A SYSTEMATIC APPROACH TO THE DEVELOPMENT OF SELF-HEALING SLAG REFRACTORY SYSTEMS

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ABSTRACT

In conventional pyrometallurgical reactors, aggressive liquid slags, salts and metals attack refractory materials leading to the continuous dissolution. The presence of corrosive slags, forced convection, and high process temperatures in the pyrometallurgical reactors may lead to the rapid degradation of the lining.

In the present study, a new methodology is being developed to enhance refractory life. The focus of the present study is on the detailed characterisation of the phase chemistry and slag interactions with refractories. The systematic approach includes the analysis of "as received" slag samples from smelters, post-mortem analysis of the end-of-life industrial refractory samples, isothermal laboratory slag/refractory interactions tests under controlled conditions, and FactSage predictions in Fe-Si-Mg-Cu-Pb-Al-Ca-Zn-O system to identify the conditions for minimum refractory wear.

The dissolution of refractory into the slag can occurs through infiltration of liquid into refractory via pores, continuous dissolution of the refractory components into the liquid phase and "washing out" refractory grains (direct dissolution), or through formation of a new solid at the slag / refractory interface, closing liquid pores and dissolution through slow solid-state diffusion. This study focuses on the modification of the slag chemistry to prevent the direct dissolution of refractory components into the slag and also to block the pores with newly formed solid phases. It has been shown that with accurate information on the slag/refractory phase equilibrium, self-healing refractory systems can be designed and operated by modification of the slag composition to obtain optimum slag/refractory combinations.

INTRODUCTION

In Kazzinc pyrometallurgical copper operation IsaSmelt is used for smelting of the sulfide concentrates, fluxes, and residues to produce slag and matte; the matte phase is converted into blister in Pierce-Smith (PS) reactor. Magnesia-chromite-based refractories are used to provide resistance to corrosion/erosion and to minimize the heat loss of reactors. The service life of the reactor lining is determined by several variables, such as, liquid bath temperature, chemical composition on of the liquid bath, liquid properties (density, viscosity, and diffusivity) and intensity of bath agitation [1-5].

IsaSmelt and (PS) converter are operated under high process temperatures and highly convective and chemically aggressive baths that can lead to rapid degradation of the refractory materials and possible unplanned shutdown. In the present study, the effects of chemistry and operational parameters have been investigated to propose strategies for increasing service life of the PS converter.

SYSTEMATIC APPROACH FOR CHARACTERISATION OF SLAG/REFRACTORY INTERACTIONS

A systematic experimental approach for the lsag / refractory interaction has been followed (see Figure 1) aimed at development of a self-healing refractory/slag process. The approach is generic and may be used for the most pyrometallurgical processes to investigate the chemical refractory degradation. The strategy is to ascertain microstructural and compositional information on the slag/refractory interactions from possible industrial sources such as end-life used bricks and slag samples. Next, phase chemistry is investigated using thermodynamic modelling followed by various experimental techniques under laboratory conditions to confirm the possible reasons and mechanisms of refractory degradation. From this, potential strategies are proposed through modification of the slag composition, operational parameters and refractory types to slow down the refractory degradation. The self-healing process of refractory/slag interaction is achieved through (1) formation of a protective solid primary phase layer on the interface between refractory and molten slag and (2) blocking the pores by formation of a secondary solid phase(s) stopping the continuous stream of infiltrated liquid slag into the refractory. Importantly, the effects of proposed changes on the whole process, such as financial performance and productivity of plants, should be investigated.

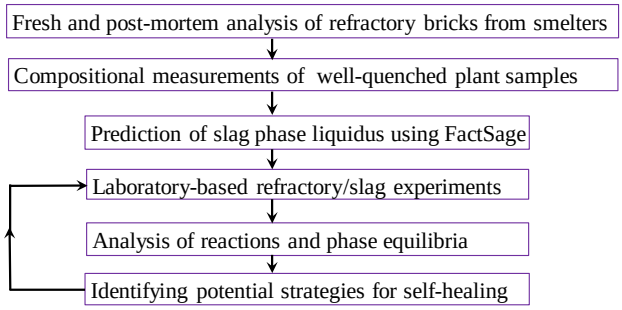

Figure 1. Systematic approach for refractory/slag investigation

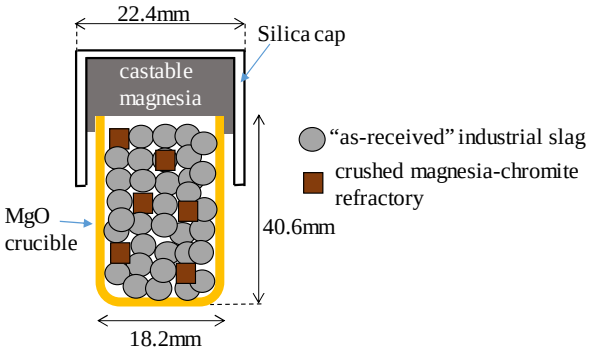

Figure 2. Isothermal equilibration approach for slag/refractory investigation

METHODOLOGY OF EXPERIMENTS AND ANALYSIS

In the present study, isothermal equilibrium experiments were performed to measure the equilibria between slag and refractory at various temperatures (Figure 2). The crushed refractory grains mixed with "as-received" slag from PS converter were placed in MgO crucibles. A silica lid was placed as a crucible cap and glued to inhibit the reactions between the furnace atmosphere and the molten slag. The whole crucible was heated to 1220 and 1180 ˚C using a tube furnace and equilibrated for 6h. After a designated time, the sample was quenched in to water. The samples were sectioned, mounted in epoxy resin, and polished for metallographic examination and microanalysis. Electron probe X-ray micro analysis (EPMA) was used to characterize the microstructures and to measure the phase compositions. An electron-probe X-ray micro-analyzer, Superprobe JEOL (a trademark of Japan Electron Optics Ltd., Tokyo) 8200L EPMA equipped with five wavelength dispersive X-ray detectors was used to determine the phase compositions. Appropriate standards were selected and the ZAF corrections were made using software supplied by JOEL.

RESULTS AND DISCUSSION

Characterization of New and Used IsaSmelt and PS Converter Bricks

The main components in the typical microstructure of a fresh magnesia-chromite brick are large fused grains (periclase plus secondary chromite, 2-4mm diameter), primary chromite (59.4 wt% Cr_2O_3, 18.9% MgO, 9.8% FeO, 11.7% Al_2O_3) and pores (Figure 3.a)

The post-mortem analysis of the PS converter used brick (Figure 3.b) indicates that the brick is fully infiltrated by the liquid phases (slag, white metal and metallic copper) meaning that channels/pores were not blocked by formation of the solid phases such spinel or forsterite. As a result, refractory could be dissolved continuously into the slag phase.

However, a relatively thick layer of spinel phase formed at the interface between IsaSmelt brick and liquid slag that slowed down the chemical dissolution of refractory into the slag phase(Figure 3.c). Also, infiltration depth of slag into the refractory is shallow indicating formation of a secondary solid phases including spinel and forsterite [(Fe, Mg)$_2$SiO$_4$] blocking the pores.

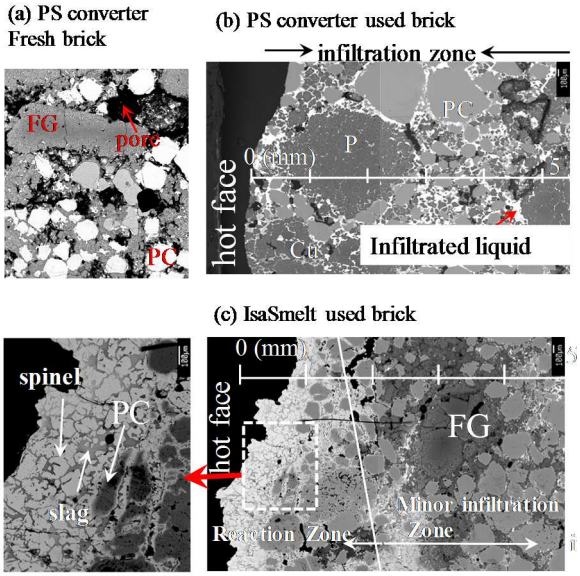

Figure 3- Back-scattered electron micrographs illustrating the microstructures of (a) fresh magnesia-chromite brick, (b) PS converter used brick taken from beneath the tuyere and (c) IsaSmelt used brick taken from slag/matte area. Fused periclase grain (FG), and primary chromite (PC) [6].

Industrial Slag Samples from IsaSmelt and PS Converter

The as-received slag samples were characterized by SEM and EPMA to ensure that the bulk composition of the industrial slag in the used brick and the laboratory tests were representative of the PS converter and IsaSmelt operations. The phase assemblage of PS converter samples consists of liquid slag and small proportion of the spinel phase (see Figure 4). In IsaSmelt plant samples, entrained matte and spinel are the typical phases within the liquid slag (see Figure 4).

Thermodynamic Modelling

To interpret the various mechanisms of refractory dissolution (i.e. direct and indirect) into slag, the thermodynamic calculations for the Fe-Si-Mg-Cu-Pb-Al-Ca-Zn-O system were undertaken using the FactSage program [7] in conjunction with the private PYROSEARCH database for condensed phases (slag, spinel, wüstite, olivine, melilite, and pyroxene) at the fixed temperature (1220 and 1170 ˚C in PS converter and IsaSmelt respectively) and fixed oxygen partial pressures (10^{-7} and 10^{-8} atm in PS converter and IsaSmelt respectively). The Fe/SiO_2 ratios of slag vs MgO in slag for the PS converter and IsaSmelt industrial slag compositions along with the FactSage outcomes [7] are illustrated in Figure 5.

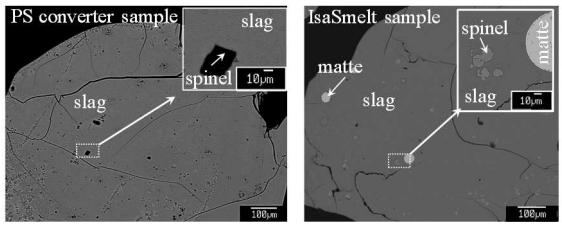

Figure 4. Typical back-scattered electron micrographs of well-quenched PS converter and IsaSmelt slag samples.

Isothermal Laboratory Static Experiments with IsaSmelt and PS Converter and Bricks

To further investigate the chemical wear mechanisms of refractory materials, the isothermal static experiments were performed immersing a magnesia-chromite refractory fingers in the liquid industrial slags of IsaSmelt and PS converter that contained in MgO crucible at temperatures of 1170 ˚C and 1220 ˚C respectively. After a designated time, the samples were quenched into water, sectioned and analyzed with SEM and EPMA [6].

As can be seen from Figure 6.a, the infiltration depth of PS converter slag into the brick is significant and no protective layer of solid phases i.e. spinel or forsterite was formed at the interface between refractory and liquid slag. This is consistent with the post-mortem analysis of the PS converter used brick (Figure 3.b).

Figure 6.b indicates the formation of a spinel [(Fe, Cu, Zn, Mg)O.(Fe, Al, Cr)$_2$O$_3$] layer at the refractory/slag interface. Pores and potential liquid channels were blocked by the formation of a secondary phases i.e. spinel forsterite [(Fe,Mg)$_2$SiO$_4$]. This observation is consistent with the post-mortem analysis of the IsaSmelt used brick (Figure 3.c).

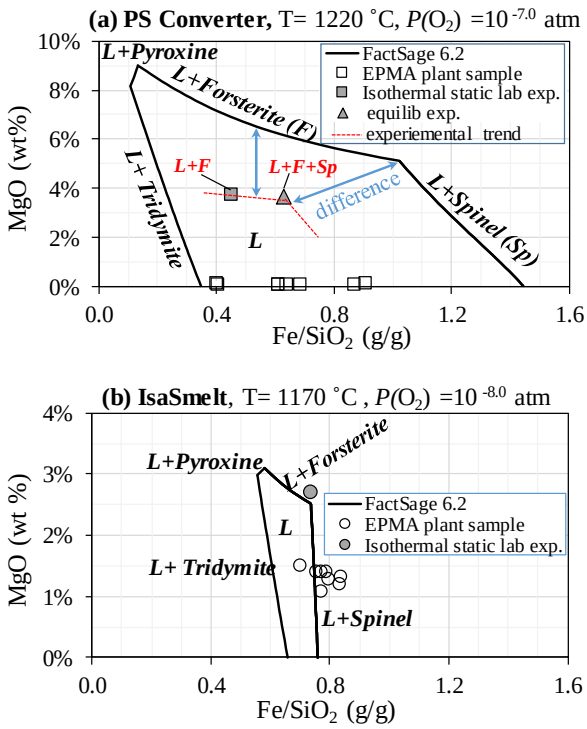

Figure 5. Liquidus presented as MgO vs Fe/SiO_2 ratio in slag plant samples, thermodynamics calculations in Fe-Si-Mg-Cu-Pb-Al-Ca-Zn-O system by FactSage [7], and isothermal laboratory experiments in (a) PS converter and, (b) IsaSmelt [6] processes. Liquid slag (L)

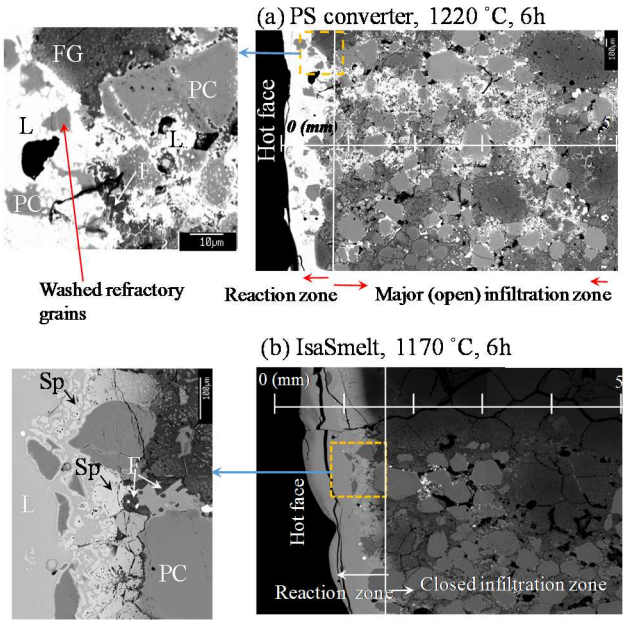

Figure 6- Back-scattered electron micrographs illustrating the microstructure of laboratory experiments with (a) PS converter slag and refractory brick at 1220 ˚C/6h immersion time, and **(**b) IsaSmelt slag and brick at 1170 ˚C/6h immersion time and,. Primary chromite (PC), liquid slag (LS), fused grain (FG), and spinel (Sp) [6].

Analysis of Reactions and Phase Equilibria

Liquidus presented as MgO concentration as a function of Fe/SiO_2 in slag indicates that the slag phase in the PS converter plant slag samples (having MgO concentration less than 0.1 wt %) is located in the fully liquid area (Figure 5.a). In the isothermal static laboratory experiments, the slag was saturated with approximately 4 wt% MgO (see Figure 5.a). The average value of the Fe/SiO_2 ratios in the plant samples and the static laboratory experiment are close. The results from post-mortem analysis, well-quenched plant samples and the laboratory test indicate that the PS converter slag is far away from any of primary phase fields of the main slag-refractory forming phases due to low MgO and Fe/SiO_2. It appears that slag chemistry and brick quality (pores, cracks, etc.) are the main degradation reason because grain bonds (mainly MgO components) are gradually dissolved into the liquid slag resulting in washing out the grains (mainly primary chromite) into the bath area (see Figure 6.a). This fast direct dissolution of refractory may be turned into the indirect dissolution by modification of operational conditions such as temperature and fluxing strategy.

Concentration of MgO in the IsaSmelt plant slag samples are between 1 to 1.5 wt pct vs Fe/SiO_2 ratios having values of 0.7-0.85 (see Figure 5.b). Formation of the protective spinel layer at the interface between refractory and slag in postmortem analysis and isothermal static lab experiments are because the liquid slag phase is located close to the liquidus - the line between the fully liquid and the liquid in equilibrium with spinel (see Figure 5.b). Compared to the PS converter brick, the indirect dissolution of the IsaSmelt refractory into the slag phase slowed down the refractory degradation.

Identification of Potential Strategies for Self-Healing and Experimental Actions

It appears that the degradation rate of IsaSmelt brick is significantly lower than that of the PS convertor due to different mechanisms of refractory dissolution. To increase the service life of the PS converter, fluxing strategy and the operational conditions may be modified to turn the direct mechanism of refractory dissolutions into the indirect. In the present study, the effect of temperature on the phase assemblage at the refractory/slag interface was investigated using isothermal equilibration approach to confirm the thermodynamic modeling trends.

In addition to the unreacted brick grains shown in Figure 7.a, the phase assemblage at 1220 ˚C equilibration experiment consists of liquid slag, forsterite and a thin layer of spinel (≈1 µm) formed at the interface between slag and primary chromite grains. The present experimental trend plotted from the isothermal static and equilibration laboratory experiments are different from FactSage predictions (see Figure 5.a). Compared to FactSage predictions [7], the highest solubility of MgO in slag to form forsterite primary phase is approximately 2.5 wt% lower for a given Fe/SiO_2 measured in the present experimental study. In addition, it appears that the spinel phase forms at lower Fe/SiO_2 ratio in slag for the fixed MgO in the present investigation (see Figure 5.a). The difference between FactSage predictions [7] and experimental results is due to a number of reasons, most important believed to be impurities in the industrial slag/refractories that were not taken into account in thermodynamic modelling.

Similar phase assemblage is observed at 1180 ˚C experiment having liquid slag, forsterite, and thicker spinel layer (≈4 µm) formed due to reaction between the primary chromite phase and liquid slag (Figure 7.b).

In addition, proportion of the newly formed phases i.e. liquid slag, forsterite and spinel was calculated using lever rule. It appeared that proportions of liquid slag, forsterite and spinel did not change significantly by decreasing temperature from 1220 ˚C to 1180 ˚C for the given Fe/SiO_2 and MgO in slag (Figure 8). As a result, it may be suggested to decrease operational temperature of PS converter without the risk of solid accumulation. This might increase the probability of the pore blockage by forsterite and formation of the spinel layer on the interface. Next, the compositions of liquid slag at 1220 ˚C to 1180 ˚C did not alter significantly (Figure 8).

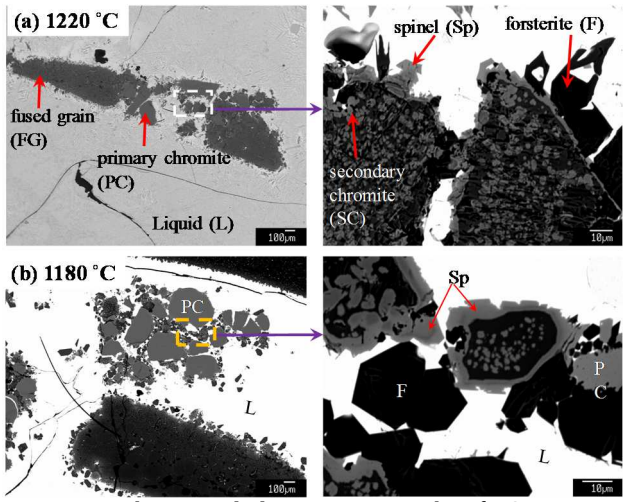

Figure 7: Back-scattered electron micrographs of PS converter slag and the crushed magnesia-chromite brick equilibrated at 6h at (a) 1220 ˚C and (b) 1180 ˚C.

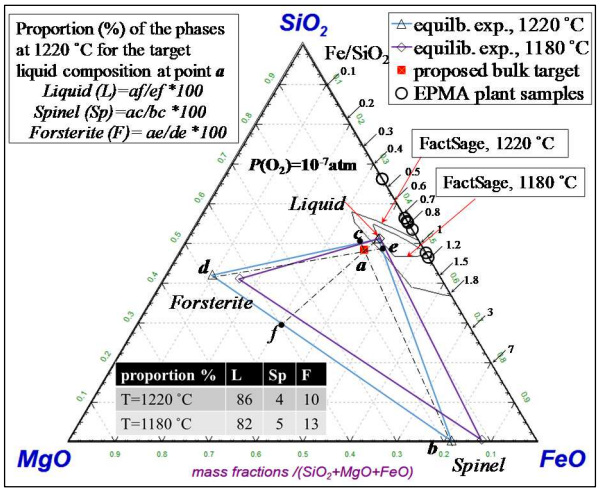

Figure 8. Projected MgO-SiO_2-FeO ternary diagram at $P(O_2)$ = $10^{-7.0}$ atm for the Fe-Si-Mg-Cu-Pb-Al-Ca-Zn-O system.

CONCLUSSION

A systematic experimental approach was used to characterize refractory/slag interactions. The approach includes microstructural and compositional analysis of the fresh/used industrial refractory, slag samples taken from smelters, and isothermal laboratory experiments followed by thermodynamic modelling. From this information, strategies are proposed/hypothesized and are experimentally tested in laboratory to confirm information on the phase chemistry of slag/refractory interactions. From this information, the strategies are proposed to decrease the chemical wear of refractory materials. Compared to the IsaSmelt, the refractory degradation in the PS converter process appeared to be more significant.

Phase analysis of the PS converter samples (used brick, slag plant samples, and isothermal static and equilibration experiments) confirmed that the dissolution mechanism of refractory into the slag is direct for the current operational conditions such as temperature and fluxing. Potential solution such as decreasing the operational temperature and fluxing strategy i.e. modification of MgO Fe/SiO_2 was suggested.

This study demonstrates a systematic approach to be considered to the design of refractory systems through fundamental understanding of the slag/refractory interaction and control of slag composition.

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