

**THERMOCHEMICAL MODELING OF REFRACTORY CORROSION IN SLAGGING
COAL GASIFIERS IN SUPPORT OF DEVELOPMENT OF IMPROVED
REFRACTORY MATERIAL**

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ABSTRACT

Slagging coal gasifiers suffer from significant attack by the coal slag on the refractory liner. To better understand the corrosive attack on the refractory the interactions were thermochemically simulated. The slag is observed to penetrate the refractory, which complicates modeling the phase behavior of the slag-penetrated interior of the refractory. To address this issue a simple strategy was adopted such that step-wise changes in composition with decreasing slag content were assumed to account for the compositional changes as slag penetrates the refractory, at least partially through its thickness. The thermochemical equilibrium calculations following this strategy typically yielded three solution phases as well as the stoichiometric crystalline phases AlPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ depending on composition/penetration. In addition, under some conditions a slag liquid miscibility gap exists such that two slag liquids co-exist.

INTRODUCTION

Coal gasification offers one of the most versatile and clean ways to convert coal into electricity, hydrogen, and other valuable energy products. The first coal gasification electric power plants are now operating commercially in the United States and in other nations, and it is predicted that coal gasification will be at the heart of future generations of clean coal technology plants for several decades into the future. For example, at the core of the U.S. Department of Energy's FutureGen prototype power plant will be an advanced coal gasifier.

Rather than burning coal directly, gasification uses partial oxidation in the presence of steam at high temperatures and pressures to react coal to CO, hydrogen, and minority hydrocarbon gases and byproducts. Thus a gasifier differs from a combustor in that the amount of air or oxygen available inside the gasifier is carefully controlled so that only a relatively small portion of the fuel burns completely.

The mineral content of the coal is liberated in the partial combustion process and this byproduct must be eliminated from the gasifier through removal from the bottom. The most common type of gasifier is a slagging gasifier where the temperatures in the gasifier exceed the melting point of the minerals in the coal and thus melt, forming a slag. Such gasifiers can operate at temperatures up to 1650°C in a reducing environment governed by the gasification process. These conditions require the use of ceramic refractories as liners to protect the combustion chamber walls from the high temperatures and contact with the corrosive slag. Currently, during combustion molten oxide slag flows along the surface of the liner and reacts with the refractory hot-face often causing relatively rapid failure.¹ Most refractories also possess significant porosity, and the slag is typically observed to infiltrate some distance into the refractory. Ex situ work in the early 1980's showed improved corrosion resistance for chromia-magnesia

and chromia-alumina spinel refractories where increasing chromia content yielded better performance.²⁻⁴ A new series of high chromia-alumina sesquioxide refractories developed at the U. S. Department of Energy National Energy Technology Laboratory in Albany, Oregon has shown significant improvement in behavior in gasifier environments.⁵ Examination of refractories after significant service life in a gasifier and from laboratory 24-hour slag-refractory cup tests have shown that during operation, the molten slag (i) dissolved the refractory, (ii) reacted with the sesquioxide to produce spinel, and (iii) penetrated into the 85% dense bodies.

Little is known about the progression of slag-refractory interactions, including the chemical thermodynamics of the reactions, the thermochemical and phase behavior of the liquid, and the nature of the resulting complex phases that form. Zhang and Lee⁶ have creatively described use of phase equilibria for comprehending refractory corrosion. Hirata, et al⁷ have developed an empirical relation for the corrosion rate in these systems. And Jak, et al⁸ have coupled experimental and thermodynamic modeling to provide a basis for obtaining a thermochemical understanding. This background sets the stage for performing thermochemical calculations that simulate corrosive attack of refractories in slagging gasifiers.

CALCULATIONAL BASIS

Thermochemical Equilibrium Calculations

The basic data were obtained from the 1996 version of the SGTE Pure Substance Database⁹ that accompanies the FactSage¹⁰ thermochemical software package used to perform the thermochemical calculations. The slag liquid as well as spinel and sesquioxide solid solution phases are important in the system equilibria, and therefore models of these needed to be included in the calculations of phases considered. These are available for use with FactSage and are based on assessments and optimizations reported in the literature.¹¹⁻¹⁷

Materials

The composition of the refractory was adopted from the Harbison-Walker AUREX[®] 95P which was developed based work with U. S. Department of Energy National Energy Technology Laboratory in Albany, Oregon 92 wt% chromia, 4.7wt% alumina, and 3.3wt% phosphate (P₂O₅).¹⁸ The slag composition was based on a simplified Pittsburgh No. 8 coal:¹⁹

Component	Wt%
SiO ₂	47
Al ₂ O ₃	25
Fe ₂ O ₃	17
CaO	6
MgO	1
Na ₂ O	1
TiO ₂	1
K ₂ O	2

Conditions

Temperature - 1450°C
Total pressure – 68 bar
Oxygen partial pressure (fixed) – 10⁻⁸ bar
No other gaseous species present
No carbon present

CALCULATIONAL RESULTS

Thermochemical equilibrium calculations were performed using the FactSage computational software package.¹⁰ Initial calculations were performed to determine the phases in solely the slag and the refractory under the conditions described above. Equilibrium states were then calculated for the combined slag and refractory, with compositions modified to simulate infiltration of slag into the refractory.

Slag

The equilibrium slag phase composition was computed at both an operating temperature of 1450°C and low temperature of 300°C. At 1450°C the slag phases were simply 7.6wt% KAlSi_2O_6 (leucite) with the remainder a single slag liquid. The slag composition under equilibrium conditions at 300°C consists of

Phase	Wt.%
Al_2SiO_5 andalusite	22.69
SiO_2 low quartz	18.98
$\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ corundum	17.49
$\text{CaAl}_2\text{Si}_2\text{O}_8$ anorthite	13.95
KAlSi_3O_8 K-feldspar	11.00
$\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$	9.63
$\text{Mg}_4\text{Al}_{10}\text{Si}_2\text{O}_{23}$ sapphire	5.30
TiO_2 rutile	0.98

Refractory

At 1450°C the refractory composition under equilibrium conditions is computed to consist of a sesquioxide (corundum) phase plus 5.7 wt% of aluminum phosphate (AlPO_4). At 300°C the FactSage database yields two sesquioxide phases that result from a solid-solid miscibility gap in the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system that is computed to form, together with 5.7 wt% of aluminum phosphate. Besmann, et al²⁰ in modeling this system indicates the miscibility gap will not extend to such a high chromia content. Recalculating the system without a miscibility gap yields a single sesquioxide phase plus the 5.7 wt% aluminum phosphate.

Refractory-Slag Equilibria

In order to simulate the interaction with slag at the refractory surface it was assumed that a 50 wt% mixture of refractory and slag equilibrated at 1450°C. As noted above, the slag is observed to penetrate the refractory, which complicates modeling the phase behavior. To address this issue a simple strategy similar to that of Lee, et al²¹ was adopted that accounted for compositional changes as slag infiltrates the refractory at least partially through its thickness. It was assumed that any non-liquid (crystalline) phases that result from an equilibrium calculation of a slag-refractory composition, for example a 50 wt% refractory-slag mixture, would precipitate and not be carried into the interior of the refractory. This would engender a compositional change in the slag liquid, and a new composition would then be utilized to interact with the refractory simulating interactions at some depth. With a starting basis of the computed 50 wt% slag and refractory phase compositions, it was then assumed that 40 wt% of the new slag composition would react with 60 wt% of refractory, thus also simulating a decrease in the amount of slag present as it penetrates the refractory. This strategy was repeated in 10 wt% increments to 10 wt% slag-90 wt % refractory. The relatively high thermal conductivity of chromia allowed the assumption that temperature was constant at 1450°C.

The thermochemical equilibrium calculations following the above strategy typically yielded three solution phases as well as the stoichiometric crystalline phases AlPO_4 and $\text{Ca}_3(\text{PO}_4)_2$, depending on

composition/penetration. In addition, under some conditions there would be a slag liquid miscibility gap and two slag liquids could co-exist. Figure 1 is a plot of the total mass of each phase at equilibrium using a 100 g basis for each calculation (the two slag liquids are combined). The effect of removing the precipitating phases as the slag penetrates the refractory can be seen in the decreasing spinel content, which no longer forms at a slag percentage below a point between 20 and 30 wt%.

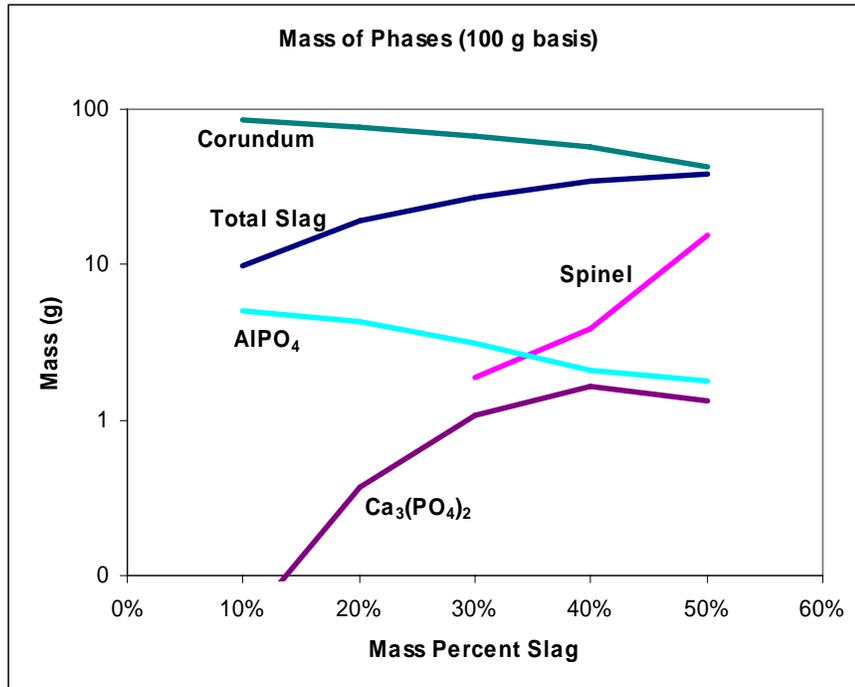


Figure 1. Mass of each phase in the equilibrated slag-refractory system under simulated conditions for penetration of the slag by the refractory (decreasing mass percent slag).

Figure 2 indicates the metal content within the slag (with the metals all present as oxides) as mass fraction versus the input mass percent slag in the simulated penetration of slag into the refractory. While most elements varied somewhat, iron in particular experienced a sharp decrease with decreasing slag content simulating slag penetration of the refractory. The small concentration of chromium in the slag behaves similarly. These are the result of iron and chromium having significant concentrations in the spinel, and as the spinel is seen to precipitate in each subsequent calculation and removed from the next calculation, quantities of these components are thus removed from the equilibria.

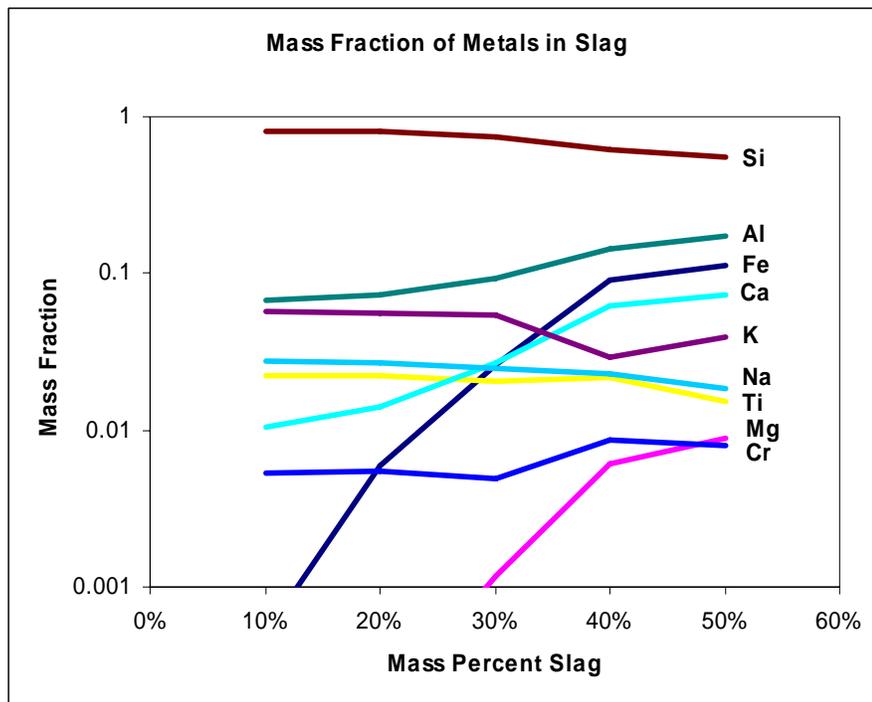


Figure 2. Mass fraction of metal as oxides in the slag phase under simulated penetration of the refractory (decreasing mass percent slag).

The metal oxide content of the spinel phase is seen in Fig. 3. The phase is no longer present at low slag contents, i.e., when the slag has significantly penetrated the refractory, so the plot extends only to 30 wt% slag. This is the effect of constituents, namely iron, precipitating in the spinel phase near the refractory surface. The iron and chrome oxide major components are relatively constant, with the minor constituents of aluminum and magnesium oxides decreasing and increasing in the phase, respectively, with slag penetration.

The sesquioxide (corundum) phase which makes up the bulk of the refractory is, of course, largely chromia. From Figure 4 it can be seen, however, that the phase picks up iron oxide from the slag, which does decrease in content further into the refractory as less is available from the slag. Alumina also appears to decrease as the slag penetrates the refractory as less is available from the slag, having been lost in precipitation of the spinel as well as due to the smaller amount of slag that is present in the calculation.

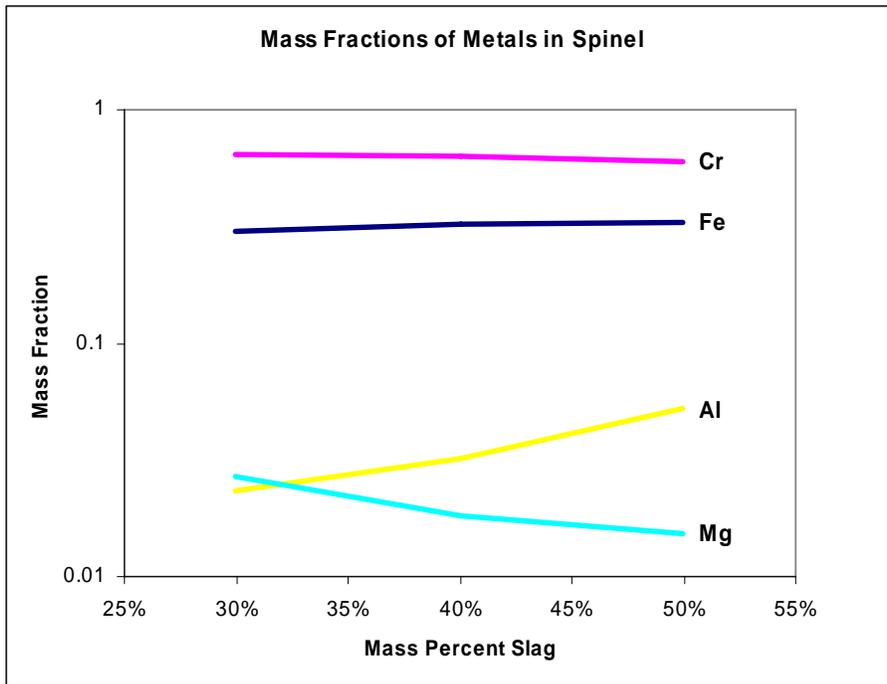


Figure 3. Mass fraction of metal as oxides in the spinel phase under simulated penetration of the refractory (decreasing mass percent slag).

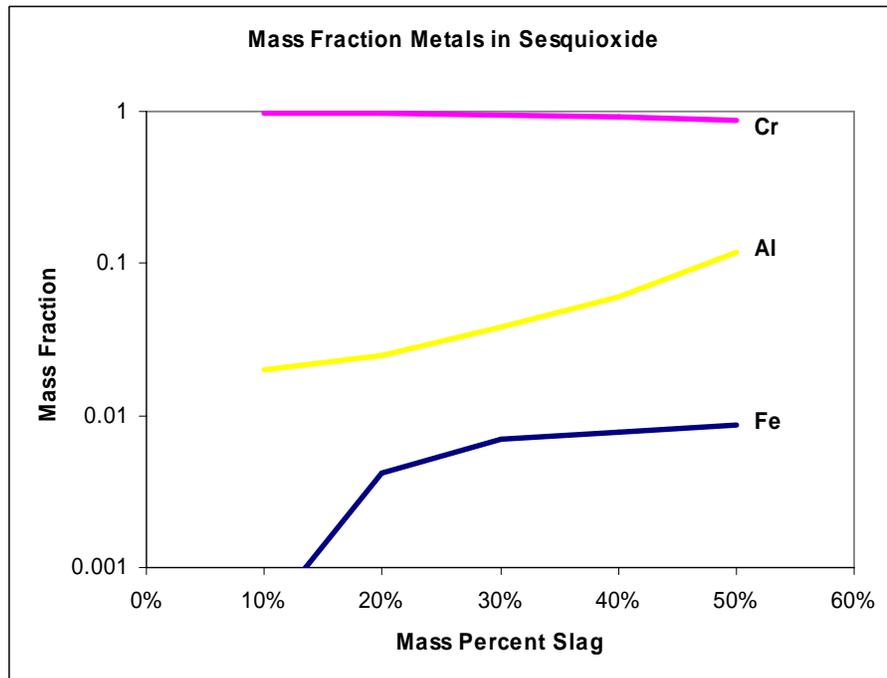


Figure 4. Mass fraction of metal as oxides in the sesquioxide (refractory) phase under simulated penetration of the refractory (decreasing mass percent slag).

LOW TEMPERATURE PHASE ASSEMBLAGES

The calculations described above at 1450°C were repeated at 300°C to simulate the slag-refractory system where the slag has penetrated the refractory to some depth and the system has now been allowed to equilibrate at low temperature. The solution phases present under these circumstances were the spinel and sesquioxide, although the spinel was not present except at high slag concentrations. Several stoichiometric phases are at equilibrium in the system under these conditions, and they are represented in Figure 5.

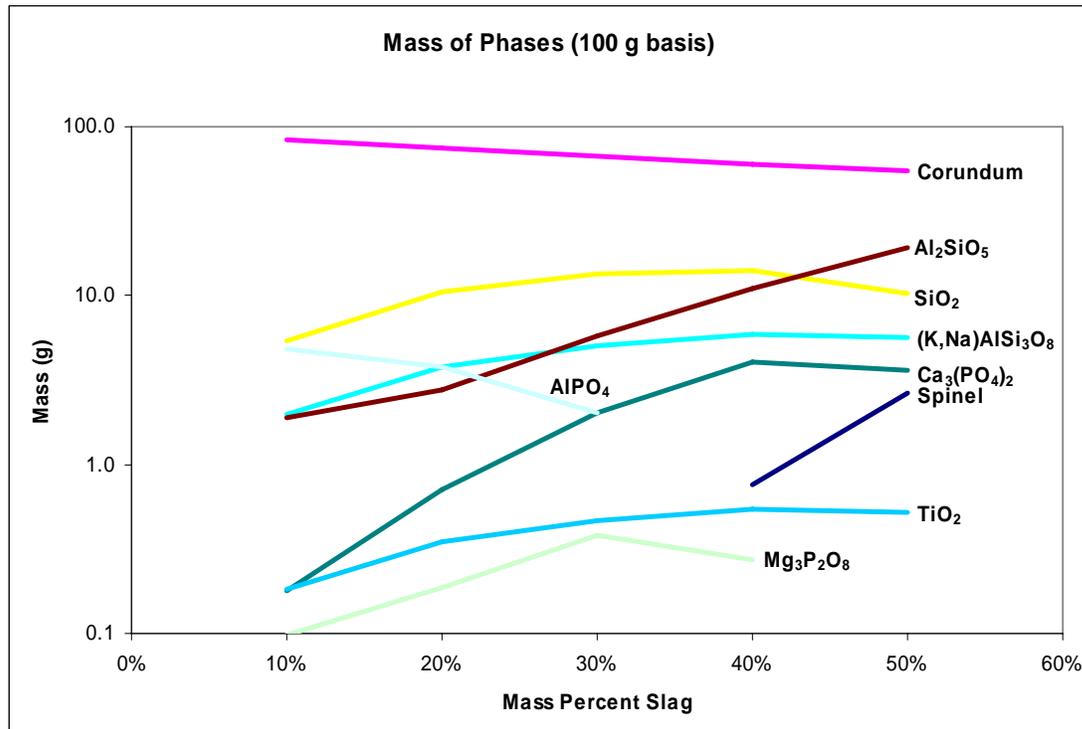


Figure 5. Low temperature (300°C) mass of each phase in the equilibrated slag-refractory system under simulated conditions for penetration of the slag by the refractory (decreasing mass percent slag)

To try to quantify attack of the refractory by the slag the equilibrium mass of the refractory constituent phases sesquioxide and aluminum phosphate at each condition of slag penetration was compared to the equilibrium mass of the constituents with no slag present. That ratio is plotted in Figure 6. From the results it appears that the sesquioxide phase is consumed to some extent by the slag near the refractory surface, but sesquioxide can also slightly gain in mass at some depth of penetration. The aluminum phosphate phase, however, loses almost 40% of its mass near the surface, which decreases to essentially no loss in the simulation when only 10% is slag. The loss of the phosphate phase, should it be an intergranular phase in the refractory, may be the controlling mechanism in refractory failure by direct slag attack.

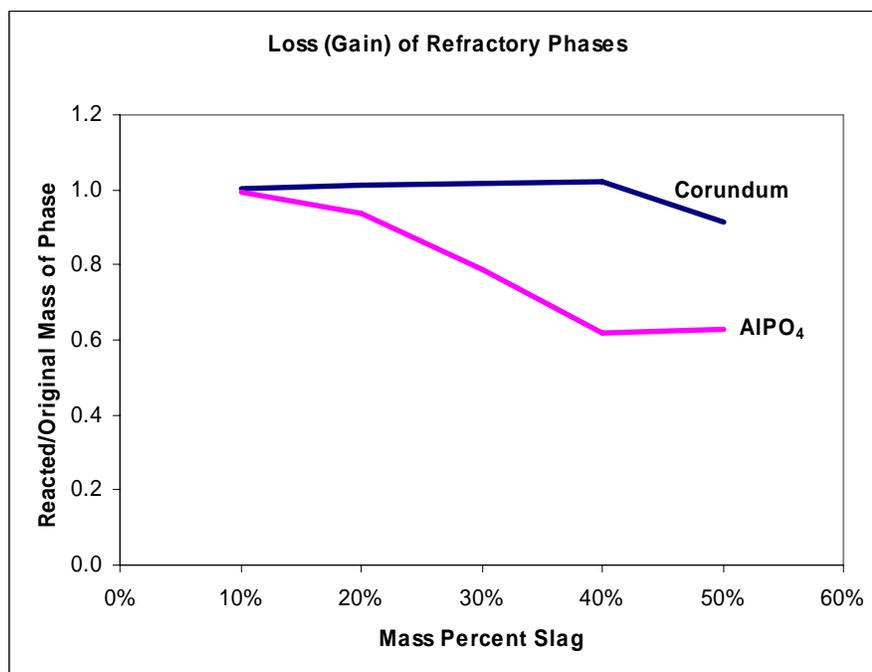


Figure 6. Mass ratio of reacted to original refractory phases sesquioxide (corundum) and aluminum phosphate under simulated penetration of the refractory (decreasing mass percent slag).

CONCLUSIONS

The thermochemical data and solution models for the constituents of a representative slag and high-chrome refractory were used in calculations to represent attack of the refractory by the slag. Penetration of the slag into the refractory was simulated by sequential calculations where precipitated phases are removed from the calculations between each step. The phases present, and the content of the solutions indicate significant compositional changes, and in particular loss of iron from the slag through the formation of a spinel phase and to a much lesser extent inclusion in the refractory sesquioxide phase. Attack of the aluminum phosphate phase in the refractory is indicated by the thermochemical calculations, and may be a controlling mechanism in refractory failure.

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