Influence of sulfur on the fate of heavy metals during clinkerization

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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

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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℃ - 1450℃ with addition of sulfur. Sulfur promotes the volatilization of Pb and Cd at the temperature from 950℃ to 1250℃ 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℃ and 1450℃, 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.

Keywords: clinker, heavy metals, sulfur, volatilization, solidification, element speciation

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 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.% to 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℃) 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 ($CaSO_4 \cdot 2H_2O$) 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 raw materials. Cu, Pb, and Cd were added to the raw mixes as CuO, PbO and CdO, respectively. S was added in two different species as sulfate (gypsum - $CaSO_4 \cdot 2H_2O$) and sulfide (CaS).

2.2. Experimental procedure

The phase composition of cement clinkers was controlled by Bogue method (see Eq. (1) – (3)) [28]. Lime saturation ratio (KH), silica ratio (SM), and alumina ratio (IM) were designed as 0.9, 2.5, and 1.6, respectively. The theoretical mineral composition was calculated to be 56% of alite (C_3S), 20% of belite (C_2S), 8.6% of aluminate (C_3A), and 10% of ferrite (C_4AF). Cement raw meals with 2.0 wt.% of Cu, Pb, or Cd were prepared and sulfur concentration was varied (0.5 wt.%, 1.0 wt.%, 1.5 wt.%, and 2.0 wt.%). Table 1 lists the formulated mixtures.

$$Lime\ saturation\ ratio\ (KH) = \frac{CaO - 1.65Al_2O_3 - 0.35Fe_2O_3}{2.8SiO_2} \tag{1}$$

$$Silica\ ratio\ (SM) = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \tag{2}$$

$$Alumina\ ratio\ (IM) = \frac{Al_2O_3}{Fe_2O_3} \tag{3}$$

Table 1

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

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

The formulated mixtures were thoroughly blended and homogenized in a mechanical planetary mixer. Then each mixture was mixed with 8% of absolute ethanol and pelletized into Ø10×50 mm cylindrical bar under 40 MPa. Each pellet was calcined from room temperature to the designated temperature at a heating rate of 10 ℃/min. When the furnace reached designated temperature, it was maintained for 45 min and then the clinkers were cooled quickly in air to the room temperature [28].

2.3. Analytical methods

The clinkers were grounded into fine powder. The clinker samples were dissolved using an acid mixture of hydrogen peroxide (H_2O_2), aqua regia, and hydrogen fluoride (HF) in a volume ratio of 2:5:2 in a microwave digestion system (ZEROM, China). The concentrations of Cu, Pb and Cd in the solutions were analyzed by flame atomic absorption spectrometry (AAS, Analytik Jena AG, Germany). The duplicate measurements were carried out, and the average values were used to calculate the volatilization percentage according to Eq. (4):

$$H = \left\{1 - \frac{K}{S/(1 - LOI)}\right\} \times 100\% \tag{4}$$

Where, H is the volatilization ratio of Cu, Pb or Cd; K (mg/kg) is the content of Cu, Pb or Cd in the clinker; S (mg/kg) is the content of Cu, Pb or Cd in raw materials; and LOI represents the loss on ignition.

The distribution of Cu, Pb and Cd in the clinker phases was investigated on the polished sections by electron probe micro-analysis (EPMA-1600, Shimadzu, Japan). The measurement was conducted with an acceleration voltage of 15.0 kV and an electron beam diameter of 1μm. The morphology of the clinkers and element analyses were investigated by scanning electron microscopy (SEM, EVO 18, Carl Zeiss, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instrument INCAx-sigth EDS-system). SEM/EDS analyses were performed with a 20 kV accelerating voltage.

Thermogravimetric analysis (TG) was used to investigate the influence of sulfur on the volatilization temperature of heavy metals. TG curves were obtained using a NETZSCH STA 449F3 instrument. TG analysis was conducted using about 20 mg of sample (chemical reagent) in alumina pans with an air purge gas flow rate of 100 mL/min, equilibration at 30°C for 10-15 min, followed by a heating rate of 10°C/min from 30°C to 1250℃ (for $CaSO_4 \cdot 2H_2O$ - up to 1400℃).

The mineralogical compositions of the samples were determined by X-ray diffraction analysis (Bruker D8). This diffractometer is equipped with Cu Kα (λ=1.5406 Å, 40 kV and 40 mA). All patterns were scanned over the range $5° < 2\theta < 70°$ using a step size of 0.02° and a count time of 0.2 s.

Selective dissolution method was used to separate silicate and interstitial phases of the clinkers [29].

3. Results and discussion

3.1. Effect of sulfur and temperature on the volatilization of Cu, Pb, and Cd

Figure 1 to 3 show the results obtained for Cu, Pb, and Cd volatilization with the addition of $CaSO_4·2H_2O$ and CaS at different temperatures. Without addition of sulfur, the volatilization ratio of Cu (Figure 1) increased from 6.0% to 20% with increasing the temperature from 950℃ to 1450℃. However, the Cu volatilization slightly increased (~ 10%) with increasing sulfur content.

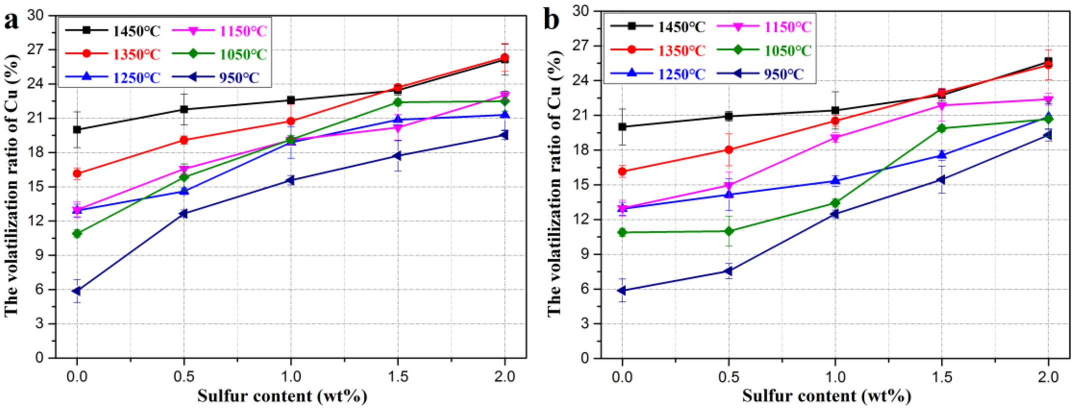


Fig. 1. Volatilization of Cu with sulfur addition: a) $CaSO_4·2H_2O$; b) CaS.

Figure 2 shows that the volatilization ratio of Pb increased from 13.4% to 86.2% with increasing the temperature from 950℃ to 1450℃ without sulfur addition. The volatilization ratio of Pb slightly increased (~ 15%) with increasing $CaSO_4·2H_2O$ content at the temperature of 950℃, 1050℃, 1150℃ and 1250℃. However, when the temperature is higher than 1250℃, the volatilization ratio of Pb decreased with increasing amount of $CaSO_4 \cdot 2H_2O$. The significant decrease of Pb volatilization was observed at 1350℃(20.2%) and 1450℃(33.4%) with the addition of 2.0 wt.% of sulfur comparing to the reference sample.

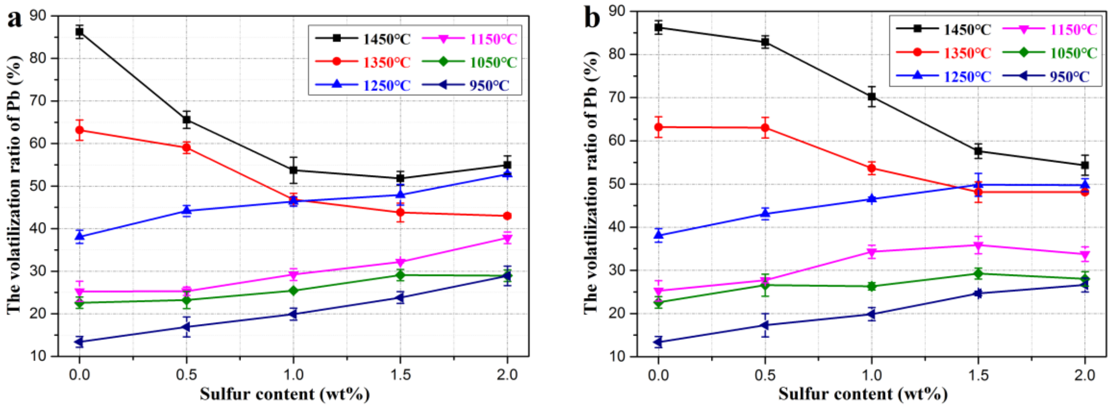


Fig. 2. Volatilization of Pb with sulfur addition: a) $CaSO_4 \cdot 2H_2O$; b) CaS.

The volatilization ratio of Cd increased from 23.9% to 59.4% with increasing the temperature from 950℃ to 1450℃ without sulfur addition (Figure 3). The volatilization ratio of Cd increased slightly (~ 12%) with increasing $CaSO_4 \cdot 2H_2O$ content at the temperature of 950℃, 1050℃, 1150℃, 1250℃ and 1350℃. However, at the temperature of 1450℃, the volatilization ratio of Cd decreased by 21.9%, with the addition of 2.0 wt.% of sulfur, compared the reference sample.

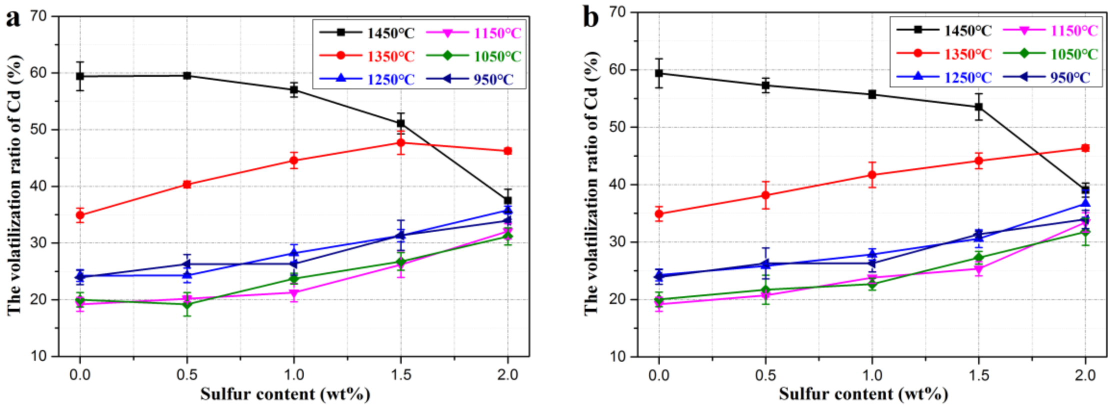


Fig. 3. Volatilization of Cd with sulfur addition: a) $CaSO_4 \cdot 2H_2O$; b) CaS.

Heavy metals were classified as volatile (Pb and Cd), semi-volatile (Zn, Sb, and Se), and non-volatile (Cr, Cu, Ni, As, Mn, and Co) elements [30]. Also, the melting and boiling temperatures of CuO (1026℃ and 2000℃) are higher than that of PbO (888℃ and 1535℃) and CdO (900℃ and 1385℃), respectively. Therefore, Pb and Cd should have a higher volatilization ratio than Cu during clinkerization that was observed in our investigation. Sulfur in cement raw meal act as flux/mineralizer lowering the temperature of the liquid phase formation, increase the amount of the melt, and decrease the viscosity and the surface tension of the melt [31, 32]. Lowering the surface tension and the viscosity of the melt, normally formed at above 1338°C (an invariant point; [33]), can increase the diffusivity of the clinkering species (including Pb-bearing and Cd-bearing species) and therefore promote the solidification of Pb and Cd. According to Taylor [28, 34], Herfort et al. [35] and Wang et al. [36], sulfur dissolved in the melt can affect the acid-base equilibrium $[MeO_4]^{5-} \leftrightarrow [MeO_6]^{9-}$ of the amphoteric elements (Me: Al^{3+} and Fe^{3+}). The displacement of this reaction to the left favors the formation of a network built from $[MeO_4]^{5-}$ and silicon tetrahedra that leads to the increase of the melt viscosity, while $[MeO_6]^{9-}$ is more mobile and promotes the decrease of the viscosity surface tension of the melt. These effects will promote the reaction among mineral phases and heavy metals. The more sulfur addition, the greater transformation degree of $[MeO_4]^{5-}$ to $[MeO_6]^{9-}$, and then the greater effect of sulfur on the volatilization/solidification of Pb and Cd will be observed. Therefore, the mineral phases of clinker might solidify more Pb and Cd, and their volatilization ratio decreased when the temperature is higher than 1350℃. CuO is hard to volatilize and might act as as flux/mineralizer itself. Therefore, the effect of sulfur on the Cu volatilization is not obvious.

Before the appearance of liquid phase during clinkerization (the temperature is lower than 1338℃), the effects of sulfur on the volatilization of heavy metals were caused by decreasing the volatilization temperature of heavy metals, that will be confirmed in Section 3.2.

It can be seen from Figure 1 (b) to Figure 3 (b) that the effect of CaS on the volatilization of Cu, Pb, and Cd is similar to that of $CaSO_4 \cdot 2H_2O$. The reason is that CaS might be oxidized to $CaSO_4$ at the temperature around 700℃ [37, 38]. The chemical reactions (1) - (5) might occur during the process of oxidation. However, the equation (1) is the main oxidation reaction due to the lowest Gibbs free energy under 700℃ (Figure 4) [37, 38]. During the preparation of clinker, most of CaS was oxidized to $CaSO_4$ around 700℃ and the mineral phases formation of clinker is higher than 1000℃. Besides, CaS is not reacting with heavy meal below the temperature of 700℃. Namely, the mechanism of the effects of CaS on the volatilization and solidification of Cu/Pb/Cd is the same as $CaSO_4$.

$$CaS + 2O_2(g) = CaSO_4 \tag{1}$$

$$CaS + 3CaSO_4 = 4CaO + 4SO_2(g) \tag{2}$$

$$CaS + 3/2O_2(g) = CaO + SO_2(g) \tag{3}$$

$$CaO + 2SO_2 + 1/2O_2(g) = CaSO_4 \tag{4}$$

$$CaS + 2SO_2 = CaSO_4 + 2S \tag{5}$$

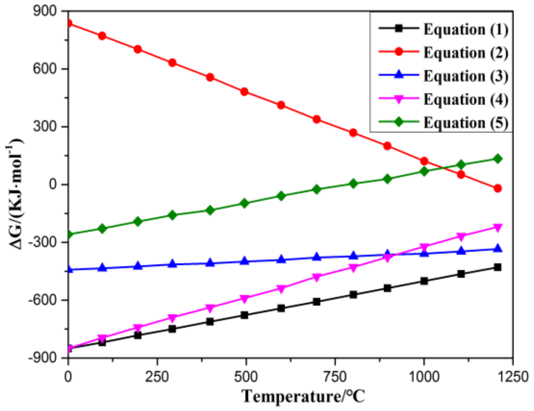


Fig. 4. Relationship between standard Gibbs free energy and temperatures of the equations (1) - (5) [37, 38].

3.2. Effects of sulfur on the volatilization temperatures of Cu, Pb, and Cd

The results from thermogravimetric analysis are shown in Figure 5. The TG curves of gypsum showed the mass losses in the temperature range from around 150°C to 700°C due to dehydration of that mineral. Gypsum start decomposing at 1200°C. Cu, Pb, and Cd start volatilizing at 1015°C, 940°C, and 1070°C, respectively. The addition of corresponding content of sulfur leads to decrease the volatilization temperatures of Cu, Pb, and Cd by 40°C, 65°C, and 35°C, respectively. Therefore, the sulfur has a positive effect on the volatilization of Cu, Pb, and Cd at the temperatures <1250°C, that confirmed the results in Section 3.1. $CaSO_4\cdot 2H_2O$ dehydrated at the temperature around 150°C and 700°C forming $CaSO_4$ and the most of CaS was oxidized to $CaSO_4$ around 700°C. $CaSO_4$ can act as mineralizer/flux changing the thermodynamic stability of CuO/PbO/CdO and, therefore, lowering their volatilization temperature.

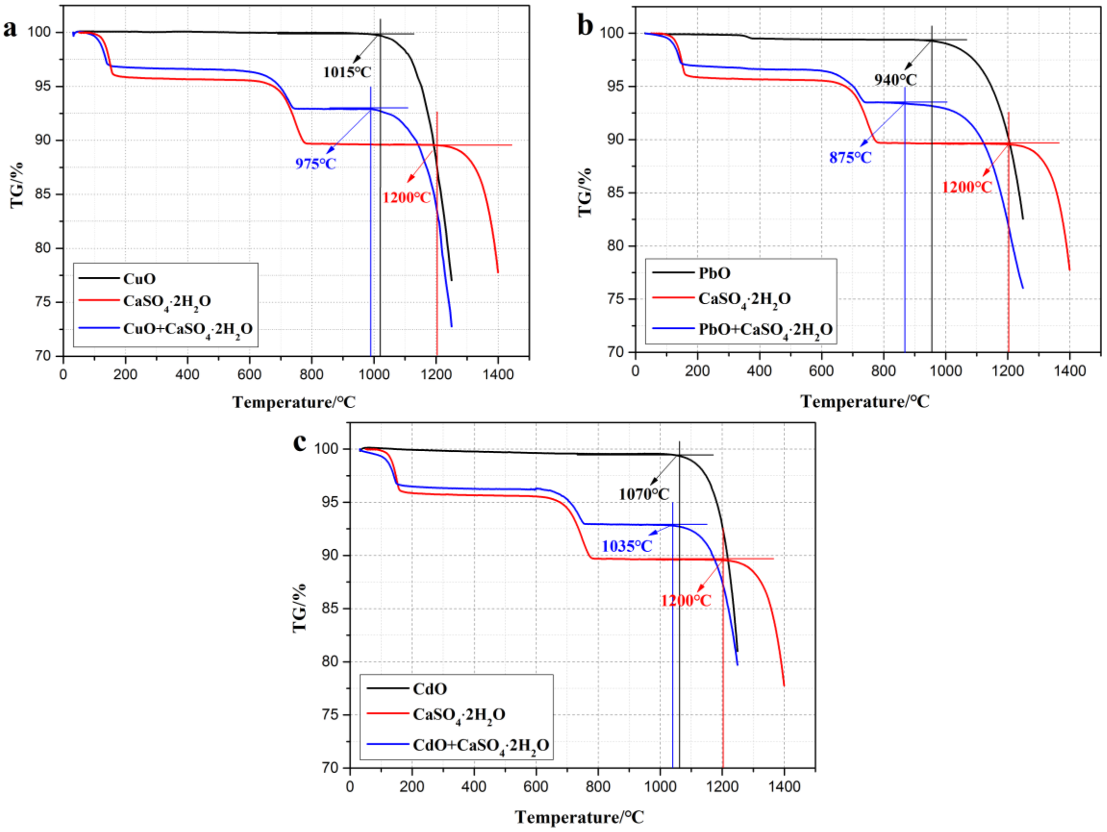


Fig. 5. TG curves of CuO, PbO, or CdO with/without $CaSO_4·2H_2O$: a) CuO with/without $CaSO_4·2H_2O$; b) PbO with/without $CaSO_4·2H_2O$; c) Cd with/without $CaSO_4·2H_2O$.

3.3. Sulfur speciation in clinker

The XRD patterns of $S_{Cu\text{-}CaSO4\text{-}2.0}$, $S_{Pb\text{-}CaSO4\text{-}2.0}$, and $S_{Cd\text{-}CaSO4\text{-}2.0}$ samples sintered at 1450℃ and their corresponding silicate and interstitial phases based on the selective dissolution method are shown in Figures 6-8. $CaSO_4$ (mainly for the S additions 1.5-2.0 wt.%) and $Ca_4Al_6O_{12}SO_4$, formed during clinkering process, were concentrated in the interstitial phases of the clinker. The content of C_3A and C_4AF in the clinker decreased but sulfoaluminate ($Ca_4Al_6O_{12}SO_4$) increased with increasing addition of sulfur. It was reported by Zhao [39] and Ma [40] that the calcium sulphoaluminate

($Ca_4Al_4O_{12}SO_4$) was formed between the temperature of 1300℃ and 1350℃ in the system of $CaCO_3$-SiO_2-Al_2O_3-Fe_2O_3-$CaSO_4$. When the temperature is higher than 1350℃, $Ca_4Al_4O_{12}SO_4$ start to decompose to C_3A and $CaSO_4$. Therefore, the main speciation of sulfur in clinker were $CaSO_4$ and $Ca_4Al_4O_{12}SO_4$. Besides, the formation of $Ca_4Al_4O_{12}SO_4$ consumed some Al, which result in the decreased content of C_3A and C_4AF.

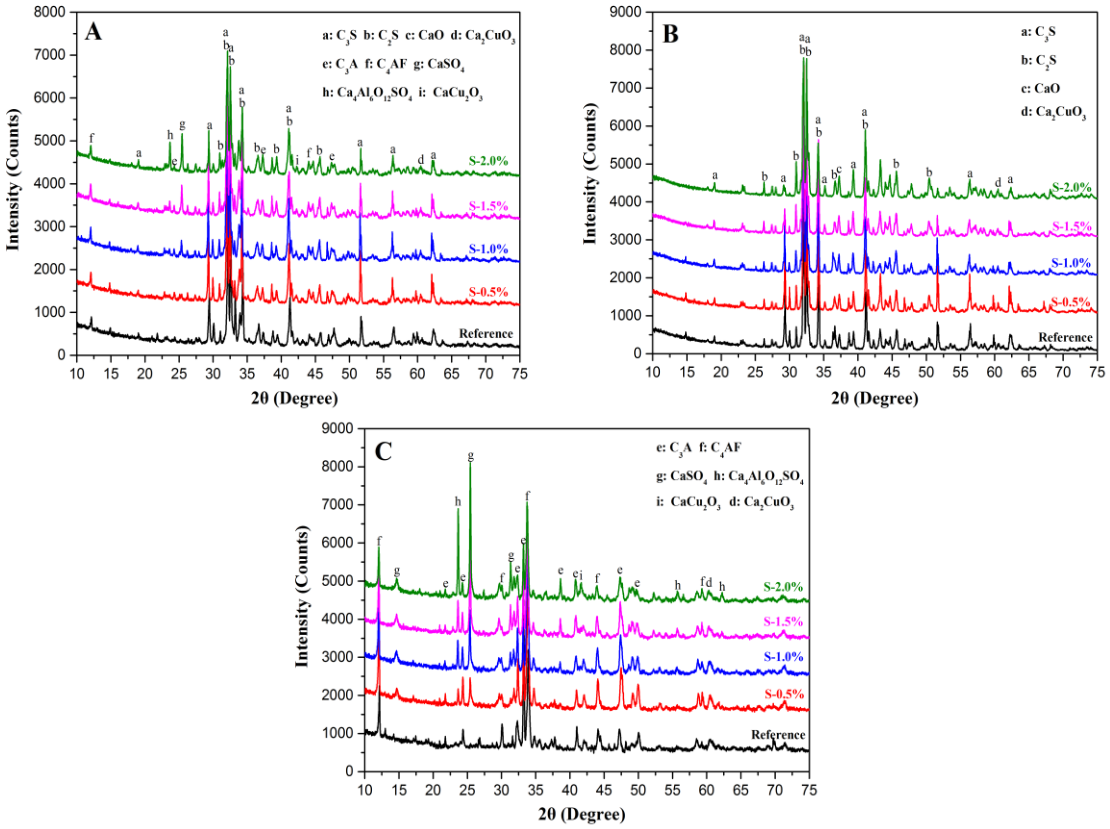


Fig. 6. XRD patterns of $S_{Cu\text{-}CaSO4\text{-}2.0}$ sample sintered at 1450℃: A) Clinker; B) Silicate phase; C) Interstitial phase.

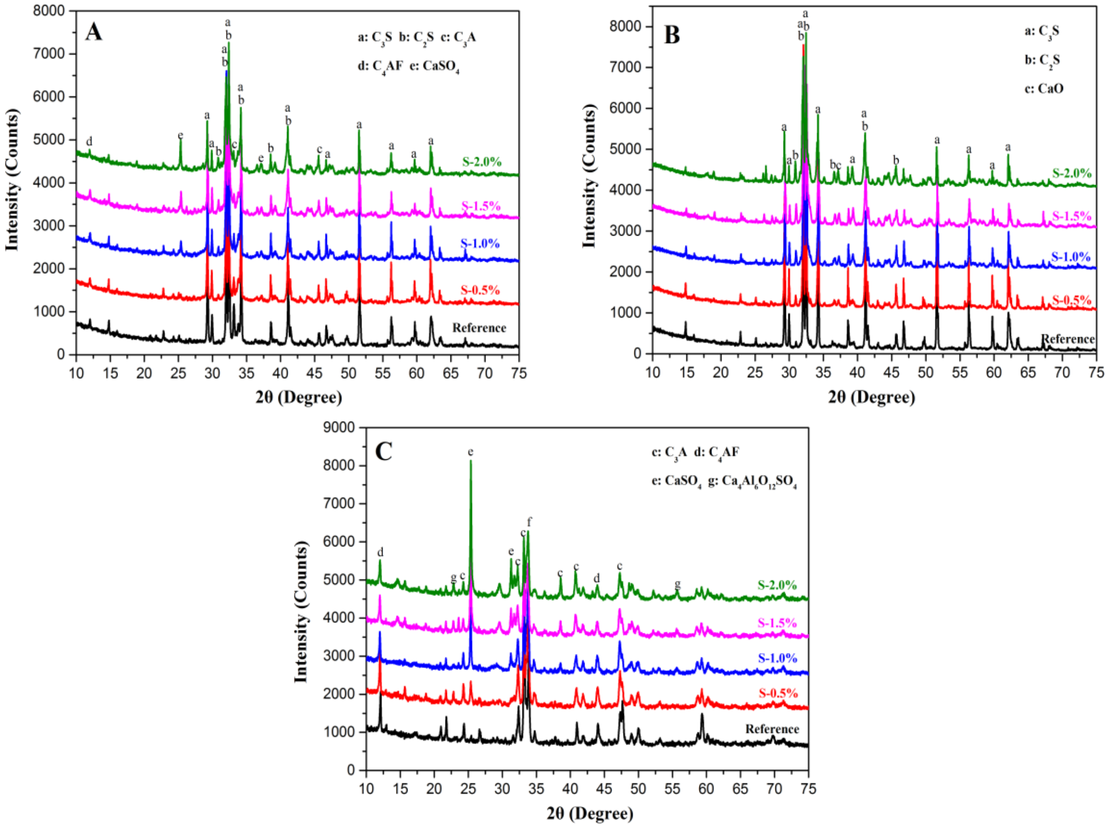
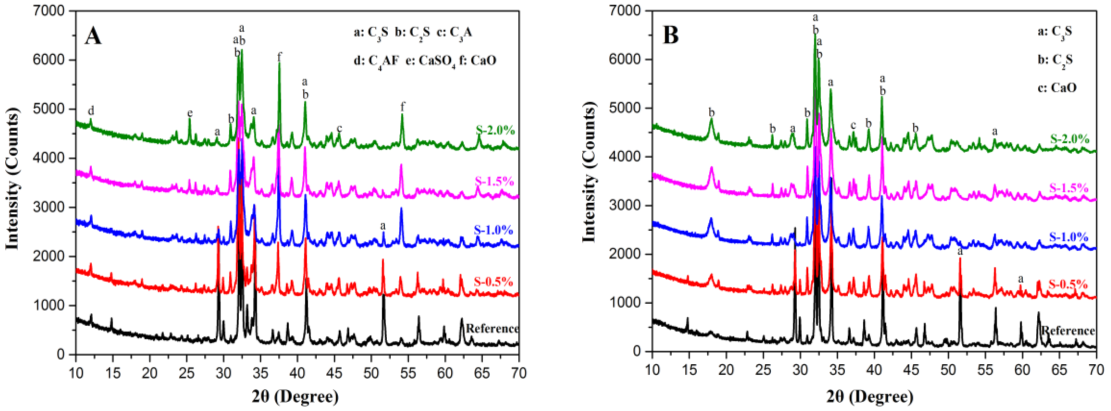


Fig. 7. XRD patterns of $S_{Pb\text{-}CaSO4\text{-}2.0}$ sample sintered at 1450℃: A) Clinker; B) Silicate phase; C) Interstitial phase.



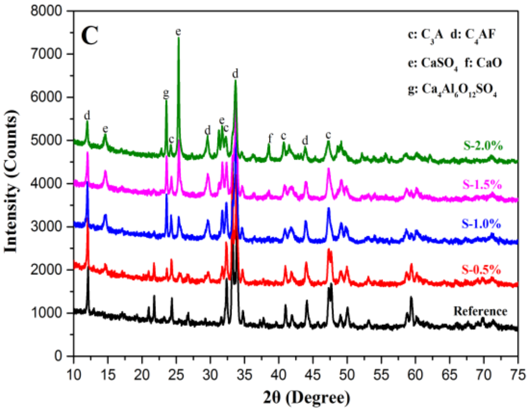
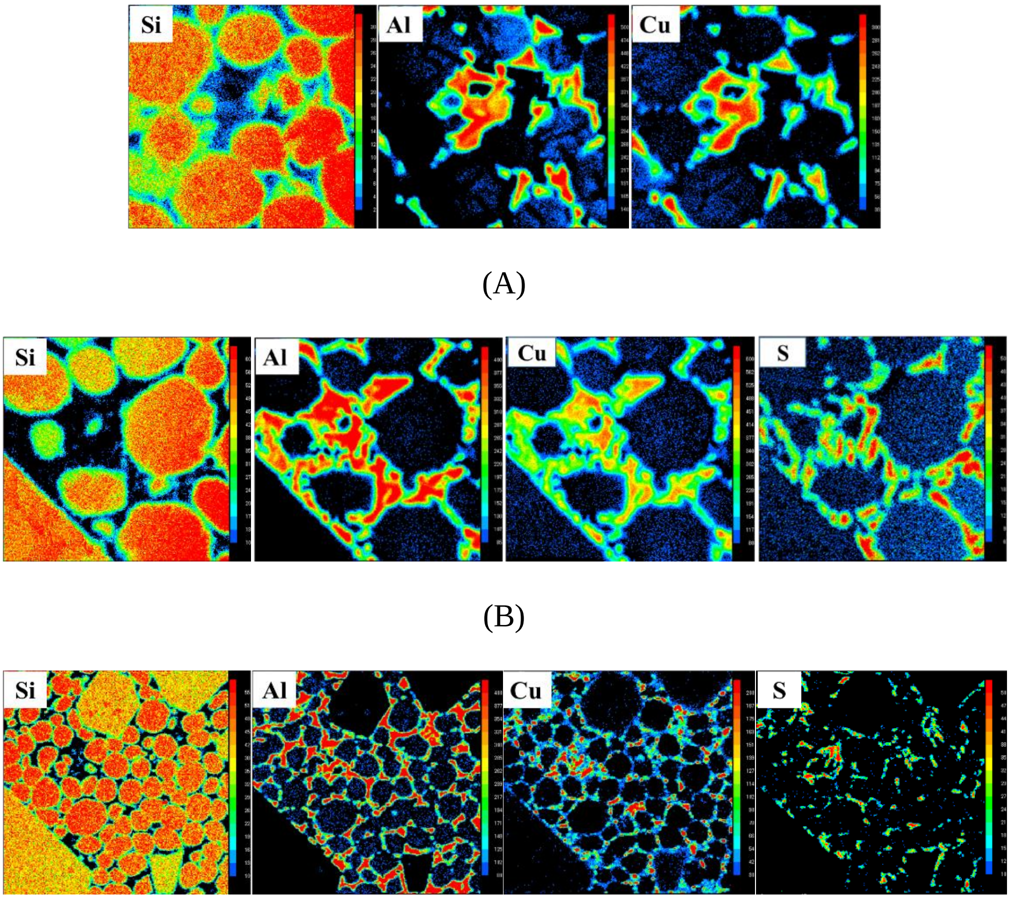


Fig. 8. XRD patterns of $S_{Cd\text{-}CaSO4\text{-}2.0}$ sample sintered at 1450℃: A) Clinker; B) Silicate phase; C) Interstitial phase.

3.4. Distribution of elements in the clinkers

3.4.1. EPMA analysis

The distribution of Si, Al, Cu, Pb, Cd and S in the clinkers are shown in Figures 9-11. Clinker consists of silicate phases (C_3S and C_2S) and interstitial phases (C_3A and C_4AF). It can be seen that the distributions of Cu, Pb, and Cd associated with Al in the clinkers. Therefore, Cu, Pb, and Cd were mainly solidified in interstitial phases of the clinker. The Cu, Pb, and Cd distributions in the clinker phases were not changed after the $CaSO_4{\cdot}2H_2O$ and CaS addition. According to the results from Section 3.3, interstitial phases mainly consist of C_3A, C_4AF and $Ca_4Al_4O_{12}SO_4$ with the addition of 2.0 wt.% of S. During clinkerization, the interstitial phases gradually become liquid phase with temperature increasing. The addition of $CaSO_4{\cdot}2H_2O$ and CaS increased the amount of the melt and decreased viscosity and surface tension of the melt, accelerating migration of heavy metals in the liquid phase, promoting ion substitution and formation of solid solutions with heavy metals, and possibly the formation of new phases. The substitution of Cu^{2+}, Pb^{2+}, and Cd^{2+} for Al^{3+} or Fe^{3+} in C_4AF and Al^{3+} in C_3A is possible. Also, formation of different solid solution by isomorphous replacement of Al^{3+} or Fe^{3+} (Al^{3+} - ionic radius 0.39-0.54 and electronegativity 1.61; Fe^{3+} - 0.63-0.92 and 1.83) by Cu^{2+} (0.57-0.73 and 1.65), Pb^{2+} (0.98-1.49 and 2.0), and Cd^{2+} (0.78-1.31 and 1.93) is probable.

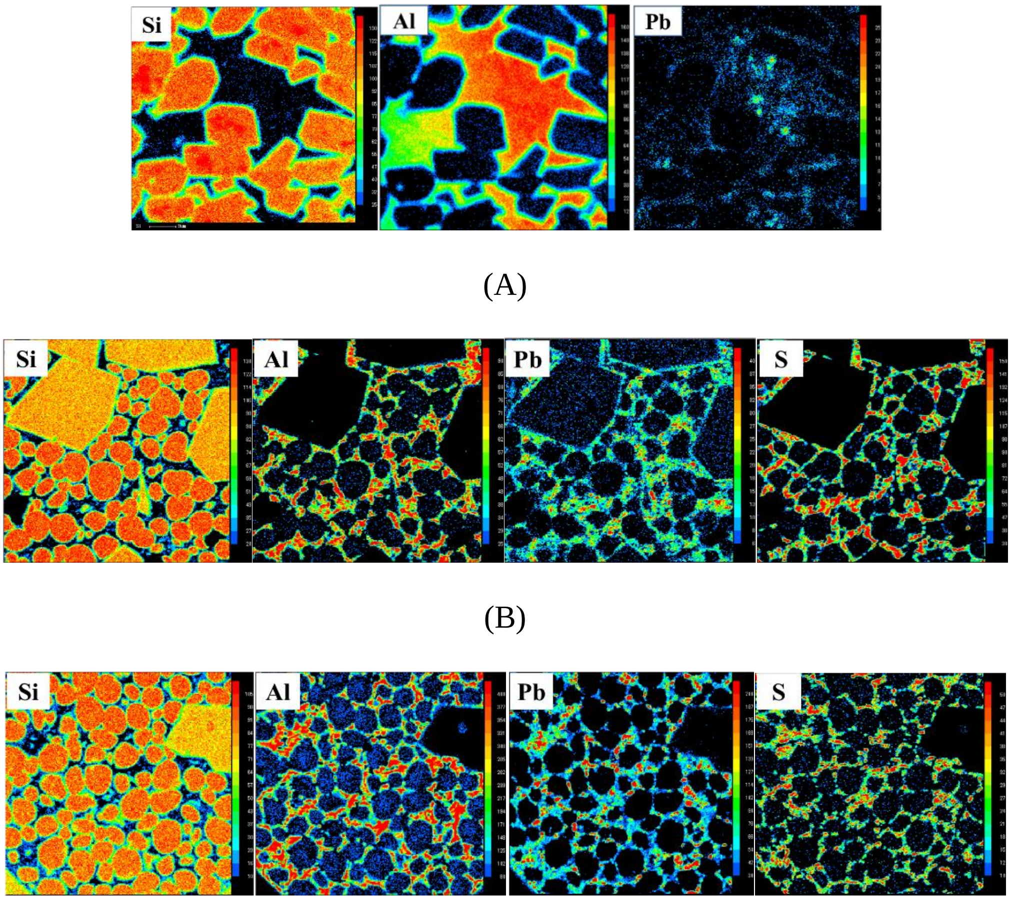


(A)

(B)

(C)

Fig. 9. An EPMA maps of the Si, Al, Cu, and S distributions in the clinkers: A) S_{Cu-S-0}; B) $S_{Cu-CaSO4-2.0}$; C) $S_{Cu-CaS-2.0}$.

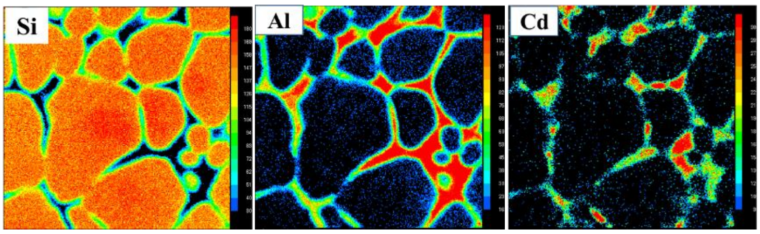


(A)

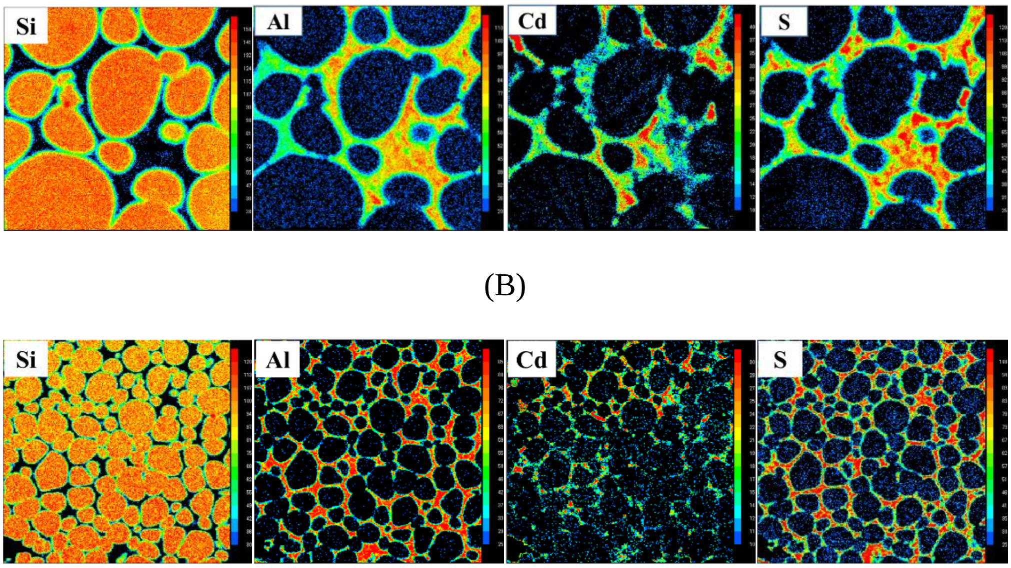
(B)

(C)

Fig. 10. An EPMA maps of the Si, Al, Pb, and S distributions in the clinkers: A) $S_{Pb\text{-}S\text{-}0}$; B) $S_{Pb\text{-}CaSO4\text{-}2.0}$; C) $S_{Pb\text{-}CaS\text{-}2.0}$.



(A)



(B)

(C)

Fig. 11. An EPMA maps of the Si, Al, Cd, and S distributions in the clinkers: A) S_{Cd-S-0}; B) $S_{Cd-CaSO4-2.0}$; C) $S_{Cd-CaS-2.0}$.

3.4.2. SEM/EDS analysis

The point chemical analysis of the polished clinker samples sintered at 1450℃ was carried out to quantitatively investigate the content of Cu, Pb, and Cd in silicate and interstitial phases. About fifty spot-analyses were performed for each sample. The results are listed in Table 2. For the sample of S_{Cu-S-0}, the content of Cu is about 0.40 wt.% and 4.53 wt.% in silicate phases and interstitial phases, respectively. The addition of 2 wt.% sulfur as $CaSO_4{\cdot}2H_2O$ and CaS had no effect on the solidification of Cu. In the sample S_{Pb-S-0}, the content of Pb is about 1.98 wt.% in interstitial phases and cannot be detected in silicate phases. However, the Pb content is about 1.10 wt.% in silicate phases and 3.65 wt.% in interstitial phases with the addition of 2 wt.% of sulfur as $CaSO_4{\cdot}2H_2O$ and CaS. About 0.26 wt.% and 2.1 wt.% of Cd were solidified in silicate phases and interstitial phases of $S_{Cd\text{-}S\text{-}0}$ sample, respectively. With the addition of $CaSO_4{\cdot}2H_2O$ and CaS, the solidified content of Cd in silicate and interstitial phases increased in about 35% and 18%, comparing to the $S_{Cd\text{-}S\text{-}0}$ sample. The results above confirmed the discussion in Section 3.1 and 3.4.1. For silicate phases of C_2S and C_3S, during clinkerization, the C_3S is formed by the combination of C_2S and free lime in the liquid phase. C_3S cannot massive formation before liquid phase appears. According to the discussion presented above, the addition of sulfur promoted the migration of heavy metals in the liquid phase, that intensified the ion substitution in C_3S and C_2S. Therefore, the incorporation content of Pb and Cd in silicate phases increased with the addition of $CaSO_4{\cdot}2H_2O$ and CaS. The mineralizing effects of $CaSO_4{\cdot}2H_2O$ and CaS for the samples added with Cu is not obvious due to good mineralizing effect.

Table 2

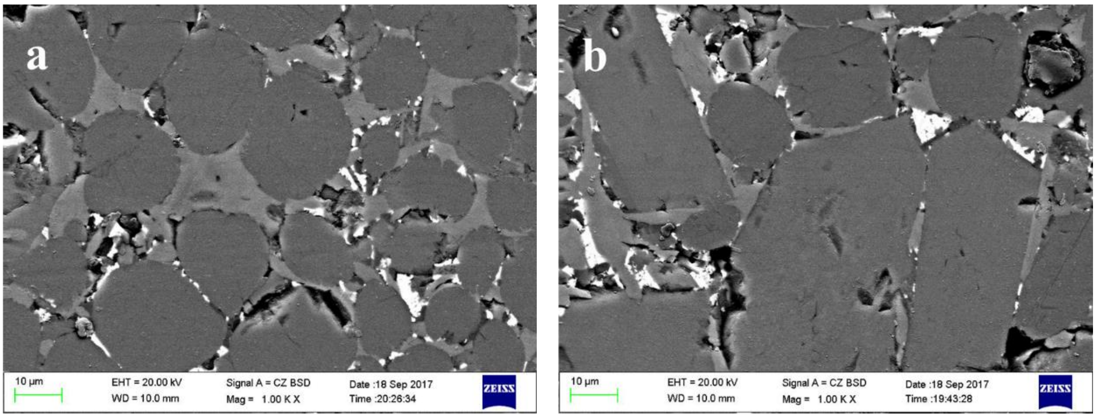
The average content of heavy metals in silicate and interstitial phases of clinker samples sintered at 1450℃(wt. %).

ID.	Heavy metals in silicate phase			Heavy metals in interstitial phase		
	Cu	Pb	Cd	Cu	Pb	Cd
$S_{Cu\text{-}S\text{-}0}$	0.40±0.13			4.53±0.26		
$S_{Cu\text{-}CaSO4\text{-}2.0}$	0.37±0.10			4.49±0.41		
$S_{Cu\text{-}CaS\text{-}2.0}$	0.38±0.12			4.28±0.35		
$S_{Pb\text{-}S\text{-}0.0}$		-			1.98±0.29	
$S_{Pb\text{-}CaSO4\text{-}2.0}$		1.10±0.18			3.68±0.38	
$S_{Pb\text{-}CaS\text{-}2.0}$		1.07±0.15			3.61±0.41	
$S_{Cd\text{-}S\text{-}0.0}$			0.26±0.09			2.05±0.28
$S_{Cd\text{-}CaSO4\text{-}2.0}$			0.35±0.11			2.42±0.32
$S_{Cd\text{-}CaS\text{-}2.0}$			0.33±0.13			2.40±0.29

Note: -, undetected; ±, standard deviation.

3.5. Effects of sulfur on the chemical forms of Cu, Pb, and Cd

According to Herfort et al. [31], at low concentration, heavy metals enter into the structure of the initial phases of the clinker (C_3S, C_2S, C_3A and C_4AF) and form different phase assemblages of solid solutions. When the content of heavy metals increases, the presence of new phases might be observed. For example, the formation of Ca_2CuO_3 and $CaCu_2O_3$ were identified by XRD in the clinkers. The scanning electron microscopy images (backscattered electron imaging detector) of the clinker samples sintered at 1450℃ (Figure 12) show that new phases were formed in the samples with the addition of $CaSO_4{\cdot}2H_2O$. From the discussion in Section 3.4, sulfur promote Cu, Pb, and Cd solidification within interstitial phases forming solid solutions. During that process, the formed solid solutions not only contained heavy metals, but also contained S, that transformed the existence forms of heavy metals in the clinker. The variable compositions of the solid solutions in the interstitial phases were shown in Table 3.



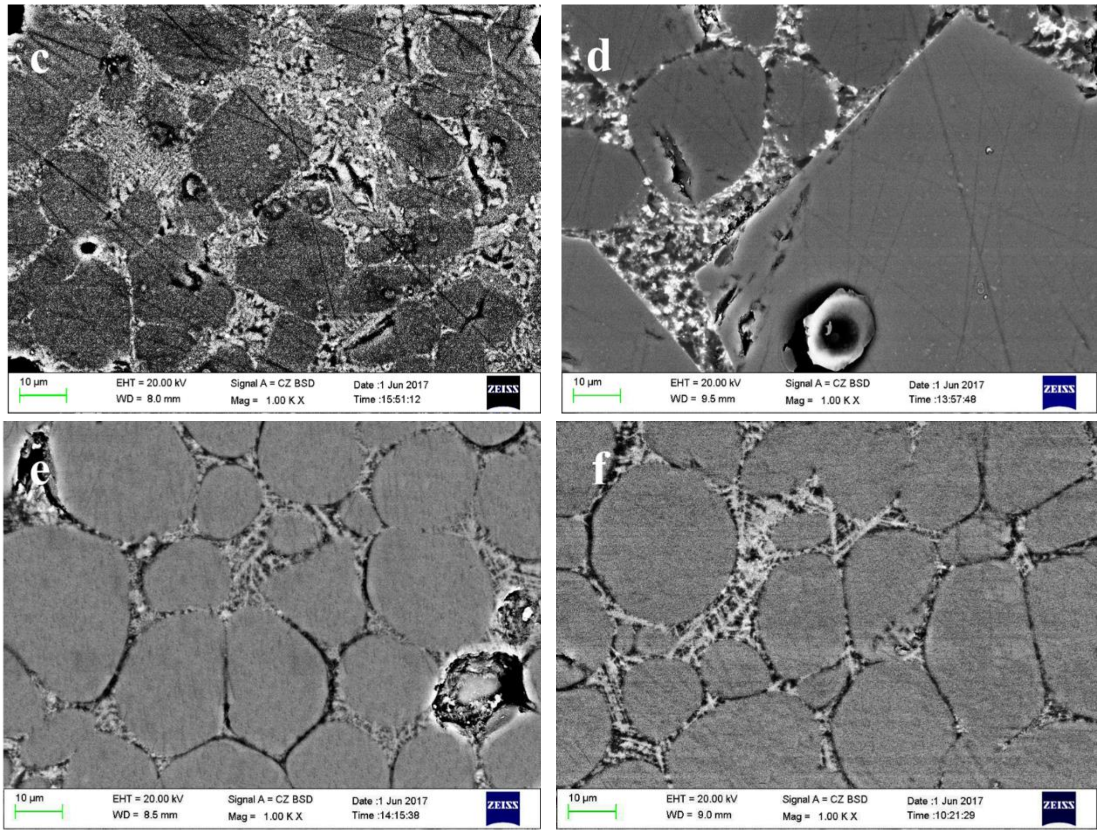


Fig. 12. Scanning electron microscopy images with backscattered electron imaging of the mineral phases: a) $S_{Cu\text{-}S\text{-}0}$; b) $S_{Cu\text{-}CaSO4\text{-}2.0}$; c) $S_{Pb\text{-}S\text{-}0}$; d) $S_{Pb\text{-}CaSO4\text{-}2.0}$; e) $S_{Cd\text{-}S\text{-}0}$; f) $S_{Cd\text{-}CaSO4\text{-}2.0}$.

Table 3

Clinker phase composition based on SEM/EDS analysis (wt.%) and empirical formula of solid solution.

Cu-S-2%	O	Al	Si	S	Ca	Fe	Cu	Formula composition
Interstitial phase	38.6	3.8	10.1	5.6	35.8	4.1	2.1	$Ca_{1.85}Fe_{0.15}Cu_{0.07}Al_{0.29}Si_{0.75}S_{0.36}O_{5.00}$
Interstitial phase	38.5	3.4	3.2	10.3	37.9	4.7	2.0	$Ca_{1.96}Fe_{0.17}Cu_{0.06}Al_{0.26}Si_{0.24}S_{0.67}O_{5.00}$
Interstitial phase	35.5	8.6	6.7	0.29	39.8	6.1	2.9	$Ca_{2.24}Fe_{0.25}Cu_{0.10}Al_{0.72}Si_{0.54}S_{0.02}O_{5.00}$
Interstitial phase	40.7	2.0	6.4	10.8	37.9	1.7	0.58	$Ca_{1.86}Fe_{0.06}Cu_{0.02}Al_{0.14}Si_{0.45}S_{0.66}O_{5.00}$
Interstitial phase	37.9	6.8	5.1	4.4	36.8	6.6	2.5	$Ca_{1.94}Fe_{0.25}Cu_{0.08}Al_{0.53}Si_{0.38}S_{0.29}O_{5.00}$
Interstitial phase	37.8	5.9	2.9	7.8	36.4	6.0	3.2	$Ca_{1.92}Fe_{0.23}Cu_{0.11}Al_{0.46}Si_{0.22}S_{0.51}O_{5.00}$
Interstitial phase	41.8	4.1	1.1	15.1	32.9	2.1	3.0	$Ca_{1.57}Fe_{0.07}Cu_{0.09}Al_{0.29}Si_{0.07}S_{0.90}O_{5.00}$
Interstitial phase	37.1	8.8	1.8	4.9	32.9	11.6	3.1	$Ca_{1.77}Fe_{0.45}Cu_{0.10}Al_{0.70}Si_{0.14}S_{0.70}O_{5.00}$
Interstitial phase	40.9	4.7	0.84	12.7	33.7	5.3	2.0	$Ca_{1.65}Fe_{0.18}Cu_{0.06}Al_{0.34}Si_{0.06}S_{0.77}O_{5.00}$

Interstitial phase	41.6	3.2	0.49	16.2	31.3	1.9	5.4	$\mathrm{Ca_{1.51}Fe_{0.06}Cu_{0.16}Al_{0.22}Si_{0.03}S_{0.97}O_{5.00}}$
Interstitial phase	46.3	1.4	0.47	20.5	29.2	1.5	0.69	$\mathrm{Ca_{1.26}Fe_{0.05}Cu_{0.02}Al_{0.09}Si_{0.03}S_{1.1}O_{5.00}}$
Cu-S-0%	O	Al	Si	S	Ca	Fe	Cu	Formula composition
Interstitial phase	31.3	8.3	2.7		35.9	18.0	3.8	$\mathrm{Ca_{2.29}Fe_{0.83}Cu_{0.15}Al_{0.78}Si_{0.25}O_{5.00}}$
Interstitial phase	31.7	11.9	0.95		34.8	17.8	2.8	$\mathrm{Ca_{2.19}Fe_{0.80}Cu_{0.11}Al_{1.11}Si_{0.09}O_{5.00}}$
Cd-S-2%	O	Al	Si	S	Ca	Fe	Cd	Formula composition
Interstitial phase	37.1	5.2	6.9	4.4	39.8	5.1	1.5	$\mathrm{Ca_{2.14}Fe_{0.20}Cd_{0.03}Al_{0.41}Si_{0.53}S_{0.30}O_{5.00}}$
Interstitial phase	34.7	11.1	2.4	0.65	37.3	13.1	0.79	$\mathrm{Ca_{2.14}Fe_{0.54}Cd_{0.02}Al_{0.95}Si_{0.20}S_{0.05}O_{5.00}}$
Interstitial phase	32.9	11.8	2.4		39.8	12.4	0.80	$\mathrm{Ca_{2.42}Fe_{0.54}Cd_{0.02}Al_{1.06}Si_{0.21}O_{5.00}}$
Cd-S-0%	O	Al	Si	S	Ca	Fe	Cd	Formula composition
Interstitial phase	33.1	8.1	7.4		40.5	10.5	0.43	$\mathrm{Ca_{2.45}Fe_{0.46}Cd_{0.01}Al_{0.72}Si_{0.64}O_{5.00}}$
Interstitial phase	34.0	8.0	8.4		40.6	7.8	1.3	$\mathrm{Ca_{2.38}Fe_{0.33}Cd_{0.03}Al_{0.69}Si_{0.70}O_{5.00}}$
Pb-S-2%	O	Al	Si	S	Ca	Fe	Pb	Formula composition
Interstitial phase	27.4	9.7	2.0		31.3	10.1	19.6	$\mathrm{Ca_{2.28}Fe_{0.53}Pb_{0.28}Al_{1.05}Si_{0.20}O_{5.00}}$
Interstitial phase	31.3	10.0	2.4	2.7	40.1	10.1	3.4	$\mathrm{Ca_{2.56}Fe_{0.46}Pb_{0.04}Al_{0.94}Si_{0.22}S_{0.22}O_{5.00}}$
Interstitial phase	34.3	7.4	2.0	4.5	34.6	8.1	9.1	$\mathrm{Ca_{2.01}Fe_{0.34}Pb_{0.10}Al_{0.64}Si_{0.17}S_{0.33}O_{5.00}}$
Pb-S-0%	O	Al	Si	S	Ca	Fe	Pb	Formula composition
Interstitial phase	30.7	14.7	1.2		35.3	11.9	6.2	$\mathrm{Ca_{2.29}Fe_{0.56}Pb_{0.08}Al_{1.42}Si_{0.11}O_{5.00}}$
Interstitial phase	29.2	15.1	2.4		41.2	10.8	1.3	$\mathrm{Ca_{2.82}Fe_{0.53}Pb_{0.02}Al_{1.53}Si_{0.23}O_{5.00}}$
Interstitial phase	29.8	14.3	2.2		39.7	13.1	0.84	$\mathrm{Ca_{2.66}Fe_{0.63}Pb_{0.01}Al_{1.43}Si_{0.21}O_{5.00}}$
Interstitial phase	31.0	13.2	3.5		42.2	9.5	0.54	$\mathrm{Ca_{2.71}Fe_{0.44}Pb_{0.01}Al_{1.26}Si_{0.32}O_{5.00}}$
Interstitial phase	31.0	13.3	3.27		38.5	12.2	1.8	$\mathrm{Ca_{2.47}Fe_{0.56}Pb_{0.02}Al_{1.27}Si_{0.30}O_{5.00}}$

4. Conclusions

The effects of sulfur on the fate of Cu, Pb, and Cd during clinkerization were discussed in this work. The main conclusions can be summarized as follow:

- Sulfur promotes the volatilization of Pb and Cd at the temperature from 950℃ to 1250℃ by decreasing the melting point of PbO and CdO. The volatilization ratio of Cu increased due to its volatilization temperature decreased with sulfur addition at the temperature from 950℃ to 1450℃. Sulfur decreased the volatilization temperature of CuO, PbO, and CdO for about 40℃, 65℃, and 35℃, respectively. Sulfur acts as a mineralizer/flux changing the thermodynamic stability of CuO/PbO/CdO and, therefore, lowering their volatilization temperature. Sulfur increased the solidification ability of clinker decreasing the volatilization ratio of Pb and Cd at the temperature of 1350-1450℃ and 1450℃, 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 found to form solid solutions with the variable compositions within interstitial phases of the clinkers. Besides, crystalline phases of Ca_2CuO_3 and $CaCu_2O_3$ were identified in the clinkers.

However, the effect of sulfur on the volatilization of Cu, Pb, and Cd might be different, if those metals present together in the system (e.g., solid wastes) due to their possible competitive effects. Therefore, further investigation of the element fate during clinkerization in multi-elemental system is required.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC, No. 5141101056) and Guangdong science and Technology Department (2014B020216002).

References

[1] China Environmental State Bulletin: 2016.

[2] China Annual Report of Comprehensive Utilization of Resources: 2015.

[3] S. Bozkurt, L. Moreno, I. Neretnieks, Long term processes in waste deposits, Sci.

Total Environ. 250 (2000) 101–121.

[4] M.J. Quina, E. Bontempi, A. Bogush, S. Schlumberger, G. Weibel, R. Braga, V. Funari, J. Hyks, E. Rasmussen, J. Lederer, Technologies for the management of MSW incineration ashes from gas cleaning: new perspectives on recovery of secondary raw materials and circular economy, Sci. Total Environ. 635 (2018) 526–542.

[5] P. Xue, A. Xu, D. He, Q. Yang, G. Liu, Fredrik Engstrom, Bo Bjorkman, Research on the sintering process and characteristics of belite sulphoaluminate cement produced by BOF slag, Constr. Build. Mater. 122 (2016) 567–576.

[6] P.E. Tsakiridis, M. Samouhos, M. Perraki, Valorization of Dried Olive Pomace as an alternative fuel resource in cement clinkerization, Constr. Build. Mater. 153 (2017) 202–210.

[7] M. Huang, X. Ying, D. Shen, H. Feng, N. Li, Y. Zhou, Y. Long, Evaluation of oil sludge as an alternative fuel in the production of Portland cement clinker, Constr. Build. Mater. 152 (2017) 226–231.

[8] B. Das, S. Prakash, P.S.R. Reddy, V.N. Misra, An overview of utilization of slag and sludge from steel industries, Resour. Conserv. Recy. 50 (2007) 40–57.

[9] D. Yan, K.H. Karstensen, Q. Huang, Q. Wang, M. Cai, Coprocessing of industrial and hazardous wastes in cement kilns: A review of current status and future needs in China, Environ. Eng. Sci. 27 (2010) 37–45.

[10] N. A. Madlool, R. Saidur, M.S. Hossain, N.A. Rahim, A Critical review on energy use and savings in the cement industries, Renew. Sust. Energ. Rev. 15 (2011) 20–42.

[11] R.K. Gupta, D. Majumdar, J.V. Trivedi, A.D. Bhanarkar, Particulate matter and

elemental emissions from a cement kiln, Fuel Process. Technol. 104 (2012) 343-351.

[12] B. Cristina, G. Gisela, A. Sofia, P. Pedro, M. Cristina, C. Otilia, Biomonitoring spatial and temporal impact of atmospheric dust from a cement industry, Environ. Pollut. 151 (2008) 292–299.

[13] P. Ch. Hsiau, S.L. Lo, Extractabilities of heavy metals in chemically-fixed sewage sludges, J. Hazard. Mater. 58 (1998) 73–82.

[14] A.P. Ghorpade, M.G. Ha, W.H. Choi, J.Y. Park, Combined calcium sulfoaluminate and ordinary portland cement/Fe(II) system for enhanced dechlorination of trichloroethylene, Chem. Eng. J. 231 (2013) 326–333.

[15] P. Tang, Y.C. Zhao, D.Z. Chen, F.Y. Xia, Volatility of heavy metals during incineration of tannery sludge in the presence of chlorides and phosphoric acid, Waste Manage. Res. 26 (2008) 369–376.

[16] Y. Ji, K. Yang, D. Xu, R. Zhou, Y. Sun, Study on Sulfur Cycle of Dynamic Equilibrium in NSP Cement Kiln System, Bull, Chinese Ceram. Soc. 30 (2011) 1023–1028.

[17] C. Chan, C.Q. Jia, J.W.Graydon, D.W. Kirk, The behaviour of selected heavy metals in MSW incineration electrostatic precipitator ash during roasting with chlorination agents, J. Hazard. Mater. 50 (1996) 1–13.

[18] S.R. Smith, A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge, Environ. Int. 35 (2009) 142–156.

[19] B. Nowak, A. Pessl, P. Aschenbrenner, P. Szentannai, H. Mattenberger, H.

Rechberger, G. Kakali, G. Parissakis, D. Bouras, A study of the burnability and the phase formation of PC clinker containing Cu oxide, Cem. Concr. Res. 26 (1996) 1473–1478.

[20] B. Nowak, S.F. Rocha, P. Aschenbrenner, H. Rechberger, F. Winter, Heavy metal removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the chloride type, Chem. Eng. J. 179 (2012) 178–185.

[21] K. Kolovos, S. Tsivilis, G. Kakali, The effect of foreign ions on the reactivity of the CaO-SiO_2-Al_2O_3-Fe_2O_3 system, Cem. Concr. Res. 32 (2002) 463–469.

[22] I. Jawed, J. Skalny, Alkalies in cement: a review, Cem, Concr. Res. 7 (1977) 719–730.

[23] A.A. Bogush, J.A. Stegemann, I. Wood, A. Roy, Element composition and mineralogical characterisation of air pollution control residue from UK energy-from-waste facilities, Waste Manage. 36 (2015) 119-129.

[24] L. Nirut, R.M. Anthony, M. Natt, Utilization of cathode ray tube waste: Encapsulation of PbO-containing funnel glass in Portland cement clinker, J. Environ. Manage. 117 (2013) 180–186.

[25] S. Yu, B. Zhang, J. Wei, T. Zhang, Q. Yu, W. Zhang, Effects of chlorine on the volatilization of heavy metals during the co-combustion of sewage sludge, Waste Manage. 62 (2017) 204–210.

[26] J. Han, M. Xu, H. Yao, Influence of calcium chloride on the thermal behavior of heavy and alkali metals in sewage sludge incineration, Waste Manage. 28 (2008) 833–839.

[27] H.C. Yang, Y.C. Seo, J.H. Kim, H.H. Park, Y. Kang, Vaporization characteristics of heavy metal compounds at elevated temperatures, Korean J. Chem. Eng. 11 (1994) 232–238.

[28] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford, New York, 1997.

[29] W.A. Gutterdge, On the dissolution of the interstitial phases in Portland cement, Cem. Concr. Res. 19 (1979) 319–324.

[30] K. Kolovos, S. Tsivilis, G. Kakali, SEM examination of clinkers containing foreign elements, Cem. Concr. Compos. 27 (2005) 163–170.

[31] D. Herfort, G.K. Moir, V. Johansen, F. Sorrentino, H.B. Arceo, The chemistry of Portland cement clinker, Adv. Cem. Res. 22 (2010) 187–194.

[32] S. Horkoss, R.Lteif, T. Rizk, Influence of the clinker SO_3 on the cement characteristics, Cem. Concr. Res. 41 (2011) 913–919.

[33] S. Telschow, F. Frandsen, K. Theisen, K. Dam-Johansen, Cement Formation. A Success Story in a Black Box: High Temperature Phase Formation of Portland Cement Clinker. Ind. Eng. Chem. Res. 51 (2012) 10983−11004.

[34] H.F.W. Taylor, Distribution of sulfate between phases in Portland cement clinkers, Cem. Concr. Res. 29 (1999) 1173–1179.

[35] D. Herfort, G.K. Moir, V. Johansen, F. Sorrentino, H.B. Arceo, The chemistry of Portland cement clinker, Adv. Cem. Res. 22 (2010) 187–194.

[36] F. Wang, D. Shang, M. Wang, S. Hu, Y. Li, Incorporation and substitution mechanism of cadmium in cement clinker, J. Clean. Prod. 112 (2016) 2292−2299.

[37] J. Wu, X. Yang, L. Yang, X. Kong, Z. Zhang, X. Wang, Study on oxidation

behaviors of CaS, Inorg. Chem. Ind. 8 (2015) 26–29.

[38] H. Xiao, J. Zhou, J. Liu, H. Fan, J. Cheng, K. Cen, Research on CaS oxidation reaction with thermogravimetric analysis, J. Zhejiang Univ. 40 (2006) 982–990.

[39] G. Zhao, J. Lin, C. Mei, K. Han, Study on formation process of sulphoalum inate calcium during high temperature desulfuration, J. Fuel Chem. Technol. 34 (2006) 665–669.

[40] S. Ma, X. Shen, L. Chen, Research on the Decomposition Kinetics of Calcium Sulphoaluminate, Bulletin of the Chinese Ceramic Society, 29 (2010) 701–704.