SILICOMANGANESE PRODUCTION – PROCESS UNDERSTANDING

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ABSTRACT

The main source of Mn in raw materials for SiMn production is Mn-ore and Mn-rich slag from the high carbon FeMn production. The amount of slag per tonne of SiMn metal is mainly determined by the ore/slag ratio. Increasing share of FeMn slag at expense of Mn-ore will lead to larger slag/metal ratio in the SiMn process. High volume of slag leads to an increased consumption of energy and probably to higher losses of metal inclusions in the final slag.

Excavation of a SiMn furnace has shown that only modest pre-reduction of Mn-ore with CO gas seems to be obtained. Nearly all reduction of MnO was finished at the top of the cokebed. Dissolution and reduction of quartz obviously takes place in the cokebed zone after the main reduction of manganese oxide is finished. Probably the 'pick up' of Si in the metal is quite fast and takes place as the metal trickles down through the cokebed towards the metal bath.

The distribution of Si between SiMn alloys and multicomponent $MnO\text{-}SiO_2\text{-}CaO\text{-}Al_2O_3\text{-}MgO$ *slags is mainly determined by the process temperature, the silica content of the slag and its R-ratio =* $(CaO+MgO)/Al_2O_3$*. As an example, the equilibrium content of Si in the alloy will increase by about 6 % if the R-ratio is reduced from 2 to 1, provided constant temperature and silica content. The effect of temperature is also considerable. The equilibrium content of silicon will increase by approximately 6 % per 50°C in the temperature range 1550°C to 1700°C. The equilibrium content of MnO in SiMn slags depends first of all on the temperature and secondly on the silica content of the slag. At 1600°C the MnO content decreases from about 9 % at silica saturation to a minimum of about 3-4% when the silica content is reduced to about 40-45%.*

1. INTRODUCTION

Manganese and silicon are crucial constituents in steelmaking, as deoxidants, desulphurizers and alloying elements. Silicon is the primary deoxidizer. Manganese is a milder deoxidizer than silicon but enhances the effectiveness due to the formation of stable manganese silicates and aluminates. It also serves as desulphurizer. Manganese is used as an alloying element in almost all types of steel. Of particular interest is its modifying effect on the iron-carbon system by increasing the hardenability of the steel.

About 93 % of all manganese produced is in the form of manganese ferroalloys. The FeMn grades are high-carbon (HC), medium carbon (MC), low-carbon (LC) and very low carbon (VLC), whereas the SiMn grades are medium carbon (MC) and low carbon (LC). The steel industry is the only consumer of these alloys. However as the average consumption of Mn in one tonne of steel is about 7 kg, this amounts to considerable tonnages.

To cover the need for manganese and silicon, the steelmaker has the choice of HCFeMn, SiMn and FeSi in a blend governed by specifications on carbon, silicon and manganese. Commonly a mixture of HCFeMn and FeSi75 is used, but a trend towards more use of SiMn is seen at the expense of the two others. This is primarily for economic reasons.

The economics of silicomanganese smelting is enhanced by minimising the loss of manganese as metal inclusions, as MnO dissolved in the slag, and by production of metal high in silicon and low in carbon. The SiMn production is typically integrated with the manufacture of HCFeMn so that the slag from the HCFeMn production is reprocessed in the production of SiMn. In this way a very high total yield of manganese is achieved.

2. SILICOMANGANESE PRODUCTION

Silicomanganese is produced by carbothermic reduction of oxidic raw materials in electric submerged arc furnaces. The same type of furnaces is used for FeMn and SiMn alloys. Operation of the SiMn process is often more difficult than the FeMn process because higher process temperature is needed. The size of the SiMn furnaces is usually in the range 15-40 MVA, giving 80-220 tonne of alloy per day.

Standard silicomanganese with 18-20 % Si and about 70% Mn is produced from a blend of HCFeMn slag with about 35 to 45% MnO, manganese ores, quartzite, (Fe)Si-remelts or off grade qualities, and coke. Sometimes minor amounts of MgO-containing minerals are added, *e.g.* dolomite [$CaCO_3 \cdot MgCO_3$] or olivine [$(MgO)_2 \cdot SiO_2$]. The discard slag from the SiMn process normally contains 5 to 10% MnO. Low carbon silicomanganese with around 30% Si is produced by upgrading standard alloy by addition of silicon wastes from the ferrosilicon industry.

Manganese ores normally contain unwanted elements that can not be removed in the mining and processing stages. Of special importance is phosphorus due to the strict demands in respect of this element both in the FeMn and SiMn alloys. Iron, phosphorus and arsenic are reduced more easily than manganese and will consequently go first into the metal. Their content in the final alloy must therefore be controlled by selection of ores. The HCFeMn slag is a very pure source of manganese because the easily reduced impurities in the ores have been taken up by the HCFeMn metal in the preceding process step. The content of impurities, like phosphorus, in SiMn alloys is therefore controlled, not only by the selection of manganese ores, but also by the relative amounts of manganese ores and HCFeMn slag in the raw material mix.

A process temperature of 1600 to 1650°C is necessary to obtain metal with sufficiently high content of Si and discard slag with low MnO. FeMn slag has a relatively low melting temperature (about 1250°C) compared with Mn-ores. Accordingly, a high share of FeMn slag will tend to give lower process temperatures[1]. When the Mn-ore starts melting at around 1350°C[2], it will contain a mixture of a solid and a liquid phase, where the solid phase is MnO. Further heating and reduction to 1550°C or more is necessary before the melting ore will mix with the slag and flow freely. With a high share of Mn-ore in the mix, the surface temperature and process temperature in the cokebed zone will be higher.

The specific power consumption for production of standard SiMn from a mixture of Mn-ore, HCFeMn slag and Si-rich metallic remelts, can typically be 3500-4500 kWh/tonne metal, dependent first of all on the amount of metallics added to the feed. The power consumption will increase with the Si-content of the metal produced, and also with the amount of slag per tonne of SiMn. Each additional 100 kg slag produced will consume additionally about 50 kWh electric energy. About 100 kWh per tonne of metal and some coke will be saved if the ore fraction in the charge is reduced to MnO by CO gas ascending from the smelt reduction zone.

3. PROCESS ZONES

The interior of the furnace may conveniently be divided into two main areas; first a preheating and prereduction zone where the charge components still are solid, and secondly the cokebed zone where ore, slag and fluxes are molten. This is illustrated in Figure 1. The sketch is based on a recent excavation of a three phase 16 MW furnace producing SiMn. The furnace was switched off during regular operation, two-thirds of the way into a new tapping cycle. No external cooling was performed. The main raw materials were Groote Eylandt lump manganese ore, FeMn slag, quartz, some dolomitic limestone and coke. The furnace was well operated prior to the shutdown. The metal contained above 18% Si and the slag about 40% SiO_2. The temperature of tapped slag was about 1600°C. With a few exceptions, the furnace load had been above 15 MW and the operating time above 95%. The excavation was therefore expected to show the interior of a well-operated furnace.

The tip of electrode A, B and C was respectively 60, 110 and 50 cm above the metal bath. As the operation was relatively good prior to the shutdown, an electrode tip position around 60 cm is assumed to have been suitable for this furnace. The electrode tip will be at the top of a correctly sized coke bed. If the coke bed gets to big, coke will will build up along the electrode leg as seen around electrode B. Too much coke was accumulated around electrode B resulting in its unwanted high position.

Under each electrode was a zone with relatively pure slag with very little coke. This has also been observed previously when HCFeMn was produced, both industrially and in pilot scale experiments[2]. Even below the coke rich electrode B there was an area with mainly slag and very little coke.

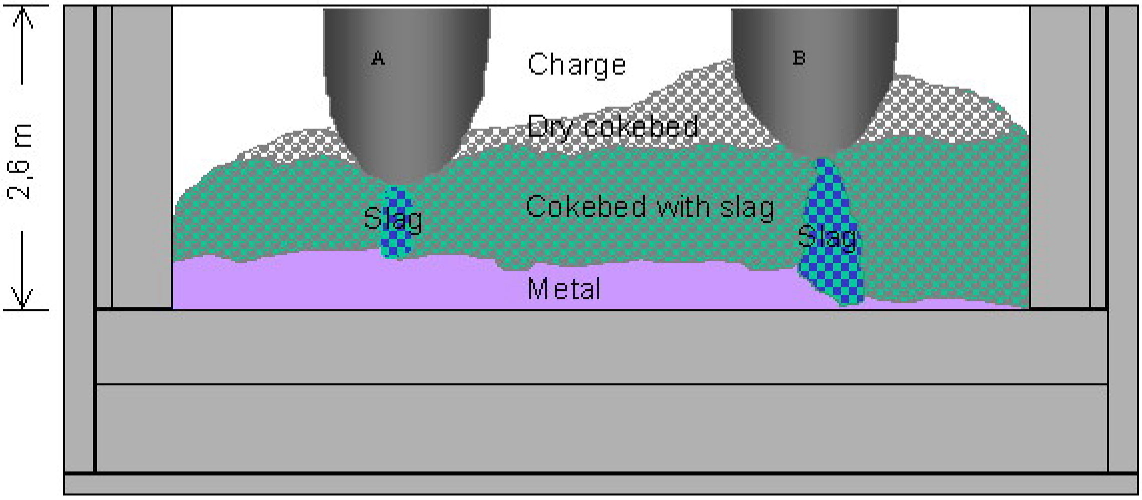

Figure 1. Zones in excavated SiMn furnace.

Loose materials were on average heaped about 20 cm above top of the furnace steel casing and lining. Sampling of the charge was carried out both manually during dig out and by taking out cores through drilling. The samples were investigated by visual judgement, XRD analyses, microprobe analyses and wet chemical analyses. MnO_2 in the ore had decomposed early to Mn_2O_3. A modest reduction to Mn_3O_4 by CO gas or by thermal decomposition had taken place just before the first signs of meltphase in the ore particles were visible at level 70 to 80 cm (level = distance below top of the furnace lining). Reduction to MnO of any significance was only observed in the charge fines constituting about 10-15% of the lumpy charge. The fine material was assumed to be either an original part of the charge mix or a result of the mechanical digging out procedure. An alternative explanation may be that brittle pre-reduced material (Mn_3O_4 + MnO) peels off successively from the surface as reduction of the ore particles takes place. There seemed to be no pattern in degree of reduction versus distance from the nearest electrode or vertical depth in the pre-reduction zone.

The main source of Mn in the charge mix for this SiMn furnace was MnO-rich FeMn slag. Initial melting and reduction of the FeMn slag had taken place 50 to 70 cm below top of the furnace lining. The FeMn slag was reduced almost to its final SiMn slag composition at level 90 cm before further reduction of the Mn-ore started. The Mn-ore is reduced separately and not via dissolution into the first melting FeMn slag. Nearly all reduction to low-Si metal and SiMn slag had been finished at level 146 which is the start of the cokebed zone and about 20 cm above the tip of the neighbouring C-electrode.

Solid quartz was present all the way down into the cokebed zone and the SiO_2 content of slag samples from this area was in the range 40 to 45%. Dissolution and parallel reduction of quartz have obviously taken place in the cokebed zone after the main reduction of manganese oxide was finished. Probably the 'pick up' of Si in the metal is quite fast and takes place as the metal trickles down through the cokebed towards the metal bath. The average content of SiO_2 in tapped slag was 40.4 %.

Only small metal inclusions in the size range from 1cm and down were found on the way down to about level 190 cm. The size of the major part of metal droplets was in the µm range. Metal with about 22 % Si was only found very close to quartz particles. Other places the Si-content was between 10 and 16 %. This is probably a result of back-reactions in the cokebed zone between metal and slag during cooling, as the average silicon content of tapped metal was close to 19 %.

The average content of MnO in tapped slag (about 6 %) was lower than in samples from the cokebed zone. This also indicates that some back-reaction between slag and metal has taken place during cooling down. This reaction is exothermic and may well proceed after shutdown.

The major part of the metal was found in the metal layer at the bottom of the furnace. The tapped metal had a Mn/Fe ratio of about 7. This is also what was found in the metal layer where the Mn/Fe ratio was between 6 and 8. The small metal droplets found in the cokebed had a much larger Mn/Fe-ratio. This is probably because the metal in the cokebed is a "secondary" product. The main part of produced metal seems to have been droplets that have drained relatively fast through the cokebed. A mixture of carbides, metal and precipitated carbon was found below the metal bath.

4. PROCESS METALLURGY

The main oxide components in raw materials for silicomanganese production are MnO, SiO_2, CaO, MgO and Al_2O_3. MnO and SiO_2 are partially reduced whereas the more stable oxides CaO, MgO and Al_2O_3 are regarded as unreducable and will go entirely to the slag phase. Even though these oxides do not take part in the reduction process, they are of great importance for the thermodynamic and physical properties of the slag phase.

The distribution of silicon and manganese between carbon-saturated Mn-(Fe)-Si-C alloys and MnO-SiO_2-CaO-Al_2O_3-MgO slags in equilibrium with CO gas is a result of simultaneous reactions taking place. In the silicomanganese process the temperature may reach 1600°C or higher, and the composition of metal and slag is assumed to approach equilibrium.

The main equilibrium reactions that controls the distribution of silicon and manganese between the slag and metal alloy are the following whether the alloy is ferromanganese or silicomanganese:

$$(MnO) + 'C' = \underline{Mn} + CO_{(g)} \tag{1}$$

$$(SiO_2) + 2'C' = \underline{Si} + 2CO_{(g)} \tag{2}$$

Parentheses indicate species present in the slag phase and underscored species in the alloy. 'C' is carbon either as graphite or in silicon carbide dependent on the Si-content of the alloy. Graphite is the stable phase coexisting with liquid Mn-Fe-Si alloy until the Si-content reaches a certain value, approx. 17-18 % Si, somewhat dependent on the temperature and the Fe-content of the alloy. At higher Si-contents silicon carbide is the stable coexisting phase. In the following the term "carbon saturated" or C_{sat} will mean an alloy saturated with either graphite or silicon carbide.

Complete slag/metal/gas equilibrium requires simultaneous establishment of equilibrium for the two reactions. Both reactions are very dependent on the temperature and the CO pressure of the system. Higher temperatures will give higher equilibrium content of Si in the metal and lower MnO content in the slag. A low CO-pressure will also favour higher content of Si in the metal and less MnO in the slag. Normally the CO-pressure is quite close to 1 atm in electric submerged arc furnaces. Calculated partial pressures of CO, SiO and Mn above Mn-Si-C_{sat} alloy in equilibrium with SiO_2-saturated slags are shown in Figure 2.

A combination of the two reactions (1) and (2) above gives the partial slag/metal equilibrium reaction, expressed by

$$2(MnO) + \underline{Si} = 2\underline{Mn} + (SiO_2) \tag{3}$$

This reaction is little dependent on temperature and independent of pressure and composition of the gas phase. The state of complete and partial equilibrium in this system has been discussed previously by Ding[3] and by Ding and Olsen[4][5][6].

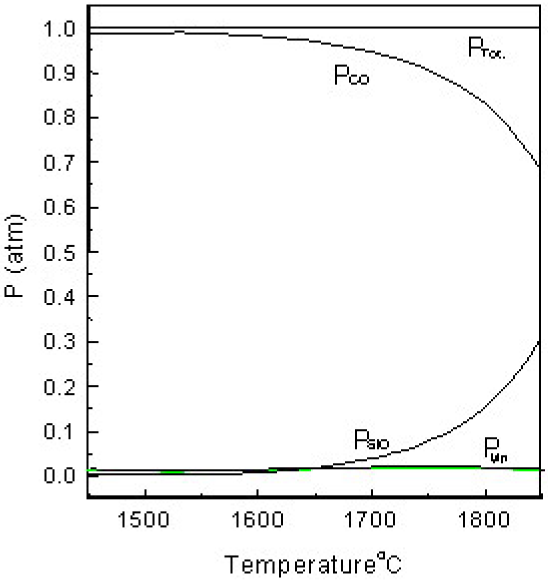

Figure 2. Calculated partial pressure of $CO_{(g)}$, $SiO_{(g)}$ and $Mn_{(g)}$ above Mn-Si-C_{sat} alloy in equilibrium with slag where a_{SiO2}=0.2. P_{tot} = 1 atm.

4.1 The manganese distribution

High process temperatures are required to produce silicomanganese alloys by carbothermic reduction of the oxide ores. The SiMn slag is a throwaway product, and loss of manganese, both as MnO and as metal inclusions in the slag, has considerable economic consequences. At complete equilibrium, the following equation has to be satisfied:

$$MnO + 'C' = Mn + CO; \qquad K_T = \frac{a_{Mn} \cdot P_{CO}}{a_{MnO} \cdot a_{'C'}} \tag{4}$$

K_T is the equilibrium constant at temperature T. The equilibrium content of MnO in the slag is mainly dependent on the temperature, the CO pressure, and also of course on the slag composition influencing the activity coefficient of MnO.

Figure 3 shows the effect of temperature and slag composition on the equilibrium content of MnO in ternary MnO-SiO_2-CaO slags[7]. Slag compositions along each curve are at equilibrium with carbon saturated alloys at the stated temperature and P_{CO}=1atm. The Si-content of the equilibrated alloy will change as the activity of silica changes along the curve. The MnO content decreases with increasing temperature and increasing content of CaO in the slag. The equilibrium content of MnO at 1600 ºC and P_{CO}=1 atm is reduced from about 10 % in silica saturated slags down to about 3 % in slag with about 60 % CaO and 40 % SiO_2. A lowering of the CO partial pressure will shift the equilibrium curve to the left, which is the same effect as of increasing the equilibrium temperature.

The effect of Al_2O_3 and MgO on equilibrium relations has been evaluated previously[4][6]. Alumina is characterised as an amphoteric oxide. When added to acid slags, Al_2O_3 will act as a basic component and give lower MnO contents, and addition to more basic slags will have the opposite effect. This is illustrated in Figure 4. The change between 'acid' and 'basic' slags takes place at about 45% SiO_2. For a typical SiMn slag with about 40% SiO_2 the overall effect of increasing Al_2O_3 (at the expense of CaO) will be to give a somewhat increased equilibrium content of MnO in the slag. The effect of MgO on equilibrium relations is less important. It was found that MnO in the slag is slightly increased when some CaO is replaced with MgO.

The MnO content of industrial SiMn slags is usually in the range 6 to 10 % whereas the equilibrium content would be about 4 %. One reason for this is that industrial slag will contain droplets of SiMn metal. The Fe content of these metal inclusions is often reported as FeO in the slag. An apparent content of say 0.3 % FeO in the slag counts for an apparent content of 2,1 % MnO in the slag if the Mn/Fe ratio in the metal is 7.

Correction for the metal inclusions will bring the real MnO content of the slag closer to its equilibrium composition. The reason for not attaining equilibrium may also be insufficient time of contact between metal, slag and solid carbon in the cokebed zone.

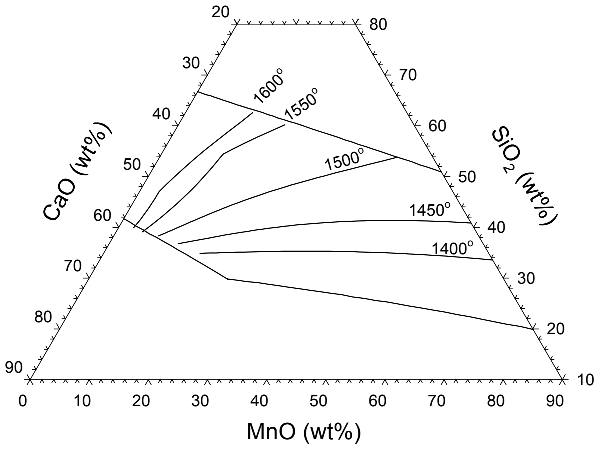

Figure 3. Complete equilibrium relations for ternary MnO-SiO_2-CaO slags in equilibrium with Mn-Si-C_{sat} alloys at P_{CO}=1atm.

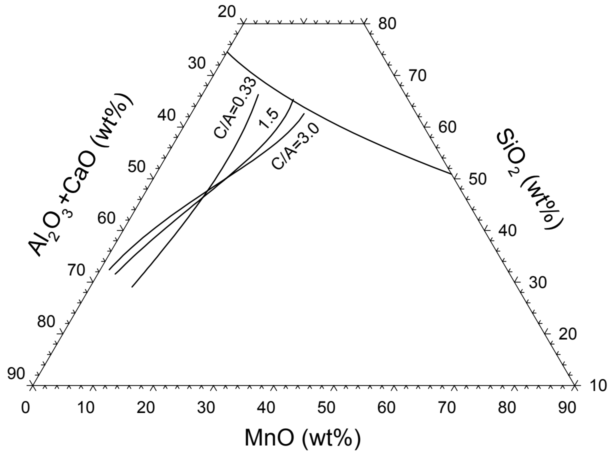

Figure 4. Sketch showing effect of Al_2O_3 addition on equilibrium content of MnO in MnO-SiO_2-CaO-Al_2O_3 slags.

4.2 The silicon distribution

$$(SiO_2) + 2C_{gr} = Si_{(l)} + 2CO_{(g)}; \qquad K_T^{(5)} = \frac{P_{CO}^2 \cdot a_{Si}}{a_{SiO_2} \cdot a_C^2} \tag{5}$$

$$(SiO_2) + 2SiC = 3\,Si_{(l)} + 2\,CO_{(g)}; \qquad K_T^{(6)} = \frac{P_{CO}^2 \cdot a_{Si}^3}{a_{SiO_2} \cdot a_{SiC}^2} \tag{6}$$

According to industrial specifications, the content of Si in commercial alloys varies from 15 to 33%. The maximum achievable Si content in an ordinary SiMn process will be about 20-22 % Si. Higher Si-content requires alloying with Si or FeSi alloys. The silica reduction proceeds to equilibrium according to either of the following reactions, the second being applicable when the silicon content of the metal at 1600°C exceeds about 17 % in Mn-Si-C_{sat} alloys:
At unit activity of C respective SiC and of CO we have:

Graphite stable: $a_{Si} = K_T^{(5)} \cdot a_{SiO_2}$

Silicon carbide stable: $a_{Si} = \sqrt[3]{K_T^{(6)} \cdot a_{SiO_2}}$

Accordingly, for both reactions, the Si-content of the alloy will only be dependent on the temperature (K_T) and the activity of SiO_2.

The maximum Si content of Mn7Fe-Si-C_{sat} alloys (weight ratio Mn/Fe=7) have been calculated assuming activity of SiO_2 = 0.2 and a total pressure (P_{CO}+P_{SiO}+P_{Mn}) of one atmosphere. As shown in Figure 2, the partial pressures of SiO and Mn are modest up to about 1700°C, so the CO pressure is quite close to unity. The result is shown in Figure 5, where the equilibrium content of Si in alloy is shown versus reduction temperature.

The Mn/Fe-ratio in metal and the silica activity in slag are both typical for SiMn production. As can be seen, the necessary temperature to reach 20 % Si in the alloy is around 1640°C, and to reach 30 % Si a temperature slightly above 1750°C would be necessary. If the CO-pressure was reduced, say to 1/3 of an atmosphere for example by dilution with nitrogen, the necessary temperature would be reduced considerably as shown in Figure 6[7].

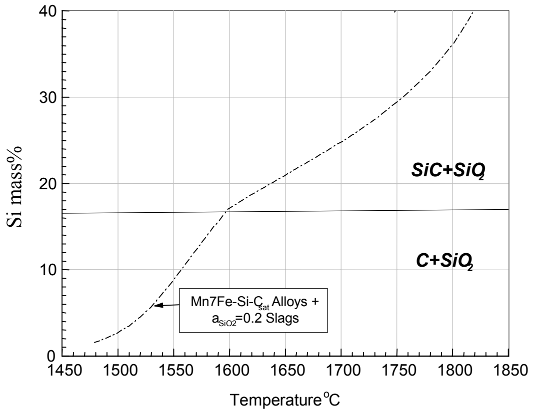

Figure 5. The equilibrium content of Si *vs.* temperature for Mn7Fe-SiC$_{sat}$ alloys in equilibrium with slags where a_{SiO2}= 0.2. P_{CO}=1 atm

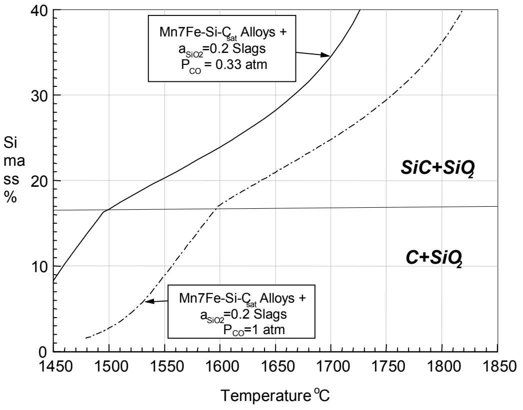

Figure 6. The equilibrium Si content of Mn7Fe-SiC$_{sat}$ alloys in equilibrium with slags where a_{SiO2}= 0.2 and gas where P_{CO}=1 and 1/3 of an atmosphere.

As already stated, the activity of SiO_2 in the slag system is very important for the Si content of the produced alloy. Iso-activity lines of SiO_2 in the system SiO_2-CaO-Al_2O_3 are shown in Figure 7. The lines representing constant silica activities in the slag are at the same time lines of constant silicon activity in equilibrated metal alloy. Note that SiC formation will take place when the SiO_2 activity exceeds approximately 0.2 at 1600°C regardless of slag and metal system. This is normal activity of SiO_2 for SiMn slags equilibrated with metal containing 18-20% Si. From the top apex of Figure 7 are drawn straight lines having constant CaO/Al_2O_3 ratios, called R-ratios. This R-ratio is much more important in SiMn production than the so-called lime basicity ratio [(CaO+MgO)/SiO_2] used by many producers. Using the R-ratio, any MgO in the slag should be added to CaO in the numerator. The lines intersect with the iso-activity lines. The position of an intersection point is defined by its SiO_2 content and the R-ratio of the slag. Corresponding Si-contents of equilibrated alloys and SiO_2-contents of slags are shown in Figure 8 for different R-ratios. This relation is based on previous experimental work[6]. The silicon content of the alloys increases fast with increasing SiO_2 in the slag up to about 18-20% Si. Then follows a slow increase until silica saturation is reached. The change in slope is a result of carbon being replaced by silicon carbide as the stable carbon-containing phase.

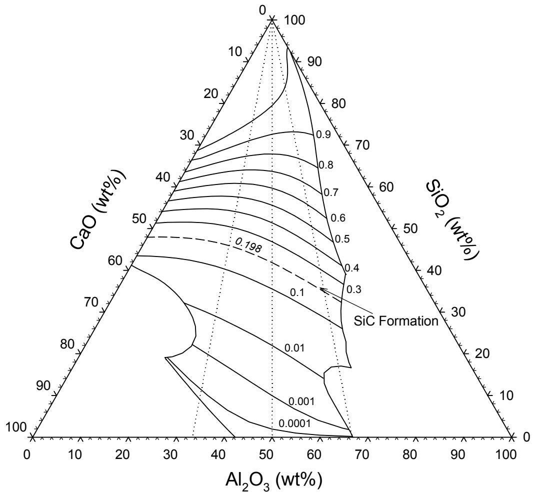

Figure 7. Calculated (FACTSage) iso-activity lines of SiO_2 in SiO_2-CaO-Al_2O_3 slags at 1600ºC intersected by lines having constant R-ratios (R=CaO/Al_2O_3).

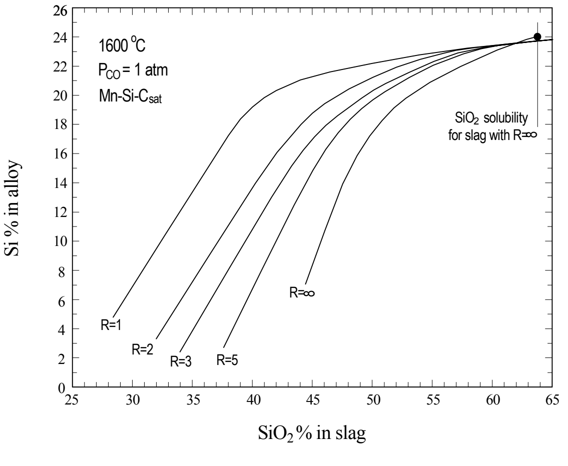

Figure 8. Distribution of silicon as a function of the R-ratio.

5. CONCLUSIONS

Excavation of a 16 MW SiMn furnace indicates that an electrode tip position of about 60 cm above the metal bath has been suitable for good operation. MnO_2 in the ore decomposed early to Mn_2O_3, but further reduction to Mn_3O_4 by CO gas or by thermal decomposition was modest. Pre-reduction to MnO of any significance was only observed in the charge fines. The MnO-rich FeMn slag was reduced almost to final SiMn slag composition before substantial reduction of melting Mn-ore started on. Nearly all reduction of MnO was finished at the top of the cokebed. Dissolution and reduction of quartz have obviously taken place in the cokebed zone after the main reduction of manganese oxide was finished. Probably the 'pick up' of Si in the metal is quite fast and takes place as the metal trickles down through the cokebed towards the metal bath.

The amount of slag per tonne of SiMn metal is mainly determined by the ore/slag ratio. Increasing share of FeMn slag at the expense of Mn-ore will lead to larger slag/metal ratio in the SiMn process. High volume of slag leads to an increased consumption of energy and probably to higher losses of metal inclusions in the final slag.

The equilibrium content of MnO in SiMn slags depends first of all on the temperature and secondly on the silica content of the slag. At 1600°C the equilibrium content of MnO decreases from about 9 % at silica saturation to a minimum of about 3-4% when the silica content is reduced to about 40-45%. The distribution of Si between SiMn alloys and multicomponent $MnO-SiO_2-CaO-Al_2O_3-MgO$ slags is mainly determined by the process temperature, the silica content of the slag and its R-ratio = $(CaO+MgO)/Al_2O_3$.

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