



# Stabilization of heavy metals in lightweight aggregate made from sewage sludge and river sediment



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## HIGHLIGHTS

- We use sewage sludge and river sediment to produce lightweight aggregate (LWA).
- We investigate the effects of  $K$  on the stabilization of heavy metals in LWA.
- Minimum heavy metals leachability can be obtained at  $K$  between 0.175 and 0.2.
- Heavy metal solidification rates above 95% in acidic solutions.
- LWA can be used as an environmentally safe material for civil engineering.

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## ABSTRACT

The primary goal of this research is to investigate the stabilization of heavy metals in lightweight aggregate (LWA) made from sewage sludge and river sediment. The effects of the sintering temperature, the  $(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$  ratio ( $K$  ratio),  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  (at fixed  $K$  ratio), pH, and oxidative conditions on the stabilization of heavy metals were studied. Sintering at temperatures above  $1100^\circ\text{C}$  effectively binds Cd, Cr, Cu and Pb in the LWA, because the stable forms of the heavy metals are strongly bound to the aluminosilicate or silicate frameworks. Minimum leachabilities of Cd, Cr, Cu and Pb were obtained at  $K$  ratios between 0.175 and 0.2. When the LWA was subjected to rigorous leaching conditions, the heavy metals remained in the solid even when the LWA bulk structure was broken. LWA made with sewage sludge and river sediment can therefore be used as an environmentally safe material for civil engineering and other construction applications.

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## 1. Introduction

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to increasing public opposition and stricter regulatory pressure because of groundwater pollution, odor emissions, soil contamination and heavy metal pollution [1–8]. Heavy metal pollution affects the use of sewage sludge [9]. Heavy metals such as Cu, Cd, Pb, Hg and Cr are found at relatively high concentrations in sewage sludge [10]. The total heavy metal content of sewage sludge is about 0.5–2.0% (dry weight), and in some cases may be as high as 4% (wet weight), particularly for metals such as Cd, Cr, Cu, Pb, Ni and Zn [11]. Therefore, land application of contaminated sludge releases heavy metals

into the soil when the sludge organic matter decomposes [12]. Fur-

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ing countries, sludge is often disposed of in open fields because of the shortage of appropriate disposal facilities, resulting in serious problems because of heavy metals leaching into groundwater, surface water and soil [14].

In recent years, various protocols for removing or stabilizing heavy metals in sewage sludge have been studied to minimize potential risks to human health and the environment. Heavy metal concentrations in sewage sludge can be reduced by chemical extraction, bioleaching, electrokinetic processes and supercritical fluid extraction [15]. An effective method for decreasing heavy metals leaching from sludge is stabilization, which can be achieved using physicochemical reactions at high temperatures or pressures. Re-use and environmental “neutralization” of waste are among the current energy-efficient and environmental-friendly methods for waste treatment [16].

Using sludge to make lightweight aggregates (LWAs) or ceramics is a promising solution because it not only avoids secondary

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pollution, but also adds value to the sludge by transforming it into a useful material [17–24]. LWA production methods have added sewage sludge or sewage sludge ash to clay. However, these methods require large quantities of clay, which is nonrenewable resource, and excessive exploitation will lead to its depletion, and may also lead to the destruction of arable land. The manufacture of clay bricks is currently prohibited in China. This has prompted research into clay substitutes for the production of LWA to contribute to both the sustainable development of natural resources and the protection of the environment.

River sediment contains  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ , which are the main components of LWA. Previously we verified that LWA produced with sewage sludge and river sediment is an effective and feasible way of reusing this “waste” [25]. To the best of our knowledge, there have only been a few studies investigating the effectiveness of heavy metals in LWAs made from sewage sludge and river sediment. Therefore, the objectives of this study were to:

- evaluate the safety of LWA made using sewage sludge and river sediment as primary materials,
- assess the effect of sintering temperature and  $K$  ratio on the stabilization of heavy metals,
- assess the effect of the oxidative conditions on leaching behavior,
- assess the effect of pH and  $\text{H}_2\text{O}_2$  on the leachability of heavy metals,
- investigate the heavy metal forms present in the LWA, and
- analyze the solidification mechanism and establish effective parameters for evaluating the application of LWA.

## 2. Materials and methods

### 2.1. Materials

Sewage sludge was obtained from the Wenchang Wastewater Treatment Plant in Harbin, China. River sediment was obtained from the Hejiagou River, which flows through Harbin.  $\text{Na}_2\text{SiO}_3$  with a modulus of approximately 3.2 was used. Sewage sludge and river sediment were dried to constant weight at  $105^\circ\text{C}$ , then ground and passed through a 0.154 mm sieve. The chemical characteristics of the sewage sludge and river sediment are shown in Table S1 (Supporting Information).

### 2.2. Methods

#### 2.2.1. Preparations of LWA

Ten grams of sewage sludge, river sediment and sodium silicate mixture, at a mass ratio of 1:1:0.1 (w/w/w), were mixed with 8 mL of water [25]. The mixture was then made into 6–10 mm pellets and dried at room temperature ( $25^\circ\text{C}$ ) for at least 5 days. The samples were dried further at  $110^\circ\text{C}$  in a blast roaster for 24 h. The samples were then prepared by heating from an initial temperature of  $25^\circ\text{C}$  at a rate of  $8^\circ\text{C min}^{-1}$  in a muffle furnace, with 10-min constant temperature periods at  $200^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $800^\circ\text{C}$ . Finally, separate samples were baked at the test temperatures ( $950$ ,  $1000$ ,  $1050$ ,  $1100$ ,  $1150$ , and  $1200^\circ\text{C}$ ) for 30 min, before being allowed to cool naturally to room temperature. The samples were stored in a desiccator before analyzing their physical properties and leachability. The LWA production process is shown in Fig. S1 (Supporting Information).

To investigate the effectiveness of the solidification of heavy metals (Cr, Cd, Pb and Cu) in the sewage sludge and river sediment during the production of LWA, a solution of heavy metals ( $\text{K}_2\text{CrO}_4$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) was added to the raw materials during the LWA pellet production. The contents of Cd, Cr, Cu and Pb were determined from analysis of activated

sludge at different locations in China as shown in Table S2 (Supporting Information). The simulated heavy metal concentrations in the raw materials (sewage sludge and river sediment mixed, at mass ratio 1:1) were: Cd  $50 \mu\text{g g}^{-1}$ ; Cr  $1000 \mu\text{g g}^{-1}$ ; Pb  $1000 \mu\text{g g}^{-1}$  and Cu  $500 \mu\text{g g}^{-1}$ .

#### 2.2.2. Characterization of LWA

##### (1) Chemical analysis

The chemical components of sewage sludge and river sediment were determined using a Philips PW 4400 XR spectrometer (X-ray fluorescence, XRF, PANalytical, Amsterdam, the Netherlands). Powder X-ray diffraction (XRD) spectra of LWA were recorded on a D/max- $\gamma\beta$  X-ray diffractometer at 50 mA and 40 kV, Cu  $K\alpha$  radiation (Rigaku, Japan).

##### (2) Heavy metal leaching test

The toxicity of the aggregate samples was determined using a modified method based on the toxicity characteristic leaching procedure [19], a standard method for determining waste leachability, and an update of the hazardous waste extraction procedure provided by the US Environmental Protection Agency. The leaching test was conducted on a solution prepared at a liquid–solid ratio of 1 L 200 g, and stirred at 110 rpm for 24 h. The supernatant was analyzed using a PerkinElmer Optima 5 300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES, Waltham, MA, USA).

## 3. Results and discussion

### 3.1. Effect of sintering temperature on the stabilization of heavy metals

To gain a better understanding of the effect of heat treatment on the leaching characteristics of heavy metals in LWAs, the LWAs were broken into pieces of different diameter ( $D$ ): (1) unbroken LWA, (2)  $2 \text{ mm} \leq D \leq 5 \text{ mm}$  and (3)  $D \leq 2 \text{ mm}$

The data presented in Fig. 1 show that the leachable Cd, Cr, Cu and Pb contents in the three different diameter LWA samples decreased significantly as the sintering temperature increased from  $950$  to  $1050^\circ\text{C}$ . The leachable Cd and Cr contents in the LWA samples of each diameter changed only slightly at sintering temperatures above  $1050^\circ\text{C}$ . The leachable Cu and Pb contents also only changed slightly at temperatures above  $1100^\circ\text{C}$ . Increasing the sintering temperature above  $1100^\circ\text{C}$  only had a minor influence on the leachability of the four heavy metals. We also observed that the smaller diameter ( $2 \text{ mm} \leq D \leq 5 \text{ mm}$  and  $D \leq 2 \text{ mm}$ ) samples prepared at temperatures between  $950$  and  $1050^\circ\text{C}$  had more leachable heavy metals, but this difference was less pronounced in samples prepared above  $1050^\circ\text{C}$ .

Samples prepared between  $950$  and  $1050^\circ\text{C}$  had relatively “loose” internal structures and semi-developed crystalline phases, so the heavy metals were not completely incorporated into the LWA and were easily leached. Sintering temperatures above  $1050^\circ\text{C}$  promoted the generation of a liquid phase followed by a crystal phase. This resulted in more efficient heavy metal solidification, with the heavy metals being locked inside the crystalline structures, even when the LWA samples were broken. Solidification of heavy metals was consistently observed for LWAs sintered above  $1050^\circ\text{C}$ .

XRD analyses identified the form of the heavy metals in the LWA and transformations of heavy metals that occurred in the heating process (Fig. 2A). The major mineral phases in the sintered samples were quartz ( $\text{SiO}_2$ ), albite ( $\text{Na}(\text{AlSi}_3\text{O}_8)$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ).

The data shown in Fig. 2B illustrate that heavy metals in the LWA were in stable forms, and that the main compounds were  $\text{Cd}_2\text{SiO}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{PbCrO}_4$ . The formation of  $\text{Cd}_2\text{SiO}_4$  reveals that Cd could enter liquid–solid phases and combine with silicate in the

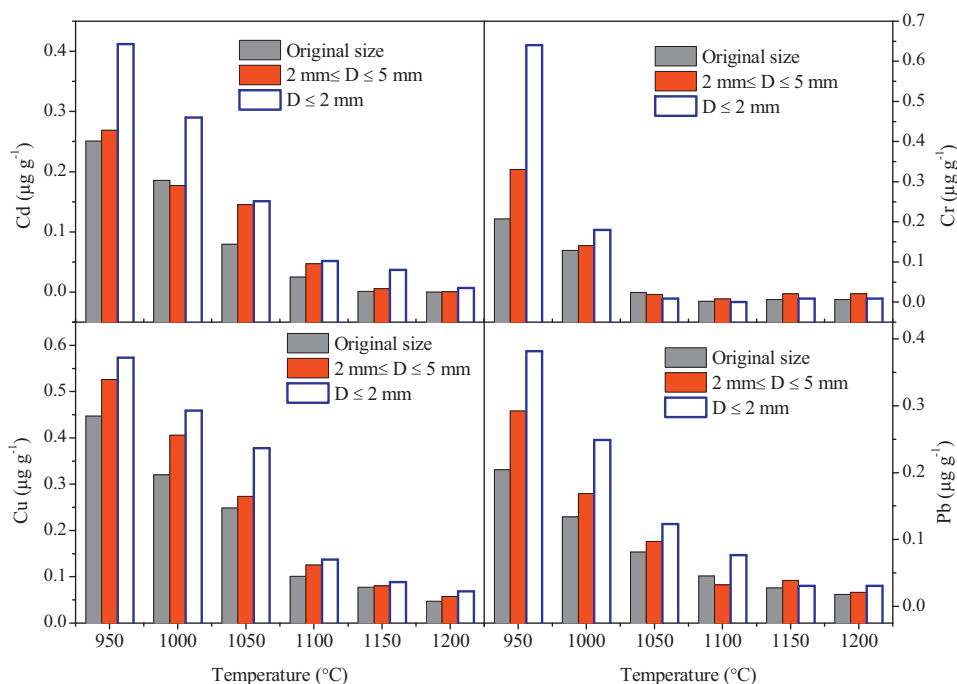


Fig. 1. Effect of sintering temperature on the leachabilities of heavy metals.

crystalline structures of the LWA during the sintering process. The formation of  $\text{Cr}_2\text{O}_3$  indicates that some  $\text{Cr}^{6+}$  was reduced to  $\text{Cr}^{3+}$ . The formation of  $\text{PbCrO}_4$  shows that  $\text{CrO}_4^{2-}$  could react with Pb at higher temperatures, enhancing the solidification efficiency of

Cr and Pb by consuming the  $\text{Pb}^{2+}$  and  $\text{CrO}_4^{2-}$  present in the raw materials [24].

The results reveal that high temperatures accelerate the formation of  $\text{CuO}$ ,  $\text{Cd}_2\text{SiO}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{PbCrO}_4$  and  $\text{PbSi}_2\text{O}_3$ , and that heavy metals solidify in the LWA. The heating process had a significant effect on heavy metal solidification, which occurred at  $1100^\circ\text{C}$ .

### 3.2. Effect of acid–basic oxides on the stabilization of heavy metals

As shown in Table S1 (Supporting Information), sewage sludge and river sediment are mainly composed of acidic ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) and basic ( $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ ) oxides. During the LWA production process,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , the framework silicate and aluminosilicate compounds that control the viscosity of the material at high temperatures, determine the overall crystalline quality and control the crystallization rate. Basic oxides,  $\text{MgO}$ ,  $\text{CaO}$ , or  $\text{Fe}_2\text{O}_3$  can lower the melting points of raw material components and promote the formation of sinter materials at low temperatures. Therefore, varying the amount of acidic or basic oxides in sludge influences the LWA properties.

Previous studies on ceramsites made from wastewater treatment sludge and drinking-water treatment sludge indicated that  $K$  ratios  $[(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)]$  had a significant effect on the ceramsite properties. The  $K$  ratio was identified as an important controlling parameter for optimizing the production of ceramsite [19,20]. Controlling the ratio of the components in the LWA production process is important, but this is difficult to achieve as the components of sewage sludge and river sediment vary according to season or district. In this study, the  $K$  ratio was controlled during the production of the LWA from sewage and river sediment, and its effect on the physical characteristics of the LWA was investigated. Figs. S2–S3 (Supporting Information) indicate that LWAs with higher bulk density and apparent density, lower water absorption and solubility in hydrochloric acid could be obtained at  $K$  ratios between 0.15 and 0.3. Therefore,  $K$  ratios have a significant effect on the compressive strength, morphology and crystalline phases of LWAs. Because the solidification of heavy

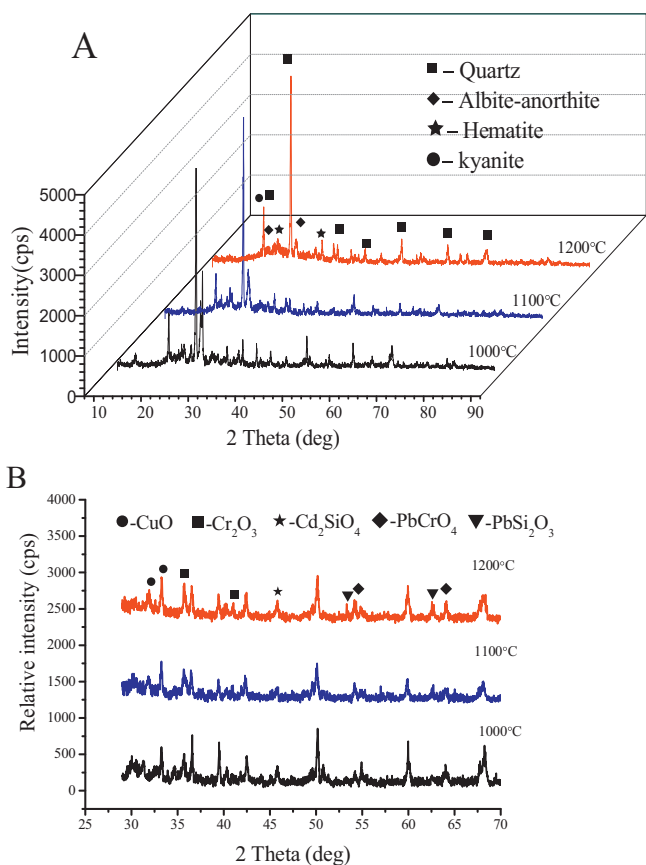


Fig. 2. (A) XRD patterns of LWAs sintered at  $1000^\circ\text{C}$ ,  $1100^\circ\text{C}$  and  $1200^\circ\text{C}$ . (B) XRD patterns of heavy metals in LWAs sintered at  $1000^\circ\text{C}$ ,  $1100^\circ\text{C}$  and  $1200^\circ\text{C}$ .

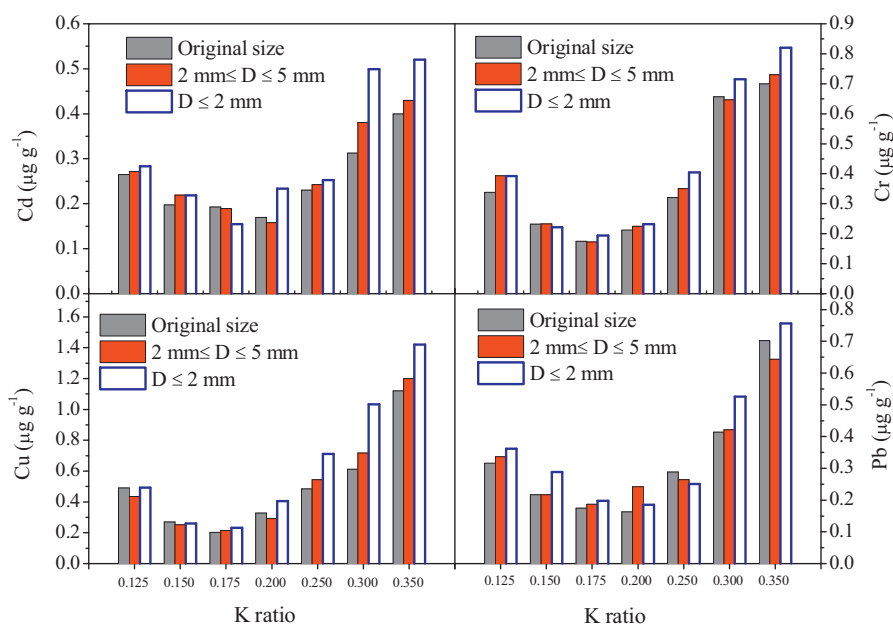


Fig. 3. Effect of  $K$  ratios on the leachabilities of heavy metals.

metals in the LWA is closely associated with the physical structure of the LWA,  $K$  ratios inevitably influence the leachability of heavy metals. The effects of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  on the stabilization of heavy metals in the LWA when the  $K$  ratio was fixed at 0.2 were also investigated (the level of the  $K$  ratios can be discretionarily selected because the main aim of this test was to find out how  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  affected the stabilization of the heavy metals in the LWA). Simulated ratios of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  were prepared by adding a range of oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ ) to the raw materials.

### 3.2.1. Effect of $K$ ratios on the stabilization of heavy metals

The results of the tests to examine the impact of  $K$  ratios on the stabilization of heavy metals are presented in Fig. 3. As  $K$  ratios increased from 0.125 to 0.35, the leachable Cd, Cr, Cu and Pb contents in the three sample sizes first decreased slightly, and then increased. Metal leachabilities were lowest when the  $K$  ratios were between 0.175 and 0.2. Variation in the heavy metal leachability was mainly caused by changes in LWA physical characteristics at different  $K$  ratios. When the  $K$  ratios are low (such as  $K = 0.125$ ) and the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents are relatively high, the LWA skeleton is "loose" and the compressive strength is weak, because the high  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents increase the sintering temperature. This means that weak physical bonds are formed between the heavy metals and the other LWA compounds, and the heavy metals leach more readily. In contrast, when the  $K$  ratios are higher (such as  $K = 0.3$ – $0.35$ ), i.e.,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$  contents are relatively high,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents are relatively low, so there are insufficient materials to form the LWA skeleton. Thus, heavy metals cannot completely solidify within the LWA because of expanded structures and semi-developed crystalline phases. This results in relatively high leachability of heavy metals. It should be noted that  $\text{Cr}^{6+}$  can replace  $\text{Ca}^{2+}$  and can solidify in the silicate matrix [26]. In this test, the  $\text{CaO}$  content in the raw material increased as the raw material  $K$  ratio increased, meaning that more  $\text{Ca}^{2+}$  was able to be substituted by  $\text{Cr}^{6+}$  in the silicate matrix, theoretically resulting in relatively low  $\text{Cr}^{6+}$  leachability. However, the leachable Cr contents increased as  $K$  increased from 0.175 to 0.35, which was in contrast to the results from the theoretical analysis. The stronger reducing conditions created by the increased  $K$  ratio and higher basic oxide ( $\text{Fe}_2\text{O}_3$ ,

$\text{CaO}$ , and  $\text{MgO}$ ) content are disadvantageous for reducing  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  [26], thereby resulting in surplus  $\text{Cr}^{6+}$ . Because  $\text{Cr}^{3+}$  combines to form stable compounds with other chemical structures more easily than  $\text{Cr}^{6+}$ ,  $\text{Cr}^{6+}$  will leach more easily than  $\text{Cr}^{3+}$ , resulting in relatively high Cr leachability with increasing  $K$  ratio. We conclude that the  $K$  ratio is an important parameter in the LWA production process.

XRD analyses were conducted to investigate the mineralogical compositions of the LWAs. From Fig. S4(A) (Supporting Information) quartz, albite-anorthite, kyanite and hematite were the major crystalline phases in the LWA at  $K$  ratios of 0.15, 0.2, and 0.35.

The XRD results shown in Fig. S4(B) (Supporting Information) show that  $\text{Cd}_2\text{SiO}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{PbCrO}_4$  were the main heavy metal forms in the LWA at the three different  $K$  ratios (cf Fig. 2B). The crystallization of these heavy metals means that Cd, Cr, Cu and Pb could permeate into the aluminosilicate or silicate matrix in the LWA during the sintering process [27]. This heat-induced transformation to a crystalline state is advantageous for the long-term stability of the metals, and the crystalline solids have an improved capacity to bind heavy metals [28].

We conclude, from XRD analyses, that varying the  $K$  ratio had no obvious effect on either the main crystalline phase or the dominant heavy metals in the LWA. However, the heavy metal solidifying efficiencies were strongly enhanced by crystallization and chemical incorporations within the aluminosilicate or silicate frameworks during the sintering process.

### 3.2.2. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$ on the stabilization of heavy metals

The curve shown in Fig. 4 shows that the leachability of Cd, Cr, Cu and Pb varies with the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. The leaching curves for Cd and Cr were similar: leaching decreased first and then increased sharply as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio decreased from 5:1 to 0.67:1. The Pb leaching increased comparatively slowly when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was above 2:1. Minimal Cd, Cr and Pb leaching was recorded when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was between 3:1 and 2:1. Because  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  have high melting points, the excessive content of either  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  increased the eutectic point of the raw materials when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was greater than 4:1 or less than 1:1, meaning that the LWAs could not be completely sintered at 1100 °C. As a

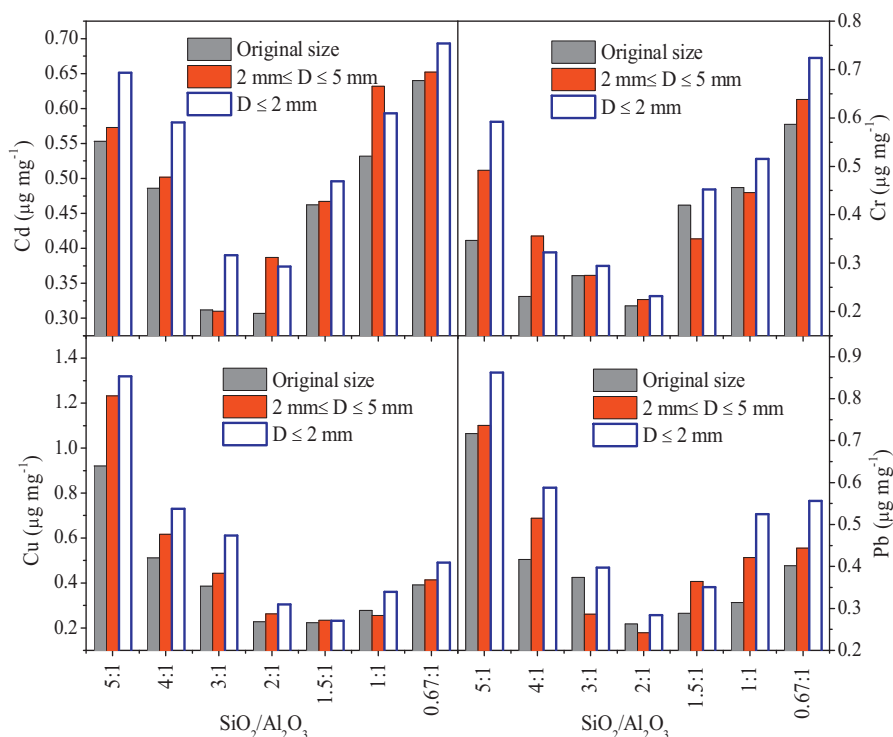


Fig. 4. Effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  on the leachabilities of heavy metals in LWAs (with  $K$  ratio of 0.2).

consequence, the LWA properties were poorer, the ability for chemical bonds to form between heavy metals and the other components was weak, and more heavy metals were leachable.

It can be seen from Fig. 4 that the leachability of Cu, which was slightly different from the leachabilities of Cr and Cd, first decreased and then slightly increased as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio changed from 5:1 to 0.67:1. This phenomenon was associated with the changing LWA physical properties at different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, similar to the reason for the variations in Cd, Cr and Pb leaching results, but may also be attributed to the special reaction between Cu and the other LWA components. As the  $\text{Al}_2\text{O}_3$  content increases (i.e.,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  decreases), more  $\text{Al}^{3+}$  can be substituted by  $\text{Cu}^{2+}$ , which then solidifies in the silicate crystal structure, thereby preventing Cu leaching (which mainly occurs in the presence of weak chemical bonds when the  $\text{Al}_2\text{O}_3$  content is higher).

Heavy metal leaching tests were conducted using LWA made with different  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  ratios (Fig. 5). As the  $\text{Fe}_2\text{O}_3$  content decreased (i.e., the  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  ratio decreased), the leachability of Cd, Cu and Pb first slowly fluctuated (at ratios between 6.5:2.3:1 and 3:2:1) and then dramatically increased (at ratios between 3:2:1 and 1.2:1.8:1), while the leachability of Cr first decreased and then increased significantly. These results suggest that a higher  $\text{Fe}_2\text{O}_3$  content favors the solidification of Cd, Cu and Pb. This may be because  $\text{Fe}_2\text{O}_3$  can lower the eutectic points of the LWA components, and can fully react with either silicates or aluminosilicates to form fine mineral groups with comparatively low eutectic points at a sintering temperature of 1100 °C. This phenomenon can enhance the formation of the liquid phase and lower the sintering points of the raw materials [27]. These reactions help to produce LWAs that have stable skeleton structures, a reduced number of cracks and bigger pores. They also promote full physico-chemical interactions between the heavy metals and the silicate or aluminosilicate matrix, and improve the solidification efficiencies of heavy metals.

The leachability of Cr differed from that of the other three metals at  $\text{Fe}_2\text{O}_3/\text{CaO}/\text{MgO}$  ratios between 6.5:2.3:1 and 3:2:1. This may

have been caused by oxidation/reduction reactions during the LWA sintering process at higher temperatures. As the  $\text{Fe}_2\text{O}_3$  content increases, more  $\text{Fe}^{3+}$  can be reduced to  $\text{Fe}^{2+}$ , restricting the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ . The leachability of Cr is fully controlled by  $\text{Cr}^{6+}$  compounds in the raw materials [28], so higher  $\text{Fe}_2\text{O}_3$  contents may have dramatically influenced the Cr solidification and leaching behaviors.

### 3.3. Effect of pH on leaching behaviors

Heavy metal leaching tests were conducted on LWA sintered at 1100 °C using leaching solutions with different pH and  $\text{H}_2\text{O}_2$  contents to investigate the stabilization of heavy metals in LWA under rigorous conditions.

Fig. 6 shows that the maximum heavy metal leachabilities were obtained at pH 1, and that the leachability of the four heavy metals substantially decreased as pH increased from 1 to 2. Minimal changes in leachability were observed when the pH was above 3. The smaller diameter ( $2 \text{ mm} \leq D \leq 5 \text{ mm}$  and  $D \leq 2 \text{ mm}$ ) samples clearly showed higher leachabilities than the unbroken LWA at pH 1.

The leaching tests indicate that low pH had a significant effect on the mobility of heavy metals in the LWA, similar to what has been reported in previous studies [19]. The acidic leaching solution (pH 1) caused the leachate to first corrode the LWA surface, affecting the stability of the heavy metals in the LWA and leading to heavy metal leaching. This phenomenon was more evident in the LWAs with diameters less than 2 mm. However, the results indicated that the solidification efficiency of heavy metals was above 95% even when the LWAs were broken (such as  $D \leq 2 \text{ mm}$ ) and when they were saturated with acid solution. This implies that strong chemical bonds were formed in the LWA, and the residual amounts of heavy metals in the sintered LWA were efficiently immobilized within the silicate or aluminosilicate matrix, making heavy metals difficult to leach, and limiting harmful effects on the environment.

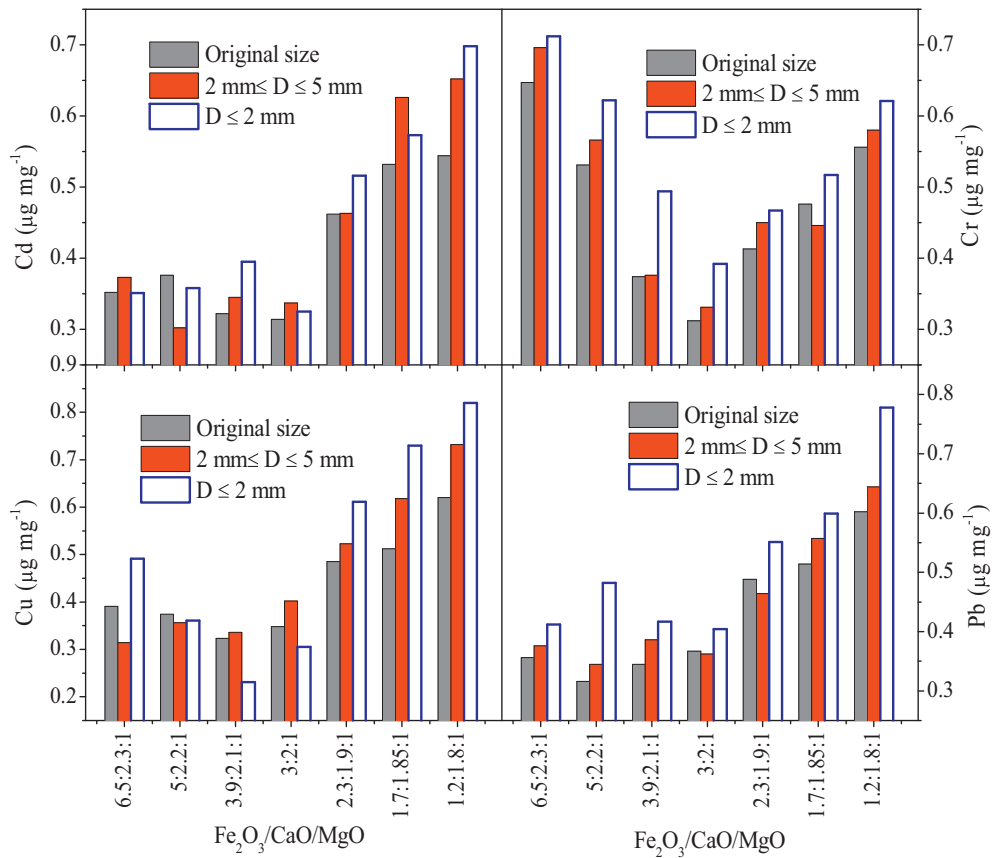


Fig. 5. Effect of  $Fe_2O_3/CaO/MgO$  ratio on the leachabilities of heavy metals in LWA (with  $K$  ratio of 0.2).

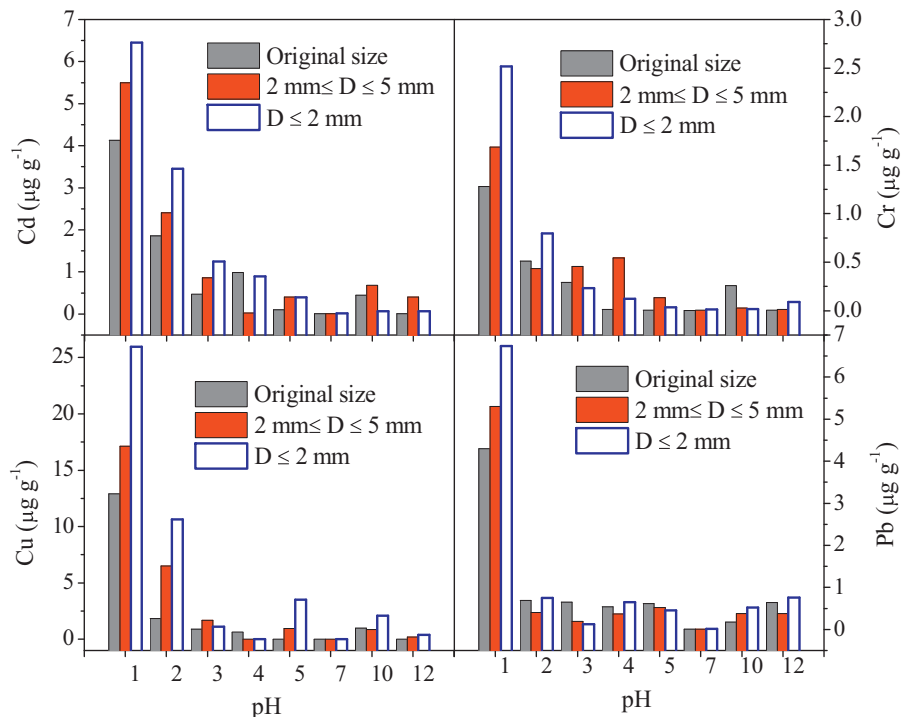


Fig. 6. Effect of pH on the leachabilities of heavy metals.

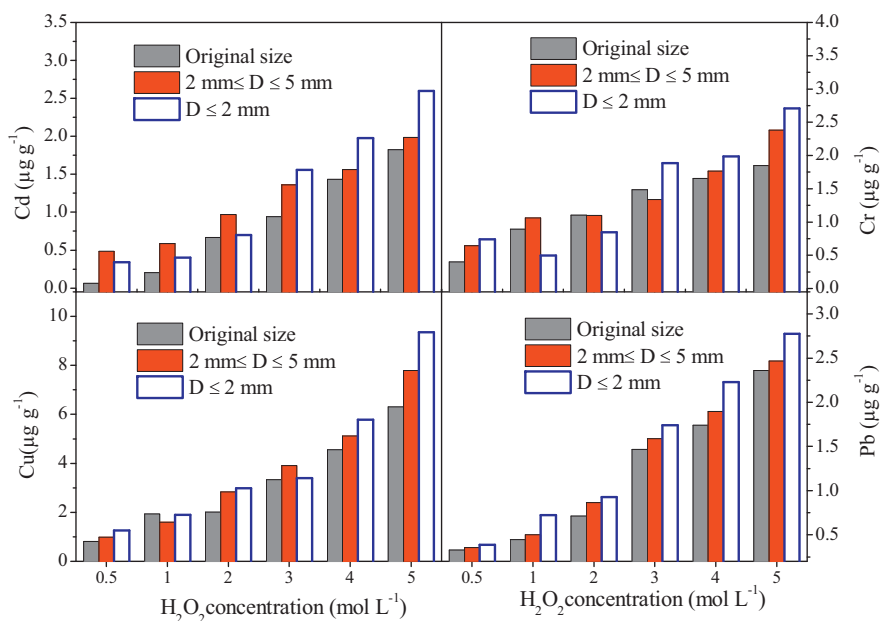


Fig. 7. Effect of  $\text{H}_2\text{O}_2$  concentration on the leachabilities of heavy metals.

### 3.4. Effect of the oxidative condition on leaching behaviors

To investigate the effect of oxidative condition on the stabilization of heavy metals in LWAs, leaching solutions with  $\text{H}_2\text{O}_2$  concentrations of 0.5, 1, 2, 3, 4 and 5 mol/L were prepared and leaching tests were conducted. Fig. 7 shows leachability data for Cd, Cr, Cu and Pb in the three different sizes of LWAs outlined earlier at  $\text{H}_2\text{O}_2$  concentrations increasing from 0.5 to 5 mol/L. The smaller diameter ( $2\text{ mm} \leq D \leq 5\text{ mm}$  and  $D \leq 2\text{ mm}$ ) samples had a slightly higher leachable content than the unbroken LWA at  $>4\text{ mol/L H}_2\text{O}_2$ .

This leaching test indicates that heavy metals were firmly solidified in LWAs because the heavy metals in the porous surface were present in stable forms, and remained stable even when the LWAs were broken. At  $\text{H}_2\text{O}_2$  concentrations above 4 mol/L, the leachate gradually corrodes and slowly destroys the LWA surface, which results in higher heavy metal leachability and reduces the solidification efficiencies of Cd, Cr, Cu and Pb. However, the heavy metal solidification efficiency was greater than 98% even when the LWAs were broken (such as  $D \leq 2\text{ mm}$ ), especially in a strong oxidizing solution (5 mol/L  $\text{H}_2\text{O}_2$ ).

The higher heavy metal solidification rate under oxidative conditions is because  $\text{Al}^{3+}$  can substitute  $\text{Si}^{4+}$  in the network tetrahedron. Therefore,  $\text{Al}_2\text{O}_3$  can enter the silica network as  $\text{AlO}_4^{4-}$  tetrahedra, replacing some of the  $\text{SiO}_4^{4-}$  groups. As a +4 valence in the tetrahedron is replaced by Al with a +3 valence, cations must supply the additional electrons required to produce electrical neutrality [29]. Therefore, a large number of cations, including Cd, Cr, Cu and Pb, enter the LWA structure in the sintering process to provide the necessary electrons [27,30]. These results indicate that most heavy metals can be solidified in the crystalline LWA structures, and are kept in the structures even when the LWAs are exposed to rigorous leaching conditions.

## 4. Conclusions

We conclude that the sintering temperature, acid–basic oxides, pH and oxidative conditions influence the leaching behavior of heavy metals in LWAs. Higher LWA sintering temperatures are advantageous for the stabilization of heavy metals, and heavy metals in LWAs are in the stable forms  $\text{Cd}_2\text{SiO}_4$ ,  $\text{Cr}_2\text{O}_3$ , CuO and

$\text{PbCrO}_4$ . Cd, Cr, Cu and Pb leachabilities are lowest at  $K$  ratios between 0.175 and 0.2, and heavy metal solidification rates remain above 95% in acidic solutions and above 98% in strong oxidative  $\text{H}_2\text{O}_2$  solutions. Heavy metals can be stabilized in LWAs, preventing their release and secondary pollution of the environment.

## Supporting information

Supporting information includes the chemical analyses of sewage sludge and river sediment (Table S1), the LWA production process (Fig. S1), average contents of heavy metals in sewage sludge at wastewater treatment plants in China (Table S2), the process of making LWA (Fig. S1) and the effect of the  $K$  ratio on the LWA physical properties (Figs. S2–S3). XRD patterns of LWAs and heavy metals in LWAs sintered at  $K$  ratios of 0.125, 0.2, and 0.35 (Fig. S4). This material is available free of charge at <http://pubs.acs.org>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.04.006>.

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