mn-C<sub>sat</sub> alloy starts at 1340°C. In the sessile drop and DTA/TGA experiments, reduction started at a much higher temperature. In addition the degree of reduction estimated from DTA/TGA experiments as 30.4% reduction for Gabonese ore, 21.7% for CVRD ore and 37.7% for CVRD sinter was well below the equilibrium data. The slow MnO reduction can be attributed to a relatively small interfacial area between the sample and the graphite substrate in the sessile drop furnace and the crucible in DTA/TGA experiments. The experimental conditions in sessile drop and DTA/TGA experiments were far from equilibrium.



Thermodynamic analysis of the reduction processes using FactSage gives an insight into the development of phases at equilibrium. The phase composition of manganese sources changed significantly upon heating and reduction, as shown in Table 4. Initially all materials contained a monoxide phase (predominantly, MnO), which disappeared as a result of MnO reduction. The ores with a high alumina content, Gabonese and CVRD ore, contained Al-spinel (predominantly  $MnAl_2O_4$ ) which was observed even at 1600°C. The mass and concentration of  $MgAl_2O_4$  in the spinel increased slightly with increasing temperature as a result of manganese oxide reduction. Assman ore, which had a relatively high MgO concentration, contained an olivine phase  $(Mn,Mg,Ca)_2SiO_4$ , which changed composition with temperature from predominantly  $Mn_2SiO_4$  to  $Mg_2SiO_4$  (72.5 wt%  $Mg_2SiO_4$  at 1500°C). At 1600°C, this phase converted to the monoxide phase with 96.1 wt% MgO. The  $(Mn,Mg)_2SiO_4$  phase (95.8 wt%  $Mn_2SiO_4$ ) was also observed in CVRD ore reduced at 1100°C. At 1100°C a major phase in the HC FeMn slag was olivine with 19.1 wt%  $Mn_2SiO_4$ . Al-spinel (99.2 wt%  $MnAl_2O_4$ ) and monoxide (95.4 wt% MnO) were also observed at this temperature together with liquid slag (see Table 3). Liquid slag became the main phase at 1200°C. The molten slag remained a major phase during the reduction of HC FeMn slag at 1600°C, while there was a very small amount of liquid slag present during the reduction of manganese ores.

The equilibrium calculations showed that under reducing conditions, melting of Assman, Gabonese and CVRD manganese ores was not complete at 1600°C. Although the major phase was liquid metal, all of the investigated ores contained solid phases that made the system heterogeneous and affected its viscosity. In contrast to the ores, smelting and reduction of HCFeMn slag at 1600 °C resulted in the formation of only molten slag and metal phases.

The metallic phase was enriched with iron at the beginning of reduction, becoming enriched in Mn with further reduction of MnO. At 1550-1600°C silica started to be reduced. Silicon in the metal phase from the reduction of HC FeMn slag reached 6.9 wt% at 1600°C, which was much higher than from the reduction of manganese ores.

In an excavation of a silicomanganese furnace [2], silica started to be reduced at 1550-1600°C when the MnO content in the slag had decreased below 10 wt%. This temperature,  $T_{10}$ , when the MnO content of the slag decreased below 10 % for each manganese source is shown in Table 7. It changed in a relatively narrow interval, from 1566°C for Assman ore to 1605°C for Gabonese ore and HC FeMn slag. The mass of metallic phase formed from the reduction of different manganese sources was significantly different. The equilibrium quantity of metal produced from 1000 kg Assman ore at  $T_{10}$  was 732 kg, while it was 288 kg if only the HC FeMn slag was used.

**Table 7:** Characteristic parameters in reduction of different manganese sources.

Mn source	Assman ore	Gabonese ore	CVRD ore	HC FeMn slag
Temperature $T_{10}$ (°C) at which MnO is reduced to 10%	1566	1605	1593	1607
Mass of metal phase at $T_{10}$ , kg/t Mn source	732	690	645	288

Differences in the phase composition of the products of the smelting/reduction of different manganese sources will affect their further processing to silicomanganese. To illustrate this difference, the equilibrium with addition of 300 kg quartz and 60 kg dolomite at 1600°C was calculated for each of the manganese sources. As shown in Table 5, this produced slags with different chemical compositions. In the smelting of Assman ore, the slag contained 5.8 wt% MnO at 1600°C, while the MnO concentration of the Gabonese and CVRD slag was much higher, 15-16 wt%. By increasing the temperature to 1650°C, the MnO content in the slag from the smelting of Assman ore was reduced to 2.4 wt %, and to less than 7 wt% in the smelting of Gabonese and CVRD ores. This is actually close to what is observed in industrial silicomanganese production. Silicomanganese alloy produced from ores at 1650°C contained 68-70 wt% Mn and 16-17 wt% Si (Table 6), with a carbon concentration in the range 2.8-2.95 wt %, which is higher than in the commercial alloy. All phases contained silicon carbide.

The equilibrium calculations showed that during reduction, solid oxide phases were present in addition to silicon carbide. After reduction of Gabonese and CVRD ores at 1600-1700°C, Al-spinel (mainly  $\text{MnAl}_2\text{O}_4$ ) was present while  $(\text{Mg,Mn})_2\text{SiO}_4$  (mainly  $\text{Mg}_2\text{SiO}_4$ ) were found after reduction of Assman ore at 1600°C. These solid phases will affect the viscosity of molten phases on the top of and in the coke bed. Their effect on furnace performance is not known.

HCFeMn slag, which is a common charge-constituent in SiMn production, resulted in a higher amount of slag than the ores. According to the equilibrium calculations, 594 kg/t HCFeMn slag was produced at 1600°C. The metal phase from the reduction of HCFeMn slag at 1600°C contained very little iron. When the HCFeMn slag was mixed with dolomite and quartz, 626 kg slag, containing 4.81 wt% MnO and 34.9 wt%  $\text{SiO}_2$  was produced at 1650°C. This slag was in equilibrium with silicomanganese with 79 wt% Mn and 17.4 wt% Si and silicon carbide. In contrast to the ores, no other solid phases were present when HCFeMn slag was reduced at 1600 °C.

Equilibrium silica concentration in the slags from the ores and HCFeMn slag at 1650°C was 25-40 wt%. Excavation of the silicomanganese furnace showed that the silica concentration in the slag at the top of the cokebed, beneath the electrode and in the final slag was about the same, 40-45 wt%. The silica reduction rate might be limited by the rate of quartz dissolution into the slag, while its reduction by the metal exchange reaction with manganese from the metal phase is relatively fast. Kinetics of silica dissolution into silicomanganese slag is unknown.

## 7 CONCLUSIONS

The melting behaviours of manganese ore heated under reducing conditions are affected by phase changes, which occur due to the increasing temperature and the reduction reactions. In a manganese ore in which MnO is the only solid phase at temperatures above 1100-1200°C, complete melting will occur when all of the MnO phase is dissolved during the course of reduction. However, during heating and reduction of the manganese ore galaxite and other phases may form, which will remain solid even at 1600°C.

Experimental investigations of Assman, Gabonese and CVRD ores and CVRD sinter revealed significant differences in their melting behaviour under reducing conditions. Laboratory measurements of the melting properties were affected by the ore rate of reduction. The difference in smelting of CVRD ore and CVRD sinter in sessile drop and DTA/TGA experiments was attributed to the physical properties of the sinter which promoted faster reduction by the graphite substrate.

Calculation of equilibrium phases in the process of reduction of manganese ores using FactSage software correctly reflects trends in the production of manganese alloys.

The temperature at which the MnO concentration in the slag was reduced below 10 wt% was in the range of 1550-1610°C. This temperature can be assigned to the top of the coke bed in the silicomanganese furnace.

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