TAP-HOLE WEAR: ANALYSIS OF DAILY AVERAGE SLAG AND METAL COMPOSITIONS OF A SINGLE SiMn SMELTER

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ABSTRACT

To test the conclusion that SiC formation through reduction of SiO_2 *in tapped slag and dissolution of carbon by tapped metal can be responsible for refractory wear in the tap-hole of a SiMn furnace, plant data over a 4 month period were analysed in more detail. Thermodynamic calculations were conducted in FACTsage 6.4, for a temperature of 1600°C. The majority of the daily average metal compositions were unsaturated in C and therefore had the potential to dissolve C-based refractory materials. A minority of metal compositions were unsaturated in SiC. All of the daily average slag compositions had the potential to consume C-based refractory materials through the formation of SiC by reaction of* SiO_2 *with carbon, at 1600°C. The calculated entrained metal content in the slag samples ranged between 1-6% by mass.*

Keywords: *tap-hole, silicomanganese, submerged arc furnace, refractory wear, FACTSage*

1. INTRODUCTION

A study [1] was conducted to determine to what extent chemical reaction between slag (and metal) and refractory materials would be responsible for tap-hole refractory wear in the tap-hole of a SiMn furnace where slag and metal are tapped typically at 1600°C through a single level tap-hole.

It was found that reaction between silicomanganese slag and carbon-based tap-hole refractory is possible. Predictions by thermodynamic calculations were supported by laboratory-scale experiments with nominally pure materials as well as industrial materials. As reaction products SiC and SiMn droplets formed.

When C-based refractory reacts with slag, if the SiC reaction product were to form an *in-situ* refractory layer at the slag/refractory interface, the potential for refractory wear by chemical reaction would be reduced [2]. However, in all experiments conducted, the SiC that formed detached from the surface of the carbon-based refractory [1] as was found by others [3].

Chemical reaction between carbon-based refractory in the tap-hole and silicomanganese slag and metal is therefore a potential wear mechanism.

During excavation of a 48 MVA submerged arc furnace used for SiMn production, it was found that the tap-hole area was one of two high refractory wear areas; the other was the furnace hearth [1]. In both high wear areas carbon-based cold ramming paste formed the crucible of the lining. Thermodynamic calculations predicted that chemical reaction between carbon-based refractory and silicomanganese slag and metal was a potential wear mechanism. Mass transfer calculations indicated that it would not be the only wear mechanism applicable.

The thermodynamic calculations in the study [1] were based on published slag and metal compositions as well as plant data where the average slag and metal compositions were calculated for daily compositions over a 4 month period – Table 1 and Table 2.

Table 2: Compositions of tapped SiMn alloy (mass percentages): typical alloy [4] and industrial alloy [1] (averages, with standard deviation in parenthesis where applicable).

	%Mn	**%Si**	**%C**	**%Fe**
Typical [4]	68	20	2	10
Industrial [1]	66.3 (0.5)	17.1 (0.8)	1.8 (0.2)	14.8 (0.6)

Table 3: Compositions of tapped SiMn slags (mass percentages): typical slag [4] and industrial slag [1] (averages, with standard deviation in parenthesis where applicable).

	%MnO	**%SiO_2**	**%Al_2O_3**	**%CaO**	**%MgO**	**%FeO**
Typical [4]	9	45	16	21	9	0
Industrial [1]	11.9 (1.8)	48.3 (0.8)	6.3 (0.7)	27.1 (1.0)	6.4 (0.4)	0

Based on these calculations, the slag can react with graphite to form solid SiC, liquid metal and gas, at 1600°C. MnO is reduced to form Mn in liquid metal and in gas; SiO_2 is reduced to form solid SiC, Si dissolved in liquid metal and SiO in the gas. Carbon would dissolve in the Mn-Si-C product.

The potential for reaction of metal with carbon was assessed by using the FSstel database in FactSage. It was found that the carbon solubility predicted with FactSage is very similar to that predicted by Tang and Olsen [5], if slightly lower (see Figure 1). Most importantly for this discussion, the silicon content at double saturation of the metal (saturation with both graphite and silicon carbide) is essentially the same (see Table 3). Metal containing more silicon than required for double saturation would tend to dissolve carbon and precipitate silicon carbide, if the metal were to come into contact with carbon. At 1600°C, the silicon concentration at double saturation is approximately 16.3% (by mass); as Table 1 indicates, typical industrially produced silicomanganese contains more silicon than this, and hence would be expected to dissolve carbon-based refractory.

Table 4: Comparison of the silicon concentration (mass percentage) in Mn_5Fe-Si-C melts at double saturation, as reported by Tang and Olsen [5], and calculated with FactSage.

Temperature (°C)	**[%Si]-double saturation**	
	Tang&Olsen	**FactSage**
1530	15.7	15.9
1630	16.6	16.6

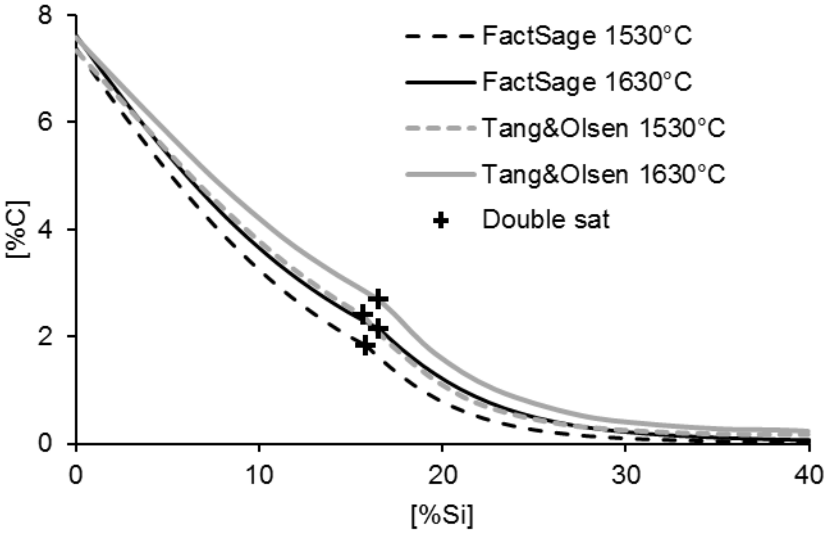

Figure 12: Carbon solubility in Mn-Fe-Si-C alloys with Mn:Fe = 5, at 1530°C and 1630°C, calculated with FactSage 6.4 (FSstel database; black lines), and by Tang and Olsen [5] (grey lines).

To test these observations (possibility of SiC formation through reduction of SiO_2 in tapped slag; dissolution of C into tapped metal), the plant data for which the averaged compositions were reported in Table 1 and Table 2 was analysed in greater details.

2. METHODOLOGY

The received daily average slag and metal analyses were normalised.

To correct the slag composition for entrained metal, it was assumed that all Fe reported in the slag analysis was present as entrained metal droplets, and that these droplets had the same composition as the daily tapped bulk metal (mainly containing Fe, Si, Mn and C). The assumption was previously validated by SEM EDS analysis on an industrial slag sample obtained from the same plant [6]. Mass balance calculations were conducted to correct the reported slag composition for FeO (recalculated to be zero), SiO_2 and MnO (recalculated, based on entrained metal mass, to be lower). As part of this calculation, the mass of metal entrained per 100g slag was estimated.

Thermodynamic calculations were conducted in FACTSage 6.4, using the FToxid, FSstel and FACTPS databases.

3. CARBON AND SILICON CARBIDE SOLUBILITY

To test whether the metal would tend to dissolve carbon, the activities of carbon (graphite reference state) and silicon carbide in the metal were calculated. The calculations were mainly performed in two ways. First, the metal was taken to be fully liquid (allowing no precipitation of solids); in this case, activities of SiC and graphite could exceed 1. Second, precipitation of solids (graphite or SiC, in this case), and changes in composition and saturation conditions were noted. Calculations were performed for 1600°C and 1550°C. In these calculations, the analysed concentrations of Si, Mn, Fe and C were used.

To give a more general indication, a graphite / silicon carbide saturation diagram for 1600˚C was also calculated for a Mn:Fe mass ratio of 4.47 (the average mass ratio of the daily average tapped metal compositions); see Figure 2. The dual saturation point at 1600˚C was found to be 2.04%C and 16.26% Si for the Si-Mn-Fe-C alloy with a Mn:Fe mass ratio of 4.47. Superimposed onto the metal saturation diagram in Figure 2 are the daily average tapped metal compositions for the 4 month period.

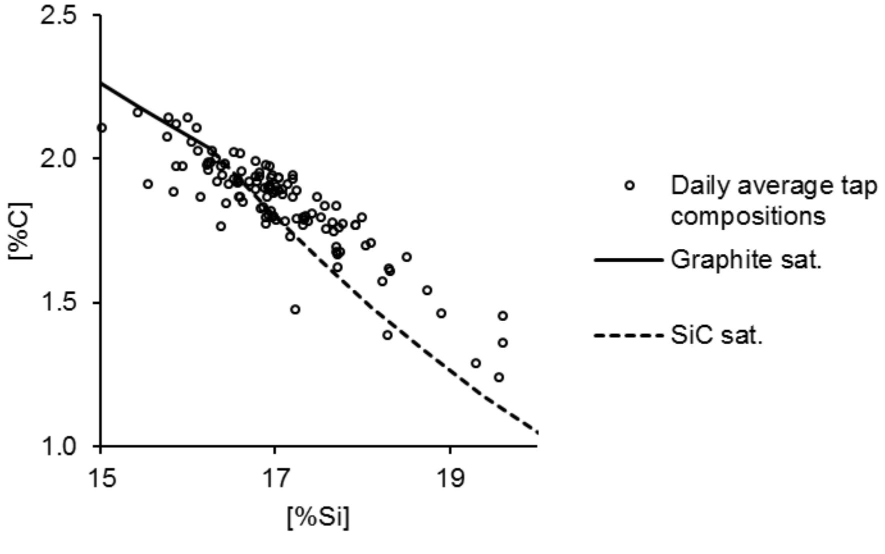

Figure 2: Carbon solubility in Mn-Fe-Si-C alloys with Mn:Fe mass ratio of 4.47 at 1600°C, calculated with FactSage 6.4 (FSstel database); compositions given as mass percentages. For silicon contents below the inflection in the curve, the stable solid phase at saturation is graphite; SiC is the stable phase at saturation for higher silicon contents. The symbols show reported daily average silicomanganese compositions over a four month period.

Figure 2 indicates that, as was the case for the average metal composition [1], many of the metal compositions were supersaturated in SiC and not saturated in C. To illustrate this differently, the calculated activities of C (with respect to graphite) and SiC are reported in Figure 3 (for the case where precipitation of solids was suppressed).

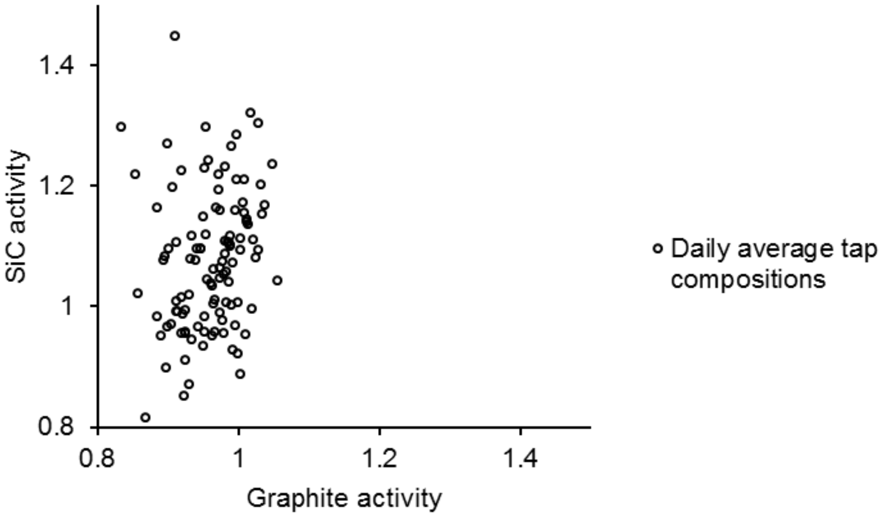

Figure 3: Activity of SiC (solid SiC as reference state) and activity of C (solid graphite as reference state) in Mn-Fe-Si-C alloys at 1600°C, calculated with FactSage 6.4 (FSstel database) for the daily average tapped metal compositions (Precipitation of solids suppressed).

Based on the calculated activities of SiC and C, for the case where precipitation of solids was suppressed, 67% of the metal taps had SiC activities greater than 1, whereas only 20% of the taps were supersaturated in graphite. In the cases where solid precipitation was allowed to proceed to equilibrium, the proportion of graphite-saturated melts was even smaller (Table 4); this is because SiC precipitation (which would occur in SiC-saturated melts) would remove carbon from solution, moving the metal composition even further from graphite saturation.

It is worth noting that the predicted proportion of graphite-saturated melts remained low even at a lower temperature of 1550°C (Table 4). This is mainly because the silicon content at double saturation does not change much upon cooling to the lower temperature (as also indicated by Figure 1). This means that lowering the metal temperature (or slight cooling of the tap block) would not necessarily help to avoid chemical wear of carbon tap blocks by silicomanganese. This contrasts with the potential for reaction of SiO_2 in the slag with carbon (next section), which would be eliminated by cooling to 1550°C.

Table 5: Calculated proportions of metal taps which remained supersaturated with SiC or graphite after solids were allowed to precipitate in the metal, for temperatures of 1550°C and 1600°C.

Temperature (°C)	**a_{SiC} = 1**	**a_C = 1**
1550	92%	10%
1600	66%	4%

4. ACTIVITY OF SLAG SPECIES

The driving force for SiC formation according to reaction 1 depends on the activity of SiO_2 in the slag, assuming unit activity for all other components.

$$SiO_2 + 3C = SiC + 2CO \quad (1)$$

Should the activity of SiO_2 in the slag be higher than the equilibrium activity (calculated to be 0.17 at 1600°C; reference state cristobalite), chemical attack of carbon refractory by SiO_2 in the slag would be possible. Calculated SiO_2 activities (for 1600°C) are reported in Figure 4: for all slag compositions the activity of SiO_2 was higher than the equilibrium activity of SiO_2 for SiC formation with C at 1600˚C i.e. all slag compositions had the potential to chemically react with C-based refractory materials. However, a decrease in temperature to 1550°C would render SiO_2 non-reactive towards carbon (Figure 4). (SiO_2 activities in the slag do change with temperature; these activities were also recalculated for 1550°C, but were found to be only slightly different from the 1600°C values shown in Figure 4.)

Figure 4 also illustrates the effect of variation in slag composition on the activity of SiO_2 in the slag for a constant SiO_2 content (mass percentage), and the expected increase in SiO_2 activity with increased SiO_2 content of the slag.

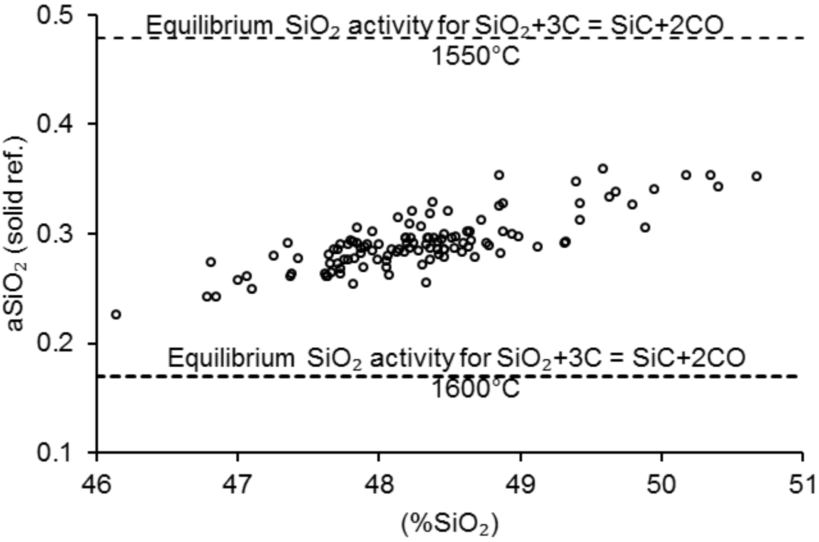

Figure 4: Activity of SiO_2 (solid SiO_2 [cristobalite] reference state) at 1600°C, calculated with FactSage 6.4 (FToxid database) as a function of SiO_2 content for the daily average tapped slag compositions. The broken lines give the equilibrium SiO_2 activities for possible reaction with carbon, at 1550°C and 1600°C.

In Figure 5 the SiO_2 contents of the tapped slag and the Si contents of the tapped metal are summarised (daily average; mass percentages) to illustrate variations in both. The Si content of the metal for dual saturation at 1600˚C (Mn:Fe ratio of 4.47; broken line) is also indicated in Figure 5, emphasising that most metal compositions have silicon concentrations greater than dual saturation.

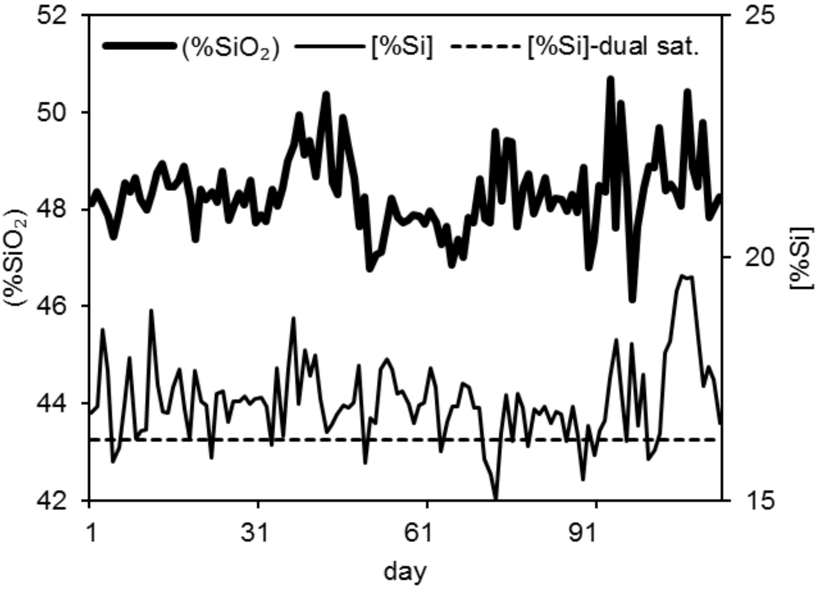

Figure 5: SiO_2 contents of the tapped slag (heavier line) and Si contents of the tapped metal (thinner line) (daily average mass percentages); also shown is the Si content of the metal for dual saturation at 1600˚C (Mn:Fe ratio of 4.47) calculated with FACTSage 6.4 (Fsstel database) (broken line).

5. METAL ENTRAINMENT

The velocity and diffusion boundary layers that are taken into account in mass transfer calculations [1] would develop near the wall inside a tap-hole due to the effects of viscosity. Muller [7] demonstrated that metal entrained in the slag phase has an effect on the effective viscosity and therefore also on the volumetric flow rate through a tap-hole. Both factors would influence the rate at which SiO_2 is transferred to the slag / refractory interface where chemical reaction between slag and metal would occur.

In Figure 6 the entrained metal concentration (g per 100g slag) in slag samples, calculated for the daily average tapped slag compositions, is presented. A distinct shift in entrainment is observed after 45 days of production (for unknown reasons).

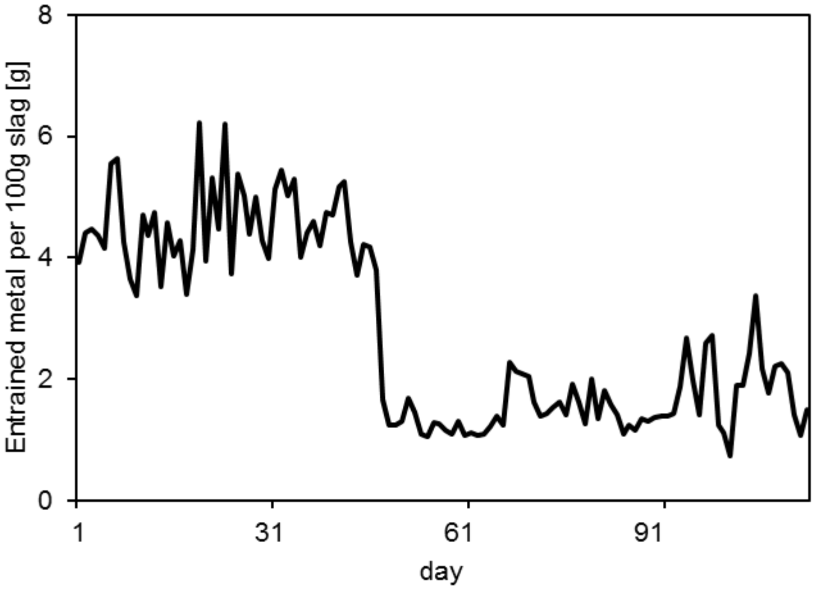

Figure 6: Calculated entrained metal (g per 100g slag) in tapped slag, calculated from % Fe reported in daily average tapped slag compositions.

6. CONCLUSIONS

During excavation of a 48 MVA submerged arc furnace used for SiMn production two high wear areas were found: the tap-hole area and the furnace hearth. Carbon-based refractory material formed the hot face refractory. Analysis of daily average tapped slag and metal compositions produced in the four months prior to excavation confirmed the potential for refractory wear through C dissolution in the metal, and SiC formation by chemical reaction with SiO_2 in the slag. Similar analysis of production data from other SiMn smelters would be useful.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

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