

# Effects of hydroxyapatite addition on heavy metal volatility during tannery sludge incineration

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**Abstract** The effectiveness of hydroxyapatite (HAP) on volatilization reducing of heavy metals during incineration of tannery sludge was investigated. The tannery sludge was treated through doped with different content of HAP, and then incinerated in the tube furnace at the temperature of 600 °C and 900 °C. The results showed that the volatilization rates decreased by 10.19 % for Pb, 10.17 % for Zn, 7.40 % for Cu and 5.33 % for Cr at 600 °C when the HAP content was raised to 20 %. At 900 °C, the volatilization rates of Pb, Cr and Cu decreased by about 40.0 %, 24.0 % and 9.0 %, respectively, while volatilization of Zn can be considered nearly unchanged at around 5 %. The heavy metals can be stabilized effectively in the incineration after the pyromorphite-like minerals were formed in the sludge doped with HAP.

**Keywords** Heavy metals · Tannery sludge · Volatilization · Hydroxyapatite · Stabilization

## Introduction

Sewage sludge is the main by-product of wastewater treatment. It was reported that the increase rate of sludge production of China was 8–10 % every year (Ma and Zhang 2010). Sludge contains abundant organics, disease-causing microorganisms and heavy metals. This is especially true for tannery sludge, which contains heavy metals in high enough

and is classified as hazardous waste. It is, therefore, of great significance to find a proper way to dispose of tannery sludge to avoid secondary pollution.

Incineration is becoming more popular throughout the world. It is expected that its role will increase in the future because it is a convenient means to achieve a large reduction of sludge volume to a small quantity of ash, the thermal destruction of toxic organic constituents and pathogens, and the recovery of the flue gas energy (Werther and Ogada 1999). However, during incineration, heavy metals are not destroyed by high-temperature thermal treatment and the air pollution control devices may not always trap the sub-micrometer metal particulate and gaseous compounds (Falco et al. 2010). Chandler et al. (2003) and Zhang et al. (2008) have shown that vaporized metals can form condensable particulates, which can then deposit on cool surfaces or be emitted in the atmosphere. It is also evident that more volatile metals such as Hg, Pb and Cd are significantly present in the stack emission, despite the scrubber stages, but in line with the volatility of the heavy metals (Van de Velden et al. 2008).

Heavy metal emissions from waste incineration plants have become a great environmental concern because of their toxicity for both human health and environment. Consequently, how to reduce the volatilization of heavy metals effectively is crucial to the sludge incineration treatment.

Recently, substantial efforts have been made to fix heavy metal in the bottom ash and decrease the heavy metals emission to the atmosphere during the incineration process by means of stabilization and absorption (Cheng et al. 2001; Naruse et al. 2003), which makes the incineration process more environmentally friendly. It was generally recognized that the apatite group minerals in nature with the formula  $A_5(PO_4)_3(F, Cl, OH)$ , where  $A = Pb, Zn, Cd, Cu$ , etc., is one of the most thermodynamically stable phosphate species (Piantone et al. 2003). The formation of apatite structure minerals through phosphate-based pre-treatment has been

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increasingly applied and plays an important role in the stabilization of heavy metal-bearing incineration residuals with less leaching (Eighmy et al. 1998; Bournonville et al. 2004; Singh et al. 2006; Sukandar et al. 2009; Quina et al. 2010). Phosphoric acid was also used to pre-treat the heavy metals-bearing waste before the incineration in order to reduce the vaporization of heavy metal at high temperature. The high efficiency of it for abatement heavy metals vaporization was pointed out by various studies (Rio et al. 2007; Tang et al. 2008a,b; Sun et al. 2011).

Likewise, hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ; HAP) was reported to have favorable stabilization on heavy metals through being partly substituted by divalent heavy metal cations (Qian et al. 2008a, b). It used to stabilize heavy metals in place of a phosphate amendment during in situ chemical remediation of contaminated soil to decrease their mobility and reduce bioavailability, and it was proved by previous research studies that HAP can effectively immobilize heavy metals in water and soil (Chen et al. 2007; Raicevic et al. 2009; Islam et al. 2010).

As an additive, mineral apatite has been shown to be the most economical and effective choice for the remediation of contaminated sites due to their ready availability, low cost and risk reduction of eutrophication (Qian et al. 2009; Mignardi et al. 2012). However, whether or not HAP addition in the sludge pre-treatment can reduce the volatility of heavy metals effectively during incineration process is merely paid attention to. In this article, we pre-treated the tannery sludge with the addition of HAP powders as a phosphate-based binder for the reduction of heavy metal volatility before incineration. The thermal behavior of pre-treated sludge and volatility characteristic of heavy metals were investigated. Moreover, the mechanisms and the reaction products resulting from chemical stabilization of tannery sludge with HAP are also discussed.

## Materials and methods

### Materials

Tannery sludge was collected from Wenzhou, China in 2011. The water contained in sludge was extracted by mechanical dewatering methods and the moisture content of the samples was decreased to about 75 %. The samples were stirred uniformly and then dried at 65 °C.

At room temperature, seven samples of tannery sludge, each weighting 30 g, were placed in beakers. The HAP nanopowders (Aladdin Chemistry Co. Ltd., <100 nm) were doped according to the different mass ratio between  $\text{PO}_4^{3-}$  and dried sludge (3 %, 5 %, 7 %, 10 %, 15 % and 20 %), respectively, together with 30 ml distilled water, and then the mixture was agitated with the magnetic stirrer to make

sure each sample was mixed thoroughly. After being aged for 7 days at room temperature, the pre-treated sludge samples were put in a drying bed at 60 °C in order to avoid moisture interference. After grinding, the size of formed products almost remained the same. Finally, the formed products were taken for incineration treatment (30 min).

### Apparatus and experimental procedure

As shown in Fig. 1, the apparatus used in this study was composed of an electric-heated tube furnace and an air supply. The heart of the furnace was a quartz tube burner, 600 mm long and 40 mm in inner diameter. A porcelain boat moved by quartz rod was designed to feed the sludge into the combustion chamber. The combustion temperature at the center inside the burner tube was monitored by a thermocouple and controlled by a programmed temperature controller. Finally, the oven is connected to two impingers filled with a solution of 5 %  $\text{HNO}_3$  allowing the collection of the volatilization fraction of the heavy metals to be determined.

Experiments were carried out by combustion of few grams of prepared samples (25 g), which were placed in a porcelain boat pushed into a quartz tube. During incineration experiments, air flow rate is fixed at 120 l/h. The influence of temperature (600 °C, 900 °C) and composition of the matrix ratio of HAP on the vaporization of heavy metals (Pb, Zn, Cu and Cr) were studied.

### Analysis methods

The bottom ash and porcelain boat was weighted after the incineration test is finished, and the boat is pulled out and cooled down, and the weight of bottom ash can be calculated through subtracted the weight of boat from the total weight. Then the ash is ground to fine powder with 69.2–138.0  $\mu\text{m}$  of  $d_{80}$ , from which 500 mg is weighed and digested in concentrated HF,  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  in pressure microwave. The concentrations of heavy metals in the aqueous solution are then analyzed by ICP (Optima2100DV; Perkin-Elmer, USA). Two parallel tests were carried out, and for each sample, two parallel digestions were conducted on and their average values are provided in the text. The vaporization percentage is calculated according to:

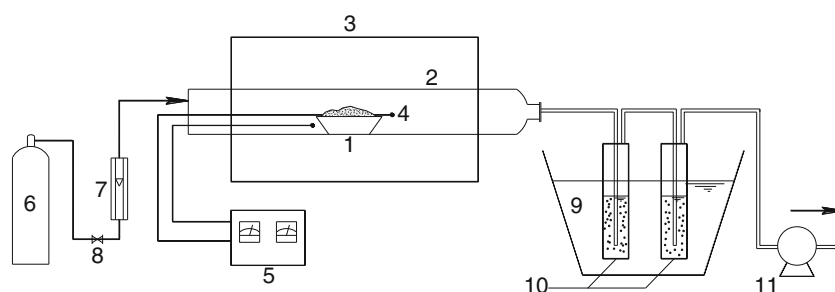
$$\text{Vaporisation (\%)} = 100 \times \frac{M_S - M_B}{M_S},$$

where,  $M_S$  is the initial metal content in sludge sample and  $M_B$  is the final metal content in the bottom ash.

The mineral phases of samples were identified by X-ray diffraction (XRD) measurement. The X-ray diffraction analysis was performed on a TD-3500 X-ray diffractometer using

**Fig. 1** Laboratory tube furnace for combustion experiment.

1 porcelain boat, 2 quartz tube, 3 tube furnace, 4 thermocouple, 5 thermocontroller, 6 air supply, 7 flow meter, 8 regulating valve, 9 water cooler, 10 impingers (5 %  $\text{HNO}_3$ ), 11 aspirator pump



MDI Jade 5.0 software (Materials Data Inc., Liverpool, CA). The operating condition of X-ray is D/max- $\gamma$   $\beta$  X-ray diffractometer. XRD patterns were obtained from  $10^\circ$  to  $80^\circ$  ( $2\theta$ ) at the scanned speed of  $6^\circ/\text{min}$ . The thermal behaviors of samples were examined by DTA – TGA using a ZRY-2P simultaneous DTA – TGA analyzer (Q600sdt, TA, USA) while the samples were heated at a rate of  $10^\circ\text{C}/\text{min}$  from  $50^\circ\text{C}$  to  $900^\circ\text{C}$  in air. Samples weighed about 10 mg in mass, and they were put into a Pt–Rh crucible. All curves were evaluated using the TA Instruments software.

## Results

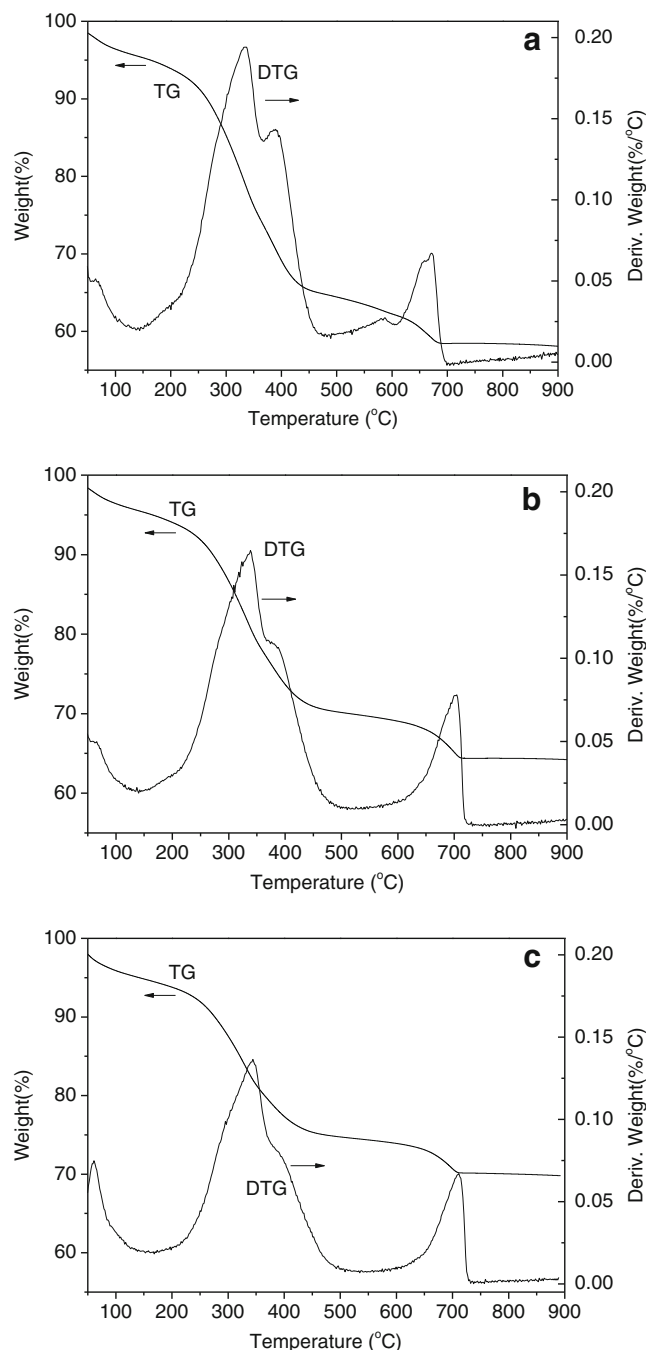
### Thermal behavior analysis

Figure 2a shows the TG–DTG curves of the tannery sludge from  $50^\circ\text{C}$  to  $900^\circ\text{C}$ . It can be seen from Fig. 2a that the DTG curve of tannery sludge changes slightly from  $50^\circ\text{C}$  to  $200^\circ\text{C}$  with the weight loss of about 6 % in TG analysis. Moreover, the DTG curve revealed two obvious peaks. Combined with the TG curve, the first peak occurs from  $250^\circ\text{C}$  to  $450^\circ\text{C}$  with about 21 % weight loss, and another peak occurs in the temperature range of  $600$ – $700^\circ\text{C}$  with about 6 % weight loss. After being finally held from  $700^\circ\text{C}$  to  $900^\circ\text{C}$ , the rate of mass loss was approximately zero.

Figure 2b and c shows the results of TG–DTG curves of pre-treated tannery sludge with addition of 10 % and 20 % HAP. Similar peaks are also observed in the DTG curves of pre-treated sludge. For the sludge with addition of 10 % HAP, the first peak occurs in the temperature range  $250$ – $450^\circ\text{C}$  and the corresponding weight loss is 17.6 %, while the other occurs in the temperature range  $600$ – $730^\circ\text{C}$ , and the corresponding weight loss is about 5.5 %. The peaks of the sludge doped with 20 % HAP also appear in the DTG curve from  $250^\circ\text{C}$  to  $450^\circ\text{C}$  with 15 % weight loss and from  $600^\circ\text{C}$  to  $750^\circ\text{C}$  with 4.3 % weight loss, respectively.

### Volatilization characteristic of heavy metals

In order to study the volatility abatement potential of heavy metals in tannery sludge, the sludge doped with different



**Fig. 2** TG–DTG curves of the tannery sludge (a) and with addition of 10 % (b) and 20 % HAP (c)

contents of HAP was carried out with incineration experiments. Figure 3 shows the relationship between the amount of HAP and the volatility percentages of zinc, lead, chromium and copper incinerated at temperature of 600 °C and 900 °C.

As shown in Fig. 3a, the influence of HAP on volatility abatement of heavy metal was rather small with addition increase from 0 % to 15 % at 600 °C. When the HAP content was raised to 20 %, the volatility percentages decrease significantly from 12.22 % to 2.05 % for zinc, from 12.9 % to 2.71 % for lead, from 10.64 % to 5.31 % for chromium and from 14.45 % to 7.05 % for copper. At 900 °C, the volatility percentage of chromium, lead and copper reduced gradually with increasing with HAP content as shown in Fig. 3b. When the content of HAP increases from 0 to 20 %, the volatility percentages decrease significantly from 36.13 % to 11.93 % for chromium, from 73.09 % to 33.13 % for lead and from 14.95 % to 5.98 % for copper. Nevertheless, the volatility percentage of Zn can be considered nearly unchanged at around 5 %.

#### X-ray diffraction (XRD) analysis

Crystal phases of the bottom ash of tannery sludge and it doped with 10 % and 20 % HAP were determined by XRD. Figures 4 and 5 show the crystal phases in the bottom ash of raw and pre-treated tannery sludge at the temperature of 600 °C and 900 °C, respectively.

At 600 °C, the crystal phases of Cr, Zn, Pb, Cu are Cr-O, Pb<sub>2</sub>O<sub>3</sub>, CuCrO<sub>4</sub> and ZnCr<sub>2</sub>O<sub>4</sub> in the bottom ash of raw sludge are as shown in Fig. 4a. When doped with HAP, the new crystal phases, such as Ca<sub>8</sub>Pb<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, Ca<sub>8</sub>Pb<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, CrPO<sub>4</sub>, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, appear in the bottom ash of sludge pre-treated with HAP as shown in Fig. 4b and c.

As shown in Fig. 5, there is no significant difference in XRD patterns of untreated sludge bottom ash between 600 °C and 900 °C. After pre-treated by HAP, XRD analysis showed that the main mineral phases of the bottom ash include Cu<sub>3</sub>(PO<sub>4</sub>)(OH)<sub>3</sub>, Ca<sub>19</sub>Cu<sub>2</sub>(PO<sub>4</sub>)<sub>14</sub>, Ca<sub>8</sub>Pb<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, CaZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O, as well as CrPO<sub>4</sub>, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> as shown in Fig. 5b and c.

#### Discussion

The reaction scheme of sludge pyrolysis is very complex, and can be considered to take place in two stages (Tang et al. 2008b). As shown in Fig. 2a, the two stages also be observed in the DTG curves, and before the first stage a weight loss is observed between 50 °C and 100 °C. It has been reported previously and can be attributed to the loss of moisture and the very light volatile materials (Tang et al. 2008b; Calvo et al. 2004). The most abundant release of volatile matter was observed in the first stage, and the most

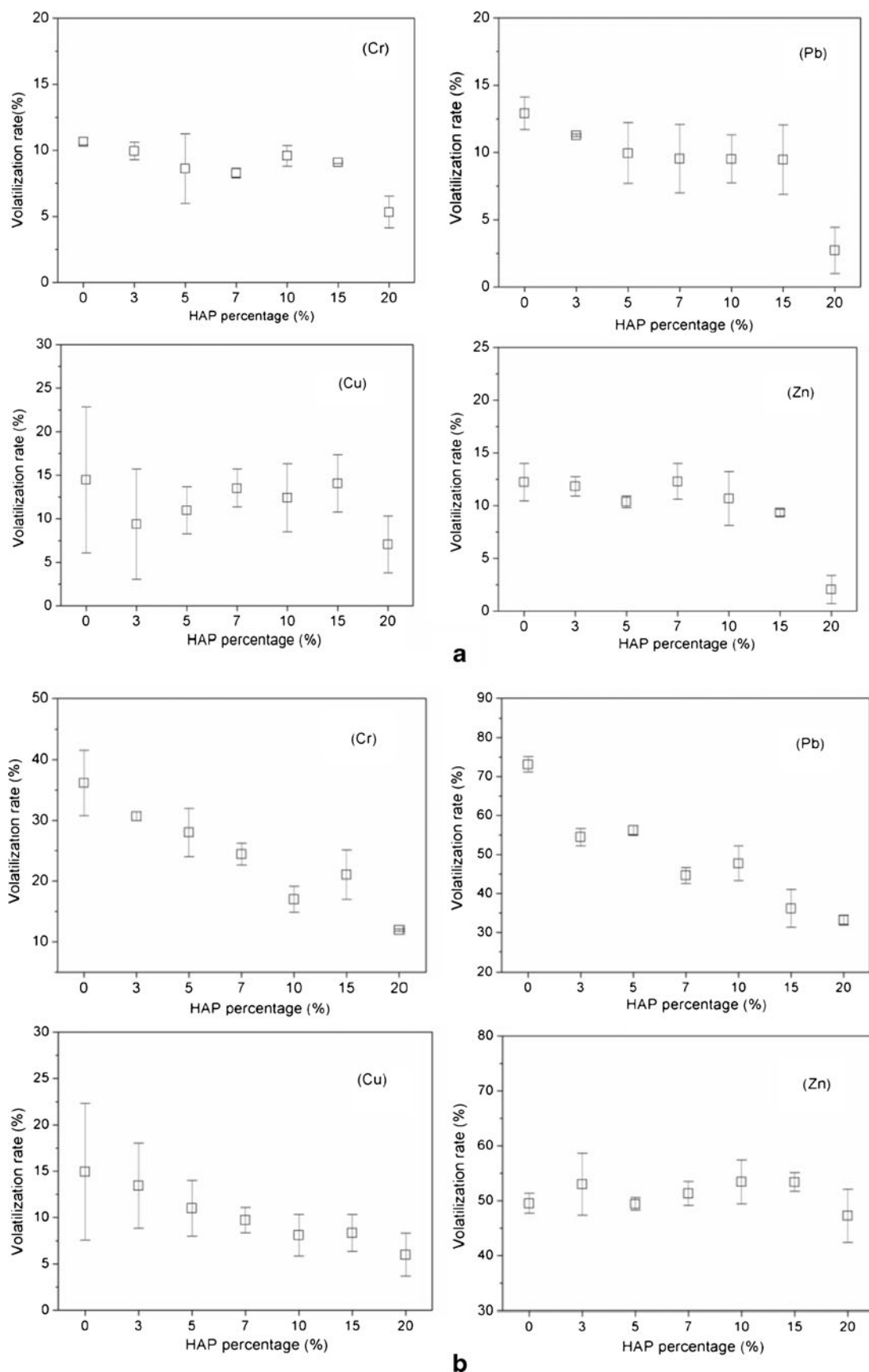
of organic matter was decomposed and devolatilized in the stage. In this stage, the peak of DTG curve have a shoulder at 380 °C which can be attributed to decomposition of more complex organic structures corresponding to a small fraction. In the second stage of sludge pyrolysis, the peak most likely corresponds to the decomposition of the carbonates (Caballero et al. 1997; Rodrigues et al. 2008).

When sludge was pre-treated through addition of HAP, the thermogravity characteristic is not changed significantly except the small change in weight loss of two stages as shown in Fig. 2b and c, due to the thermostability of HAP. According to the literatures report, calcium zinc HAP, calcium cadmium HAP and HAP decomposed and lost structure water when temperature exceeded 600 °C (Qian et al. 2008a, b; Sugiyama et al. 1999), which also was responsible for the change of weight loss in the second stage.

As shown in Fig. 3, the heavy metal volatilization rate decreased with the increase of HAP content as a whole at 600 °C. It can be seen that the high efficiency to abate the heavy metal volatilization can be achieved when the content of HAP increases to 20 %. Especially, the volatilization of Zn and Pb decreased significantly. Combined with the XRD patterns (Fig. 4), it can be found that formations such as Ca<sub>8</sub>Pb<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and CaZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O were formed after doped with HAP at 600 °C. On the other hand, Cu and Cr was also immobilized to a certain extend by HAP and the volatilization rates of Cu and Cr reduced 7.05 % and 5.33 %, respectively, as shown in Fig. 3a. The much more thermostable phosphate minerals, such as CrPO<sub>4</sub> Cu<sub>2</sub>(PO<sub>3</sub>)<sub>4</sub>9H<sub>2</sub>O and Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, were formed according to XRD patterns in Fig. 4.

During incineration at 900 °C, the high efficiency of volatilization abatement of Pb, Cr and Cu was also achieved except Zn, and the volatilization rates of Pb, Cr and Cu decreased by about 40.0 %, 24.0 % and 9.0 %, respectively. The pyromorphite-like minerals, such as Cr<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CaZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O and Ca<sub>8</sub>Pb<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, were also formed in the bottom ash of pre-treated sludge by HAP. These minerals kept a stable structure even at 900 °C. Hence, it revealed that it was the formation of pyromorphite-like minerals that contributed to the volatilization, reducing heavy metals in the tannery sludge pre-treated with HAP.

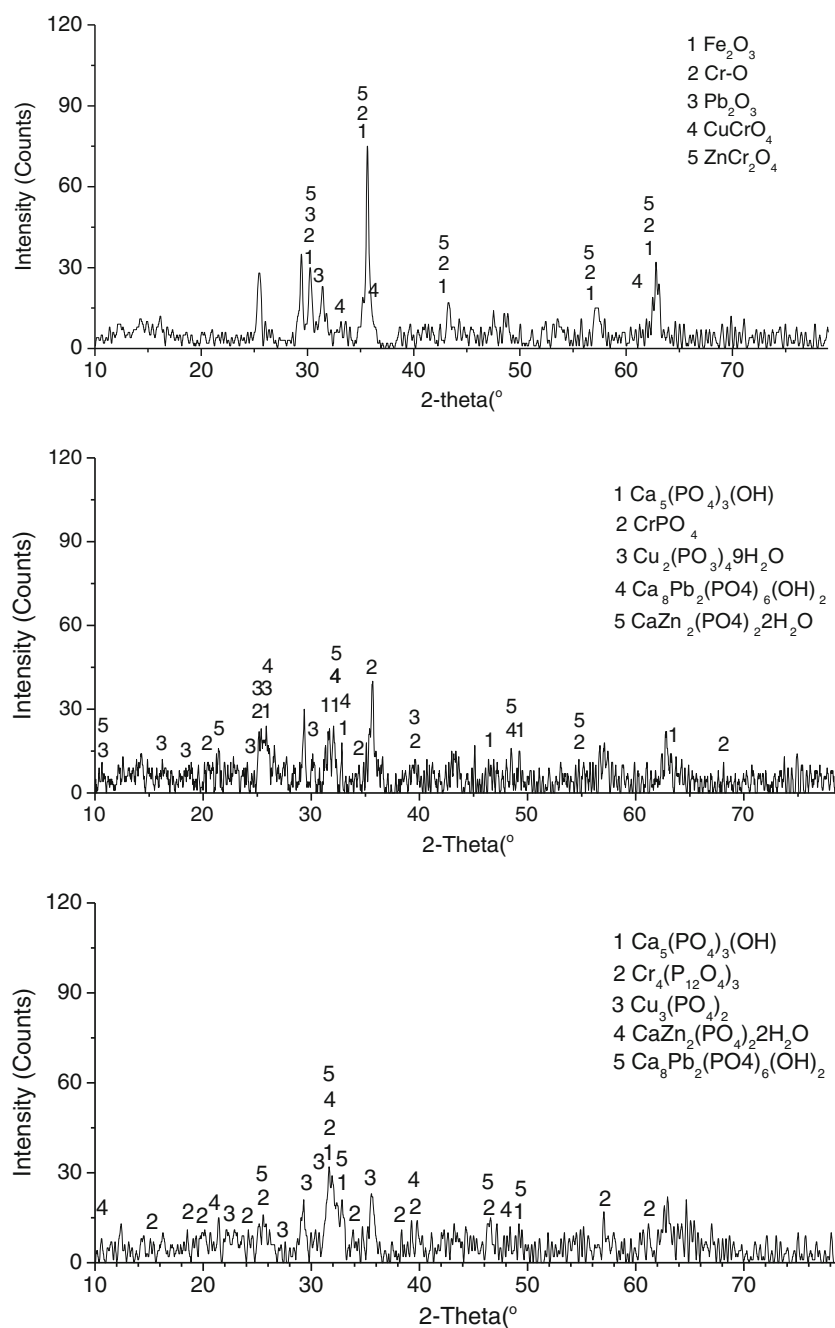
Previous research suggested that the reaction mechanisms for metal immobilization by phosphate minerals (i.e., HAP, phosphate rock) include: (a) ion exchange, (b) surface complexation, (c) dissolution of the original phosphate minerals and precipitation of new metal phosphates, and (d) substitution of Ca in phosphate by other metals during recrystallization (co-precipitation) (Jeanjean et al. 1994; Ma et al. 1994; Xu et al. 1994). Moreover, Mignardi et al. (2012) pointed out that the proposed mechanism of HAP in immobilizing Cd, Zn, Pb and Cu involves both surface complexation of the heavy metals on the phosphate grains and partial dissolution of the HAP and precipitation



**Fig. 3** Volatilization percentages of heavy metal during thermal treatment of pre-treated sludge at 600 °C (a) and 900 °C (b)

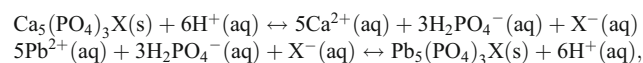


**Fig. 4** X-ray diffraction patterns of the bottom ashes of untreated sludge (**a**) and sludge doped with 10 % (**b**) and 20 % (**c**) HAP at 600 °C



of heavy metal-containing phosphate. However, it was also suggested by previous studies that the mechanisms of Cu, Cd, and Zn immobilization by phosphate amendments are quite different (Ma et al. 1994; Da Rocha et al. 2002; Raicevic et al. 2009). According to Figs. 4 and 5, CaPbHAP appeared in the bottom ash as a major mineral phase at 600 °C, and the structure water was thermally lost partly to form  $\text{Pb}_3(\text{PO}_4)_2$  at 900 °C. Pb immobilization by HAP contributed to the formation of a new lead and calcium phosphate solid solution, CaPbHAP, which was in agreement with the results of Mavropoulos et al. (2002). It indicated that the main immobilization mechanism for Pb was due to the

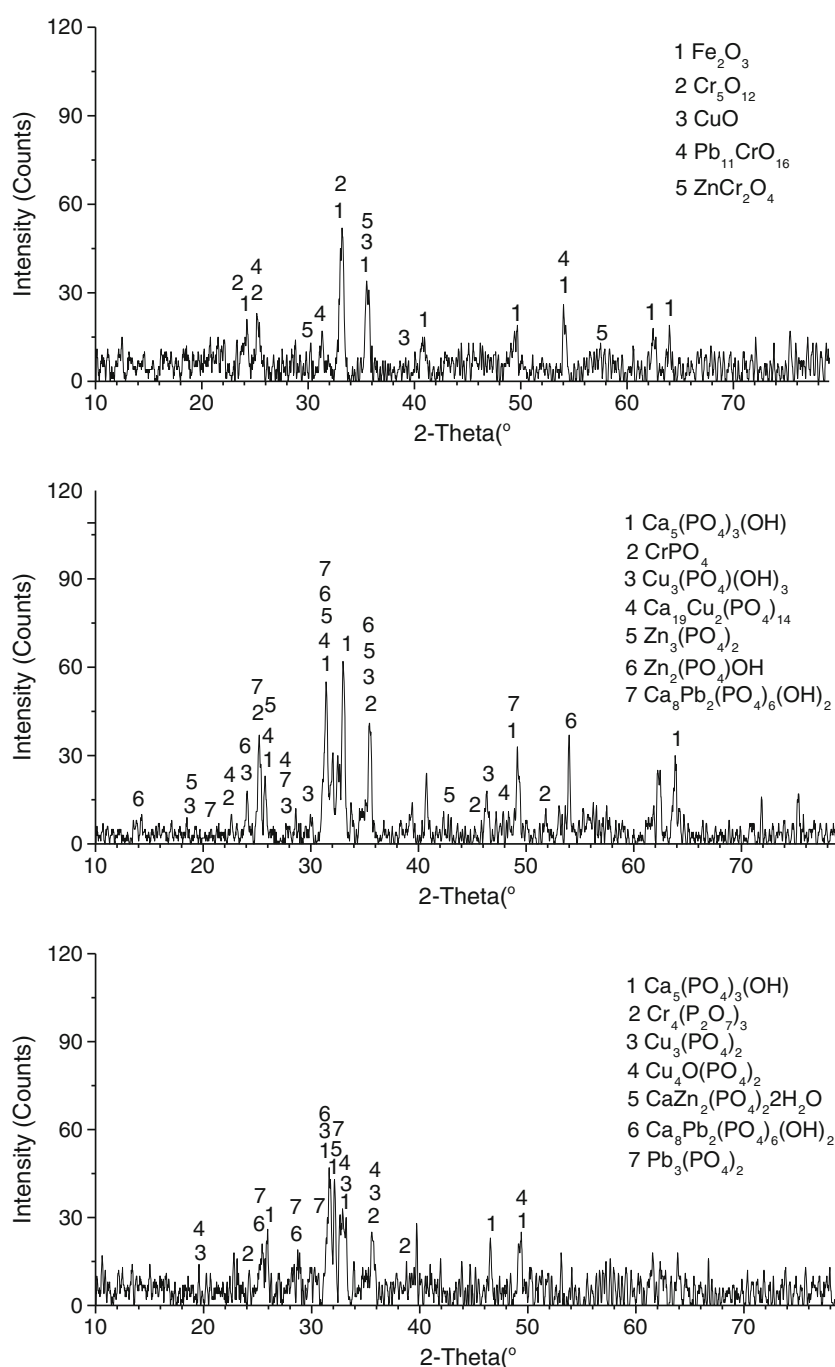
dissolution/precipitation as reported by Hettiarachchi et al. (2001), and the process can be expressed as follows:



where  $\text{X} = \text{F}^-$ ,  $\text{OH}^-$ , or  $\text{Cl}^-$ .

Hence, Pb can be stabilized effectively by HAP in the incineration process at the temperature of 600 °C and 900 °C, respectively, as shown in Fig. 3. Xu et al. (1994) suggested that surface complexation and calcium–zinc HAP co-precipitation were the primary processes in the

**Fig. 5** X-ray diffraction patterns of the bottom ashes of untreated sludge (a) and sludge doped with 10 % (b) and 20 % (c) HAP at 900 °C



immobilization of Zn by HAP, while ion exchange and solid diffusion might be secondary processes. Several studies experimentally determined similar immobilization mechanisms for Zn (Raicevic et al. 2009; Mignardi et al. 2012). Accordingly, it can be inferred that the good stabilization of Zn achieved at 600 °C was attributed to a surface complex mechanism, and XRD analysis did not detect any new minerals of Zn as major phase. The presence of  $\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  detected by XRD (Fig. 4) as a minor phase confirmed the occurrence of secondary processes such as ion exchange and solid diffusion. At the incineration temperature of 900 °C,

volatilization of Zn decreased slightly with the increase of HAP. It could be due to the lower thermostability of surface complex compounds. Most of  $\text{Zn}^{2+}$  on HAP was still volatilized at 900 °C because Zinc is the most volatile metal. A small fraction that substituted  $\text{Ca}^{2+}$  in the HAP to form the  $\text{CaZnHAP}$  was stabilized even at 900 °C.

Similar fixation mechanism for Cu was obtained by Šljivić et al. (2009) and Mignardi et al. (2012): Cu stabilization involved both surface complexation on the phosphate grains and partial dissolution of HAP and precipitation of heavy metal-containing phosphates. XRD patterns showed

Cu metal phosphate minerals as minor phases ( $\text{Cu}_3(\text{PO}_4)_2$ ,  $\text{Cu}_2(\text{PO}_3)_4 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}_{19}\text{Cu}_2(\text{PO}_4)_{14}$  and  $\text{Ca}_{18}\text{Cu}_3(\text{PO}_4)_{14}$ ), which implied that the mechanism of surface complexation had a major role in stabilization of heavy metal. It was also proved that it is thermodynamically favorable for dissolved Pb to react with P to form Pb phosphate, but less so for Zn and Cu to form Zn and Cu phosphates (Cao et al. 2009). These complex compounds cannot abate the volatilization of Cu further at high temperature due to its lower thermostability than that of pyromorphite-like minerals. On the other hand,  $\text{CrPO}_4$ ,  $\text{Cr}_4(\text{P}_{12}\text{O}_4)_3$ , and  $\text{Cr}(\text{P}_2\text{O}_7)_3$  was also identified by XRD as minor crystalline phase in the bottom ash of pre-treated tannery sludge at incineration temperature of 600 °C and 900 °C. Thus it can be inferred that structure recombination between Cr and HAP might take place in the incineration after dissolution/precipitation. These pyromorphite-like minerals are quite stable, and thus it can be illustrated that the formation of insoluble pyromorphite-like minerals did substantially abate Cr from volatilization in pre-treated tannery sludge.

Therefore, Pb can be stabilized more effectively than other heavy metals by HAP during incineration as shown in Fig. 3, because it can form pyromorphite-like minerals more easily with HAP. It was also consistent with the literature report that apatite is extremely effective at immobilizing  $\text{Pb}^{2+}$  but less effective for  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  (Boisson et al. 1999; Chen et al. 2003; Cao et al. 2003; Melamed et al. 2003; Seaman et al. 2001).

## Conclusion

This study investigated the effectiveness of HAP in volatilization reducing of heavy metal during incineration of tannery sludge. The results revealed that the decrease of volatilization rates of heavy metals during incineration were significant at 600 °C in the presence of 20 % HAP. At 900 °C, the high efficiency of volatilization abatement of Pb, Cr and Cu was also achieved except Zn. The chemical mechanisms governing the volatilization behaviors of heavy metals in pre-treated tannery sludge in the incineration process was proposed through XRD analysis. After doped with HAP, heavy metals react with HAP through complexation of metal ions onto the surface of phosphate grains, dissolution/precipitation. The heavy metals can be stabilized effectively in the incineration after the pyromorphite-like minerals were formed. The efficiency of HAP for stabilizing heavy metals during incineration depends on the inclination of heavy metals to form the pyromorphite-like minerals due to its much more thermostability than that of the complex compounds. Pre-treatment tannery sludge with proper amount of

HAP can be considered among the measures to abate heavy metals volatilization in the process of tannery sludge incineration.

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