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SO_2, NO_x, HF, HCl and PCDD/Fs emissions during Co-combustion of bituminous coal and pickling sludge in a drop tube furnace

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ABSTRACT

The influence of co-combustion of bituminous coal and pickling sludge on SO_2, NO_x, HF, HCl and PCDD/Fs emissions was studied in a drop tube furnace. To simulate the combustion condition of suspension firing boilers, the experiment was performed at 1100–1400 °C with the share of sludge in the feed ranging from 0 to 10% by weight. The combustion characteristics of coal and of blended fuels were studied by TG analysis. The results showed that the average combustion efficiency of co-combustion of bituminous coal and pickling sludge in the drop tube furnace is larger than 99%. SO_2, NO_x and HCl emissions had an increasing tendency with the temperature rising, but HF emissions were not sensitive to temperature. SO_2 and HF emissions had a rising trend with increasing share of sludge, while NO_x and HCl emissions had an opposite trend. No obvious effect of temperature and the share of sludge on the total TEQ of PCDD/Fs was found, and the emissions of the seventeen congeners were basically stable under different experimental conditions. TG results showed that the combustion characteristics of coal and blended fuels were basically the same. XRD results showed that the ash composition changed significantly with the addition of sludge. Compared to the national standard, when co-combusting of bituminous coal and pickling sludge in commercial power plant, desulphurization and denitrification equipment, activated carbon injection and baghouse should be provided.

1. Introduction

In China, the amount of hazardous waste has been growing rapidly in recent years. In 2014, approximately 3600 tons of hazardous waste were produced, mainly from Nonmetal Mineral Products, Chemical Products, Medical and Pharmaceutical Products, and Metal Products, etc. [1]. This amount is obviously grossly underestimated. However, due to the lack of disposal facilities, nearly 800 tons of this waste was not disposed of properly. Pickling sludge is a kind of residue generated from the neutralization of acid pickling wastewater [2], and it belongs to HW17 in the National Hazardous Waste List [3]. Since the metal pickling process uses sulfuric and hydrofluoric acids, pickling sludge contains large amounts of $CaSO_4$ and CaF_2 [2]; therefore, it is difficult to directly recycle the sludge back to the steelmaking process. Nowadays, hundreds of hazardous waste disposal technologies exist all over the world, but due to the lack of land resources and the strict environmental regulations in developed countries, integrated incineration is one of the most important methods for the disposal of hazardous waste. About 78% of hazardous wastes are burned in Japan, and there are 239 hazardous waste incinerators in the European Union [4]. According to data from the EPA (Environmental Protection Agency, USA), there were 271 hazardous waste incinerators in the USA in 2012 [5].

Co-combustion treatment is defined as combusting two or more fuels at the same time for energy production, with the purpose of using waste as the secondary fuel being to dispose of it [6]. The advantages of co-combustion of fuel and waste materials include: the reduction of CO_2 emissions from fossil fuels, disposal of waste materials with more efficient environmental protection equipment, and eliminating the need for waste incinerators. However, due to the fact that the compositions of various fuels are different, co-combustion of two fuels can lead to positive or negative synergy effects [6]. To determine the influence of adding a secondary fuel on suspension-firing boilers, series of investigations have been carried out using hazardous waste, solid recovered fuel (SRF) and municipal sewage sludge (MSS) as secondary fuels.

During the co-combustion process, the impact of using a secondary fuel depends on many factors, such as the nonmetallic and mineral element content, physical and chemical properties, and combustion characteristics. Previous studies on co-combustion

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have used are hazardous waste [7–12], sewage sludge [13–20] and solid recovered fuel [21–27] as secondary fuels. Generally, due to the lower calorific value and poorer combustion characteristics of the secondary fuel, the combustion efficiency and the temperature at furnace center would decline during the co-combustion process. When co-firing petroleum sludge and coal in a tangentially-fired pulverized coal boiler, the combustible content in the ash produced increase from 9.48% to 10.69% [8], and lots of H_2 and CO are generated due to incomplete combustion, which leads to a decrease in temperature at the furnace center of about 20–90 K [9]. In many European power plants, the amount of sewage sludge is usually below 10 wt.% and there are only slight differences compared to combustion of coal alone [13]. When co-combusting coal and SRF, the combustion efficiency drops with the addition of SRF; this is mainly because the SRF particles are partly agglomerated [23].

Furthermore, it has been shown that the emission of pollutants such as SO_2 and NO_x in the flue gas may be influenced by the composition of fuels and the temperature of the furnace during co-combustion. Additionally, the relatively high content of the inorganic elements F and Cl in waste may also cause problems. According to a study by Li [7], the emission of SO_2 and NO_x basically remains unchanged; however, Wu's study [23] shows that SO_2 and NO_x emission is clearly affected by the addition of SRF and additives. Other studies show that the emission of hydrogen chloride will increase due to the high chlorine content in waste [26], and that during the combustion process of hazardous wastes, a large amount of polychlorinated dibenzo-p-dioxins and dibenzofurans(PCDD/Fs) may be release to the surrounding environment [28]; this is the primary source of PCDD/Fs emissions in China [29]. Due to the large amount of $CaSO_4$ and relative high heavy metal content in pickling sludge, the ash composition is expected to change significantly during the co-combustion process. According to Zhang [30], more than 90% of non-volatile heavy metals such as Cr, Ni and Mn will be present in ash after co-combustion.

The objective of the current study is to investigate the influence of the furnace temperature and the sludge content on the combustion characteristics and pollutant emissions in the flue gas during co-combustion of bituminous coal and pickling sludge. To simulate the combustion conditions of suspension firing boilers, experiments were performed in a drop tube furnace and the bituminous coal was co-combusted with different amounts of pickling sludge (0, 2, 5, and 10 wt.%) at different temperatures (1100, 1200, 1300, and 1400 °C). TG analysis was used to study the combustion characteristics of coal and blended fuels. XRD techniques were used to study the composition of bottom ash.

2. Experimental section

2.1. Materials

A bituminous coal and a pickling sludge were chosen as the fuels. The pickling sludge used in the experiments was obtained from a hazardous waste treatment plant in Huzhou, Zhejiang province. Both coal and sludge were being ground into a powder of particle size >200 mesh. The proximate and ultimate analysis data of bituminous coal and pickling sludge are given in Table 1. The Cl and F content in both fuels are determined by using high temperature combustion hydrolyzing method (GB/T 3558-2014, GB/T 4633-2014) and an ion chromatography method (792 Basic IC, Switzerland. Metrohm company). It can be seen that the volatile, fixed carbon and heat values of the sludge are lower than those of the coal, but that the ash and F content in the sludge is higher. Both fuels were dried for at least 12 h at 105 °C before they were sent into the reactor.

2.2. TG analysis

TG analyses of coal with different amounts of sludge (0, 2, 5, and 10 wt.%) were performed in a thermo-gravimetric analyser (Mettler-Toledo TGA/SDTA851e). Approximately 10 mg of air-dried fuel was used for each analysis. Air was used as a reaction gas with a flow rate of 80 ml/min. The heating rate was set to 20 °C/min, and the sample was heated from 25 °C to 1000 °C.

2.3. Setup-drop tube furnace

The co-combustion experiments were performed in a drop tube furnace to simulate the combustion conditions in suspension-firing boilers. A schematic diagram of the drop tube furnace is shown in Fig. 1. A weight-loss feeder (MT-112, K-TRON company) was used, in order to ensure a feeding error of less than 0.5%. An alundum tube (1.2 m long, 40 mm diameter) was used as the combustion reactor, and 12 surrounding heating elements were divided into three layers to control the temperature of the combustion area. The experimental fuels were sent into the reactor by primary air, and secondary air was adjusted to obtain a good combustion condition. The flue gas was collected through the sampling aperture and the bottom ash was gathered from the bottom ash chamber.

During experiments, the feeding rate of the fuels was set to 36 g/h. By changing the flow rate of secondary air, the oxygen content in the flue gas was adjusted to nearly 10% for the different experiments. The duration of each experimental condition was 2 h, with a 1 h adjusting and stabilizing process followed by a 1 h sampling and measuring process. The emission concentrations of CO, CO_2, O_2, NO_x, SO_2, HF and HCl in the flue gas were measured on-line using a Gasmet FT-IR (DX-4000, Finland Gasmet). PCDD/Fs gas samples were collected on XAD-2 in the filter and adsorbed in toluene, which was cooled by ice bath. The extraction, concentration, clean-up procedure, and analysis process of PCDD/Fs samples used in this experiment were carried out as described in a previous study [31] according to US EPA method 1613 [32].

2.4. Experimental matrix

For the purposes of studying the effect of temperature and simulating the combustion conditions in suspension firing boilers, the combustion temperatures during the experiments were set to 1100, 1200, 1300, and 1400 °C, respectively. As the heat value of sludge is low (0.075 MJ/kg), the highest composition of sludge used in the mixed fuel was 10 wt.%. In addition, pure coal and mixtures containing 2 and 5 wt.% sludge were also studied.

Table 1
Proximate and ultimate analysis of bituminous coal and pickling sludge (Mass%).

Sample	Proximate analysis (%)					Ultimate analysis (%)						
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{net,ad}$(MJ/kg)	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}	F_{ad}	Cl_{ad}
Coal	4.66	20.65	26.61	48.08	24.58	62.29	3.90	7.17	1.02	0.31	0.01	0.04
Sludge	1.50	89.15	9.25	0.1	0.08	0.86	0.46	1.32	0.38	6.33	0.08	0.04

ad, air-dried basis; M, moisture; A, ash; V, volatile; FC, fixed carbon