



Research article

The precipitation of metallic iron from coal ash slag in the entrained flow coal gasifier: By thermodynamic calculation



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ABSTRACT

A smooth slag flow out of gasifier bottom is key to a reliable operation of entrained flow gasifier. Therefore, avoiding slag blockage at the bottom of gasifier is very essential. Under the gasifier reduction operation conditions, precipitation of metallic iron from the liquid slag sometimes occurred. This solidified slag resulted in the gasifier outlet blockage. Consequently, gasifier operation has to stop. In this study, the thermodynamic software FactSage was used to predict the behavior of iron in the liquid slag within the temperature range of gasifier normal operation. From the results of this study, the mechanism of iron precipitation was revealed. The study showed that due to the higher reducing gas ratio in the syngas, the precipitation of metallic iron only occurred in the pulverized coal gasifiers instead of the coal water slurry gasifiers. When weight ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is too low, or CaO content is too high in the slag, Fe^{2+} is not able to be saturated in the liquid phase. As a result, precipitation of metallic iron from slag was observed. A β value ($\beta = \text{Si}^{4+} / (\text{Ca}^{2+} + \text{Al}^{3+})$, mole basis) of 1.25 was regarded as the boundary of metallic iron precipitation when 18.4% Fe_2O_3 content in coal ash. Finally, a metallic iron precipitation predicting model was given by using ternary phase diagram to guide the feedstock selection for the coal application in the entrained flow gasifiers.

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1. Introduction

China is the largest coal consumer in the world, accounting for approximately 50% of the total annual coal consumption [1]. In order to increase the energy efficiency and reduce the environmental pollution, gasification, a clean way for coal conversion, is gaining more and more interest in China [2]. The entrained flow gasifier is the most widely used gasification technology for the coal chemical industry because of large scale capability and high efficiency. To ensure continuous operation of the entrained flow gasifier, the viscosity of the coal ash must be sufficiently low for slag tapping, optimally between 15 Pa·s and 25 Pa·s at the tapping temperature between 1350 °C and 1500 °C [3]. Most importantly, the sudden increasing viscosity during slag tapping should be avoided by the increasing of solids or crystallization in the liquid slag [4].

The flow behavior of slag depends on the chemical composition of coal ash. Coal ashes consist mainly of four major oxides, namely SiO_2 , Al_2O_3 , Fe_2O_3 and CaO, which usually account for 90% of the composition

of coal ash [5,6]. Typically, the flow temperature of the coal ash increases with the increasing SiO_2 and Al_2O_3 contents due to the formation of minerals with high melting point, such as mullite, corundum and quartz [7,8]. The flow temperature decreases with increasing CaO until 30% since low-temperature eutectic is formed. When further increasing CaO, the remaining CaO leads to the increase of flow temperature again [9]. The network former (Si^{4+}) increases the viscosity of slag by forming a network structure. The network modifier (Ca^{2+} and Fe^{2+}) decreases the viscosity by breaking and losing the structure. The Al^{3+} in the melts behaves as amphoteric, network former or network modifier. The effect of Al^{3+} on viscosity depends on the content of Si^{4+} [10]. Therefore, the S/A ($S/A = \text{SiO}_2/\text{Al}_2\text{O}_3$, weight basis) ratio is used for evaluating the effect of Al^{3+} on viscosity [11]. The effect of iron oxide on the viscosity depends on its valence. Fe^{2+} acts as network modifier which decreases the viscosity, while Fe^{3+} works as amphoteric which can either decrease or increase the viscosity [10]. However, the effect of metallic iron on slag viscosity is not clear. In ash fusion temperatures test, the ash cone in the strong reducing atmosphere shows a skeleton structure due to the formation of metallic iron. Therefore, the shape of ash cone is not changed at high temperatures [12]. In the entrained flow gasifier, the content of reducing gas is approximately 70%, or

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more [13,14]. The slag lump containing metallic iron appeared at the outlet of entrained flow gasifier, would block the gasifier and result in the gasifier shut-down [15]. It is assuming that the formation of metallic iron leads to the sudden increase of slag viscosity due to the significant change of liquid slag composition and solid/liquid proportion [16]. Therefore, it is important to avoid the formation of metallic iron in the actual gasifier operation.

Several studies have been made on the metallic iron precipitation from coal ash slag in a reducing atmosphere. The reducing atmosphere described in the literatures includes the real gasification atmosphere and the simulated reducing atmosphere (60% CO/40% N₂, 90% H₂/10% CO₂ and 100% H₂) [12,17,18]. The reduction of iron in the slag takes place both on the gas/slag interface and also in the bulk of slag. The content of metallic iron is manipulated by the diffusivity of O²⁻ [17] and the dissolved CO in the slag [19]. When the pyrite is added to the coal ash, the content of metallic iron is decreased due to the formation of FeS and Fe_{1-x}S [18]. However, to our knowledge, the critical condition for metallic iron precipitation from coal ash slag in the real gasification atmosphere has not been reported. Therefore, the selection of feedstock for gasifier is lacking theoretical guidance to avoid the iron precipitation.

The iron precipitation can be determined by thermodynamic calculation. In this study, FactSage is employed to investigate the effect of metallic iron precipitation in coal ash under the thermodynamic equilibrium conditions in the entrained flow gasifiers. The possibility of preventing iron precipitation was investigated through adjusting the coal ash chemical composition. In the end, ternary diagrams are given to illustrate that the ash composition may lead to iron precipitation. As such it can be used for guiding the feedstock selection for entrained flow gasifiers.

2. Experimental

2.1. Coal sample and its characterization

A typical coal, enriched of iron from Yanzhou, China, (denoted as YZ coal) was selected in this work. The proximate analysis, ultimate analysis and total sulfur contents of this coal were performed according to the Chinese standards (GB/T212-2008, GB/T476-2001, and GB/T214-2007). The results were listed in Table 1. The ash composition of YZ coal was conducted via X-ray fluorescence (XRF) based on ASTM D6349. The results are presented in Table 2.

2.2. Simplified treatment during calculation

The properties of coal ash are mainly influenced by the four major components (SiO₂, Al₂O₃, Fe₂O₃ and CaO). The four oxides in the YZ coal ash were normalized to 100% and listed in Table 3. In order to cover the main range of coal ash composition in China, using YZ coal as basis, a series of ashes with different Fe₂O₃ content, different α

Table 1
Proximate and ultimate analysis (wt%) of YZ coal.

Proximate analysis (ad)				Ultimate analysis (daf)			S _{t,d}
M	A	V	FC	C	H	N	
1.1	12.9	38.7	47.3	76.0	5.4	1.1	2.8

ad: air dry base; daf: dry and ash-free base; S_{t,d}: total sulfur (dry base).

Table 2
Chemical composition of YZ ash (expressed as wt% of metal oxides).

Content										Others
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂		
34.5	18.8	16.0	17.7	1.8	0.5	0.3	7.9	0.6	1.8	

Table 3
Component (g) of the solid phase used for thermodynamic calculation.

Sample	Component					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	α	S/A
YZ ash	39.6	21.6	18.4	20.4	0.33	1.8
<i>Ashes of different Fe₂O₃ content</i>						
Fe_6	45.6	24.9	6.0	23.5	0.33	1.8
Fe_7	45.1	24.7	7.0	23.2	0.33	1.8
Fe_8	44.7	24.4	8.0	23.0	0.33	1.8
Fe_9	44.2	24.1	9.0	22.7	0.33	1.8
Fe_10	43.7	23.9	10.0	22.5	0.33	1.8
Fe_11	43.2	23.6	11.0	22.2	0.33	1.8
Fe_12	42.7	23.3	12.0	22.0	0.33	1.8
Fe_13	42.2	23.1	13.0	21.7	0.33	1.8
Fe_14	41.7	22.8	14.0	21.5	0.33	1.8
Fe_15	41.3	22.5	15.0	21.2	0.33	1.8
Fe_16	40.8	22.3	16.0	21.0	0.33	1.8
Fe_17	40.3	22.0	17.0	20.7	0.33	1.8
Fe_18	39.8	21.7	18.0	20.5	0.33	1.8
Fe_19	39.3	21.5	19.0	20.2	0.33	1.8
<i>Ashes of different α values</i>						
α_0.03	51.2	28.0	18.4	2.4	0.03	1.8
α_0.13	46.7	25.5	18.4	9.4	0.13	1.8
α_0.23	42.9	23.4	18.4	15.3	0.23	1.8
α_0.33	39.7	21.7	18.4	20.3	0.33	1.8
α_0.43	36.9	20.2	18.4	24.5	0.43	1.8
α_0.53	34.5	18.8	18.4	28.3	0.53	1.8
α_0.63	32.4	17.7	18.4	31.5	0.63	1.8
α_0.73	30.5	16.7	18.4	34.4	0.73	1.8
α_0.83	28.8	15.8	18.4	37.0	0.83	1.8
<i>Ashes of different S/A ratios</i>						
S/A_0.5	20.4	40.8	18.4	20.4	0.33	0.5
S/A_1.0	30.6	30.6	18.4	20.4	0.33	1.0
S/A_1.5	36.8	24.5	18.4	20.4	0.33	1.5
S/A_2.0	40.8	20.4	18.4	20.4	0.33	2.0
S/A_2.5	43.8	17.5	18.4	20.4	0.33	2.5
S/A_3.0	45.9	15.3	18.4	20.4	0.33	3.0
S/A_3.5	47.6	13.6	18.4	20.4	0.33	3.5
S/A_4.0	49.0	12.3	18.4	20.4	0.33	4.0

ratio and different S/A ratio were prepared. These samples' ash compositions were also listed in Table 3. A new index, α (in Eq. (1)), is introduced first time, to describe the change of ash composition at fixed Fe₂O₃ content.

$$\alpha = \frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \tag{1}$$

in this equation, oxides are expressed as weight percentage.

Based on type of feedstock, entrained flow gasifiers can be divided into two types, pulverized coal process (dry feed) and coal water slurry process (slurry feed) [20,21]. The atmosphere in both gasifiers is very different. In this study, we chose the Shell gasifier for dry feed process and the Texaco gasifier for slurry feed process on thermodynamically modelling. The raw syngas, contains the main reducing gases CO and H₂, and the main oxidizing gases CO₂ and H₂O was considered in the calculation. In Table 4, the gas compositions, employed during calculation, were listed for both Texaco gasifier (denoted as (a)) and Shell gasifier, (denoted as (b)). The content of H₂S and residual carbon greatly varies in different operation conditions, so the effect by the minor components was not considered in this study.

Table 4
Component (g) of the gas phase used for thermodynamic calculation.

Atmosphere	Component			
	CO	CO ₂	H ₂	H ₂ O
(a)	821.1	565.9	57.0	219.2
(b)	1138.3	66.2	41.4	47.2

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