Fuel xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Inhibition of lignite ash slagging and fouling upon the use of a silica-based additive in an industrial pulverised coal-fired boiler: Part 2. Speciation of iron in ash deposits and separation of magnetite and ferrite

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HIGHLIGHTS

- The use of silica additive caused a remarkable change on the speciation of iron.
- Fe^{3+} was precipitated out of silica matrix upon the cooling and oxidation.
- The magnetic particles formed bear various morphologies.
- The ferrites achieved contain less impure SiO_2 and Al_2O_3.
- The external silica cannot be simply treated as inherent silica.

ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 15 May 2014
Accepted 25 June 2014
Available online xxxx

Keywords:
Pulverised lignite
Silica additive
Iron
Slagging

ABSTRACT

This study for the first time reported the speciation of iron in ash deposits collected from the combustion of a pulverised lignite mixed with external silica in an industrial 30 MW_{th} boiler. The iron speciation was conducted by the use of Mössbauer spectroscopy, Quantitative XRD, and SEM-EDX couple with elemental mapping. In addition, the magnetic particles were separated from fly ash deposits, and their yields and properties were compared with those reported in the literature. As has been confirmed, the addition of external silica caused a remarkable change on the speciation of iron in ash deposits. In the fireside slag, the quantities of highly molten Fe^{2+}-slag and Fe^{3+}-slag were reduced, whereas the contents of fully oxidised hematite and Fe^{3+}-silicate were improved remarkably. The latter two species possesses high melting points and viscosity, and are therefore more difficult to melt to trigger the slagging. These changes are thought to be mainly contributed from the reactions between external silica additive and ash-forming metals, as well as the variation of fluid dynamics and particle residence time in the boiler. The formation of magnetite was also promoted noticeably in the silica additive case, due to a gradual oxidation of Fe^{2+} cation and precipitation of Fe^{3+} – bearing magnetite/ferrites out of the high-viscosity silica matrix, upon a gradual cooling and oxidation in flue gas. The highly molten species were agglomerated with external silica to form coarse clusters that rarely underwent supercooling when the external silica was added into coal. The ferrites achieved after the use of external silica contain less impure SiO_2 and Al_2O_3 than those separated from raw coal fly ashes in the literature. The external silica cannot be simply treated as the inherent silica in a high-rank bituminous coal. Its properties such as contents of impurities, structure and size are apparently pivotal in the capture of Fe^{2+}/Fe^{3+} cations and their speciation.

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1. Introduction

In a typical pulverised coal-fired boiler, the iron-bearing molten species including Fe^{2+}-glass, pyrrhotite and FeO–FeS eutectics have the potential to trigger the initial stage of ash slagging [1]. The ash particles with more than 5 wt% Fe_2O_3 are prone to melt and stick to heat exchanger surface at approximately 1177 °C that is below the temperatures of volatile flame and flue gas in the vicinity of coal burners [2]. Upon the growth of ash slag deposits, more of the heat flux derived from coal flame will move upwards, which in turn intensities ash fouling propensity and water tube corrosion in the convection zone in a boiler.

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http://dx.doi.org/10.1016/j.fuel.2014.06.075
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Please cite this article in press as: Dai B-Q et al. Inhibition of lignite ash slagging and fouling upon the use of a silica-based additive in an industrial pulverised coal-fired boiler: Part 2. Speciation of iron in ash deposits and separation of magnetite and ferrite. Fuel (2014), http://dx.doi.org/10.1016/j.fuel.2014.06.075

The most common iron-bearing minerals in coal include pyrite (FeS_2), siderite ($FeCO_3$) and clay minerals, with their fractions varying greatly with coal rank [1,3]. The amorphous goethite (α-FeOOH) was also found as ultrafine mineral grains embedded in some low-rank lignites such as Victorian brown coal [4]. Ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) was detected in some coals as well [3]. The mechanisms underpinning the transformation of these minerals, and the influences of oxidising and reducing conditions on these mechanisms, have been discussed extensively. Based on the association of minerals with carbonaceous matrix, the iron-bearing species undertake the following transformation routes:

Excluded species [5,6]

Pyrite initially decomposes into pyrrhotite at approximately 530 °C and then oxidise to molten FeO–FeS at 1080 °C. Siderite decomposes into wüstite (FeO) at 1370 °C. For either FeO–FeS or wüstite formed, it further oxidises into magnetite (Fe_3O_4) and hematite (Fe_2O_3) under oxidising condition, or persists under reducing condition. Ankerite is supposed to convert into magensioferrite spinel ($MgFe_2O_4$) upon decomposition [3].

Included species [5,6]

Both pyrite and siderite behave as for their external counterparts in the case there is no contact with alumina-silicates, although their oxidation is delayed by char combustion. However, upon the contact and interaction with alumina-silicates on the receding char surface, molten glassy eutectics are formed [7], which are initially Fe^{2+}/FeS-glass formed in the locally reducing environment, much of which subsequently transform to Fe^{3+}-glass under oxidising condition, or remain intact in a gasification environment.

Little interaction between excluded mineral grains and included ash species [7,8]

This assumption was supported by calculations of coagulation rates based on Brownian diffusion. In other words, the glass formation occurs primarily by the agglomeration of included iron and alumina-silicates and their sintering.

Following these established knowledge, it is referable that the silica additive, mixed with coal physically in this study, should behave as for excluded minerals that interfere little on the transformation of the included Fe-bearing mineral species. It should not even interact with the inherent excluded minerals either, according to the classic ash formation mechanism [8]. This is clearly not the case as explored in the first paper of this study, where the alteration on overall properties of individual ash deposits upon the use of silica additive has been confirmed [9]. In particular, the fireside slag has been reduced remarkably by the use of silica additive. As iron is the trigger for ash slagging, it is pivotal to examine the detailed changes on the speciation of iron upon the mixing of silica with coal. As far as the authors are aware, the knowledge on this area is still scarce, although many case studies on different 'raw coals" and interaction between inherent minerals species without the introduction of external species have been conducted intensively.

This paper is complementary to the first part of this study by detailing the speciation of iron upon the use of silica additive into a lignite-fired pulverised coal boiler. For the speciation of iron, Mössbauer spectroscopy (MS), quantitative XRD (QXRD), and SEM-EDX coupled with elemental mapping on both surface and cross-section of ash particles have been employed. The magnetic species (*e.g.* magnetite, magnesioferrite spinel) in ash deposits were also separated to quantify the change on their mass and structure upon the use of silica additive. Finally, thermodynamic equilibrium modelling based on the use of FactSage 6.4 was conducted to interpret the experimental observations and clarify the mechanisms underpinning the transformation of inherent iron upon the interference of external silica.

2. Experimental

2.1. Coal combustion facility and ash sampling

This is the same as mentioned in the part 1 [9] and our previous work on the combustion of raw coal without the use of additive [10].

2.2. Annealing clay at laboratory horizontal tube furnace

To clarify the effect of iron contaminant in clay on the speciation of iron in coal ash deposits, the same clay as used for industrial scale test was annealed at a laboratory horizontal tube furnace at 1000 °C and 1300 °C. The annealing of clay was achieved in two ways, a direct heating of clay with furnace together at 10 °C/min from room temperature to set point, which was kept on hold for 3 h then; a prior heating of furnace to the set temperature, and clay sample was then pushed into the hot furnace for 3 h on hold. For either method, the cooling of the annealed clay was accomplished by leaving it on a cold marble surface to cool down naturally, which usually takes about 30 min. In other words, the cooling rate is quite slow here. This is to mimic a slow cooling in flue gas rather than fast quenching on cold water tube surface in a coal-fired boiler. For each annealed clay sample, apart from being analysed by XRD, it was also treated by a dry magnet separation method to pull out any magnetic particles within it.

2.3. Iron speciation and quantification methods

Same as other elements, iron in ash deposits was quantified by a pre-calibrated XRF. The speciation of iron was achieved by the use of Mössbauer spectroscopy, following the method described previously [10]. Quantitative XRD was also conducted based on the Rievfield least squares fitting method and through the use of a commercial software, Siroquant 3.1. The XRD spectra were collected from Philips 1130 using a current of 25 mA and a volatage of 40 kV. SEM-EDX and elemental mapping were used to observe the microstructures of iron-bearing particles.

2.4. Thermodynamic equilibrium modelling

This was conducted by the use of FactSage 6.4, Phase diagram module to draw $FeO–Fe_2O_3–SiO_2$ phase diagrams as a function of $SiO_2/(FeO + Fe_2O_3)$ molar ratio. The databases including FToxid-SLAG A and FToxide-SPINA were included. The latter database comprises Fe_3O_4, $(Fe^{3+}O_2)^-$ and $(Fe_2^{3+}O_5)^{4-}$.

3. Results and discussion

3.1. Mössbauer spectroscopic characterisation

Fig. 1 illustrates the Mössbauer spectra for three ash deposits collected from the combustion of coal mixed with silica. The corresponding quantitative results are tabulated in Table 1, where the results for raw coal ash deposits cited from previous paper [10] are included for comparison. Regarding the raw coal fire-side slag labelled G, its initial dense layer is dominated by Fe^{3+}-slag (57%)

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