

INITIAL MELTING AND REDUCTION OF ORE AND FLUXES AT THE TOP OF THE COKE BED DURING SiMn-PRODUCTION

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ABSTRACT

The conditions at the boundary of the coke bed are believed to be important for the operation of SiMn furnaces and an understanding of these conditions can be used to explain why the furnace performance varies with the ore type. In this work a possible mechanism for the initial melting and reduction in this zone is proposed and discussed. This is based on a review of literature of MnO reduction with a focus on furnace excavations and pilot plant experiments. It is assumed that the conditions under which the slag starts to drain down in to the coke bed determines the temperature at the top of the coke bed.

Four different charge mixtures for SiMn production, based on single Mn sources, have been calculated. The investigated Mn sources are Assmang ore, Comilog ore, CVRD sinter and HCFeMn slag. Quartz and dolomite are used as fluxes. The liquidus temperatures for the calculated charge mixtures are compared with melting temperatures for the ores reported in literature. The melting temperatures for all the ores are higher than the liquidus temperature of their charge mixture.

In industrial excavations and pilot scale experiments nearly all MnO is reduced at the top of the cokebed. Parameters of importance for the temperature at the boundary of the cokebed and for the MnO reduction in this zone are discussed.

INTRODUCTION

SiMn is primarily produced by carbothermic reduction of oxidic raw materials in electric submerged arc furnaces. The typical alloy composition is min 65% Mn, 15-19% Si and max 2% C. The main Mn sources are various lump Mn ores and agglomerated Mn fines in addition to HCFeMn slag. The main Si sources are quartz in addition to SiO₂ in the Mn ore and in the HCFeMn slag. Various fluxes are added to adjust the slag composition. Coke is normally used as a reductant. The process temperature is around 1650°C.

Reactions

The important reactions for the production of SiMn and HCFeMn in submerged arc furnaces, have been extensively studied and are described by several authors [1, 2, 3]. The main overall reactions that control the distribution of silicon and manganese between slag and alloy are:



Brackets denote species in the slag phase and underlining denote species in the metal phase. As stated by Tranell *et al.* [3], more investigations are required to establish the detailed reaction mechanism for these reactions. A literature survey of possible reaction mechanisms are given by Jafar [17]. This paper focus on the effect of different ores in the cokebed zone, where a liquid slag is present, and it is sufficient to base the discussion on the overall reactions (1) and (2).

In a system with simultaneous reduction of MnO and SiO₂, the slag/metal exchange reaction, which is a combination of reaction (1) and (2), must in addition be taken in to account.



The equilibrium in reaction (1) between MnO in slag and Mn in the alloy is not always established. The exchange reaction (3) that is little dependent of temperature [1, 2] is often considered to be faster than the carbothermic reactions and partial slag/metal equilibrium can be established. The carbothermic reactions (1) and (2) depend strongly on temperature, with a higher temperature producing a higher silicon content in the alloy and a lower MnO content in the slag.

Properties of Slags and Mn-Source

The slag composition affects both the silica and the manganese activities and the amount of solid MnO in the slag at a given temperature. The importance of the alumina content and basicity are shown by Tang and Olsen [4] and Zhao *et al.* [5]. Reduction starts below the liquidus temperature in the two phase area where solid MnO is present in the liquid slag phase. The liquidus lines in the MnO-SiO₂-Al₂O₃ system are illustrated in Figure 1. The content of CaO and MgO must also be included when the liquidus temperature is estimated.

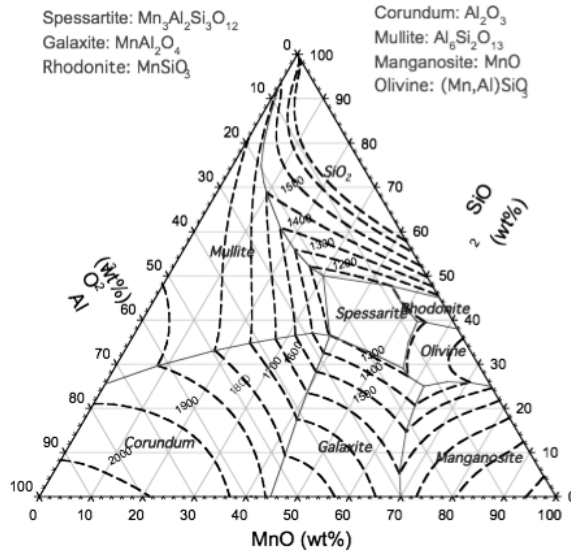


Figure 1: Phase and liquidus relations for the MnO-SiO₂-Al₂O₃ system

The Mn sources are either HCFMn slag or Mn ores. The Mn ores are composed of one or a mixture of different minerals [5], both Mn containing minerals, such as Pyrolusite (MnO₂), BraunitelI (7(Mn,Fe)₂O₃CaSiO₃), Manganite (MnOOH) and other mineral species as Quartz (SiO₂). An overview over the Mn-minerals is given in Olsen *et al.* [1].

The Cokebed Zone

Excavation of an industrial furnace by Olsen and Tangstad [2] has shown the existence of a cokebed where the final reduction to Mn and Si takes place. The cokebed consists of molten ore, fluxes and alloy together with solid coke [6]. The existence of the cokebed and its properties under different conditions is observed in several pilot scale experiments [7, 8, 9]. They also show that most of the MnO-reduction takes place at the top of the cokebed and that nearly all the Mn ore is reduced in this zone, while SiO₂ is reduced to Si in the cokebed as illustrated in Figure 2. In the excavation by Olsen and Tangstad [2] dissolution and reduction of quartz appeared to take place in the cokebed zone after the main reduction of manganese oxide was completed.

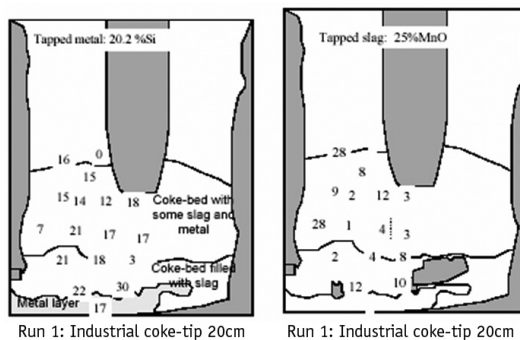


Figure 2: MnO and Si distribution in cokebed from pilot scale experiment [7]

Industrial experience [8, 16] indicates that the operation and performance of a submerged arc furnace is affected by the Mn source. Since most of the MnO-reduction takes place at the top of the cokebed, variation between the Mn sources that affects their behaviour in this zone, can be one of the causes for this difference. In this work a possible mechanism for the initial melting and reduction at the boundary of the cokebed is proposed and discussed. The discussions are based on calculation of the melting conditions for four different charge mixtures.

METHODOLOGY

A hypothesis for the reaction mechanisms at the boundary of the coke bed is made by a qualitative evaluation of results from literature, especially the results from the pilot scale [7, 8, 9] and industrial excavations [2, 15]. This hypothesis is described in the chapter: *Reactions at the boundary of the cokebed*. Based on this hypothesis the conditions at the boundary of the cokebed are calculated for industrial production of SiMn in four different cases with different Mn-sources. The compositions of these charge mixes at the boundary of the coke bed are calculated and their liquidus temperatures found, in the chapter *Composition of charge mixtures and liquidus temperature with use of different Mn-sources*.

In the results and discussion part, these results are compared with softening and melting temperatures found in literature. On the basis of these results and the presented hypothesis the conditions at the boundary of the coke bed is discussed and further work to test out this hypothesis is proposed. The focus of this paper is a qualitative description of possible reactions in this zone.

Reactions at the Boundary of the Cokebed

The rather small zone at the boundary of the cokebed where most of the MnO reduction takes place is believed to affect the operation of the furnace significantly. The properties of the Mn source and the charge mix can determine the conditions in this zone. Possible reaction mechanisms in this zone are:

- Solid ore, fluxes and slag remains at the boundary of the cokebed until the viscosity of the charge is low enough to let it drain between the coke particles. The temperature where the charge starts to flow is reached when both the amount of solids and the viscosity of the liquid phase are low enough. The solids are charge materials that have not melted or dissolved, or solid MnO in equilibrium with the MnO containing slag. The temperature where the charge or partially reduced charge has a low enough viscosity to flow down through the coke bed determines the temperature at the top of the coke bed.
- Reduction of MnO from the charge may start as soon as there is a liquid phase present. The equilibrium MnO content depends on the temperature and the slag composition. The MnO content in the slag at the boundary of the cokebed depends on the temperature where the charge starts to drain in to the cokebed and the initial charge composition. Silica reduction is of little importance until the process temperature is above around 1550°C. Only when the temperature at the boundary of the cokebed is higher than this, is it possible for the silica reduction to start here, otherwise it takes place in the bulk part of the cokebed.
- The maximum process temperature in the cokebed is determined by the total energy input and the energy required for melting and reduction together with the volume of the cokebed. The difference between the maximum process temperature and the

temperature in the boundary zone of the cokebed is determined by how much of the total energy input is used for heating and reduction in this zone. The temperature and the reduction work done in the bulk of the cokebed strongly depend on the.

Composition of Charge Mixtures and Liquidus Temperature with Use of Different Mn-Sources

The charge mixtures required to produce SiMn with 18% Si from each of four different Mn sources, Comilog ore, and Assman ore, CVRD sinter and HCFEMn-slag are calculated.

The chemical composition of these Mn sources used in further calculations, are shown in Table 1. The properties of these raw materials have been investigated earlier [8, 10, 11, 12, 13]. The composition of specific samples used in these investigations and not average or typical ores are used. To ease the comparison between the Mn sources and between these and the charge mixture, their Mn contents are reported as MnO and their Fe contents as Fe.

Table 1: Chemical composition of investigated Mn sources

Element	Assman ore10	Comilog ore10	CVRD sinter8	HCFEMn slag12
MnO	62,2	66,1	63,3	39,3
Fe	11,2	2,4	7,9	0,2
SiO ₂	2,8	4,3	7,2	23,6
CaO	6,7	0	0,7	16,7
MgO	0,3	0	0,4	4,4
Al ₂ O ₃	0,5	5,8	10,5	12,5
K ₂ O	0,03	0,8	1,4	

For each of these Mn sources a charge mixture that in addition to the alloy will give a slag with a desired composition is calculated. Based on Olsen *et al.* [1] it is assumed that a final slag with 38% SiO₂, and slag basicity ($\frac{CaO + MgO}{SiO_2}$) above 0,8 is necessary to produce

SiMn with 18 % Si. It is assumed that the slag will contain 10 % MnO. The calculations are in principles simple mass balances, but since several iterations are required, they are made with a calculation program [8]. The calculations are based on the following principles.

First the obtained slag composition and the slag/alloy ratio for 1 ton of each Mn source is calculated, based on the following:

- All Fe in the raw materials goes to the alloy as Fe
- All CaO, MgO, Al₂O₃ and K₂O in the Mn sources and additives go to the slag
- The only additives are Quartz with 100% SiO₂, and Dolomite with 100% (Ca,Mg) (CO₃)₂. The contribution of slag components from the coke is not included
- The slag contains 10 % MnO
- The slag composition for each Mn-sources is calculated and adjusted by addition of Quartz and

Dolomite until it reaches 38% SiO₂, and a slag basicity ($\frac{CaO + MgO}{SiO_2}$) above 0,8.

- The initial composition and amount of slag is now known
- Mn from the raw material that do not end as MnO in the slag, goes together with Fe to the alloy

- The alloy composition is adjusted to reach 18% Si
- The initial composition and amount of the alloy is now known
- If all SiO_2 in the raw materials is consumed, the calculation is finished. If it is a surplus of SiO_2 the calculations must be repeated until the requirements for both slag and alloy are met
- Final slag composition and slag/alloy ratio is calculated.

The calculated slag composition and slag/alloy ratios are shown in Table 2. They differ from ore to ore. In industrial production, a mixture of different Mn-sources is normally used to optimize the slag/alloy ratio and the alloy composition. In this work, each charge is based on a single Mn-source in order to illustrate the difference between them. In the work by Leroy [11] only ores without flux were used in experiments and similar calculations.

Table 2: Final slag composition with the different Mn sources

Element	Assman ore	Comilog ore	CVRD sinter	HCFEMn slag
Basisity (CaO + MgO) / SiO_2	1,27	0,80	0,80	0,86
R (CaO + MgO) / Al_2O_3	13,71	1,61	1,59	1,69
Slag/alloy ratio	0,20	0,48	0,84	2,03

When the slag and alloy compositions and the slag/alloy ratio are calculated, the amount of all the elements except C and O are known. It is assumed that when the charge reach the cokebed, all iron oxide is reduced to iron, the higher manganese oxides are reduced to MnO and CO_2 has dissociated from the carbonates. The composition of the liquid oxide phase at the boundary of the cokebed can then be calculated. The charge compositions with using different Mn sources are shown in Table 3.

The liquidus temperatures for each of these slag compositions are estimated from Tang and Olsen [4] and shown in Table 3.

Table 3: Composition of charge mix at the boundary of the cokebed before the reduction starts

Element	Assman ore	Comilog ore	CVRD sinter	HCFEMn slag
MnO	60,3	55,8	46,3	35,8
SiO_2	32,4	30,5	33,7	33,6
CaO	6,5	4,6	7,2	15,2
MgO	0,3	4,3	5,1	4,0
Al_2O_3	0,5	4,9	7,7	11,4
Basisity (CaO + MgO) / SiO_2	0,21	0,29	0,36	0,57
Basisity 2 (CaO + MgO) / ($\text{SiO}_2 + \text{Al}_2\text{O}_3$)	0,21	0,29	0,36	0,43
A/S				
$\text{Al}_2\text{O}_3 / \text{SiO}_2$	0,02	0,16	0,23	0,34
MgO / CaO	0,05	0,93	0,70	0,26
R (CaO + MgO) / Al_2O_3	13,6	1,82	1,59	1,69
Liquidus temperature °C	1400	1350	1300	1200

RESULTS AND DISCUSSION

Melting Temperatures

The reduction of MnO will first start when the ore has melted. In Table 4 the temperatures where the initial softening starts and the melting temperature for each of the Mn sources are compared with the liquidus temperatures for the corresponding charge mix. The liquidus temperatures for the charge mixes is a result of this investigation as described in the chapter *Composition of charge mixtures and liquidus temperature with use of different Mn-sources* and also presented in Table 3, while the softening and melting temperature are taken from literature.

The softening and melting temperatures for the ores have been studied by several authors [8, 9, 10, 11, 12, 13]. The melting temperatures used in the discussion below, shown in Table 4 are based on the works of Gaal *et al.* [12, 13]. The melting temperature of the ore may differ from the melting temperature of a slag with the same chemical composition as the ore since the ore is an inhomogeneous mixture of individual minerals with different melting temperatures.

Table 4: Melting properties of the ores

Element	Assman ore	Comilog ore	CVRD sinter	HCFEMn slag
Temperature, °C, of initial softening of Mn sources [12, 13]	1450	1490	1350	1220
Temperature, °C, of final melting of Mn sources [12, 13]	1510	1540	1410	1230
Liquidus temperature, °C, charge mix	1400	1350	1300	1200

Conditions at the Boundary of the Cokebed

According to the hypothesis presented earlier in this paper, the temperature and the MnO content at the boundary of the coke bed is affected by the melting temperature of the ore and the liquidus temperature of the charge.

If the melting temperatures for the Mn sources are higher than the liquidus temperature for the charge mix, the charge is expected to be able to trickle down into the cokebed as soon as it has melted and before much of the MnO has had time sufficient to be reduced. When the liquidus temperature is higher than the melting temperature, MnO reduction must at least go to the point where all solid MnO particles have disappeared, e.g. liquidus must be reached, before the molten and partially reduced charge mix will be able to drain into the cokebed. With only a liquid phase present, the viscosity of this phase will determine at which MnO- content, the slag will drain into the cokebed.

For all of the calculated charge mixtures, both the softening and the melting temperature of the Mn-source were, as shown in Table 4, higher than or nearly equal to the liquidus temperature. Therefore, in the investigated cases, the temperature at the boundary of the cokebed is not believed to be determined by the liquidus temperature of the charge mixture.

When these charge mixtures are molten, they are above the liquidus temperature and are not prevented from trickling down in the cokebed by solid MnO particles in equilibrium with the liquid slag phase. No further MnO reduction is thus necessary to let these mixtures flow down into the coke bed. However industrial excavations [2] and pilot scale experiments [7, 8, 9] show that this is not the case. In these, MnO in the molten charge is reduced before it drains into the cokebed, and the slag at the boundary of the cokebed has nearly the same MnO content as the final slag. This can be a result of reduction during

melting or very fast reduction as soon as the charge mix has melted. A liquid phase with a high viscosity or slow dissolution of quartz particles can also result in a higher temperature and longer retention time at the boundary of the cokebed. Further investigations are needed to clarify this.

Recent DTA/TGA investigations by Gaal *et al.* [13], have shown reduction during melting and that the temperature where the reduction starts varies from ore to ore. Such reduction during melting may explain the low MnO content in the cokebed observed in furnace excavations [4, 7, 8, 9].

How low viscosity that is required for the liquid phase to be able to drain into the cokebed is not clear. This must be clarified by experiments and compared with the viscosities of the actual charge mixtures at the melting temperature to determine the importance of the viscosity on the temperature at the top of the cokebed. A model for calculation of viscosity is presented by Tang and Tangstad [14].

In industrial excavations [2, 15] undissolved quartz particles have been reported in the cokebed. This indicates that the properties of the cokebed and especially the top of the cokebed are affected by the dissolution rate of quartz into the liquid. Solid quartz will only result in a higher effective viscosity if it disintegrates and is suspended in the liquid phase. Otherwise the liquid phase may drain between larger quartz lumps. The amount of quartz added, varies from ore to ore and the importance of the dissolution rate will also differ between the ores. In the case where not all of the quartz has dissolved, the silica activity will be lower than given by the calculated slag composition. It must be emphasised that since the existence of solid quartz is a result of kinetics and not thermodynamics, the activity is not unity although solid quartz is present. The lowered silica activity affects the silica reduction. Experimental studies of dissolution of quartz will give more information about the importance of this parameter.

Before it is possible to calculate the degree of MnO and SiO₂ reduction at the boundary of the coke bed, and their reduction mechanism within the coke bed, the temperature and conditions at the boundary of the coke bed with the use of different ores must be further clarified.

CONCLUSIONS

A hypothesis that describes the conditions and the reactions at the boundary of the coke bed during SiMn production in a Submerged Arc Furnace is presented. Here it is assumed that the temperature on the top of the coke is determined by the temperature where the oxide phase has low enough viscosity to trickle down in the coke bed. The temperature must at least be so high that the charge mix is melted. If the melting temperature for the Mn-sources is higher than the liquidus temperature for the charge mix, the temperature at the top of the coke bed must be equal to or higher than the melting temperature for the Mn sources. Otherwise it must be at least as high as the liquidus temperature for the charge mix. A high viscosity of the melted phase may prevent drainage of the melted charge mix into the cokebed until the temperature is further increased. The MnO content in the slag at the top of the cokebed is assumed to depend both on the temperature and the total composition of the charge mix in this zone. According to this hypothesis the conditions at the top of the coke bed depends on the Mn-source. The furnace performance will then vary with the Mn source used.

The conditions at the top of the coke bed is, based on the presented hypothesis, calculated for four different charge mixes based on different Mn sources. The investigated Mn sources are Assman ore, Comilog ore, CVRD sinter and HC slag. For all these the melting temperature of the ore is higher than the liquidus temperature for the charge mix. For the

calculated cases, the temperature at the boundary of the coke bed is therefore determined by the melting temperature of the ore and not the liquidus temperature for the charge mix.

Furnace excavations [2, 7, 8, 9] show that most of the MnO reduction in a SiMn furnace takes place at the boundary of the cokebed. The parameters that determine the conditions in this zone should therefore be further clarified. The work presented in this paper indicated that the most important parameters are softening and melting temperatures of the Mn-sources, the extent of reduction during melting, the dissolution rate of quartz, the viscosities of the different charge mixtures and the viscosity required for drainage of the slag through the cokebed.

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