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Effects of sulfur on lead partitioning during sludge incineration based on experiments and thermodynamic calculations

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ABSTRACT

Experiments in a tubular furnace reactor and thermodynamic equilibrium calculations were conducted to investigate the impact of sulfur compounds on the migration of lead (Pb) during sludge incineration. Representative samples of typical sludge with and without the addition of sulfur compounds were combusted at 850 °C, and the partitioning of Pb in the solid phase (bottom ash) and gas phase (fly ash and flue gas) was quantified. The results indicate that three types of sulfur compounds (S, Na_2S and Na_2SO_4) added to the sludge could facilitate the volatilization of Pb in the gas phase (fly ash and flue gas) into metal sulfates displacing its sulfides and some of its oxides. The effect of promoting Pb volatilization by adding Na_2SO_4 and Na_2S was superior to that of the addition of S. In bottom ash, different metallic sulfides were found in the forms of lead sulfide, aluminosilicate minerals, and polymetallic-sulfides, which were minimally volatilized. The chemical equilibrium calculations indicated that sulfur stabilizes Pb in the form of $PbSO_4$(s) at low temperatures (<1000 K). The equilibrium calculation prediction also suggested that SiO_2, CaO, TiO_2, and Al_2O_3 containing materials function as condensed phase solids in the temperature range of 800–1100 K as sorbents to stabilize Pb. However, in the presence of sulfur or chlorine or the co-existence of sulfur and chlorine, these sorbents were inactive. The effect of sulfur on Pb partitioning in the sludge incineration process mainly depended on the gas phase reaction, the surface reaction, the volatilization of products, and the concentration of Si, Ca and Al-containing compounds in the sludge. These findings provide useful information for understanding the partitioning behavior of Pb, facilitating the development of strategies to control the volatilization of Pb during sludge incineration.

1. Introduction

Sewage sludge production is increasing rapidly with the development of wastewater treatment facilities (Patryk et al., 2014). In China, the annual discharge of sludge (80% water) is estimated to be more than 20 million tons (Dai et al., 2013). Currently, more than 16 million tons of sludge is abandoned without further treatment, which has caused serious environmental pollution (Duan et al., 2012). Therefore, it is urgent to take effective measures to address sludge in China.

Land filling, agricultural utilization, and incineration are the main disposal methods for sewage sludge (Zhan et al., 2014). Compared with landfill and agricultural utilization, incineration is preferred for volume reduction, destruction of organic pollutants and energy recovery (Samolada and Zabaniotou, 2014). In China, sludge incineration mainly uses the following methods: (1) power generation by the co-combustion of municipal solid waste (MSW) and sludge or co-firing sludge and coal, (2) use raw materials for cement after the sludge is incinerated in a rotary kiln, and (3) performing independent incineration after the sludge is dried, etc. For these methods, co-combustion is the mainstream thermo-chemical treatment because of its low cost. The cost is based on the application of mature MSW equipment and technologies (Hong et al., 2013). However, in the process of sludge–coal or sludge-MSW co-combustion, the complexity and variability of the sludge, the MSW, and the coal for combustion, will result in the emissions of secondary pollutants such as nitrogen oxides, volatilization of heavy metals, and metal–chemical complexes. This is especially true in the presence of chloride and sulfur. Among these pollutants,

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heavy metal emissions cannot be effectively removed by exhaust gas-cleaning devices (Degereji et al., 2013; Lin and Ma, 2012). Furthermore, during waste incineration, the heavy metals in waste cannot be destroyed. They then volatilize during incineration and condense later to form metal compounds and submicron metallic particles as the flue gas is cooled (Meylan and Spoerri, 2014).

Previous studies (Luan et al., 2013; Jiao et al., 2011; Zhang et al., 2008) indicated that the partitioning behavior of heavy metals during waste incineration is influenced by the composition of the gas stream, the incineration temperature, the concentration of metals in the waste, and the concentration of chlorine (Cl), sulfur (S), phosphorus (P), H_2O, and so on. Because both raw sludge and dewatered sludge have high moisture levels and low heating values, adding auxiliary fuel is necessary for independent sludge incineration or the co-combustion of sludge with MSW and coal. In China, the addition of sulfur containing coal is a common practice in the co-combustion of sludge with MSW because of its low cost (Cheng et al., 2007). The effect of chlorides on the transfer of heavy metals has been investigated (Chiang et al., 1997; Han et al., 2008; Li et al., 2010); nevertheless, there have been few reports of experimental studies on the effect of sulfur on heavy metal characteristics during sludge incineration. In fact, knowing which form of sulfur is in the MSW is very complicated because of the usage of sulfur compounds in many industries, such as textiles, pigments, rubber, papermaking, detergents, soaps, among others. Statistical data show that the sulfur concentration in the MSW of 12 cities is approximately 0.09%, whereas in some cities it ranges between 0.18% and 1%, reaching as high as 6% in some MSW or other solid wastes amenable to incineration (Xi et al., 2002; Li et al., 2003; Tan et al., 2007). Furthermore, the sulfur concentrations in 7 types sludge from China have been listed in the literature (Li et al., 2006; Ran et al., 2008; Wang et al., 2007; Deng et al., 2008) and are between 0.17% and 5.63%. During sludge–coal or sludge-MSW co-combustion, the sulfur concentration in the fuel could be more than that in the sludge. Although the concentration of sulfur in the sludge is often lower, it still plays an important role and affects the transformation of heavy metals.

In general, most heavy metals form sulfides or sulfates in the presence of sulfur at temperatures below 700 °C (Chen et al., 1998a,b). The sulfur present in the coal may interact with heavy metals, such as Pb, and affect their emissions during sludge–coal co-combustion. In principle, sulfur can delay heavy metal volatilization when the incineration temperature is below 800 °C (Verhulst et al., 1996). Liu and Sun (2010a, 2010b) and Liu et al. (2012) carried out a theoretical study on heavy metal volatilization. However, a study performed by Hasan and Hermann (2000) indicated that a theoretical study could not precisely predict heavy metal transformations. The computed results were often contrary to experimental results, especially when certain important parameters were ignored. Because co-combustion of sludge with sulfur-containing coal or MSW is commonplace in China, the impact of sulfur compounds on heavy metal partitioning during sludge incineration is an important issue to study.

Lead (Pb) is one of the most heavily regulated heavy metals in the standard for pollution control on the MSW incineration, in which the Pb emission concentration limit is 1.6 mg/m^3 in China under standard state at a concentration of 11% (v/v) O_2, 0.358 mg/m^3 in Germany under standard state at a concentration of 11% (v/v) O_2, 0.1 mg/m^3 in USA under standard state at a concentration of 7% (v/v) O_2, and 0.06 mg/m^3 in Sweden under standard state at a concentration of 10% (v/v) O_2. Recently, the emission and leaching of Pb from ash have received considerable attention (Jiao et al., 2011; Fraissler et al., 2009; Asthana et al., 2010) as part of understanding, through experiments and thermodynamic calculations, how different factors affect heavy metal behavior characteristics. Previous studies (Fraissler et al., 2009; Liu and Sun, 2010a) on the migration and transformation of heavy metals indicate that the thermodynamic equilibrium method is effective.

Due to the limited knowledge on Pb partitioning in sludge incineration, the objective of this study was to experimentally quantify the impact of sulfur on the partitioning of Pb under simulated incineration conditions and to understand its species and removal characteristics using sorbents based on the thermodynamic calculations. Representative samples of the sludge generated in the city of Guangzhou were incinerated in a tubular furnace reactor, which serves as a model of a fixed-bed waste incinerator. The impact of various sulfur compounds on the partitioning of Pb between the solid phase (bottom ash) and the gas phase (fly ash and flue gas) was measured. The results are helpful for better understanding the emission of Pb from the co-combustion of sludge with coal or MSW and developing effective heavy metal control strategies.

2. Materials and methods

2.1. Sample collection and preparation

Dehydrated sludge was collected from a wastewater purification plant in a developmental zone in Guangzhou, Guangdong province, China. Every day, this plant treats 30,000 m^3 of wastewater from both domestic (30%) and industrial (70%) sources and uses conventional waste treatment processes common in most municipal activated sludge systems, including bio-treatment and physicochemical treatment technology. The dehydrated sludge had a moisture content of 80% and a pH of 6.35. The samples were air-dried at room temperature and then ground and homogenized with an agate mortar. The homogenized sludge samples were passed through a sieve with a mesh size of <75 μm and stored in jars at room temperature. Table 1 shows the properties of the dried sewage sludge employed. From Table 1, it can be seen that the volatile matter content was higher than 50%, which made sludge incineration easy. Additionally, the concentrations of S and Cl were 2.55% and 0.21%, respectively, which affects the migration of Pb during sludge incineration.

Table 1
Properties of dried sewage sludge employed.

Proximate analysis (air dry %)	
Moisture	8.73
Ash	31.33
Volatile	56.12
Fixed carbon	3.82
Ultimate analysis (air dry %)	
N	4.48
C	33.73
H	5.25
O	22.98
S	2.55
Cl	0.21
Mineral matters (air dry %)	
SiO_2	28.41
CaO	3.71
Al_2O_3	4.14
MgO	0.25
Fe_2O_3	2.19
K_2O	1.36
Trace metal (mg kg^{-1})	
Pb	81.20
Ni	220.8
Mn	1844
Cr	191.4
Cu	5845
Zn	987.0
Cd	3.26