PHASE CHEMISTRY OF DIGOUT SAMPLES FROM A FERROSILICON FURNACE

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ABSTRACT

Phase chemical analysis of a set of digout samples from a 57 MVA ferrosilicon furnace provided valuable insight into the mechanism whereby buildup may form in the furnace hearth and taphole areas under conditions of operational instability. The samples were recovered during a partial sidewall rebuild of the tapholes areas. The electrode crater did not extend all the way to the tapholes; instead a 'false bottom' with several blow holes separated the cavity behind the tapholes from the crater. Although it was not possible to enter the furnace samples could be taken from the 'false bottom' and the banks around the taphole.

Analysis of the samples by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) showed the presence of:

- *Significant quantities of slag containing silicon carbide and refractory oxide phases. The slag is highly enriched in alumina and contains the following oxide phase assemblages:*
  - *$Ca_2Al_2SiO_7$ (C_2AS); $CaAl_2Si_2O_8$ (CAS_2); $CaAl_{12}O_{19}$*
  - *$Ca_2Al_2SiO_7$ (C_2AS): $CaAl_4O_7$*
  - *$Ca_2Al_2SiO_7$ (C_2AS); $CaAl_2Si_2O_8$ (CAS_2); Al_2O_3*
  - *$CaAl_2Si_2O_8$; $Al_6Si_2O_{13}$; slag*
- *Sialon and possibly silicon oxy-carbide. This may be the first documented occurrence of sialon in a ferrosilicon furnace.*
- *Intimate intergrowths of SiC and $CaAl_2Si_2O_8$. It is inferred that these intergrowths formed in-situ at temperatures below the liquidus temperature of the slag.*

A general feature of the samples is that they are heterogeneous in composition and, consequently, phase distribution. EDS area analyses indicate that the alumina content may vary by as much as 30% (absolute) over a matter of hundreds of micron. Such variability suggests that the slag did not crystallize under equilibrium conditions and it is likely that significant alteration took place once the slag was at least partly solidified. The most likely alteration mechanism that may result in the formation of a high-alumina residue is SiO fuming from the slag at temperatures that are too low for SiO to react with SiC to form Si and CO. Apart from SiO fuming, less Al was reduced from the slag during the period of instability, further contributing to a high overall alumina content in the furnace slag.

1. INTRODUCTION

Until recently, Siltech operated 2 high-grade ferrosilicon furnaces near Newcastle in South Africa. Furnace A is rated at 42 MVA, typically operating at a load of 27-28 MW. Furnace B is rated at 57 MVA, typically operating at a load of 31 MW (105 kA, 0.93 mΩ).

Furnace B experienced patting problems in September 2009, leading to a partial reconstruction of two tapholes and the lining surrounding the tapholes in June 2010. During the repairs sampling was done of the hearth buildup material and banks surrounding the tapholes to

determine why the banks were so refractory and difficult to penetrate when the tapping difficulties were experienced in September 2009. It stands to reason that the phase chemistry of the banks during sampling in June 2010 may have been different from the condition of the banks in September 2009 but valuable information would still be obtained with regard to the refractory nature of this material, even though the dig out samples cannot be directly related to the furnace blockage that was experienced.

2. OPERATIONAL DATA FROM THE PERIOD JUNE TO SEPTEMBER 2009

Siltech noticed gradual changes in the performance of furnace B over a period of almost 3 months leading up to the September 2009 tapping problems. The systematic decrease in the aluminium content of the hot metal was particularly profound (figure 1) and was mirrored by the metal-to-slag ratio (figure 2). At the resolution of the data the SEC did at first not significantly increase but from September 2009 it trended above 10 MWh/t metal (figure 3).

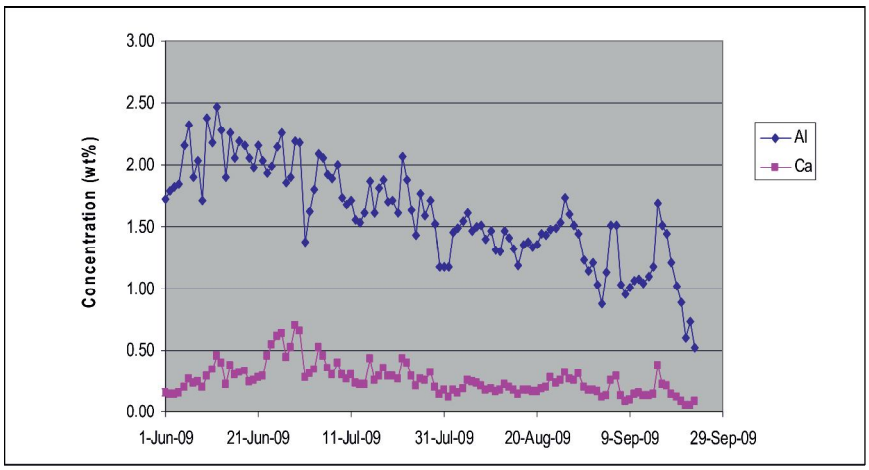

Figure 1: Aluminium and calcium in hot metal from Furnace B for the period 1 June to 23 September 2009

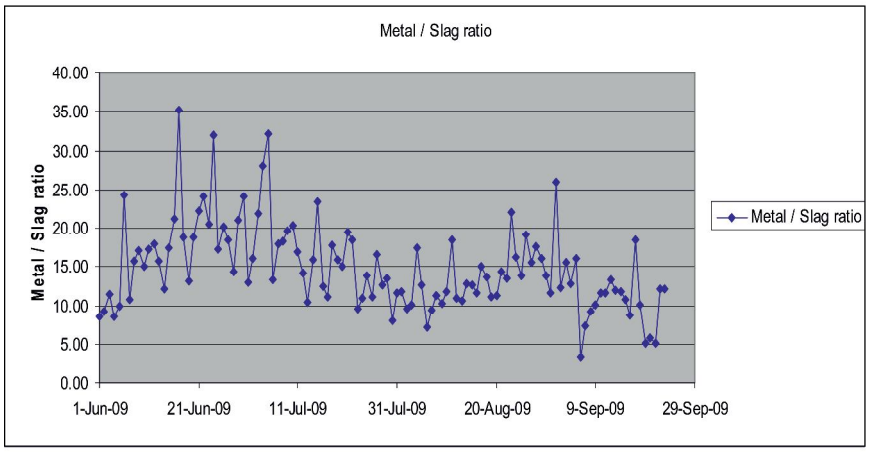

Figure 2: Metal-to-slag ratio over the period 1 June to 23 September 2009

The trends in metal composition and metal-to-slag ratio are indicative of lower temperatures in the active reduction zone in the electrode craters and would normally be associated with an

increase in electrode resistance (figure 4) [1]. Because the Siltech furnaces are operated under resistance control the electrode immersion must have decreased to maintain the resistance setpoint of about 0.93 mΩ.

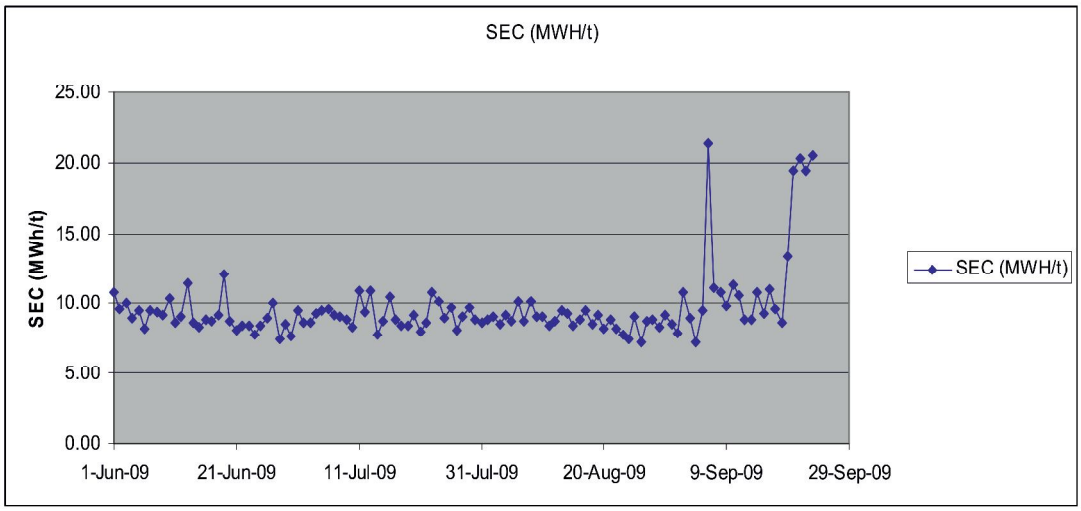

Figure 3: SEC over the period 1 June to 23 September 2009

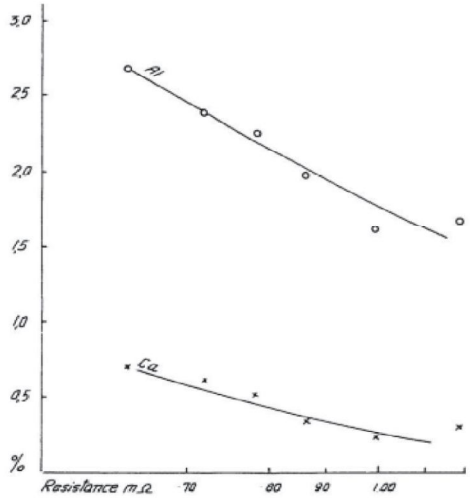

Figure 4: Relationship between metal composition and electrode resistance in high-grade ferrosilicon [1]

3. PHASE CHEMISTRY OF THE DIG-OUT SAMPLES

The digout samples were prepared for Scanning Electron Microscopy (SEM) and phase analysis by Energy Dispersive Spectroscopy (EDS). Powder X-ray Diffraction was used to confirm the phases present in selected samples.

The taphole samples revealed pertinent information on the reasons for tapping problems:

- The presence of significant quantities of slag containing silicon carbide and refractory oxide phases between the electrode crater and taphole. The slag is unexpectedly enriched in alumina containing the following oxide phase assemblages:
  - $Ca_2Al_2SiO_7$ (C_2AS); $CaAl_2Si_2O_8$ (CAS_2); $CaAl_{12}O_{19}$

- $Ca_2Al_2SiO_7$ (C_2AS): $CaAl_4O_7$
- $Ca_2Al_2SiO_7$ (C_2AS); $CaAl_2Si_2O_8$ (CAS_2); Al_2O_3
- $CaAl_2Si_2O_8$; $Al_6Si_2O_{13}$; slag
- The presence of Sialon and possibly silicon oxy-carbide (figure 5). Silicon oxy-carbide and silicon oxy-nitride compounds were previously reported from the digout of ferrosilicon furnaces [2, 3] but this may be the first documented occurrence of sialon in a ferrosilicon furnace. Sialon is stable to very high temperatures under inert conditions (approximately 2800°C), further contributing to the refractory nature of the samples.
- The ubiquitous presence of intimate intergrowths of SiC and $CaAl_2Si_2O_8$ (the intergrowth was identified on the basis of a consistent 1-to-2 atomic ratio of Ca-to-Al and an oxide total in excess of 100%). It is inferred that these intergrowths formed in-situ at temperatures below the liquidus temperature of the slag.

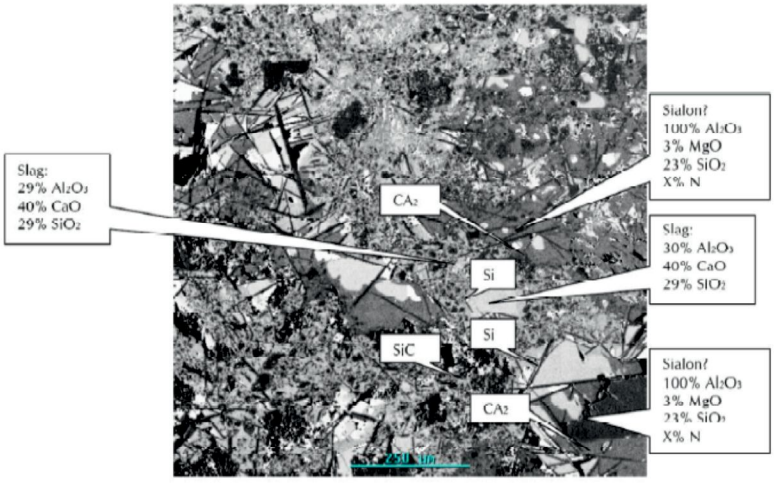

Figure 5: Backscattered electron image illustrating silicon being replaced by CA_2 or slag, as well as sialon platelets in a matrix of slag and SiC. Sialon is characterised by the absence of Ca and the presence of Mg and N (in the sialon analysis all elements are arbitrarily expressed as oxides). An equaliser filter was applied to enhance grey levels

A general feature of the samples is that they are heterogeneous in composition and, consequently, phase distribution. EDS area analyses indicate that the alumina content may vary by as much as 30% (absolute) over a matter of hundreds of micron. Such variability suggests that the banks / buildup did not form under equilibrium conditions and it is likely that significant alteration took place once the material was at least partly solidified. The most likely alteration mechanism that may result in the formation of a high-alumina residue is SiO fuming from the slag at temperatures that are too low for SiO to react with SiC to form Si and CO (the reaction SiO + SiC = Si + CO, which is stable at temperatures above approximately 1800°C figure 8). Apart from SiO fuming, less Al was transferred to the metal in the period before the September 2009 incident (figure 1), further increasing the overall alumina content in the furnace slag.

Striking examples of slag alteration and localized variability are found around droplets of silicon that are being 'replaced' by slag that predominantly comprises CA_6 or Al_2O_3 (figure 6 and figure 7). It is postulated that these replacement textures are the result of SiO generation from the slag according to the following reaction:

$$Si\ (liquid) + SiO_2\ (in\ slag) = SiO\ (gas) + SiO_2\text{-depleted slag} \quad (1)$$

which is equivalent to the reaction $Si+SiO_2=2SiO$ in the Si-O system. The reaction is favoured by low partial pressures of SiO (figure 8). In the presence of SiC, SiO_2 will oxidize Si at temperatures below about 1800C (at higher temperatures the reaction $SiO+SiC=Si+CO$ will stabilize Si).

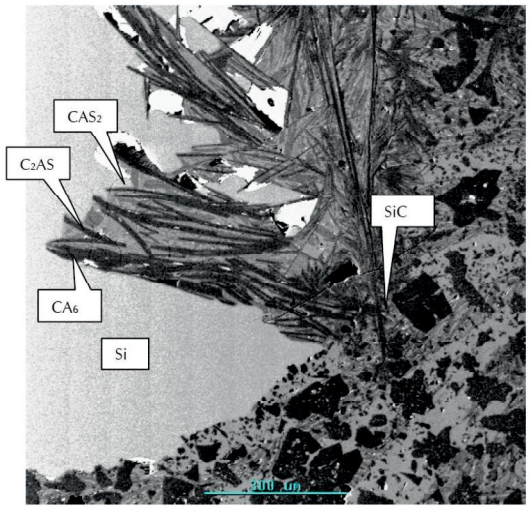

Figure 6: Backscattered electron image illustrating the replacement of Si by CA_6, C_2AS and CAS_2

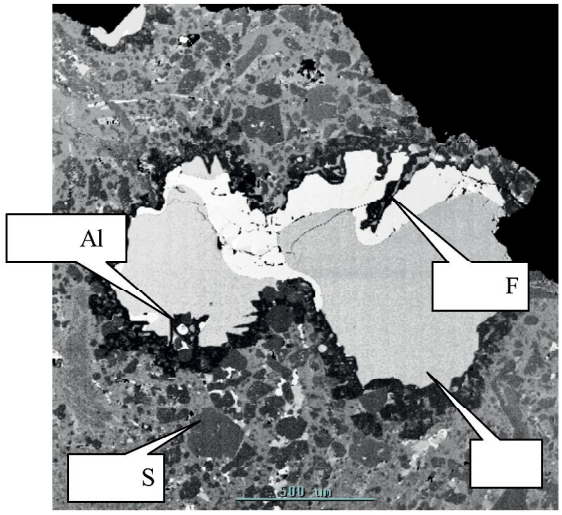

Figure 7: Backscattered electron image of Al_2O_3 (corundum) crystals surrounding metal droplets. The resorbed appearance of the Si suggests that it is being replaced by corundum

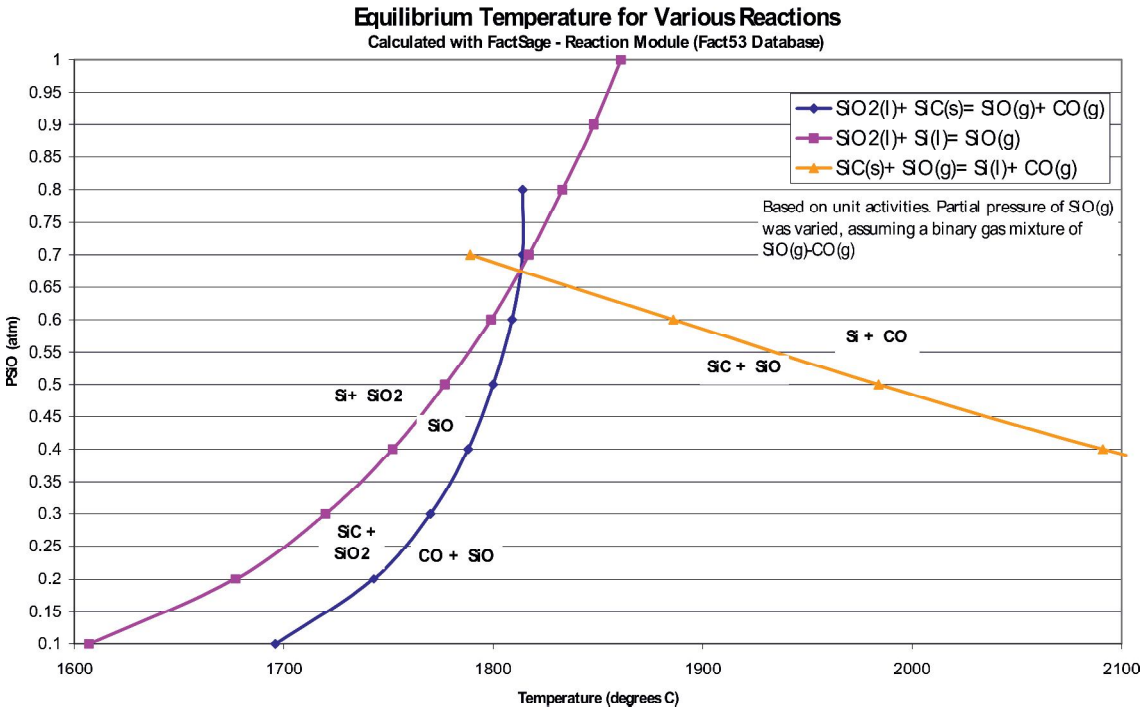

Figure 8: Subset of univariant reactions in the system Si, C and O. The reaction $Si+SiO_2=2SiO$ (pink curve) may explain the replacement of Si droplets by alumina-rich slag. At temperatures below about 1800°C (the temperature of the invariant point), SiO released by the reaction $Si+SiO_2=2SiO$ will not be able to react with SiC

The samples that show 'replacement' of Si by alumina-rich slag typically contain composite metal droplets comprising Si and $FeSi_2$. $FeSi_2$ and Si are the equilibrium crystallization products of high-grade ferrosilicon and these composite droplets are inferred to represent solidified high-grade ferrosilicon. The eutectic between FeSi and Si is at about 1230°C and it is inferred that the replacement of Si by high-alumina slag took place at temperatures below the eutectic, i.e., at low partial pressures of SiO. Phase relationships suggest that the solidus temperature of the slag is in the range of 1400° to 1500°C, confirming that significant slag alteration took place below the solidus temperature. Sub-solidus alteration supports the observation of significant compositional differences over short distances and also the porous nature of some samples (e.g., CA_6-rich zones in some samples).

The solidus triangles defining the SiO_2-depled oxide phase assemblages are outlined in figure 9. It is immediately evident that the samples are significantly enriched in alumina relative to typical furnace slag that would run at about 70% SiO_2. The equilibrium solidus temperatures of the phase assemblages are in the range of 1400 to 1500°C. Liquidus temperatures in those parts of the samples containing CA_6 and Al_2O_3 may be as high as 1900 to 2000°C.

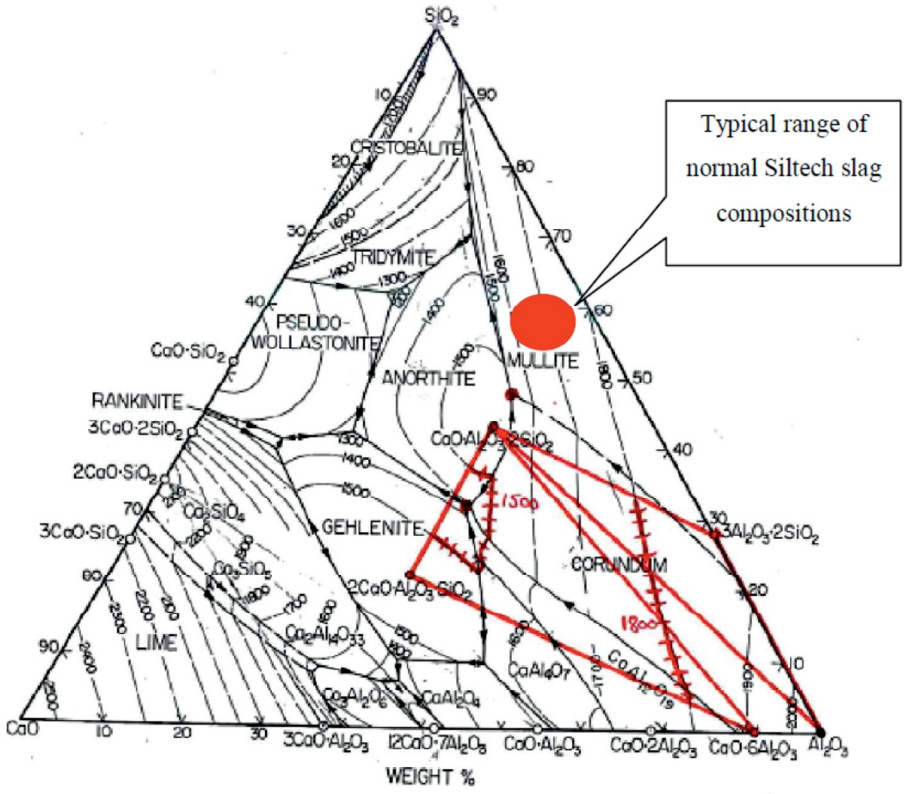

Figure 9: Phase diagram of the system SiO_2-CaO-Al_2O_3. The solidus triangles defining the SiO_2-depleted phase assemblages are highlighted in red. The solidus temperatures of the invariant assemblages are marked by dots. The 1500°C and 1800°C liquidus isotherms are marked to provide a sense of liquidus temperatures for the oxide assemblages

The phase chemical data for the samples clearly indicate that apart from the presence of highly refractory SiC, the high alumina content of the banks served to significantly increase the liquidus temperature, especially where localised formation of CA_6, Al_2O_3 and sialon had taken place.

4. ROOT CAUSE

An explanation of the events that caused the blockage is based on the following observations:

- A systematic decrease in the Al content of the hot metal, and an associated increase in the slag to metal ratio over an extended period of time prior to the event. These trends indicate that the furnace started producing more slag at the expense of metal prior to the event.
- The presence of a large amount of slag with an anomalously high alumina content in the furnace hearth
- The presence of a large amount of SiC associated with slag in the furnace hearth.

A probable explanation for the events is based on a decrease in electrode immersion over a period of about 3 months before the blockage finally developed after extensive down-time immediately before the incident. To maintain a constant electrode resistance, conditions in the furnace (electrode crater and bath) must have become electrically more conductive, possibly because of a change in gas composition in the crater and or a accumulation of slag and SiC (volatile suboxides of aluminium, e.g., Al_2O may be implicated in a change in crater conditions). As conditions in the bath became more conductive, electrode immersion decreased, resulting in the formation of more slag, which would further decrease the electrode resistance. At the same time volatilization of SiO increased the alumina content of the slag, increasing the liquidus temperature and further increasing the conductivity of the slag and possibly the vapour pressure of Al_2O in the crater. At the same time temperatures in the furnace hearth were too low for SiO to react with SiC and the SiC inventory increased. Ultimately, shallow electrode immersions driven by a bath with high electrical conductivity and a significant inventory of refractory slag and silicon carbide led to the catastrophic blockage.

Systematic work on the relationship between the PVI operating point, electrode tip position and bath chemistry is recommended to refine the control philosophy, especially when unstable furnace conditions are encountered.

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[2] Andersson, M. Reaction Mechanisms in the ferrosilicon production process. MSc. Thesis, Luleå University of Technology, 2009.

[3] Tranell, G., Andersson, M., Ringdalen, E., Ostrovski, O., Steinmo, J.J. Reaction zones in a FeSi75 furnace – Results from an industrial excavation. INFACON XII, 709-715, 2010.