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Effects of $CaCO_3$ on slag flow properties at high temperatures

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HIGHLIGHTS

- Effects of limestone on coal samples of different Si/Al were carefully studied.
- The essences of influences on AFTs, slag viscosity, temperature of critical temperature and type of slag were discussed.
- The prediction methods are raised for guiding the use of limestone.
- A new method for predicting critical temperature is presented.

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ABSTRACT

Experiments were conducted on the selected ashes with different additions of $CaCO_3$ for understanding the effects on slag flow properties including ash fusion temperatures, slag viscosity, temperature of critical viscosity and type of slag. ICP-AES, XRD and FTIR analyses were applied to determine the component and structure of the slags. Factsage was used to calculate liquidus temperatures in the SiO_2–Al_2O_3–CaO–FeO system and to predict formed mineral matters and proportion of solid phase as a function of temperatures. The results show that the liquidus temperature calculated by Factsage well predicts the variation of ash fusion temperatures. Slag viscosity behavior changes with increasing addition of $CaCO_3$ because the formation process of solid phase is different. The Fourier transform infrared (FTIR) spectrum indicates that Ca^{2+} leads to break polymerized Si–O–Si into Si–O, so the increasing Ca^{2+} in slag results in the decrease of viscosity above liquidus temperature. Below liquidus temperature, solids content decreases with increasing addition of $CaCO_3$ above the temperature of critical viscosity (T_{cv}). Meanwhile, it is found that the rate of solid formation is related with T_{cv} and a new prediction method of T_{cv} based on that was proposed. Moreover, the type of slag changed with addition of $CaCO_3$ was predictable by XRD analysis. The prediction on ash fusion temperature, T_{cv} and type of slag is expected to serve as a reference for adding flux to regulate coal/ash properties suitable for slag tapping gasification technology.

1. Introduction

The need for higher efficiency of future power generation and chemical production leads to increased interest in IGCC technologies, especially in advanced gasification technology such as entrained-flow gasifier [1–6]. In the gasifier, under high temperatures over 1400 °C and strong turbulence, organic matter in coal is completely combusted and gasified in a short time, and the mineral matter in coal transforms into ash. The ash becomes liquid slag owing to the melting and reactions of its component mineral matter at high temperature [2]. Slag fluid properties are much more important for entrained-flow gasifiers with liquid slag-removal process than the conversion of organic matter in coal.

Continuous slag tapping is the key for the successful operation for different entrained flow gasifiers (GE, Shell, Prenflo, GSP, Texaco, Eagle) [3–21], so the flow properties of slag and the influence of additives on them at high temperature are of great importance. Generally, ash fusion temperature and slag viscosity curve are used for describing the slag flow properties. Ash fusion temperatures (AFTs) are referred for slag tapping in GE gasifier. Operating temperature is above the flow temperature (FT) of coal ash, and the FT should not be higher than 1300 °C. Slag viscosity vs. temperature curve is applied for slag tapping in the membrane wall gasifiers, such as Shell and GSP gasifiers. It is generally accepted that the slag viscosity must be in a certain range for not only slag tapping but also membrane wall design [4]. Two aspects were considered from slag viscosity curve including viscosity dependence on temperature and the temperature of critical viscosity (T_{cv}). For example, the viscosity is required in 2.5–25 Pa s at temperatures from 1300 to 1500 °C. Besides, T_{cv} should be at least 150 °C lower than

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Table 1
Chemical composition of coal ashes (wt%).

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	Si/Al
YC	56.98	27.33	4.92	5.19	0.98	1.05	1.06	0.43	2.08
SL	60.82	22.89	3.86	3.82	2.55	1.13	1.82	1.10	2.66
FG	61.08	18.10	5.25	7.48	2.12	0.97	1.76	0.46	3.37

Table 2
Ash content and fusion temperatures of samples.

Samples	Ash content/A_d (wt%)	AFTs (°C)			
		IDT	ST	HT	FT
YC	15.30	1404	1427	1443	1496
SL	14.05	1306	1353	1357	1372
FG	4.57	1180	1206	1224	1318

the temperature of 2.5 Pa s. However, slag properties of most coals, especially lignite in Northwest China did not satisfy the requirement for slag tapping. In hence, fluxing agent is used to adjust slag properties and limestone is the widely used one in China for its abundance and low cost. Thus, it is necessary to understand the influence of limestone on slag properties including AFTs, slag viscosity and T_{cv}, for continuous operation of the various gasifiers at the expected temperature range.

Generally, two methods, both experimental and thermodynamic calculation are used to study AFTs of coal ash with addition of limestone [4–9]. Hurst et al. [4] used the ternary equilibrium phase diagrams to study the fluxing effect addition of $CaCO_3$ on Australian coal ashes. Song et al. [5] examined the effect of CaO as pure compounds on the AFTs of coal ash with Factsage. It was found that when the content of CaO was over 35%, the AFTs increased quickly with more CaO. The similar phenomenon is also noticed by other researchers, but the minimum AFTs appears at different content of CaO for various Si/Al coal ashes [9]. Since the AFTs also increased with adding limestone, the proper selection of flux amount is important for gasification operation. Seggiani [6] provided a method from chemical composition to predict the effect of adding minerals (such as CaO) on AFTs. Jak et al. [7] also applied the thermodynamic computer package Factsage to predict AFTs and found that they do correlate with the liquidus temperatures. However, much fewer attempts have been made so far with regards to proper flux ratio based on the AFTs of raw coal aiding with thermodynamic calculation.

Viscosity of most slags exponentially decreases with increasing temperature and irregularly decreases with adding limestone. The decrease is mainly caused by the variation of solid phase in melted slag [9–12]. Wu et al. [13] studied the effect of solid particles on liquid viscosity by adding solids into silicate liquid. The amount and type of solid phase precipitated in melt slag showed significantly influence on slag viscosity. Ilyushechkin [11] found that below the liquidus temperature, slag viscosity increased sharply with the increasing amount of solids. The sharp increase of viscosity with relatively low Si/Ai ratio (<2) slag was due to solid level or size of the crystal, and a high Si/Al ratio slag was solid precipitation. The alkaline earth metal oxides (e.g. CaO) mostly acted as network modifiers to reduce the slag viscosity. Song et al. [12] also found that solids amount in melted slag decreased with the increasing CaO content which resulted in viscosity decreasing.

The T_{cv} is another critical factor of slag flow behavior. T_{cv} indicates a point of abrupt change in the viscosity–temperature curve when solid phase in liquid slag begins to crystallize and to separate out from the liquid phase [14]. It is also assumed that T_{cv} indicates the boundary between crystal-affected viscosity and viscosity not affected by the presence of crystals [15]. Some slags exhibit the classical behavior of a glass that a continuous increase in viscosity as the temperature decreases and the slag is referred as glassy slag. Others show a rapid increase of viscosity when the temperature is lowered below T_{cv}, which is referred as plastic slag or crystalline slag [16]. Many researchers [4–9] used CaO or $CaCO_3$ as fluxing agent to study their effect on slag viscosity. Although these results can give good guide in gasification, yet little work has been published regarding essences for the effect of flux on slag viscosity, T_{cv} and type of slag.

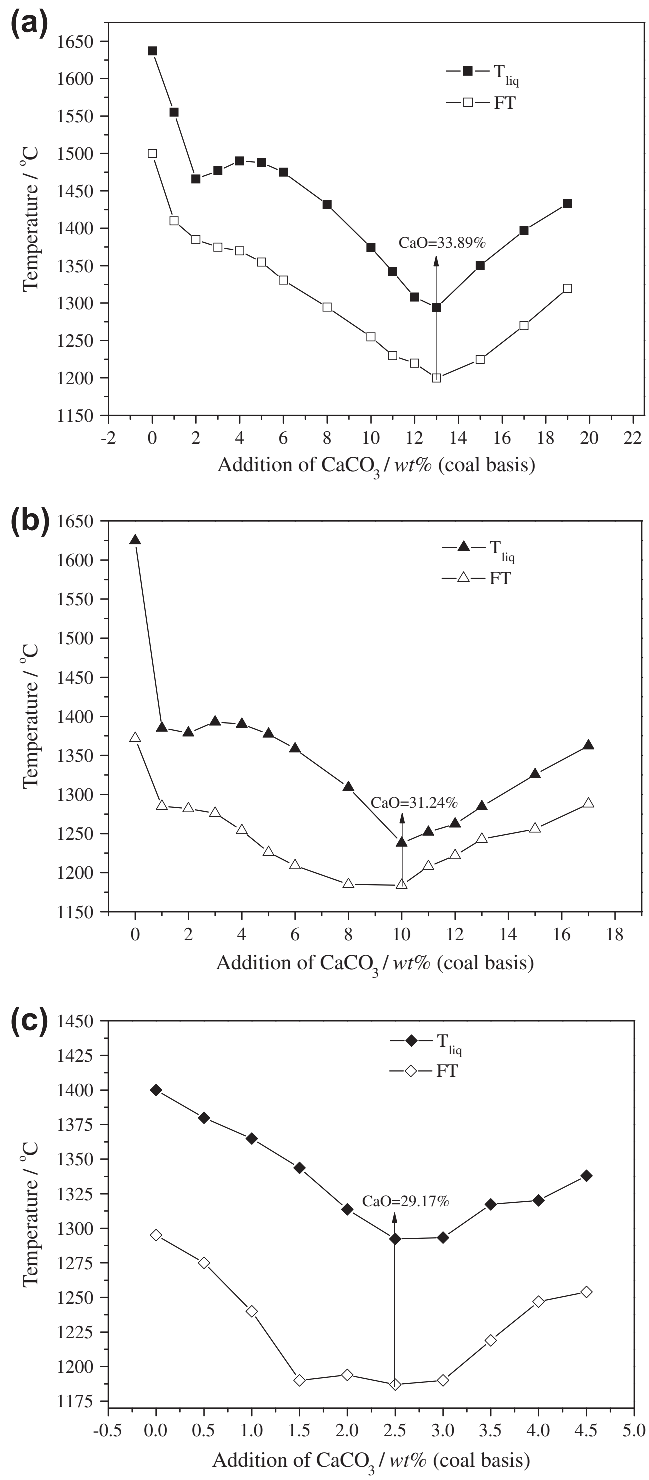

Fig. 1. Flow temperature *vs* addition of $CaCO_3$ curves. (a) YC; (b) SL; (c) FG.