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Influence of sulfur on the fate of heavy metals during clinkerization

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HIGHLIGHTS

- Clarifying effects of S on the volatilization of Cu, Pb and Cd during clinkerization.
- S decreased the volatilization temperature of Cu, Pb and Cd.
- S increased the solidification ability of clinker to Pb and Cd at 1450 °C.
- S was concentrated in interstitial phases of the clinkers.
- Cu, Pb and Cd were mainly solidified in interstitial phases forming solid solutions.

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ABSTRACT

The fate of heavy metals during clinkerization is of crucial significance to the solid waste utilization, environmental management, and sustainable development. This paper presents a laboratory scale simulation that aims to investigate the effects of sulfur on the fate of Cu, Pb, and Cd during clinkerization. The sulfur-bearing phases ($CaSO_4 \cdot 2H_2O$ and CaS) and metal oxides were mixed with cement raw meal in appropriate ratios to produce clinkers. The volatilization and solidification of Cu, Pb and Cd were investigated using atomic absorption spectrometry, thermogravimetric analysis, X-ray diffraction analyses, electron probe X-ray microanalysis, and scanning electron microscopy. The volatilization of Cu slightly increased in the temperature range 950 °C–1450 °C with addition of sulfur. Sulfur promotes the volatilization of Pb and Cd at the temperature from 950 °C to 1250 °C by decreasing the melting point of PbO and CdO. Sulfur increased the solidification ability of clinker decreasing the volatilization ratio of Pb and Cd at the temperature of 1350–1450 °C and 1450 °C, respectively. Both forms of sulfur ($CaSO_4 \cdot 2H_2O$ and CaS) have similar effect on the Cu/Pb/Cd volatilization. Sulfur concentrated in interstitial phases of the clinkers mainly as $Ca_4Al_6O_{12}SO_4$ and $CaSO_4$. Cu, Pb and Cd were mainly solidified within interstitial phases of the clinkers forming solid solutions with the variable compositions. Cu was also present in alite and belite and as crystalline phases of Ca_2CuO_3 and $CaCu_2O_3$ in the clinkers. This research can help to improve understanding of the fate of heavy metals and provide a guideline for risk assessment during the co-processing of solid wastes in cement kiln.

1. Introduction

Due to the rapid development of modern industry and city, significant amount of solid wastes (SW) are being produced every day, for instance, 3.28 billion tons of industrial SW, 173 million tons of municipal solid waste (MSW) and 25 million tons of sludge were produced in China in 2016 [1]. About 77% of the solid wastes were transported to the landfills and waste incineration facilities [2]. However, solid wastes can be considered as secondary raw fuels and/or materials in the cement industry, for example, in co-processing of solid wastes in the cement kiln [3–6]. By the implementation of co-processing, the natural resources can be saved and carbon dioxide emissions can be reduced [7–10]. Nevertheless, most of the solid wastes contain heavy metals that could be volatilized and move with flue gas into the atmosphere during clinkerization, polluting the environment and threatening human health [11–13]. Therefore, it is important to study the volatilization of

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heavy metals during co-processing of solid wastes in the cement kiln.

The previous studies carried on heavy metal emissions from solid wastes co-processing indicated that the fate of heavy metals strongly depended on the waste composition, particularly on the content of chlorine and sulfur in the solid wastes and cement raw meal [14,15]. The content of sulfur in the cement kiln is about 0.5 wt%–2.0 wt%, that mainly come from raw fuels (e.g., coal) and materials (e.g., limestone containing sulfide minerals) combustion [16]. The content of sulfur in the cement kiln might increase due to co-processing of solid wastes with high content of sulfur. Therefore, the detailed investigation of the effect of sulfur on the fate of heavy metals in co-processing of solid wastes in the cement kiln are required. Chan et al. [17], Smith [18], and Nowak et al. [19,20] focused on the effect of sulfur (such as Na_2SO_4 and K_2SO_4) on the volatilization of heavy metals during the burning of solid wastes. However, the temperatures investigated were relatively low (<1200 °C) comparing to the Portland cement clinker production (T = 1450 °C). Moreover, cations from the sulfates such as Na^+ and K^+ might influence on the clinkering process, volatilization and solidification of heavy metals [21,22].

Heavy metals like Cu, Pb, and Cd commonly exist in the solid wastes such as Pb-Zn slag, residues from MSW incineration facilities and sewage sludge [23–25]. Heavy metals might volatilize and move with flue gas into the atmosphere. Pb and Cd are easy to volatilize during the thermal treatment process of solid wastes [17,20,26,27]. CuO is known to act as flux and/or mineralizer in the clinkerization because it decreases the melting temperature considerably and favours the combination of free lime [20,28].

In this research, the effects of sulfur on the fate of Cu, Pb, and Cd was emphasized and the binary system of clinker-heavy metal in the study of co-processing of SW in cement kiln was developed to ternary system of clinker-heavy metal-sulfur, which is more coincident with the condition of co-processing of SW in cement kiln. Two sources of sulfur as gypsum ($CaSO_4·2H_2O$) and calcium sulfide (CaS) were used in our experiments. The relationships among sulfur sources, volatilization and solidification of Cu/Pb/Cd, and mineral phases of clinker were investigated. This paper can help to improve understanding of the fate of heavy metals in presence of sulfur and provide a guideline for risk assessment during the utilization of solid wastes in cement kiln.

2. Materials and method

2.1. Materials

Cement raw materials such as $CaCO_3$, SiO_2, Al_2O_3, and Fe_2O_3, were supplied by pure chemical reagent in order to eliminate the effects of impurity ions such as Na^+, K^+, and Cl^- in the industrial

Table 1
The formulated mixtures with Cu, Pb, Cd, and sulfur (wt%).

ID.	Cu	Pb	Cd	$CaSO_4·2H_2O$/CaS (S: wt%)
S_{Cu-S-0}	2.0	0	0	0
$S_{Cu-CaSO4-0.5}$/$S_{Cu-CaS-0.5}$	2.0	0	0	0.5
$S_{Cu-CaSO4-1.0}$/$S_{Cu-CaS-1.0}$	2.0	0	0	1.0
$S_{Cu-CaSO4-1.5}$/$S_{Cu-CaS-1.5}$	2.0	0	0	1.5
$S_{Cu-CaSO4-2.0}$/$S_{Cu-CaS-2.0}$	2.0	0	0	2.0
S_{Pb-S-0}	0	2.0	0	0
$S_{Pb-CaSO4-0.5}$/$S_{Pb-CaS-0.5}$	0	2.0	0	0.5
$S_{Pb-CaSO4-1.0}$/$S_{Pb-CaS-1.0}$	0	2.0	0	1.0
$S_{Pb-CaSO4-1.5}$/$S_{Pb-CaS-1.5}$	0	2.0	0	1.5
$S_{Pb-CaSO4-2.0}$/$S_{Pb-CaS-2.0}$	0	2.0	0	2.0
S_{Cd-S-0}	0	0	2.0	0
$S_{Cd-CaSO4-0.5}$/$S_{Cd-CaS-0.5}$	0	0	2.0	0.5
$S_{Cd-CaSO4-1.0}$/$S_{Cd-CaS-1.0}$	0	0	2.0	1.0
$S_{Cd-CaSO4-1.5}$/$S_{Cd-CaS-1.5}$	0	0	2.0	1.5
$S_{Cd-CaSO4-2.0}$/$S_{Cd-CaS-2.0}$	0	0	2.0	2.0

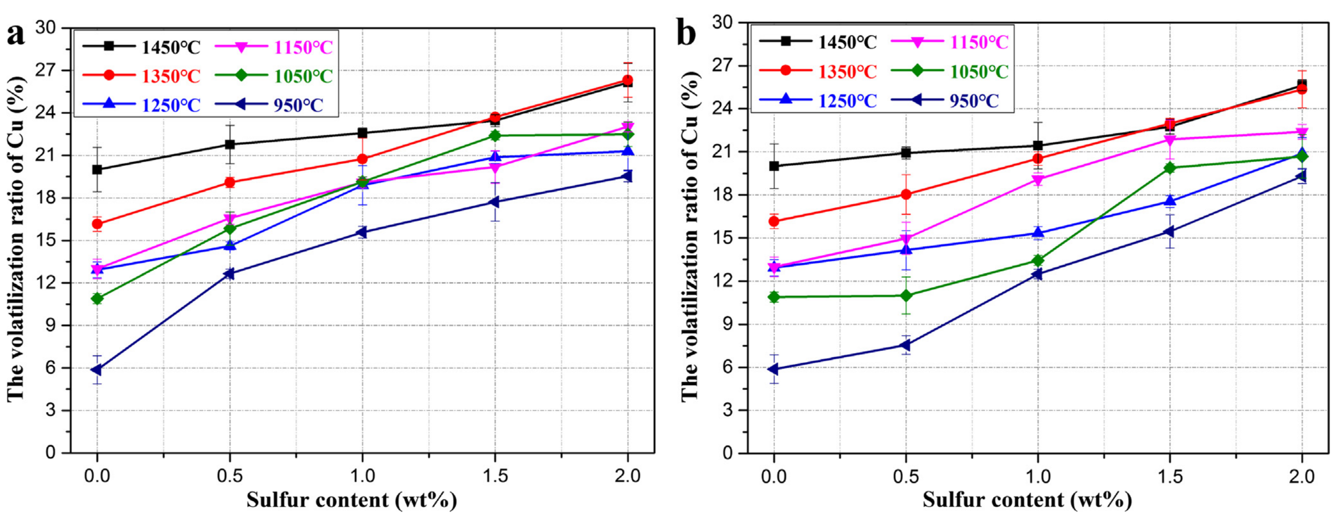

Fig. 1. Volatilization of Cu with sulfur addition: a) $CaSO_4·2H_2O$; b) CaS.