THE EFFECT OF ALUMINA IN FERROMANGANESE SLAG

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ABSTRACT

The composition of ferromanganese slag is very important as it determines the slag/metal equilibrium relations including MnO content of final slag, melting relations and slag viscosity. The slag composition is further expected to influence the process temperature. The properties of ferromanganese slags are suitably described by its basicity and A/S mass ratios. The influence of slag basicity has been discussed in the previous papers. The present paper will discuss the effect of Al2O3 on melting relations, viscosity and MnO-content of final slag. This discussion will be based on assessed thermochemical databases and a recently developed viscosity model.

1. INTRODUCTION

Alumina is one of the major constituents in ferromanganese slags. It is thermochemically stable in the ferromanganese furnace and goes almost completely to the slag phase. The presence of alumina will mainly influence phase relations and activities of MnO and SiO_2 in the oxide systems and finally affect the smelting process. It is also expected to influence the viscosity of liquid slag. The effect of alumina on equilibrium conditions has been studied previously in the laboratory[1]. The general conclusions based on the experimental observations have later been confirmed by thermodynamic simulations[2].

Olsen[3] has found that industrial high-carbon ferromanganese slags with basicities in the range 0.4-0.8 have compositions very close to the measured liquidus lines[4] . Slag/metal equilibrium seems to be established in industrial furnaces, whereas the slags are far from the slag/metal/gas complete equilibrium compositions. Liquidus temperatures at fixed basicities and Al_2O_3/SiO_2 mass ratios in the MnO-SiO_2-Al_2O_3-CaO-MgO slag system have been measured earlier[4] . However, the experimental data only cover relatively high temperatures (1450-1550°C) and a limited range of compositions.

Viscosity is another important factor influencing the content of MnO in slag phase. When changing from one raw material base to another resulting in higher viscosity of the primary slag, the flow rate of slag into coke bed will initially be hampered. However, the energy input in this area is constant and the temperature of primary slag will increase since less energy is used for melting and reduction. The temperature will increase until the “new slag” has the same viscosity as the previous slag. The viscosity may thus affect the process temperature and the final MnO content in the slag. Little knowledge exists about slag viscosities close to the liquidus boundaries of ferromanganese slags.

The present paper will discuss the effect of Al_2O_3 on slag smelting properties and slag/metal equilibrium relations based on assessed thermodynamic databases[2][6]. A SINTEF database[2] that covers the Mn-Fe-Si-C the metallic system has been employed for the thermodynamic properties of metallic phases. The FACT oxide database[6] has been used to describe the non-ideal behaviour of liquid and solid oxide phases. The equilibrium calculations have been carried out using the commercial software FactSage[5]. The influence of alumina on the viscosity has been evaluated using a recently developed viscosity model[8].

2. THE EFFECT OF ALUMINA ON SLAG SMELTING PROPERTIES

The A/S ratio and the slag basicity have previously been suggested to evaluate the influence of alumina on the thermochemical properties of ferromanganese slags[3][7] . The calculated influence of Al_2O_3 on the liquidus temperatures and compositions in the MnO-rich domain is schematically shown in Figure 1:. MnO occupies one apex in the ternary diagram since MnO is the only oxide to be reduced. The top and left apexes are occupied by SiO_2 and Al_2O_3, respectively, in order to show the effect of A/S ratios on the liquidus lines. The amount of the basic oxides, CaO and MgO, is kept constant. The dash-dotted lines represent slags with fixed A/S ratio. Similar to basicity lines discussed previously[3][7] , the A/S line define "reduction paths" of certain ore mixtures, since only MnO is substantially reduced.

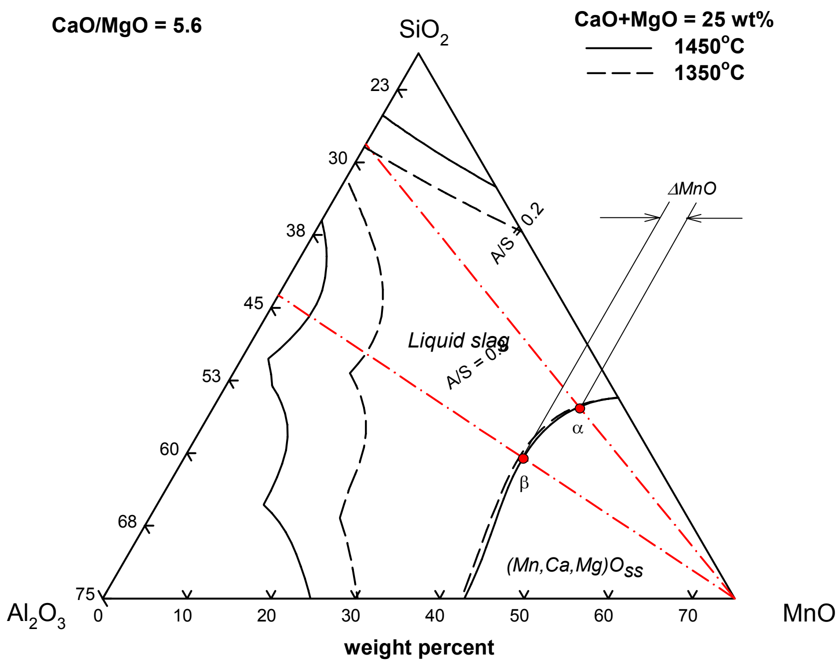

Figure 1: Figure 1:Illustration of the effect of A/S ratio on the liquidus line

The effect of the A/S ratio on the liquidus content of MnO can readily be seen from the diagram by comparing the intersection points between the A/S lines and liquidus boundaries. For example, two different A/S ratio lines intersect the 1450^{o}C liquidus line at α and β, respectively. The difference in A/S ratio has only a slight effect on the liquidus content of MnO. Increasing A/S ratio from α(A/S=0.2) to β(A/S=0.8) results in a reduction ΔMnO of the liquidus content of manganese oxide in the slag. Comparing the two liquidus lines, solid for 1450^{o}C and dashed for 1350^{o}C, shows that the liquidus surface raises steeply in the MnO-rich domain.

Figure 2:(a) and (b) show the effect of the A/S ratio on the liquidus content of MnO provided fixed basicities. Changing the A/S mass ratio from 0.2 to 0.5 reduces the solubility of MnO in liquid slag with about 5 wt%. Further increase in the A/S ratio has practically no influence on the liquidus MnO composition. It is easy to draw the conclusion from Figure 2: that the effect of basicity on the MnO solubility is larger than that of the A/S ratio. A change in the basicity from 0.4 to 0.8 lowers the solubility of MnO in the slag considerably.

Figure 3: demonstrates the effect of slag basicity on the liquidus content of MnO for a fixed A/S ratio 0.5. According to the definition of slag basicity, the sums of acid and basic oxides occupy respectively the top and left apexes in the ternary diagram. The dash-dotted lines represent two oxide mixtures having different basic-

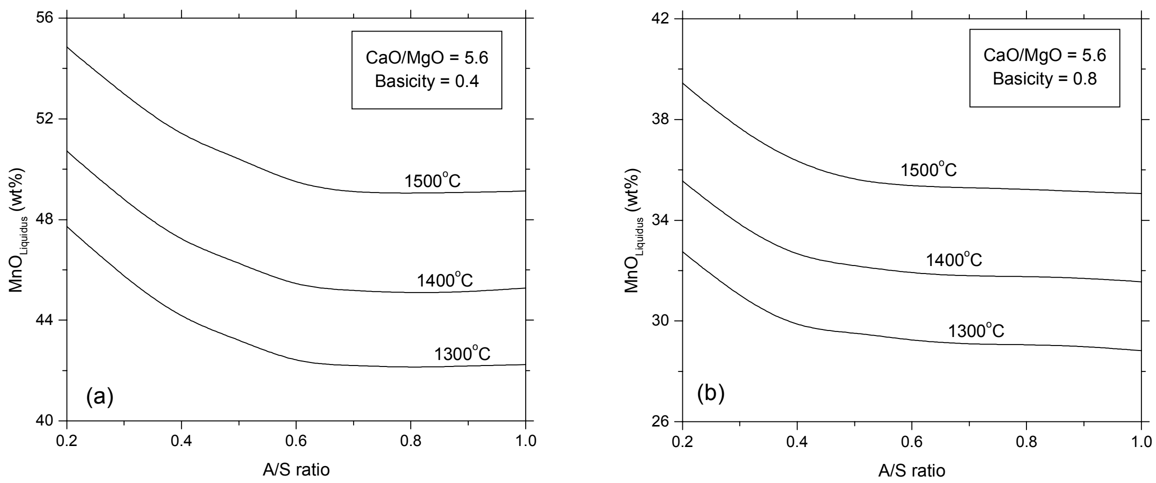

Figure 2: Influence of A/S ratio on the liquidus MnO composition with fixed basicity for the MnO-SiO_2-CaO-MgO-Al_2O_3 slag

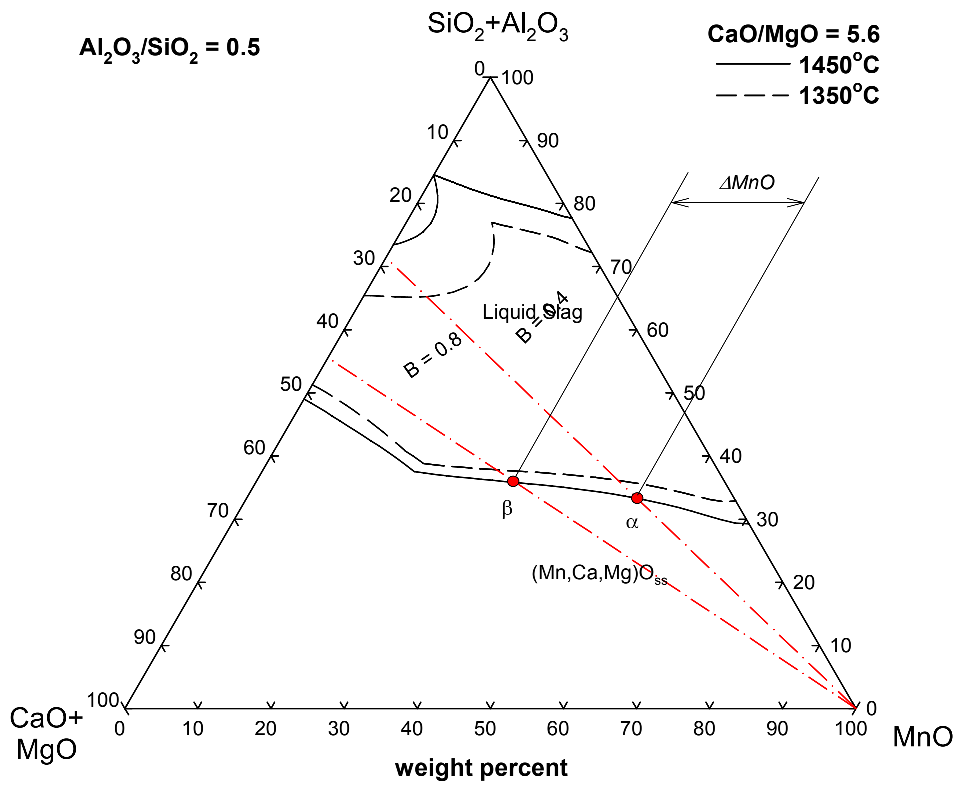

Figure 3: Illustration showing the effect of slag basicity on the liquidus content of MnO at fixed temperatures

ities. The more acid slag intersects the liquidus boundary at point α while the more basic slag at point β. The difference in liquidus MnO contents is shown as "ΔMnO" in the figure. It appears that the more acid ore mixture has the higher liquidus content of MnO.

The liquidus temperature for a certain ore mixture is of importance for the ferromanganese process temperature. The effects of the A/S ratio and of the slag basicity on the liquidus temperature is calculated and shown in Figure 4: and Figure 5:, respectively. The primary crystallized solid phases are also indicated in the figures. Figure 4: shows that increasing the A/S ratio from 0.4 up to 1.0, at a fixed MnO content at 35 wt%, has no virtual influence on the liquidus temperature. Figure 5: shows that increasing the slag basicity, on the other hand, leads to a continuous rise the liquidus temperatures. An approximate increase of 100-200°C in liquidus temperature is expected for every 0.2 increase in basicity units from 0.2 to 1.0 for a fixed MnO content.

3. EFFECT OF ALUMINA ON THE EQUILIBRIUM RELATION

The effect of Al_2O_3 on the slag/metal equilibrium relations has been examined and is shown in Figure 6:(a) and (b). The measured data[1][3] are not superimposed for the sake of clarity. Figure 6:(a) shows the effect of A/S ratio on equilibrium MnO concentration provided fixed basicity 0.4, while Figure 6:(b) demonstrates the same for a fixed basicity 0.8. In an earlier investigation[3] it was found that the A/S ratio has relatively little influence on the equilibrium content of MnO. The influence of the A/S ratio on the equilibrium MnO content is analogous to that on the liquidus MnO compositions as shown in Figure 2:. Changing the A/S ratio from 0.6 to 1.0 has little influence on the equilibrium MnO in slag phase. Varying the A/S mass ratio from 0.2 to 0.5 results in the reduction of equilibrium MnO content around 5-6 wt%. Comparing Figure 6:(a) with (b), it is concluded that a change in the basicity from 0.4 to 0.8 is able to reduce 15-18 wt% of MnO in the slag.

The effect of A/S ratio on the equilibrium content of silicon in the Mn-Si-C_{sat} metal phase is shown in Figure 7:. Increasing addition of Al_2O_3 to a slag with fixed content of SiO_2 leads to more Si being reduced to the metal phase. Increasing temperature brings on slight increase of Si content of liquid alloy. The influence of basicity on the equilibrium Si content is more complicated due to the amphoteric nature of alumina. As can be seen in Figure 7:, two curves intersect at A/S ratio around 0.7. For more basic slags, increasing basicity enhances Si reduction, whereas the opposite effect applies to the more acid slags assuming the same SiO_2 content.

4. EFFECT OF ALUMINA ON THE VISCOSITY OF LIQUID SLAG

The effect of Al_2O_3 on the viscosity of liquid ferromanganese slag has been evaluated using the recently developed viscosity model[8]. Detailed description of the viscosity model is given in another publication[8] at this conference.

Viscosity is defined as a measure of the ability of one layer of molecules to move over an adjacent layer of molecules. Liquid silicate melts contain various 3-dimensional structural units based on SiO_4^{4-} tetrahedra. Addition of alumina to the silicate melt will modify the network structure and consequently change its viscosity. Detail analyses are presented elsewhere[8].

Figure 8: shows the combined effect of the A/S ratio and the basicity on the viscosity of liquid slag with fixed content of SiO_2+ Al_2O_3 at constant temperature. Both the A/S ratio and the basicity influence the slag viscosity considerably. Changing the A/S ratio from 0.4 to 0.8 leads to decrease the viscosity. This is due to the fact that increasing A/S ratio means decreasing the SiO_2 contents for slags having fixed SiO_2+ Al_2O_3 content. Increasing the basicity from 0.2 to 1.0 results in considerable decrease in slag viscosity. The effect of the A/S ratio on slag viscosity is relatively stronger for the more acid slags.

It is well known that viscosity of liquid slag also depends on temperature. The effect of temperature on the viscosity of ferromanganese slags is moderate in the temperature range from 1200 to 1500°C. As shown in Figure 9:, every 100°C increase in temperature brings on about 0.2 poise decrease in the viscosity. For the more acid slag, the effect of temperature on the viscosity is stronger than for the more basic slags.

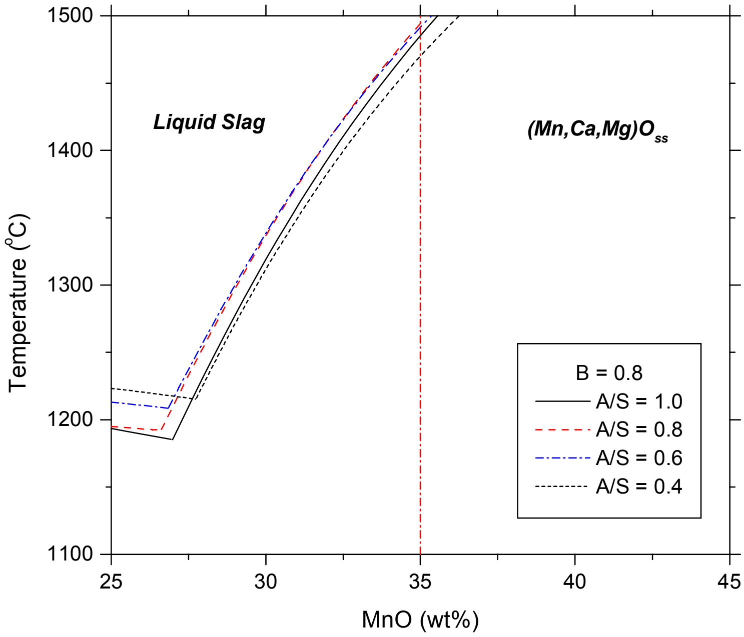

Figure 4: Influence of A/S ratio on the liquidus temperature of the MnO-SiO_2-CaO-MgO-Al_2O_3 ferromanganese slag

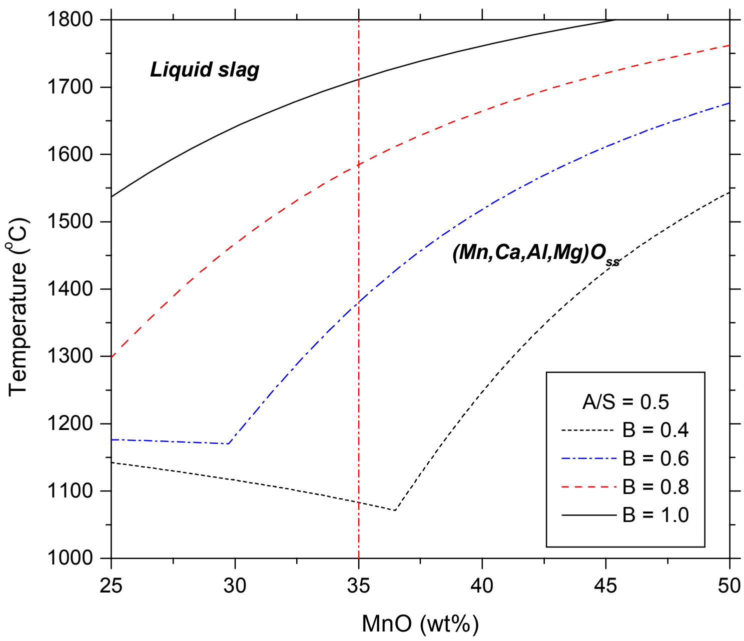

Figure 5: Influence of basicity on the liquidus temperature of the MnO-SiO_2-CaO-MgO-Al_2O_3 ferromanganese slag

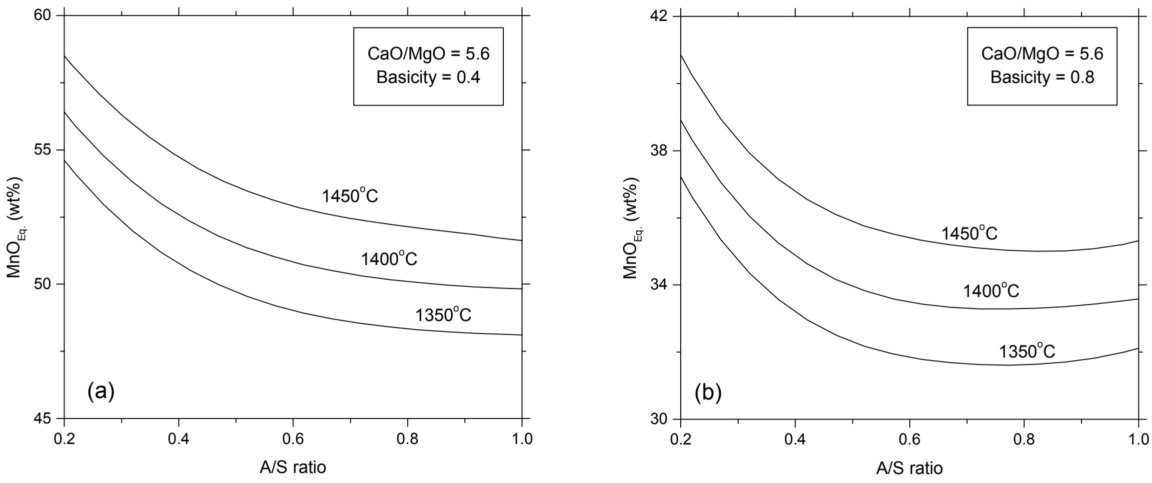

Figure 6: Effect of A/S ratio on the equilibrium MnO content

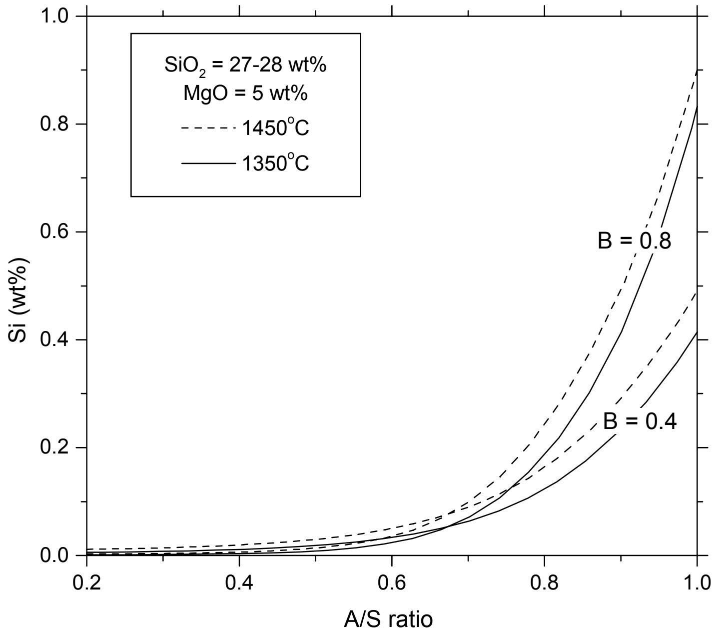

Figure 7: Effect of A/S ratio on the equilibrium silicon content

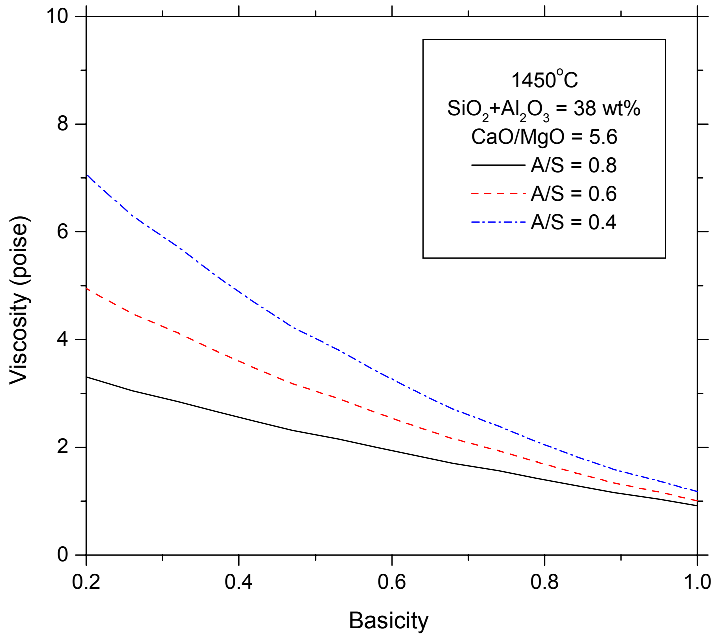

Figure 8: Effect of A/S ratio and basicity on the viscosities of ferromanganese slag

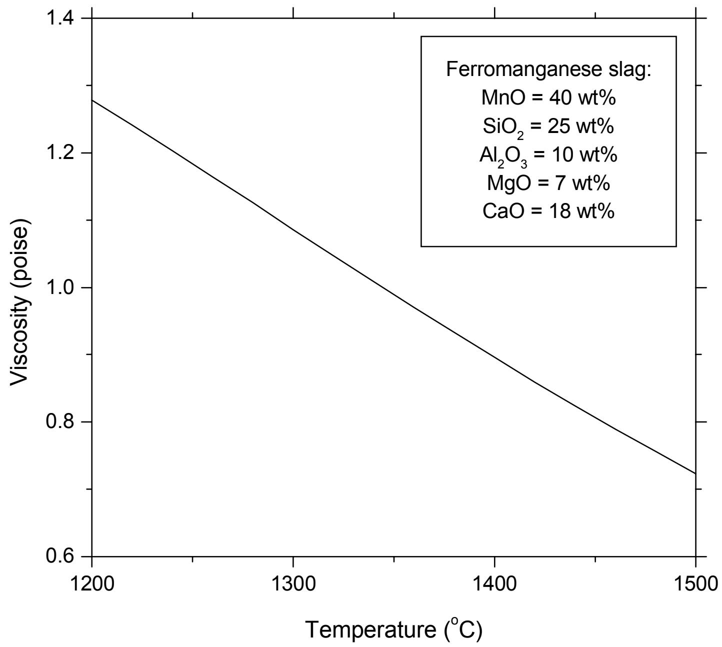

Figure 9: Effect of temperature on the viscosity of typical ferromanganese slag

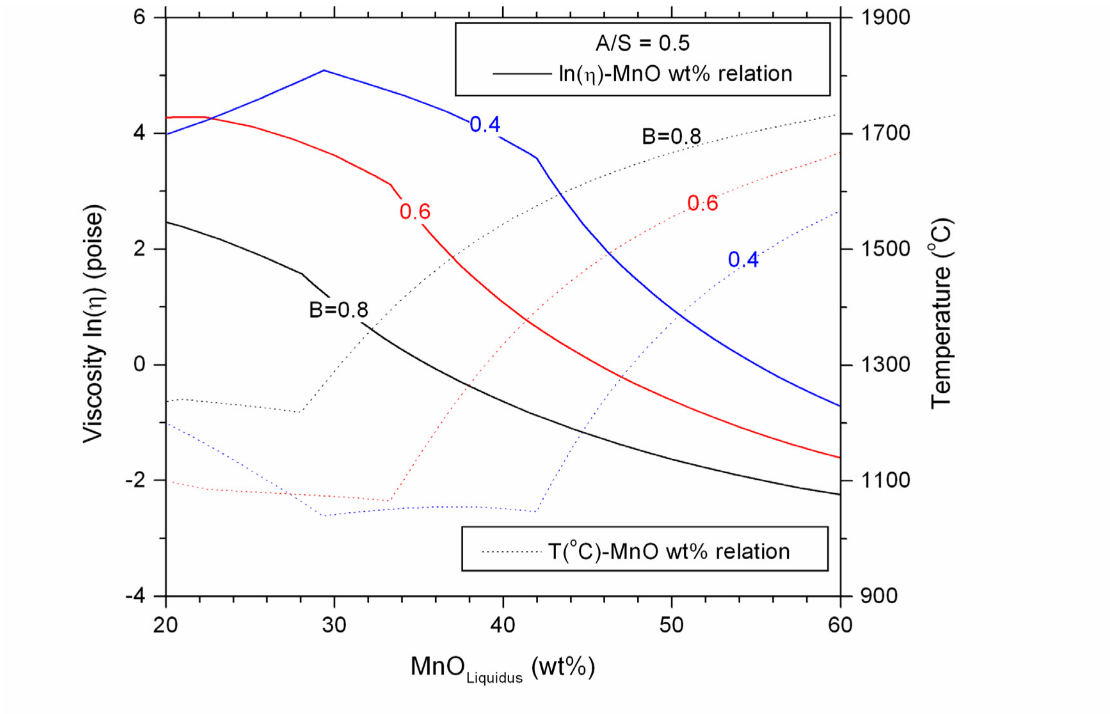

Figure 10: Calculated viscosities along the liquidus with fixed A/S ratio and basicity (solid lines). The dotted lines represent the corresponding temperature in the solid lines

As discussed above, industrial ferromanganese slags have compositions close to the liquidus composition. Therefore it is of practical importance to recognize viscosities of slags at their liquidus composition at various temperatures. Figure 10: is an example showing the viscosity as function of liquidus MnO content at different temperatures. The calculated liquidus temperature vs. MnO content relations is shown as dotted lines in the figure. It is evident that an acid operation tends to increase the viscosity of "primary liquid slag". This is primary due to the fact that the more acid slag contains more SiO_2. The viscosity of pure liquid SiO_2 is several orders of magnitudes higher than that of pure alumina and other oxides. Increasing MnO content, on one hand breaks the SiO_4^{4-} network and on the other hand increases liquidus temperature, results in the decrease in viscosity of liquid slag. This shows that the viscosity is not "sensitive" to the MnO content.

5. CONCLUSIONS

The influence of alumina on the liquidus temperature of ferromanganese slags and their MnO contents has been studied based mainly on assessed thermochemical databases. It has been found that the A/S ratio has only slight effect on the liquidus temperature and MnO content. The slag basicity, as influenced by the alumina content of the slag, is on the other hand important for the liquidus temperature and composition.

Slag/metal equilibrium calculations also confirm that the equilibrium MnO content is relatively little dependent on the A/S ratio but strongly dependent on the basicity ratio. A more basic operation results in reduced MnO content. Increasing A/S ratio at fixed SiO_2 content leads to increased silicon content in the metal phase.

The A/S ratio also plays a relatively important role on the viscosity of liquid ferromanganese slag. Increasing alumina addition to the acid slag leads to increase in slag viscosity considerably. However, viscosity of the more basic slag is not sensitive to the alumina addition. Increasing temperature may reduce the viscosity of acid slag significantly whereas the effect of temperature on the basic slag is relatively small. Viscosities of ferromanganese slags close to the liquidus temperatures and compositions are strongly dependent on its basicity. Increasing basicity results in substantial decrease in viscosity.

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