



Full Length Article

Effect of mineral reaction between calcium and aluminosilicate on heavy metal behavior during sludge incineration



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ABSTRACT

Calcium-based additives such as lime, portlandite and limestone are widely applied in solid waste incineration for desulfurization. However, calcium may affect emission of heavy metals. In this study, effects of mineral reaction on the transference of copper and zinc during sludge combustion are investigated. Sludge from a chemical fiber factory was blended with lime as an additive in different mass fractions. The incineration tests were performed in a tube furnace at temperatures of 600–1100 °C. Then the ash was digested into two methods to clarify two retention forms of heavy metals. The X-ray diffraction shows that the calcium from additive converted to calcite, amorphous calcium, gehlenite and anorthite successively as temperature rising. The two-step digestion reveals that minerals above change the distribution of heavy metals between different forms. The residual form of both two heavy metals increases with temperature upgraded, while the leachable form presents an opposite trend. Calcium stimulated the volatility of copper at all temperatures but took positive effect on volatility of zinc only at 600 °C and promoted its retention at higher temperatures. With consideration of retention forms, mineral composition and temperature, it is suggested that through reactions with aluminosilicate, calcium changes heavy metals transference to a different extent. Competition by calcium to produce aluminosilicate inhibits retention of heavy metals, but zinc can be together with calcium as eutectic aluminosilicate at higher temperatures. Surface morphologies were detected by scanning electronic microscopy and energy dispersive spectrometer, confirming the effect of calcium.

1. Introduction

Huge amount of solid waste such as sludge has been disposed over the world. Sludge usually contains harmful substances, including pathogens, organics and heavy metals that cannot be treated casually. For energy-saving and emission-reduction, sludge treatment is supposed to achieve aims of reducing, reusing and recycling. Incineration is widely used as an efficient treatment for solid waste, but flue gas results in some secondary pollutants, such as acid gases, heavy metals, dust and dioxin [1].

Heavy metals from fuel are not eliminated after thermal treatment, but exist in flue gas, fly ash and slag. Some of them such as lead, cadmium, copper and zinc called “semi-volatile heavy metals”, are usually vapor at high temperature, then under lower temperature condense into very fine particulates (often smaller than 1 μm, even 0.1 μm) which can easily escape from air pollutant control device [2]. To reduce their emissions into atmosphere, it is effective to fix them in the bottom ash or sorbents. The effects of different combustion conditions and fuel components are different on the behaviors of heavy metals [3,4]. Co-

combustion of sludge and various fuel such as coal, biomass has become a popular research area. During co-combustion process the transference of heavy metals are also not the same because of different species and quantity of fuel composition and different combustion conditions [5–8]. For example, moisture can prolong ignition, that means high temperature continues in longer time, promoting the volatility of heavy metals [9]. Some studies pointed out that by forming low boiling point chlorine, both organic chlorine (PVC, etc.) and inorganic (HCl, NaCl, etc.) can increase volatility of heavy metals through different mechanisms [10]. Elements like silicon, aluminium and phosphorus can be combined with heavy metals at high temperature to become very stable form [11,12]. For instance, proved to be an effective heavy metal adsorbent, kaolin can form stable production with heavy metals at high temperature [13–16]. In a drop furnace for sludge incineration, Yao et al. chose kaolin as adsorbent to capture heavy metals in flue gas [17–19]. In addition, some minerals with phosphorus also can fix heavy metal. Tang et al. used hydroxyapatite to immobilize heavy metals during combustion of tannery sludge 11. In a word, the difference of elements or minerals in the fuel with its additive can be one of the

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dominant factors for behaviors of heavy metal.

Copper and zinc are demonstrated to cause teratogenesis and threaten healthy potentially. Additionally, copper can be the catalyst for formation of dioxin in furnace [20,21]. Thus, it is still deserved to study their behaviors during combustion. Previous studies have explained how chloride, sulfur, moisture and reaction atmosphere impact on their volatility [22]. Calcium is one of the most common elements in the fuel composition, and many studies have indicated that calcium influences behaviors of heavy metals. Lime as a calcium-based additive can also be used as a heavy metal adsorbent [4,8]. It is generally believed that the existence of silicon and aluminium is beneficial to fix heavy metals [23–26], but previous study tended to focus on the effect of single oxide (like CaO, SiO₂, Al₂O₃) and the effect of calcium on their formation of aluminosilicate has not been further studied, so it is desired to find the relation between calcium and heavy metals to form aluminosilicate.

In this paper, the behaviors of zinc and copper in sludge incineration are investigated. Lime was added in the sludge as a calcium-based additive. Volatility and different retention forms in the ash of copper and zinc in the combustion process were investigated. Moreover, the mechanism of effect by calcium on copper and zinc to form aluminosilicate was discussed.

2. Materials and method

2.1. Materials

The sludge was sampled from a chemical fibre factory. Dried before in the factory, it only had 6.2% moisture. Its dry base composition analysis is listed in Table 1. Ash yield of sludge is 58.2%, where silicon oxide and aluminium oxide occupy high proportion, and the ratio of Si and Al atoms is very close to 1:1.

Lime as an additive was milled and sieved into less than 0.2 mm. The sludge was blended with such additive of 1%, 3% and 5% mass fraction which were respectively marked as C1, C3 and C5. Untreated sludge was marked as N.

2.2. Method

The sample weight 1.0 g was placed in a quartz ark, which is heated in a horizontal tube furnace to simulate combustion process, and the air flow rate is 10 L/min constantly. Heating temperatures were set at 600, 700, 800, 900, 1000 and 1100 °C. The quartz ark was sent into the tube furnace at the setting temperature and maintained for 20 min, then stop heating and cool down to 110 °C before the removal. Parallel tests were carried out for 3 times, and the data were averaged to refer in this paper.

The ash was digested into two methods. First method is to leach the ash in aqua regia. Second method is to digest the ash in HNO₃-HCl-HF-HClO₄. The heavy metal concentrations of solution were analysed by an atomic absorption spectrometer (AAS, WA2081, China). The

Table 1
Composition of sludge (dry base).

Approximate analysis/%			Element analysis/%						
Volatile matter	Ash yield	Fixed carbon	N	C	H	O	S	Cl	
31.9	58.2	9.9	3.01	21.05	2.74	14.3	0.51	0.11	
Mineral in ash/% (Expressed as oxide)								Heavy metals/ mg·kg ⁻¹	
SiO ₂	Al ₂ O ₃	CaO	P ₂ O ₅	Fe ₂ O ₃	TiO ₂	K ₂ O	Cu	Zn	
43.15	38.25	4.73	4.14	3.5	1.6	1.28	103	742	

distribution of heavy metals is divided into two parts: volatility and retention. And the retention part is also divided into two forms: leachable form and residual form. Those are calculated according to:

$$Volatility (\%) = \frac{M_s - M_2}{M_s} \times 100\% \tag{1}$$

$$Retention (\%) = 1 - Volatility \tag{2}$$

$$Leachable Form (\%) = \frac{M_1}{M_s} \times 100\% \tag{3}$$

$$Residual Form (\%) = \frac{M_2 - M_1}{M_s} \times 100\% = Retention - Leachable Form \tag{4}$$

where M_s (mg/kg) is the initial content in the sample, M_1 (mg/kg) is the content in solution of the first method and M_2 (mg/kg) is the content in solution of the second method.

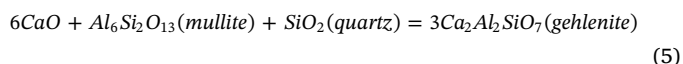
To acknowledge whether the additive had affected the combustion process then further impacted on the behaviors of heavy metal [27], thermal analysis of sludge combustion was measured on a thermogravimetry (TG, STA409PC, German) for sample N and C5. Each sample weight 10 ± 0.5 mg was placed into a crucible, and then heated from ambient temperature to 1000 °C at the rate of 10 °C/min. The air flow rate was 100 mL/min. Derivative thermogravimetry (DTG) analysis was calculated at the same time.

The mineral phase in ash was identified by X-ray diffraction (XRD, ARL X-TRA, Switzerland). The surface morphologies for the ash of sample N and C5 at 900 °C were detected by scanning electronic microscopy and energy dispersive spectrometer (SEM-EDS, Ultra Plus, German).

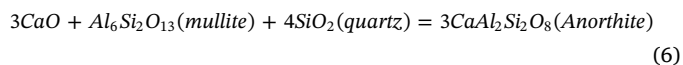
3. Result and discussion

3.1. Changes in the mineral matter

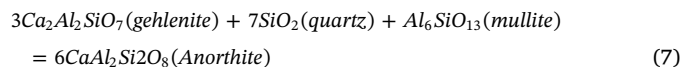
The X-ray diffraction patterns of sludge and its ash are shown in Fig. 2. Mullite and quartz are the main minerals of sludge. Berlinite and anhydrite were also detected. Below 700 °C, the crystal phases do not change significantly. Then at 800 °C, gehlenite was observed, whose calcium might come from amorphous calcium (Eq. (5)) that presents no peak in the curve [28]:



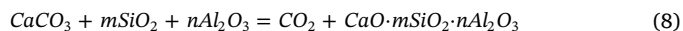
From 900 °C, anorthite was confirmed and its peaks became intense, indicating its large amount formation (Eq. (6)):



At 1100 °C, the anhydrite peak disappeared, while the yeelimite was found in turn. Meanwhile, the gehlenite also disappeared that might convert to anorthite (Eq. (7)):



With additive, more calcium remained in the sludge ash. The lime might absorbed the moisture in the air and formed portlandite, comparing the 20 °C curves in Fig. 1 and Fig. 2. At 600 °C, the diffraction peaks of calcite and anhydrite was intense. This can be ascribed to the production of CO₂ and SO₂ during combustion; At 700 °C, calcite was decomposed, and except anhydrite there is no mineral containing calcium, due to the formation (Eq. (8)) of amorphous anorthite [28]:



At 800 °C, compared to Fig. 1, anorthite had already been generated caused by combination of calcium, mullite and quartz (Eq. (6)). Under

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