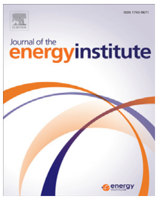
Journal of the Energy Institute xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: http://www.journals.elsevier.com/journal-of-the-energy-institute



Effects on enrichment characteristics of trace elements in fly ash by adding halide salts into the coal during CFB combustion

Q4 Shilin Zhao[*], Yufeng Duan, Meng Liu, Chenping Wang, Qiang Zhou, Jianhong Lu

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, 210096, China

ARTICLE INFO

Article history:
Received 13 October 2016
Received in revised form
14 December 2016
Accepted 20 December 2016
Available online xxx

Keywords:
Trace elements
Enrichment characteristics
Halide salts
Coal combustion

ABSTRACT

The effects on enrichment characteristics of trace elements (TEs) in fly ash by adding halide salts into the coal during coal combustion were conducted on a 6 kW_{th} circulating fluidized bed (CFB) experimental device. Results show that unburn carbon content in fly ash has little relationship with the concentration of TEs namely Hg, As, Pb, Cr and Mn. All the TEs are enriched in fly ash for the raw coal CFB combustion. Concentration of Hg and Mn increases with increasing the addition amount of $CaCl_2$, NH_4Cl and NH_4Br. As, Pb and Cr enrich in fly ash more strongly when adding more $CaCl_2$ into the coal while more addition of NH_4Cl and NH_4Br leads to the decrease of their enrichment compared to addition amount of 0.1 wt%. On the whole, putting halide salts into the coal results in the TEs enriched in fly ash, which benefits for TEs removal during the coal combustion. Combining this method with the chemical sequential extraction or thermal treatment of the fly ash will be a promising way to realize the TEs removal and their recovery.

1. Introduction

Coal is the main primary energy in the world, which occupies about 30% in the total energy consumption [1]. In China, the coal production and consumption account for 49.6% and 50.6% of the total coal amount in the world at the same period by the year of 2014 [2]. Trace elements (TEs), content of which is less than 100 ppmw, emitted from coal combustion can generate great harm on the environment and human health [3–5]. U.S. Clean Air Act Amendments and the European Union have listed some trace elements as the key toxic air pollutants, such as As, Pb, Cd, Hg [6,7]. With the extensive growth of the industry and economy in China, more than 30 serious poisoning cases associated with TEs have happened since 2009, including Cd, As, Pb pollution incidents in Hunan, Shandong, and Sichuan province, respectively [8].

For the removal of the mercury emitted from coal-fired power plant, many researchers have done lots of works, including mercury occurrence in coal [9,10], mercury transformation during the coal combustion [11–13], coal pre-treatment before burning [14,15], adjusting the boiler operation parameters [16,17] and injecting oxidizing agent or adsorbent into the coal, furnace, flue gas duct [18–21], etc. However, related reports about the control for other trace elements emitted from coal-fired power plants are little. Recently, TEs removal in the field coal-fired power plant mainly depends on the conventional air pollution control devices (APCDs), like selective catalytic reduction (SCR), electrostatic precipitator (ESP), fabric filter (FF) or wet flue gas desulfurization (WFGD). Due to the difference in the coal samples, boiler output, and APCDs installation structures, etc., the overall removal rate across the APCDs is different and unstable [22–24]. Therefore, many works should be done to achieve the ultra-low emissions for the coal-fired power plant which includes TEs. Coal combustion with halogens, such as bromine or chlorine, is considered as one of the most effective ways to remove mercury form coal combustion [25–27]. Zhuang et al. [25] cofired the subbituminous coal with a $CaCl_2$ additive to study the mercury transformation during the coal combustion, finding that the added $CaCl_2$ could result in almost 50% oxidized mercury. Pan et al. [26] injected NH_4Cl into the furnace to study the effects on mercury transformation under Cl atmosphere, results of which showed that the proportion of both the gaseous Hg^{2+} and Hg^0 decreased while Hg^p increased. Cao et al. [27] found that 300 ppm HCl added in the flue gas could achieve 40% Hg^0 oxidation in a slipstream reactor. The impact

---

[*] Corresponding author. Fax: +86 025 83795652.
E-mail address: slzhao_seu@163.com (S. Zhao).

http://dx.doi.org/10.1016/j.joei.2016.12.003

Please cite this article in press as: S. Zhao, et al., Effects on enrichment characteristics of trace elements in fly ash by adding halide salts into the coal during CFB combustion, Journal of the Energy Institute (2016), http://dx.doi.org/10.1016/j.joei.2016.12.003

extent on Hg^0 oxidation for hydrogen halogens were ranked in the order of HBr > HI > HCl > HF. However, there is no report about the effects of halogen additives on the other TEs except mercury in the coal combustion process.

For the fly ash produced from waste incineration, chemical sequential extraction and thermal treatment may realize the TEs recovery and make the fly ash be reused [28–30]. Liu et al. [31] removed the TEs from MSS fly ash by thermal and chlorination, finding that the added chlorinating agents could improve the TEs removal rate dramatically. Based on this, lots of benefits such as TEs control in the coal-fired power plant, TEs recovery and reuse of the fly ash can be acquired if that putting the halogens into the coal can achieve the enrichment of the TEs in the fly ash.

In this study, the experiments about coal combustion with $CaCl_2$, NH_4Cl and NH_4Br additive were conducted on a 6 kW_{th} CFB experimental device, the object of which is to study the effects of halide salts addition on the TEs enrichment characteristics in the fly ash. The concentration of the TEs including Hg, As, Pb, Cr, Mn was determined by the mercury analyzer and the ICP-MS. XRF and EDS were used to analyze the chemical composition of the fly ash. The migration and transformation mechanism of TEs in the coal combustion process with/without halide salt addition were also discovered. The main purpose is to improve our basic understanding of the underlying migration and transformation processes of TEs during the coal combustion and provide a theoretical basis for the way to remove the TEs emitted from coal burning.

2. Experimental section

2.1. Coal samples preparation

The anthracite in Guizhou province was used in this study, the proximate and ultimate analysis of which was shown as Table 1.

According to the classification standard based on the chlorine content in coal (MT/5597-1996, China), this kind of anthracite belongs to the extremely low-chlorine coal. Based on the sulfur content in the Chinese coal with the range of 0.2 wt%–8 wt% [32], the coal studied in this work belongs to the low sulfur coal.

Previous work [33,34] found that when the chlorine content in the coal exceeded 0.3 wt%, it would accelerate corrosion and shorten the service life of the boiler and stack. Therefore, this study selected $CaCl_2$, NH_4Cl and NH_4Br as the coal additive with chlorine or bromine addition amount of 0.1 wt%, 0.2 wt% and 0.3 wt% respectively, accounting for the coal on the mass fraction.

The specific coal samples preparation process can be found in the reference [35]. The fly ash in the flue gas was defined as *x*-additive, where *x* represents the chlorine or bromine addition amount, wt%.

2.2. Experimental setup and procedure

The coal samples combustion were conducted on a 6 kW_{th} CFB experimental device, schematic diagram of which was shown as Fig. 1. The structural parameter about this device was described in the reference [35]. In the apparatus, T1–T7 were the temperature sites along the furnace body. P1 and P2 were the pressure points, which were set at the bottom and top of the furnace, respectively. Combining the parameters of T1-T7, P1, P2 and the content of O_2, CO, CO_2 from the ecomJ2KN flue gas analyzer, the coal samples could be burned stably. Fly ash in the flue gas was sampled for 2 h for every coal sample by the isokinetic sampling. During the combustion, the bed temperature of the CFB combustor was kept at 900 °C with the excess air ratio of 1.4.

2.3. Analysis methods

Mercury in the coal and fly ash was detected by the Leeman Laboratories Hydra II C mercury analyzer. The content of the other TEs (i.e. As, Pb, Cr, Mn) in solid samples like the coal and fly ash was detected by the EPA Method 6020a. About 0.1 g of each sample was digested by a mixture of acids (HNO_3:HCl:HF = 3:1:1) in a microwave oven, and then the inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the concentration of As, Pb, Cr, Mn, which was according to the methods reported in Zhao et al. [36]. The carbon content in the sample was determined by the burning weight-loss method, which was reported in Xin et al. [37]. X Ray Fluorescence (XRF) and Energy Dispersive Spectrometer (EDS) were used to analyze the chemical composition of the fly ash.

3. Results and discussion

3.1. Content of TEs in the raw coal

The concentration of the TEs in the raw coal was shown as the Table 2. Compared with the average content of the TEs in the Chinese and the world's coal [38,39], Cr and Mn are similar. Hg and Pb in the coal of China are higher than that in the world's coal while As is lower. Except Cr, the concentration of the other TEs namely Hg, As, Pb and Mn in the raw coal is lower than the average value in the Chinese coal. The difference in the content of the TEs in the coal is due to the different post-depositional and coalification processes [40].

Table 1
Proximate and ultimate analyses of the Guizhou anthracite.

Ultimate analysis/wt%					$Q_{net,ar}$	Proximate analysis/wt%				Cl	F
C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	MJ/kg	FC_{ar}	V_{ar}	A_{ar}	M_{ar}	%	μg/g
57.28	2.25	3.47	0.70	1.32	21.62	58.42	6.60	31.24	3.74	0.006	135

$Q_{net,ar}$: Low heating value at the received base; ar: As received base.

Please cite this article in press as: S. Zhao, et al., Effects on enrichment characteristics of trace elements in fly ash by adding halide salts into the coal during CFB combustion, Journal of the Energy Institute (2016), http://dx.doi.org/10.1016/j.joei.2016.12.003