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# Properties of freeze linings formed during the production of manganese ferro-alloys

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**Abstract** – Any furnace operation needs to establish a working crucible, irrespective of the original lining materials. The formation of a stable crucible from process materials in front of the hot face of the original lining material is commonly referred to as a freeze lining. The properties of the materials that form this freeze lining are different from those of the metal and slag being generated during the reduction process. This paper presents findings from work carried out on freeze lining materials recovered from a silicomanganese furnace.

*Keywords:* freeze lining properties, submerged arc furnace, silicomanganese

## INTRODUCTION

One essential factor in the operation of any furnace is that the refractory lining needs to contain the process for an extended period. Commercial considerations dictate an acceptable campaign life, although this can vary significantly based on the product type, product value, and annual quantity. In the case of silicomanganese, lining campaigns can be as little as three years and as much as twenty years, depending on factors which include the design basis, the raw materials, operator skills, and control tools available.

A lining can be as simple as carbon ramming paste installed against ceramic brick. More structured linings include carbon block and carbon brick systems, with or without graphite. Lining selection ultimately depends on the budget available and the required campaign life.

A furnace with three electrodes arranged in triangular configuration generally does not result in uniform energy distribution at the perimeter. One guideline used in lining selection is the average hearth power density, presented in units of $kW/m^2$ of open hearth area. However, taking account of electrode proximity to the lining, a second consideration is the electrode to sidewall power intensity expressed in MW/metre from electrode surface to sidewall hot face. These two factors may be used as a guide during hearth design and to estimate campaign life. Evidently, linings in low-powered furnaces last longer. However, as productivity is proportional to power input, operating companies generally aspire to higher-power operations. In this regard, and maintaining a balance between risk and reward, there are manganese alloy furnaces in operation today with a range of hearth power density from 150 $kW/m^2$ to 500 $kW/m^2$. The challenge of process containment is greater for furnaces operating above 300 $kW/m^2$.

High-powered furnaces depend on the formation and maintenance of a freeze layer onto the hot face of the lining in contact with the process. Once formed and maintained, lining life can be greatly extended. A stable freeze lining depends on the refractory materials and the boundary conditions, namely process temperature at the hot face, and cooling conditions at the cold face. The composition of this freeze lining in industrial furnaces is, however, not well documented.

## SILICOMANGANESE FREEZE LINING

The linings of five similarly sized furnaces used to produce silicomanganese were core drilled, and the positions of these cores have been documented. The original refractory lining sidewall thickness was about 550 mm, except inside the abutment containing the tap-hole blocks where the thickness had been increased to about 1000 mm.

The cores contained the original lining materials (graphite, carbon, and ceramic) as well as frozen process material. Cores extracted from the sidewalls at six elevations confirmed that the original thin wall lining was intact after up to 16 years of service. In some parts on the circumference and at certain elevations, the hot face ceramic had been replaced partially by frozen process material. The depth of the freeze layer in front of the original lining was estimated from core data and is summarised in Table I.

**Table I:** Freeze layer thickness

| | At level of tap-hole | At electrode tips | Above electrode tips | Above normal slag zone |
|---|---|---|---|---|
| Between tap-holes | 250 mm | 200 mm | 200 mm | na |
| At tap-holes | 300 mm | 250 mm | 300 mm | na |
| Closest to electrode no.2 | 700 mm | 700 mm | 700 mm | 200 mm |
| Between electrode nos. 2 & 3 | 700 mm | 700 mm | 700 mm | 200 mm |
| Closest to electrode no.3 | 700 mm | 700 mm | 700 mm | 200 mm |

The original lining within the abutment was also generally intact, although there were some indications of hot-face wear around the tap blocks.

Previous work has shown that there are variations in the composition of the freeze lining, with metal, slag, and raw materials combining to form the working lining. The core details for one of the elevations, level 3 on furnace M4, are reproduced in Figure 1.

Positions NW, N, and NE are within the tap-block abutment and therefore show more carbon brick at depth. The other three locations, namely SW, S, and SE, show the original ceramic cover in front of the carbon brick. Freeze lining materials are evident at the hot face.

A more detailed investigation has been carried out on the freeze lining from core M4/SE/3, a 350 mm section of slag freeze close to electrode no.2 at an elevation corresponding to the position of the electrode tip. The make-up of this core is described in Table II.

**Table II:** Core M4/SE/3

| Lining material | Graphite tile | Carbon brick | Ceramic brick | Loose material | Frozen slag | Loose material |
|---|---|---|---|---|---|---|
| Thickness from inside of shell (mm) | 70 | 230 | 230 | 270 | 350 | 100 |
| Cumulative thickness (mm) | 70 | 300 | 530 | 800 | 1150 | 1250 |

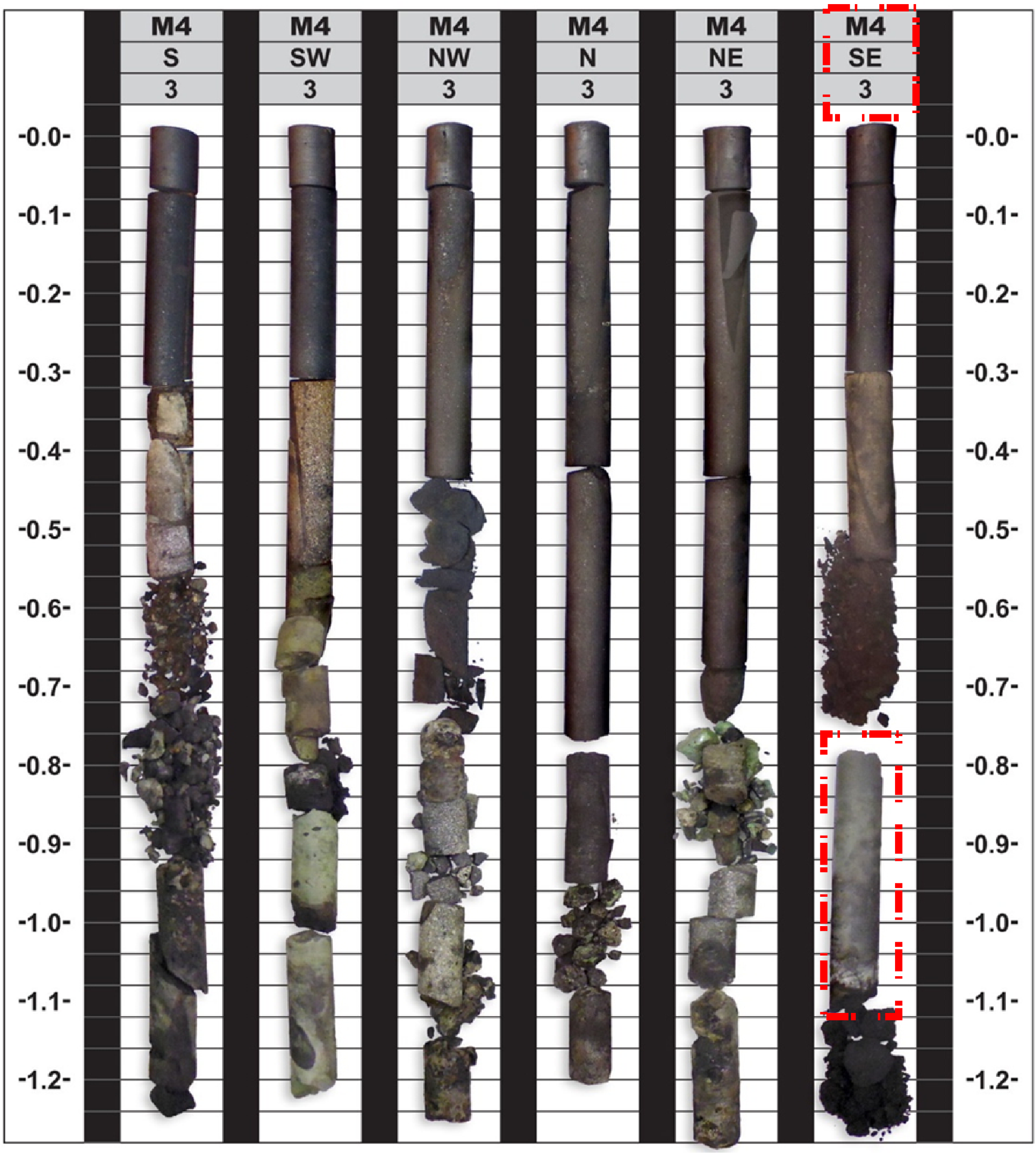


**Figure 1:** Cores recovered on Furnace M4 at elevation 3

Some samples of the loose material were analysed and found to contain varying amounts of carbon, most likely devolatilised coal, as well as quartz and partially processed manganese ore, all mixed with slag. The recovery of cores also sometimes resulted in fracture if the material was brittle. As a result, there were gaps in the cores, but these gaps did not necessarily relate to the absence of a freeze lining structure. Solid sections do, however, confirm existence of a freeze lining.

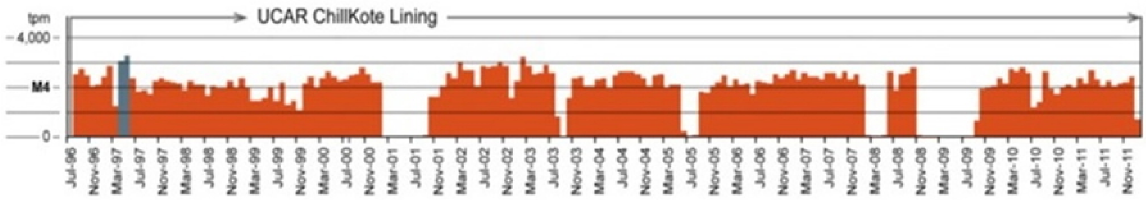


**Figure 2:** Operational performance on furnace M4 between 1996 and 2012

The furnace (M4) had two major and three minor shutdowns during the life of the lining, as shown in Figure 2. Any of the five shutdowns (identified as periods of zero production) could have caused partial removal to the working lining. The freeze section analysed might therefore have been built up over a 15 year period with discontinuities attributed to furnace shut-downs and restarts.

The 350 mm sample from M4/SE/3 was sliced into 30 sections of which 14 were analysed by Scanning Electron Microscopy (SEM) and by X-Ray Diffraction (XRD). These 14 samples were uniformly spaced along the length of the original core. The results are presented in the following figures. The mineral types were identified as either silicates or aluminosilicates. Others amounted to 1 percent or less, except for a single oxide phase in sample no.3.

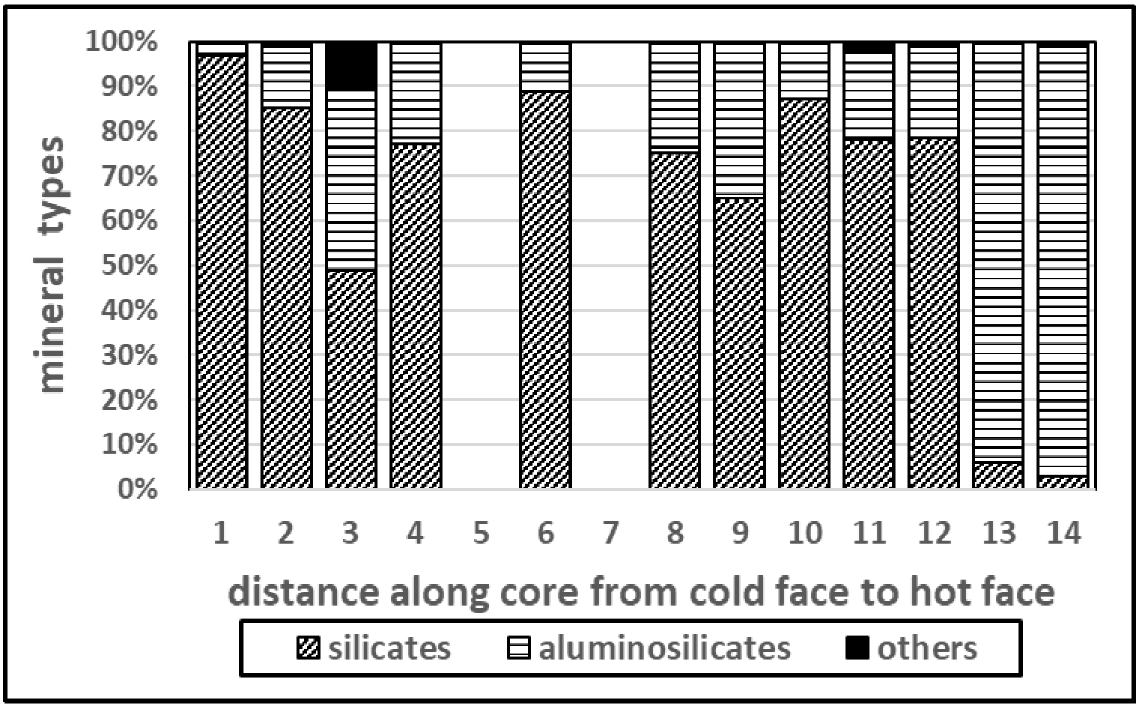


**Figure 3:** Mineral types

Barium was found only in the silicates. Manganese, iron, calcium, magnesium, sodium, and potassium appeared in both silicates and aluminosilicates. Aluminosilicates dominate at the hot face even though process slag is low in alumina.

The oxygen required for the oxides of silicon, aluminium, calcium, magnesium, barium, sodium, and potassium was calculated. Phosphorus and sulphur were assumed to form phosphides and sulphides of manganese and iron. Total oxygen was insufficient for all of the remaining iron and manganese to be present as monoxides. A metallic phase has therefore been estimated to be present within the freeze lining.

Manganese and iron are both high at the cold face, and in most cases higher than the levels in the process slag. Metallics were estimated to be present across the length of the core sample, lower at the hot face.

The concentrations of the four main slag-forming oxides, namely $SiO_2$, $Al_2O_3$, CaO, and MgO, are inversely proportional to the manganese and iron levels. The high level of alumina at the hot face corresponds with the presence of aluminates, as shown in Figure 4.

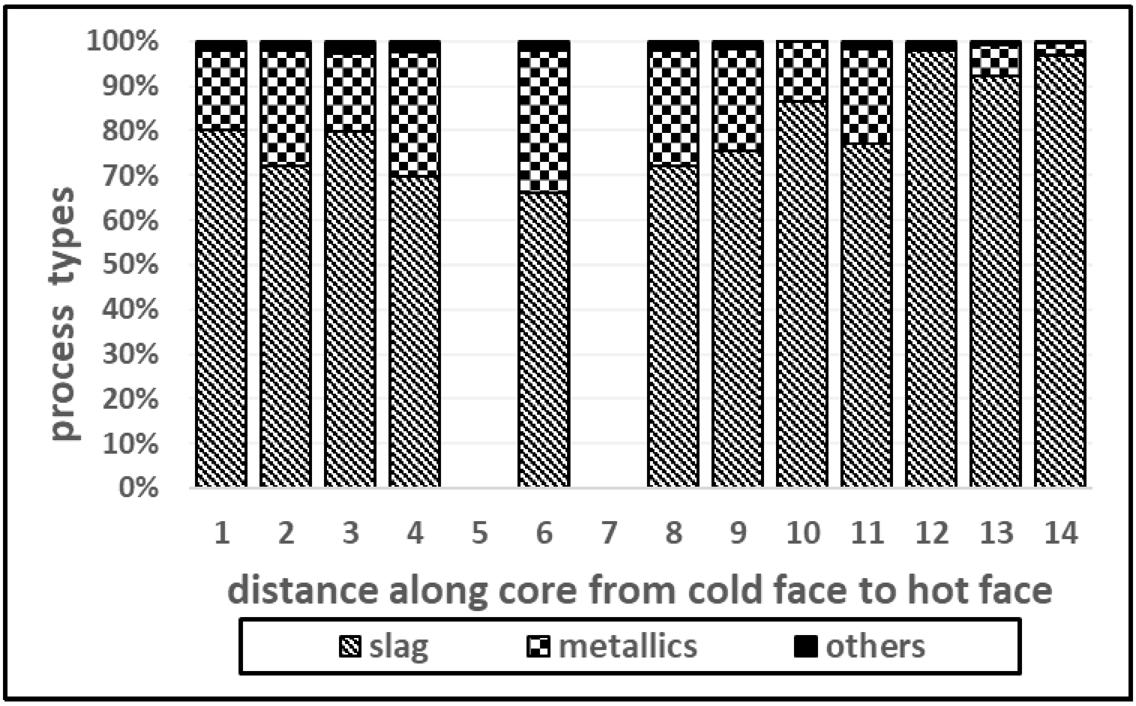


**Figure 4:** Process materials

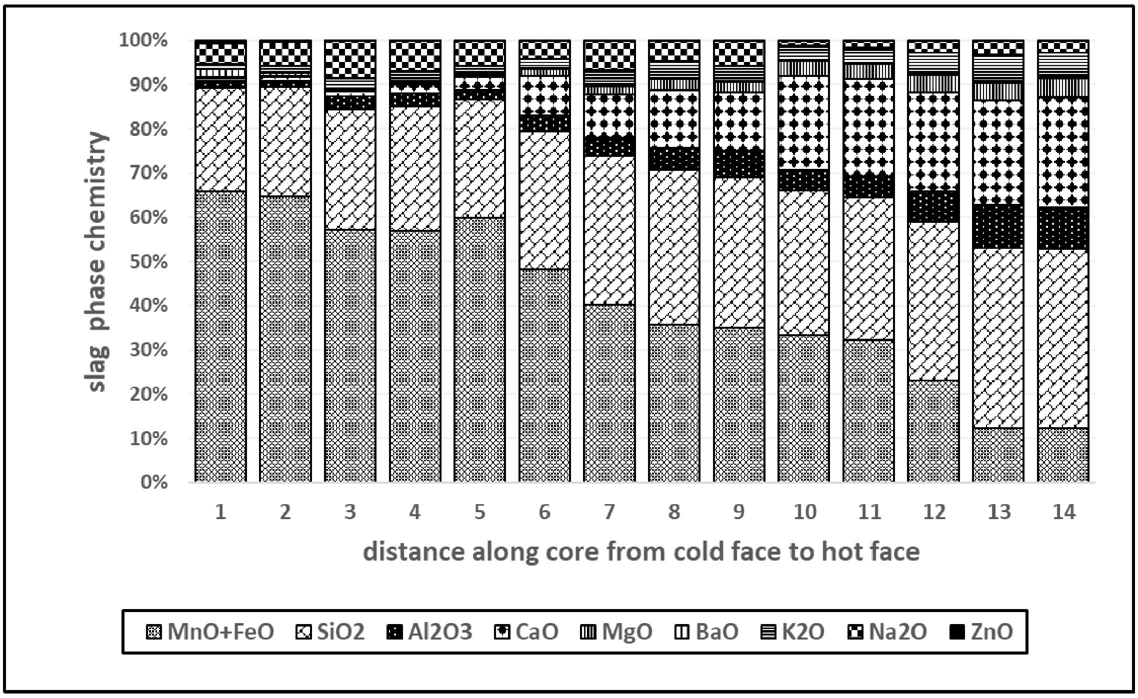


**Figure 5:** Slag chemistry

Zinc oxide was found to be present only at the cold face of the freeze lining. The levels of alkali oxides in the freeze lining core indicate concentration from raw materials, and there is an inverse relationship between sodium oxide and potassium oxide from cold face to hot face. Barium oxide concentrations are higher at the cold face.

Overall, it is noted that there are significant chemical differences in freeze lining material from cold to hot face, and that the freeze material does not have the same chemistry as the regularly tapped process slag.

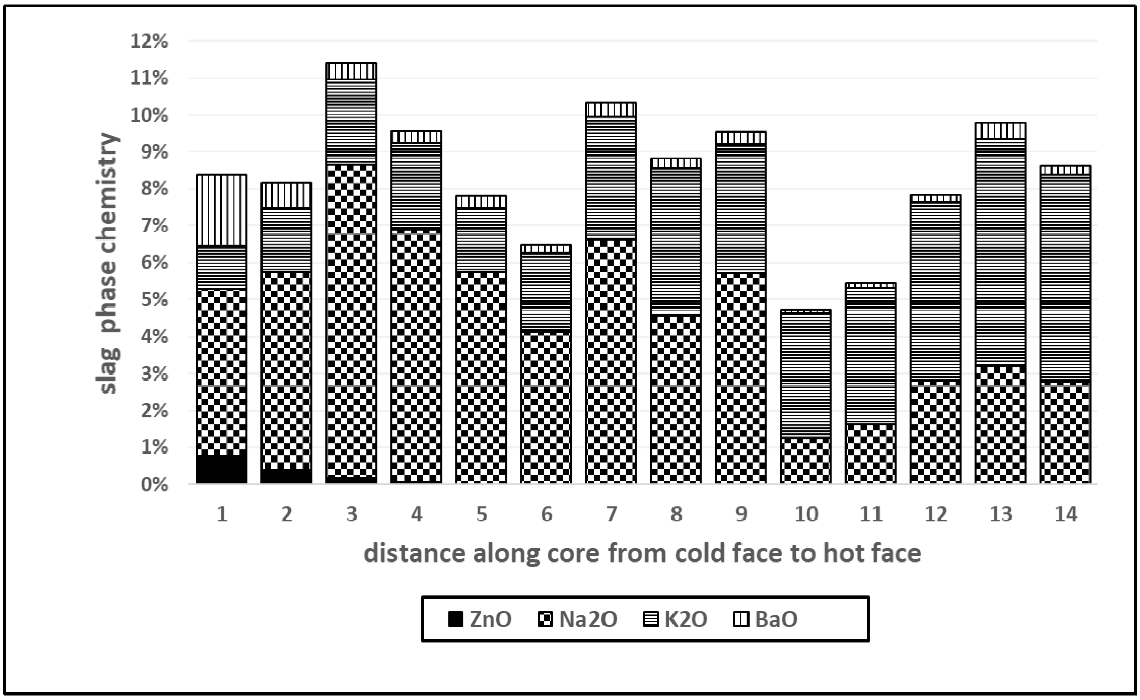


**Figure 6:** Minor oxide slag chemistry

The circulation of alkali metal oxides in the burden of a submerged arc smelting furnace has been documented. In the temperature range of 750°C to 950°C, zinc, potassium, and sodium may all exist in a reducing atmosphere such as in the burden of a smelting furnace. However, their migration towards cooler regions of the furnace, and conversion into more stable compounds is to be expected. While it is beyond the scope of this paper to review the formation mechanisms, it is adequate to highlight the fact that oxides of zinc, sodium, and potassium have all accumulated in the silicomanganese freeze lining at concentrations which vary across its length.

## FURNACE DETAILS

The freeze lining will have been built up over time, with the gradual solidification of compounds settling out from the process slag and trapping metallics during this process. Nevertheless, the thermal conductivity of the different types of materials recovered from the freeze lining indicates a range of between 1.0 and 2.4 W/mK at room temperature. As shown in Table I, the thickness of the freeze lining was uniform. Considering typical thermal conductivity values for ceramic brick at temperatures expected in the freeze lining, an assessment has been carried out of the thermal profile within the working lining.

The process factors and boundary conditions for these furnaces were as follows:

Average power: 14 MW
Maximum power: 16 MW
Hearth power density: 250 kW/m$^2$
Electrode to sidewall power intensity: 2.2 MW/m
Open shell water cooling
Process freeze in front of thin wall lining: 700 mm
Process freeze within tap block abutment: 250 mm

With this set of parameters, an average sidewall energy flux of around 3000 W/m² has been estimated, equivalent to the rate of transfer of energy of around 350 kW to the cooling water. This is equivalent to about 2.5 percent of input power.

It is to be expected that freeze lining thickness will decrease as either or both of hearth power density and electrode to sidewall power intensity increase. There are both theoretical and practical limits to the efficiency of energy removal by water at the cold face of the lining.

There is a maximum power input for a furnace with any given set of dimensions producing a specific product while meeting with acceptable lining campaign life. These furnaces producing silicomanganese could have operated successfully at a hearth power density of up to 400 kW/m² while maintaining a smaller freeze lining and still providing long service life. It is estimated that operating this size of furnace at an average of 22 MW would have created significant productivity gains while maintaining lining integrity. At 22 MW, an increase in sidewall energy flux to around 5000 W/m² has been estimated, equivalent to the rate of transfer of energy of around 600 kW to the cooling water. This is equivalent to a reduction in freeze lining thickness from 700 mm to 450 mm, and a small increase in energy transfer to about 2.7 percent of input power.

## CONCLUSIONS

This evaluation of lining performance in a 16 MW silicomanganese furnace has shown that the freeze lining:

- prevented any damage to the original lining materials over a 16 year campaign
- transferred about 2.5 percent of input power to the cooling water while in steady state
- is non-homogeneous and contains metallics as well as slag
- has a relatively low thermal conductivity and can provide a hot face which insulates the original lining to a temperature well below 400°C
- absorbs zinc and alkali oxides, confirming their migration through the furnace

The depth of the freeze lining also indicated that this furnace could have operated as successfully at 22 MW, a significant factor in furnace design for high-productivity performance.

## NOTE

Sample chemistries were analysed by Energy Dispersive Spectroscopy (EDS) using 2* Oxford Instruments X-Max 150 mm² Silicon Drift Detectors on a Zeiss Sigma HD Analytical Scanning Electron Microscope in the School of Earth and Ocean Sciences at Cardiff University. Prior to analysis, samples were coated with a 10–15 nm thick layer of carbon to prevent charging. Data was acquired at 20 kV with a nominal beam current of 2 nA. Backscatter electron (BSE) imaging was performed using a 5 channel multi diode detector.

Samples were imaged using BSE, and chemically mapped using EDS to determine the types and abundances of minerals present. Mapping was performed with a step size of 7 to 11 µm, with 70 to 80 fields which were montaged to form a single region for each sample. Sample-specific BSE images and element maps for each element identified were also provided. A layered map of Al, Fe, Mn, and Si is also included for each sample.

Mineral abundances were calculated using the *Analyse Phases* function in the Oxford Instruments Aztec software. This function works by thresholding individual elements to distinguish the different minerals present. Due to variable cation substitution within mineral phases, it was difficult to assign a name to most minerals identified in the element maps. Instead, the minerals have mostly been named as oxides, silicates, or aluminosilicates, with the prefix of major cations (above 2.5 wt%) listed in order of decreasing abundance. Identification of some minerals was complicated by spectral mixing with surrounding phases. Any minerals with an abundance less than 1 vol.% were referred to as trace. Trace minerals that were identified but could not be thresholded include jacobsite, alabandite, apatite, and quartz.

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