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Characteristics and catalytic actions of inorganic constituents from entrained-flow coal gasification slag

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ABSTRACT

The morphology, mineralogy, and elemental distribution of inorganic constituents from two entrained-flow coal gasification slags were mainly investigated to understand the physico-chemical characteristics of the two slags. The fully molten and partly molten inorganic components in the coarse slag tend mainly to co-exist in the overlapping bulk of lumps and agglomerates, whereas the two ones in the fine slag almost tended to be discretely presented in spherical particles and agglomerates, respectively. The trace elements (Pb, As and Zn) with great volatile behaviors were easily concentrated into the fine slag. Summarily, the inorganic constituents in gasification slags predominantly contained crystalline components (silicates, aluminosilicates, and Ca–Fe and Fe oxides) and vitreous components (Ca–Fe-aluminosilicate glass). Simultaneously, a rough distribution model for main ash-forming elements in gasification slags was proposed. Also, the catalytic actions of inorganic constituents in the two gasification slags were assessed using a thermo-gravimetric analyzer. It was found that the inorganic constituents in gasification slags can take a distinct catalytic action on the carbon gasification, mainly due to the predominant presence of these catalytic components (Ca–Fe and Fe oxides). A higher gasification reactivity of the coarse slag was mainly ascribed to a higher content of its catalytic components, compared to the fine slag.

1. Introduction

Currently, the entrained-flow coal gasification technology such as GE (Texaco), Shell, GSP and OMB (Opposed multi-burner gasification technology), has become one of the leading clean coal technologies. Gasification slag is a by-product from entrained-flow coal gasification. In order to achieve "zero emissions" of the gasification technology, the environmentally safe utilization of GS by-products must be addressed and developed. Generally, the coarse component in slag, which is a vitreous, dense and abrasive solid with a relatively low carbon content, can be used for many applications such as polishing media, roofing granules, cement kiln feed, landscaping, road surface coating, as well as a cement additive [31], and the fine component in slag, which is in the form of irregularly shaped particles with a highly developed pore structure and a significantly high carbon content, can be beneficiated and then recycled as a supplemental combustion fuel or used as an adsorbent or a precursor for activated carbon [1]. However, it should be noted that the utilization of the slag depends intensively on its unique physico-chemical characteristics. Therefore, the detailed characterization on the physico-chemical properties of slags is highly imperative and significant.

Thus far, special reports on the characteristics of entrained-flow coal gasification slag were very scarce, and there were only several reports [31,33,34]. Wu et al. [31] found that the morphology of the residual carbon in the coarse slag was similar to that in the fine slag, and was also comparable to partly combusted chars produced in a drop tube furnace (DTF). Xu et al. [33] considered that a higher ordering of carbon layers and a lower content of catalytic components were the main reasons for the lower reactivity of the unburned carbon in the fine

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slag compared to that in the coarse slag. Zhao et al. [34] observed that fine inorganic matters in slag tended to exist in spherical shape, whereas the residual carbon tended to stay as loose floccules, and found that the reactivity of the carbon in the fine slag was lower than that in the coarse slag. Obviously, these results are quite dispersive and are not enough to deeply understand its essential characteristics, which can provide some fundamental supports for its efficient and reasonable utilization. Therefore, there is still a strong need to do more studies on the topic.

Typically, a standard entrained-flow coal gasification process produces two types of slags, coarse slag and fine slag [31,33]. Normally, both coarse slag and fine slag are roughly composed of residual carbons (namely residual chars) and inorganic constituents. Thus, to understand fully the characteristics of slags, a series of important investigations such as the physico-chemical characteristics of residual carbons and inorganic constituents as well as the interactions of the two ones, should be carried out in detail. Recently, the physico-chemical characteristics of residual carbons from two entrained-flow coal gasification slags were investigated specially by our research group [28]. Consequently, considered as a successive task, this study mainly focuses on these investigations of characteristics and catalytic actions of inorganic constituents to further understand the characteristics of entrained-flow coal gasification slags.

2. Materials and methods

2.1. Details of gasification slag samples

Two kinds of gasification slags (GSs), namely coarse slag (CS) and fine slag (FS), were obtained from a commercial GE (Texaco) gasification unit located in Shanghai Coking Co., Ltd. of China. The original coal for the gasifier was Shenhua coal of China (proximate analysis data (dry basis): ash content of 6.66%, volatile content of 33.22%, fixed carbon content of 60.12%; ultimate analysis data (dry basis): carbon content of 71.23%, hydrogen content of 6.08%, total sulphur content of 0.35%, nitrogen content of 0.99%). The schematic process of the GE coal gasification unit was same as that described by two literatures [31,33]. As stated in the two literatures, the CS and the FS were, respectively, sampled from the outlet of the lock-hopper and the filter of the fine slag removal. Samples were collected during a period of 2 days at 2 h intervals, and then were mixed to produce a single composite sample. A routine coning and quartering method was applied repeatedly to reduce the sample to a size suitable for conducting laboratory analyses. During the period of sampling, the operation parameters for the gasifier are as follows: coal water slurries with a concentration of 60–62%, coal consumption of about 950 t/day (i.e., a load of about 95%), gasification temperature of about 1320 °C, and gasification pressure of about 4 MPa. The proximate and ultimate analyses, the calorific values (CV), and the ash compositions (in main oxides) of the two GSs were determined according to the Chinese standards of GB/T 212-2008, GB/T 476-2008, GB/T 213-2008 and GB/T 1574-2007. Their losses on ignition (LOI) were carried out by a thermo-gravimetric analyzer (TGA, Setaram TG-DTG/DSC) at 900 °C and O_2 atmospheres (99.9 v/v%). Table 1 gives the elementary properties of the two GSs.

2.2. Characterization for morphologies of inorganic constituents in GSs

A scanning electronic microscopy coupled with an energy dispersive spectrometry (SEM/EDS, JEOL JSM-6360LV) was used to investigate the morphologies and the surface element compositions of inorganic constituents in each GS.

2.3. Characterization for distributions of inorganic elements in GSs

In order to detect the inorganic elements as far as possible, the ash samples from each GS after being dried at 105 °C for 3 h and finely crushed to below 180 μm were prepared using the ashing treatment at a relatively low temperature of 600 °C and O_2 atmosphere (99.9 v/v%) for 24 h in a muffle furnace. The ash samples from the CS and the FS are, respectively, termed as CSA and FSA.

The ash samples from each GS were analyzed using an X-ray fluorescence spectrometer (XRF, X-Lab 2000). Due to the heterogeneity of ash samples, the XRF analysis for each ash sample was conducted thrice and the mean value was used as the indicator for the concentration of each detectable element in ash samples. The concentration of each detectable element in the GS was calculated on the basis of the XRF analysis of ash samples and the total mass of the GS before and after the low-temperature ashing treatment.

An enrichment factor (EF) was usually used to characterize the inorganic element distributions in different slags. Dahl et al. [5] used an EF (defined as the ratio between the total element concentration in the fly ash and that in the bottom ash) to characterize the element

Table 1
Elementary properties of two GSs.

Samples	Proximate analysis (d, wt%)			Ultimate analysis (d, wt%)				LOI[d](wt%)	CV[e] (MJ/kg)
	A[a]	V[b]	FC[c]	C	H	S	N		
CS	78.39	4.69	16.92	20.95	0.07	0.27	0.27	20.49	7.74
FS	62.71	7.75	29.54	33.01	0.47	0.45	0.46	35.57	9.51
Samples	Ash compositions in main oxides								
	SiO_2	CaO	Fe_2O_3	Al_2O_3	Na_2O	SO_3	MgO	K_2O	TiO_2
CS	35.81	22.98	19.67	12.35	2.71	1.47	1.27	0.87	0.71
FS	43.52	17.02	12.31	15.97	3.19	2.46	1.51	1.21	0.98

[a] Content of ashes.
[b] Content of volatile matters.
[c] Content of fixed carbons.
[d] A weight loss percentage on ignition (900 °C, 30 min).
[e] High calorific value.