

Prediction of coal slag foaming under gasification conditions by thermodynamic equilibrium calculations

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Abstract—In slagging gasifiers, slag foaming can cause serious operational problems, so there is a need for investigation into the conditions causing slag foaming. Viscosity experiments were carried out examining viscosity, extent of swelling and Fe formation. Although extensive swelling was not observed, FeO reduction was observed under an N₂/CO gas atmosphere, but not under CO₂/CO. In order to predict FeO reduction conditions in the gasifier, a model for an adiabatic equilibrium gasifier was developed. The gas composition, the amount of gas to slag, and P_{O₂} were calculated for a slurry-feed gasifier, and the results of the calculation were used to predict the reduction of FeO in slag by using FactSage. Under typical gasification conditions for Denisovsky coal, the predicted P_{O₂} in the gasifier was not low enough to cause FeO reduction. The FactSage simulation for the viscometer conditions predicted no FeO reduction under a CO/CO₂ atmosphere, but did predict Fe formation under CO/N₂ conditions. At a 20% CO concentration, FeO reduction starts at temperatures above 1,600 °C. Since the slag has a low viscosity at 1,600 °C, the oxygen bubble may have escaped as it formed. Therefore, slag foaming, caused by FeO reduction in the slag, can only occur when the right conditions of viscosity and oxygen partial pressure are met.

Key words: Gasification, Slag, FeO Reduction, Foaming

INTRODUCTION

In the entrained flow type of gasifiers, slag viscosity is an important parameter which determines gasification conditions [1,2]. Slag viscosity has been determined experimentally under isothermal conditions or under slow cooling rates, and the viscosity data were used to determine the gasification temperature, making sure there was continuous flow and, therefore, continuous removal of slag. In dry-feed gasifiers, which operate at temperatures well above 1,500 °C, the viscosity is used as related to the refractory lifetime; the lower viscosity slag penetrates more into the refractory, causing chemical corrosion and spalling of the refractory. Isothermal measurements do not, however, render any information on slag viscosity behavior under rapid cooling conditions, such as the condition at the slag tap of the gasifier.

As the cooling rate increases, the viscosity at a given temperature decreases, and the slag remains fluid to quite a low temperature. The low viscosity helps the slag flow out of the slag tap, so it was not a concern until one particular coal, Denisovsky coal, was tested. Denisovsky coal, which is a Russian sub-bituminous coal, was one of the nine coals tested under the project, "Development of Fundamental Technologies for the IGCC Systems," funded by the Korean Ministry of Commerce, Industry and Energy [3,4]. All nine coals were tested in two pilot scale entrained flow gasifiers: a 3-ton/day dry-feed gasifier at the Institute of Advanced Engineering (IAE), Suwon, Korea, and a 1-ton/day slurry-feed gasifier at the Korean Institute of Energy Research (KIER), Taejeon, Korea.

While the Denisovsky coal slag did not cause any operational problems at the high temperature of the dry-feed gasifier, slag foaming occurred in the slurry-feed gasifier, filling up most of the volume of the gasifier vessel, and resulting in its shut-down.

Slag foaming was also observed in the laboratory during viscosity measurements. Under 2 °C/min cooling, the swelling of coal slag was observed but was not extensive; the slag remained inside the crucible, but filled the space which had been occupied by the rotor. The slag contained a large number of small spherical pores throughout the sample. At 10 °C/min cooling, the slag showed excessive swelling; it not only filled the rotor space, but also expanded above the crucible. The portion extruded above the crucible had a rust colored coating of relatively high strength. The hardness of the slag decreased towards the bottom of the crucible, becoming very brittle, to the point that it could be crushed by hand. Many big spherical pores were observed at the bottom of the crucible. The spherical pores suggested gas formation inside the slag, and the metallic iron balls found in the lower part of the crucible confirmed that the reduction of FeO to metallic iron caused the swelling.

The conditions for slag foaming were investigated in this paper. The viscosity of the synthetic slag was measured at two cooling rates, 2 and 10 °C/min, and the cooled slag was examined for pore and Fe formation. FactSage equilibrium analyses were carried out to determine the conditions for FeO reduction to Fe.

EXPERIMENTAL

Slag sample: Synthetic slag was formulated by using the composition of Denisovsky slag. Only the major components were used, and the concentrations of dissolved refractory components such as Cr₂O₃ and ZrO₂ were excluded. The composition of the synthetic slag is shown in Table 1 along with Denisovsky coal properties. One

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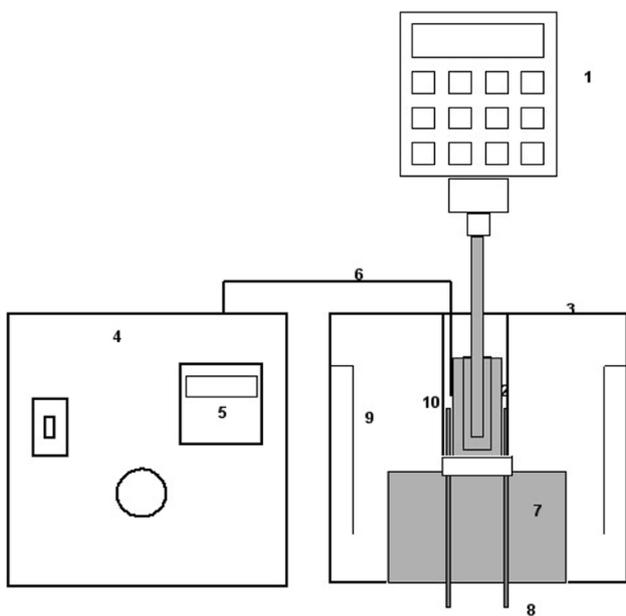
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Table 1. Composition of synthetic Denisovsky slag

Proximate analysis (wt%), as-received basis						
Moisture	Volatile matter	Fixed carbon	Ash			
8.8	20.1	59.1	12.1			
Ultimate analysis (wt%), moisture-free basis						
C	H	N	S	Ash		
74.2	4.7	0.72	0.34	13.24		
Ash composition ^a						
SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
51.9	27.1	5.7	9.7	1.5	0.5	1.8

^aAlso the synthetic slag composition.

**Fig. 1. Schematic of a high temperature viscometer.**

1. Viscometer (Brookfield HB-DVIII)
2. Alumina cell (Cup & Rotor)
3. Lindberg blue/M furnace
4. Control box
5. Temperature controller
6. B-type thermocouple
7. Alumina support plate
8. N₂/CO gas inlet tube
9. Heating elements
10. Mullite tube

can see that the slag had high concentrations of SiO₂ and Al₂O₃, and a low concentration of CaO. High purity chemicals in fine powder form were mixed and shaped into small spheres by using water-based glue for easy feeding and melting. The agglomerated synthetic ash was dried for 10 hours before feeding into the crucible at 1,600 °C.

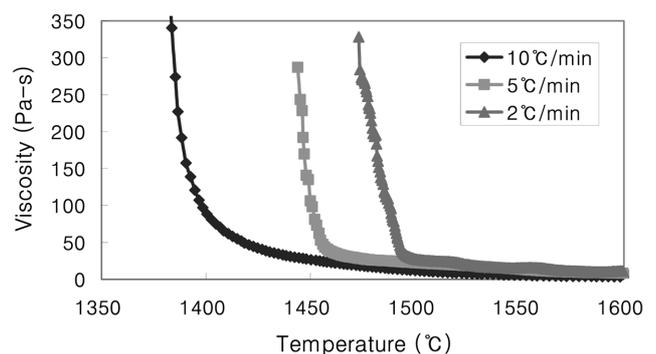
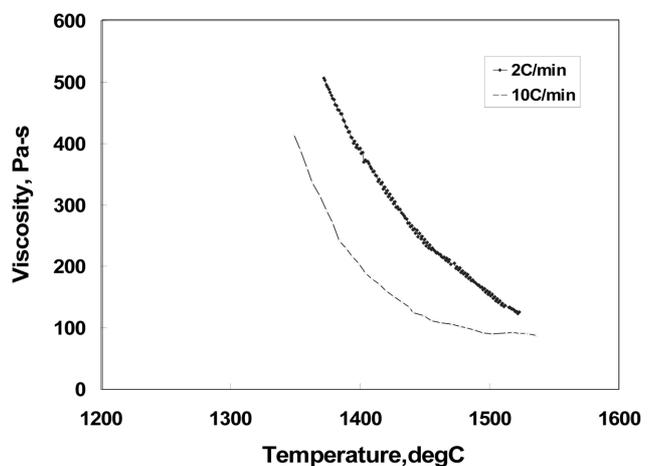
Viscometer: a Brookfield HB-DVIII viscometer with a Searle type coaxial cylindrical cell was used in viscosity measurements [5]. The schematic of the viscometer is shown in Fig. 1. The cell (stationary crucible and rotor) was made of high-density alumina and was placed in a high temperature furnace with a maximum attainable temperature of 1,600 °C. In order to simulate a reducing atmosphere, 80/20 (volume%) mix of CO₂/CO or N₂/CO was injected from the bottom of the furnace at 1,000 cm³/min. Once the

furnace and the cell were heated to 1,600 °C, we slowly fed approximately 55 g of slag samples into the crucible, making sure the slag was completely melted before the next feeding. When all the slag was fed and the rotor assembled, the temperature of the furnace was lowered at rates ranging from 2 to 10 °C/min. The viscosity was recorded every 12 s at a constant shear rate of 10 rpm, until the torque on the rotor reached 90% of the maximum measurable by the viscometer. The rotor was then removed from the molten slag and the whole assembly was allowed to cool naturally. The cooled slag was examined for the extent of swelling, pore formation, and Fe formation.

RESULTS AND DISCUSSION

1. Viscosity of the Synthetic Slag and the Extent of Swelling

Fig. 2 shows the viscosity as a function of temperature under cooling rates of 2, 5 and 10 °C/min. As expected, a lower viscosity was observed under the rapid cooling conditions, extending the fluid region to about 1,400 °C when the slag was cooled at 10 °C/min. As compared to the Denisovsky slag data shown in Fig. 3, the viscosity of the synthetic slag was lower than that of Denisovsky slag, and had more of the crystalline slag characteristics. At 10 °C/min cooling, the viscosity of the synthetic slag was lower than that of

**Fig. 2. Effect of cooling rate on the viscosity of synthetic slag under reducing atmosphere.****Fig. 3. Viscosity of Denisovsky coal slag as a function of temperature at two cooling rates [5].**

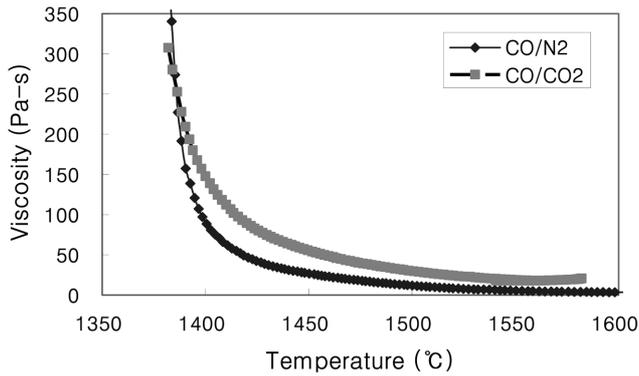


Fig. 4. Effect of gas atmosphere on the viscosity of synthetic slag at 10 °C/min cooling.

Denisovsky coal slag at temperatures higher than 1,400 °C, while, at temperatures lower than 1,400 °C, the viscosity rapidly increased, showing much higher viscosity than that of Denisovsky coal slag.

The viscosity was also affected by the gas atmosphere. Fig. 4 shows the changes in the slag viscosity when the 80/20 mole% of CO₂/CO and N₂/CO gas mixtures were used as a reducing gas. The slag under N₂/CO atmosphere showed lower viscosity than that under CO₂/CO. Based on the acid/base theory, the slag was expected to exhibit a lower viscosity under reducing conditions, where an acid component, Fe₂O₃, is reduced to a base, FeO. Therefore, one can expect that the N₂/CO gas mixture forms a stronger reducing atmosphere than CO₂/CO.

When cooled, the slag under CO₂/CO gas formed a homogeneous glass phase without any crystalline phase. While other coal slags

showed an empty space in the middle created by rotor removal, in this case, the rotor space was refilled with the slag but the severe swelling seen in Denisovsky slag (See Fig. 5(a)) was not observed. Furthermore, we did not find any evidence of FeO reduction.

The slag under N₂/CO gas also formed a glass phase with the rotor space being refilled with slag. Fig. 5 shows the cross sectional view of the synthetic slag after the viscosity measurements under N₂/CO gas. The swollen Denisovsky coal slag is presented for comparison. Even though the extensive swelling seen in the Denisovsky coal slag was not observed, a number of small pores were formed inside the slag, and the evidence of FeO reduction was easily found: a large spherical ball of metallic iron was observed at the bottom of the crucible.

Table 2 summarizes the experimental observations on swelling and FeO reduction under various cooling rates and gas atmospheres. The extensive swelling observed in the Denisovsky coal slag was not observed in any of the experiments with the synthetic slag, while the FeO reduction was observed under 5 and 10 °C/min cooling in a N₂/CO atmosphere.

The difference in the extent of swelling between the Denisovsky slag and the synthetic slag samples can be explained by the difference in viscosity. When the reduction of iron oxides starts, oxygen bubbles form and can move upward more readily in the slag matrix with the lower viscosity, and escape through the top surface. The terminal velocity of the bubble movement can be described according to the following equation [6]:

$$v_i = \frac{2R^2 \rho g}{9\mu}, \quad (1)$$

where R is the bubble radius, ρ the slag density, g the gravitational

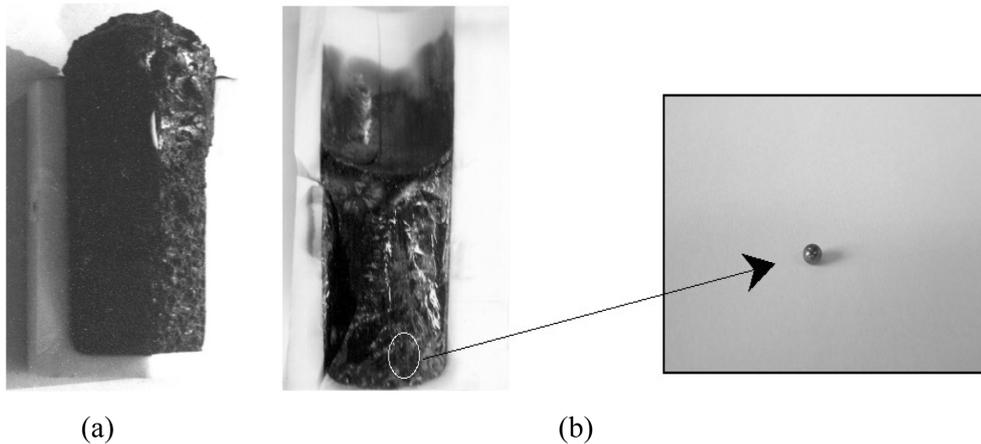


Fig. 5. Slag after cool down (a) swollen Denisovsky slag after 10 °C/min cooling and (b) synthetic slag with Fe ball formed from the reduction of iron oxide.

Table 2. Slag swelling and FeO reduction observed under CO/CO₂ and CO/N₂ atmospheres

Cooling rate	CO/CO ₂		CO/N ₂		
	2 °C/min	10 °C/min	2 °C/min	5 °C/min	10 °C/min
Swelling	×	×	×	×	×
The formation of Fe	×	×	×	○	○

Note: O: observed, X: not observed

constant, and μ is the slag viscosity. For a 1 mm bubble, the time required to travel through 4 cm of 20 Pa-s slag melt and reach the surface is roughly 3.7 min, while it takes 37 min through a 200 Pa-s slag melt.

As the gas formed from the molten slag is transferred to bubbles, the bubbles expand with the expansion rate affected by mechanical forces such as the internal and external pressures of the bubble, surface tension, and inertia and viscous forces. Assuming (1) constant fluid density, viscosity and surface tension; (2) the liquid behaves as a Newtonian fluid; (3) liquid density \gg gas density; bubble radius \ll distance between bubbles, and (4) viscous force \gg inertial force [7-9], the simplest bubble growth rate is expressed as the following:

$$\frac{dr}{dt} = \frac{r}{4\mu} \left(P_b - P - \frac{2\sigma}{r} \right), \quad (2)$$

where r is the bubble radius; μ is the liquid viscosity; P_b is the pressure inside the bubble; P is the external pressure; and σ is the surface tension. As shown above, the bubble expansion rate is inversely proportional to the viscosity, and the bubble expansion is limited under a high viscosity condition such that no foaming will be observed. Slag foaming, therefore, seems to require a low enough viscosity for bubble expansion, but not so low as to allow bubble movement. Based on the viscosity data of Denisovsky slag and the synthetic slag, a viscosity higher than 400 Pa-s appears to be the high viscosity to inhibit the bubble growth, while a viscosity lower than 100 Pa-s is the low viscosity for foaming.

2. Determination of P_{O_2} Required for FeO Reduction

For the thermodynamic equilibrium prediction of the reduction of FeO in the gasification slag, the gas composition and the weight (or molar) ratio of gas to slag are important input parameters, and need to be applied accurately to simulate the gasification condition. The amount and composition of syngas from the slurry feed slagging gasifier were calculated as a function of temperature, assuming an adiabatic equilibrium gasifier at 4,052 kPa (40 atm): the resulting synthesis gas was assumed to be in equilibrium at the given temperature. Four element mass balance equations, three equilibrium relations, and one energy balance equation are obtained and are solved simultaneously. The O_2 injection was assumed to be controlled to achieve a desired gasifier temperature. The equations are

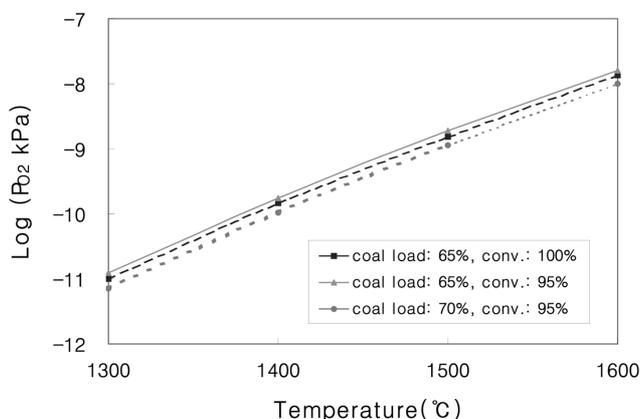


Fig. 6. Effects of slurry loading and coal conversion on the predicted O_2 partial pressure.

summarized in the appendix. Denisovsky coal composition was used for input parameters, and the slurry loading and the carbon conversion were varied.

The P_{O_2} in the gasifier was calculated as a function of temperature while the coal loading in the slurry was varied from 65 wt% to 70 wt%, and the coal conversion from 95% to 100%. As can be seen in Fig. 6, P_{O_2} increases as the temperature increases, showing a value of 10^{-11} at 1,300 °C, and 10^{-8} kPa at 1,600 °C. As expected, the higher coal loading and conversion gave lower P_{O_2} , but the effects were not significant. P_{O_2} for 65% slurry and 95% conversion was 1.76×10^{-10} kPa at 1,400 °C, for 65% slurry and 100% conversion 1.45×10^{-10} kPa, and for 70% slurry and 95% conversion 1.04×10^{-10} kPa.

The simulation of FeO reduction in the slag requires an extensive thermodynamic database on slag components and slag equilibrium models. We used the FactSage program, which is the most commonly used package program for slag equilibrium calculations [10]. Using the gas composition predicted for the gasifier at 1,400 °C with 65% Denisovsky coal slurry and 100% conversion using the model in the Appendix, the P_{O_2} and the equilibrium composition of the slag system were calculated. The predicted crystalline phase formation in the slag is shown in Fig. 7. Formation of Na-containing phases and mullite was predicted at temperatures above 1,450 °C. However, FeO reduction was not predicted, and FeO remained in the slag phase, showing that the P_{O_2} in the gasifier is not low enough to cause FeO reduction to Fe under adiabatic equilibrium conditions. Since there was no oxygen produced from FeO reduction, the calculated P_{O_2} from FactSage simulation was identical to the value obtained from the adiabatic equilibrium gasification model. The possible explanations for slag foaming observed in the 1-ton/day gasifier include (1) locally reducing conditions were formed when unreacted carbon remained in the slag and (2) less than the required O_2 was injected, lowering the P_{O_2} .

3. Prediction of P_{O_2} and FeO Reduction Under the Viscometer Conditions

P_{O_2} and the equilibrium composition of the slag under the viscosity measurement conditions were calculated, and the results were compared with the experimental observation. The composition of synthetic slag was used for input parameters for FactSage. Since

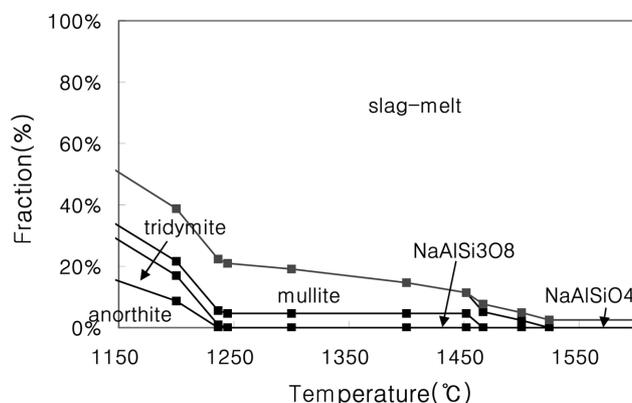


Fig. 7. Prediction of crystalline phase formation in the slag as a function of temperature under gasification with 65% coal slurry and 100% conversion.

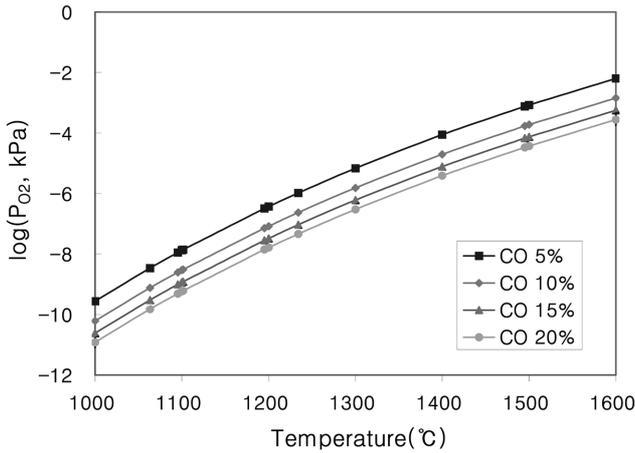


Fig. 8. Effect of CO/CO₂ ratios on the predicted O₂ partial pressure.

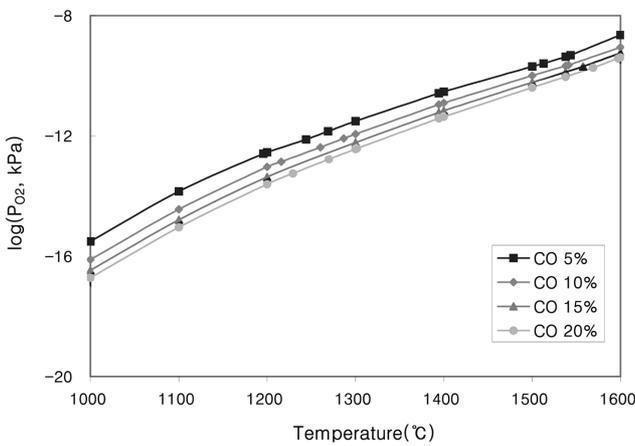


Fig. 9. Effect of CO/N₂ ratios on the predicted O₂ partial pressure.

the sweep gas of 1 liter/min cannot be used in equilibrium system simulation, 55 g of slag with 100 mol of gas mixture was used as the base case, and the effects of gas composition and the slag/gas ratio were examined. The amount of syngas formed per 1 g slag from the gasification of typical bituminous coal gasification is roughly between 1 to 2.5 mol, depending on the ash contents.

Fig. 8 shows the changes in P_{O_2} under CO₂/CO gas as a function of temperature for varying CO contents from 5 mol% to 20 mol%. P_{O_2} increases as % CO decreases, and the lowest P_{O_2} at 1,400 °C was 3.9×10^{-6} kPa at 20% CO. When the slag to gas ratio was varied while keeping CO concentration at 20%, the P_{O_2} did not change. The reduction of FeO was not predicted under any ratios of CO₂/CO considered. The formation of Fe containing crystalline phase was not predicted at the viscosity measuring temperatures: FeO remains in the slag up to 1,100 °C and then formation of Fe₂Al₄Si₅O₁₈ (Ferrocordierite) is predicted.

Fig. 9 shows the effect of gas composition on P_{O_2} under an N₂/CO atmosphere. Again, P_{O_2} increases at higher CO concentrations, showing 10^{-12} kPa at 1,400 °C at 20% CO concentration. Unlike the case under CO₂/CO, the slag/gas ratio also affects P_{O_2} : as the amount of gas increases relative to slag, P_{O_2} decreases. Under N₂/CO conditions, FeO reduction at temperatures between 1,300 and

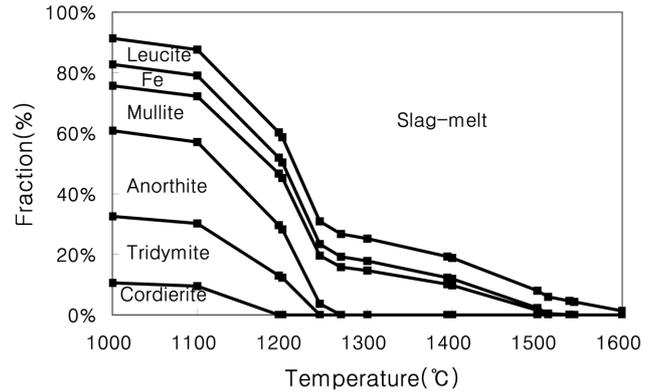


Fig. 10. Prediction of crystalline phase formation in Denisovsky coal slag under CO/N₂ (5/95) atmosphere.

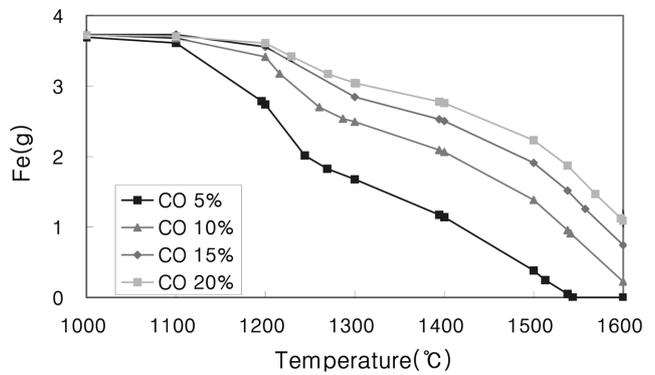


Fig. 11. Effect of CO/N₂ ratio on iron oxide reduction temperature.

1,600 °C was predicted. Therefore, the formation of extra O₂ from the slag changed the overall P_{O_2} , but its impact became smaller when there was a large amount of gas in the system. As the relative amount of gas decreased, the O₂ from the slag can change P_{O_2} more significantly.

Fig. 10 shows the crystalline phase formation in the slag under a 5/95 CO/N₂ atmosphere. Under this condition, Fe formation starts at 1,600 °C along with the formation of mullite and leucite, a potassium-containing phase. The amount of Fe gradually increases as the temperature decreases. Fig. 11 shows the amount of reduced Fe formed as a function of temperature at various concentration of CO in a CO/N₂ mixture. At higher CO concentrations, the initial temperature of FeO reduction increases. At a 20% CO concentration, which gives the lowest P_{O_2} among the conditions considered, the reduction begins at a temperature higher than 1,600 °C, and about 1 g of Fe was formed at 1,600 °C. This result explains the experimental observation of Fe formation without swelling under a 20/80 CO/N₂ mixture. The temperature of the slag viscosity is low at 1,600 °C and the bubble may have readily escaped the slag melt as it formed.

CONCLUSIONS

The conditions for slag foaming were investigated. Viscosity experiments were carried out, and the viscosity, the extent of swelling and the formation of Fe were examined. Although extensive swell-

ing was not observed, FeO reduction was observed under an N₂/CO gas atmosphere, but not under CO₂/CO. FactSage simulations for the viscosity measuring conditions correctly predicted that the P_{o2} under CO₂/CO gas mixtures was not low enough to cause FeO reduction in the slag, while with the P_{o2} under N₂/CO it is possible to have FeO reduction. The FactSage prediction for a gasifier, combined with an adiabatic equilibrium gasification model, did not, however, agree with the observations.

The viscosity of the slag is also important in slag foaming. When FeO reduction occurs in slag which has a high enough viscosity to inhibit bubble movement, but low enough to allow bubble expansion, slag foaming can occur. The viscosity range for slag foaming is roughly between 100 and 400 Pa-s.

APPENDIX

Adiabatic Equilibrium Gasification Modeling for P_{o2} Calculation

Mass Balances

$$\text{Basis: 1 mol syngas: } \sum y_i = 1 \quad (\text{A1})$$

$$\text{C balance: } \frac{1 \text{ s}(0.482)}{w} = y_{\text{CO}_2} + y_{\text{CO}} + y_{\text{CH}_4} \quad (\text{A2})$$

$$\text{H balance: } \text{s}(0.35) \left(\frac{2}{18} \right) + \text{s}(0.0304) = 2y_{\text{H}_2\text{O}} + 2y_{\text{H}_2} + 4y_{\text{CH}_4} \quad (\text{A3})$$

$$\text{O balance: } 2x + \frac{\text{s}(0.35)}{18} + \frac{\text{s}(0.0447)}{16} = 2y_{\text{CO}_2} + y_{\text{CO}} + y_{\text{H}_2\text{O}} + y_{\text{O}_2} \quad (\text{A4})$$

where y_i : mole fraction of i

s : weight fraction of coal in coal-water slurry

w : coal conversion

x : moles of O₂ injected.

Equilibrium Relations



$$K_{p1} = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} \quad \ln(K_{p1}) = \frac{3,380}{T} - 5.082 \quad (\text{A5})$$



$$K_{p2} = \frac{y_{\text{CO}_2}}{P^{0.5} y_{\text{CO}} y_{\text{O}_2}} \quad \ln(K_{p2}) = \frac{33,580}{T} - 19.078 \quad (\text{A6})$$



$$K_{p3} = \frac{y_{\text{CH}_4} y_{\text{H}_2\text{O}}}{P^2 y_{\text{CO}} y_{\text{H}_2}^3} \quad \ln(K_{p3}) = \frac{27,269}{T} - 60.576 \quad (\text{A7})$$

Equilibrium constants, $K_{p,i}$, were obtained by fitting the ΔG of each reaction to a linear relationship of $\ln(K)$ vs. $1/T$ in the temperature range between 1,300 and 1,500 °C. P is the gasifier pressure.

Energy Balance: Adiabatic gasifier $H_{out} - H_{in} = 0$

$$T_{ref} = 298 \text{ K} \quad H_{in} = \sum_{j=1}^1 \Delta H_{fj}(298) \quad j = \text{water, coal} \quad (\text{A8})$$

$$H_{out} = \sum_{i=1}^6 H_i = \sum_{i=1}^6 y_i (\Delta H_{fi} + \int_{298}^T C_{pi} dT) \quad (\text{A9})$$

$\Delta H_{f,cool}$ is assumed to be equivalent to Carbon and, therefore, $\Delta H_{f,cool} = 0$.

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