

# Gasifier Refractories, Coal Slags, and Their Interaction

Kyeising Kwong <sup>1)\*</sup>, James Bennett <sup>1)</sup>, and Jinichiro Nakano <sup>1),2)</sup>

*1) National Energy Technology Laboratory, US Department of Energy, 1450 SW. Queen Ave., Albany, OR 97321 USA*

*2) URS Corp, P.O. Box 1959, Albany, OR 97321 USA*

**Abstract:** Gasification offers a clean, efficient, and flexible way to convert carbon based materials into electricity, hydrogen, and other chemical products. The conventional commercial hot face Cr<sub>2</sub>O<sub>3</sub> gasifier refractory materials; which are used to protect the outer steel containment shell from gasification environment attack, suffer from chemical dissolution and slag penetration causing chemical corrosion and structural spalling. The effects of chemical corrosion and structural spalling are to reduce refractory service life. Several years ago, The National Energy Technology Laboratory, (NETL) US DOE developed a phosphate containing Cr<sub>2</sub>O<sub>3</sub> refractory and demonstrated it can dramatically decrease slag penetration depth and extend refractory service life in laboratory cup, rotary drum tests, and field test panels. Coal is one of the major feedstock in gasifiers. Slag properties from impurities in coal affect not only the operation of a gasifier, but also the performance of a Cr<sub>2</sub>O<sub>3</sub> refractory liner. US coal slag properties were thermodynamically investigated, including liquidus temperature, viscosity, primary phase precipitation, and solid content at temperatures from 1300 to 1600 °C in 20 °C increments. Slag interactions with Cr<sub>2</sub>O<sub>3</sub> refractory were studied in laboratory tests, thermodynamic calculations, and post mortem analyses of spent gasifier refractories. Post mortem analysis of commercial and NETL developed refractories were conducted by XRD, ICP, and SEM to determine the failure mechanisms, to study the reaction between gasifier slags and refractories, and to evaluate the performance of NETL developed phosphate containing refractories.

**Key words:** IGCC Gasification, coal, slag, Cr<sub>2</sub>O<sub>3</sub> refractories, phosphate

## 1. Introduction

Gasification is a process converting organic or fossil based carbonaceous materials into carbon monoxide, hydrogen, carbon dioxide and methane; and is often achieved in a high pressure/high temperature reaction vessel (slagging gasifier) fed with carbon, water and oxygen. In a gasifier, the non-volatile mineral impurities in the carbon feedstock are liquefied at the elevated temperature, forming a corrosive slag. Refractory linings are used to protect the steel vessel from the attack by corrosive gases, molten slag, and abrasive wear; as well as to insulate the vessel from energy loss during gasification. The service life of refractory liners for gasifiers has been identified by users as a critical barrier to IGCC system economics, reliability, and on-line availability [1]. The gasifier operating conditions and slag chemistry have significant impacts on the performance of refractories.

Slagging gasifiers are typically operated between 1300 and 1600 °C at pressures of 2.75 MPa (400 psi) or more, with flowing molten slag that can exceed 10 tons/hour. The operating temperature depends on the liquidus temperature, ash fusion temperature, and viscosity characteristics of the ash. The hot-face refractory lining inside a slagging gasifier must have the following characteristics to withstand the gasifier's hostile conditions:

- High temperature resistance
- Slag corrosion resistance
- Slag penetration resistance
- Erosion resistance from the injected slurry
- Phase stability in oxidizing and reducing atmosphere
- Thermal shock resistance from gasifier shutdowns and temperature excursions
- High temperature creep resistance

Material research in the 70's to 80's suggested high chrome content in refractory (75 weight percent, wt pc or higher) should be used in such severe environments [2]. Currently, refractory lifetime ranges between 3 and 36 months varying in different areas. Figure 1 shows that factors affecting the service life of refractory liner such as chemical and physical properties, fabrication flaws, brick installation quality, gasifier operational conditions, and gasifier design. This paper will only discuss the material issues related to the refractory. The degradation of the gasifier refractories with coal slag can be attributed to chemical corrosion and physical wear, which can interact with each other and can have a synergistic effect.

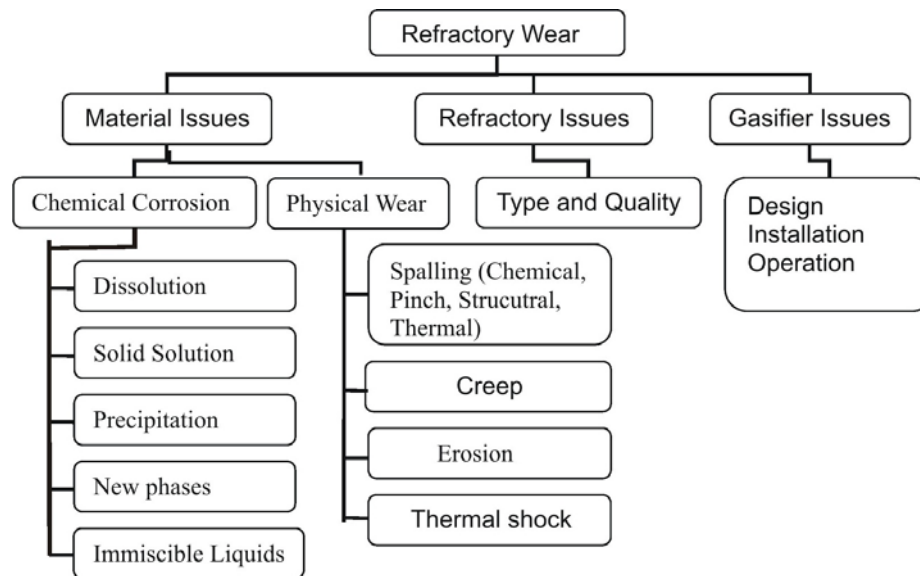


Fig. 1 Factors affecting the service life of a gasifier refractory liner

## 2. Gasifier Atmosphere

Synthetic gas (syngas) compositions in gasifiers may vary with different products (table 1)[3]. Thermodynamic calculations using HSC Chemistry® were performed to predict the oxygen partial pressure in the gasifier based on the syngas compositions listed in table 1 (Figure 2). Results indicated that the oxygen partial pressure in a gasifier ranges from  $10^{-7}$  to  $10^{-9}$ . The oxygen potential in gasifiers affects: (i) the valence state of transition oxides in the slag; (ii) oxide basicity; (iii) the basicity of slags; and (iv) the melting point of the slags. Therefore, the oxygen potential in the gasifier influences slag-refractory reactions and the compound formation.

Table1 Examples of synthetic gas constituents

	PSI Wabash	Tampa Polk	Exxon Singapore	Motiva Delaware
H <sub>2</sub> (by Vol)	24.8	37.2	44.5	32.0
CO	39.5	46.6	35.4	49.5
CH <sub>4</sub>	1.5	0.1	0.5	0.1
CO <sub>2</sub>	9.3	13.3	17.9	15.8
N <sub>2</sub> +Ar	2.3	2.6	1.4	2.2
H <sub>2</sub> O	22.7	0.3	0.1	0.4

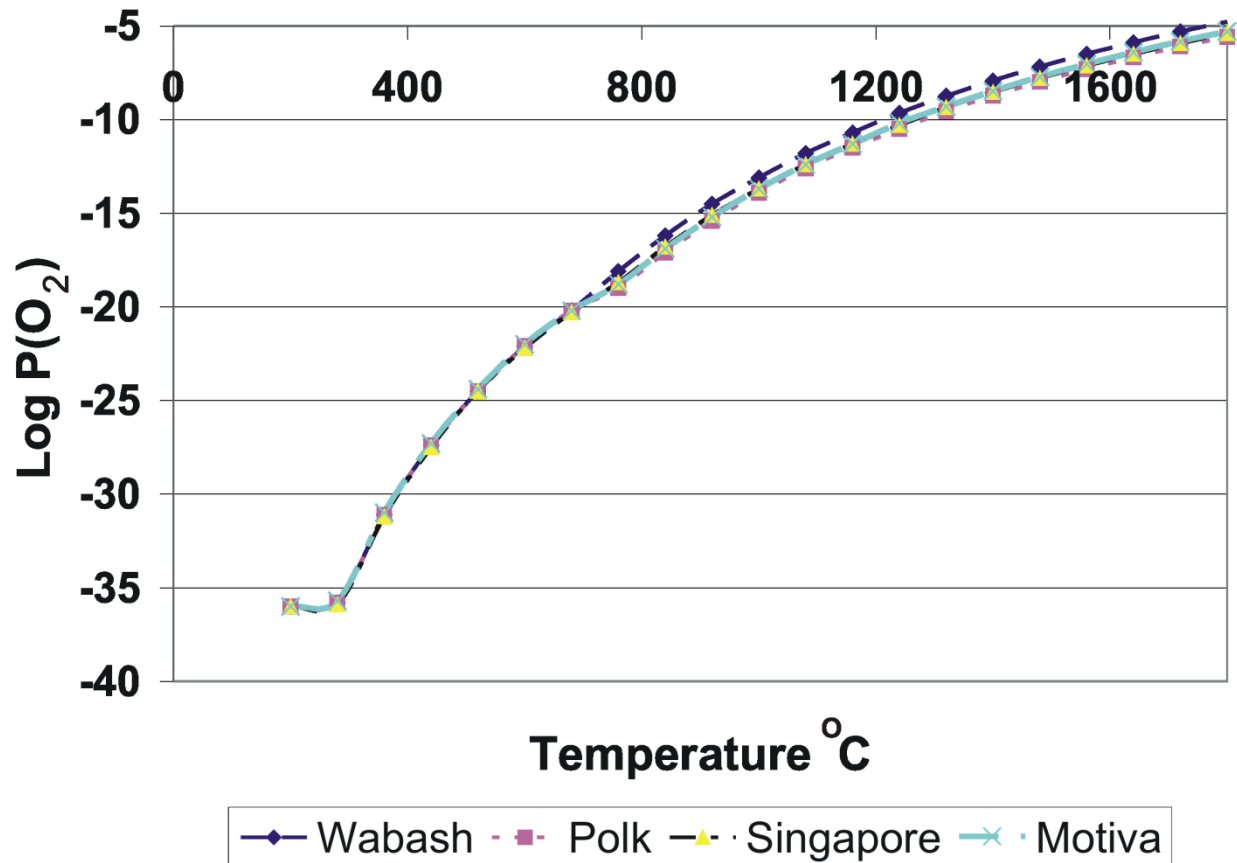


Fig. 2 The variations of oxygen partial pressure with temperature in gasifiers

### 3. Refractory Liner Materials Studied

Post mortem analysis was conducted on a number of spent gasifier commercial Cr<sub>2</sub>O<sub>3</sub> refractories to determine causes of failure. The high chromia (86-95 wt% Cr<sub>2</sub>O<sub>3</sub>) refractories studied contained from 5-10 wt% Al<sub>2</sub>O<sub>3</sub> and/or ZrO<sub>2</sub>. Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> can interact at elevated temperature to form a complete solid solution. Un-reacted coarse Al<sub>2</sub>O<sub>3</sub> grains, however, are often observed in the refractory microstructure. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD), optical microscopy, and wet chemical analysis were used to determine slag penetration, phase transformations, and internal crack initiation sites. Figure 3 shows typical void/crack formation on a spalled surface of a commercial chromia gasifier refractory caused by slag infiltration during use. The postmortem analyses

[4] of spent refractory indicated that many small cracks were observed on the leading edge of the slag penetration area and that these small cracks tend to link with each other to form a larger one, such as the one shown 40 mm below hot face.  $\text{Cr}_2\text{O}_3$  refractory is very susceptible to thermal shock and slag penetration may make it more vulnerable because of the decrease of porosity and the density difference between penetrated and un-penetrated areas. Thermal cycling exacerbates the cracking problems, leading to structural spallings.



**Fig. 3** Crack formation in a high  $\text{Cr}_2\text{O}_3$  refractory removed from a gasifier

This implies that the service life of  $\text{Cr}_2\text{O}_3$  refractory could be improved if slag penetration can be reduced or stopped. Researchers at NETL conducted numerous trials to solve the spalling problem; such as improving the microstructure of hot face refractories, evaluating non-wetting materials, promoting sintering, and adding phosphates. NETL researchers found that phosphate additives to the  $\text{Cr}_2\text{O}_3$  refractories decreased slag penetration in laboratory tests. Phosphate additives are commonly used by the refractory industry, especially in ramming mixes or castable, where they enhance the bond strength from room to high temperatures. Phosphate additives in  $\text{Cr}_2\text{O}_3$  refractory were made with the goal of reacting with molten penetrated slag, high in calcium silicates, to form highly siliceous melts that would slow or stop slag penetration due to increasing network bonding, resulting in higher viscosity.

Field trials were conducted on the phosphate containing refractory versus conventional refractory. Result indicated that the performance of NETL developed  $\text{Cr}_2\text{O}_3$  refractory lining has reduced structural spalling and less wear. The conventional non-phosphate containing refractory suffered from greater structural spalling/cracking, while the NETL developed  $\text{Cr}_2\text{O}_3$  refractory materials were flawless and less corroded (figure 4).



Fig. 4 Phosphate containing refractory (middle) versus conventional refractory (left) after field trials with a virgin brick (right) for comparison.

#### 4. US Coal Slag

A coal quality database was published by USGS [5] listing coal properties of United States coals. This report recorded 136 parameters including location and sample description, analytical data from ASTM tests, and USGS tests for major-, minor-, and trace elements from 7,430 coal samples that represent complete-bed thicknesses at various localities. From this data, ash chemistry of 11 oxide components from 4503 coal samples were compiled and are listed in table 2

Table 2 –Average US coal ash chemistry

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
Avg	43.4	23.0	3.7	17.3	1.11	0.03	0.66	1.71	1.15	0.43	3.93
Max	93.0	46.0	42.0	88.0	19.00	1.50	13.00	6.80	5.60	9.70	37.00
Min	7.4	1.6	0.1	0.3	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Std	11.8	6.9	4.7	14.3	1.12	0.07	1.07	0.96	0.50	0.58	4.80

Figure 5 shows the classification of coal ash and indicates that most of US coal ash belong to Siallic and Ferrisialic groups ranging from high to low acid. This means that most US coal ash originated from aluminosilicates such as clay, quartz-cristobalite-tridymite, mica minerals, K-feldspar, and iron oxides-hydroxides, or iron containing glass. However, this classification cannot yield detailed engineering information about the slag characteristics. Therefore, a ternary phase diagram (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO) was used to explore slag characteristic. As previously mentioned, slag contains 11 oxides, which can be categorized in 3 groups as acidic, neutral and basic oxides. Figure 6 shows that the isothermal liquidus lines and primary phase regions in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO system, and shows about 4500 data points which were drawn on the phase diagram of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO using the assumption that SiO<sub>2</sub> represents the summation of all acidic oxides, and FeO all basic oxides. This figure estimates that some US coal slag have very high liquidus temperature (above 1600 °C) and the most should have mullite as their primary phase. Spinel (hercynite FeO-Al<sub>2</sub>O<sub>3</sub>) is another possible major primary phase, but should not occur at high temperature (1400 °C). In addition, it was noted that some coal slag can be completely molten

before temperature of 1300 °C are reached. This figure also indicates that the ratio of acidic oxides (majority is SiO<sub>2</sub>) to neutral oxide (Al<sub>2</sub>O<sub>3</sub>) range from 5.6 to 1.2.

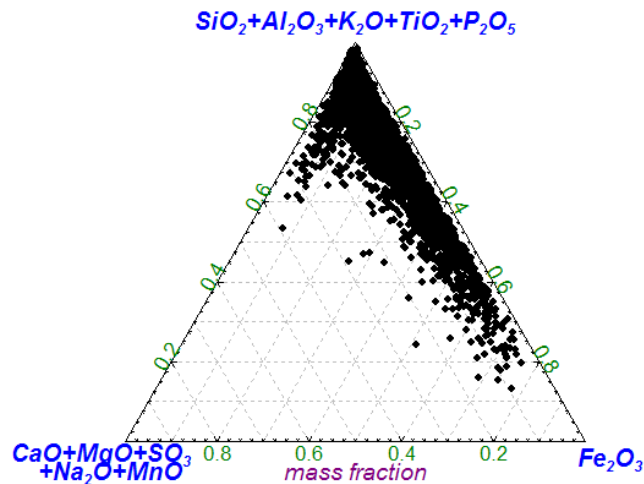


Fig. 5 Classification of US coal ash

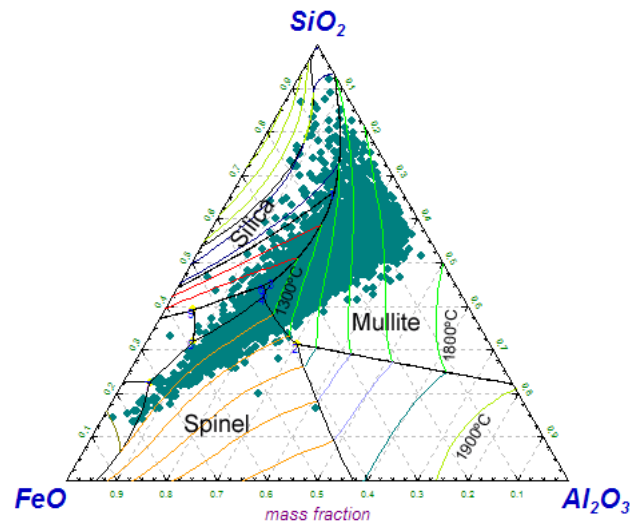


Fig. 6 The phase diagram of SiO<sub>2</sub>-FeO-Al<sub>2</sub>O<sub>3</sub> and the US coal slag chemistry distribution

Basicity is another important index used to define the characteristics of slags. It is often used as a means of selecting the best refractory material for use in slagging conditions. In general, acidic refractory should be selected for acidic slags, and basic refractory for basic slags. However, neutral refractory may be considered for use with acidic slag because acidic refractory generally do not have good physical properties at high temperatures.

There are different ways to calculate the basicity of slag. The way used in this paper, called the excess base method, adopted the following equation:

$$B^{XS} = \sum x_i b_i + x_2 b_2 + x_3 b_3 + \dots$$

where

x: the mole fraction of oxide species present in the coal ash

b: constants related to the ion-oxygen attraction for specific oxides

Oxides	CaO	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	MgO	FeO
b <sub>i</sub>	6.05	-6.31	-4.97	-0.2	4.8	4.0	3.4

The excess base method takes into account iron and other oxides present in coal ash except Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and SO<sub>3</sub>. Figure 7 shows the calculated results of basicity distribution of US coal slag. Using the excess base method, the majority of US coal slag is acidic with less than three percent of them classified as neutral or basic (value more than 0).

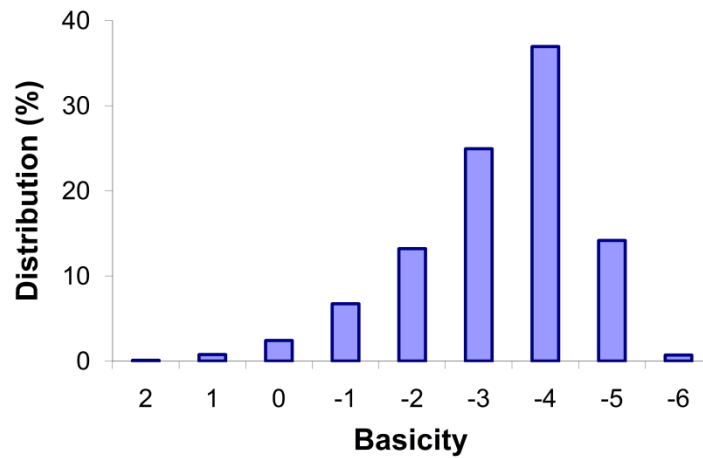


Fig. 7 The basicity distribution of US coal slag

The saturation of an oxide component in a slag is important to slow refractory corrosion where an oxide component is a primary phase; an oxide is most likely to be saturated in the slag if the gasifier temperature is lower than the slag melting point (liquidus temperature). Primary phases can be estimated by experiment, phase diagrams, thermodynamic calculations or models using all the information. Thermodynamic calculations were performed using a commercially available software, Factsage™, to find the liquidus temperature, primary phase, and solid content of the 4500 coal slags at temperature from 1300 to 1600 °C in 20 °C increments and at the oxygen partial pressure 10<sup>-8</sup> atm. Result indicated that about 50% of coal slags have a theoretical liquidus temperature above 1600 °C. Results also indicated that primary phases in coal slag were mullite, quartz, kaliophilite (KAlSiO<sub>4</sub>), anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), corderite, corundum, pyroxene, and spinel. Among them, mullite is the major primary phase in slag with 72% of the coal slags having it as their primary phase (figure 8). Some primary phases in figure 8 show zero percentage because their percentages are less than 0.5, and were rounded to zero in the

mathematic operation. In addition, thermodynamic calculations also point out that 11% of coal slags have their liquidus temperature below 1300°C (no primary indicated in figure 8).

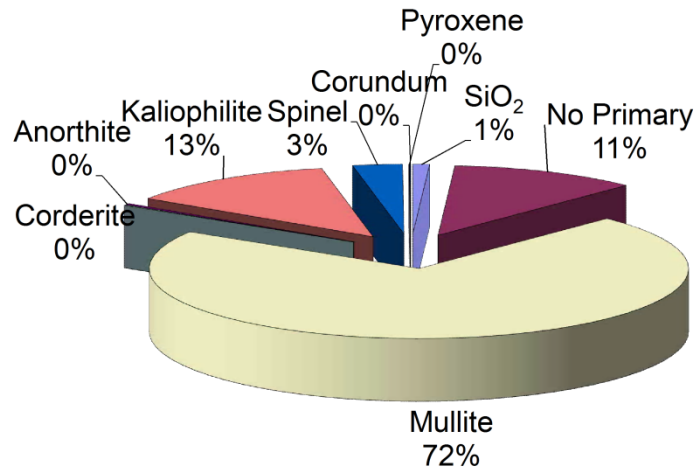


Fig. 8 The distribution of primary phase of US coal slag

## 5. The interaction of gasifier refractory with US coal slag

Illinoise #6 coal, Powder River Basin coal, Al<sub>2</sub>O<sub>3</sub> refractory and Cr<sub>2</sub>O<sub>3</sub> refractory were selected for thermodynamical studies of the interaction between refractories and US coal slags. Illinois #6 and Powder River Basin coals have been frequently cited as feedstock for gasifiers [6,7]. Illinois #6 coal is a bituminous coal and contains about 13 % water, in contrast, Powder River Basin coal is a sub-bituminous coal with 30% water. Illinois #6 and Powder River Basin coal slag chemistry are shown in table 3. Generally, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> are considered as neutral oxides when used for refractory liners. Al<sub>2</sub>O<sub>3</sub> refractory is very popular and used in many applications, while, Cr<sub>2</sub>O<sub>3</sub> refractory is used primarily in glass fiber and gasification industries. Factsage was used to calculate thermodynamic interactions between Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> refractories and Illinois #6 coal from 1300 to 1600 °C in a gasifier atmosphere (Fig. 9 and 10).

Figure 9 shows that Illinois #6 coal slag completely melts at around 1300 °C and that increases in temperature will dissolve Al<sub>2</sub>O<sub>3</sub> refractory dramatically. For example, 100 gm of Illinois slag will dissolve 25 gm Al<sub>2</sub>O<sub>3</sub> refractory at 1600 °C before it reaches an equilibrium condition. This figure also shows that mullite or CaAl<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> may be formed in the interaction zone of slag and Al<sub>2</sub>O<sub>3</sub> refractory. Figure 10 shows that 100 gm Illinois slag dissolves 10 gm of Cr<sub>2</sub>O<sub>3</sub> refractory at 1600 °C and that spinel (or FeCr<sub>2</sub>O<sub>4</sub>) will form after slag interacts with Cr<sub>2</sub>O<sub>3</sub>. Post mortem analysis by SEM and EDX of interaction between coal slag and Cr<sub>2</sub>O<sub>3</sub> refractory removed from a commercial gasifier confirmed the formation of spinels, which are FeAl<sub>2</sub>O<sub>4</sub> and FeCr<sub>2</sub>O<sub>4</sub>. Figures 9 and 10 demonstrate that Cr<sub>2</sub>O<sub>3</sub> has better corrosion resistance than Al<sub>2</sub>O<sub>3</sub>.

Table 3 Illinois #6 and Powder River Basin Coal Slag Chemistry

Wt%	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>
Illinois #6	54.31	18.00	14.04	10.33	1.18	0.41	1.69	0.05
Powder River Basin	32.15	16.48	4.55	34.14	9.77	2.61	0.31	0.00

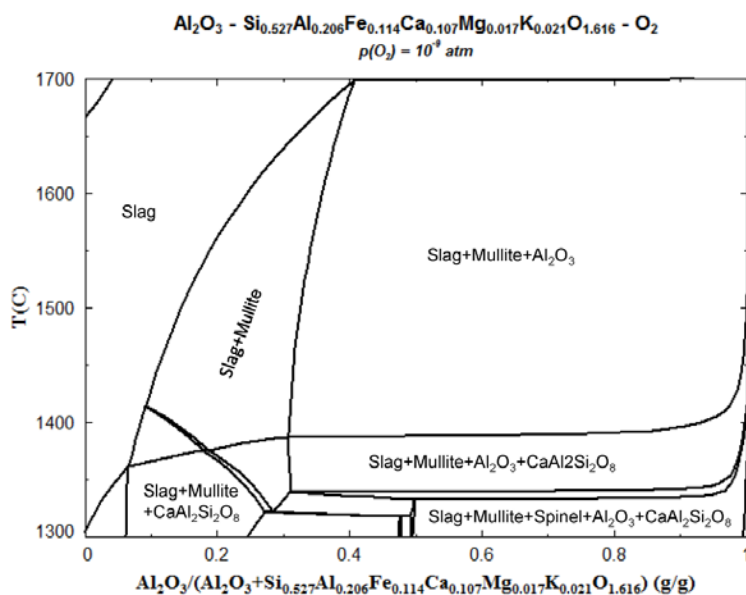


Fig. 9 Thermodynamical calculations of the interactions between Al<sub>2</sub>O<sub>3</sub> refractory and Illinois #6 coal slag.

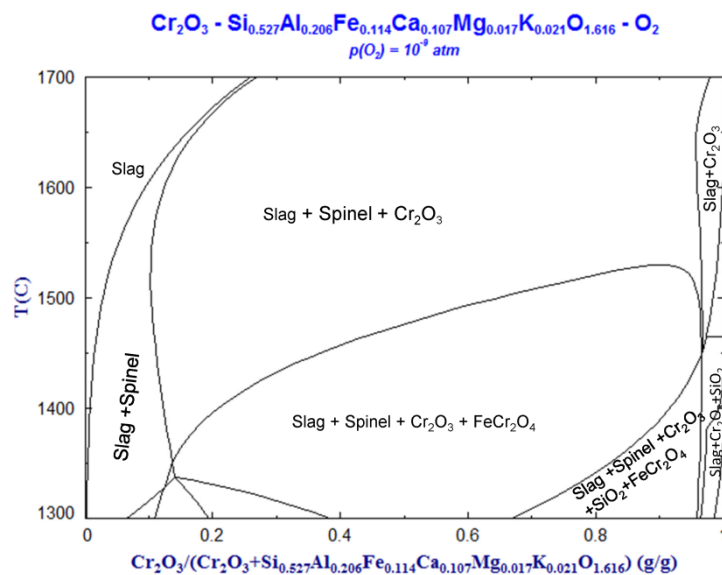


Fig. 10 Thermodynamical calculations of the interactions between Cr<sub>2</sub>O<sub>3</sub> refractory and Illinois #6 coal slag

Figure 11 shows the interaction between Powder River Basin coal slag and  $\text{Cr}_2\text{O}_3$  refractory at a temperature range from 1300 to 1600 °C in a gasification atmosphere. This figure indicates that Powder River Basin coal slag is complete molten by 1430 °C and that a minor amount of  $\text{Cr}_2\text{O}_3$  dissolves into the slag at 1600 °C.

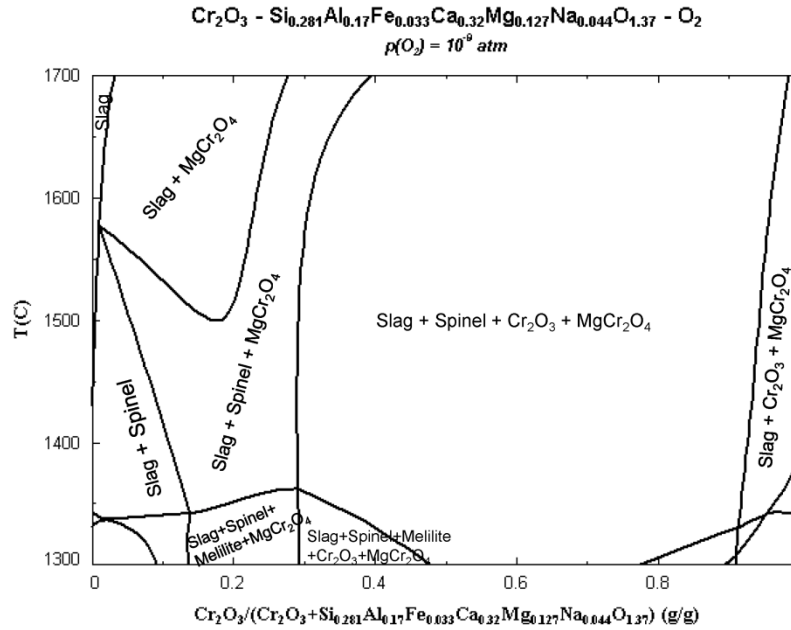


Fig. 11 Thermodynamical calculations of the interactions between  $\text{Cr}_2\text{O}_3$  refractory and Powder River Basin coal slag

As previously mentioned, the NETL developed phosphate containing  $\text{Cr}_2\text{O}_3$  refractory has better structural spalling resistance than traditional commercial  $\text{Cr}_2\text{O}_3$  refractory because it reduces slag penetration into the refractory. Post mortem chemical analysis indicated that slag penetration into pores of the  $\text{Cr}_2\text{O}_3$  refractory material contained primarily  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and a depletion of  $\text{FeO}$  in the slag. Phosphate additives in the  $\text{Cr}_2\text{O}_3$  refractory reacted with molten penetrated slag, calcium silicates, to form highly siliceous melts that would slow or stop slag penetration due to increasing network bonding. Figure 12 (a, b, and c) shows  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{CaO}$ - $\text{P}_2\text{O}_5$  liquidus projections where  $\text{P}_2\text{O}_5$  was set to a constant concentration of 1, 3, and 7 wt% separately. Figure 12a, with a 1 wt%  $\text{P}_2\text{O}_5$  concentration, indicates that the lowest liquidus temperature in the phase diagram is less than 1300 °C. While, Figure 12 c, with a 7 wt%  $\text{P}_2\text{O}_5$  concentration, shows that the lowest liquidus temperature is around 1400 °C and the liquid composition was changed. Figure 12 indicates that the  $\text{P}_2\text{O}_5$  increased the liquidus temperature of penetrated acidic slag. Figure 13 shows post mortem SEM analysis at the depth of 6-8 mm below the hot face, where the existence of  $\text{AlPO}_4$  was noted. It was thought  $\text{AlPO}_4$  was responsible for slowing or stopping slag penetration because of the phase diagrams in Figure 12.

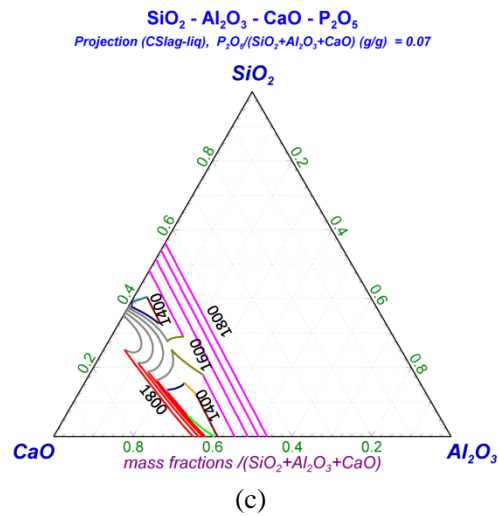
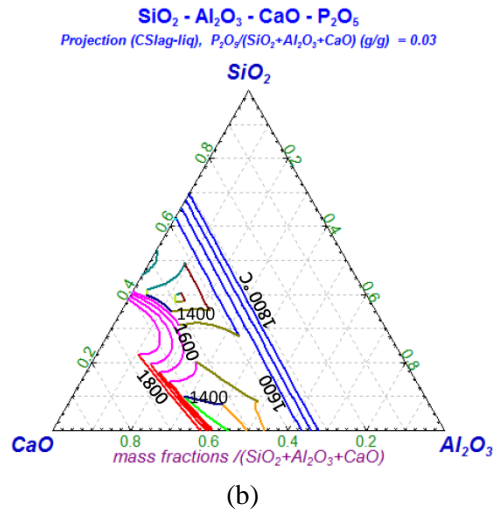
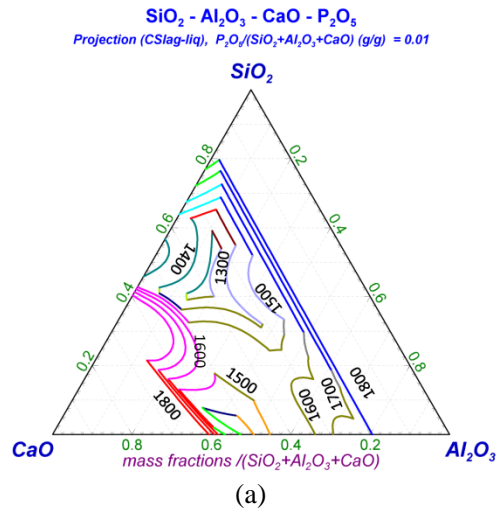


Fig. 12 The phase diagrams for SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-P<sub>2</sub>O<sub>5</sub> system containing (a) 1; (b) 3; and (c) 7 percent P<sub>2</sub>O<sub>5</sub> separately.

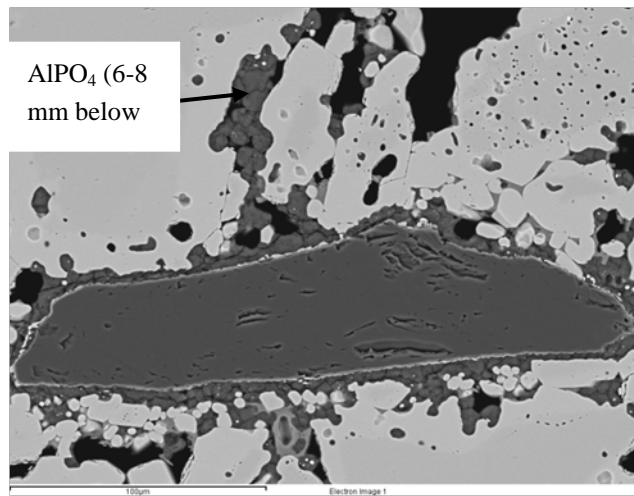


Fig. 13 SEM micrograph of NETL developed phosphate containing  $\text{Cr}_2\text{O}_3$  refractory after exposure to slag in a field trial

## 6. Conclusions

Statistical analysis showed that most of US coal ash belongs to Siallic and Ferrisialic groups ranging from high to low acid from sources of aluminosilicates such as clay, quartz-cristobalite-tridymite, mica minerals, and K-feldspar. The excess basicity calculation indicated that the majority of US coal slag is acidic, with less than three percent neutral or basic. US coal slag properties were thermodynamically investigated, including liquidus temperature, primary phase precipitation, and solid content at temperatures from 1300 to 1600 °C in 20 °C increments. Results indicated that mullite is the major primary phase in US coal slag. It implied that  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  saturation are possible when the temperature is below the liquidus temperature. Thermodynamic studies also proved that  $\text{Cr}_2\text{O}_3$  has better corrosion resistance than  $\text{Al}_2\text{O}_3$ , and that phosphate additives can increase the liquidus temperature of penetrated slag. The National Energy Technology Laboratory (NETL), US DOE developed a phosphate containing  $\text{Cr}_2\text{O}_3$  refractory and demonstrated it can dramatically decrease slag penetration depth and extend refractory service life. Post mortem analysis revealed the existence of  $\text{AlPO}_4$  at the location of 6-8 mm below the hot face; the maximum depth of slag penetration. It was thought  $\text{AlPO}_4$  slowed or stopped slag penetration.

**Disclaimer:** "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

## References

- [1] G.Stiegel, and S. Clayton, "DOE Gasification Industry R& D Survey: A Perspective of Long Term Market Trends and R&D needs" Proceedings from the Gasification Technologies 2001 Annual Meeting, San Francisco, CA.
- [2] J. Bonar, C. Kennedy, and R. Swaroop, "Coal-Ash Slag Attack and Corrosion of Refractories" Am Ceram Soc Bull. 1980, 59(4), p473-478.
- [3] B. Jones "Gas Turbine Fuel Flexibility For A Carbon Constrained World" Workshop on Gasification Technologies Bismarck, ND June 28, 2006.
- [4] K.S. Kwong, A. Petty, J. P. Bennett, R. A. Krabbe, H. H. Thomas, Wear Mechanisms of Chromia Refractories in Slagging Gasifiers International Journal of Applied Ceramic Technology, 2007, 4(6), p503–513.
- [5] L.J. Bragg, J.K. Oman, S.J. Tewalt, C.J. Oman, N.H. Rega, P.M. Washington, R.B. Finkelman, U.S. Geological Survey open-file report 97-134 .
- [6] K. Natesan and M. Thiele. Influence of Water Vapor and Slag Environments on Corrosion and Mechanical Environments on Corrosion and Mechanical Properties of Ceramic Materials. Eleventh Annual Conference on Fossil Energy Materials: May 20-22, 1997. Part 1 p57-69.
- [7] T.M. Strobel, J. P. Hurley, Coal-ash Corrosion of Monolithic Silicon Carbide-based Refractories by Fuel Processing Technology, 1995, 44 (1-3), p201-211.