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The effects of gasification feedstock chemistries on the infiltration of slag into the porous high chromia refractory and their reaction products

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HIGHLIGHTS

- Slags with compositions resembling ash derived from coal and petroleum coke were synthesized.
- Infiltration of synthetic slags was simulated with a thermal gradient induced in the refractory.
- The slag–refractory interactions under coal gasification conditions were investigated.
- The products of the slag–refractory interaction were examined and their formation was discussed.

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ABSTRACT

Synthetic slags with compositions representative of carbonaceous feedstock derived from coal and petroleum coke were infiltrated into 90%Cr_2O_3–10%Al_2O_3 refractory material with a temperature gradient induced along the penetration direction of the slag. Experiments were conducted with a hot-face temperature of 1723 K (1450 °C) in a CO/CO_2 gas mixture with a ratio of 1.8, which corresponded to an approximate oxygen partial pressure of 10^{-8} atm. Interactions between the slags and the refractory produced solid-solution spinel layers on the top interfaces of the refractory samples, whose chemistries reflected the compositions of major constituents of the starting slags. $FeCr_2O_4$ formed when samples were infiltrated with slag composition rich in FeO, which was typical for coals derived from eastern USA. $(Mg,Fe)Cr_2O_4$ formed when samples were infiltrated with slags, containing considerable concentrations of both MgO and FeO that were common in western US coals. In slags resulted from substituting 50% (by weight) of the coal feedstock by petcoke, similar solid solution phases formed as the pure coal counterparts, but with addition of V_2O_3, which originated from the petcoke feedstock. The chromium spinel layers, to a reasonable extent, limited infiltration by hindering the slag from flowing into the porous microstructure of the refractory and the formation mechanisms of the product layers were discussed. The $Fe(Cr,V)_2O_4$ layer that formed in the presence of petcoke ash exhibited an uneven morphology. As compared to the FeO rich slags, MgO rich slags penetrated further beyond the protective layers and into the refractory. Both of these phenomena could lead to increased refractory spallation rates in actual gasification conditions.

1. Introduction

Entrained-flow gasification converts mixtures of carbon-based materials such as coal, biomass, and petroleum coke into synthesis gas (syngas), a fuel rich in carbon-monoxide and hydrogen gases. The flexibility to utilize a wide breadth of feedstock options can provide increased fuel flexibility and potentially greater reduction in CO_2 emissions when used with carbon capture and storage. However, with operation temperatures and pressures as high as 1600 °C and 2.8 MPa, the mineral impurities from the feedstock fuse together into slag, which attack the porous refractory lining that shields the external steel casing of the gasifier [1]. After slag infiltrates into the refractory, variations in the chemical and physical properties of the materials cause cracks and voids to form near the refractory surface to the point of penetration [2,3].

Penetration of molten slag into refractory is controlled by temperature, gasification atmosphere, refractory porosity, slag composition and interfacial surface properties of the slag with respect to microstructure and chemistry of the refractory material [4]. This

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analysis focuses upon understanding how slag composition influences the slag infiltration into porous refractory.

Petroleum coke (petcoke) is a carbonaceous by-product from petroleum processing. Petcoke has high energy value, high carbon content and lower impurity content than coal, and hence it has become an attractive alternative feedstock for gasifiers. As shown in the worldwide petcoke usage data in ref. [5], the increase is significant over the recent years and is projected to continue to grow. The total ash content of coal is typically around 10 wt%, whereas that of petcoke is 1–2 wt% [6]. However, one disadvantage with petcoke is its significant amount of vanadium oxides such that it may require the addition of additives such as limestone or silica sand to maintain required slag flow characteristics in the system. This can be further complicated where petcoke is used in a fuel blend, with coal. The compositions of the consequent slags depend on the source of petcoke and the coal that it is blended with. Some typical compositions of a few petcoke slags can be found in Ref. [7].

Vanadium has a number of valence states, which are strongly dependent on the temperature and oxygen partial pressure in the gasifier. However, the thermodynamic data and phase diagrams of VO_x in slag solutions are sparse in public databases [8], which render limited understanding of the thermo-physical properties such as change of slag viscosity and the mechanism by which vanadium-containing slags interact with refractory materials [7]. Although the trade may consider petcoke slags to possess similar behaviors to those of the coal slags [7], this has yet to be evaluated experimentally and extensively.

A number of refractory materials have been considered or evaluated for use with coal and petcoke feedstock in slagging gasifier environments, such as sintered or fused cast alumina-silicate, high alumina, chromia–alumina, chrome–magnesia, alumina, and magnesia, as well as SiC refractory materials [9–13]. Each of these refractory materials has its own merits and disadvantages in terms of corrosion and wearing. Alumina refractories are not used in slagging gasifiers with petcoke-containing feedstock because vanadium found in petcoke slags can aggressively attack alumina refractories, rapidly decreasing service life. Based on laboratory-scale tests and industry trials, chromia-containing refractories were found to have the best overall properties and performance to be used as hot-face refractory material, including refractories made with Cr_2O_3–Al_2O_3, Cr_2O_3–Al_2O_3–ZrO_2, and Cr_2O_3–MgO systems [13–15]. Therefore, this study only considered high chromia refractory, i.e. 90%Cr_2O_3–10%Al_2O_3.

Representative slag chemistries were chosen and synthesized to simulate potential gasification feedstocks and their infiltration behaviors into 90%Cr_2O_3–10%Al_2O_3 refractory were studied using microscopy and diffraction techniques to identify product phases and changes in morphology.

2. Materials and methods

2.1. Materials

Synthetic slags with compositions, resembling those created by the mineral impurities in representative feedstock for entrained-flow slagging gasifiers, were used in this investigation. Representative slag compositions [7,16] were selected by taking averages of ash constituents derived from petroleum coke (petcoke) and eastern and western coal feedstock from the United States, with the former having a more acidic ash composition and the latter being more basic. The slag compositions were determined for the feedstock blends: 100% eastern coal (EC), 50 wt% eastern coal – 50 wt% petcoke (ECP), 100% western coal (WC), and 50 wt% western coal – 50 wt% petcoke (WCP) feedstock. The ash contents of eastern coal, western coal and petcoke feedstocks are 10%, 9%, and 1%, respectively. The ECP and WCP slags are similar to their EC and WC counterparts, but contain minor additions of V_2O_3.

Oxide powders were weighed and mixed to their appropriate ratios, then pre-melted in a high-density Al_2O_3 crucible at 1500 °C for 2 h in a CO/CO_2 gas mixture with a ratio of 1.8 (corresponding to an oxygen partial pressure of approximately 10^{-8} atm) in order to ensure that the oxidation state of Fe and V ions were maintained constant. The slag was cooled at roughly 20 °C/min by lowering the sample and the surrounding Al_2O_3 furnace tube out of the hot-zone. The slag was then extracted from the crucible and ground into roughly 2 mm particles. The desired target compositions and the experimentally achieved compositions are summarized in Table 1.

Commercial 90%Cr_2O_3–10%Al_2O_3 refractory bricks with fused grains were cored into cylindrical cups for accepting the slag. The outer dimensions of the samples were machined to a diameter of 5.08 cm and a height of 11.11 cm. The cup portions of the samples were machined to a diameter of 3.18 cm and a height of 3.49 cm. The composition of the refractory is summarized in Table 2.

3. Experimental methods

To verify the constituents and characteristics of the starting materials, the synthetic slags and the refractory in their virgin states were examined using an FEI Quanta 600 environmental scanning electron (ESEM) microscope with energy dispersive

Table 1
Target compositions and experimentally achieved compositions of synthetic slags. Experimental compositions were analyzed using XRF. Results are presented in oxide mol%.

	Slags	Al_2O_3	SiO_2	FeO	CaO	MgO	Na_2O	K_2O	V_2O_3	Basicity CaO/SiO_2
EC	Target	18.30	53.70	15.90	7.67	2.31	1.02	1.1		
	Pre-melted	19.07	53.08	15.19	7.79	2.13	0.82	1.90		0.15
ECP	Target	17.51	52.09	15.46	7.86	2.37	1.07	1.09	2.55	
	Pre-melted	17.15	51.13	14.91	9.04	2.50	0.90	1.71	2.66	0.18
WC	Target	10.48	32.50	9.42	29.30	11.45	6.12	0.74		
	Pre-melted	10.60	32.89	8.31	29.66	11.64	6.15	0.75		0.90
WCP	Target	10.18	32.14	9.44	28.19	11.00	5.76	0.77	2.52	
	Pre-melted	14.10	31.28	7.44	28.79	9.07	5.54	1.07	2.70	0.92

Table 2
Composition of 90%Cr_2O_3–10%Al_2O_3 refractory. Results are presented in oxide mol%.

	Al_2O_3 (%)	SiO_2 (%)	Cr_2O_3 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Na_2O (%)
90%Cr_2O_3–10%Al_2O_3	9.87	0.05	89.65	0.21	0.13	0.09	0