

Correlation between the critical viscosity and ash fusion temperatures of coal gasifier ashes☆



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ABSTRACT

Coal gasification yields synthesis gas, an important intermediate in chemical manufacturing. It is also vital to the production of liquid fuels through the Fischer-Tropsch process and electricity in Integrated Gasification Combined Cycle power generation. Minerals naturally present in coal become molten in entrained-flow slagging gasifiers. Molten coal ash slag penetrates and dissolves refractory bricks, leading to costly plant shutdowns. The extent of coal ash slag penetration and refractory brick dissolution depends on the slag viscosity, the gasification temperature, and the composition of slag and bricks. We measured the viscosity of several synthetic coal ash slags with a high-temperature rotary viscometer and their ash fusion temperatures through optical image analysis. All measurements were made in a carbon monoxide-carbon dioxide reducing atmosphere that approximates coal gasification conditions. Empirical correlation models based on ash fusion temperatures were used to calculate critical viscosity temperatures based on the coal ash compositions. These values were then compared with those obtained from thermodynamic phase-transition models. An understanding of slag viscosity as a function of ash composition is important to reducing refractory wear in slagging coal gasifiers, which would help to reduce the cost and environmental impact of coal for chemical and electricity production.

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1. Introduction

Coal gasification is an important industrial chemical process. Synthesis gas, a mixture of hydrogen, carbon monoxide and carbon dioxide, is produced from coal and steam as the net product of several chemical reactions outlined in Table 1 [1]. For over a century, chemical manufacturers have used synthesis gas as a feedstock to produce ammonia, alcohols, and synthetic fuels [2]. More recently, it was found that the amount of sulfur, nitrogen oxides, and particulates emitted by Integrated Gasification Combined Cycle (IGCC) electrical power plants could be reduced significantly by using synthesis gas as a fuel for gas turbines [3]. In addition, carbon dioxide is readily captured from pre-combustion synthesis gas [4,5]; consequently, a net reduction in carbon dioxide emissions by IGCC power plants may be realized through coal gasification and pre-combustion carbon capture. The development of improved carbon capture and storage capabilities for future IGCC power plants continues to be an active topic of research today [6,7]. An improved understanding of coal ash slag formation is a key factor in enabling the design and operation of entrained-flow gasifiers with greater efficiency and reliability.

Coal is a complex mixture of organic and inorganic compounds. During gasification, the organic compounds are converted to synthesis gas while the inorganic compounds become coal ash. A survey of bituminous coals produced in the United States reports a range of 1 to 23% (mass/mass) ash content of moisture-free coal, with an average sample containing approximately 10% (mass/mass) ash [8]. Coal ash minerals encompass oxides, sulfides, and carbonates of silicon, aluminum, iron, calcium, magnesium, sodium, potassium, and trace elements such as titanium. While over 120 minerals have been identified in coal, only 8 are common constituents: quartz (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite ($(\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$), montmorillonite ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$), chlorite ($(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg,Fe})_3(\text{OH})_6$), pyrite (FeS_2), calcite (CaCO_3), and siderite (FeCO_3) [9]. The proportion of these mineral constituents varies considerably for coal ashes, depending on the geographic origin of the coal. The difference in coal ash compositions causes substantial variability in their viscosity as a function of temperature. Coal ash management is an important issue for coal gasifier operation, given the high temperatures needed for efficient synthesis gas production.

Gasification temperatures range from 950 to 1100 °C for fluid-bed gasifiers, and 1300 to 1600 °C for entrained-flow gasifiers [10]. Fluid-bed gasifiers are suitable for gasifying low-rank coals; however, synthesis gas produced by fluid-bed gasifiers often contains volatile coal tars. Depending on the intended use, an additional clean-up step may be needed to remove the coal tars from the synthesis gas [11]. In

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Table 1

Principal coal gasification chemical reactions [1]. Carbon exists in coal as a solid, while oxygen, steam and all reaction products are gases.

Partial coal combustion:	$2C + O_2 \rightarrow 2CO$
Boudouard reaction:	$C + CO_2 \rightleftharpoons 2CO$
Water-gas shift reaction:	$C + H_2O \rightleftharpoons CO + H_2$
Carbon monoxide shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$

comparison, entrained-flow gasifiers are capable of handling a wider range of coals, have better carbon conversion efficiency, and produce tar-free synthesis gas [1]. Due to the higher operating temperatures found in entrained-flow coal gasifiers, coal ash minerals agglomerate to form a molten slag that must be removed periodically. This is typically accomplished by tapping, where the molten slag flows through a tap hole into an ash hopper; the slag is then quenched and collected for disposal.

In a typical entrained-flow gasifier, the optimal slag tapping viscosity is approximately 80 to 150 P (1 P = 0.1 Pa·s), while the maximum slag viscosity for continuous flow is 250 P [12]. Slag viscosity varies as a function of coal ash composition and gasifier operating temperature. Control of the molten slag viscosity is typically achieved by adding fluxing minerals to the slag [13,14], coal blending [15], or by adjusting the gasifier operating temperature [16]. In order to do so effectively, it is necessary to understand how the slag viscosity changes as a function of composition and temperature.

2. Literature review

Coal ash slags are similar in their composition and transport properties to magmas, glasses, and slags [17]; therefore, the study of coal ash slags yields data relevant to the study of molten silicates in general. Conversely, several concepts and models from the study of molten silicates are useful in understanding how changes in composition and operating temperature affect coal ash slag viscosity. More specifically, the study of local silicate structure through optical basicity measurements [18] is important in understanding the effect of coal ash slag composition on the viscosity of fully molten slags [19–23]. In addition, the thermodynamics and kinetics of solid phase formation in molten silicates are important factors in understanding the transition from Newtonian to non-Newtonian flow at the critical viscosity temperature.

2.1. Viscosity of fully molten silicates

Fully molten silicates, including coal ash slags, contain numerous SiO_4 tetrahedrons interlinked by Si–O–Si bonds (Fig. 1). The extent of

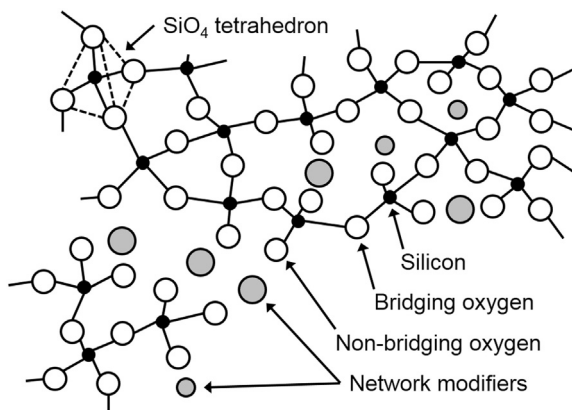


Fig. 1. Covalent polymeric networks found in molten silicates. SiO_4 tetrahedrons are linked by bridging oxygens to form a wide range of structures. The presence of cationic network modifiers breaks down the network, forming non-bridging oxygens to maintain overall charge balance. The decrease in degree of polymerization leads to a decrease in viscosity.

SiO_4 polymerization has a strong effect on viscosity, due to the fact that larger polymeric structures are more likely to become entangled, thereby impeding the shear flow of the melt [24]. The extent of polymerization in a silicate melt is affected by the presence of network modifiers: alkali metal oxides, alkaline earth metal oxides or transition metal oxides. Network modifiers convert bridging Si–O–Si bonds to nonbridging terminal oxides through Lewis acid–base reactions with the anionic SiO_4 network [18]. Increasing the concentration of network modifiers present in the melt decreases its degree of polymerization, thereby decreasing its viscosity.

Changes in the electron density around oxygen atoms in the SiO_4 anions due to network modifiers can be assessed indirectly through optical basicity measurements [25]. Optical basicity is measured spectroscopically as the ratio of the shift in the ultraviolet absorption maximum of a probe ion (Th^{+} or Pb^{2+}) in the modified silicate network relative to the shift in a reference oxide (CaO) [26]. An increase in the optical basicity of a slag is associated with a decrease in its viscosity [19,20], consistent with the formation of nonbridging terminal oxides and the breakup of large polymeric structures. The effect of composition on the viscosity of molten silicates has been studied extensively, and several local network structure models have been developed for fully molten silicates [27–29]. These models typically account for the effect of network modifiers by calculating the acid-to-base ratio in the molten silicate, where silica (SiO_2), alumina (Al_2O_3), and iron(III) oxide (Fe_2O_3) are acidic oxides, and network modifiers (e.g. Na_2O , K_2O , Li_2O , CaO, MgO, MnO, FeO) are basic oxides.

The composition of the molten coal ash slag is known to play an important role in its viscosity. Interestingly, coal ash slags can be modified chemically during gasifier operation, resulting in measureable changes in viscosity. The reduction of iron(III) oxide to iron(II) oxide converts an acidic oxide to a basic oxide, which lowers the slag viscosity. The oxygen partial pressure inside a coal gasifier is typically on the order of 10^{-8} to 10^{-9} atm (1 to 0.1 mPa), sufficient to reduce most of the iron present in slags to a Fe^{2+} state. A decrease in slag viscosity was observed by Folkedahl and Schobert in their study on the effect of reducing atmospheres on the viscosity of coal ash slags [30]. The effect of oxygen partial pressure on coal ash slag viscosity highlights the importance of matching experimental parameters to gasifier operating conditions in data collection.

While high-temperature rotary viscometry is typically employed to measure the viscosity of fully molten coal ash slags (see Section 2.4), a number of other approaches have been reported in the literature. Stanmore and Budd [31], as well as Buhre et al. [32], proposed the use of thermomechanical analysis as an alternative to rotary viscometry for fully molten coal ash slags; instead of torque, the force required to force the slag up into an annular region of defined geometry is measured instead. Buhre et al. noted that the approach is not suitable for testing subliquidus slags, as non-Newtonian slag flow leads to an erroneous interpretation of the thermomechanical data.

2.2. Critical viscosity temperature

The service life of refractory bricks lining the interior of gasifiers can be prolonged by lowering the gasification temperature [33]; however, if the slag is cooled below its liquidus temperature, nucleation and growth of one or more solid phases becomes thermodynamically favorable. The formation of a solid phase can cause the molten slag to become a non-Newtonian fluid. The viscosity of a non-Newtonian fluid is a function of shear rate due to the interactions between solid particles suspended in the liquid phase; moreover, the shear rate dependence may itself vary as a function of time. The critical viscosity temperature (T_{cv}) is defined as the temperature at which solid phase formation causes a transition from Newtonian to non-Newtonian flow in molten coal ash slags [34]. Johnson reviewed viscosity data for slagging gasifier operations, and proposed a Bingham plastic model to describe the non-Newtonian slag flow [35]. A Bingham fluid is a viscoplastic substance which yields

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