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Solidification and leaching behaviours of Cr^{6+} in sludge ceramsite

G.R. Xu*, J.L. Zou, G.B. Li

School of Municipal and Environmental Engineering, Harbin Institute of Technology, P.O. Box 2602,
Harbin, Heilongjiang Province, China

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Abstract

Making lightweight ceramsite with sewage sludge is a new effective approach for disposal of sludge. However, there is a concern as to whether the heavy metals such as Cr^{6+} in sewage sludge can be solidified in ceramsite after sintering. The configuration of Cr^{6+} in ceramsite was analyzed by X-ray diffraction (XRD) and leaching tests were conducted to determine the effects of sintering temperature, pH and H_2O_2 concentration on the stabilization of Cr^{6+} in ceramsite. The results show that leaching of Cr^{6+} changes little at temperatures above 900 °C, and both pH and H_2O_2 concentration have some effects on the leaching of Cr^{6+}. Leaching test results indicate that Cr^{6+} is stabilized in ceramsite and cannot be easily released to the environment again as secondary pollution, which eliminates the concern for its application. XRD analysis of ceramsite sintered at 1000 °C reveals that the main compounds of Cr^{6+} in ceramsite are Cr_2O_3 and $FeCrO_4$. The test results provides a better understanding of the factors that affect the mobility of Cr^{6+}, and show it is a safe way to make ceramsite with sludge as an additive.

Keywords: Ceramsite; Heavy metal; Cr^{6+}; Sewage sludge; XRD

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1. Introduction

Wastewater treatment in activated sludge plants (ASPs) results in production of large amounts of wet sludge and the quantity of hazardous sewage sludge increases rapidly due to rapid urbanization. Organic substances in sewage sludge create many environmental concerns such as leachate and soil contamination. In addition, these organic substances lead to excessive propagation of microorganisms, such as red tides in the ocean. Therefore, an effective stabilization method must be discovered to reduce adverse impacts of sewage sludge on humans and ecosystems [1,2].

There are also many kinds of heavy metals in sewage sludge. The existence of hexavalent chromium (Cr^{6+}) is one of the several toxic heavy metals that deserve serious attention. Data collected from excessive oral administration of Cr^{6+} with animals have documented cases of growth retardation, and liver and kidney failures [3,4]. So the technology for treatment of hazardous sewage sludge is becoming increasingly important [5–7].

Some factors, such as waste, cost, legislation and technology, limit the choices of disposal of sewage sludge. A few years ago, sewage sludge could be used directly in agriculture as fertilizer, but such usage is hampered by the legal criteria due to high content of heavy metals in sewage sludge [8]. Another approach is incineration [9–13], but it cannot easily be conducted due to emissions and expensive off-gas treatment. Several studies have reported the characteristics of glass-ceramics made of sewage sludge ashes [1,14]. Sewage sludge ash has been compacted and fired at different temperatures (1350–1450 °C) to produce a range of sintered ceramic materials [1].

It is difficult to find a new technology for disposal of sludge due to the operational demerits and high cost of the treatment [7,15]. Utilizing of sludge as an additive for making ceramsite is as a more sustainable way for disposal of sludge relative to landfilling and incineration, and offers a significant potential for reducing the cost of sludge treatment [16].

The ceramsite evaluated in this study was made with the following components: (1) clay characteristics as shown in Table 1; (2) water glass (sodium silicate) with modulus of 3.2; (3) dried

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* Corresponding author. Tel.: +86 45186282559; fax: +86 45186282559.
E-mail address: xgr@hit.edu.cn (G.R. Xu).

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Table 1
General physicochemical characteristics of clay

Chemical composition (wt.%)								
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	H_2O
≤65.0	≥25.0	≤2.5	≤1.2	≤1.2	<0.4	<0.5	<0.5	<10.0

Physical properties			
Particle size (μm)	Plastic index	Linear shrinkage (%)	Moisture (%)
>5	4.0	8.5–12.0	≤15.0

sewage sludge made of wet sewage sludge dried at 105 °C until invariable mass and then manually crushed, and consists of 35% of inorganic matter in form of metal, non-metal oxidation and salt, and 60% of organic matter in form of death bio-solid, and 5% of water content. The optimized process parameters are as follows: dried sludge/clay (wt.%) of 33%, water glass/clay (wt.%) of 15%, sintering temperature of 1000 °C and sintering time of 10 min [16]. Chemical compositions of the ceramsite sintered at 1000 °C are as shown in Table 2.

The main concerns are whether sewage sludge containing heavy metals such as Cr^{6+} can be utilized for making ceramsite, and whether it is safe to use ceramsite as filter media and other purposes according to the environmental safety criterion [16]. So, the aim of the present study is to investigate the effect of sintering temperature (800 °C, 850 °C, 900 °C, 950 °C, and 1000 °C), pH (0, 1, 2, 3, 4, 5, 6, 7, 9, and 12), and H_2O_2 concentration (0, 1 mol L^{-1}, 2 mol L^{-1}, 4 mol L^{-1}, 6 mol L^{-1}, 8 mol L^{-1}, and 10 mol L^{-1}) on Cr^{6+} solidified in ceramsite.

2. Methods

2.1. Main apparatus

Main apparatus: SX2-10-12 muffle furnace (Shanghai, China); YK-60 grain machine (Shanghai, China); DHG-9070A oven (Shanghai, China); 752 spectrophotometer (Shanghai, China); PHILIPS crushing machine; SHA-A constant temperature shaker (Jiangsu, China); Perkin-Elmer Optima 5300DV Inductively Coupled Plasma Atomic Emission Spectrometer (USA) and D/max-γ β X-ray diffractometry (Japan).

Table 2
Components of the ceramsite sintered at 1000 °C (wt.%)

SiO_2	64.46
Al_2O_3	19.52
Na_2O	6.984
Fe_2O_3	2.41
P_2O_5	2.23
CaO	1.23
TiO_2	1.14
K_2O	1.03
MgO	0.59
ZnO	0.09
MnO	0.04
CuO	0.03
BaO	0.03

Table 3
Average contents of Cr^{6+} in sewage sludge at different wastewater treatment plants (mg kg^{-1})

Site (China)	Cr^{6+}
Changsha	436.5
Shanghai	1.13–70.0
Wuhan	72.0–78.6
Anyang	95.0
Gaobei	179.6
Shenyang	147.8

2.2. Analytical methods

The dried sludge was obtained from the lab and the content of Cr^{6+} is less than 5 mg kg^{-1}. The synthetic contents of Cr^{6+} in dried sludge were according to the basic data obtained through analysis of sewage sludge at different places in China as shown in Table 3. The solution of K_2CrO_4 was added to the dried sludge and the synthetic contents of Cr^{6+} in dried sludge were 100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1}, and 1000 mg kg^{-1}. Then the wet sludge was dried at 105 °C until invariable mass. The ceramsite was made with the dried chromium sludge as an additive. The samples of the dried material were put into a muffle furnace, heated to the preset temperature, using a heating rate of 8 °C min^{-1}. The maximum temperature was held for 10 min and then the samples were allowed to cool down to room temperature.

Leaching tests were implemented according to an updated method [17]. Leaching is a process in which contaminants transfer from a stabilized matrix to liquid medium. Therefore, the leaching tests play a major role in the determination of the leaching behaviours of heavy metal according to the environmental impact regulation. Leaching rate is often used to evaluate the leachability of waste and it is defined as a ratio of the leaching content of heavy metal (Cr^{6+}) to the total heavy metal (Cr^{6+}) content in ceramsite, and can be calculated according to the following Eq. (1).

$$\text{Leaching rate (\%)} = \frac{\text{Leaching content of } Cr^{6+}}{\text{Content of } Cr^{6+} \text{ in ceramsite}} \quad (1)$$

Chromium (Cr^{6+}) in the sludge and sintered ceramsite was extracted by acid digestion (using $HNO_3/HClO_4/HF$) according to USEPA SW3050. The concentration of Cr^{6+} in the leachate was measured by using a Perkin-Elmer Optima 5300DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The crystalline phases of ceramsite and chemical configuration of Cr^{6+} in ceramsite were analyzed by a D/max-γ β X-ray diffractometer with 50 mA and 40 kV, Cu Kα radiation (XRD).

3. Results and discussion

3.1. Effect of sintering temperature on the leaching behaviours of Cr^{6+}

The leaching experiments were conducted with the ceramsite (initial contents of Cr^{6+} in dried sludge were 0 mg kg^{-1},

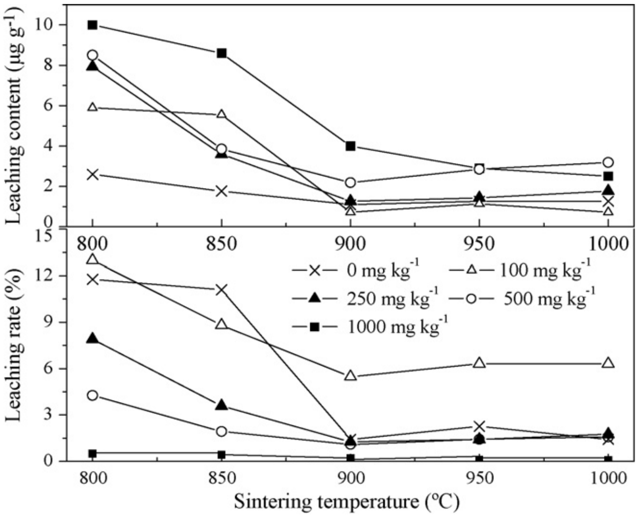

Fig. 1. Relation of sintering temperature and leaching behaviours of Cr^{6+}.

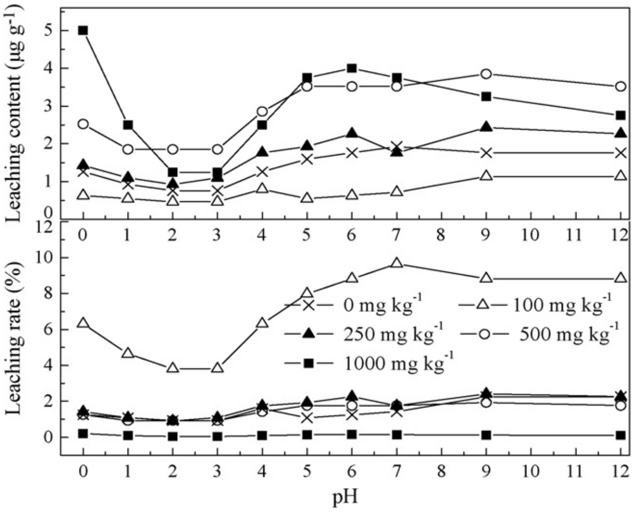

Fig. 2. Relation of pH and leaching behaviours of Cr^{6+} (12 h leaching).

100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1} and 1000 mg kg^{-1}, respectively), which were sintered at the temperature of 800–1000 °C with an interval of 50 °C. 5 g samples of sintered ceramsite were added to 100 mL of deionized water (L:S = 20:1), and the mixture was stirred for 12 h to reach equilibrium. The samples were filtered, and the concentration of Cr^{6+} in the leachate was measured.

It can be seen from Fig. 1 that the leaching rates of Cr^{6+} of the five specimens (0 mg kg^{-1}, 100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1}, and 1000 mg kg^{-1}) decrease as the sintering temperature gradually increases. The leaching rates of Cr^{6+} have a turning point at 900 °C and the solidification of Cr^{6+} is better as sintering temperature is greater than 900 °C. It can be also seen from Fig. 1 that leaching contents of Cr^{6+} of the five specimens decrease as the sintering temperature gradually increases.

It can be obtained a conclusion from Fig. 1 that there is a significant effect of sintering temperature on the solidification of Cr^{6+} in ceramsite as the sintering temperature is above 900 °C. At a temperature below 900 °C, crystals growth and sintering in a nucleation process are negligible due to high viscosity of the mixture; but at a temperature above 900 °C, the nuclei can act as the centres of crystallization and have their effect on the solidification of Cr^{6+} and the rate of phase formation. The formation of liquid phase above 900 °C improves the mechanical strength of ceramsite. So, Cr^{6+} can be solidified in the reticular structure (Si–O–Al) of ceramsite and cannot be easily leached from ceramsite no matter what is the initial content of Cr^{6+} in sludge. The results are similar with the report of utilizing sludge as a raw material for ceramic production [14].

The sintering temperature shows a significant influence on the results of leaching tests and the ceramsite made with chromium sludge can be sintered at a temperature above 900 °C to solidify Cr^{6+} and to reach the requirements of the environmental impact regulation. The following pH-dependent and H_2O_2-dependent leaching test of Cr^{6+} and XRD analyses were conducted with ceramsite sintered at 1000 °C.

3.2. Effect of pH on the leaching behaviours of Cr^{6+}

It is known that in pH range of 3–10, equilibrium conditions stipulate nearly complete conversion of trivalent chromium (Cr^{3+}), whether in precipitated or dissolved form, to hexavalent chromium (Cr^{6+}) [18]. Therefore, there is no need to consider the influence of Cr^{3+} in the leachate.

It can be seen from Figs. 2 and 3 that the minimum leaching rates and leaching contents of Cr^{6+} of the five specimens (0 mg kg^{-1}, 100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1} and 1000 mg kg^{-1}) are obtained as pH 2 or pH 3 (either after 12 h or 36 h leaching). Leaching rates and leaching contents of Cr^{6+} gradually increase as pH above 3, and both of them in the neutral and alkalinous condition are greater than those in the acidic condition. It can be seen from Figs. 2–3 that the effect of higher pH ($pH > 3$) on the leaching characteristics of Cr^{6+} is greater than lower pH ($pH < 3$) and the leaching rates almost do not change as the leaching time increases 24 h.

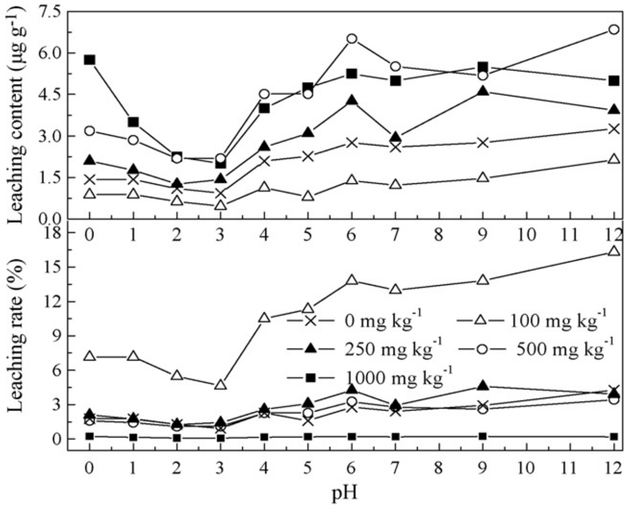

Fig. 3. Relation of pH and leaching behaviours of Cr^{6+} (36 h leaching).

The results show that pH has a significant effect on the leaching characteristic of Cr^{6+} due to it can influence the characteristics of the components in the surface, which causes the mobility of Cr^{6+} in ceramsite. The release of Cr^{6+} from the sintered ceramsite not only depends on the initial contents of Cr^{6+} present in the sludge, but also depends on the minimum solubility of each chromium compounds such as chromate and Cr_2O_3 [10]. The characteristics and contents of Cr^{6+} in ceramsite are affected by the presence of Cr_2O_3 inside due to the rigidity of ceramsite increases as the amounts of chromium oxides increase. The formation of liquid phases at 1000 °C reduces the number of pores in ceramsite, which hinders initiation of any crack and also improves the rigidity of ceramsite, and so Cr^{6+} can be solidified in the reticular structure (Si–O–Al) of ceramsite and cannot be easily leached from ceramsite either in acidic or alkalinous condition.

3.3. *Effect of H_2O_2 concentration on the leaching behaviours of Cr^{6+}*

It can be seen from Fig. 4 that the maximum leaching rates and leaching contents of Cr^{6+} of the five specimens (0 mg kg^{-1}, 100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1}, and 1000 mg kg^{-1}) are obtained when H_2O_2 concentration is 1 mol L^{-1}. The strong oxidative condition (H_2O_2 concentration >1 mol L^{-1}) does not have a significant influence on the solidification of Cr^{6+} for the five specimens as shown in Fig. 4 and the little presence of Cr^{6+} in the leachate need not to be taken into account of the environmental impact according to the protocol in China. It is also apparent that the content of Cr^{6+} in the sludge does not play an important role in determining the content of Cr^{6+} in the leachate. Most of Cr^{6+} is deoxidized to Cr^{3+} (Cr_2O_3) at 1000 °C and Cr_2O_3 can be used as crystal nucleus for the growth of other crystals, and so, both Cr^{6+} and Cr^{3+} are stabilized in the structure of crystalline network [10].

The results provide both qualitative and quantitative guidance for indicating the influence of oxidative condition on the leaching characteristics of Cr^{6+}. In the current case, the necessity for controlling the oxidation–reduction condition during the usage process of ceramsite is clearly documented.

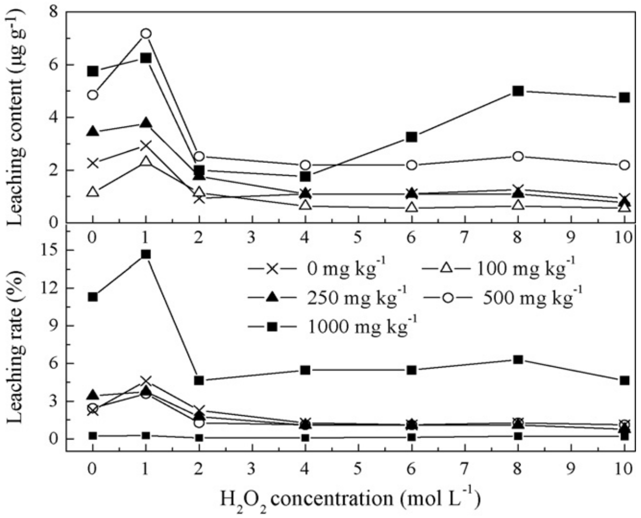

Fig. 4. Relation of H_2O_2 concentration and leaching behaviours of Cr^{6+}.

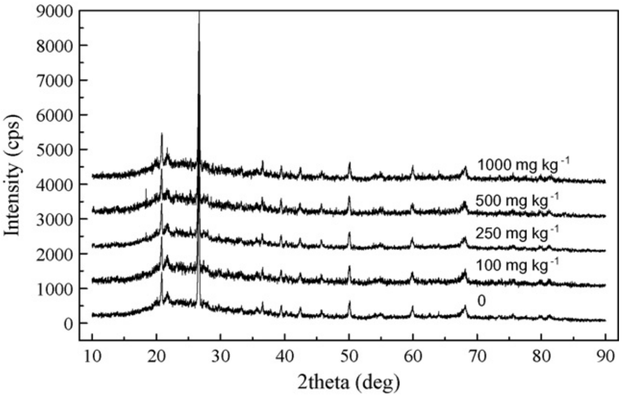

Fig. 5. XRD patterns for ceramsite with different contents of Cr^{6+} (1000 °C).

3.4. *X-ray diffraction analyses*

XRD analyses of the five powdered samples (0 mg kg^{-1}, 100 mg kg^{-1}, 250 mg kg^{-1}, 500 mg kg^{-1}, and 1000 mg kg^{-1}) are performed to indicate the crystalline phases of ceramsite and the configuration of Cr^{6+} in ceramsite. The analyses were conducted by using an XRD patterns database (International Centre for Diffraction Data, ICDD). It can be seen from Fig. 5 that the main crystalline phases of the five ceramsite sintered at 1000 °C are Quartz (α-SiO_2), Kyanite (Al_2SiO_5) and Albite ($NaAlSi_3O_8$) at the angle of 0–90°. The changes in Cr^{6+} content do not have any effect on the formation of crystals and the peaks of major crystalline phases of the five specimens are similar to each other as shown in Fig. 5. The chemical compositions of the five specimens in turn are SiO_2, Al_2O_3, Na_2O, Fe_2O_3, P_2O_5 and TiO_2, etc. The XRD analyses result shows that the chromium in ceramsite is in the form of steady chromium oxides and the main compounds of chromium are Cr_2O_3 and $FeCrO_4$.

4. Conclusions

It can be concluded from the results and discussion above that there is a significant influence of sintering temperature, pH, and H_2O_2 concentration on the leaching characteristics of Cr^{6+} solidified in ceramsite. Leaching results showed that the concentration of Cr^{6+} in the leachate for all solidified ceramsite samples was lower than the limit specified by the China EPA standards and the leached Cr^{6+} from ceramsite is not deleterious to the environment. Chromium (Cr^{6+}) is stabilized in ceramsite and cannot be easily released into the environment again to cause secondary pollution. The results confirm that it is a safe way to make ceramsite with sewage sludge containing heavy metal (Cr^{6+}).

The results is helpful to understand the leaching mechanism of Cr^{6+} under varying conditions, and to make a comprehensive judgment of the environmental impact of sludge-based ceramsite during their service life or any secondary service life. Further studies should be performed to study the leaching behaviours of various heavy metals in ceramsite made with sewage sludge as an additive.

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