

## Stabilization of heavy metals in ceramsite made with sewage sludge

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### Abstract

In order to investigate stabilization of heavy metals in ceramsite made with sewage sludge as an additive, the configuration of heavy metals in ceramsite was analysed by XRD and while leaching tests were conducted to find out the effect of sintering temperature (850 °C, 900 °C, 950 °C, 1000 °C, 1100 °C, and 1200 °C), pH (1, 3, 5, 7, 9, and 12), and H<sub>2</sub>O<sub>2</sub> concentration (0.5 mol L<sup>-1</sup>, 1 mol L<sup>-1</sup>, 1.5 mol L<sup>-1</sup>, 3 mol L<sup>-1</sup>, and 5 mol L<sup>-1</sup>) on stabilization of heavy metals (Cd, Cr, Cu, and Pb) in ceramsite. The results indicate that leaching contents of heavy metals do not change above 1000 °C and sintering temperature has a significant effect on stabilization of heavy metals in ceramsite; leaching contents of heavy metals decrease as pH increases and increase as H<sub>2</sub>O<sub>2</sub> concentration increases. XRD analysis reveals that the heavy metals exist in steady forms, mainly Pb<sub>2</sub>O(CrO<sub>4</sub>), CdSiO<sub>3</sub>, and CuO at 1100 °C. It is therefore concluded that heavy metals are properly stabilized in ceramsite and cannot be easily released into the environment again to cause secondary pollution.

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**Keywords:** Ceramsite; Sewage sludge; Leaching test; Stabilization; Heavy metals

### 1. Introduction

Sewage sludge partially removes heavy metals in wastewater through sedimentation of suspended solids, metal precipitation and metal adsorption to biomass. It is therefore of great significance to find a proper way to dispose sewage sludge to avoid secondary pollution. Until recently sewage sludge was allowed to be used directly in agriculture as fertilizer, but this is now hampered by the legal criteria for high concentration of heavy metals [1]. Another commonly used way is thermal [2–6], which involves incineration, gasification, and pyrolysis as a means of disposal.

Solidification/stabilization are an alternative solution for disposal of sewage sludge containing heavy metals [5,7]. Solidification/stabilization (S/S) technologies are the processes used to treat inorganic and organic waste materials, in which waste materials are mixed with various binding media to obtain a new product with improved physical properties.

Much works have been done on the characteristics of glass–ceramics made of sewage sludge ashes [8–10]. Sewage sludge ash has been compacted and fired at different temperatures to produce a range of sintered ceramic materials [11,12]. Ceramic and glass technologies are considered to be the most versatile for rendering hazardous waste inert because they destroy organic matter and immobilize heavy metals in a stable matrix [9].

Sintering stabilization is one of the methods to reduce the leachability of heavy metals in waste materials without increasing the volume of stabilized products [13]. The aim of sintering stabilization is to form a new, less soluble and more geochemically stable mineral phase in leaching environments [14]. This process can be used to produce ceramsite with sewage sludge as additive which has the potential to reduce the cost of sludge treatment [15]. The main concern is whether it is safe to use ceramsite made with sewage sludge containing heavy metals.

The aim of the present work is to obtain valuable information about the chemical speciation of heavy metals in ceramsite and their potential environmental risks by studying the leaching behaviour of heavy metals in ceramsite whose chemical composition is shown in Table 1.

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Table 1  
Chemical components of ceramsite sintered at 1000 °C (wt%)

SiO <sub>2</sub>	64.46
Al <sub>2</sub> O <sub>3</sub>	19.52
Na <sub>2</sub> O	6.984
Fe <sub>2</sub> O <sub>3</sub>	2.41
P <sub>2</sub> O <sub>5</sub>	2.23
CaO	1.23
TiO <sub>2</sub>	1.14
K <sub>2</sub> O	1.03
MgO	0.59
ZnO	0.09
MnO	0.04
CuO	0.03
BaO	0.03

## 2. Materials and methods

### 2.1. Main apparatus

SX<sub>2</sub>-10-12 muffle furnace (Shanghai, China); YK-60 granulator (Shanghai, China); DHG-9070A oven (shanghai, China); 752 spectrophotometer (shanghai, China); PHILIPS crushing machine; SHA-A constant temperature shaker (Jiangsu, China); D/max-γ β X-ray diffractometry (Japan) and Perkin-Elmer Optima 5300DV inductively coupled plasma atomic emission spectrometer (U.S.A.).

### 2.2. Analytical methods

Wet sewage sludge with heavy metals added is dried at 105 °C until invariable mass and used as additive to make ceramsite for determination of the stabilization of Cd, Cr, Cu, and Pb.

The reference sludge was made with heavy metals by adding metal solutions (Cd(NO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>CrO<sub>4</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, and CuSO<sub>4</sub>) into dried sludge, mixing and allowing them to react for 30 d. The contents of Cd, Cr, Cu, and Pb were designed according to the basic data obtained through analysis of activated sludge at different places in China as shown in Table 2 above. The synthetic metal solutions was prepared by dissolving 0.05 g L<sup>-1</sup> of Cd<sup>2+</sup>, 0.1 g L<sup>-1</sup> of Cr<sup>6+</sup>, 0.1 g L<sup>-1</sup> of Pb<sup>2+</sup>, and 0.5 g L<sup>-1</sup> of Cu<sup>2+</sup> in water. Simulated heavy metal concentrations were prepared by adding tested heavy metal compounds into sludge. The contents of heavy metals added into the sewage sludge are as shown in Table 3 below.

The toxicity of ceramsite samples was determined using toxicity characteristic leaching procedure (TCLP), a standard method used to determine waste leaching toxicity, updated on the

Table 2  
Average contents of heavy metals in sewage sludge at wastewater treatment plants (mg kg<sup>-1</sup>)

Site (China)	Cd	Cr <sup>6+</sup>	Cu	Pb
Changsha	8.1	436.5	331.25	151.8
Shanghai	0.19–5.55	1.13–70	101–426	59.5–129
Wuhan	0.70	72–78.6	148.4	55.1
Gaobei	42.20	179.6	300	937.40
Shenyang	11.82	147.8	274.53	306.82

Table 3  
Contents of heavy metals in reference sludge

Added content (mg kg <sup>-1</sup> )	Cd	Cr	Cu	Pb
Minimum	1	100	100	50
Medium	25	500	250	500
Maximum	50	1000	500	1000

basis of hazardous waste extraction procedure (EP) by USEPA. Leaching is a process used to determine if a contaminant is transferred from a stabilized matrix to a liquid medium. Therefore, the leaching test plays a leading role in assessing the environmental impact of a specific way of disposal.

The leaching test was conducted with the solution prepared at a liquid–solid ratio of 1 L/200 g, and stirred at 110 rpm for 24 h or 30 d. The supernatant was analyzed by ICP-AES and the crystalline phase of the heavy metals in ceramsite was analyzed by XRD.

## 3. Results and discussion

### 3.1. Effect of sintering temperature on characteristics of heavy metals in ceramsite

It can be seen from Fig. 1(Cd) that the leaching content of Cd in three specimens (1 mg kg<sup>-1</sup> Cd, 25 mg kg<sup>-1</sup> Cd, and 50 mg kg<sup>-1</sup> Cd) decreases in 24 h or 30 d as sintering temperature increases. At a temperature below 1000 °C, crystal growth and sintering in a nucleation process are negligible due to high viscosity of the mixture; but at a temperature ≥ 1000 °C, these nuclei can act as centres of crystallization and have their effect on the phase formation rate, and at a temperature above 1000 °C, formation of liquid phase reduces the number of pores in ceramsite as a consequence of higher percentage of fine particles in the specimens, which hinders initiation of any crack and improves the mechanical strength of ceramsite. The results are similar to the reports of utilizing sludge as a raw material for ceramic production [9,10].

It should be noted that of the four heavy metals, chromium has the highest leaching content reduction rate and is the element most sensitive to sintering temperature as shown in Fig. 1(Cr). The increase in sintering temperature has a slight influence on the leaching results of Cr at 1000 °C, 1100 °C, and 1200 °C; and there is an obvious relationship between sintering temperature and leaching of Cr at 850 °C, 900 °C, and 950 °C.

The relatively lower leaching content of Cu is obtained at a temperature between 900 °C and 1000 °C by leaching for 24 h (Fig. 1(Cu)), and leaching content of Cu decreases as the sintering temperature increases at the 30th day.

The effect of sintering temperature on the leaching content of Pb is evaluated for both 24 h and 30 d. It should be noticed that Pb in ceramsite (50 mg kg<sup>-1</sup> Pb, 500 mg kg<sup>-1</sup> Pb and 1000 mg kg<sup>-1</sup> Pb) is in the form of plumbous compound and cannot be easily released from ceramsite made at a sintering temperature above 950 °C (Fig. 1(Pb)).

It can be seen from Fig. 1 that significant reductions of heavy metals can be achieved during the leaching test. The mobility of Cd, Cr, Cu, and Pb in ceramsite can be reduced by the sin-

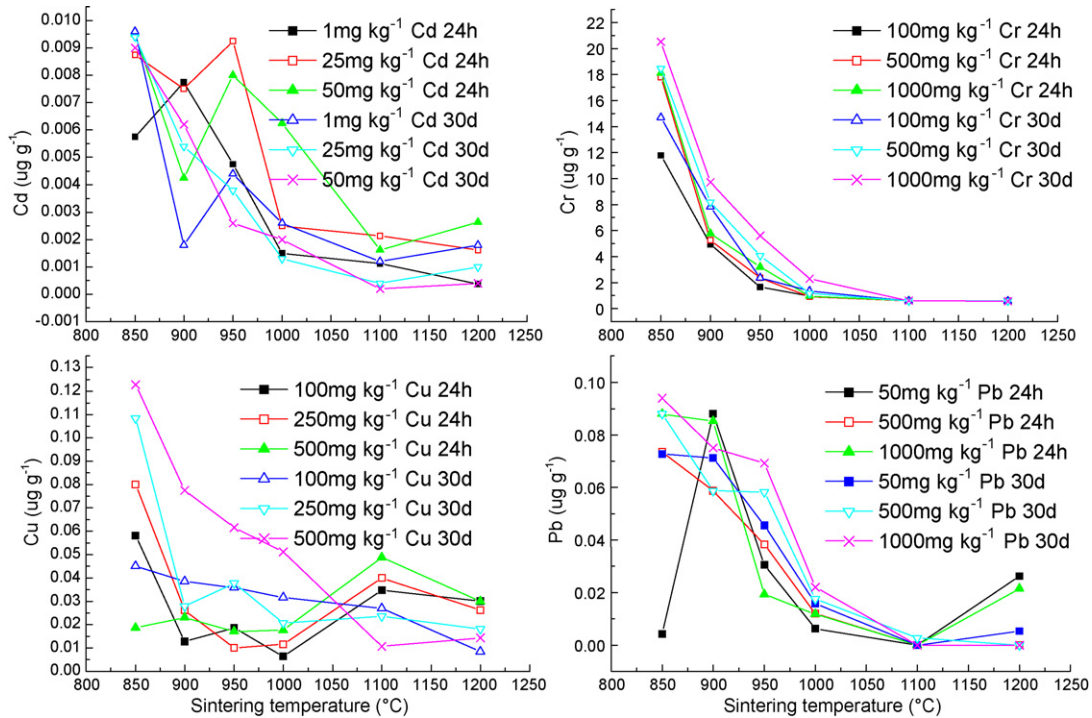


Fig. 1. Leaching contents of Cd, Cr, Cu and Pb in ceramsite with influence of sintering temperature.

tering process at a temperature above 950 °C, which as it has been experimentally shown that sintering can be used to produce ceramsite and stabilize the heavy metals [5].

The following pH-dependent and H<sub>2</sub>O<sub>2</sub>-dependent leaching tests of heavy metals are conducted with ceramsite made by sintering at 1000 °C.

### 3.2. pH-dependent leaching

It can be seen from Fig. 2(Cd) that the maximum leaching content of Cd is achieved at the 24th hour or on the 30th day when pH is 1. By average, the leaching content of Cd on the 30th day is higher than that at the 24th hour. The effect of higher pH

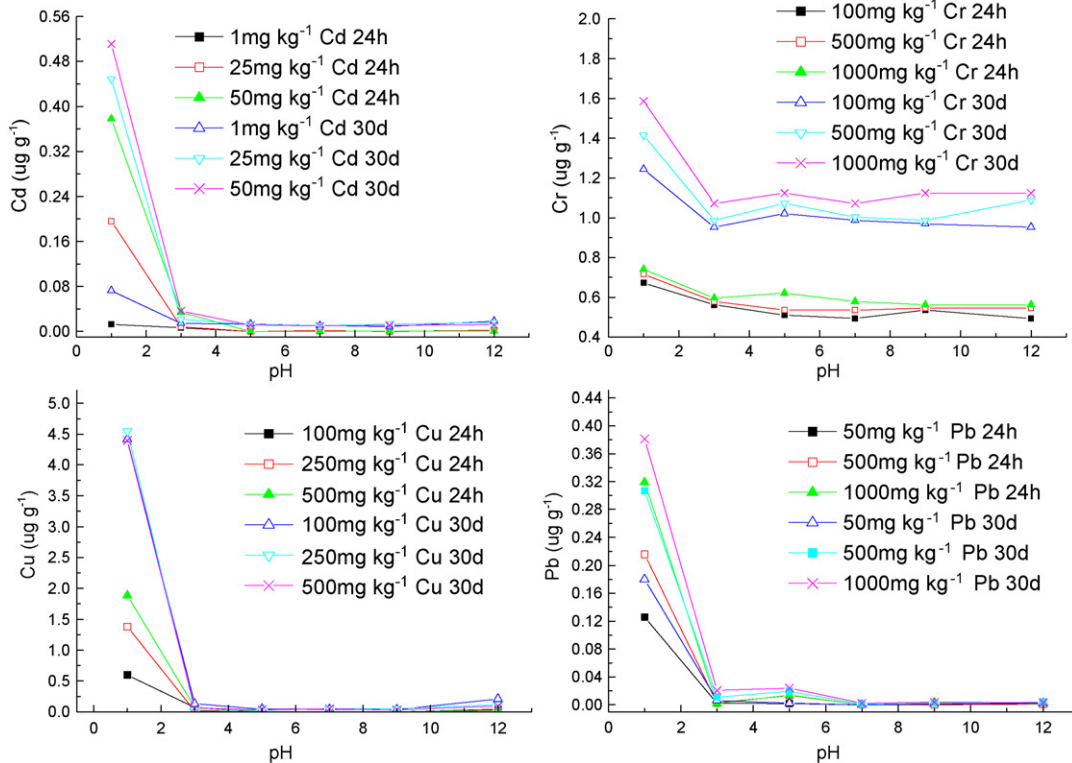


Fig. 2. Leaching contents of Cd, Cr, Cu, and Pb in ceramsite with influence of pH.

on the leaching content of Cd is weaker than the effect of pH 1 and the leaching content almost does not change as pH increases when  $\text{pH} > 3$ .

The cumulative amounts of Cr leached from ceramsite on the 30th day are about twice as much as those of the 24th hour. It can be seen from Fig. 2(Cr) that Cr cannot be easily released during the pH-dependent leaching test for 30 d. Most of  $\text{Cr}^{6+}$  is deoxidized to  $\text{Cr}^{3+}$  ( $\text{Cr}_2\text{O}_3$ ) [3] which can be used as a crystal nucleus for growth of other ion crystals at a temperature  $\geq 950^\circ\text{C}$ , and so, both  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  are stabilized in the structure of a crystalline network.

It can be seen from Fig. 2(Cu) that the leaching content of Cu stabilized in ceramsite increases by 100–260% on the 30th day, and the increasing rate of leached heavy metals can be higher than 200% at a pH of 1.

Fig. 2(Pb) shows that the maximum leaching contents of Pb is achieved in three specimens ( $50\text{ mg kg}^{-1}$  Pb,  $500\text{ mg kg}^{-1}$  Pb, and  $1000\text{ mg kg}^{-1}$  Pb) when pH is 1. The maximum leaching content of Pb for the 24th hour or the 30th day are  $0.1258\text{ }\mu\text{g g}^{-1}$  and  $0.18\text{ }\mu\text{g g}^{-1}$ ,  $0.2158\text{ }\mu\text{g g}^{-1}$  and  $0.3066\text{ }\mu\text{g g}^{-1}$ ,  $0.3186\text{ }\mu\text{g g}^{-1}$  and  $0.3812\text{ }\mu\text{g g}^{-1}$ , respectively.

The pH-dependent leaching tests indicate that the relationship between metal mobility and pH based on distilled water batch test is complicated, and the solubility of some heavy metals may have nothing to do with pH [13], and other minor influences on the leaching test are generally caused by quantity and type of soluble anions leached from ceramsite.

### 3.3. Effect of $\text{H}_2\text{O}_2$ on characteristics of heavy metals in ceramsite

It can be seen from Fig. 3(Cd) that the leaching content of Cd increases as the  $\text{H}_2\text{O}_2$  concentration increases, which can attribute to either an enrichment of Cd in a distinct mineral phase of minor solubility in ceramsite, or an equilibrium phase leaching in the leachant ( $\text{H}_2\text{O}_2$ ).

As shown in Fig. 3(Cr), the experimental results follow the same trends, and influence of oxidative condition on Cr is minor. Chromium in ceramsite is in the form of a steady oxide of chromium and the main compound of Cr is  $\text{Cr}_2\text{O}_3$  [3]. The characteristics of ceramsite may be affected by the presence of  $\text{Cr}_2\text{O}_3$  inside; the number of pores in ceramsite decreases as amounts of chromium oxides and higher dispersion of alkaline oxides increase.

Fig. 3(Cu) shows an increase in leached content of Cu as the  $\text{H}_2\text{O}_2$  concentration increases, although there are many scattered dots. To understand the cause for this increase, heavy metal (Cu) is studied by comparing their formation of reaction products. The leaching content of Cu does not change much with  $\text{H}_2\text{O}_2$  concentration increases, which suggests the formation of similar reaction products in all ceramsite.

It can be seen from Fig. 3(Pb) that leaching time does not have an important influence on the leaching content of Pb. The study on the internal structure of ceramsite made of sewage sludge, adherent and clay materials indicates that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in raw material can form a Si–O–Al reticulation structure in the sintering process, which Pb can transfer into, and high sintering

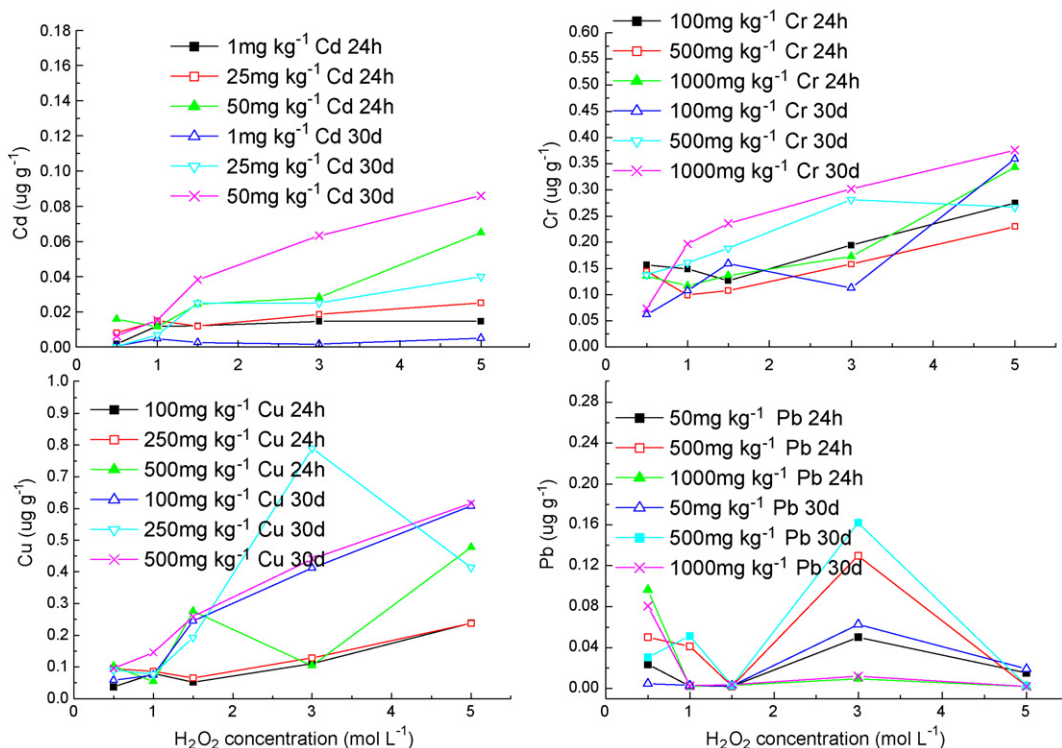


Fig. 3. Leaching contents of Cd, Cr, Cu, and Pb in ceramsite with influence of  $\text{H}_2\text{O}_2$  concentration.



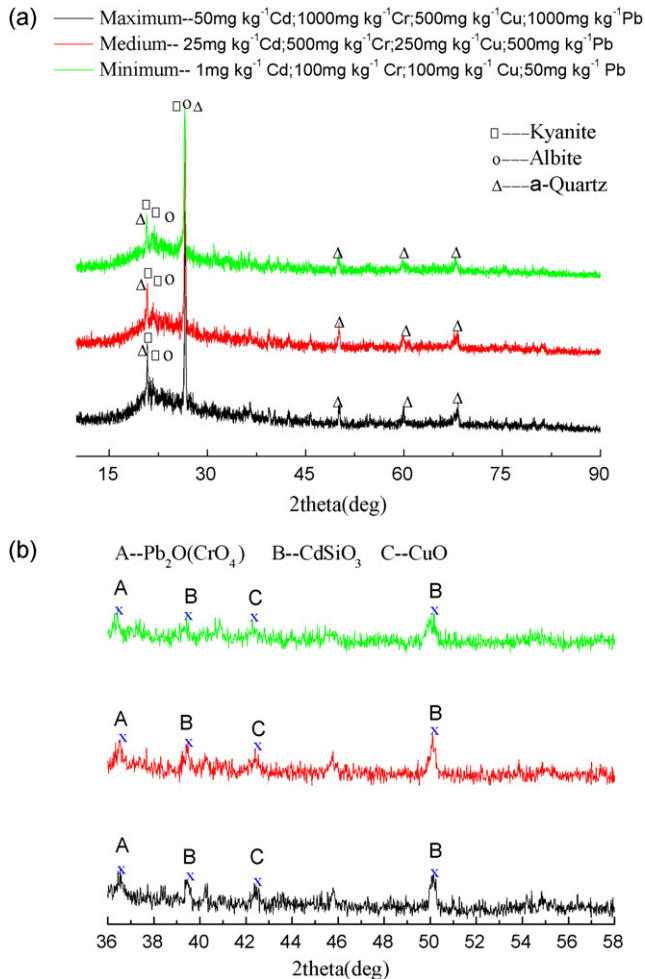


Fig. 4. XRD patterns for ceramsite with different contents of heavy metals.

temperature promoted this transformation, so that Pb cannot be easily leached from ceramsite.

### 3.4. X-ray diffraction analyses

The S/S process should be optimized so that regulatory requirements can be satisfied by taking into account the effect of sintering temperature on the leaching process. So samples sintered at 1100 °C with different contents of heavy metals added (minimum, medium, and maximum) are selected for analysis of their phase transformation.

The crystalline phases of the three ceramsites are kyanite (Al<sub>2</sub>SiO<sub>5</sub>), albite (NaAlSi<sub>3</sub>O<sub>8</sub>), and quartz (α-SiO<sub>2</sub>) detectable at the angle of 0–90° as shown in Fig. 4(a). No significant crystalline transformation occurs and the crystalline phases at 1100 °C are effectively bonding as a result of liquid phase existence, because the glassy phase formation at 1100 °C is leading to a finer and more densified microstructure in ceramsite. The decrease of viscosity of glassy phase in ceramsite may enhance the diffusion of kyanite species from the inner region to the outer region of ceramsite and the results are similar to the reports of utilizing sewage sludge or Al-rich sludge as a raw material for ceramic production [10,16]. Cr and Pb in ceramsite are in steady

form and the main compound is phenicochroite (Pb<sub>2</sub>O(CrO<sub>4</sub>)) as shown in Fig. 4(b). Cd and Cu are in the form of cadmium silicon (CdSiO<sub>3</sub>) and copper oxide (CuO).

## 4. Conclusion

It can be concluded from the results and discussion above that pH, H<sub>2</sub>O<sub>2</sub> concentration and sintering temperature have a significant influence of on the leaching behaviour of the heavy metals in ceramsite. It can be seen from all the figures that the leaching contents of Cd, Cr, Cu, and Pb from ceramsite follow a similar trend and the approximate sequence of leaching contents of heavy metals is maximum > medium > minimum.

The changes in composition of leachant solution (acidic, neutral, alkaline, and oxidative) have an important influence on the leaching content of heavy metals and the main immobilization capacity is related to the sintering temperature. The sintering process is useful to retain fractions larger than 90% of Cd, Cr, Cu, and Pb usually considered hazardous, concluding its binder suitability to constitute a solidification/stabilization process for sewage sludge containing heavy metals to achieve valuable ceramsite.

The stabilization process of ceramsite must be performed to satisfy the safety requirements and it is safe to use sewage sludge as additive to make ceramsite. Heavy metals are properly stabilized in ceramsite and cannot be easily released into the environment again to cause secondary pollution.

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