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Kinetic study of heavy metals Cu and Zn removal during sewage sludge ash calcination in air and N_2 atmospheres

Rundong Li*, Zhenyu Zhai, Yanlong Li, Tianhua Yang, Yang Chen

College of Energy and Environment, Shenyang Aerospace University, The Key Laboratory of Clean Energy in Liaoning Province, Shenyang, China

HIGHLIGHTS

- The in-depth study on the kinetics of heavy metals removal from SSA with $MgCl_2$ was completed.
- Cl-addition is beneficial to remove Cu/Zn during thermo-treatment of SSA to get fertilizer with low heavy metal toxic.
- The reaction activation energy of both Cu and Zn in an air atmosphere was lower than in N_2.
- Sub-step chlorination reduced the reaction requirement of the activation energy.

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ABSTRACT

Heavy metal control is essential during the thermochemical recovery of phosphorus (P) from sewage sludge ash (SSA). For medium volatile heavy metals, i.e. Cu and Zn, the effect of chlorine additive was complicated and more sensitive to temperature variation. So, in the in-depth study on the removal kinetics of Cu and Zn was necessary. Thus, the studies described in this paper considered the experiments and kinetic models of Cu and Zn removal in SSA through calcination under different atmospheres and temperatures. The results showed that within 15 min, the removal of Cu and Zn was more effective at the same temperature in air than in N_2. The result is consistent with kinetic analysis: Reaction activation energy of both Cu and Zn in an air atmosphere is lower than in N_2. In addition, the reaction orders, energy and frequency factors of Cu and Zn removal reaction during SSA calcination at high temperature with air and N_2 atmosphere were calculated.

1. Introduction

It is estimated that approximately 7.91 million tons of dry sewage sludge (SS) are produced annually, and this amount is likely to increase more than 10% annually in China [1–4]. Although most SS is currently landfilled after incineration, this option results in the loss of the valuable phosphate in SS [5,6]. The amount of phosphate rock and the quality of mineral phosphate resources is constantly decreased [7]. Therefore, new methods must be developed because P is an essential element, and the resources of P are not renewable. SSA is a significant potential P-source due to its huge amount and large P content [8]. However, direct application of SS in agriculture as a P-fertilizer cannot be achieved in the presence of organic pollutants and heavy metals [9,10]. Incineration treatment for SS can degrade the organic pollutants completely [11]. However, heavy metals are also enriched in SSA [12].

In order to achieve phosphorus enrichment and removal of heavy metals, Adam et al. 2009, Vogel & Adam, 2011 and Vogel et al. 2013 and others had done a lot of research [6,10,11]. It was found that: For heavy metals that are difficult to volatilize, i.e. Cr and Ni, the effect of chlorine additive was very little; For heavy metals that are easy to volatilize, i.e. Pb and Cd, a little chlorine additive can make heavy metals evaporate almost completely; For medium volatile heavy metals, i.e. Cu and Zn, the effect of chlorine additive was complicated. So, in the in-depth study on the removal kinetics of Cu and Zn was necessary.

Therefore, further research on heavy metal removal, especially kinetic and thermodynamic mechanisms, is required [13]. Investigated a local CFD kinetic model of Cd vaporization during municipal solid waste (MSW) incineration. However, the huge difference between MSW and SSA, especially the high P content in SSA, has significant influence on the kinetics of heavy metal volatilization [14]. The extensive research on kinetics has mainly focused on the

* Corresponding author.
E-mail address: rdlee@163.com (R. Li).

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Table 1
The proximate and ultimate analysis of SS.

Proximate analysis (wt%, as air-dried)				Ultimate analysis (wt %, as air-dried)			
M_{ad}	A_{ad}	FC_{ad}	V_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}
6.35	30.23	7.92	55.50	42.49	6.79	6.63	1.22

kinetics of MSW incineration or SS pyrolysis and seldom on SSA calcination [15]. Thus, an in-depth study on the kinetics of heavy metals removal is conducted during SSA calcination under different technological conditions, including temperature, atmosphere and time. The results provide a theoretical basis for the harmless and highly efficient P-resources recovery in SSA, which has not been researched previously in this related field.

2. Materials and methods

2.1. Materials

SS used in the experiment was taken from a municipal wastewater treatment plant in Dalian City, Liaoning Province, China. The SS used was produced from the A2/O pool and the second pond in the SS dewatering system. The moisture content of the original SS was 79%, the industry analysis result of SS is shown in Table 1 [16]. After drying at 105 °C for 48 h, the dried SS was triturated and sieved with 100 mesh (150 μm) and was burned in a muffle furnace at 850 °C for 2 h with the addition of CaO at a mix ratio of 20:1 SS:CaO. Then, SSA was collected after sieving with 100 mesh. The additives, including CaO and the Cl-donor ($MgCl_2$), were of technical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. (China). The mixture was then homogenized. The heavy metal contents in the SS and SSA samples are given in Table 2, the heavy metals leaching toxicity of SSA is shown in Table 3.

2.2. Experimental apparatus

The samples were thermal-chemically treated in a gastight, lab-scale tube furnace (length: 1100 mm, inner diameter: approximately 75 mm, high-quality aluminous material). A corundum boat was used to hold the well-mixed powder of SSA and additives (SSA weight = 5 g, particle size < 150 μm) and was placed into the tube furnace to calcinate in air (oxidable atmosphere) or N_2 (inert atmosphere) at a rate of 500 ml/min at 950 °C, 1000 °C and 1100 °C. The off-gas was absorbed by combined installation (deionized water, 5% HNO_3 + 10% H_2O_2, 4% $KMnO_4$ + 10% H_2SO_4, silica gel). The chemical composition of the SSA was analyzed by X-ray fluorescence (XRF). The heavy metals in SSA before and after calcination were measured by inductively coupled plasma-atomic emission spectrometry (PerkinElmer Analyst ICP-OES 8300) after total digestion (HNO_3/HCl/HF [17]). Three replications of the whole extraction test were performed for each sample.

2.3. Correlation theory of kinetics

The kinetic study of the SSA calcination is complex because there are more components in SSA, and the removal of heavy metal involves heat transfer, mass transfer and physicochemical reactions. This paper is based on the following assumptions: (i) The mixed system of SSA is transformed into a unitary system, i.e., studying the kinetic model of a single metal removal in thermal treatment without considering the mutual effect of metals in SSA. (ii) Homogeneous SSA system, i.e., the heavy metals in the SSA have a uniform distribution. (iii) Simplify the intermediate reactions, i.e., only the initial concentration of SSA is considered. The transfer percentage between the reactant and product was replaced by the removal efficiency of heavy metals. (iv) The transformation percentage of the reaction (α) was replaced by removal efficiency of heavy metals, i.e.,

$$\alpha = \frac{\varphi_t}{\varphi_{max}} \times 100\% \quad (1)$$

where φ_t is the removal rate of heavy metals at moment t, and φ_{max} is the maximum rate of volatiles.

3. Results and discussion

3.1. Elicitation experiment of the kinetic study

3.1.1. Influence of atmosphere

Fig. 1 shows that the removal of the heavy metals Cu and Zn varies with the atmosphere: 95.6% of Cu and 91.8% of Zn can be removed from phosphorus-enriched sewage sludge ash., and two kinds of metal in nitrogen slightly higher than that of the air, only 5% Cl-addition for Cu is significant higher for N_2. This is similar to the study of Christian Vogel and Christian Adam et al. The addition of a very small amount of chlorine can make the removal of copper and zinc more than 90%. However, the results in Fig. 1 conflict with the stepwise chlorination theory (i.e., the O_2 in the air atmosphere will react with a Cl-donor to form Cl_2 at first, then the formed Cl_2 will

Table 2
Heavy metal contents and standard deviations (averages of five replicates) of the SS (dry) and average SSA samples and chemical compositions of the average SSA samples.

Major composition(SSA)		Heavy metals				
Substance	Mass fraction (%)	Substance	Concentration (ppm)			
			SSA	SD	SS	SD
SiO_2	25.61	Cd	4.1	0.1	3.0	0.1
Al_2O_3	13.53	Pb	104.9	2.0	86.4	2.4
Fe_2O_3	11.99	As	48.5	1.0	51.3	1.8
MgO	5.5	Zn	3830.0	46.2	2277.3	36.2
CaO	17.54	Cu	13160.0	42.5	5248.2	31.4
K_2O	3.81	Cr	2201.6	36.6	935.0	20.4
P_2O_5	16.63	Ni	843.5	20.1	342.5	13.9
SO_3	5.25					

Table 3
The heavy metals leaching toxicity of SSA.

Heavy metals	Cd	Pb	As	Zn	Cu	Cr	Ni
Leaching concentration (mg/L)	0.46	0.08	28.65	466	1074	1203	157
Leaching limit concentration of TCLP (mg/L)	1	5	5	25	15	5	20