

THE EFFECTS OF ATMOSPHERE AND ADDITIVES ON COAL SLAG VISCOSITY

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ABSTRACT

The viscosities of a Powder River Basin slag were measured in air, air + 10% water vapor, and a reducing atmosphere. The temperature of critical viscosity (T_c), below which the viscosity increases dramatically, was approximately 1250°C in air and air + water vapor, but dropped to 1180°C when measured in the reducing atmosphere. Since the corrosivity of the slag is much higher when its viscosity is low, the slag will be highly corrosive at the substantially lower temperature in reducing gas. The addition of alumina increased viscosity and T_c , making the slag less corrosive, while magnesia additions dropped viscosity but increased T_c . These changes imply that magnesia additions will make the slag slightly more corrosive in its liquid range, but that the slag will harden and become less corrosive at a higher temperature than without the magnesia addition. The changes in T_c were more substantial when measured in the presence of water vapor in the case of alumina additions, but less substantial in the case of magnesia additions.

INTRODUCTION

As coal reacts in an energy system, the inorganic material in the coal reacts to form silica-rich ash. If the temperature of the ash is high enough, it will completely fuse, forming a molten slag. This slag is very erosive and corrosive to energy system materials with which it comes in contact. The viscosity of the coal ash slag determines its flow rate which affects its erosivity, and the diffusivity of ions within the slag which affects its corrosivity. Several phenomenological models based on linear regression analysis of slag composition-versus-viscosity data have been developed to predict the viscosity of coal ash slags in combustor systems.¹⁻⁴ However, these models only work well in predicting slag viscosity at the conditions under which the composition-versus-viscosity data were developed, and it is not well understood how far the predictions can be extended to other system conditions such as variations in local atmosphere. In addition, the models do not predict the temperature at which crystallization starts in the slag, known as the temperature of critical viscosity T_c , below which the viscosity sharply rises. This means that the minimum temperature to which the models can be applied or to which slag can be expected to flow is not well known.

In this article, we report the impact of three gas compositions, each of which may be expected in various regions of a coal-fired boiler, on the viscosity and critical temperature on a high-calcium coal slag produced from a Powder River Basin coal. We also demonstrate how these properties can be manipulated with the use of coal additives in order to reduce their corrosiveness to energy system materials.

EXPERIMENTAL

The viscosity of the slags were measured under three atmospheres: air, air + 10% water vapor, and $H_2/CO/CO_2$ (31/45/24). In addition, reagent-grade magnesium oxide (45 wt%) or aluminum oxide (20 wt%) was added to the slags under both air and air + 10% water vapor conditions. Viscosities were measured with a Haake RV-2 Rotovisco system with a DMK 50/500 dual measuring head, which is a rotating bob viscometer. In this system, the torque on the viscometer bob is converted to an electrical signal to a computer, which controls the rotation at 64 rpm. For oxidizing atmosphere tests, the bob was fabricated from platinum-rhodium (90/10) alloy. For reducing atmosphere tests, the bob was fabricated from molybdenum. In both cases, the bob was 22 mm long with a 30° taper at both ends. The top of the bob terminated in a 16-mm-long, 6-mm-diameter shaft accommodating a 420-mm-long by 3-mm-diameter stem. The bob was immersed until the slag just covered its top. The coal slags were prepared by melting ash powders at 1500°C in air in a platinum crucible and quenched on a brass plate at room temperature. The glasses were crushed, put into alumina crucibles, and heated to 1500°C. The viscosity of the slags were measured over the range of 10 to as high as 4000 poise unless crystallization was seen to occur along the walls of the alumina container, at which point the measurements were terminated. Measurements were started at a temperature of at least 100°C above the temperature of critical viscosity, and the temperature was decreased in 20°C intervals. The bob was rotated in the slag for approximately 40 minutes after each temperature was reached before a reading was taken. The viscometer was calibrated with National Bureau of Standards silicate glasses 710 and 717. The accuracy of the tests is approximately $\pm 5\%$. Compositions of the original ash is listed in Table 1.

TABLE 1

Compositions of Coal Ashes, wt% oxide basis	
	Oxide Coal
SiO ₂	38.8
Al ₂ O ₃	20.8
Fe ₂ O ₃	6.1
TiO ₂	1.5
P ₂ O ₅	1.1
CaO	23.2
MgO	6.5
Na ₂ O	1.4
K ₂ O	0.3
SO ₃	ND ¹

¹ Not detected.

RESULTS AND DISCUSSION

Figure 1 shows the viscosity-versus-temperature curves for the Powder River Basin coal slag in air, air + 10% moisture, and reducing conditions. The curves are very similar for both the air and air + moisture tests, with T_c approximately 1250°C and the viscosity of each slag around 20 poise at 1400°C. However, under the reducing conditions, T_c dropped considerably to 1180°C, and the viscosity of the slag at 1400°C was only around 5 poise. These changes cannot be explained merely by the reduction of iron in the slag from a network former (3+ ion) to a network modifier (2+ ion) since there is so little in the slag.

Figure 2 shows the effects of the additions of alumina and magnesia to the slag when measured in air. As expected, the addition of a network former like alumina increased the viscosity of the slag at 1400°C from 20 to 40 poise. In addition, the temperature of critical viscosity was increased dramatically from 1250°C for the original ash to 1330°C with the alumina addition. X-ray diffraction showed the formation of plagioclase ([Ca,Na][Al,Si]₂O₆) and spinel (MgAl₂O₄) crystals in the melt below T_c . In contrast, the addition of magnesium, a network modifier, to the melt decreased its viscosity as expected, but increased T_c even more, to around 1350°C. Crystals forming in that melt included spinel and monticellite (CaMgSiO₄). The changes in viscosity indicate that alumina additions would decrease the corrosivity of a Powder River Basin slag, while magnesia additions may slightly increase corrosivity. However, because T_c is increased in each case, either addition would dramatically lower slag corrosivity at material temperatures 80° to 100°C higher than the T_c of the slag alone.

Figure 3 shows the effects of the additions of alumina and magnesia to the slag when measured in air + 10 moisture. As was true for the measurements in air, adding alumina raised the viscosity and T_c of the slag but much more substantially, with the viscosity increased by 60 poise at 1400°C while T_c rose by 140°C. This increase in viscosity would reduce the corrosivity of the slag to energy system materials, dramatically reducing the corrosivity of the slag at temperatures below 1400°C. The additions of magnesia also created similar changes as when measured in air. The viscosity of the slag at 1400°C dropped by approximately 10 poise, but T_c rose by only 50°C to 1310°C.

CONCLUSIONS

The viscosity and T_c of a Powder River Basin slag is not substantially different when measured in air or in air + 10% water vapor, but both are substantially reduced when measured in an H₂/CO/CO₂ atmosphere. The reduction is more than would be expected from the conversion of iron from a 3+ ion to a 2+ ion. Adding alumina, a network former, increased viscosity and T_c when measured in air, but more substantially when measured in air + 10% water vapor. The addition of magnesia, a network modifier, to the slag dropped the viscosity and raised T_c , but the change in T_c was less substantial in air + water vapor than when measured in air alone. Either addition will have small effects on corrosivity of the slags above T_c , but will dramatically reduce corrosivity below the new T_c of the modified slags. Also, since combustor gas contains more water vapor than air alone, we suggest that in order to gauge the effect of additives on slag viscosity accurately, viscosity measurements should be made in an atmosphere containing water vapor.

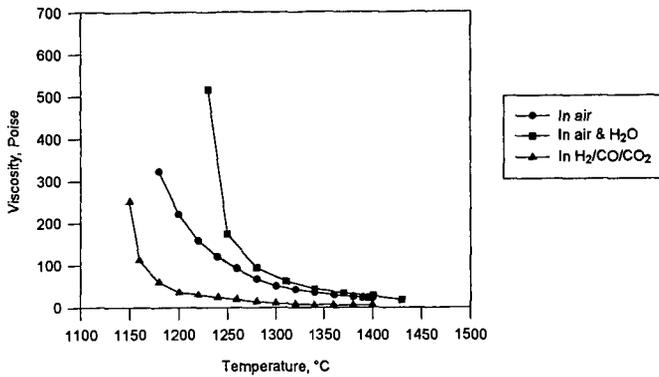


Figure 1. Viscosity-versus-temperature curves for the Powder River Basin coal slag in air, air + 10% moisture, and reducing conditions.

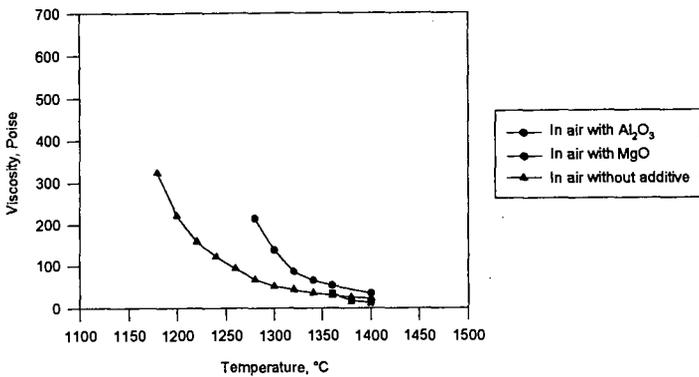


Figure 2. Viscosity-versus-temperature curves measured in air for the Powder River Basin coal slag, slag plus alumina, and slag plus magnesia.

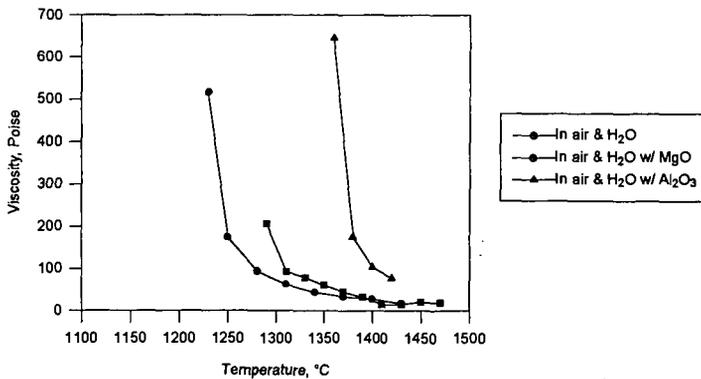


Figure 3. Viscosity-versus-temperature curves measured in air + 10% moisture for the Powder River Basin coal slag, slag plus alumina, and slag plus magnesia.

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