

MELTING BEHAVIOUR OF Mn SOURCES - EFFECT ON FURNACE PERFORMANCE

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ABSTRACT

During production of Mn alloys in Submerged Arc Furnaces (SAF) most of the reduction takes place at the top of the coke bed. The conditions in this zone are crucial. Results of several studies of melting and reduction in this zone are presented and discussed. The temperature at the top of the coke bed is assumed to be determined by the temperature where the slag has viscosity low enough to drain into the coke bed. It is shown that this temperature will increase when the temperature for initial melting of the charge mixture increases. Charge mixtures with a high temperature for initial melting will thus give a high temperature at the top of the coke bed.

The temperature for initial melting has been measured for several Mn sources. The investigations show that the temperature where the Mn sources start to melt, the softening temperature vary between the different sources from around 1250 °C to nearly 1600 °C. It decreases with increasing amount of acidic oxides in the ore. Heat-treated ores will have lower melting temperatures than the ores they are made from. Addition of quartz will decrease the melting temperature while it will increase when dolomite is added. Materials that soften at lower temperatures will be reduced at lower temperatures. When produced slag from two pilot experiments with HCFMn production were compared, % MnO in slag was higher in the experiment where low melting Mn-source was used. A high temperature at the top of the coke bed is believed to be beneficial for SiMn production, but this has not been further discussed.

1. INTRODUCTION

Manganese alloys are important constituents in steel production. The two main products are HCFMn and SiMn. In 2013 global production of Mn-alloys was 13.1 mln. tons [1], distributed with around 70% as SiMn and 30% as FeMn. Mn alloys are mainly produced in submerged arc furnaces (SAF) by carbothermic reduction of oxidic raw materials. Heat needed for smelting and reduction is supplied by electrical energy through the electrodes. Manganese ores and sinters are the main Mn sources. In SiMn production HCFMn slag is in addition used as Mn source and quartz is the main Si-source. Fluxes as dolomite and limestone are added to adjust the properties of the final slag. Several carbon sources are used as reductants, coke is the most common and the major source used in Norway. HCFMn is produced at temperatures around 1400 -1500°C while the temperature is around 1600 – 1650°C in SiMn production. The process and reactions are described in detail by Olsen et al [2].

During production of manganese alloys, the submerged arc furnace can be divided into two main reaction zones [Ошибка! Закладка не определена.] as illustrated in Figure 1. Their existences have been confirmed by excavation of industrial furnace [3]. In the upper part of the furnace, in the prerelution zone, the raw materials are solid and MnO₂, Mn₃O₄ and Mn₂O₃ are reduced to MnO by ascending CO-gas. In the lower part of the furnace, in the coke bed, slag and metal are liquid and the final reduction of MnO to Mn and in silicomanganese production, SiO₂ to Si, takes place by reaction (1)–(3).

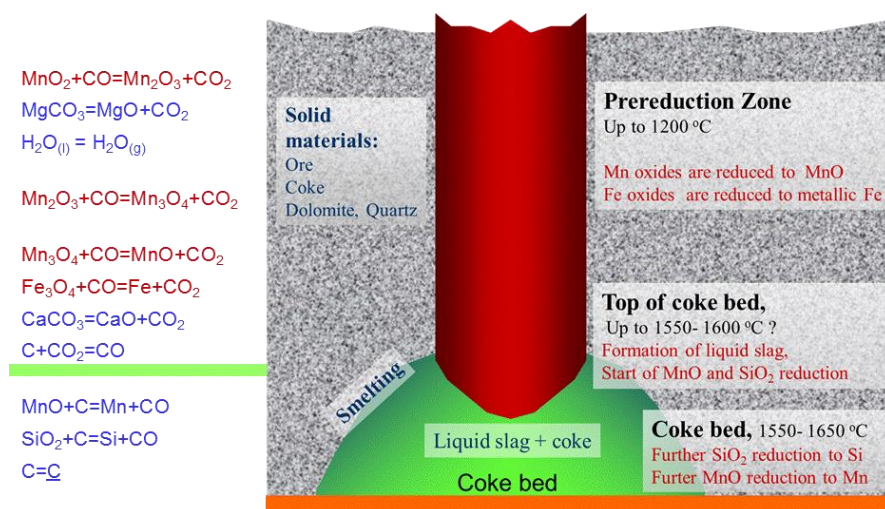


Figure 1: Main reactions in SAF for SiMn production (based on drawing from Tangstad [Ошибка! Залкада не определена.])



Pilot experiments [4], [5], [6] have shown that most of the reduction takes place at the top of the coke bed. Knowledge about the conditions in this zone is therefore important when production of manganese alloys is discussed. Several aspects of melting and reduction at the top of the coke bed have been studied at Sintef and NTNU the last years and reported in various publications. The newest results are in the PhD work by Brynjulfen [7]. The current paper will sum up and discuss the results from earlier investigations with main focus on the work by Brynjulfen. The aim is to describe conditions at the top of the coke bed, how this is affected by various raw materials and to discuss their implications on the final reduction to Mn alloys.

2. EXPERIMENTS AND METHODS

Results from several different works which have mostly been published earlier will be presented. Details about the experimental methods can be found in the cited papers. The methods used by Brynjulfen [Ошибка! Залкада не определена.] are described briefly below. These are: determination of melting properties by sessile drop apparatus, bulk melting experiments in induction furnace and investigation of reaction mechanisms in pilot scale furnace.

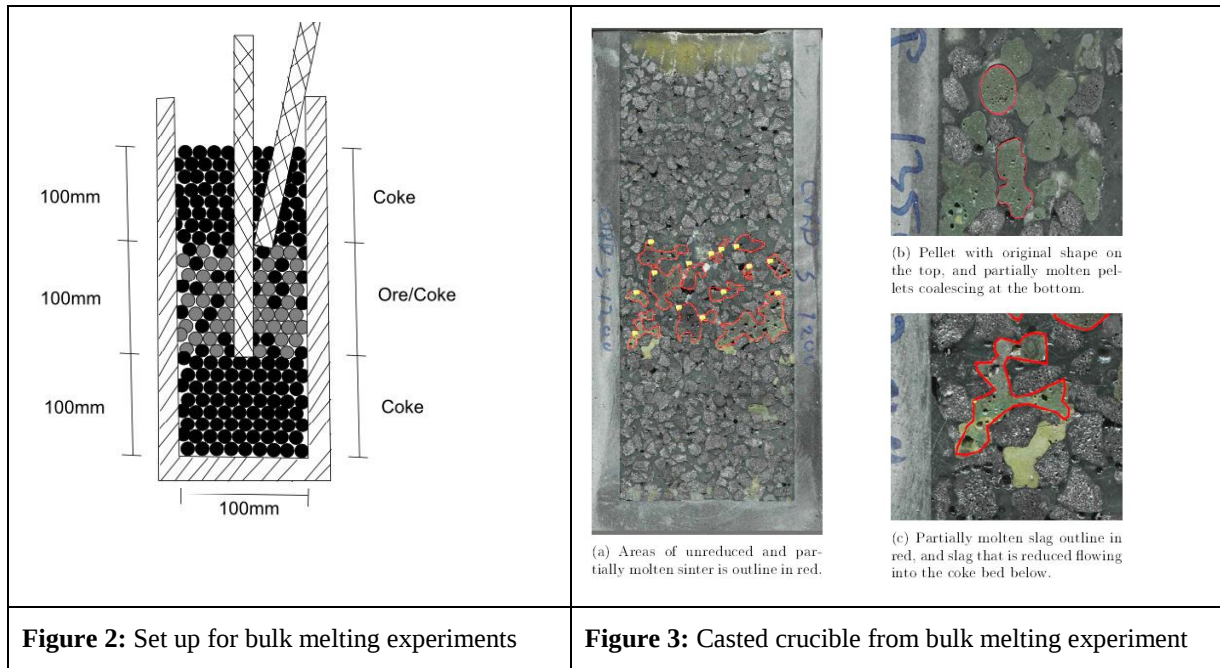
4.1 Sessile drop experiments

When melting properties are measured in the sessile drop apparatus, a 10-50 mg ore sample placed on a graphite substrate is heated in CO-atmosphere. In this case it was heated to 1100 °C and held at this temperature for 30 minutes to complete pre-reduction, then heated further 5 °C/ min until complete melting. Changes of sample shape is recorded by video and coupled to measured temperatures. The melting properties are determined by visual analysis of the recorded data:

- Start of melting - when the shape of the particle has lost the sharp edges
- Final melting - when the droplet is round, with no artefacts

4.2 Bulk softening and melting

When melting properties are measured by bulk softening and melting, a 500g sample consisting of 10-15mm ore particles mixed with coke is placed on the top of a coke bed in a graphite crucible. The set up shown in Figure 2 is used. The crucible was heated to 1200 °C and held at this temperature for 30 minutes to complete pre-reduction, then heated around 20 °/min to the designated temperature and then cooled down. The cold crucible was filled with epoxy and a cross section cut through the centre. Amount of unreduced, softened and reduced ore in the coke bed was determined by area analysis as illustrated in Figure 3. A series of experiments were stopped at different temperatures to determine the change in melting and reduction with increasing temperature.



4.3 Pilot experiments

The pilot scale experiments were run in a 400 kVA furnace at SINTEF /NTNU with a top and bottom electrode. The setup is shown in Figure 4. The lining was designed with respect to an excavation technique where it is possible to make cast cross sections of the furnace. Two experiments for production of HCFeMn were run, one experiment with 100 % Gabonese sinter as Mn- source and one where the Mn-source was a mixture of 50 % Gabonese sinter and 50 % Gabonese ore. In both experiments limestone was added to obtain a basicity of 0.7. The experiments were run for 8 hours at a power of 150 kW and 8 tappings. After the experiment, the furnace was cooled down, filled with epoxy and a cross section was cut through the centre of the furnace. Samples were taken out from the cross section and investigated by EPMA. Composition of tapped slag and metal was determined by chemical analysis.

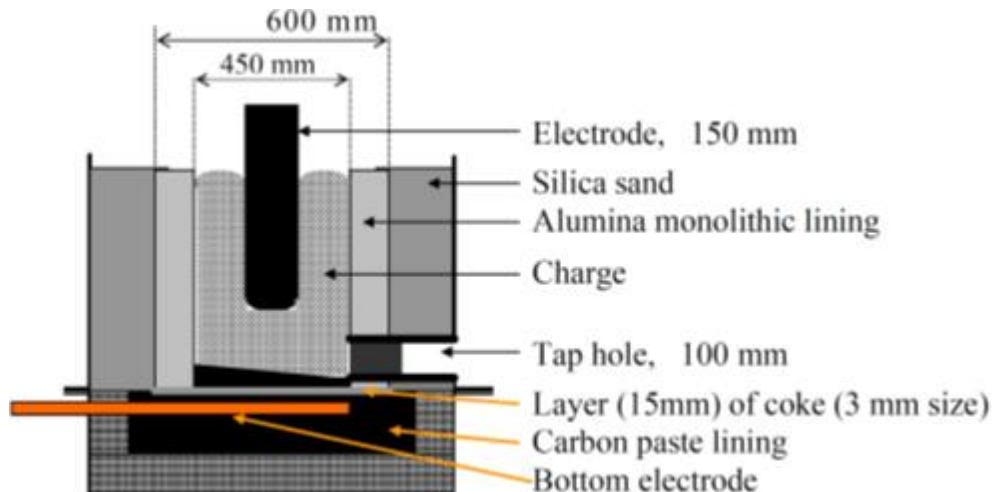


Figure 4: Set up for pilot furnace.

3. MELTING AND REDUCTION OF Mn SOURCES

3.1 Conditions at the top of the coke bed

The coke bed consists of solid coke mixed with liquid metal and slag. Heat is generated by ohmic resistance in solid coke, and most of the electrical energy supplied to the furnace is consumed in this zone. At the top of the coke bed initial slag is formed by melting and reduction of the Mn-sources and dissolution of the fluxes. When their viscosity is low enough, the materials will drain into the coke bed. Furnace excavations [Ошибка! Закладка не определена.] and pilot exper-

iments [Ошибка! Закладка не определена., Ошибка! Закладка не определена., Ошибка! Закладка не определена.] have shown that most of the reduction takes place at the top of the coke bed. Conditions here as temperature, compositions of liquid phases and rate for dissolution of solid phases affects the degree of reduction at the top of the coke bed and the composition of the phases in the coke bed.

The temperature at the top of the coke bed is believed to be determined by the temperature needed for the slag to drain into the coke bed. This has not yet been shown experimentally. In pilot experiments with HCFMn production [Ошибка! Закладка не определена.] temperatures around 1100–1200°C were measured just above the coke bed and around 1500–1600°C inside the coke bed just below the top, varying with the type of raw materials used. The measurements have low accuracy, but confirm the large temperature gradient at the top of the coke bed indicated by the large MnO reduction observed industrially and in pilot experiments.

The temperature required to obtain a slag with low enough viscosity to drain down in the coke bed, depends on the viscosity of the liquid phase and its amount of solids. The solid particles can either be solids in equilibrium with the liquid phase or solid particles that due to kinetics have not dissolved in the liquid phase. Experiments in sessile drop furnace [8] have shown that metal will drain down in the coke bed independent of the slag and therefore not affect the conditions in this zone. Reduction of MnO to alloy will reduce the total MnO content in the slag and amount of solid MnO-containing phases in equilibrium with the slag. This is illustrated in Figure 5 showing reduction path, A-B, under equilibrium conditions for a charge mixture with composition A. Until liquidus is reached, the slag is a mixture of solid MnO particles dispersed in the liquid phase as shown in the micrograph. The slag will drain down in the coke bed when the amount of solids is sufficiently low given that the liquid phase has low enough viscosity. The temperature where this is achieved is determined by the composition of the charge mixture. At equilibrium, the temperature at the top of the coke bed is therefore determined by the composition of the charge mixture. If equilibrium is not reached, the temperature will be higher.

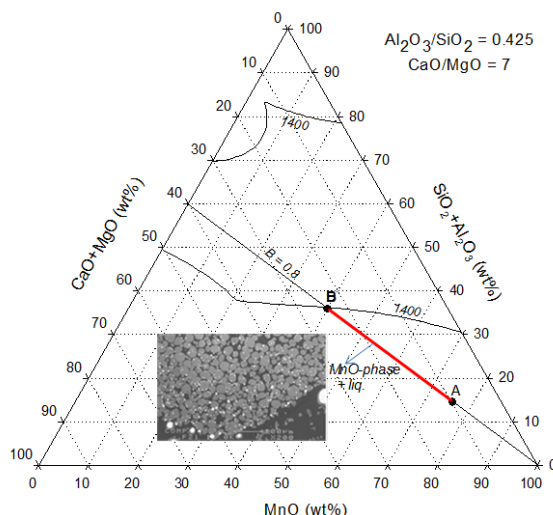
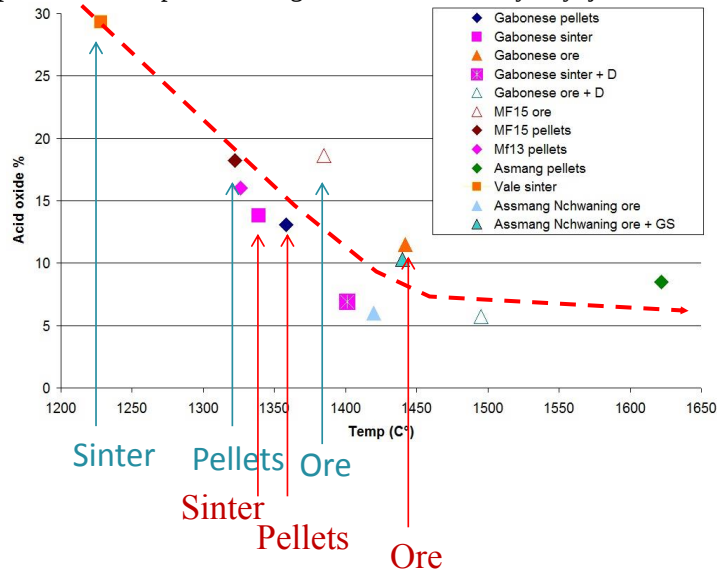


Figure 5: Reduction path under equilibrium conditions for MnO slag with micrograph showing the mixture of solid and liquid phases along line A-B

A higher temperature at the top of the coke bed than given by the liquidus temperature of the charge mixture can be caused by slow dissolution of fluxes in the slag phase. Another probable cause is that the solid phases in the ore are not equilibrated during heating and that a higher temperature than liquidus is required to form the first liquid phase. Too slow dissolution of solid MnO in the liquid slag to obtain equilibrium ratio between the two phases will also give a higher temperature for drainage of the slag into the coke bed.

In a comparison [9] of liquidus temperatures for typical charge mixtures and measured temperature for complete melting of the ores, the liquidus temperature for the charge mixture were lower than the melting temperature of the ores. Melting properties and especially the temperature of incipient melting of the ores, are assumed to be of importance for the conditions at the top of the coke bed. Melting properties of various types of manganese ores have been measured by different methods. Since melting and reduction takes place simultaneously, both properties are included in the measurements.

Temperature of incipient melting of ores measured by Brynjulfson [Ошибка! Залкадка не определена.] was,



as shown in

Figure 6, found to increase with decreasing amount of acidic oxides. This effect of acidic oxides can result from a higher amount of liquid phase present at low temperature in more acidic ores as illustrated in Figure 7 and Figure 8.

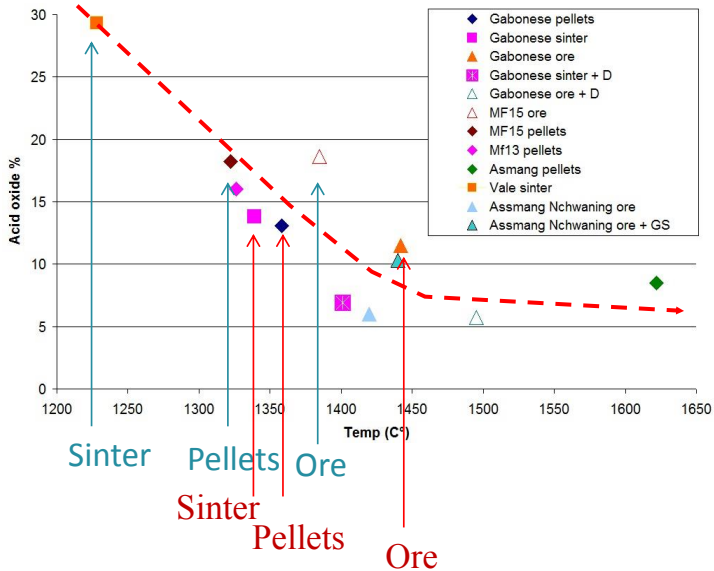


Figure 6: Temperature for initial melting as a function of % of acidic oxides in different ores

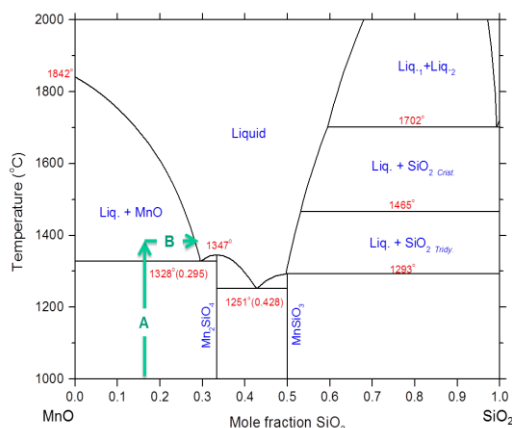


Figure 7: MnO-SiO₂ phase diagram.

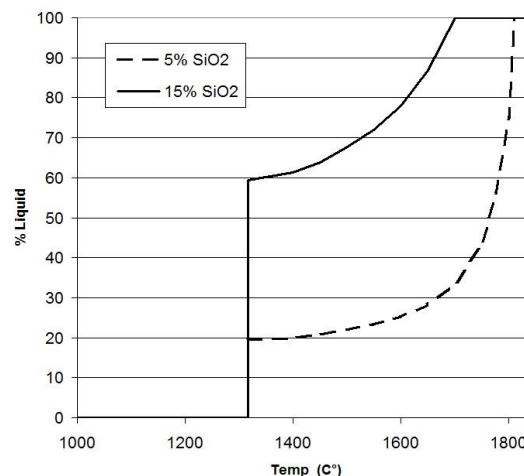
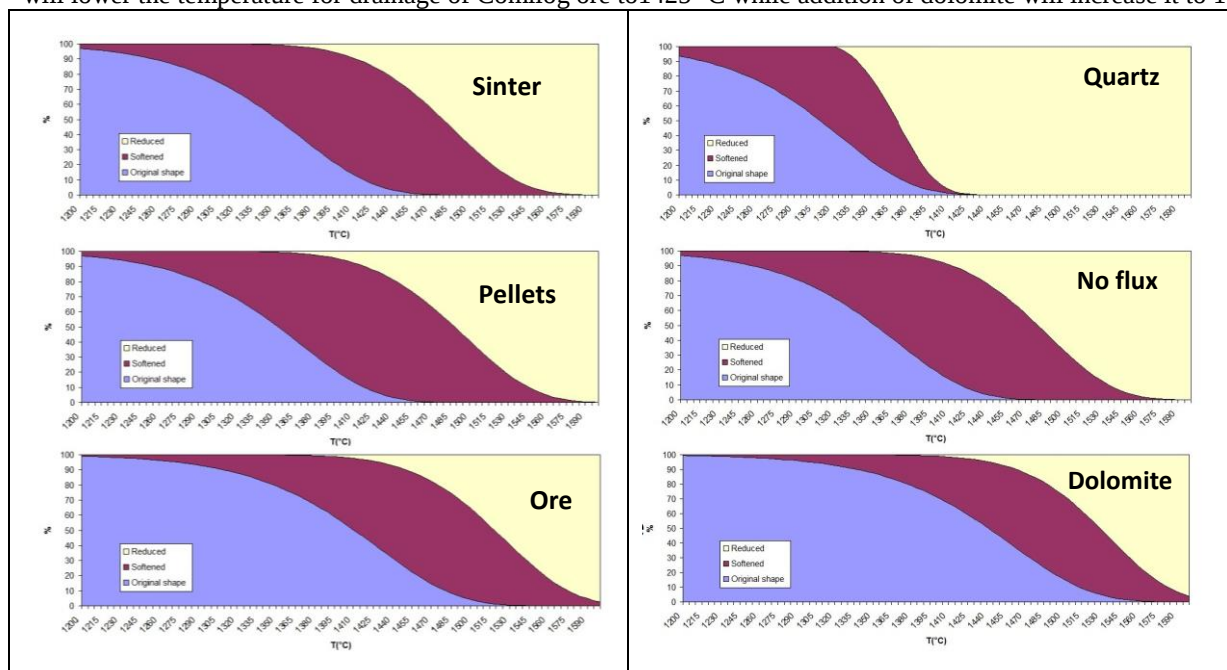


Figure 8: % Liquid formed as a function of temperature for different SiO₂ contents in a MnO-SiO₂ system.

Addition of dolomite increased the melting temperature while it decreased when quartz was added. The experiments also showed that heat-treated agglomerates started to melt at lower temperatures than the raw ores with the same chemical composition. During the heat treatment low melting phases as tephroite (Mn_2SiO_4) and galaxite (MnAl_2O_3) had formed and the temperature for initial melting was lowered. The difference in melting temperature for the ores with same chemical composition shows that initial melting does not take place under equilibrium. The temperature for initial melting can then not be calculated from the chemical composition of the ore. It is affected by the phases present in the solid ore as well as the size of the individual phases.

MnO is reduced from the liquid phase simultaneously with further melting and dissolution of solid particles in the liquid slag. Reduction during melting was investigated in bulk smelting experiments simulating the conditions at the top of the coke bed [Ошибка! Закладка не определена.]. Relative amounts of unreduced ore, softened ore and reduced ore at different temperatures are compared in Figure 9A for Comilog ore, Comilog pellets and Comilog sinter. In Figure 9B the Comilog ore without fluxes and with quartz and with dolomite is compared. The lower initial melting temperatures for heat-treated ores found in the sessile drop experiments were confirmed by bulk melting tests. The temperature needed to reduce all the ore shown by the yellow area in Figure 9, vary between the different cases. At the temperature where MnO is reduced below a certain amount the slag will drain into the coke bed and this is assumed to be the temperature at the top of the coke bed. Level of MnO reduction needed for drainage is not clear: If it is assumed that the limit is $\text{MnO} < 10\%$ the following temperatures can be found. While Comilog ore will drain into the coke bed at around 1580°C, heat-treated ores as sinter and pellets will drain into the coke bed at around 1550°C. Addition of quartz will lower the temperature for drainage of Comilog ore to 1425 °C while addition of dolomite will increase it to 1600°C.



A: Comilog sinter, pellets and ore	B Comilog ore without fluxes and with quartz and with dolomite
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Figure 9: Amount of unreduced, softened and reduced ore at different temperatures for Comilog ore, sinter and pellets (A) and for Comilog ore with no fluxes, addition of quartz and addition of dolomite (B)

The cases with lowest softening temperatures for the ores had also the lowest reduction temperature, but the differences between the cases were larger for softening temperature than for reduction temperature. Based on the bulk smelting experiments, the degree of reduction at different temperatures was calculated and modelled. The temperature for 50% reduction of the ores found in bulk smelting experiments is in Figure 10 compared to temperature for initial melting measured with sessile drop. Ores that start to melt at lower temperatures are reduced and drain into the coke bed at lower temperature. It was also found that ores that melt at a low temperature will have a higher reduction rate than ores that melt at a higher temperature.

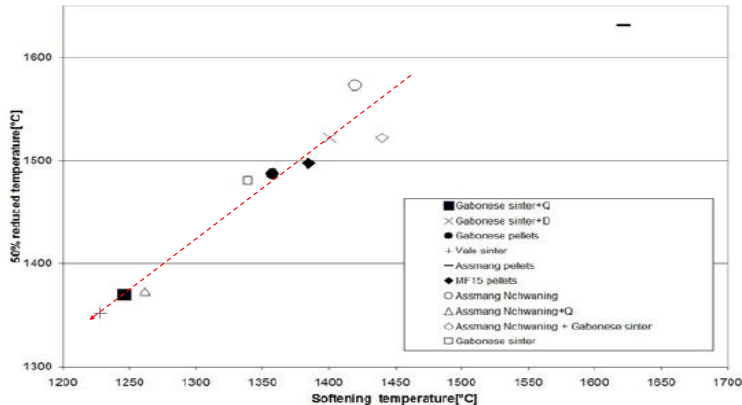


Figure 10: Temperature for 50% of reduction measured by bulk melting experiments as a function of softening temperature measured by sessile drop

Industrially, it has been shown that the slag is tapped close to the liquidus composition as illustrated in the case in Figure 5. A higher temperature is required if either the dissolution of the solid phase in the liquid slag or reduction from the liquid slag is slow. The solid phase in equilibrium with the liquid can in addition to MnO be Mn_2SiO_4 , MnAl_2O_4 or other [Ошибка! Закладка не определена.] depending on the composition of the ore. Dissolution rate for the solid is expected to be affected by the phase. Analysis of industrial data and thermodynamic calculations by Ostrovski [10] showed that in HCFMn production the solid phase was close to equilibrium with the liquid phase while the liquid slag phase and alloy were not in equilibrium. If this reduction is the slowest step, the reduction rate and the temperature for reduction of the ores will be determined by the rate for reduction of MnO from the liquid slag. The current investigations indicate that initial melting of the ores is slower. The correlation between reduction temperature and temperature for initial melting indicate that formation of a liquid phase and not the reduction of MnO from the liquid phase is rate determining step. The difference between ore pellets and sinter indicates that this is not a result of the chemical composition of the ore, but the phases are present.

The decrease in melting temperature with quartz addition and the increase with dolomite addition show that although the temperature for initial melting is mainly a result of change in composition it is also affected by the solid phases that are present. Reactions in solid state between flux and ore can have formed new phases that affect the melting conditions. Dissolution of the fluxes in the first liquid that is formed and changes in the melting temperature due to this is another and may be more probable explanation. The decrease in melting temperature by addition of quartz then indicate formation of a liquid phase in amounts too low to be detected by the experimental method at temperatures lower than reported for initial melting in the experiments. Temperature for initial melting and reduction temperature are correlated when fluxes are added similarly as for ores. So also when fluxes are added, formation of liquid phase seems to be the step determining the temperature for melting and reduction. In SiMn production where quartz is added slag and alloy are according to Ostrovski [Ошибка! Закладка не определена.] contrary to in HCFMn production close to equilibrium.

The above analysis of published results showed that the temperature where solids in an mixture of solid and liquidus reduced so the slag will drain into the coke bed, vary with the temperature for initial smelting of the ore. It is mainly a result of the liquidus temperature of the mixture. But the temperature will have some deviation from this and, it will increase with decreasing amount of acid oxides in the ore. Addition of quartz to the charge mixture will decrease the temperature while it is increased by addition of dolomite.

3.2 Effect on furnace performance of melting and reduction properties

The top of the coke bed is defined as the interface between coke mixed with solid ore and coke mixed with a liquid phase. The temperature at the top of the coke bed is therefore assumed. The temperature in the bulk coke bed is determined by the energy density in the coke bed, e.g. the size of the coke bed and the energy input. The temperature in the coke bed will hence be the same or higher than the temperature at the top of the coke bed. Most of the reduction takes place at the top of the coke bed, and the temperature here is therefore crucial for furnace performance and products.

HCFeMn slag has traditionally been assumed to be tapped at liquidus temperature [Ошибка! Закладка не определена.] with %MnO given by liquidus composition. Pilot experiments by Brynjulfesen [Ошибка! Закладка не определена.] comparing HCFeMn production from Comilog ore and from Comilog sinter showed that with use of low melting raw materials as sinter, the slag will not necessarily be tapped at liquidus composition. With the use of Comilog ore, the temperature at the top of the coke bed was high enough for CaO to dissolve and a basicity of 0.65 was obtained in the slag. It was then reduced to a liquidus MnO content of 33 % and the tapped slag had this MnO content. When Comilog sinter with the lower melting temperature was used, the temperature at the top of the coke bed was too low to dissolve CaO, the liquidus MnO content was 55% and slag with this MnO content drained into the coke bed. The slag dissolved CaO while draining into the coke bed and a basicity of 0.65 was reached in the tapped slag. But while draining through the coke bed MnO in the slag was not reduced to the new liquidus composition. When low melting raw materials were used, MnO content in the slag was 40%. The reduction path is illustrated in Figure 11.

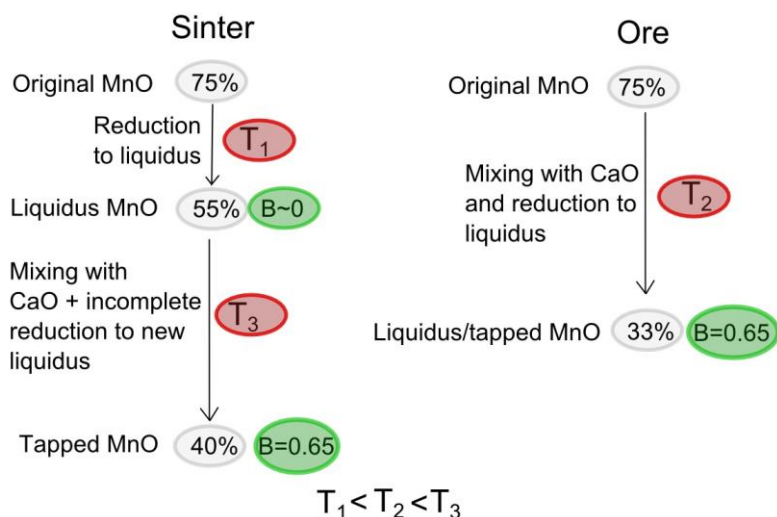


Figure 11: Reduction of low melting sinter compared to ore.

In SiMn production, SiO_2 must be reduced to Si and a higher temperature is required. In the experiments by Brynjulfesen, quartz dissolved easily in the initial slag. Analysis by Ostrovski [Ошибка! Закладка не определена.] showed that equilibrium between slag and alloy was achieved while the slag was not in equilibrium with quartz and Maroufi showed that mass transfer in the slag was rate determining [11]. A higher temperature at the top of the coke bed is in both cases assumed to be beneficial to allow more of the SiO_2 reduction to take place here. This hypothesis still needs to be verified.

The discussion in paragraph 3.1 showed that use of raw materials with higher temperature for initial melting will give a higher temperature at the top of the coke bed. This effect has been seen industrially in HCFeCr production as a correlation between melting properties of ores and Si-content in alloy [12]. Ores with a low content of acid oxides have high melting temperatures and would from this be expected to have an advantage in SiMn production. Heat treatment of the ores as sintering and pelletising lowers the melting temperatures and is expected to give a disadvantage. Addition of quartz that is needed in SiMn production will lower the melting temperature and reduce some of the advantage of the basic ores. Experimental studies of the effect of various ores and ore properties is needed to clarify their effect on the temperature on the top of the coke bed and how this will affect SiMn production.

3.3 Melting properties of raw materials for Mn-alloy productions

Melting properties of industrial Mn-sources can, based on the discussion above, affect furnace performance and product quality in the production of Mn-alloys, especially SiMn production. Temperature for initial melting is one of the most important parameters. Melting properties have been measured at Sintef and NTNU for several industrial Mn sources. [Ошибка! Закладка не определена., Ошибка! Закладка не определена., 13, 14]. Some of the published results are presented in Table 1 to Table 4 to give an overview over melting properties than can be expected for the dif-

ferent ores. Results from the different investigations are presented in separate tables since there might be small differences in measurement procedure between the different measurement campaigns. The reported temperatures for initial melting vary from 1220°C to 1622°C. The melting properties are presented to indicate the differences that can be expected in industrial manganese sources. The background for the observed differences between these sources is thus not further discussed here.

Table 1 Melting temperatures for Mn sources measured by sessile drop [Ошибка! Закладка не определена.]

Material	Initial melting °C	Complete melting °C
Assmang ore	1450	1510
Comilog ore	1490	1540
CVRD sinter	1350	1410
HCFEMn slag	1220	1230

Table 3 Melting temperatures for Mn sources measured by sessile drop [Ошибка! Закладка не определена.]

	Initial melting °C	Complete melting °C
Nchwaneng A	1478	1600
Nchwaneng B	1519	1628
Nchwaneng C	1521	1550
Nchwaneng D	1450	1560
Gloria A	1588	1702
Gloria B	1512	1674

Table 2 Melting temperatures for Mn sources measured by sessile drop [Ошибка! Закладка не определена.]

Material	Initial melt-ing °C	Complete melting °C
Assmang ore	1446±70	1513±57
Gabonese ore	1485±11	1538±9
CVRD ore	1461±13	1494±23
CVRD sinter	1395±85	1489±132

Table 4 Melting temperatures for Mn sources measured by sessile drop [Ошибка! Закладка не определена.]

	Initial melt-ing °C	Complete melting °C
Gabonese ore	1442	1531
Gabonese sinter	1339	1498
Gabonese pellets	1358	1516
CVRD ore MF15	1385	1505
CVRD pellets MF15	1322	1421
CVRD sinter	1228	1305
Assmang Nchwaneng ore	1420	1624
Assmang Gloria pellets	1622	1683

4. CONCLUSIONS

When Mn alloys are produced in SAF, most of the reduction takes place at the top of the coke bed. The temperature in this zone is determined by the temperature where the slag has viscosity low enough to drain into the coke bed. When no flux is added, this temperature has been found to depend on the temperature for initial melting of the Mn sources. Addition of quartz will decrease the temperature for initial melting while it will increase when dolomite is added.

Temperature for initial melting of Mn-sources is not only determined from their composition as the liquidus temperature for the mixture. Heat-treated ores have lower melting temperatures than the ore they are made from. The temperature for initial melting will decrease with increasing amount of acidic oxides in the ore. For industrially used Mn-sources, the temperature varies from below 1250°C to above 1600°C. Materials that melt at a low temperature will have a higher reduction rate and obtain high enough reduction to drain into the coke bed at a lower temperature than materials with a higher temperature for initial melting. Melting and reduction properties were determined by two different methods that were correlated.

Dolomite and limestone will not dissolve in the slag at the top of the coke bed if the temperature is too low. This will give a low basicity and high MnO content in the slag at the top of the coke bed. This led in pilot experiments to higher MnO content in the tapped slag. In two pilot experiments comparing HCFEMn production from ore with sinter made from the same ore, use of sinter gave a higher MnO content in the tapped slag.

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