# Phase Relations in Ferromanganese Slags during Melting and Reduction

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## ABSTRACT

Melting and reduction of various manganese ores have been studied in a laboratory scale graphite tube furnace. Charge mixtures were heated in reducing atmosphere to temperatures from 1200°C to 1500°C. After completed runs, the solidified slags were studied in an Electron Probe Micro Analyzer. The manganese ores will go through stages as sintering and softening before reaching the incipient reduction temperature which is about 1335°C for BHP ore. At this temperature the various original phases in the ore are transformed into a liquid phase and a solid MnO phase. The MnO phase, being present as clouds of solid spheres in the liquid, defines the chemical activity of MnO and influences physical properties like the viscosity of the mixture. The amount of solid MnO phase decreases as the reduction proceeds until the liquidus composition is reached. With a lime basicity of about 1 and $Al_2O_3/SiO_2$ ratios of 0.6 and 1.4 (BHP ore and Comilog ore respectively), the solid phase will be present down to 30-40% MnO. Any MgO in the mixture dissolves preferably in the solid MnO phase where its content increases almost linearly with increasing reduction. The MnO content in the liquid phase will at the same time decrease slightly with increasing degree of reduction.

## INTRODUCTION

High carbon ferromanganese is produced in electric submerged arc furnaces. The raw materials are blends of manganese ores and fluxes and carbonaceous reducing agents. Typical fluxes are quartzite, limestone and dolomitic limestone. The upper part of the submerged arc furnace is a prereduction zone where the materials are solid. Here the higher oxides of manganese are reduced to MnO by the CO gas formed in the lower part of the furnace. As the charge reaches the high temperature zone, the ore will melt down and reduction to Mn metal takes place. This zone has a stoichiometric surplus of carbon and is called the coke bed zone. The reactions taking place in the different zones of the furnace have been discussed earlier by Tangstad et al (1995). The slag and alloy produced may be tapped simultaneously from the same tap hole or separately from different slag and metal tapholes.

The characteristics of the charge materials are of main importance for the reactions taking place in the prereduction zone, which mainly determine the power and carbon consumption, and the reactions in the hearth zone, which determine the stability of operation and the manganese yield. The main reaction in the heart zone is the reduction of MnO in the liquid slag with coke:

$$MnO_{slag} + C_{coke} = Mn_{metal} + CO_{gas}$$

Previously Olsen et al. (1995) investigated the equilibrium relations in the production of manganese alloys, and Skjervheim et al. (1995) the kinetics of MnO reduction in slags with less than 45% MnO. The aim of the present investigation have been to elucidate the mechanism of slag formation and to study phase relations during reduction of various manganese ores.

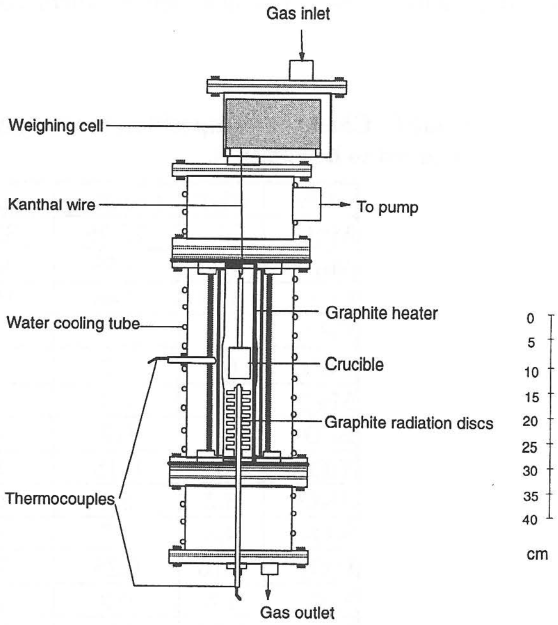


**Figure 1. The graphite tube furnace with thermobalance.**

## EXPERIMENTAL

A carbon crucible was charged with ore, flux and coke. The chemical composition of the materials used is shown in Table I. The crucible with the sample was heated in a graphite tube furnace, which was flushed with CO gas during the experiment. The furnace is shown in Figure 1.

Melting and reduction experiments were carried out. Slag formation was studied in the melting experiments where the charge mixture was heated at an average heating rate of 200°C/hour to temperatures between 1200 and 1400°C. In the reduction experiments the charge was heated as fast as possible, which was from room temperature to the maximum temperature in about 12 minutes. The temperature range investigated was 1350-1500°C. The weight loss of the sample was continuously recorded by a thermobalance, and the degree of reduction was controlled by the holding time at max. temperature. About 15 melting and 80 reduction experiments were performed. After completed runs the samples of slag and metal were analysed by an Electron Probe Micro Analyzer (EPMA). Uncrystalline, glassy slags and homogeneous metal were analyzed with a single beam method which is the most accurate. Fine crystalline areas were analyzed by the area method. In coarse crystalline areas, the composition and area fraction of each phase was determined. It was assumed that the area fraction equals the volume fraction, and the total composition was calculated. The area fraction was determined by the EPMA or in an optical microscope. Three to six area fractions were measured for every sample. The average value was used for further calculation.

The degree of reduction, expressed as the remaining content of MnO (in solid + liquid phase), was calculated based on material analyses and weight loss measured by the thermobalance.

## RESULTS AND DISCUSSION

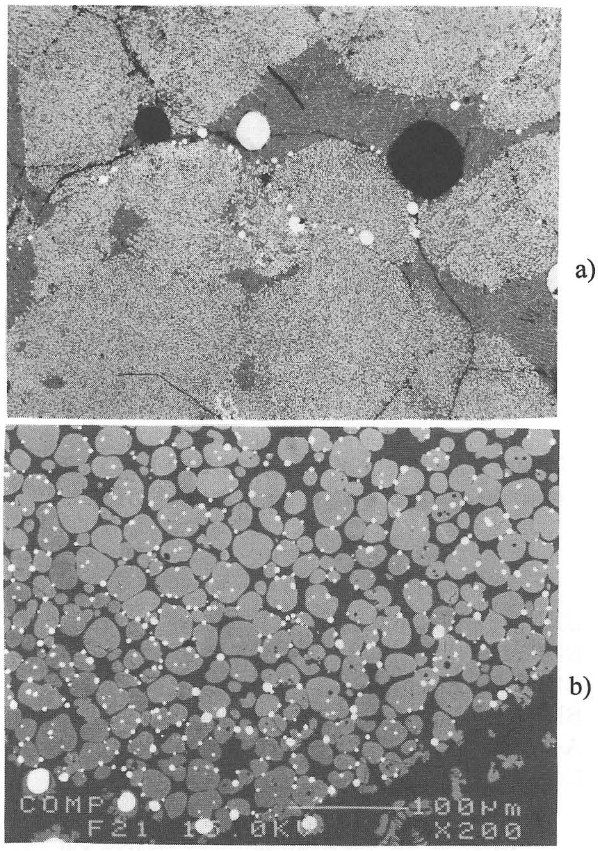
### Slag formation of BHP ore

Prereduction of higher manganese oxides and iron oxides takes place in solid state as BHP ore is heated in reducing atmosphere. The iron content is reduced to metallic, and the higher manganese oxides are completely reduced to MnO. The prereduced ore contains a variety of phases. Large grains of MnO phase and smaller grains of $SiO_2$ are embedded in a matrix containing a variety of different phases.

The ore particles will go through different stages during further heating. These stages are sintering, softening and slag formation, Tangstad (1996). Sintering starts around 1200°C and softening takes place from 1270°C. The temperature of slag formation is around 1335°C where the ore is transformed into a liquid in coexistence with manganosite (MnO). A typical solidified slag sample is shown in Micrograph 1. The white areas are metal prills and the black area pores. The solidified slag can be divided into two areas, one area

**Table I. Chemical composition of manganese ores and flux agents used. The deviation from 100% is assumed to be volatiles.**

| wt.% | BHP | Comilog | Asman48 | Dolomite | Magnesite | Limestone |
|---|---|---|---|---|---|---|
| **$MnO_2$** | 76.3 | 75.26 | 33.67 | | | |
| **MnO** | 4.24 | 3.55 | 38.57 | 0.05 | 0.19 | 0.18 |
| **$Fe_2O_3$** | 3.95 | 4.46 | 15.03 | | | |
| **FeO** | | | | 0.25 | 1 | 0.13 |
| **CaO** | 0.2 | 0.2 | 4 | 34.31 | 1.54 | 53.62 |
| **MgO** | 0.4 | 0.3 | 0.8 | 16.75 | 84.62 | 0.04 |
| **BaO** | 1.1 | 0.2 | 0.3 | 0.01 | 0.01 | 0.01 |
| **$TiO_2$** | 0.16 | 0.15 | 0.05 | 0.07 | 0.07 | 0.05 |
| **$Al_2O_3$** | 3.2 | 5.2 | 0.2 | 0.29 | 0.78 | 0.24 |
| **$SiO_2$** | 4.8 | 3.7 | 5.3 | 1.71 | 2.95 | 6.01 |
| **$P_2O_5$** | 0.16 | 0.25 | 0.02 | 0.01 | 0.05 | 0.01 |
| **$K_2O$** | 1.8 | 0.8 | 0.1 | 0.04 | 0.04 | 0.03 |
| **Zn** | 0.02 | 0.04 | 0.01 | 0 | 0.01 | |
| **Pb** | 0.01 | 0.01 | 0.01 | 0.02 | 0.03 | 0.03 |
| **Sum** | 96.34 | 94.12 | 98.06 | 53.51 | 91.29 | 60.35 |



**Micrograph 1. Solidified slag sample from BHP ore at a) 16 times and b) 200 times magnification (white prills - metal, black area - pores, grey spheres and dendrites - MnO phase, dark grey phase - slag phase).**

with spherical MnO particles in a matrix, and next a crystalline area. The crystalline area consists of MnO dendrites in a matrix. The spherical MnO phase has remained solid all the time, whereas the MnO dendrites and other crystals have been precipitated during solidification.

Reduction of MnO will first take place when the slag is sufficiently fluid, that is from around 1335°C when the main liquid phase is formed. As the temperature of incipient reduction is somewhat dependent on the heating rate, it is expected that this temperature will be 1335°C or higher in an industrial furnace.

The BHP ore contains only small amounts of iron. After completed reduction of the iron to metallic, about 90% of the BHP ore consists of MnO, $SiO_2$ and $Al_2O_3$. The MnO content is above 76%. As the ore is further heated in reducing atmosphere, it will change into solid MnO particles and a liquid phase according to the MnO-$SiO_2$-$Al_2O_3$ phase diagram presented by Muan and Osborne (1966), Figure 2. The overall composition of the prereduced BHP ore is indicated by the letter **X**. At 1400°C the liquid phase will have a composition as indicated by the letter **A** in the figure. Then, according to the phase diagram, the slag will contain a solid MnO phase and a liquid phase with 64% MnO. As the reduction proceeds, the amount of the solid phase decreases. At a certain degree of reduction the solid MnO phase will be completely consumed. In this ternary system the composition of the liquid is only dependent on the temperature and is not influenced by the degree of reduction as long as the solid phase is present.

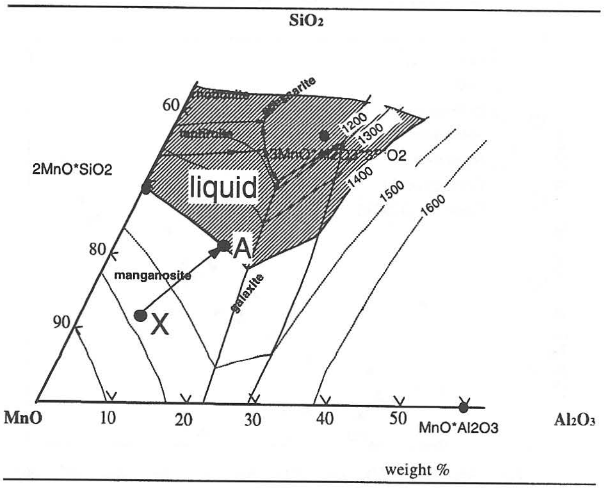


**Figure 2. Part of MnO-$SiO_2$-$Al_2O_3$ phase diagram from Muan and Osborne (1966).**

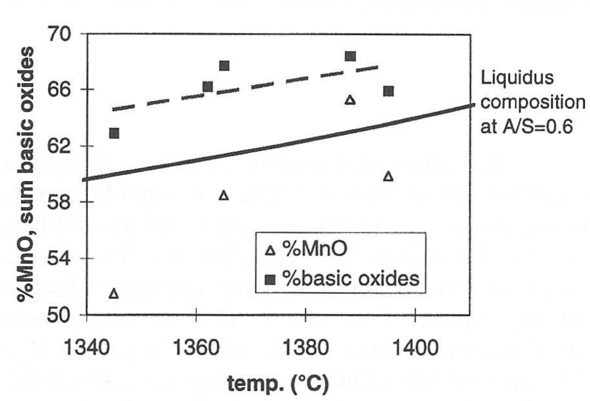


**Figure 3. Liquidus composition versus temperature. Liquidus content of MnO according to phase diagram MnO-$Al_2O_3$-$SiO_2$ (A/S=0.6) (solid line). Liquidus content of Σbasic oxides, BHP ore (broken line).**

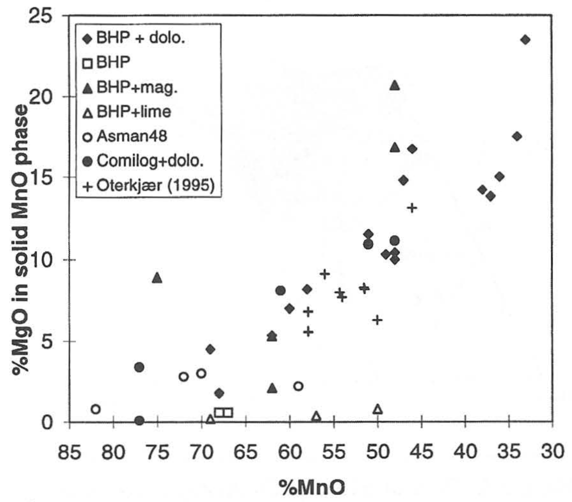


**Figure 4. MgO content (%) in the (Mn,Mg)O solid solution versus the content of remaining unreduced MnO (1350-1500°C).**

The influence of the temperature on the liquidus compositions is estimated from the $MnO\text{-}SiO_2\text{-}Al_2O_3$ phase diagram, and is shown as the solid line in Figure 3. The A/S ratio is 0.6 as in BHP ore. The liquidus composition is expressed by the percentage of MnO in the liquid phase. However, the BHP ore also contains small amounts of basic oxides such as CaO, MgO, $K_2O$. The small amount of these components are estimated to equally substitute MnO, e.g. $1\%K_2O \approx 1\%MnO$, and to influence the liquidus temperature in the same way, leading to a lower content of MnO in the liquid phase. The observed liquidus composition for BHP ore, expressed by the percentage of $\Sigma$(basic oxides), is shown as the broken line in the same Figure 3. The liquidus content of $\Sigma$(basic oxides) is on average 5% higher than the liquidus content of MnO in the ternary system. However, the isotherms in the three component phase diagram are only estimated according to Muan and Osborne (1966), and hence the experimental values may be more correct.

## Reduction Experiment

6 different charge mixtures were chosen for experiments to investigate phase relations during reduction at temperatures between 1350 and 1500°C. Mixtures, with the following A/S ($Al_2O_3/SiO_2$-ratio) and lime basicities (LB=$(CaO+MgO)/SiO_2$) were studied:

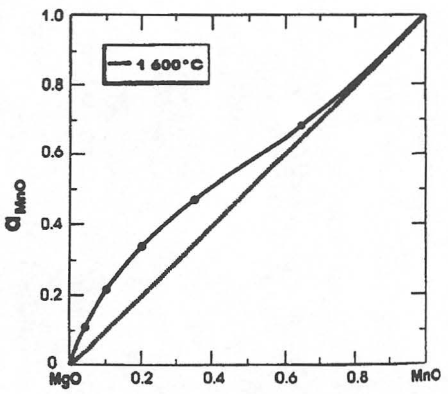


**Figure 5. Activity of MnO in MnO-MgO solid solution at 1600°C (Geldenhuis et al., 1992).**

| | A/S | LB |
|---|---|---|
| BHP ore + dolomite | ≈0.6 | ≈1 |
| BHP ore | ≈0.6 | ≈0.1 |
| BHP ore + magnesite | ≈0.6 | ≈1 |
| BHP ore + limestone | ≈0.6 | ≈1 |
| Asman48 | ≈0.1 | ≈0.9 |
| Comilog + dolomite | ≈1.4 | ≈1 |

Most of the experiments were carried out with BHP ore + dolomite. In most of the investigated systems there are 5 main components: $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaO\text{-}MgO$. Any CaO will mainly dissolve in the liquid phase. The CaO content in the solid MnO phase will be less than 1%. MgO, on the other hand, will preferably dissolve in the solid phase. For charge mixtures with low MgO contents, such as BHP ore, Asman48 and BHP and limestone, the MgO content in the solid phase will of course be low. However, in the other charge mixtures, the MgO content will increase almost linearly in the solid phase with increasing degree of reduction as illustrated in Figure 4. Solid and liquid phases in slag samples from Oterkjær (1995) were also investigated in the EPMA. In these slag samples the lime basicities and $Al_2O_3/SiO_2$ ratios were in the range 0.6-0.9 and 0.3-0.65 respectively. No temperature dependency was proved within the error deviation of the analyses. According to Figure 5 the solution properties of the MnO-MgO system is nearly ideal down to about 65 mole% MnO, or 77 wt.% MnO. Accordingly the activity of MnO in the slag equals the mole fraction of MnO in the solid phase.

When MgO is present in the charge, the liquid phase will change its composition during reduction. This is shown in Figure 6 where the MnO content in the liquid decreases from about 45% down to 32% MnO as the total amount of unreduced decreases from 70 to 32%

MnO. The increase of MgO in the solid phase (Fig.4) and decrease of MnO in the liquid phase (Fig.6) with increasing degree of reduction may be explained in principle by studying the MnO-MgO-$SiO_2$ phase diagram, Figure 7. A charge composition as indicated by the letter X is reduced. As the overall slag composition follows the arrow from point X, the solid solution and the liquid phase will change composition as indicated by the line B and the line A, respectively.

The solid solution phase is completely consumed at a certain degree of reduction, dependent on the composition of the original charge mixture. Table II shows the observed contents of MnO and Σbasic oxides as the solid phase is completely consumed. Roughly it can be said that the basic oxides substitute each other. For a fixed $Al_2O_3/SiO_2$ ratio, as is for example the case for all experiments with BHP ore, the solid phase disappears somewhere between 60 and 68% Σbasic oxides. At higher $Al_2O_3/SiO_2$ ratios, e.g. Comilog ore, it disappears at a lower basicity, and at lower $Al_2O_3/SiO_2$ ratios, e.g. Asman48 ore, at a higher basicity. The liquidus compositions in the five component system, MnO-MgO-CaO-$SiO_2$-$Al_2O_3$, are not known. However, MnO and MgO have a similar chemical effects, and the phase diagram for the system MgO-CaO-$SiO_2$-$Al_2O_3$ can be used to estimate trends in the liquidus compositions. The liquidus temperature decreases considerably when MnO is substituted for MgO in this four component system. The experimental values are therefore compared with the 1900°C liquidus composition in Figure 8.

The liquidus temperature does not change significantly when CaO is substituted for MgO in the four component system MgO-CaO-$SiO_2$-$Al_2O_3$. It is therefore supposed to be a valid assumption that the

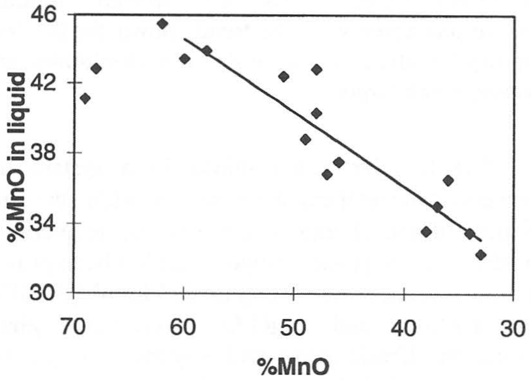


**Figure 6. MnO content (%) in the liquid phase versus the content of remaining unreduced MnO (1350-1500°C). (Mixture: BHP ore and dolomite).**

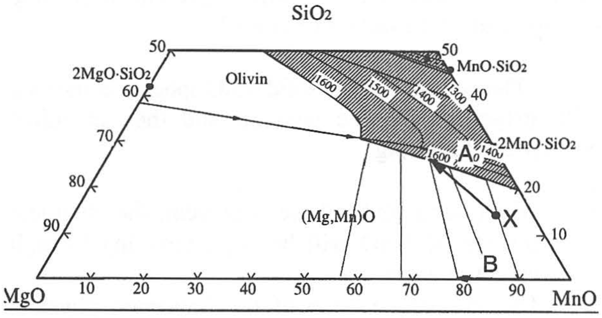


**Figure 7. MgO-MnO-$SiO_2$ phase diagram from Muan and Osborne (1966). Tie lines (dotted lines) from Geldenhuis et al. (1992).**

**Table II. The content of MnO and Σbasic oxides when the solid solution phase is completely consumed.**

| Charge mixture | A/S-ratio | temp. (°C) | %MnO | % total basic oxides |
|---|---|---|---|---|
| **BHP and dolomite** | ≈ 0.6 | 1400 | 33-36 | 63-64 |
| **BHP and dolomite** | ≈ 0.6 | 1450 | <32 | <63 |
| **BHP and dolomite** | ≈ 0.6 | 1500 | 35-36 | 64-65 |
| **BHP** | ≈ 0.6 | 1400 | >60 | >67 |
| **BHP and mag.** | ≈ 0.6 | 1500 | 27<%MnO*<48 | |
| **BHP and lime.** | ≈ 0.6 | 1400 | 33-36 | ≈68 |
| **Asman48** | ≈ 0.1 | 1400 | ≈48 | ≈71 |
| **Asman48** | ≈ 0.1 | 1500 | ≈51 | ≈71 |
| **Comilog and dolo.** | ≈ 1.4 | 1400 | 31<%MnO<40 | 55-58 |
| **Comilog and dolo.** | ≈ 1.4 | 1500 | <42 | <62 |

* Calculated values

basic oxides substitute each other within a certain composition range. The experimental liquidus compositions agree with the trend shown for the four component system in Figure 8. The amplitudes are, however, much larger.

The liquidus compositions in a system are dependent on the temperature. However, within the error deviation of the chemical analyses, no temperature dependency of the phase compositions has been proven in this investigation. According to the $MnO-MgO-SiO_2$, $MnO-CaO-SiO_2$ and $MgO-CaO-SiO_2-Al_2O_3$ phase diagrams, the $\Sigma$basic oxides will only increase by about 3% for every 100°K increase in temperature. This probably explains the apparent lack of temperature dependency observed.

In the production of high carbon ferromanganese a high-MnO-slag practice is often used. For a slag with a lime basicity of about 1, the MnO content is typically between 30 and 40%. When comparing this with data in Table II, it is apparent that the solid solution phase, mainly consisting of MnO, will be present in the slag during most of the reduction period.

The presence of the solid MnO spheres in the slag will influence both the physical and the chemical properties of the slag:

- When solid MnO phase is present, the chemical activity of MnO will be high, resulting in high reduction rates.
- The viscosity is one of the important physical properties which is affected by the presence of solid MnO particles. When solid particles are present in a liquid the viscosity will be high and may be given by the equation given by Brinkman (1952):

$$\mu=\mu_f(1-\epsilon)^{5/2}$$

where $\mu$ is the viscosity of the slag, $\mu_f$ is the viscosity of the liquid and $\epsilon$ is the volumetric fraction of solid MnO phase.

When discussing reaction rates and coke bed relations in a ferromanganese furnace, the influence of the solid MnO spheres on the viscosity and the MnO activity must be considered.

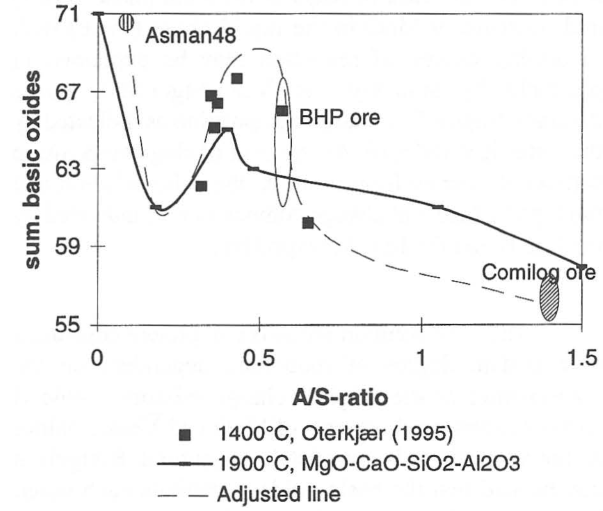


**Figure 8. Experimental liquidus compositions compared with 1900°C liquidus composition in the $MgO-CaO-SiO_2-Al_2O_3$ system.**

## CONCLUSIONS

Small scale experiments in a graphite tube furnace have been carried out to investigate melting and phase relations of BHP ore during heating in reducing atmosphere up to 1400°C. The ore sinters at about 1200°C and is softened at about 1270°C. The incipient reduction temperature of the ore is reached around 1335°C, as the ore is transformed into a liquid in coexistence with solid MnO spheres.

Phase relations during reduction were investigated in experiments with 6 different charge mixtures at temperatures between 1350 and 1500°C. With a lime basicity of about 1 and $Al_2O_3/SiO_2$ ratios 0.6 and 1.4, the solid MnO spheres are present down to overall contents of 30-40 %MnO. For a lower A/S ratio, e.g. about 0.1, the solid MnO spheres will be present down to 50% MnO. This means that the solid MnO spheres are present during most of the reduction period in high-MnO-slag operation practice. MgO in the charge mixture dissolves primarily in the solid MnO phase where the MgO content increases almost linearly with increasing degree of reduction. At the same time the concentration of MnO in the liquid phase decreases slightly with increasing degree of reduction.

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