JOURNAL OF MATERIALS SCIENCE **37** (2002) 531 – 538

Initial stages of coal slag interaction with high chromia sesquioxide refractories

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Slagging coal gasifiers operate at temperatures as high as 1650°C in a reducing environment, requiring combustion chambers to be lined with refractories. The liner materials of choice are semi-porous high chromia refractories. Recently, a new series of high-chromia aluminia sesquioxide refractories have been developed. Both long term and short term tests are being conducted to evaluate the performance of these materials. In this study, the initial stage of slag-refractory interactions was analyzed. Samples of gasifier slag were compacted and placed upon the surface of these new chromia refractories and the temperature was raised consistent with start-up operating conditions of commercial gasifiers. The slag was completely molten by the time the furnace achieved a temperature consistent with gasifier operation conditions: 1350°C. Measurement of the slag contact angle, slag spread along the slag-refractory interface, and the loss of slag due to slag infusion into the refractory were monitored by camera. Analysis suggests a single phenomenon with an activation energy of approximately 54 kcal may be the controlling factor. Cross-section analysis of the sample and analysis of slag chemistry indicate that slag infusion preceded the slag-refractory interface front movement and that the iron component of the slag was becoming concentrated at the slag-refractory interface leading to the formation of a chromium-iron spinel phase. Results of these short term tests are critical in characterizing and understanding the results long term slag-refractory interactions. © *2002 Kluwer Academic Publishers*

1. Introduction

Slagging coal gasifiers operate at temperatures as high as 1650°C in a reducing gas environment. These conditions require the use of ceramic refractories as liners to protect combustion chamber walls. During combustion, the coal feedstock impurities become molten oxides (slag), come into contact with the liner, and react with the refractory at the liner hot-face. Laboratory studies in the early 1980's using chromia-magnesia and chromia-alumina spinel refractories showed improved corrosion resistance with increasing refractory chromia concentration [1–4]. Recently, a new series of high chromia alimina sesquioxide refractories have been produced and are currently being evaluated for used in gasifiers. Examination of refractories after several years of 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 soinel, and (iii) penetrated into these 85% dense sesquioxides [5–8]. However, little is known about the initial stage of slag-refractory interaction, which includes surface wetting and penetration mechanism and rates.

In this study, pellets of compacted commercial gasifier slag powder were set on blocks of sesquioxide refractory, placed in a controlled, reducing gas atmosphere, and heated. The slag-refractory interaction was monitored as the slag melted and reacted with the refractory surface. The slag wetting of both refractory surface and slag penetration into the refractory by infusion through the refractory porosity were measured. The slag began to soften or melt at approximately 950°C and was totally molten by 1350°C. The slag began to infuse into the refractory shortly after becoming molten. Although the contact angle began to decrease with increasing temperature from 1350°C, wetting (contact angle less than 90°) did not occur until 1450°C. Activation energies associated with (i) the rate of change in contact angle, (ii) the increase in slag-refractory interface profile width, and (iii) the infusion of slag into the refractory by capillary wicking suggest a single phenomenon may be controlling these events. In addition to slag infusion, the chemical composition of the slag surface and infused changed. The slag's iron component became concentrated near the slag-refractory interface, resulting in the formation of a chromium-iron spinel phase.

2. Experimentation

To characterize the initial stages of slag interaction with high-chromia alumina refractories, slag powder obtained from the TECO coal gasifier demonstration plant in Tampa, Florida, USA., were pressed into

TABLE I Slag chemistry

	C	O	Si	Fe	Al	Ca	K	Ti
Wet chemistry analysis of slag prior to testing								
wt%	24.8	28.5	16.7	11.9	5.9	2.9	1.4	0.2
at.%	40.6	35.0	11.6	4.2	4.3	1.4	0.7	0.1
SEM-EDX analysis of surface slag, at.% (EDX does not measure carbon or oxygen)								
Slag prior to tests			52	19	19	6	0.6	
Center of slag bubble			55	19	19	7	0.5	
Inner region			45	15	20	16	0.8	
Near contact angle			30	32	16	10	1.7	

2.5 gram pellet cylindars: 10 mm in diameter by 10 mm tall. The slag pellet chemistry is presented in Table I. The pellets were placed upon pieces of high-chromia/alumina refractories (AUREX 75 and AUREX 90, Harbinson-Walker Refractory Company, Vandalia, MO USA 63382) approximately 25 mm square by 15 mm thick and placed in an environmentally controlled tube furnace with viewing ports on either end. A reducing atmosphere was controlled by maintaining a constant flow of 50 : 50 argon/CO gas with a flow rate through the tube of approximately 1.0 liter per hour. In the first set of tests the furnace was heated to 1550°C at approximately 100°C per hour. During these tests no slag-refractory wetting began until 1450°C. A second series of tests was conducted in which the slag-refractory combinations were heated to 1450°C and the temperature held.

The slag-refractory interaction was monitored using a KODAK MDS1000 digital video camera equipt with a zoom lens. The pictures were stored on a computer hard drive, from which they could be retrieved, processed, and analyzed. A series of welding filter lens were inserted at appropriate temperatures to prevent saturation.

After the furnace run, the slag-refractory samples were removed, cross-sectioned, and examined using a scanning electron microscope with SEM equipt with energy and-wavelength dispersion analytical capabilities to determine slag penetration depth and slag chemistry both on the slag surface and interior (Table I).

3. Data and analysis

Slags used in this experiment was a bottom slag provided by a commercial gasifier and typical of those produced in a slagging coal gasifier, including the presence of approximately 40 at% of unburned coal (carbon) [5, 6]. The slag wasThe refractories used in this study were the same as those used as liners in gasifier combustion chambers: AUREX-75 and −90. These refractories are 75 and 90 wt% chromia (approximately 60 and 80 mole% respectively) with the remainder alumina and a small quantity of binder (<2 wt%) and were formed by sintering oxide particles to form bricks that are approximately 85% dense. The 15% porosity is composed of interconnected channels and pores [8].

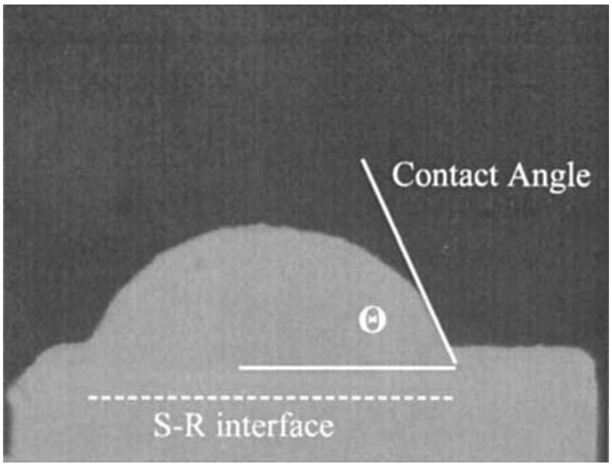

Figure 1 Schematic showing the measurement of contact angle and slag-refractory interface profile width.

From the computer-stored photographs, three measurements were taken to determine the slag-refractory interaction: (i) the contact angle at the point of slag-refractory-gas interface, (ii) the cross-section profile width at the slag-refractory interface, and (iii) the cross-sectional area of the molten slag (Fig. 1). The first two measurements are standard techniques for determining surface wetting [4, 9–14]. The third was used as a means of measuring the slag penetration into the refractory.

Much of the experimental design and analysis is consistent with Sessile drop experiments and analysis [14]. However the purpose and design of this study was to understand the slag-refractory interactions occurring in commercial operations. Thus, in contrast to the normally accepted practice for Sessile drop studies of surface wetting, where a carefully prepared, polish solid, flat surface is used, the surface in this study was that of a commercial refractory with 15% porosity. Both the surface roughness and the porosity were expected to affect the rate of slag wetting [13, 14]. However, when the time data points were plotted, the change in contact angle, contact diameter, and slag profile area, on average, were uniform and continuous with respect to time and temperature.

Examination of the slag-refractory sample profiles as a function of temperature and time showed several stages of pellet deformation and interaction of slag with the refractory. During the rise in furnace temperature, the pellets went through several stages of alteration before forming a complete melt (Fig. 2). At approximately 950°C, the pellet began to show regions of local solid softening. The pellet appeared to undergo a continuous transformation from solid to liquid, possibly resulting from the formation of glassy phases, until the slag became fully liquid and assumed a semi-spherical

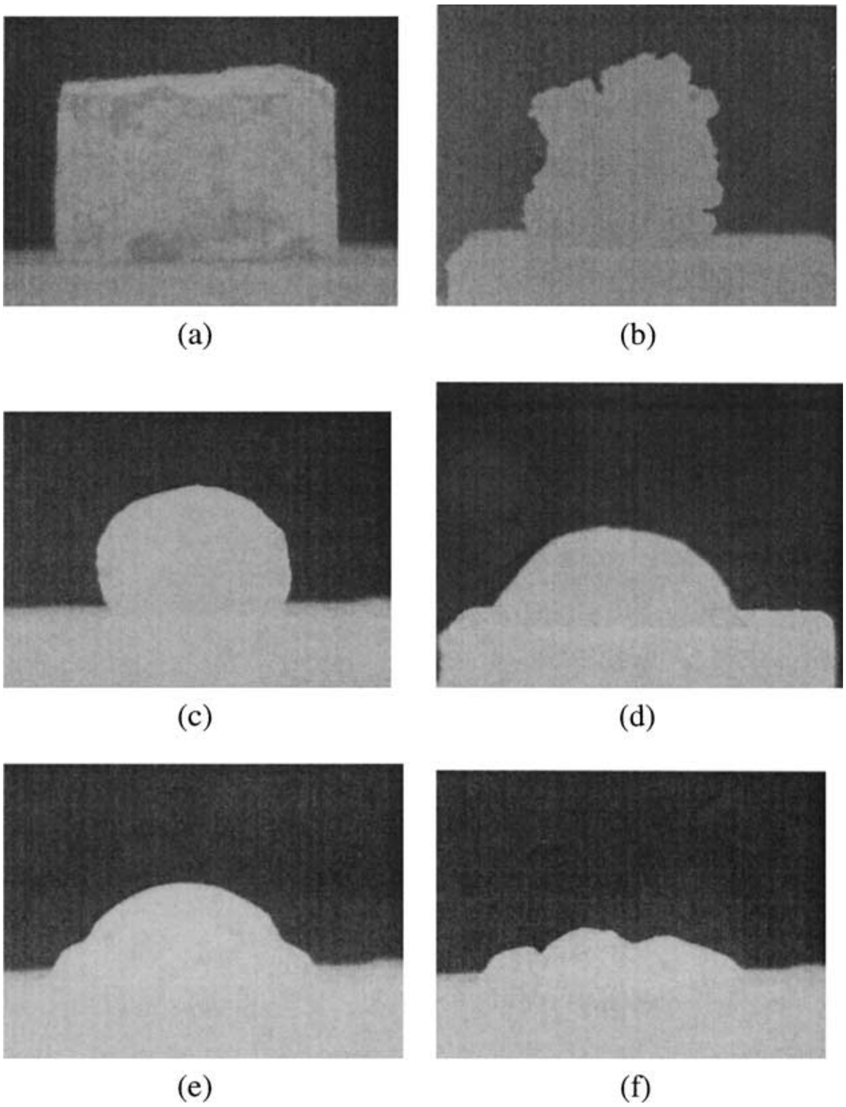

Figure 2 Profiles of slag in furnaces on AUREX-90 refratory temperature hold test. (a) temperature 750°C, sample dimension is 10 mm in diameter, (b) temperature 1000°C, (c) temperature 1400°C, (d) temperature 1450°C, hold time 0 minutes, (e) temperature 1450°C, hold time 10 minutes, (f) temperature 1450°C, hold time 78 minutes.

geometry at approximately 1350°C. When the slag became completely molten, the area of contact had shrunk, the contact angle decreased from 90° (while the slag pellet was solid) to greater than 90°. The contact angle decreased as the temperature increased and the profile width at the slag-refractory interface increased (Fig. 3). The molten slag did not wet to the refractory (i.e., the contact angle remained greater than 90°) until the furnace temperature reached approximately 1450°C. The wetting continued and the contact angle continued to decrease with increasing temperature up to 1550°C, the upper limit of this study. In the temperature hold tests, the furnace was placed on hold at 1450°C, (approximating a classical Sessile drop experiment). Shortly after reaching 1450°C, the molten slag began to wet the refractory. The region associated with the slag-refractory wetting expanded, extending the profile width of the molten slag/refractory interface. NOTE, 1450°C is approximately the eutectic temperature associated with the formation of the iron-chromium spinel phase [15]. For both the Aurex-75 and Aurex-90 refractories, the contact angle began to decrease shortly after reaching 1350°C. Shortly after the initial stage of wetting, a small portion of the slag at the slag-refractory interface began to form a small bulge or protrusion and to pull out from the bulk of molten slag semi-spherical shell. The decrease in bulge contact angle was consistent with increasing slag-refractory interface profile width and width increasing experimental time and temperature (Fig. 3). The bulk of the molten liquid kept a spherical shape and an extension of the spherical profile to the refractory interface produced a contact angle that changed little from 90° and remained relatively constant with increasing temperature and/or time.

A measure of the molten slag profile area showed that initially there was little change in the area. However, once the slag became completely molten at temperatures below 1100°C, the profile area began to decrease with time and temperature. The slag infiltration may be associated with surface reaction/wetting which began at approximately 1350°C. NOTE, CaO – Cr_2O_3 forms several liquid phases above 1000°C [15]. During both the temperature ramp tests and the temperature hold tests, there was a strong correlation between the continuous decrease in wetting contact angle, an increase in interface profile width, and a loss of profile

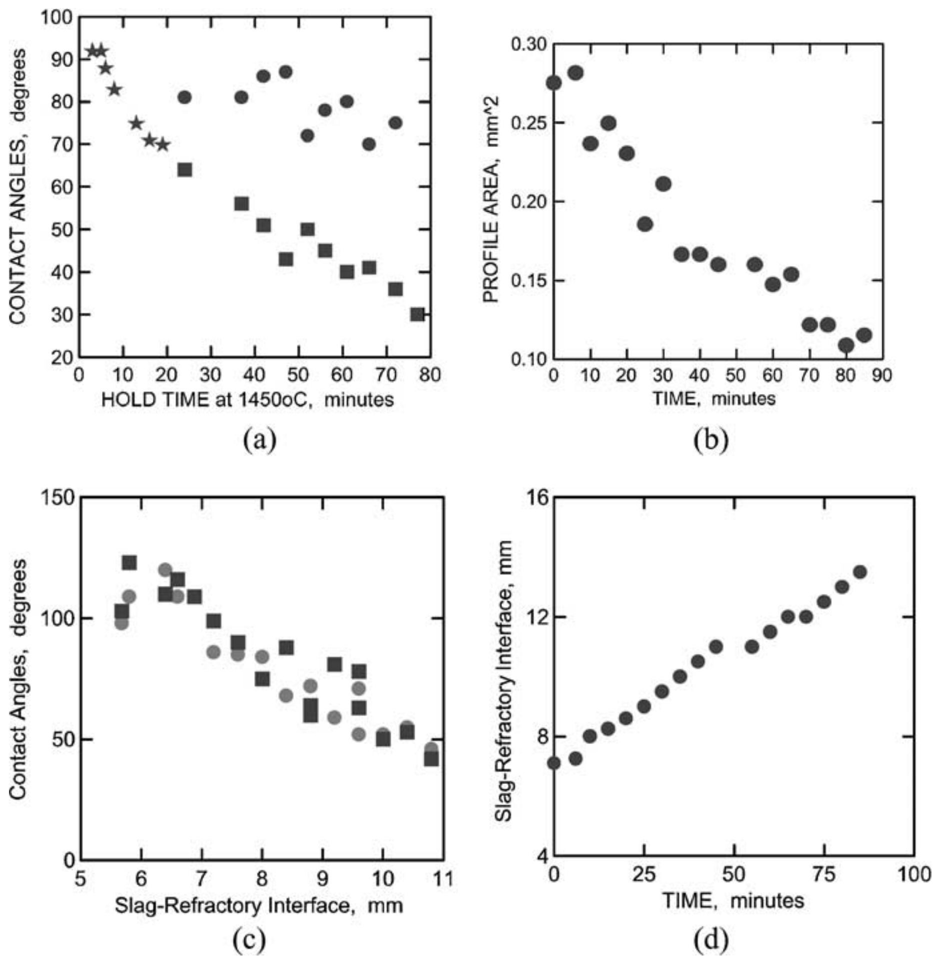

Figure 3 Data graphs. (a) Change in contact angles during experiment with temperature hold tests on AUREX-75. ★ single contact angle, ● contact angle determined from extension of molten slag profile, ■ contact angle at the outer point of slag-refractory interaction, (b) change in slag profile area with time during temperature ramp tests, (c) relationship between the outer contact angle and the extension of slag-refractory interface profile width with time during a temperature ramp tests, ● left angle ■ right angle. (d) change in slag-refractory interface profile width during temperature hold experiment.

area (Fig. 3). After the slag began to wet the refractory and a significant portion of the slag had penetrated into the refractory, the molten slag profile was no longer smoothly curved, but began to develop local ungulations

SEM-EDX examination of the slag surface after the test showed the slag chemistry changed from the outer edge of contact angle inward (Fig. 3). Slag chemistry in the center changed little from pre-melting concentrations. Slag at the outer edge of the slag refractory interface was significantly higher in iron concentration than the bulk slag. A similar increase in potassium and titanium concentrations was observed, although the overall concentration levels were low. Beyond the slag-refractory surface interface the refractory surface chemistry showed the presence of silicon and calcium indicating subsurface slag infusion had occurred.

Cross-section examination of the samples showed that the slag completely wetted to the refractory surface, filling in the refractory surface roughness. The slag penetrated to a depth of approximately 1.5 mm into the refractory within the 1–2 hours of the experiment, and penetration had occurred prior to the surface slag-refractory interaction developed (Fig. 4). Below the slag-refractory interface, the slag infused into the porous refractory forming a semi-spherical penetration profile which extended approximately 1 mm ahead of the slag-refractory wetting. Scanning-electron-microscopy wavelength dispersion elemental mapping showed a continuous iron rich layer at the surface of the refractory. This iron-rich layer on the chrome sesqioxide phase may to be the precursor of the chromium-iron spinel layer observed in longer duration tests [5–8]. And, although the diffused slag had penetrated beyond the surface slag-refractory interface, the iron elemental map did not show the presence of iron in the diffused slag except under the slag-refractory interface.

Measurements of the change in slag-refractory interface profile width, contact angle, profile area, and semi-sphere radius as a function of temperature and time were used to determine activation energies using analytical techniques established for Sessile drop wetting studies [10, 11, 14]. Analysis for both sets of experimental conditions and both refractories showed a consistent value activation energy of approximately 54.2, ±1.0 kilocalories for all tests (Table II). Regression analysis for the data had a statistical R^2 fit between 0.94 and 0.99.

Analysis of the slag infusion profile for the samples that were held at 1450°C showed the diffusion depth to

TABLE II Activation energy determination

	Experimental conditions			
	Temperature ramp		Temperature hold	
Parameters used	Aurex-75	Aurex-90	Aurex-75	Aurex-90
Interface profile width	53.3	54.2	53.9	54.4
Contact angle	54.5	53.5	54.2	58.0
Profile area	54.0	53.8	54.0	53.7
Semi-sphere radius	53.7	54.1	53.6	54.2

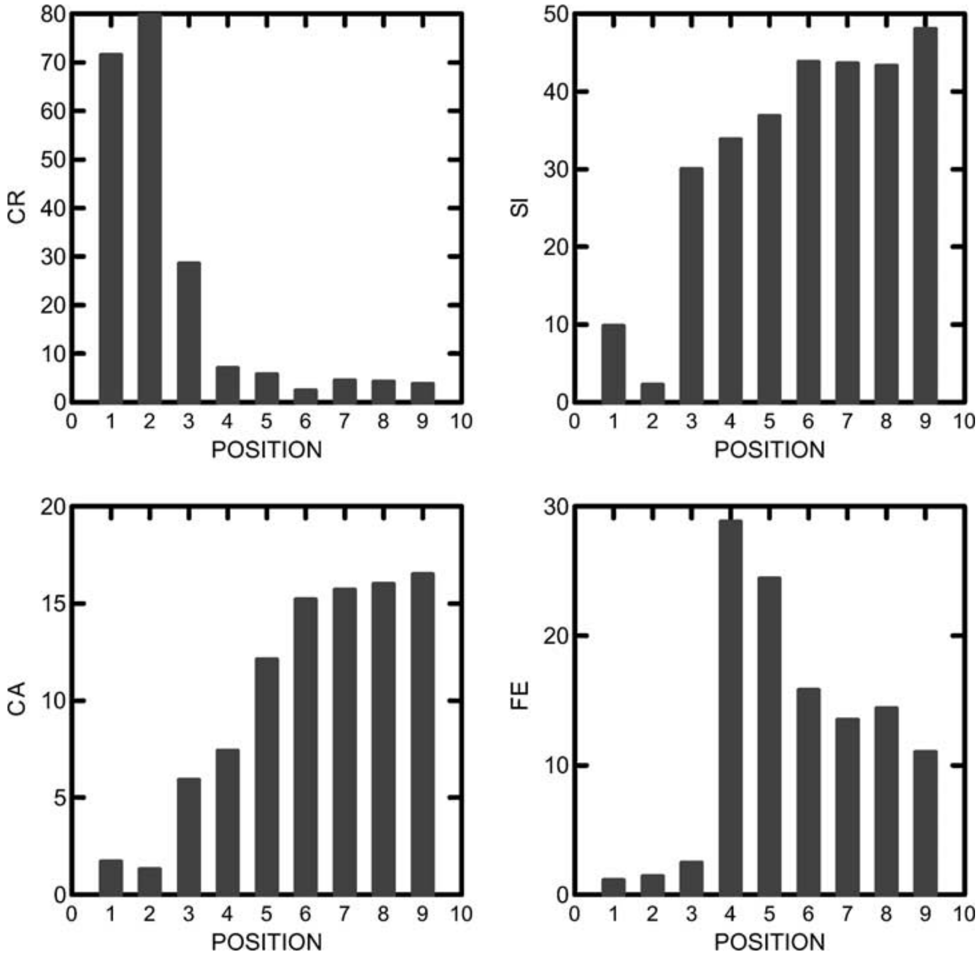

Figure 4 SEM-EDX measurement of slag surface chemistry after temperature hold tests on AUREX-90 refractory: Positions are approximately 0.5 mm apart. Position 1 is approximately one millimeter ahead of the slag-refractory surface interface. Position 3 is the slag at the contact angle. Positions 4, 5, ... are positions proceeding into the center of the slag, (a) chromium outer positions 1 and 2 have the concentration of the AUREX-90 refractory, (b) silicon outer positions 1 and 2 indicate the presence of silicon due to internal slag infusion. Interior positions 3, 4, ... show a gradual increase in concentration as one proceeds in to the center of the slag, (c) calcium concentration profile was similar to silicon, (d) iron concentration is highest at the point of the slag wetting, position 4, and rapidly decreases as one moves towards the center of the slag.

be a function of two variables with respect to the depth of the slag-refractory interface. The dominant factor was related to the square root of the interface depth and accounted for greater than 99% of the penetration depth. However, analysis of the residuals of this single value relationship between penetration depth and square-root of the interface depth showed the residuals had a definite parabolic shape with respect to interface length; hence, the need to include a second factor. Because the temperature was held constant during this test, the square-root depth relationship can be associated with time. Similarly, the second factor, the parabolic or quadratic component of the profile, can be explained as being associated with the lateral expansion due to wetting of the slag-refractory interface. Thus, the measured diffusion depth is a function of the time the slag was over a particular point and the movement of the slag-refractory interface, which expanded with time. There are two components to the diffusion depth profile: (i) one proportional to the time associated with the slag over a point, and (ii) a second associated with the time it takes the slag to reach the diffusion point.

4. Results and discussion

Previous slag-refractory cup studies [5–8] using this same gasifier slag and high chromium sesquioxide refractories have shown that significant slag penetration (>5 mm) can occur in 24 hours at 1550°C. In these previous studies, in addition to slag infusion into the refractory, the slag both dissolved the chromium sesquioxide refractory and reacted with the sesquioxide particles forming chromium-iron spinels at the slag-refractory interface. This study was designed to characterize the initial stages of the slag-refractory interaction and to provide insight into: slag wetting, penetration, and chemical reaction with the refractory.

Control of the gas environment is important. In the coal gasifier combustion chamber, as coal feed stock, the iron contaminant present in the coal is predominantly in the form of iron sulfides. During combustion in a gasifier, these iron-sulfides oxidize to produce iron oxide (FeO), which reduces the slag melting point and increases slag viscosity [16]. In this study, the Ar/CO reducing atmosphere ensured retaining the iron ions in the Fe^{+2} state. FeO reacted with the high chromium sesquioxide refractory forming a chromium-iron, $FeO\text{-}Cr_2O_3$, spinel phase [17]. (In an oxidizing atmosphere, iron-sulfides oxidize to form the iron oxide spinel, Fe_2O_3, that reacts with chromia, Cr_2O_3, to form the sesquioxide phase $(Cr,Fe)_2O_3$ [1, 17].) Note: while both the iron and chromium spinel and sesquioxide phases have melting temperatures above the combustion chamber temperature of 1550°C, iron oxide, FeO, has the lower melting point, 1370°C Fe2O3 $T_{\text{m.p.}} = 1595$°C [18]. Examination of high chromia refractories removed from commercial operations after approximately two years of operation have only detected the presence of the chromium-iron spinel phase.

Slag underwent several changes during thermal heating. At approximately 900°C, the compacted powder slag pellet began to shrink, densified, and show signs of consolidating. With continued heating the slag pellet profiles continued to show localized regions of particle consolidation, possibly forming amorphous slag particles which continued to soften, or the particles reacted, consolidated, and formed low melting oxides. These reactions continued until approximately 1375°C when the pellets were completely liquid and assumed a spherical shape. The gradual change in the slag pellet shape is consistent with predictions obtained from the phase diagrams for combinations of different oxide blends [15].

Analysis of slag-refractory interaction data from the two different refractories showed little difference as did the data from the temperature ramp and temperature hold experiments showed little difference. Thus all results were analyzed together. The following discussions will be presented without test distinction.

During the initial stage of heating the slag samples, the contact area of the slag-refractory interface contracted and the contact angle changed from the 90° when the pellet was solid to greater than 100°, i.e., consistent with the bulk of the molten slag not wetting the refractory. The overall profile of the molten slag remained semi-spherical during the rest of the thermal cycle. (At the highest temperature and after extended times, the majority of the slag had infused into the refractory, the remaining slag could no longer support a semi-spherical shape. Fig. 2) Slag samples being fully molten above 1350°C is consistent with the commercial slagging gasifiers where all the coal slag is molten while in the combustion chamber.

With increasing temperature, the slag-refractory interface area continued to increase and the contact angle continued to decrease. At approximately 1440°C, the contact angle reached 90°; shortly thereafter the molten slag began to wet the refractory and a small bulge or protrusion began to extend from the ends of the semi-spheres at the slag-refractory interface. The contact angle of these protrusions continued to decrease as the slag-refractory interface area continued to increase. The contact angle of the general spherical shape of the molten slag to the slag-refractory interface changed only slightly with time and temperature (Figs 2 and 3). The change in slag profile suggests that there is a localized difference in surface tension, possibly due to difference in the local slag chemistry.

After the tests, the slag surface showed the chemistry of the slag at the edge of the slag-refractory interface to be different from the chemistry at the center of the slag (Fig. 4). The elemental concentration of the outer regions of the slag had significant higher concentrations of elements that increase silica viscosity (Fe, Ca, and K). Within several millimeters of the outer edge, the slag surface chemical composition changed to that of the slag composition prior to testing. (Note: SEM-EDX was not capable of measuring oxygen or carbon, so the compositions presented in Table II have been normalized for the elements measured.) The change in slag chemistry is consistent with the change in slag profile. The development of the protrusions is thus possibly due to the localized change in slag chemistry.

In addition to the change in contact angle and interface area, the profile of the molten refractory decreases in area with increasing temperature and time. The loss of profile area is attributed to slag infusion/diffusion into the refractory [3–7]. Cross-section examination of the refractory after the test showed the infused slag front extending significantly ahead of the surface slag. The shape of the infused slag had a profile consistent with slag diffusion and movement of the slag-refractory interface. SEM-EDX elemental mapping (Fig. 5) showed the slag silicon, aluminium, calcium, and potassium compositions to be uniform throughout the infused slag region. However, the surface slag iron concentration was present only where the slag was present on the refractory, and was limited to a small infusion depth at the interface region. The change in infused slag chemistry is consistent with the change in the surface slag chemistry wherein there was a preferential affinity for slag to infuse into the refractory leaving behind a higher concentration of iron in the slag above. This enrichment of iron at the front of the slag-refractory interface would influence the surface tension and liquid viscosity.

Several theories may explain the change of contact area and contact angle with temperature and time [4, 9, 10, 11]. These relationships are based upon thermodynamic relationships and allow determination of an activation energy for various phenomena. In this study the thermodynamic value determined from these two relationships and the activation energy determined for the change in profile area and semi-spherical radius are relatively consistent, approximately 54 kcal., suggesting that one mechanism may account for all four

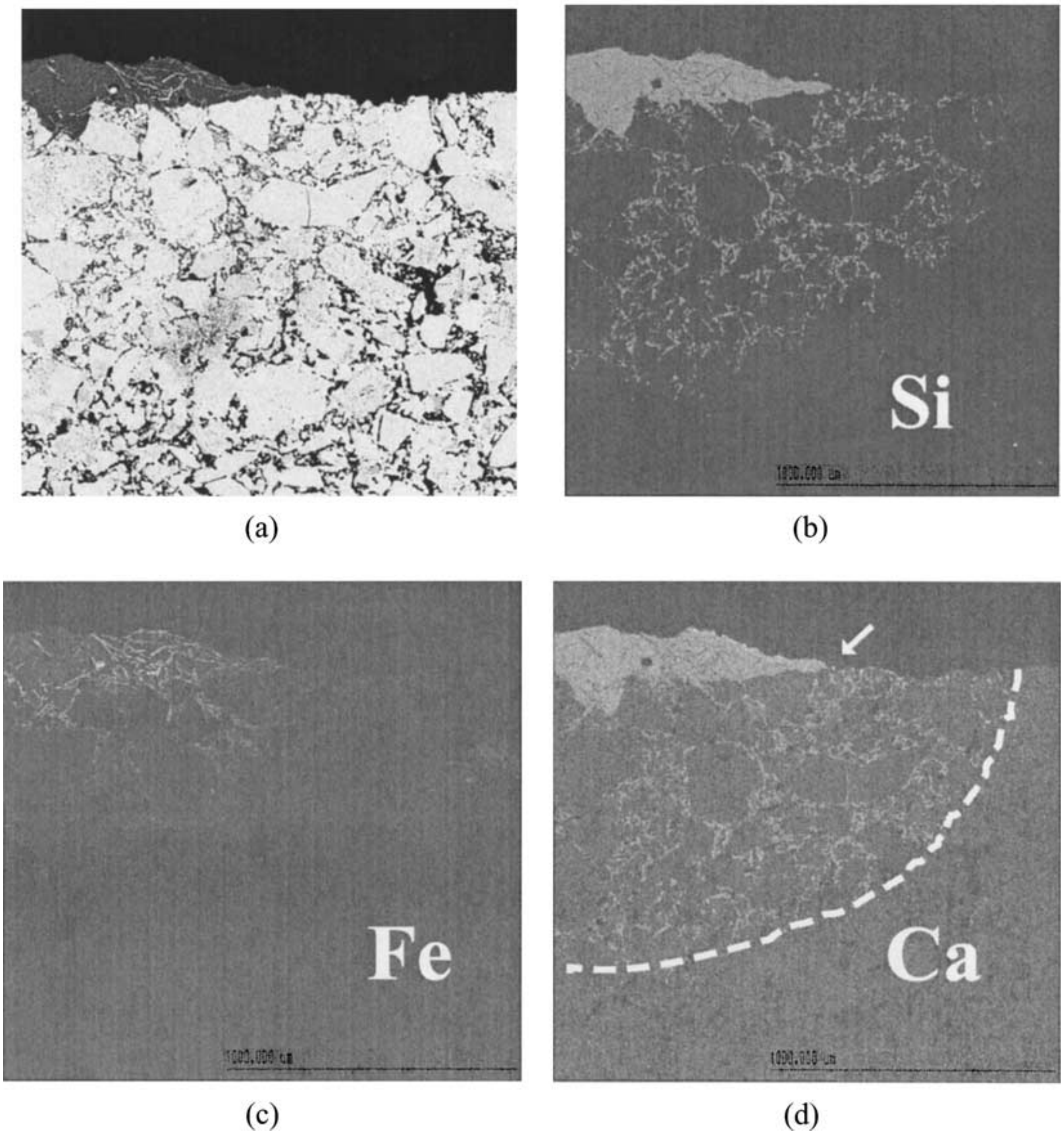

Figure 5 Scanning electron micrographs of cross-section ater temperature ramp test on AUREX-90. (a) Back scatter image showing the refractory porosity and microstructure and the surface slag, (b) Silicon elemental map showing the depth and extent of the slag infusion, (c) Iron elemental map showing the limited iron infusion, (d) Calcium elemental map showing the slag infusion profile, the extent of surface slag-refractory wetting (arrow), and the extent of slag infusion ahead of the surface slag wetting.

phenomena. Using the activation energy associated with depth of slag penetration for this study, a diffusion depth of approximately 5–7 mm is predicted for a 24 hour slag-refractory cup test, which was identical to that previously reported [5–8] and the 70–100 mm penetration also consistent with the observed depth of slag penetration in the "spent" refractories removed from demonstration commercial gasifier power stations after approximately two years operation [7, 8].

4.1. Summary

Characterization of the initial stages of slag-refractory interaction consistent with all the observations and data in this study is that shortly after the slag became molten, the slag began to wick into the narrow capillary channels of the 85% dense refractory. The change in the contact angle and the change in slag-refractory interface area was the result of both local wetting of the capillary within the refractory narrow channels and smaller pores and along the refractory surface. However, the local capillary action of the slag being pulled or the wicking action of the slag into the refractory appears to be stronger. As the slag is wicked into the refractory it infused along all the possible paths both vertical and horizontal, not just those directly below the slag-refractory interface, but along those continuous pores at the edge of the slag-refractory interface, ahead of the contact area. From the observed difference in surface and interior slag-refractory interactions, it is apparent that the dominant slag-refractory wetting mechanism is due more to slag infusion or wicking into the refractory than to change in surface wetting along the refractory outer surface. This understanding of the difference in capillary versus surface wetting is consistent with closer examination of the slag infused region for longer time test and spent refractories [8]. Larger pores are often not completely filled with slag, whereas small pores and the narrow channels between particles are almost always filled.

The rate of slag infusion is dependent upon the chemistry of the slag. The lower the iron concentration the greater the wicking action. The results of this study can not determine if the change in slag iron chemistry changed the wetting, slag surface tension, and/or slag viscosity. However, the observed localized changes in slag composition, especially the iron concentration, and the closely related change in physical properties at the slag-refractory interface could explain (i) the change in surface profile, (ii) the appearance of the protrusions, and (iii) the change in the contact angle ahead of the protrusion, (iv) the contact angle associated with the bulk molten slag remaining relatively unchanged and (v) the development of the chromium-iron spinel phase. The change in slag chemistry and the resulting concentration of iron in the upper portion of the infusing slag is consistent with the observation of longer term slag-refractory cup tests in which the infused slag was essentially free of iron and a uniform layer of chromium-iron spinel phase developed at the slag-refractory layer [5–8].

5. Conclusion

The initial phase of reactions between coal slag and high chromium sesquioxide gasifier liner refractories was analyzed and characterized. At the temperatures used in the gasifiers, >1350°C, the slag is completely molten. The refractories have approximately 15% porosity. Slag infusion began shortly after the slag became molten, although wetting at the slag-refractory interface did not occur until approximately 1440°C. Analysis of the change in contact angle, of the rate of expansion of the slag-refractory interface, and of the slag infusion into the refractory as a function of time and temperature suggest that they may be controlled by a single phenomenon with an activation energy of approximately 54 Kcal: the capillary pull of slag into the refractory. Cross-section examination of the infused slag shows a parabolic profile that reached an infusion depth of approximately 1.5 mm in one hour. However, what may be more important to the understanding of the infusion process, the front of the infusion slag profile extended significantly beyond (approximately 1 mm) the slag-refractory surface interface. Elemental analysis of the surface slag composition as well as SEM-EDX elemental profiles showed the iron component of slag becoming concentrated at the slag-refractory interface and the formation of a chromium-iron spinel phase on the chromium sesquioxide phase. The results observed in this study are consistent with, and help explain, the longer term slag-refractory interaction reported in previous cup tests and analysis of refractories removed after years of operation in commercial power facilities.

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*Received 13 March
and accepted 28 August 2001*