Environmental and Carbon Dioxide Issues

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Influence of chlorine on the fate of Pb and Cu during clinkerization

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ABSTRACT

The fate of heavy metals during clinkerization is of crucial significance to the utilization of solid waste as fuels and raw materials in cement kiln producing clinker. A ternary system of clinker-heavy metal-chlorine was developed that is more coincident with the condition of co-processing of solid waste in cement kiln. The main goal of this study was to investigate the relationships among chlorine, volatilization and solidification of Cu/Pb, and mineral phases of the clinker during clinkirization. The $AlCl_3 \cdot 6H_2O$ (chlorine source) and PbO/CuO were mixed with cement raw meal in appropriate ratios to produce co-processed clinkers. The

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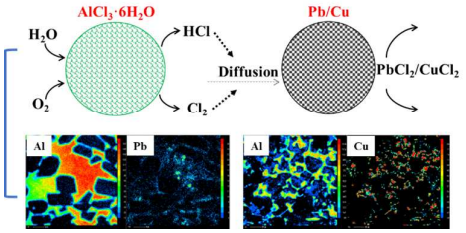
volatilization and solidification of Pb and Cu were investigated experimentally using a combination of atomic absorption spectrometry, electron probe micro-analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy, optical microscope, thermogravimetric and X-ray diffraction quantitative analyses. The volatilization ratios of Pb and Cu increased up to 46.18% and 34.04%, respectively, with increasing $AlCl_3 \cdot 6H_2O$ content up to 1.6%. comparing to the cement mixtures without $AlCl_3 \cdot 6H_2O$ addition (Pb and Cu volatilisation ratios are 49.90% and 27.21%, respectively). Pb and Cu oxides can be transformed into Pb and Cu chlorides, that are not stable and have high vapor pressure. Pb and Cu are mainly concentrated in the interstitial phases of the clinker. The addition of $AlCl_3 \cdot 6H_2O$ led to increase the crystal size of alite and belite. X-ray diffraction quantitative analyses proved that the content of silicate phase increased with the corresponding content of interstitial phases decreased during clinkerization with the addition of $AlCl_3 \cdot 6H_2O$, that decreased the ability of clinker to solidify Pb and Cu in the produced clinkers. This research can help to promote understanding of the fate of heavy metals during the cement kiln co-processing of solid wastes and meaningfully for energy conservation and sustainable development.

Key words: energy; chlorine; heavy metals; clinkerization; volatilization; mineral phases

TOC/Abstract Art



Synopsis

The relationships among chlorine, volatilization/solidification of Pb and Cu, and mineral phases of the cement clinker were demonstrated, which is essential for the utilization of solid waste as fuels and raw materials in cement kiln.

1. Introduction

The cement industry consumes around 2% of global primary energy use and produces 5-7% of anthropogenic CO_2 emissions worldwide. China's cement industry accounted for more than half of the world's total cement production.[1] Meanwhile, China produced 3.28 billion tons of industrial solid waste, 173 million tons of municipal solid waste (MSW) and 25 million tons of sludge in 2016.[2] Solid wastes can be considered as secondary raw fuels and/or materials in the cement industry. The cement kiln, known to consume a large quantity of energy and raw materials, promotes to use solid waste (SW) as fuels and raw materials in replacement for traditional materials used during the manufacturing process.[3-4]

However, the content of chlorine and heavy metals in SW are much higher than that of in traditional raw fuels and materials (e.g., coal and limestone).[5-6] Previous studies carried out on heavy metal emissions from waste incineration indicated that the volatilization of heavy metals depends on the composition of the wastes, the

physicochemical properties of heavy metals, and the compounds formed during incineration.[7-8] In particular, the waste-derived chlorine significantly affects the heavy metal emissions by the formation of volatile metallic chlorides.[9-10] Therefore, during the utilization of solid waste as fuel and raw material in cement kiln, heavy metals volatilization may be promoted by chlorine. Volatilized heavy metals can move with flue gas to concentrate on the wall of kiln, precalciner and cyclones, and then even exhaust into the atmosphere, which have serious effects on cement production and environment.[11-14] Accordingly, understanding the influence of chlorine on the fate of heavy metals in clinkerization is significant for the co-processing of solid wastes in the cement kiln.

Available literatures mainly focused on the effects of chlorides (such as NaCl and KCl) on the volatilization of heavy metals during the solid wastes incineration.[15-18] However, the incineration temperatures are relatively low (<1000˚C) and incineration environment and raw materials are different comparing to the cement clinker production (T=1450°C). Additionally, cations from the chlorides such as Na^+ and K^+ will have some effects on the process of clinkerization and then affect the volatilization and solidification of heavy metals.[19-20] Besides, $AlCl_3 \cdot 6H_2O$ is commonly exist in the municipal solid waste such as sewage sludge and industrial solid waste such as red mud.[17,18,21] Therefore, in order to eliminate influence of cations (such as Na^+ and K^+) on the clinkerisation process, $AlCl_3 \cdot 6H_2O$ (additionally, aluminum is one of the constituent elements of clinker) was selected as chlorine source in this study.

Pb and Cu commonly exist in the solid wastes such as Pb-Zn slag and sewage sludge[22-23] that have the potential threat to volatilize and move with flue gas into the atmosphere. Pb is one of the highly toxic heavy metals and can easily volatilize during the heat treatment of solid waste. In cement clinkering, CuO is known to act as mineralizer because it decreases the melt temperature considerably and favours the combination of free lime.[20, 24]

Yu *et al.*[22] studied the effects of chlorine on the volatilization of heavy metals during the co-combustion of sewage sludge. Author showed that chlorine increased the volatilization ratio of heavy metals during clinkerization. Fukuda *et al.*[25] focused in a melt-differentiation mechanism to understand the crystallization behavior of aluminates, other than the effects of chlorine on the fate of heavy metals during clinkerization. Therefore, the binary systems of clinker-heavy metal or heavy metal-chlorine have been investigated in previous works of co-processing of solid waste in cement kiln. In this study, a ternary system of clinker-heavy metal-chlorine was developed that is more coincident with the condition of co-processing of solid waste in cement kiln. The main goal of this study was to investigate the relationships among chlorine, volatilization and solidification of Cu/Pb, and mineral phases of the clinker during clinkirization. The results obtained in this study can give some suggestions to reduce the volatilization of Cu and Pb by adjusting mineral compositions of the clinker when co-processing of chlorine-contained solid waste in the cement kiln.

2. Materials and methods

2.1. Materials

Cement raw materials such as limestone, clay, and iron tailing, were supplied by the Yue Bao cement plant (China). Table 1 summarizes the chemical compositions of cement raw materials determined by X-ray fluorescence (XRF) analysis.

Table 1

Chemical compositions of the raw materials (%).

Material	Chemical composition								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	P_2O_5	LOI	Others
Limestone	4.36	BDL	1.64	53.07	0.47	0.44	0.04	39.69	0.29
Clay	65.32	17.34	4.71	1.21	0.48	0.9	0.14	0.04	9.87
Iron tailing	34.45	4.29	30.87	26.87	0.25	0.04	0.05	0.03	3.15

Note: BDL – below detection limit which is 0.01%, LOI: loss on ignition.

Table 2 summarizes the content of Pb, Cu, and Cl in the raw materials analyzed by atomic absorption spectrometry (Analytik Jena AG, Germany) after total acid digestion. Although the concentrations of Pb and Cu in clay are 49 mg/kg and 19 mg/kg respectively, they are far away below the detection limit of electron probe micro-analysis (EPMA) and energy dispersive spectrometer (EDS). Therefore, exogenous heavy metals of Pb and Cu were added to the raw mixes as PbO and CuO.

Table 2

Concentrations of Pb, Cu, and Cl in the raw materials (mg/kg).

Elements	Limestone	Clay	Iron tailing
Pb	1.1	49	2.7
Cu	3.9	19	3.0
Cl	1.0	1.3	2.2

2.2. Apparatus

Figure 1 shows a laboratory apparatus used for cement clinker production. The furnace is an alundum tube with length of 120 cm and inner diameter of 7.0 cm. The temperature of heating area of the alundum tube is monitored by a thermocouple and controlled automatically. A quartz-fiber filter was set up next to the alundum tube. The filter is 99.99% effective for the removal of 0.3 μm particles. The sampling train consisted of six impingers was situated after the filter. Heavy metals and their compounds in the flue gases were trapped by using a modified standard method.[26] The first impinger was empty. The second and third impingers were filled with a combined solution of 5% HNO_3 and 10% H_2O_2 for trapping most of the Pb and Cu and their compounds from the gases. The fourth and fifth impingers were filled with 4% $KMnO_4$ and 10% H_2SO_4 to capture trace element. The final impinger was filled with silica gel to remove the moisture content from the gases.

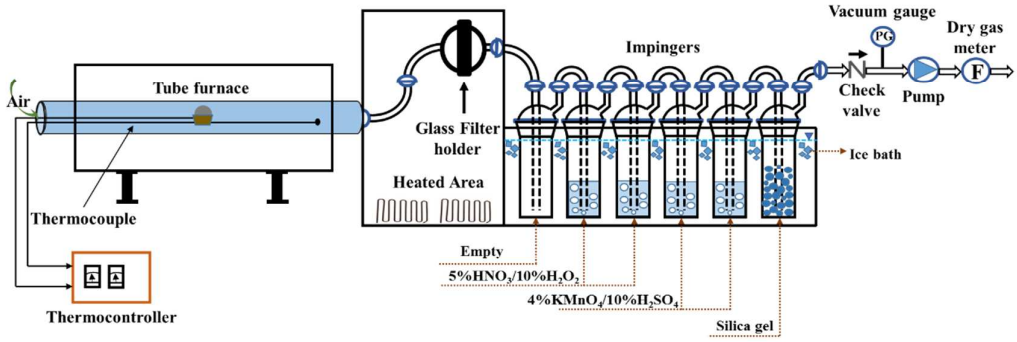


Fig 1. Laboratory apparatus used for cement clinker production.

2.3. Experimental procedure

The phase composition of cement clinkers was controlled by Bogue method[27] (Eq. (1) – (3)). 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 tricalcium silicate (C_3S), 20% of dicalcium silicate (C_2S), 8.6% of calcium aluminate (C_3A), and 10% of calcium alumino-ferrite (C_4AF). Cement raw meal with 1.0% of Pb or Cu were prepared and $AlCl_3 \cdot 6H_2O$ was added at percentages of 0.4%, 0.8%, 1.2%, and 1.6% by mass of raw meal. Table 3 lists the formulated mixtures.

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

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

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

Table 3

Formulated mixtures with Pb, Cu, and $AlCl_3 \cdot 6H_2O$.

ID.	Pb (wt. %)	Cu (wt. %)	$AlCl_3 \cdot 6H_2O$ (Cl: wt. %)
$S_{Ref.}$	0	0	0
S_{Pb}	1.0	0	0
$S_{Pb-0.4}$	1.0	0	0.4
$S_{Pb-0.8}$	1.0	0	0.8
$S_{Pb-1.2}$	1.0	0	1.2
$S_{Pb-1.6}$	1.0	0	1.6
S_{Cu}	0	1.0	0
$S_{Cu-0.4}$	0	1.0	0.4
$S_{Cu-0.8}$	0	1.0	0.8
$S_{Cu-1.2}$	0	1.0	1.2
$S_{Cu-1.6}$	0	1.0	1.6

The formulated mixtures were thoroughly blended and homogenized in a mechanical planetary mixer. Then each mixture was mixed with 8% of water and pelletized into Ø10×50 mm cylindrical bar under 40 MPa. Each pellet was calcined at 900°C, then heated up to 1450°C with a heating rate of 10°C/min, and maintained at 1450°C for 30 min. Then the clinkers were cooled quickly in air to the room temperature.

2.4. Analytical methods

The clinkers were grounded into fine powder. The prepared clinkers 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 the microwave digestion system (ZEROM, China). The concentrations of Pb and Cu in the solutions were analyzed by flame atomic absorption spectrometry (AAS, Analytik Jena AG, Germany). The duplicate measurements were carried out for prepared clinkers, and the average values were used to calculate the volatilization percentage according to Eq. (4):

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

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

The distribution of Pb and Cu in the clinker phases was investigated on the polished (Tegramin-25 polishing machine, Struers, Denmark) sections by an electron probe micro-analysis (EPMA-1600, Shimadzu, Japan). The polishing process was as

follows: sandpaper of #250-mesh for 2min, #800-mesh for 5min, #1200-mesh for 10min, #2000-mesh for 15min, and then #4000-mesh for 20min. The measurement was conducted with an acceleration voltage of 15 kV and an electron beam diameter of 1μm. the detection limit of mapping by EPMA for Cu and Pb was about 0.1wt.%. 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 20kV accelerating voltage. The detection limit of EDS for Cu and Pb from the polished samples of clinkers with using long counting times was about 0.05wt.%.

Thermogravimetric analysis (TG/DTG) was used to investigate temperature conditions and mass changes as well as the effect of $AlCl_3 \cdot 6H_2O$ on the sintering reactions of the clinker. Thermogravimetric analysis was carried out for the samples of $S_{ref.}$, S_{Pb}, $S_{Pb\text{-}1.6}$, S_{Cu} and $S_{Cu\text{-}1.6}$. TG and DTG curves were obtained using a NETZSCH STA 449F3 instrument. Runs were conducted using about 20 mg of sample 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 1450°C.

The morphology of mineral phases of the clinkers was observed by a Carl Zeiss GmbH 37081optical microscope (Germany). The samples were cross-sectioned and polished, and the surface of the cross-section was etched by nitric acid dissolved in the alcohol with a volume fraction of 1.0%.

The qualitative and quantitative mineralogical compositions of the clinkers 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). A K-value method was adopted to quantify the amount of mineral phases in clinker according to the previous report[28-29] and α-Al_2O_3 was used as the internal standard. 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.

3. Results and discussion

3.1. Volatilization of Pb and Cu with $AlCl_3 \cdot 6H_2O$

Figure 2 shows the results obtained for Pb and Cu volatilization. The volatilization ratios of Pb and Cu from the S_{Pb} and S_{Cu} samples are 49.90% and 27.21%, respectively. The volatilization ratios of Pb and Cu increased with increasing $AlCl_3 \cdot 6H_2O$ content. The most significant increase of element volatilization was observed for Pb (46.18%) and Cu (34.04%) with the addition of 1.6% of Cl comparing to the reference sample (Figure 2).

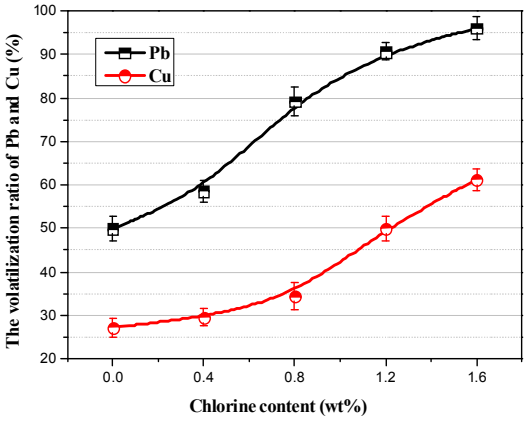


Fig. 2. Volatilization of Pb and Cu with $AlCl_3 \cdot 6H_2O$.

Therefore, the volatilization of Pb and Cu depend strongly on the addition of

$AlCl_3 \cdot 6H_2O$. A schematic diagram of the distribution of Pb or Cu and $AlCl_3 \cdot 6H_2O$ in a pellet and the potential reactions between Pb/Cu and $AlCl_3 \cdot 6H_2O$ are shown in Figure 3. $AlCl_3 \cdot 6H_2O$ release chlorine-containing gas (HCl) with temperature increasing according to the reactions in Figure 3.[15] According to Dong et al.,[15] Pb and Cu are assumed to be present as oxides at the envisaged temperature (1000°C). The chemical reactions show the conversion of PbO and CuO into volatile metal chlorides (Figure 3).[22,30,31]

The boiling points of PbO and CuO are quite high comparing to the correspondent $PbCl_2$ and $CuCl_2$ (Figure 4). Therefore, the addition of $AlCl_3 \cdot 6H_2O$ has a positive effect on the volatilization of Pb and Cu.

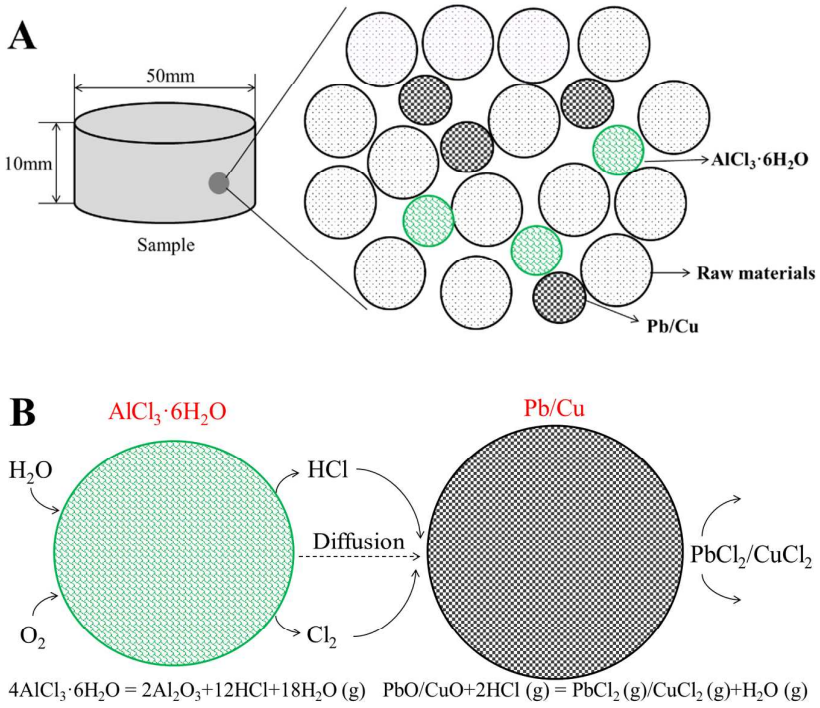


Fig. 3. Schematic diagram of the distribution of Pb/Cu and $AlCl_3 \cdot 6H_2O$ in a pellet (A) and potential reactions (B).

Figure 2 shows that Pb is more volatile than Cu at the same content of $AlCl_3 \cdot 6H_2O$. The reason is that the melting points and boiling points of PbO and $PbCl_2$ are lower than that of CuO and $CuCl_2$, respectively (Figure 4).

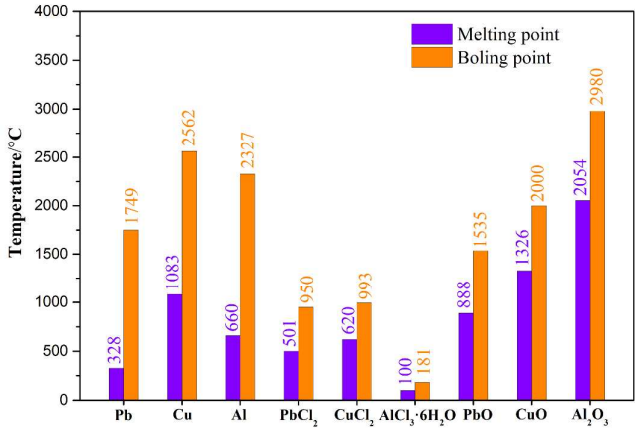


Fig. 4. Melting and boiling points of chemical compounds.

3.2. Solidification of Pb and Cu with $AlCl_3 \cdot 6H_2O$

The element distribution maps of Si, Al, Fe, and Pb in the S_{Pb} clinker are shown in Figure 5. It can be seen that the distributions of Pb, Al and Fe in the clinker are similar. Thus, Pb was mainly solidified in the interstitial phases of the clinker. Due to the high volatilization of Pb, especially in the $S_{Pb\text{-}1.2}$ and $S_{Pb\text{-}1.6}$ clinkers, the distribution of Pb in the mineral phases is difficult to be confirmed by EPMA. Therefore, point chemical analysis was carried out to investigate the solidification of Pb in the $S_{Pb\text{-}0.8}$ clinker (Figure 6) and the results are listed in Table 4. Pb was detected in the interstitial phases but not in the silicate phase of the clinker. Consequently, the addition of $AlCl_3 \cdot 6H_2O$ has no effect on the solidified position of Pb.

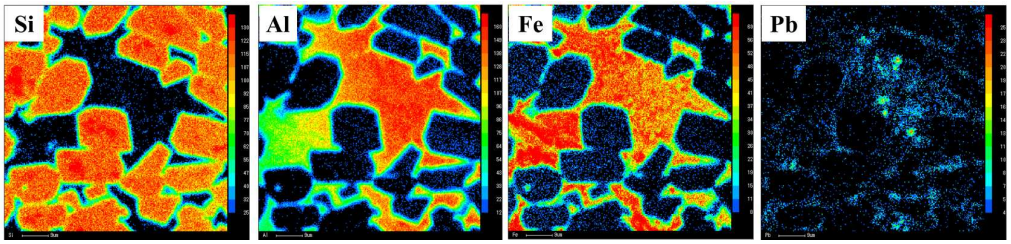


Fig. 5. An EPMA maps of distribution of Si, Al, Fe, and Pb in S_{Pb} clinker.

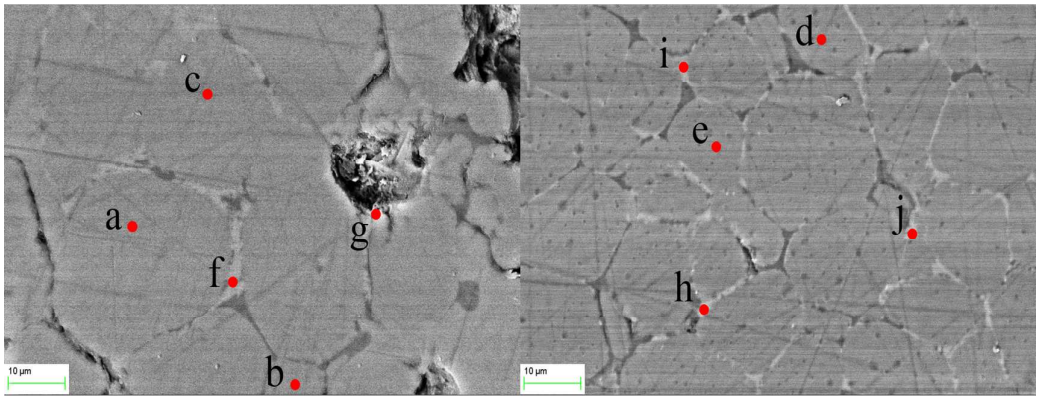


Fig. 6. Photomicrograph of a backscattered electron image of mineral phases in the $S_{Pb-0.8}$ sample.

Table 4

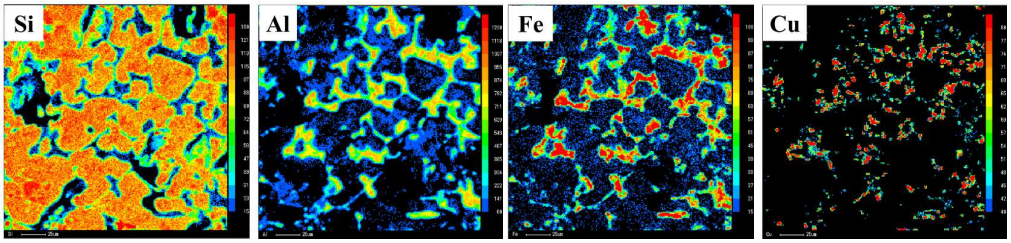
Composition of clinker phases from $S_{Pb-0.8}$ sample by SEM/EDS (%).

Elements	Points in silicate phase					Points in interstitial phase				
	a	b	c	d	e	f	g	h	i	j
Ca	42.31	44.66	41.73	45.91	40.84	35.20	37.29	35.88	32.84	35.14
O	41.23	38.65	41.95	37.52	42.62	39.98	37.88	37.79	39.86	33.79
Si	14.46	14.77	14.37	14.53	14.26	6.61	5.59	5.89	3.18	2.59
Al	1.29	1.25	1.14	1.21	1.19	9.45	9.37	8.08	13.03	15.29
Fe	0.49	0.46	0.62	0.65	0.19	6.49	7.11	8.14	7.79	8.88
Pb	-	-	-	-	-	0.13	0.10	0.09	0.11	0.14
Others	0.22	0.21	0.19	0.17	0.59	2.14	2.67	4.13	2.71	3.27

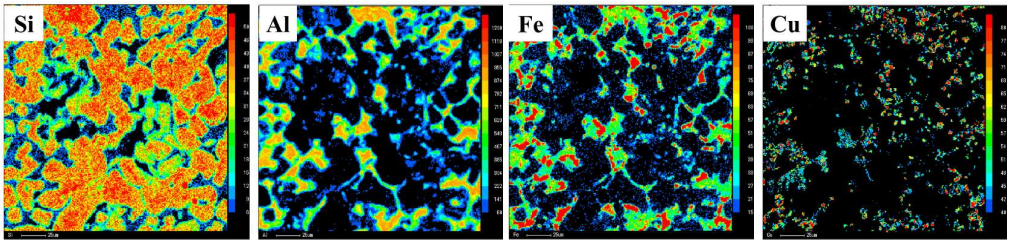
Note: -, undetected; Error bars: Ca, ±2.1; O, ±2.7; Si, ±1.8; Al, ±0.12; Fe, ±0.33; Pb,

±0.14.

The element distribution maps of Si, Al, Fe, and Cu in the S_{Cu} and $S_{Cu-0.8}$ clinkers are shown in Figure 7. Cu was concentrated in the interstitial phases of the clinker (Figure 7A), similar to Pb. The Cu distribution in the clinker phases was not changed after $AlCl_3 \cdot 6H_2O$ addition. Therefore, the solidified position of Cu was not affected with the presence of $AlCl_3 \cdot 6H_2O$.



(A)



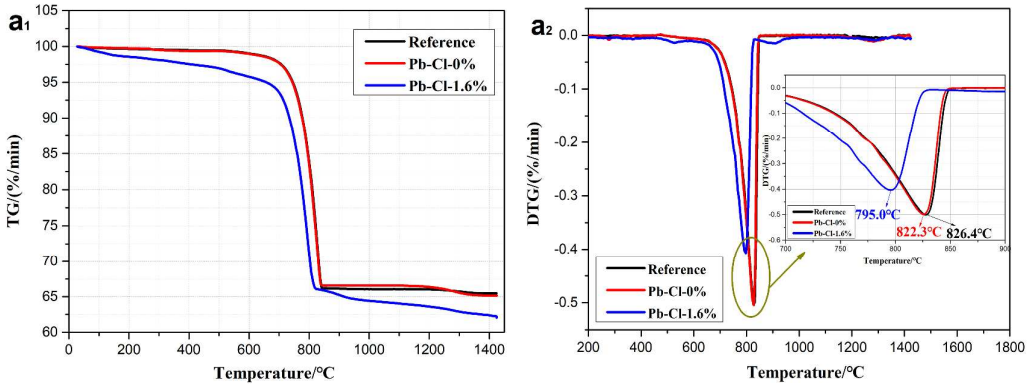
(B)

Fig. 7. An EPMA maps of distribution of Si, Al, Fe, and Cu in clinkers: A) S_{Cu}; B) $S_{Cu-0.8}$.

3.3. Influence of $AlCl_3 \cdot 6H_2O$ on the decomposition temperature of limestone

The formation of each mineral phases during the process of clinkerization relates to the reactions among CaO, SiO_2, Al_2O_3 and Fe_2O_3. The reactions are affected by the

formation rate of CaO that comes from the decomposition of calcium carbonate (e.g., limestone).[20] The results from thermogravimetric analysis are shown in Figure 8. The endothermic pick at 826.4°C for the reference sample corresponds to decomposition of $CaCO_3$. The decomposition temperature of limestone in the cement mixtures doped with Pb or Cu (e.g., S_{Pb} and S_{Cu} samples) decreased about 5°C comparing to the S_{ref} sample. The addition of 1.6 wt.% of $AlCl_3 \cdot 6H_2O$ (e.g., $S_{Pb\text{-}1.6}$ and $S_{Cu\text{-}1.6}$ samples) lead to decrease of the $CaCO_3$ decomposition temperature significantly (about 30°C lower than for the reference sample). $AlCl_3 \cdot 6H_2O$ played the role as a mineralizer accelerating the decomposition of $CaCO_3$. According to other research,[20] the incorporation of chlorine in the cement raw meal could promote the decomposition of $CaCO_3$, decrease temperature of the first liquid phase formation, increase the amount of the melt, and accelerate the rate of the reactions occurring in the solid state.



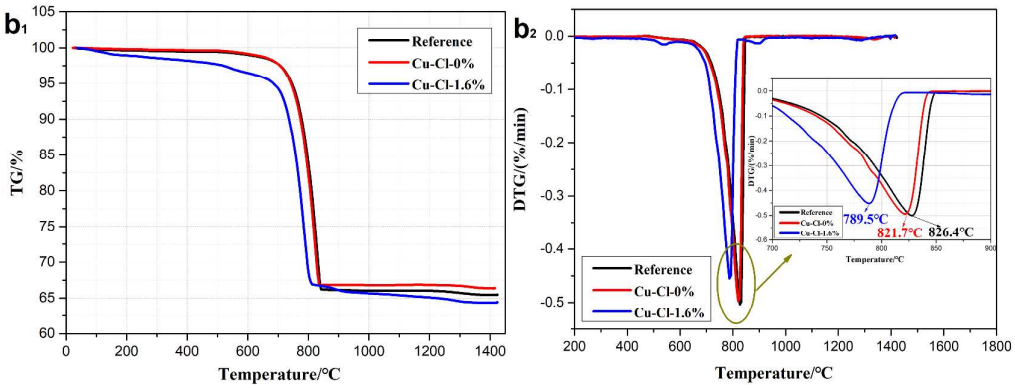


Fig. 8. TG-DTG curves of the following cement mixtures: a_1) TG curves of $S_{ref.}$, S_{Pb} and $S_{Pb\text{-}1.6}$; a_2) DTG curves of $S_{ref.}$, S_{Pb} and $S_{Pb\text{-}1.6}$; b_1) TG curves of $S_{ref.}$, S_{Cu} and $S_{Cu\text{-}1.6}$; b_2) DTG curves $S_{ref.}$, S_{Cu} and $S_{Cu\text{-}1.6}$.

3.4. Influence of $AlCl_3 \cdot 6H_2O$ on the crystal sizes of alite and belite

The optical photomicrographs of the $S_{ref.}$, S_{Pb}, $S_{Pb\text{-}1.6}$, S_{Cu}, and $S_{Cu\text{-}1.6}$ clinkers are given in Figure 9. All investigated clinkers consist of main silicate minerals such as alite (C_3S), belite (C_2S), and interstitial phases including matrix of calcium aluminate (C_3A) and calcium aluminoferrite (C_4AF). The fifty typical micrographs were taken for each sample in order to estimate the crystal sizes of alite and belite (Table 5). The average crystal sizes of alite and belite in the $S_{ref.}$ clinker are in the range of 15-25 μm and 10-20 μm, respectively. There were not visible changes in the alite and belite crystal sizes for the S_{Pb} and S_{Cu} samples. However, the crystal sizes of alite and belite in the $S_{Pb\text{-}1.6}$ and $S_{Cu\text{-}1.6}$ clinkers increased considerably comparing to the S_{Pb}, S_{Cu}, and $S_{ref.}$ samples.

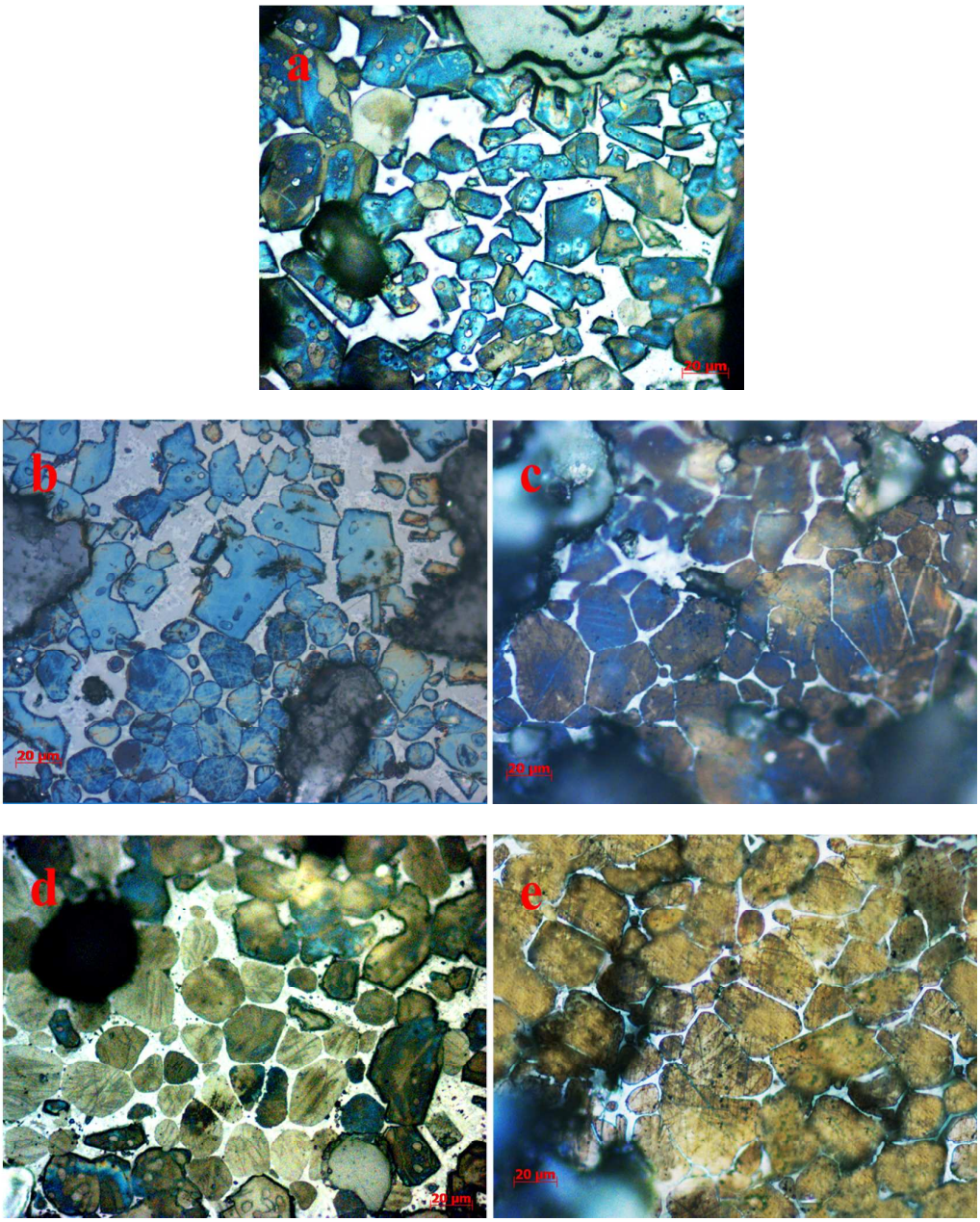


Fig. 9. Optical photomicrographs for the clinkers: (a) $S_{Ref.}$; (b) S_{Pb}; (c) $S_{Pb\text{-}1.6}$; (d) S_{Cu}; (e) $S_{Cu\text{-}1.6}$.

Table 5

Size and shape of alite and belite crystals in clinkers

ID.	Alite	Belite

	Size (μm)	Shape	Size (μm)	Shape
$S_{ref.}$	15-25	Angular, elongated, prismatic	10-20	Small, roundish
S_{Pb}	15-30	Prismatic, angular	10-25	Small, roundish
$S_{Pb-1.6}$	30-50	Large, compact, prismatic, angular	20-30	Large, round, compact
S_{Cu}	15-30	Prismatic, angular	10-25	Small, roundish
$S_{Cu-1.6}$	30-50	Large, compact, prismatic, angular	20-30	Large, round, compact

According to Taylor et al.,[27] Kacimi et al.[32] and Wang et al.,[33] chlorine dissolved in the melt can affect the acid-base equilibrium $[MeO_4]^{5-} \leftrightarrow [MeO_6]^{9-}$ of the amphoteric elements (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, and then promote the silicate crystals (e.g., C_3S and C_2S) formation and growth.

3.5. Influence of $AlCl_3 \cdot 6H_2O$ on the mineral composition of the clinker

X-ray diffraction is a reliable and precise method to quantify the relative phase content in the Portland cement clinker.[34] The content of silicate and interstitial phases of the clinkers were determined by quantitative XRD analysis and the results are listed in Figure 10 and Table 6. The content of silicate phase is 79.2% with 54.2% C_3S and 25.0% C_2S for the reference sample, which is consistent with the calculated mineral composition by Bogue method. For the samples of S_{Pb} and S_{Cu}, the main peaks intensity of C_3S in the XRD patterns (Figure 10) increased a little bit and the content of C_3S is slightly higher but contents of C_2S, C_3A, and C_4AF are slightly

lower than for $S_{Ref.}$. Addition of 1.6 wt.% of $AlCl_3 \cdot 6H_2O$ leads to significant increase the main peaks intensity and content of C_3S, about 10 wt.% higher than for reference clinker. Amount of C_2S decrease in 1.65 wt.% for the $S_{Pb\text{-}1.6}$ clinker and in 2.68 wt.% for the $S_{Cu\text{-}1.6}$ clinker comparing to $S_{Ref.}$. The content of C_3A and C_4AF (interstitial phases) decreased considerably (about 8 wt.%) for both $S_{Pb\text{-}1.6}$ and $S_{Cu\text{-}1.6}$ clinkers (Table 6). Combined with the results in Section 3.2, Pb and Cu were concentrated in interstitial phases of the clinker and being not affected by the addition of $AlCl_3 \cdot 6H_2O$. It can be obtained that chlorine decreased the ability of clinker to solidify Pb and Cu during clinkerization. Accordingly, to increase the solidification of Cu and Pb in clinker, the content of interstitial phases in clinker should be increased properly through adjusting the KH, SM, and IM by Bogue method[26] during the co-processing of chlorine-contained solid waste in cement kiln.

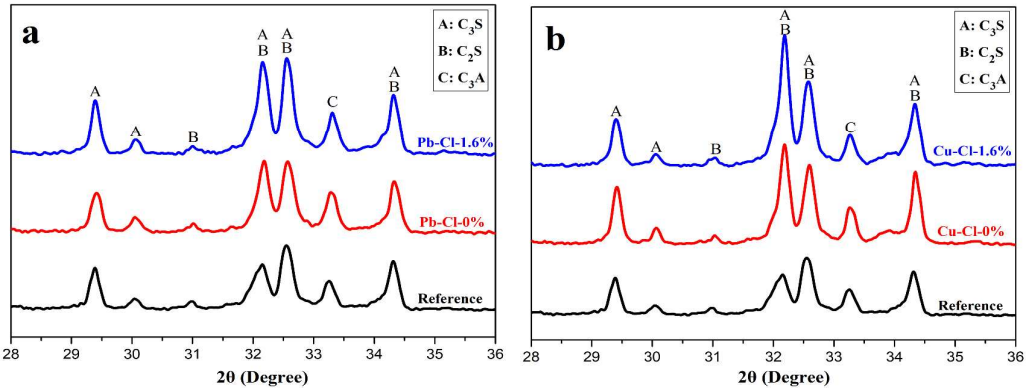


Fig. 9. XRD patterns of clinker. a) $S_{ref.}$, S_{Pb} and $S_{Pb\text{-}1.6}$; b) $S_{ref.}$, S_{Cu} and $S_{Cu\text{-}1.6}$.

Table 6

Mineral composition of the clinkers, wt.%

ID.	Silicate phase		Interstitial phase		
	C_3S	C_2S	C_3A	C_4AF	Others
$S_{Ref.}$	54.2±0.8	25.0±0.6	9.6±0.3	8.3±0.5	2.8±0.2
S_{Pb}	56.4±0.6	23.5±0.7	9.4±0.2	8.2±0.4	2.4±0.3
$S_{Pb\text{-}1.6}$	64.9±0.4	23.4±0.3	5.0±0.4	4.6±0.5	2.2±0.1
S_{Cu}	55.8±0.5	24.1±0.4	8.9±0.6	8.0±0.6	3.2±0.3
$S_{Cu\text{-}1.6}$	64.7±0.9	22.3±0.2	3.8±0.2	6.2±0.8	3.0±0.4

4. Conclusions

The relationships among chlorine, volatilization and solidification of Cu/Pb, and mineral phases of the clinker during clinkirization were investigated and discussed in this work. The main conclusions can be summarized as follow:

- Chlorine has a significant effect on the volatilization of Pb and Cu in clinkerization. The volatilization ratios of Pb and Cu increased up to 46.18% and 34.04%, respectively, with increasing $AlCl_3 \cdot 6H_2O$ content up to 1.6%. comparing to the cement mixtures without $AlCl_3 \cdot 6H_2O$ addition (Pb and Cu volatilisations are 49.90% and 27.21%, respectively).
- Pb and Cu were concentrated in the interstitial phases of the clinker and being not affected by the addition of chlorine.
- The crystal formation and growth of alite and belite were promoted by chlorine. The crystal sizes of alite and belite increased about 100% and 70%, respectively, when the content of chlorine was 1.6%. The content of C_3S increased about 10 wt.% with the corresponding content of interstitial phases decreased about 8 wt.% during clinkerization with the addition of 1.6% Cl.
- Chlorine decreased the ability of clinker to solidify Pb and Cu by decreasing the

content of interstitial phases in clinkerization.

However, there are some experiments and questions that deserve to be done and discussed in the future. Firstly, determination of the effects of chlorine on the volatilization of Pb and Cu in this study was at the temperature of 1450□. Indeed, the cement raw meal will undergo different temperature ranges during the process of being sintered to clinker. Therefore, the study of the chlorine effect to the volatilization of Pb and Cu at different temperatures during clinkerization is required. Secondly, the effect of chlorine on the volatilization of Pb and Cu may be different, if Pb and Cu exist simultaneously due to their possible competitive effects. Therefore, it is interesting to investigate the effect of chlorine on the volatilization of heavy metals from mono-elemental system to multi-elemental system in the future.

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References

(1) Zhang, S.; Ernst, W.; Wina C. Evaluating co-benefits of energy efficiency and air pollution abatement in China's cement industry. Appl. Energ. 2015, 147, 192-213.

(2) China Environmental State Bulletin: 2017.

(3) Dong, J.; Chi, Y.; Tang, Y.; Wang, F.; Huang, Q. Combined Life Cycle Environmental and Exergetic Assessment of Four Typical Sewage Sludge Treatment Techniques in China. Energy Fuels. 2014, 28, 2114–2122.

(4) Rahman, A.; Rasul, M. G.; Khan, M. M. K.; Sharma, S. Impact of alternative fuels on the cement manufacturing plant performance: an overview. Procedia Eng. 2013, 56, 393–400.

(5) Maria del, M. C. M.; Linda, K. N.; Flemming, J. F.; Peter, G.; Kim, D. J. Review: Circulation of Inorganic Elements in Combustion of Alternative Fuels in Cement Plants. Energy Fuels. 2015, 29, 4076–4099.

(6) Qiu, Q.; Jiang, X.; Lv, G.; Lu, S.; Ni, M. Stabilization of Heavy Metals in Municipal Solid Waste Incineration Fly Ash in Circulating Fluidized Bed by Microwave-Assisted Hydrothermal Treatment with Additives. Energy Fuels. 2016, 30, 7588–7595.

(7) Chanaka, U. W. D.; Andrei, V.; Apostolos, G.; Grzegorz, L.; Victor W. C.; Teik-Thye, L. Fate and distribution of heavy metals during thermal processing of sewage sludge. Fuel. 2018, 226, 721–744.

(8) Mu, Y.; Amirhomayoun, S.; Takayuki, S. Utilization of waste natural fishbone for heavy metal stabilization in municipal solid waste incineration fly ash. J. Clean. Prod. 2018, 172, 3111–3118.

(9) Zain, A. S. B.; Li, R.; Li, Y.; Gao, H.; Teerawat, S.; Teng, W.; Sunel, K.; Liang, Z. New advancement perspectives of chloride additives on enhanced heavy metals removal and phosphorus fixation during thermal processing of sewage sludge. J.

Clean. Prod. 2018, 188, 185–194.

(10) Ke, C.; Ma, X.; Tang, Y.; Zheng, W.; Wu, Z. The volatilization of heavy metals during co-combustion of food waste and polyvinyl chloride in air and carbon dioxide/oxygen atmosphere. Bioresource Techonl. 2017, 244, 1024-1030.

(11) Krzysztof, F.; Agnieszka, R.; Anna, G.; Malgorzata, J. K. The presence of contaminations in sewage sludge–The current situation. J. Environ. Mange. 2017, 203, 1126–1136.

(12) Quina, M. J.; Bontempi, E.; Bogush, A.; Schlumberger, S.; Weibel, G.; Braga, R.; Funari, V.; Hyks, J.; Rasmussen, E.; Lederer, J. 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. 2018, 635, 526–542.

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

(14) Gupta, R. K.; Majumdar, D.; Trivedi, J. V.; Bhanarkar, A. D. Particulate matter and elemental emissions from a cement kiln. Fuel Process. Technol. 2012, 104, 343–351.

(15) Dong, J.; Chi, Y.; Tang, Y.; Ni, M.; Nzihou, A.; Weiss, H. E.; Huang, Q. Partitioning of Heavy Metals in Municipal Solid Waste Pyrolysis, Gasification, and Incineration. Energy Fuels. 2015, 29, 7516–7525.

(16) Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Xiang, J.; Hu, S.; Yao, H. Mechanism on heavy

metals vaporization from municipal solid waste fly ash by $MgCl_2 \cdot 6H_2O$. Waste Manage. 2016, 49, 124–130.

(17) Nowak, B.; Pessl, A.; Aschenbrenner, P.; Szentannai, P.; Mattenberger, H.; Rechberger, H.; Hermann, L.; Winter, F. Heavy metal removal from municipal solid waste fly ash by chlorination and thermal treatment. J. Hazard. Mater. 2010, 179, 323-331.

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

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

(20) Kolovos, K.; Tsivilis, S.; Kakali, G. The effect of foreign ions on the reactivity of the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ system. Cem. Concr. Res. 2002, 32, 463–469.

(21) Lu, Q.; Dong, W.; Wang, H.; Wang, X. A Novel Way to Synthesize Yttrium Aluminum Garnet from Metal-Inorganic Precursors, J. Am. Ceram. Soc. 2002, 85, 490–492.

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

(23) Jiang, Y.; Lin, T. C.; Shi, C.; Pan, S. Characteristics of steel slags and their use in cement and concrete–A review. Resour. Conserv. Recy. 2018, 136, 187–197.

(24) Ludwig, H. M.; Zhang, W. Research review of cement clinker chemistry. Cem.

Concr. Res. 2015, 78, 24–37.

(25) Fukuda, K.; Matsunaga K.; Bessho, T.; Yoshida, H. Melt Differentiation Induced by Zonal Structure Formation of Calcium Aluminoferrite in a CaO-SiO_2-Al_2O_3-Fe_2O_3 Pseudoquaternary System. J. Am. Ceram. Soc. 2005, 88, 954–962.

(26) U.S. Environmental Protection Agency (USEPA), Method 29–Determination of Metal Emissions from Stationary Sources, Office of Air Quality Planning and Standards, Washington, D.C, 1996.

(27) H. F. W. Taylor, Cement Chemistry, second ed. Thomas Telford, New York, 1997.

(28) Li, J.; Yu, Q.; Wei, J.; Zhang, T. Structural characteristics and hydration kinetics of modified steel slag. Cem. Concr. Res. 2011, 41, 324–329.

(29) Guilherme, A. C.; Thais, L. T. S.; Ana Paula, B. R.; Adenilson, O. S.; Lisandro, P. C. On the quantitative phase analysis and amorphous content of triacylglycerols materials by X-ray rietveld method. Chem. Phys. Lipids. Available online, 2018.

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

(31) Liu, J.; Chen, J.; Huang, L. Heavy metal removal from MSS fly ash by thermal and chlorination treatments. Sci. Rep. 2015, Article number: 17270.

(32) Kacimi, L.; Simon-Masseron, A.; Ghomari, A.; Derriche, Z. Reduction of clinkerization temperature by using phosphogypsum. J. Hazard. Mater. 2006, 37, 129–137.

(33) Wang, F.; Shang, D.; Wang, M.; Hu, S.; Li, Y. Incorporation and substitution

mechanism of cadmium in cement clinker. J. Clean. Prod. 2016, 112, 2292–2299.

(34) Witte, M. Lesch, C. On the improvement of measurement accuracy of retained austenite in steel with X-ray diffraction. Mater. Charact. 2018, 139, 111–115.