Inhibitory effects of CaO / Fe₂O₃ on arsenic emission during sewage sludge pyrolysis

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Abstract: This work aimed to investigate effects and reaction mechanisms of CaO / Fe₂O₃ on emission behaviors of arsenic during sewage sludge pyrolysis. The results showed that 24.8~54.2%, 26.4~60.4% and 27.7~63.1% of arsenic escaped from three samples when pyrolysis process happened at 723, 923 and 1123K respectively. And the sludge which contained higher calcium and iron contents released less arsenic than others. External CaO and Fe₂O₃ were added into the sewage sludge to study their effects on arsenic emissions during pyrolysis, where both of them inhibited arsenic emission effectively, especially at high temperatures. With the help of thermogravimetry analysis and X-ray fluorescence, inhibitory mechanisms of CaO / Fe₂O₃ on arsenic emission during sewage sludge

pyrolysis were studied. CaO could react with As_2O_3 , As_2S_3 and NaAsO_2 to form nonvolatile substances, such as $\text{Ca}(\text{AsO}_2)_2$; while Fe_2O_3 could react with NaAsO_2 to generate certain substances which was stable below 1123 K.

Keywords: Arsenic (As); Sewage sludge; Pyrolysis; Calcium oxide (CaO) / Iron oxide (Fe_2O_3); Inhibitory mechanisms

1. Introduction

Sewage sludge is considered as a disturbing problem all over the world (J.Wether;T.Ogada, 1999) even it could be taken as an alternative renewable fuel resource (Fytili & Zabaniotou, 2008). Pyrolysis of sewage sludge attracted lots of attentions of researchers (Liu et al., 2015), because it is one of the most effective and clean ways to recover energy and nutrients from sewage sludge (Fytili & Zabaniotou, 2008; Park et al., 2010; Song et al., 2014) and also the first and fundamental step in gasification, combustion (Hu et al., 2015). However, arsenic concentrated in sewage sludge volatilizes easily (Yao et al., 2004) and usually transforms from organic forms into more toxic inorganic forms (Jomova & Valko, 2011) during the process of pyrolysis, affecting the quality of bio-oil or bio-gas (Leng et al., 2015) , and threatening human health for its carcinogenic characteristics (Ito et al., 2001; Mohan & Pittman, 2007). A deep understanding of the arsenic release behaviors during sewage sludge pyrolysis is essential.

Numerous researchers investigated the arsenic emission characteristics of coals during the thermal treatment, which could help to understand the arsenic emission of sewage sludge during the process of pyrolysis. Various factors, such as temperatures and duration time were reported to influence the devolatilization process, which further affected the arsenic releasing behavior (Guo et al., 2004). Several researchers already found that arsenic emission characteristics during coal combustion or

pyrolysis processes related with reaction temperatures and chemical compositions of materials (Guo et al., 2004; Liu et al., 2009). However, compared with coals, sewage sludge contains more volatile matters, less fixed carbon (Folgueras et al., 2004; Otero et al., 2008; Stelmach & Wasielewski, 2008), and different forms of arsenic (Liu et al., 2009; Stietiya & Wang, 2011), which might lead to diverse arsenic releasing behaviors during pyrolysis.

Calcium and iron were reported to play important roles to inhibit arsenic escaping from coals during thermal treatments (Guo et al., 2004; Lu et al., 2004; Wang & Tomita, 2003). Lu (Lu et al., 2004) found that the arsenic release was suppressed by calcium oxide during coal pyrolysis. And it was observed that the coal which contained more iron and calcium compounds released less arsenic during the thermal conversion process (Guo et al., 2004). To explain the inhibitory phenomena, reaction mechanisms between As and Fe / Ca were explored by some researchers. Jadhav et al. (Jadhav & Fan, 2001) found that CaO could react with arsenic trioxide (As_2O_3) and oxygen (O_2) to generate $\text{Ca}_2\text{As}_2\text{O}_7$ and $\text{Ca}_3\text{As}_2\text{O}_8$. Shen et al. (Shen et al., 2015) maintained that CaO could react with arsenic compounds to form $\text{Ca}(\text{AsO}_2)_2$ above 1273 K by calculation. Zhang et al. (Zhang et al., 2015) believed that As_2O_3 steam could be absorbed by ferric oxide (Fe_2O_3) and transformed to iron arsenate (FeAsO_4). However, most of these experiments were only conducted to investigate the interactions between As_2O_3 and CaO / Fe_2O_3 , and some of above interactions were put forward in oxygen atmosphere. These mechanisms are not enough or appropriate to

describe the inhibitory phenomena of arsenic emission during sewage sludge pyrolysis, because the composition of arsenic-compounds in sewage sludge is so complicated and oxygen is not supposed to be existed during pyrolysis. Not only As_2O_3 , but also As_2S_3 and arsenites were found widely existed in sewage sludge (Caballero et al., 1997; Mahuli et al., 1997), all of which were able to release during the process of pyrolysis. To the best of authors' knowledge, inhibitory mechanisms of arsenic emission based on the reactions of As_2S_3 , arsenites and metal oxides during pyrolysis are still unsatisfied.

To investigate arsenic releasing behaviors, three sewage sludge collected from municipal wastewater treatment plants in Wuhan, China were studied. Releasing characteristics of arsenic in sewage sludge during pyrolysis were analyzed by measuring the arsenic amount in chars prepared at different conditions. In addition, CaO and Fe_2O_3 were added into the sewage sludge to explore the inhibitory effects of extrinsic metal oxides on arsenic emission respectively. Finally, reactions between As_2S_3 / NaAsO_2 with CaO / Fe_2O_3 were studied by a synchronous thermal analyzer (STA) and an X-ray Fluorescence Spectrometer (XRF) to explore possible inhibitory mechanisms of CaO and Fe_2O_3 on arsenic emission.

2. Methods

2.1 Materials

Three types of sewage sludge collected from Tangxunhu, Shahu, and

Longwangzui municipal wastewater treatments in Wuhan, China were labeled as ST, SS and SL. All samples were dried to constant weight at 378 K and pulverized to a size less than 200 μ m for subsequent analysis and experiments. The ultimate / proximate analysis of samples and chemical compositions of ashes derived from sludge were listed in **Table 1** and **Table 2**. And the arsenic concentration of SS, ST and SL were 14.01 ± 0.39 , 14.42 ± 0.33 and 12.26 ± 0.48 mg/kg respectively.

2.2 Pyrolysis of sewage sludge

The pyrolysis experiment was conducted in a horizontal tube furnace with 0.25 ± 0.01 g of sludge sample used in each batch. And 1 L/min pure nitrogen (99.999%) was inlet into the reactor at least for 15 min to guarantee an inert atmosphere before each run. During the pyrolysis process, the samples were moved into the reacting zone from the cooling zone immediately with heating rates at 700~1000 K/s when the target temperature was reached. The sewage sludge were pyrolyzed for 25, 15 and 10 min at 723, 923 and 1123 K respectively until the weight loss rates of all sludge were below 1 % / min. The physical characteristics of chars at 1123 K were determined by a specific surface area analyzer (ASAP 2020M, Micromeritics) to investigate the physical characteristics of chars produced from different samples.

Chars obtained from pyrolysis of ST, SS and SL were named as STC, SSC, SLC, respectively. And the emission ratio of arsenic (R) was defined as

$$R = C_T \times \frac{W_T}{C_0} \times W_0$$

Where C_T and C_0 represent arsenic concentrations of chars produced at T temperature and original sewage sludge respectively, while W_T and W_0 represent the corresponding weight of chars and sludge.

After the pyrolysis of raw sewage sludge, one of the representative samples, ST, was blended with Fe_2O_3 / CaO (Sinopharm Chemical Reagent) with a mass ratio of 4:1 and pyrolyzed at 723, 923, 1123 and 1323 K to explore impacts of metal oxides on the releasing behavior of arsenic. All the tests were conducted for at least three times to ensure the reliability of data.

2.3 Quantification of Arsenic

An 50 ± 0.1 mg of sewage sludge and chars were digested by 10 ml nitric acid (HNO_3) (UP-S pure, Jingrui) and 2 ml hydrofluoric acid (HF) (UP-S pure, Jingrui) at 448 K in a Microwave Digestion System (Sineo Microwave chemistry Technology) according to the EPA Method 3052 (USEPA, 1996). The concentrations of arsenic in samples were measured by an inductively coupled plasma mass spectrometry (ICP-MS) (ELAN DRC-e, PerkinElmer). All the tests were conducted in triplicate.

2.4 Interaction mechanisms between arsenic compounds and metal oxides

In order to investigate the effects of CaO / Fe_2O_3 on As_2S_3 and arsenites emission, analytical pure As_2S_3 / NaAsO_2 (Alfa and Sinopharm Chemical Reagent) was added into CaO / Fe_2O_3 and mixed uniformly in a mortar with a mass ratio 1:3. 10 ± 0.2 mg

pure materials and mixtures were pyrolyzed from ambient temperature to 1373 K at 20 K/min in a STA (STA 8000, PerkinElmer) respectively. Products were then detected by an X-ray Fluorescence Spectrometer (XRF, EDAX Inc.).

Two parameters (α_E, α_C) are introduced, where α_E and α_C respectively represents the measured and calculated weights of mixtures. α_C is defined as the weights of the mixtures when no reactions are assumed to happen between CaO / Fe₂O₃ and As₂S₃ / NaAsO₂:

$$\alpha_C = \alpha_{i,t} \times \mu_i + \alpha_{j,t} \times \mu_j$$

Where μ_i and μ_j represent the weight ratio of As₂S₃/NaAsO₂ and CaO / Fe₂O₃ in mixtures, $\alpha_{i,t}$ and $\alpha_{j,t}$ stand for the weight of these substance thermal treated alone at t time.

3. Results and Discussion

3.1 Arsenic emission characteristics during pyrolysis

Figure 1 gives arsenic emission characteristics during sewage sludge pyrolysis for the three kinds of sludge. 24.8%, 39.5% and 54.2% of arsenic escaped from SL, ST and SS at 723K respectively. And the emission ratio of arsenic accelerated slightly with the temperature increased, which was similar with the arsenic emissions during the coal pyrolysis (Lu et al., 2004). As₂O₅ and organic arsenic compounds would decompose to As₂O₃ (Kakitani et al., 2004) which released easily at a low temperature during the pyrolysis (Cuypers et al., 2009; Helsen et al., 2004). In this study, As₂S₃ whose

melting point is 573 K was also one of the origins that caused arsenic to release at a low temperature. It was noticed that SL released the least arsenic at the same temperature, despite the three samples contained similar amount of arsenic. When the temperature increased from 723 to 1123 K, arsenic emission ratio of SL enhanced only 3%, which was much lower than ST and SS (14% and 10%). These differences must be caused by the diverse physical structures of chars or chemical compounds in sewage sludge (Zeng et al., 2001).

The physical properties of chars at 1123 K were represented in **Table 3**. The BET surface area and pore volume of STC were found to be the largest among the three samples, while the surface areas and pore volumes of SSC and SLC were similar. According to Zeng's study (Zeng et al., 2001), only considering physical characteristics of chars, those chars with more abundant pore structures were expected to release arsenic more easily than chars with poor physical properties during the process of pyrolysis. But this conclusion could not be used to explain the phenomenon that SL released the least arsenic among the three samples. Chemical reactions must play a major role in influencing the arsenic releasing behavior during pyrolysis.

High contents of calcium and iron contents might be one of the reasons that SL released less amount of arsenic than the other two sludge. ST added with CaO or Fe₂O₃, named as ST-CaO or ST-Fe₂O₃ respectively, were pyrolyzed, and arsenic releasing behaviors of these mixtures were investigated during pyrolysis.

3.2 Impacts of CaO and Fe₂O₃ on arsenic emission

The arsenic releasing curves of ST, ST-CaO and ST-Fe₂O₃ are showed in **Fig. 2**. It was observed arsenic emission ratios of ST-CaO (25.5%, 28.3%, 33.3%, 30.4% at 723, 923, 1123 and 1323 K) and ST-Fe₂O₃ (32.1%, 28.4%, 29.3%, 37.1% at 723, 923, 1123 and 1323 K) were much lower than STC (39.5%, 46.4%, 53.3%, 88.1% at 723, 923, 1123 and 1323 K), which indicated that CaO and Fe₂O₃ did have the ability to inhibit arsenic release during pyrolysis. And inhibitory effects of CaO / Fe₂O₃ on arsenic emission were intensified with the increasing temperature, especially at 1323K where CaO and Fe₂O₃ restrained 57.8% and 51.1% arsenic releasing from the sludge respectively. CaO restrained the arsenic releasing more effectively than Fe₂O₃ at 723 K. But when it reached at higher temperatures, CaO did not show more excellent inhibitory effects than Fe₂O₃. According to literatures, sulfur dioxide formed during the pyrolysis of sludge above 973K (Karayildirim et al., 2006) competes with As₂O₃ to react with CaO (Chen et al., 2015) which would obstruct the capture of As₂O₃ by CaO. Different arsenic release behaviors of these two mixtures must be caused by different inhibitory mechanisms between arsenic compounds and CaO / Fe₂O₃.

3.3 Interaction mechanisms between arsenic compounds and metal oxides

To understand these inhibitory mechanisms, As₂S₃ and arsenites (represented by NaAsO₂) which were reported widely existed in sewage sludge (Carbonell-Barrachina et al., 2000; Masayasu, 2007) were put in a simultaneous thermal analyzer and co-pyrolyzed with CaO / Fe₂O₃, and weight losses of them were monitored on line.

The weight loss curves of mixtures (As_2S_3 / NaAsO_2 and CaO / Fe_2O_3) during the pyrolysis are presented in **Fig. 3**. If no chemical reactions occurred between As_2S_3 / NaAsO_2 and CaO / Fe_2O_3 , α_c should be equal to α_E . The experimental data showed that α_c and α_E differed from each other when CaO and As_2S_3 was pyrolyzed together (**Fig. 3a**). α_E remained unchanged until 896 K, where a slight weight loss was observed due to the decomposition of CaCO_3 . Two reactions were supposed to have happened during the pyrolysis of this mixture according to the Gibbs free energy changes of reactions.

From above, it can be concluded that CaO is able to control arsenic emission by reacting with As_2S_3 and As_2O_3 .

Interactions between As_2S_3 and Fe_2O_3 are presented in **Fig. 3b**. The trends of α_c and α_E curves in this picture were similar as **Fig 3a**, but α_E in **Fig. 3b** was much lower than α_c in the temperature range from 723 to 896 K.

By calculation, As_2S_3 firstly react with Fe_2O_3 to form As_2O_3 in low temperature range (equation 3), and then As_2O_3 is solidified by Fe_2O_3 (equation 4). However, the reaction rates of the equation 4 are much lower than equation 2 (When the rate constant of reaction 2 is 1.283×10^{16} , the rate constant of reaction 4 is only 15.54). Instead of reacting with Fe_2O_3 , majority of As_2S_3 escaped from the mixture, leading to nearly the same value of α_E and α_c in the end. It can be concluded that Fe_2O_3 has little ability to inhibit As_2O_3 emission during the process of pyrolysis at low temperature. This could

help explain the phenomenon that ST-CaO exhibited a better performance than ST-Fe₂O₃ to inhibit arsenic emission at 723K.

In **Fig. 3c**, α_E was found to be almost the same with α_C in a relatively low temperature range when CaO and NaAsO₂ was co-pyrolyzed. But as the temperature exceeded 1123 K, α_E remained constant whereas α_C decreased rapidly, suggesting that CaO could also react with NaAsO₂ and control arsenic emission effectively.

It was observed from **Fig. 3d** that there was a huge difference between α_E and α_C above 800K. Obviously, reactions have occurred between Fe₂O₃ and NaAsO₂. α_E remained constant at 90.4% from 960 to 1134K, indicating that some substances were generated. When the temperature increased above 1200 K, α_E started to decrease rapidly again and the value of α_E was nearly equal with α_C at 1373 K, indicating that the substance formed would volatilize or decompose at high temperatures. This was the reason that more arsenic released from STC-Fe₂O₃ at 1323K than 1123 K during sewage sludge pyrolysis.

The XRF results were presented in **Fig. S2**. CaO had the ability to react with As₂S₃, to form thermal stable compounds, which was in accord with the analysis above. Arsenic was also found in the products of NaAsO₂ with CaO at 1073 K and the products of NaAsO₂ and Fe₂O₃ at 973 K, suggesting that CaO and Fe₂O₃ had the ability to restrain arsenic escaping from arsenites at different temperatures.

From above analysis, inhibitory mechanism of CaO / Fe₂O₃ to arsenic emission during pyrolysis was presented in **Fig. 4**. During pyrolysis process (723 to 1323 K), about 39.5% to 88.1% of arsenic compounds evaporated from sewage sludge. CaO / Fe₂O₃ could control arsenic emission by reacting with arsenic compounds during the pyrolysis. Both of Fe₂O₃ and CaO are able to react with As₂S₃ to form As₂O₃.

Comparing to Fe_2O_3 , CaO has better activity with As_2O_3 to form thermal stable compound. Therefore, in this aspect, CaO shows a stronger ability to restrain As_2S_3 release than Fe_2O_3 . On the other hand, NaAsO_2 could interact with CaO / Fe_2O_3 to generate compounds difficult to release below 1123K. Adding CaO / Fe_2O_3 into sewage sludge is a potential method to restrain arsenic migrating into gas or oil during the process of pyrolysis.

Conclusion

24.8~54.2%, 26.4~60.4% and 27.7~63.1% of arsenic escaped from three kinds of sewage sludge when pyrolysis process happened at 723, 923 and 1123K respectively. Both calcium and iron oxides could restrain arsenic release, and their inhibitory effects on arsenic emission were stronger when the reacting temperature increased. CaO could react with As_2O_3 , As_2S_3 and NaAsO_2 to form thermal stable compounds, like $\text{Ca}(\text{AsO}_2)_2$, and Fe_2O_3 had the ability to inhibit NaAsO_2 decomposition by generating certain substances stable below 1123 K. Adding CaO or Fe_2O_3 into sewage sludge is considered to be a potential method to control arsenic emission during sewage sludge pyrolysis.

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Table list

Table 1. Ultimate and proximate analysis of sewage sludge

Table 2. Chemical compositions of ashes (at, %) derived from three kinds of sewage sludge

Table 3. Physical properties of chars at 1123 K

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Figure 1. The emission characteristics of arsenic during sewage sludge pyrolysis

Figure 2. Impact of external Ca/Fe oxides on arsenic releasing characteristics during pyrolysis process

Figure 3. Weight loss of As_2S_3 / NaAsO_2 and CaO / Fe_2O_3 mixtures during pyrolysis

Figure 4. Inhibitory mechanism of CaO / Fe_2O_3 to arsenic emission during pyrolysis

Table 1

Sample	Proximate analysis (wt%, air-dried basis)				Ultimate analysis (wt%, air-dried basis)					
	Moisture	Volatile	Fixed	Ash	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen ^a	C/O
			carbon							
ST	5.64	40.62	5.96	47.78	23.26	3.90	4.23	0.62	14.57	2.13
SS	6.51	48.61	9.36	35.52	18.63	2.57	3.29	0.82	32.66	0.76
SL	2.86	21.09	1.76	74.29	11.17	1.86	1.44	0.23	8.15	1.83

a. Calculated by difference

Table 2

Materials	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	Others
ST	1.29	3.19	10.61	63.76	9.75	1.86	1.84	5.37	1.31	1.02
SS	1.35	3.82	9.56	60.13	7.86	5.28	2.11	6.92	1.98	0.99
SL	1.97	1.91	11.42	69.88	1.8	0.7	1.83	8.19	1.53	0.77

Table 3

Materials	BET surface area / (m^2 / g)	Pore volume / (cm^3 / g)	Pore diameter / (nm)
STC	15.014	0.077	20.36
SSC	8.179	0.045	21.53
SLC	8.971	0.058	25.33

Fig. 1

Fig. 2

Fig. 3

Fig. 4