Effects of chlorine on the volatilization of heavy metals during the co-combustion of sewage sludge

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Abstract

To clarify the volatilization of heavy metals (Cu, Ni, Pb, and Zn) in sewage sludge during co-combustion in cement kiln, effects of addition and types of four chlorides and temperature on the volatilization of heavy metals in raw meal with 25 wt.% sewage sludge were investigated. The results showed that the volatilization of Cu, Ni, and Pb increased significantly with increase of chlorides addition, while no obvious change in the volatilization of Zn was observed. The effectiveness of chlorides on the volatilization of heavy metals depended on their release capacity of chlorine radicals and the chlorine combined capacity of heavy metals. Higher calcination temperature resulted in dramatically increase in the volatilization of heavy metals due to easier formation of volatile heavy metal chlorides. The results will provide a guideline for co-combusting heavy metals contained solid wastes in cement kiln on the basis of security.

1. Introduction

The use of cement kilns for disposing heavy-metal-containing sewage sludge is promising, attributed to advantages, such as high temperatures (1450 °C) and long residence times (greater than 1200 °C for several seconds), surplus oxygen during and after combustion, good turbulence and mixing conditions, as well as no generation of by-products (e.g., slag, ashes, or liquid residues) (Yang et al., 2014; Mokrzycki et al., 2003).

Several studies (Stephan et al., 1999; Eckert and Guo, 1998; Qijun et al., 2003) have reported that heavy metals can be solidified in clinker and hydration products, which in turn make it difficult to leach out. Moreover, during the co-combustion of sludge in cement kilns, heavy metals can volatilize and move with flue gas into the atmosphere, which will directly pollute the environment. Hence it is necessary to clarify the volatilization behavior of heavy metals during the co-combustion of sludge in cement kiln, which can provide a guideline for appropriately handling solid wastes containing heavy metals on the basis of security.

Previously, heavy metals have been known to be classified into volatile (Pb and Cd), semi-volatile (Zn, Sb, and Se), and non-volatile (Cr, Cu, Ni, As, Mn, and Co) heavy metals (Yang et al., 1994). The content of chlorine in sewage sludge changed from ppm (Park et al., 2010) to one percent (Toledo et al., 2005; Samaras et al., 2008), and the types of chlorine salt consist mainly of alkali metal and alkaline earth metal chlorides (Werther and Ogada, 1999) and ferric chlorides (Wang et al., 2001), and etc.. In a municipal solid waste (MSW) incineration plant, the evaporation rates of Cd, Cu, Pb, and Zn in fly ash have been reported to be markedly shifted by the addition of NaCl at an incineration temperature range of 670–1000 °C (Jakob et al., 1996). Increase in the chlorine content from either organic chlorides (polyvinyl chloride) or inorganic chlorides (NaCl and KCl, and FeCl₃) will increase the amount of heavy metal (Cd, Zn, Cr, and Cu) partitioned to the fly ash (Wang et al., 1999; Tang et al., 2008; Wang et al., 2001). The gas/solid transformation temperature of Cu has been reported to clearly decrease while that of Zn is maintained a similar level, attributed to the present of calcium chloride (Han et al., 2008). Without the use of a chlorinating agent, only 40% of Zn has been reported to removed, as compared with the removal of 90% of Pb and Cd and 70% of Cu. In contrast, approximately 90% of Pb, Cd, and Zn have been removed from electrostatic precipitator ash after treatment at 1000 °C for 30 min with the addition of calcium chloride (Chan et al., 1996). The removal of heavy metals depended on the chlorine release ability (Chan et al., 1996) and the binding energy (Luan et al., 2013) of chlorides. Most of inorganic chlorides are more effective than organic chlorides, such as PVC (Wang et al., 1999; Li et al., 2015). Furthermore, CaCl₂ and MgCl₂ were generally

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more effective for heavy metal removal than NaCl, as CaCl₂ and MgCl₂ first form HCl and/or Cl₂ by reacting with H₂O and/or O₂ (indirect chlorination), while NaCl directly chlorinates (Nowak et al., 2012).

From the above studies, the volatilization of Cu, Ni, Pb, and Zn is possibly improved by chloride, which is inevitable presented in the raw materials of cement kiln. Nevertheless, Available literatures mainly focused on the effects of chlorine on the volatilization of Cu, Ni, Pb, and Zn during incineration of sewage sludge at relatively low temperatures (<1000°C). However, sewage sludge was subjected to high temperature (950–1450°C) during co-combustion in cement. In addition, various chlorine sources are contained in sludge, which will play different roles in the volatilization of heavy metals. To the best of our knowledge, few studies have been conducted to distinguish the effect of differential chloride sources on the volatilization of heavy metal. For clarifying the effects of chlorine on the volatilization of Cu, Ni, Pb, and Zn, different addition and types of chlorides (AlCl₃·6H₂O, FeCl₃·6H₂O, CaCl₂, and NaCl) were used in the raw meal, and the volatilization of heavy metals was determined under different conditions (use of different chlorides and sintering temperature).

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. The original sewage sludge from wastewater treatment is produced by Anaerobic-Anoxic-Oxic Technology. The moisture content of original sewage sludge from wastewater treatment is produced by Anaerobic-Anoxic-Oxic Technology. The moisture content of original sewage sludge was determined under different conditions (use of different chlorides and sintering temperature).

2.2. Sample preparation

In this study, Lime saturation ratio (KH), Silica ratio (SM), and Alumina ratio (IM) values of raw meal with 25.00 wt.% sewage sludge were designed as 0.9, 2.5, and 1.6, respectively. By the Bogue calculation (Lawrence, 1998) (Eqs. (1)–(3)), the compositional parameters of cement clinkers were controlled. The theoretical mineral composition was calculated to be 56% C₃S, 20% C₂S, 8.6% C₆A, and 10% C₅A. Raw materials were prepared and four inorganic chlorides (AlCl₃·6H₂O, FeCl₃·6H₂O, CaCl₂, and NaCl) were added at percentages of 0 wt.%, 0.4 wt.%, 0.8 wt.%, 1.2 wt.%, and 1.6 wt.% by mass of raw meal. Table 3 lists the mixtures thus designed.

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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<td>3.92</td>
<td>1.31</td>
<td>1.12</td>
<td>8.76</td>
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<tr>
<td>Clay</td>
<td>58.97</td>
<td>16.12</td>
<td>180.95</td>
<td>6.80</td>
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<tr>
<td>Iron tailing</td>
<td>2.96</td>
<td>13.34</td>
<td>2.71</td>
<td>13.24</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>1750.98</td>
<td>206.59</td>
<td>66.08</td>
<td>885.64</td>
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</tbody>
</table>

* Dry weight basis (constant weight at 105°C).

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Cl</th>
<th>P₂O₅</th>
<th>LOI*</th>
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<tbody>
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<td>Limestone</td>
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<td>0.44</td>
<td>0.02</td>
<td>0.04</td>
<td>39.69</td>
<td>0.27</td>
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<tr>
<td>Clay</td>
<td>65.32</td>
<td>17.34</td>
<td>4.71</td>
<td>1.21</td>
<td>1.24</td>
<td>0.25</td>
<td>0.02</td>
<td>0.04</td>
<td>9.84</td>
<td></td>
</tr>
<tr>
<td>Iron tailing</td>
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<td>4.29</td>
<td>30.87</td>
<td>26.87</td>
<td>0.25</td>
<td>0.02</td>
<td>0.02</td>
<td>0.07</td>
<td>3.13</td>
<td></td>
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<tr>
<td>Sewage sludge</td>
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<td>9.77</td>
<td>7.85</td>
<td>13.33</td>
<td>0.96</td>
<td>1.6</td>
<td>0.05</td>
<td>33.04</td>
<td>2.89</td>
<td></td>
</tr>
</tbody>
</table>

* LOI, Loss on ignition (Chinese national standard method GB/T 176-2008).

Note: *, un-detected.

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Cl</th>
<th>P₂O₅</th>
<th>LOI*</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>4.36</td>
<td>1.64</td>
<td>53.07</td>
<td>0.47</td>
<td>0.44</td>
<td>0.02</td>
<td>0.04</td>
<td>39.69</td>
<td>0.27</td>
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<td>1.6</td>
<td>0.05</td>
<td>33.04</td>
<td>2.89</td>
<td></td>
</tr>
</tbody>
</table>

Note: *, un-detected.

a Dry weight basis (constant weight at 105°C).

Fig. 1. X-ray diffraction pattern of sewage sludge.

Lime saturation ratio (KH) = \( \frac{\text{CaO} - 1.65\text{Al}_2\text{O}_3 - 0.35\text{Fe}_2\text{O}_3}{2.8\text{SiO}_2} \) (1)

Silica ratio (SM) = \( \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \) (2)

Alumina ratio (IM) = \( \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \) (3)
temperatures, the chlorine content was maintained at 1.2%, and the temperatures were set as 950°C, 1050°C, 1150°C, 1250°C, 1350°C and 1450°C (as discussed in Section 3.2).

2.3. Analytical methods

The calcined samples were dissolved using an acid mixture of hydrogen peroxide (H₂O₂), aqua regia, and hydrogen fluoride (HF) in a volume ratio of 2:5:2 in the digestion instrument (ZEROM, China).

ContrAA 700 high-resolution atomic absorption spectrometer (Analytik Jena AG, Germany) equipped with an acetylene-air burner (10 cm slit) was used for the determination of copper, nickel, lead and zinc. Hollow cathode lamps were used as the radiation source with a lamp current of 3.0, 5.0, 5.5, and 6.0 mA for Cu, Ni, Pb, and Zn, respectively. The wavelength was adjusted 324.8, 232.0, 283.3, and 213.9 nm for Cu, Ni, Pb, and Zn, respectively. As well as spectral slit width were adjusted 0.5, 0.2, 0.8, 0.5 nm for Cu, Ni, Pb, and Zn, respectively. Integrated absorbance with an integration time of 3 s was used for signal evaluation (Aydemir et al., 2011; Galbeiro et al., 2014).

Duplicate measurements were carried out for calcined samples, and the average values were used to calculate the volatilization percentage according to Eq. (4):

\[ H = \left( 1 - \frac{K}{S/(1 - \text{LOI})} \right) \times 100\% \]  

where H represents the volatilization ratio of heavy metals; K (mg·kg⁻¹) represents the content of heavy metals in the cement clinker; S (mg·kg⁻¹) represents the content of heavy metals in raw materials; and LOI represents the loss on ignition.

An analysis of variance (ANOVA) of obtained data was conducted with R Software (The R Project for Statistical Computing), version 3.3.1.

3. Results

3.1. Effects of chlorine on the volatilization of Cu, Ni, Pb, and Zn

Fig. 2 shows the data obtained for heavy metal volatilization in present of AlCl₃·6H₂O. The volatilization ratios of Cu and Ni increased with increasing AlCl₃·6H₂O content. While the volatilization ratios of Pb changing slightly with increasing chlorine content of greater than 0.4%. The most significant improvement was observed for the volatilization ratio of Cu; 33.1%, Ni; 24.5%, and Pb; 17.7% as compared with that of the reference sample. Nevertheless, chlorine marginally affected the volatilization of Zn.

Fig. 3 shows the relationship between the volatilization ratio of heavy metals by the addition of FeCl₃·6H₂O. With increasing amount of Cl from 0% to 1.6%, the volatilization ratio of Ni

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>AlCl₃·6H₂O</th>
<th>FeCl₃·6H₂O</th>
<th>CaCl₂</th>
<th>NaCl</th>
</tr>
</thead>
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<td>M0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>A4</td>
<td>0.91(0.4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>A8</td>
<td>1.82(0.8)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>A12</td>
<td>2.72(1.2)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>A16</td>
<td>3.63(1.6)</td>
<td>1.93(0.4)</td>
<td>–</td>
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</tr>
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<td>F4</td>
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<td>3.86(0.8)</td>
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<td>F8</td>
<td>–</td>
<td>5.80(1.2)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>F12</td>
<td>–</td>
<td>7.73(1.6)</td>
<td>–</td>
<td>–</td>
</tr>
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<td>C4</td>
<td>–</td>
<td>–</td>
<td>0.63(0.4)</td>
<td>–</td>
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<tr>
<td>C8</td>
<td>–</td>
<td>–</td>
<td>1.25(0.8)</td>
<td>–</td>
</tr>
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<td>C12</td>
<td>–</td>
<td>–</td>
<td>1.88(1.2)</td>
<td>–</td>
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<td>C16</td>
<td>–</td>
<td>–</td>
<td>2.50(1.6)</td>
<td>–</td>
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<td>N4</td>
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<td>–</td>
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<td>0.66(0.4)</td>
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<tr>
<td>N8</td>
<td>–</td>
<td>–</td>
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<td>1.32(0.8)</td>
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<td>N12</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.98(1.2)</td>
</tr>
<tr>
<td>N16</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.64(1.6)</td>
</tr>
</tbody>
</table>

* Represents the content of chlorine as compared to that of raw meal.
significantly increased from 31.5% to 63.6%. The volatilization ratio of Cu changed slightly when the chlorine content was more than 0.8%. Moreover, with increasing chlorine content, the volatilization ratio of Pb significantly increased, followed by changing slightly with increasing chlorine content of greater than 0.8%. Similar to that observed in Fig. 2, the volatilization ratio of Zn almost exhibited changed slightly, corresponding to a volatilization ratio of approximately 60%.

As can be observed in Fig. 4, the volatilization behavior of heavy metals caused by the addition of CaCl2 was similar to that caused by the addition of AlCl3·6H2O. With increasing amount of Cl from 0% to 1.6%, the volatilization ratio of Cu significantly increased from 26.7% to 59.3%, while that of Ni exhibited almost no change with increasing chlorine content of greater than 0.8%. For the facile volatilization of heavy metals, the volatilization ratio of Pb increased from 61.4% to 80.7% when the addition of chlorine increased from 0% to 1.2%, whereas that of Zn was almost unchanged.

The effect of the addition of NaCl on the volatilization behavior of heavy metals was also investigated. As shown in Fig. 5, with increasing NaCl, the increase in the volatilization ratio of Cu (22.2%) and Ni (25.9%) was similar to those observed with the addition of AlCl3·6H2O, FeCl3·6H2O, and CaCl2. Nevertheless, the volatilization ratio of Pb almost exhibited little change, while that of Zn slightly decreased with increasing chlorine content of greater than 0.4%.

3.2. Effects of temperature on the volatilization of Cu, Ni, Pb, and Zn

Figs. 6–9 show the relationship between the temperatures and volatilization ratio of Cu, Ni, Pb as well as Zn in the incineration process. As can be observed from Fig. 6, the volatilization ratio of Cu increased greatly when the temperature increased from 950 °C to 1150 °C. With the addition of CaCl2, 45.2% of Cu was released at 950 °C; while at 1250 °C, 58.5% of Cu was released. Nevertheless, the amount of Cu evaporated only increased slightly at temperatures greater than 1250 °C.

Ni, which had a volatility similar to that of Cu, exhibited clear dependency on sintering temperature and chloride type, as shown in Fig. 7. That is, at temperature less than 1050 °C, less than 52% of Ni was volatilized, and the volatilization ratio of Ni increased to 61.1% with the addition of CaCl2. FeCl3·6H2O was very effective for Ni removal. At 950 °C, the volatilization ratio reached 48.3%; at temperatures greater than 1150 °C, the volatilization ratio possibly reached 61.3%. The addition of NaCl resulted in a Ni removal of greater than 46.4% at 1050 °C; moreover, at 1450 °C Ni removal of greater than 57.4% was achieved.
The volatilization of Zn with temperature.

As can be observed in Fig. 8, Pb can be easily volatilized during calcination. The volatilization ratio of Pb increased greatly when the temperature increased from 950 °C to 1050 °C. More than 44.8% of Pb was released at 950 °C, and up to 74.68% at 1050 °C with the addition of CaCl₂. On the other hand, the amount of Pb removed was less and did not exceed 65% with the addition of NaCl. At temperatures of greater than 1150 °C, greater than 80% of Pb was always volatilized with the addition of FeCl₃·6H₂O, as compared with NaCl, were significantly more effective for the volatilization of Zn, as shown in Fig. 9. With AlCl₃·6H₂O and FeCl₃·6H₂O, the volatilization of Zn was achieved approximately similar results, and both AlCl₃·6H₂O and FeCl₃·6H₂O, as compared with NaCl, were significantly more effective for the volatilization of Zn, as shown in Fig. 9. With AlCl₃·6H₂O, greater than 54.5% of Zn was released at 950 °C, and up to 63.1% at 1450 °C. On the other hand, NaCl typically exhibited a negative effect or almost no effect on Zn removal; especially at low temperatures, Zn removal was high instead.

4. Discussion

In order to understand effectiveness of the addition and type of chlorides, and temperature on the volatilization of heavy metals, the results of the experiment were analyzed by ANOVA study as shown in Table 4. The addition and types of chlorides demonstrated a strongly positive correlation (ANOVA, P < 0.05) with the volatilization of Cu, Ni, and Pb. For instance, the F values of the addition of chlorides in ANOVA study were 296.14 for Cu, 163.235 for Ni, and 41.727 for Pb. However, no significant correlation (ANOVA, F = 0.789, P > 0.05) existed between the addition of chlorides and the volatilization of Zn. In addition, there was strongly correlation (ANOVA, P < 0.05) between temperature and the volatilization of heavy metals. The volatilization of Cu was strongly positive correlation between the interaction of addition and type of chlorides, while the interaction of chlorides type and temperature had a modest influence on the volatilization of Ni.

To be useful as chlorinating agents, chlorides RCl₂ (R = Al, Fe, Ca, and Na) should release chlorine-containing gas (HCl) when they react with water according to the following general reactions:

\[ \text{RCl}_2 + \text{H}_2\text{O} (g) = \text{RO} + 2\text{HCl}(g) \]  \hspace{1cm} (5)

According to a previous study (Chou et al., 2009), heavy metals are assumed to be present as oxides at the envisaged temperature. The following of chemical reaction can account for the conversion of heavy metal oxides (MO) into volatile heavy metal chlorides (MCl₂) (M = Cu, Ni, Pb, and Zn):

\[ \text{MO} + 2\text{HCl}(g) = \text{MCl}_2(g) + \text{H}_2\text{O}(g) \]  \hspace{1cm} (6)

From the results, the added chlorides affect the removal of both Cu and Ni in a positive manner. Cu was predominantly present in MSW fly ash as Cu (II) (Tian et al., 2008); it was assumed that Cu was present as Cu (II) in sewage sludge. High amounts of chloride caused an increase in Cu and Ni volatilization, as shown in Figs. 2 and 3, attributed to the fact that the affinity of Cu and Ni for chlorine was greater than that of Zn for chlorine (Yan et al., 2001), and Cu was either volatile in the form of the chloride trimer (CuCl₃) and the monomer CuCl (Fraissler et al., 2009), or reacted first to form CuCl₂, followed by reduction to CuCl (Li et al., 2009). The removal of Zn appeared to be almost complete, i.e., more amounts of added chloride will not result in the increase of the evaporated amount. By contrast, the removal of Cu, Ni, and Pb in the treated sample might consequently continue to further increase with high amounts of chlorine. Pb was the most volatile metal, followed by Zn, which was removed by greater than 60% even without the use of chloride. The results obtained herein are consistent with those reported by Marani et al. (2003). Low amounts of Pb in sewage sludge would predominantly result in good heavy metal removal. Therefore, for reducing the emission of heavy metals into the atmosphere, the content of chlorine in raw meal should be strictly controlled during the co-combustion of sludge in cement kiln systems.

It is more difficult for sodium chloride, as compared to calcium chloride, to release Cl radicals (Chan et al., 1996; Tang et al., 2008). Hence, the increased volatilization percentages of heavy metals with the added NaCl are less than those spiked with CaCl₂. The maximum volatilization ratios of Cu with the addition of CaCl₂ and NaCl were 59.3% and 48.9%, respectively, as shown in Fig. 2. For some heavy metals (such as Zn), NaCl resulted in slightly decreased removal (Fig. 5 or Fig. 9), which was similar to that reported (Mattenberger et al., 2008) previously (increasing amounts of KCl decreased the removal of Cd, Cr, Cu, Ni, Pb, and Zn from sewage sludge ash). Probably, NaCl forms negative azeotropes with heavy metal chlorides (Nowak et al., 2012). When heavy metals such as Cu and Zn are present in high amounts in sewage sludge, they are possibly present as stable compounds (Nowak et al., 2010), which are hardly affected by Cl. These azeotropes or stable compounds probably wrap around the heavy metal surface, making it difficult for gaseous compounds (such as HCl) to diffuse inside heavy metal. As a result, Cl is not available for further reactions with Cu and Zn.

The volatilization of heavy metals with chlorides at different temperatures was also investigated. High temperature facilitated the formation of heavy metal chlorides, as well as their evaporation.
and diffusion inside the pellets. From Figs. 6–8, with increasing incineration temperature from 950 °C to 1450 °C, the volatilization of Cu, Ni, and Pb was enhanced. At a calcination temperature of greater than 950 °C, four different chlorides played an increasingly important role in the vaporization of Cu and Ni because chloride releases Cl radicals more easily when subjected to high thermal decomposition. As a result, the diffusion of Cl radicals is easier, and Cu or Ni is easily combined to form volatile chlorides. Thus, the volatilization ratio of Ni (NaCl) significantly increases to 17.6% with increasing temperature from 1050 °C to 1150 °C, as shown in Fig. 3. For volatile heavy metals, the volatilization ratio of Pb (CaCl2) increased to 66.7% at temperatures of greater than 950 °C. Zn exhibited a different tendency. Basically, no change in volatilization was observed at a calcination temperature of greater than 950 °C. As the temperature exceeds a certain value, heavy metals hardly volatilize. In the presence of Si and Fe, one part of heavy metals, such as Ni and Zn, possibly exists as heavy metal salts NiFe2O4 and ZnSiO4, respectively (Fraissler et al., 2009; Stucki and Jakob, 1998); while another part of heavy metals possibly solidifies in cement clinker minerals.

### 5. Conclusions

1. The addition of chlorides has strongly positive effect on the volatilization of Cu, Ni, and Pb. When the addition of CaCl2 increased from 0% to 1.2%, the volatilization ratio of Cu and Ni increased approximately 30%. However, chlorides did not exert a significant effect on the volatilization of Zn.

2. AlCl3·6H2O, FeCl3·6H2O, and CaCl2 were typically more effective for the removal of heavy metal volatilization compared with NaCl. Maximum volatilization ratio of heavy metals at 1450 °C were 60.8% for Cu (AlCl3·6H2O), 63.6% for Ni (FeCl3·6H2O), 83.0% for Pb (FeCl3·6H2O), and 67.5% for Zn (FeCl2·6H2O).

3. The higher the temperature, the easier formation of volatile heavy metal chlorides, resulting in dramatically increase in the volatilization of Cu, Ni and Pb. More than 44.8% of Pb was volatilized at 950 °C and increased to 74.68% at 1050 °C in the present of CaCl2.

### Acknowledgements

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### References


### Table 4

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<thead>
<tr>
<th>Factor</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorides addition</td>
<td>296.14***</td>
<td>162.35***</td>
<td>41.72***</td>
<td>0.789***</td>
</tr>
<tr>
<td>Chlorides type</td>
<td>33.51</td>
<td>15.068</td>
<td>19.981</td>
<td>12.143</td>
</tr>
<tr>
<td>Temperature</td>
<td>183.27</td>
<td>43.45</td>
<td>91.9***</td>
<td>12.105</td>
</tr>
<tr>
<td>Chlorides addition × type</td>
<td>15.18</td>
<td>2.638</td>
<td>3.171</td>
<td>3.991</td>
</tr>
<tr>
<td>Chlorides type × temperature</td>
<td>12.12</td>
<td>2.74</td>
<td>3.888</td>
<td>3.307</td>
</tr>
</tbody>
</table>

Note: ns: not significant.

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.


