



# Effects of natural and modified calcium-based sorbents on heavy metals of food waste under oxy-fuel combustion

Chuncheng Ke, Xiaoqian Ma\*, Yuting Tang, Fangfang Tang, Weihua Zheng

Guangdong Province Key Laboratory of Efficient and Clean Energy Utilization, School of Electric Power, South China University of Technology, 510640 Guangzhou, China

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## ABSTRACT

Performance of natural and modified calcium-based sorbents for heavy metals for food waste under oxy-fuel combustion in a lab-scale tubular furnace was carried out. The effects of furnace temperature, sorbents type, and CO<sub>2</sub>/O<sub>2</sub> ratio on adsorption of heavy metals were investigated. Increasing the furnace temperature helped fixing Al in the bottom ash, but increased the volatilization of Zn. The results showed that heavy metals captured by sorbents highly depended on the metals types. Nature and modified CaO had excellent performance for Al capture while CaCO<sub>3</sub> could not absorb Al. Neither CaCO<sub>3</sub> or CaO could not use as sorbents for the Cr capture. CO<sub>2</sub>/O<sub>2</sub> ratio highly affected the capture of Cr and Zn but had no influence on Al, and the decrease of CO<sub>2</sub>/O<sub>2</sub> ratio would help capturing Cr and Zn. This work contributes to the heavy metals controlled by Ca-based sorbents during municipal solid waste oxy-fuel combustion.

## 1. Introduction

Being as the biggest component of municipal solid waste (MSW), food waste shares a proportion of 55.86% according to the result of Zhou et al. (2014), which is an average of 79 research papers. 203.6 million tons of MSW were collected in China in 2016 (China Statistical Yearbook, 2017), that was 119.7 Gmillion tons of food waste need to be disposed and it will grows year by year. Many researchers had studied the disposition of food waste, anaerobic digestion was the hottest topics (Nguyen et al., 2016; Ren et al., 2018; Xiao et al., 2018). However, since the difficulty of collection and longtime dispose, incineration has lots of advantages comparing with anaerobic digestion and becomes the main disposal method in China. According to the Thirteenth Five-year Plan of China (National Development and Reform Commission, 2016), by the end of 2020, the incineration capacity will reach 50% share of national urban waste disposal capacity. Waste incineration is becoming the trend of development of MSW in China, thus it is important to ensure that the waste incineration power plants are environmentally friendly. Waste incineration power plants are not only the most suitable dispose for MSW but also contribute to solving current energy shortage problem.

For waste incineration, one of the most challenging work is to reduce pollution. The concentration of heavy metals in MSW is relatively high compared with other solid fuels such as biomass and coal (Sorum

et al., 2003). Heavy metal emission is one of environmental protection problems which need high attention during MSW incineration. The State Environmental Protection Administration of China has set cadmium (Cd)'s emission standard for MSW incinerators at 0.1 mg/m<sup>3</sup>, and the total amount of antimony (Sb), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn) and nickel (Ni) is set at 1 mg/m<sup>3</sup>. Heavy metal pollution not only causes damage to the environment such as degrades the quality of the atmosphere, water bodies, and food crops, but also harmful to human health because they are not biodegradable and can accumulate in human body and cause chronic poisoning (Jamil et al., 2010; Prasad et al., 2008). It is worth study not only because of the stricter emission standards, but also for the harmonious development of human and nature.

Sorbent control is an effective way to control heavy metals pollution because bottom ash is easily collected. Ca-based sorbent are widely used for SO<sub>2</sub> adsorption (Chen et al., 2009; Wang et al., 2002) and heavy metals capture (Chen et al., 1999; Tang et al., 2016). Lu and Wang (2005) used NaCl solution to modify CaCO<sub>3</sub> and calcined at 900 °C under N<sub>2</sub> atmosphere and found that modified calcium-based sorbents had better Cd absorption than unmodified sorbents. Heavy metal controlled by sorbents is to capture heavy metals through physical adsorption and chemical adsorption, so the purpose of modified sorbents is to enhance the physical adsorption capacity or chemical adsorption capacity. Chen and Wey (1996) indicated that operating

\* Corresponding author at: School of Electric Power, South China University of Technology, 510640 Guangzhou, China. Tel.: +86 20 87110232; fax: +86 20 87110613.

E-mail address: [epxqma@scut.edu.cn](mailto:epxqma@scut.edu.cn) (X. Ma).

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temperature, chloride content and sorbent size are three most important factors affecting sorbent capacity. Zheng et al. (2018) found that limestone modified with  $K_2CO_3$  improved the capture performance for Cr and Cu, whereas limestone modified with  $Al_2(SO_4)_3$  showed an enhanced capture performance for Cr, Cu, Pb and zinc (Zn).

Oxy-fuel combustion is a promising technology to storage carbon and has gained a lot of concerns and considerable research (Chen et al., 2015; Gao et al., 2016; Tran et al., 2016). Significant changes happened when combustion atmosphere was switched to oxy-fuel combustion from air combustion. Researches (Hong et al., 2009; Pak et al., 2010) found that oxy-fuel combustion technology was an innovative combustion technology that could control  $CO_2$ ,  $SO_2$  and  $NO_x$  emissions simultaneously. Tang et al. (2016) used individual tire rubber and polyethylene found that the replacement of  $N_2/O_2$  atmosphere by  $CO_2/O_2$  atmosphere could decrease the volatilization rate of heavy metals. Our previously study (Ke et al., 2017) presented the volatilization of heavy metals of co-combustion of food waste and polyvinyl chloride (PVC), found that the replacement of  $N_2/O_2$  atmosphere by  $CO_2/O_2$  atmosphere decreased the volatilization rate of Cd and Cr but increased Zn. However, no research focus on the heavy metals adsorption by sorbents for the food waste under oxy-fuel combustion. In order to improve the environmental performance of MSW incineration and the development of oxy-fuel combustion, efficient sorbents and the heavy metals adsorption mechanism during food waste combustion in  $CO_2/O_2$  atmosphere need further study.

So far, the study of sorbent capture performance of food waste combusted under  $CO_2/O_2$  atmosphere has not been carried out and the adsorption mechanism of modified sorbent still needs to be explored. This paper studied the performance of natural and modified calcium-based sorbents for heavy metals for food waste under oxy-fuel combustion in a lab-scale tubular furnace. The effects of furnace temperature, sorbents type, and  $CO_2/O_2$  ratio on adsorption of heavy metals were investigated. The results provide important information for the development of heavy metal sorbents for food waste incineration, and it is of great significance to the development of oxy-fuel combustion and management of MSW oxy-fuel combustion.

## 2. Materials and methods

### 2.1. Materials

Because food waste is a complex heterogeneous mix, the types and concentration of heavy metal in food waste vary from one location to another. The components of food waste used in this paper were leaf vegetable, stem, fruit, rice noodle, bone and shell, and their percentage were 24.5%, 15.0%, 16.0%, 18.0%, 5.2%, 12.8% and 8.5%, respectively. It was typical food waste in Guangdong Province according to Ma et al. (2009), and the oil and other component like plastic bag were excluded. The food waste samples were obtained from canteen in South China University of Technology (SCUT).

Calcium oxide (CaO) and calcium carbonate ( $CaCO_3$ ) were selected as two calcium-based sorbents matrix, and sodium carbonate anhydrous ( $Na_2CO_3$ ) was selected as the modified reagent. CaO and  $Na_2CO_3$  were purchased from Tianjin Fuchen Chemical reagents Factory (Tianjin City, China), and  $CaCO_3$  was purchased from Guangzhou Chemical reagent Factory (Guangzhou City, China). All the chemical reagents are analytical reagent (A.R.) and the total amount of heavy metals is less than 0.005% for CaO, 0.0005% for  $Na_2CO_3$  and 0.001% for  $CaCO_3$ , which make sure no introduction of heavy metals during the experiments.

For modified sorbents, total mass of 50.0 g CaO or  $CaCO_3$  with three different  $Na_2CO_3$  mass ratio of 0%, 10%, and 25% added were added into magnetic stirring apparatus (Tianjin City, China), then 150 ml ultrapure water were also added. The solution was stirring in magnetic stirring apparatus for 4 h. When stirring finished, solid particles were filtered from the solution and dried at 105 °C in the dry oven for 24 h.

All the experimental materials except natural CaO and  $CaCO_3$  were dried at 105 °C in a dry oven until its weight maintained steady. A DFY-300 pulverizer (Wenling Linda Machinery Co. Ltd., Zhejiang Province, China) was used for pulverization process. After pulverization, the food waste was passed through a sieve with a mesh size of 178  $\mu m$ , then dried at 105 °C for 4 h and stored in desiccators. Vario EL-II chons elemental analyzer (Elementar Analysensysteme GmbH, Germany) was used for ultimate analysis. GB/T 28731-2012 criterion and MA260S electronic balance (Shanghai Second Balance Instrument Factory, Shanghai, China) were used for proximate analysis. The weight percentage of C, H, N, S and O for food waste were 40.41%, 5.16%, 3.02%, 0.12% and 32.63%, respectively. And the percentage of O was calculated by difference. For proximate analysis, the volatile matter, fixed carbon and ash of food waste were 67.73%, 13.61%, and 18.66% for air dry basis. All the experiments were conducted twice with a standard deviation less than 3% to ensure the reliability of the experimental results.

### 2.2. Apparatus and methods

#### 2.2.1. Combustion experiments

Mixture of  $CO_2$  and  $O_2$  by volume ratio are used as feed gas to simulate oxy-fuel combustion atmosphere, and the purity of gases are higher than 99.99%. Combustion of samples in all different atmospheres ( $80CO_2/20O_2$ ,  $70CO_2/30O_2$  and  $60CO_2/40O_2$ ) was conducted in a lab-scale tubular furnace, the experiment apparatus was also employed in our previous studies (Ke et al., 2017; Tang et al., 2016; Zheng et al., 2018). Incineration experiments in the tubular furnace with small quantities of synthetic waste, to a certain degree of precision, to simulate the complex processes in the furnace of a MSW incinerator (Wochele and Stucki, 1999). Three different mass fractions of Ca-based sorbents (0%, 5%, and 10%) were added to the food waste sample to study the effects of natural and modified sorbent on capture of heavy metals of food waste. The total flow rate of the feed gas was 1 L/min. For each experiment, when the tubular furnace reached the desired temperature (700 °C, 800 °C or 900 °C), a sample holder was pushed into the central region of tubular furnace which loaded a total weight of  $0.50 \pm 0.001$  g sample. All the samples combusted at desired temperature for 15 min. After 15 min, the sample holder with bottom ash was immediately moved out of the tubular furnace and cooled to room temperature, then the bottom ash was moved into digestion oven for subsequent analysis.

#### 2.2.2. Analysis of heavy metal in ash

Aluminum (Al), Cr and Zn concentrations in the original food waste and combustion ash of food waste combusted with or without sorbents were analyzed. An Inductively Couple Plasma – Optical Emission Spectrometry (ICP-OES, Agilent Technologies Co. Ltd, U.S.A) was used to determine the Al, Cr and Zn concentrations in the bottom ash after microwave digestion. Analytical reagent and ultrapure water were used.

## 3. Results and discussions

### 3.1. Heavy metal volatilization character of food waste without sorbent

Eq. (1) was used to calculate the volatilization rate (VR) of heavy metal:

$$VR = ((C_{fuel} - C_{ash})/C_{fuel}) \times 100\% \quad (1)$$

where  $C_{fuel}$  and  $C_{ash}$  were the contents of heavy metals in the original food waste sample and the ash residue after 15 min combustion, respectively.

The content of Al, Cr and Zn in the combustion ash of food waste combusted in  $80CO_2/20O_2$  atmosphere without sorbent were presented in Fig. 1. The results showed that under different furnace temperature,

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