

## Stabilization of Heavy Metals in Ceramsite Obtained from Blast Furnace Slag and Sewage Sludge

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To develop the application of the manufacturing of the ceramsite from blast furnace slag and sewage sludge, the stabilization of Cu and Ni is studied under some experimental environment such as the preheating and sintering temperature, pH and HNO<sub>3</sub> condition. The results show that with the increase of the preheating temperature, the leaching concentration and leaching rate of Cu and Ni have a significant decrease especially the temperature from 300 to 400 °C. The influence of the preheating temperature on the leaching concentration and leaching rate is obvious. The leaching concentration of Cu and Ni gradually decreases as the sintering temperature increases and the sintering temperature has a important influence on the leaching concentration. The leaching rate of Cu and Ni gradually declines with the increase of the sintering temperature when the contents of Cu and Ni only are 100 mg kg<sup>-1</sup>. As pH = 1, both the leaching concentration and leaching rate of Cu and Ni are maximum. Except pH = 1, the influence of the variation of pH on the leaching concentration and leaching rate of Cu and Ni is very less. The oxidative condition of HNO<sub>3</sub> has not a obvious influence on the leaching concentration and leaching rate except the HNO<sub>3</sub> concentration = 0.5 mol L<sup>-1</sup>.

**Key Words:** Ceramsite, Blast furnace slag, Sewage sludge, Heavy metal, Stabilization.

### INTRODUCTION

With the economic rapid growth of the modern society, the solid wastes become more and more around the world because of people's manufacture and life<sup>1,3</sup>. There are many toxic matters especially heavy metals, which are harmful for people's health existing in these solid wastes, such as blast furnace slag and sewage sludge. In order to decrease the leaching dose of the heavy metals from blast furnace slag and sewage sludge which are not sintered in high temperature, the ceramsite was made from the blast furnace slag and sewage sludge and sintered under high temperature to solidify the heavy metals. The studies on the stabilization of heavy metals in solid wastes especially sewage sludge have been conducted by many researchers, but the studies on that in blast furnace slag alone or the combination of blast furnace slug + sewage sludge (BFS+SS) are less than sewage sludge alone.

The treatment of municipal wastewater results in the production of huge amounts of sewage sludge and in recent years, the quantity of the total sludge generated all over the world has increased dramatically<sup>4</sup>. The studies on the leaching behaviour and the stabilization of heavy metal from sewage sludge have been carried out by several researchers. Ashish *et al.*<sup>4</sup> studied the various bioleaching behaviour in different modes of operation and the various important aspects such as

pathogen destruction, odor reduction and metal recovery from acidic leachate. Montse and Joan<sup>5</sup> studied the leaching of Cu, Zn and Ni from three contrasted Mediterranean forest soils treated with sewage sludges and the relationships between metal mobility and soil properties. Xu *et al.*<sup>6,7</sup> studied the effects of sintering temperature, (Fe<sub>2</sub>O<sub>3</sub> + CaO + MgO)/(SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>) (defined as F/SA ratios), pH and oxidative condition on the stabilization of Cu, Cr, Cd and Pb in sludge ceramsite. The result showed that the leaching contents of these heavy metals will not change above 1000 °C; the leaching contents of Cd, Cu and Pb increase as the F/SA ratios increase; the leaching contents of heavy metals decrease as pH increases and increase as H<sub>2</sub>O<sub>2</sub> concentration increases.

Blast furnace slag is a by-product of the manufacture of pig iron from iron ore, limestone and coke. The liquid slag is rapidly cooled by quenching to obtain an almost completely amorphous material. Its chemical composition mainly depends on the composition of the iron ore and potentially contains 27-40 % SiO<sub>2</sub>, 30-50 % CaO, 5-15 % Al<sub>2</sub>O<sub>3</sub> and 1-10 % MgO<sup>8</sup>. As for the immobilization of heavy metals in slag, the leaching tests are employed to investigate the immobilization behaviours of the slag based geopolymer mortar and the result showed that the slag based geopolymer mortar can effectively immobilize Cu and Pb heavy metal ions<sup>9</sup>.

TABLE-1  
ELEMENTS ANALYSES

Elements	Si	Ca	Al	Mg	Fe	K	Na	P	Sb
BFS (w-%)	10.06	19.05	6.20	3.78	0.77	0.59	0.31	0.13	4.26
SS (w-%)	9.24	1.39	2.97	0.53	3.68	1.48	0.22	0.33	0.42
Clay (w-%)	16.68	0.69	6.28	0.78	3.19	0.99	0.63	0.05	–
Elements	Mo	Sn	Ti	Mn	Cd	Se	Pd	O	C
BFS (w-%)	1.94	1.94	0.56	0.16	0.02	–	–	45.48	4.75
SS (w-%)	1.09	1.64	0.32	0.07	–	0.10	0.09	30.69	45.69
Clay (w-%)	0.07	1.10	0.33	–	–	–	–	52.08	17.13

From the discussion above, the studies on the development of BFS+SS or blast furnace slag alone ceramsite and its leaching behaviour of heavy metal are less than sewage sludge alone. The objective of this paper is to observe the variation of the leaching behaviour of the heavy metals in the ceramsite manufactured from blast furnace slag and sewage sludge during the different experimental environment such as the preheating and sintering temperature, pH and HNO<sub>3</sub>. Meanwhile, the safety of the sintered ceramsite which will be applied for the treatment of water and waste water will be verified by this study.

## EXPERIMENTAL

Blast furnace slag in this paper is obtained from the energy factory of MA STEEL group, MaAnShan, China. Blast furnace slag is a type of granular residue which is produced by water quickly cooling in the process of steel making in blast furnace. Sewage sludge is produced from dewatering workshop of Jiangxinzhou Wastewater Treatment Plant, Nanjing, China. In this plant, wastewater treatment technology is made of primary sedimentation basin, A/O and secondary sedimentation basin and the sludge dewatered by pressure filter comes from the excess sludge of secondary sedimentation basin. Clay is obtained from the work site in the 3rd Bridge of Yangtze River, Nanjing, China and the plasticity index of clay is over 17.

The chemical compositions of three raw materials mentioned above are shown in Table-1.

The raw materials are ground by SF-130C pulverizer (made in China) at sizes below 100 μm that are sufficiently fine to be mixed homogeneously. Three sorts ceramsite in the following experiments defined as SSA, SSB and SSC, respectively, are manufactured by the methods as shown in Table-2.

TABLE-2 SAMPLES CONTENTS AND RATIOS					
Type of ceramsite	Cu (mg kg <sup>-1</sup> )	Ni (mg kg <sup>-1</sup> )	BFS (w-%)	SS (w-%)	Clay (w-%)
SSA	100	100	20	50	30
SSB	300	300	20	50	30
SSC	500	500	20	50	30

CuSO<sub>4</sub>·5H<sub>2</sub>O and NiSO<sub>4</sub>·6H<sub>2</sub>O are dissolved in water solution, which is poured into the mixture of three raw materials. The raw materials are used by DZ-60 pelletizing machine (made in China) to pelletize ceramsite with particle sizes of 4-6 mm and left in a room at a temperature of about 20 °C for 4 days and then the samples were dried at 105 °C in a drying

oven for 24 h. The samples are sintered in different temperatures in a muffle furnace (Sx2-12-12, made in China). The variation of pH is adjusted by H<sub>2</sub>SO<sub>4</sub> and NaOH. The different concentrations of HNO<sub>3</sub> are diluted by concentrated nitric acid. The leaching behaviour is tested by horizontal vibration method (HJ557-2010, Chinese national standard). The chemical compositions of the raw materials are measured by electron energy disperse spectroscopy (INCA 250 EDS, UK). The concentration of heavy metals which leach from the ceramsite to the water solution is measured by plasma spectrometer(J-A1100, US).

## RESULTS AND DISCUSSION

**Effect of preheating temperature on leaching behaviour of heavy metals in ceramsite:** To evaluate the effect of the preheating temperature on the leaching behaviour of Cu and Ni, the experiment on SSA, SSB and SSC chose as samples is conducted at the same duration 20 min and different temperatures: 300, 400, 500 and 600 °C. The results are shown in Figs. 1 and 2.

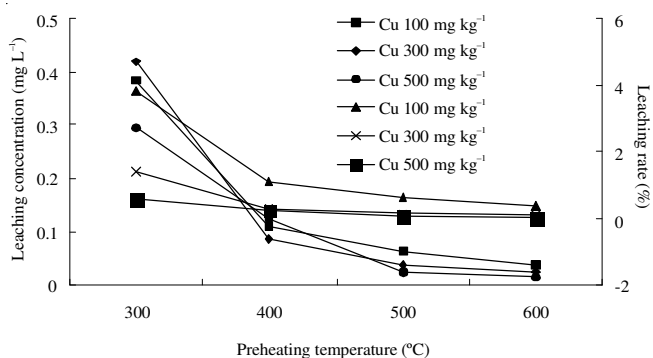


Fig. 1. Effect of preheating temperature on leaching behaviour of Cu<sup>2+</sup>

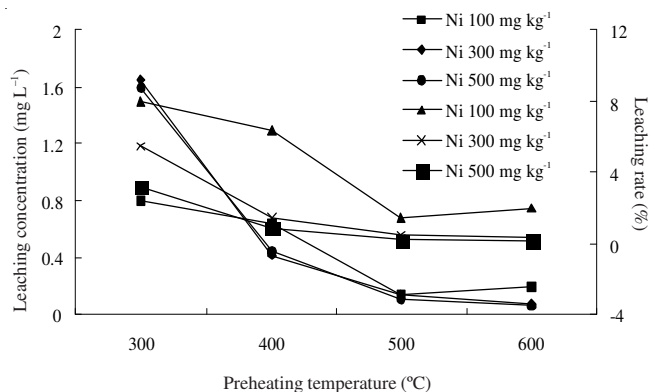


Fig. 2. Effect of preheating temperature on leaching behaviour of Ni<sup>2+</sup>

It can be seen from Figs. 1 and 2 that the leaching concentration and leaching rate of Cu and Ni gradually decreases when the preheating temperature varies from 300 to 600 °C. But from 300 to 400 °C the decrease of the leaching concentration and leaching rate of Cu and Ni is more than from 400 to 600 °C. When the preheating temperature is 300 °C, according to the content of Cu the order of the leaching concentration of Cu is 500, 100, 300 mg kg<sup>-1</sup> and the most is 300 mg kg<sup>-1</sup>. When the preheating temperature is 600 °C, the order of the leaching concentration of Cu is 500, 300, 100 mg kg<sup>-1</sup> and the found maximum for 100 mg kg<sup>-1</sup>. The order of the leaching rate of Cu is always 500, 300, 100 mg kg<sup>-1</sup> and the found maximum for 100 mg kg<sup>-1</sup> which ever preheating temperature it is. According to the content of Ni the order of the leaching concentration of Ni is 100, 500, 300 mg kg<sup>-1</sup> and the found maximum for 300 mg kg<sup>-1</sup> when the preheating temperature is 300 °C. The order of the leaching concentration of Ni was 500, 300, 100 mg kg<sup>-1</sup> and the found maximum for 100 mg kg<sup>-1</sup> when the preheating temperature is 600 °C. The variation of the order of the leaching rate of Ni was identical to Cu.

The explanation of the above phenomenon is that with the increase of the preheating temperature, the water molecule especially bound water is volatilized from the ceramsite, which is more solid than before so that the Cu and Ni is difficult to leach from the ceramsite and the volatilization is the most from 300 to 400 °C. Meanwhile, the ceramsite is easy to solve in the water solution at the lower preheating temperature owing to its incomplete sintering so that the content of heavy metals increases. As the preheating temperature and the content of Cu and Ni increase, the solidification of heavy metals become more effective so that the leaching rates of Cu and Ni are the least when the content of Cu and Ni is the most (500 mg kg<sup>-1</sup>).

**Effect of sintering temperature on leaching behaviour of heavy metals in ceramsite:** To examine the effect of the sintering temperature on the leaching behaviour of Cu and Ni, the experiment on SSA, SSB and SSC chose as samples is carried out at the following condition: preheating temperature (400 °C) and duration (20 min) and sintering temperature (900, 1000, 1050 and 1100 °C) and duration (20 min). The result is as following Figs. 3 and 4.

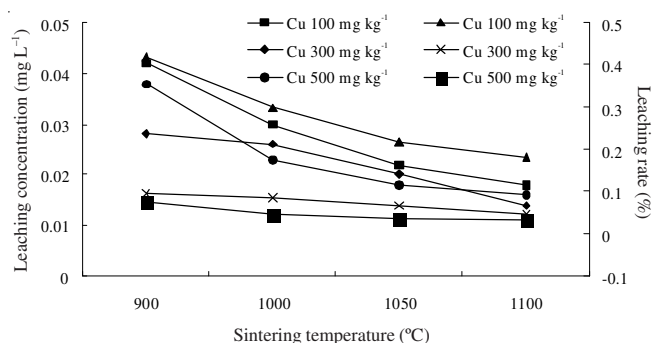


Fig. 3. Effect of sintering temperature on leaching behaviour of Cu<sup>2+</sup>

It can be seen from Figs. 3 and 4 that with the increase of the sintering temperature, the leaching concentration of Cu and Ni gradually decreases. From 900 to 1000 °C the variation of the curve of Cu and Ni is very sharp but from 1050 to 1100 °C the variation become much gentle so that the difference of

the leaching concentration of Cu and Ni is very less when the sintering temperature is 1100 °C. When the content of Cu and Ni is 100 mg kg<sup>-1</sup>, the variation of the leaching rate is sharp but the variation is less as the content of Cu and Ni is 300 mg kg<sup>-1</sup> and 500 mg kg<sup>-1</sup>. Meanwhile, the final order of the leaching rate of Cu and Ni is 100, 300 and 500 mg kg<sup>-1</sup> (the most is 100 mg kg<sup>-1</sup>). The reason of above phenomenon is that as the sintering temperature increases, the inner small pores of the ceramsite gradually are melted to become larger pores so that the ceramsite is more dense. In fact, with the increase of the sintering temperature, the complex compounds of Cu and Ni are formed and the types of them may be different at different temperature. The crystal of Cu and Ni begin forming when the sintering temperature is below 1000 °C and the crystals of Cu and Ni basically have been formed at the sintering temperature of 1000 °C.

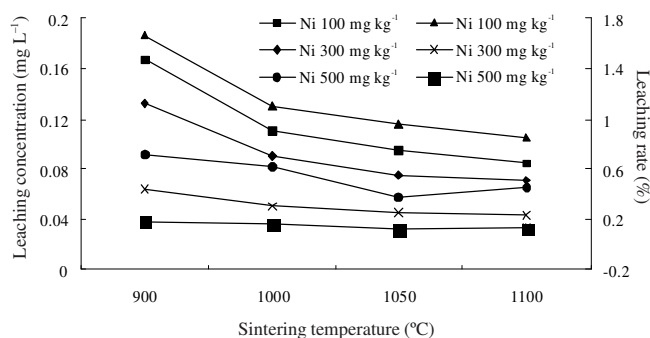


Fig. 4. Effect of sintering temperature on leaching behaviour of Ni<sup>2+</sup>

**Effect of pH on leaching behaviour of heavy metals in ceramsite:** To observe the effect of pH on the leaching behaviour of Cu and Ni in the ceramsite, the experiment on SSA, SSB and SSC chose as samples was conducted at the following conditions: preheating temperature (400 °C) and duration (20 min), sintering temperature (1000 °C) and duration (20 min) and pH (1, 3, 5, 7 and 9). The results are as following Figs. 5 and 6.

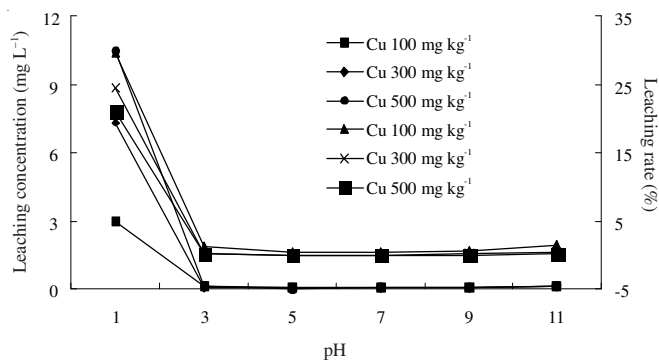


Fig. 5. Effect of pH on leaching behaviour of Cu<sup>2+</sup>

It can be seen from Figs. 5 and 6 that when pH is from 1 to 3, the leaching concentration of Cu and Ni dramatically decreases, but the variation of the leaching concentration is very less remaining below 0.5 mg L<sup>-1</sup> as pH > 3. When pH = 1, the order of the leaching concentration of Cu and Ni is 500, 300, 100 mg kg<sup>-1</sup> (the content of Cu and Ni) and the maximum was 500 mg kg<sup>-1</sup>. The difference of the leaching concentration

among the different content of Cu and Ni almost negligible as  $\text{pH} > 3$ . The order of the leaching rate of Cu and Ni was the same as 100, 300, 500  $\text{mg kg}^{-1}$  and the maximum was 100  $\text{mg kg}^{-1}$  when  $\text{pH} = 1$ . The variation of the leaching rate of Cu and Ni is identical to the variation of the leaching concentration as  $\text{pH}$  is from 1 to 11. The above phenomenon indicates that the relationship between heavy metals mobility and  $\text{pH}$  is complicated and the solubility of heavy metals in the ceramsite is dramatically influenced by lower  $\text{pH}$  such as  $\text{pH} = 1$ , also reported in previous studies<sup>7</sup>. The explanation of above phenomenon is that the pores are slowly filled by the solution containing Cu and Ni so that the  $\text{pH}$  in the pores gradually decreases especially at  $\text{pH} = 1$  and Cu and Ni in this region start to leach from the ceramsite. The initial released metals likely originate from the outer surface of the ceramsite. The residual amounts of Cu and Ni in the sintered ceramsite appear to be efficiently immobilized within the silicates or aluminosilicates matrix. This implies that stronger chemical bonds are formed between these heavy metals and the components in ceramsite, making heavy metals difficult to be leached.

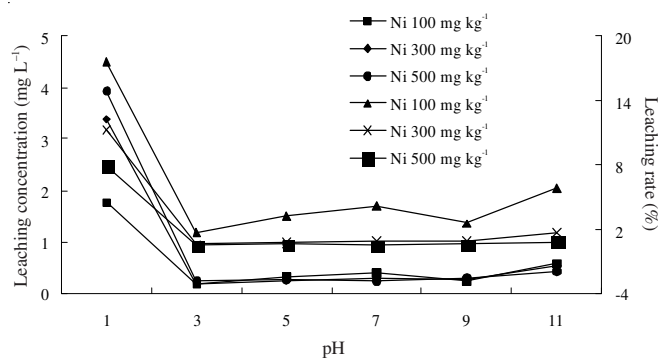


Fig. 6. Effect of  $\text{pH}$  on leaching behaviour of  $\text{Ni}^{2+}$

**Effect of  $\text{HNO}_3$  concentration on leaching behaviour of heavy metals in ceramite:** To examine the effect of oxidative condition on the leaching behaviour of Cu and Ni in the ceramsite, the experiment on SSA, SSB and SSC chose as samples is carried out at the following condition: preheating temperature ( $400\text{ }^\circ\text{C}$ ) and duration (20 min), sintering temperature ( $1000\text{ }^\circ\text{C}$ ) and duration (20 min) and  $\text{HNO}_3$  (0.5, 1.0, 1.5, 2, 2.5 and 3.0  $\text{mol L}^{-1}$ ). The results are shown in Figs. 7 and 8.

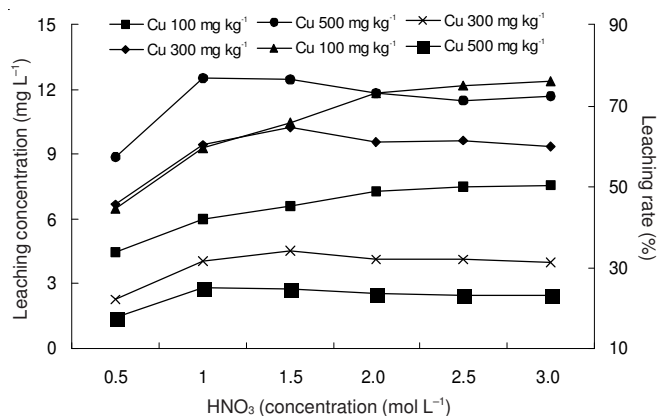


Fig. 7. Effect of  $\text{HNO}_3$  on leaching behaviour of  $\text{Cu}^{2+}$

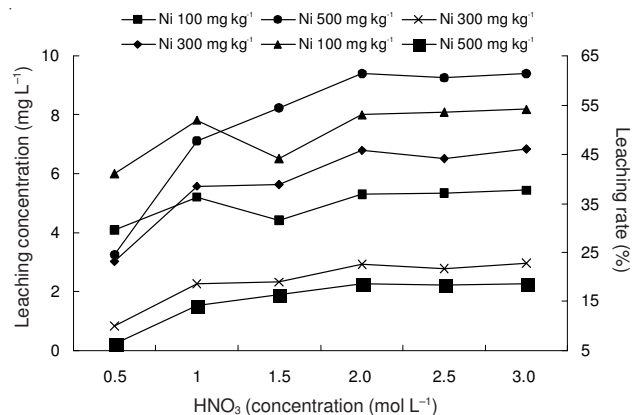


Fig. 8. Effect of  $\text{HNO}_3$  on leaching behaviour of  $\text{Ni}^{2+}$

It can be seen from Figs. 7 and 8 that when the  $\text{HNO}_3$  concentration increases from 0.5 to 1.0  $\text{mol L}^{-1}$ , the leaching concentrations of Cu and Ni from the ceramsite have a sharp rise. But as the  $\text{HNO}_3$  concentration is more than 1.0  $\text{mol L}^{-1}$ , the leaching concentration of them increased slowly especially Cu. When the content of Cu and Ni are both 100  $\text{mg kg}^{-1}$ , the leaching rate gradually increases with the increase of the  $\text{HNO}_3$  concentration, in contrast, the variations of the leaching rate of Cu and Ni have little difference as the contents of them are 300 and 500  $\text{mg kg}^{-1}$ . The result indicates that the influences of the  $\text{HNO}_3$  concentration on the leaching concentration and rate almost negligible. The reason of above changes is that during the sintering process, the Si may be substituted for the Al in a network tetrahedron, contributing to the stability of the network. Therefore,  $\text{Al}_2\text{O}_3$  can enter the silica network as  $\text{AlO}_4^{4-}$  tetrahedra to replace some of  $\text{SiO}_4^{4-}$  groups<sup>10</sup>. These complex chemical reactions need the incorporation of many cations including Cu and Ni into the structure<sup>11</sup>. Therefore, even put in the high  $\text{HNO}_3$  concentration, the ceramsite structures still have good binding ability and heavy metals cannot be easily leached from the ceramsite to the leachant.

## Conclusion

Based on the above discussion, the following conclusions may be drawn as follows:

(1) With the increase of the preheating temperature, the leaching concentration and leaching rate of Cu and Ni have a significant decrease especially the temperature from 300 to  $400\text{ }^\circ\text{C}$ . The influence of the preheating temperature on the leaching concentration and leaching rate is very obvious.

(2) The leaching concentration of Cu and Ni gradually decreases as the sintering temperature increases and the sintering temperature has a important influence on the leaching concentration. The leaching rate of Cu and Ni gradually declines with the increase of the sintering temperature when the contents of Cu and Ni are 100  $\text{mg kg}^{-1}$ , in contrast, as the contents of Cu and Ni are 300 and 500  $\text{mg kg}^{-1}$ , respectively the variations of the leaching rate are very less.

(3) As  $\text{pH} = 1$ , both the leaching concentration and leaching rate of Cu and Ni are the maximum. When  $\text{pH}$  varies from 3 to 7, the changes of the leaching concentration and leaching rate are not obvious. Except  $\text{pH} = 1$ , the influence of the variation of  $\text{pH}$  on the leaching concentration and leaching rate of Cu and Ni is very less.

(4) When the  $\text{HNO}_3$  concentration increases from 0.5 to  $1.0 \text{ mol L}^{-1}$ , the leaching concentration and leaching rate of Cu and Ni have a sharp rise, in contrast, the variation of them is not significant as the  $\text{HNO}_3$  concentration  $> 1.0 \text{ mol L}^{-1}$ . In general, the oxidative condition of  $\text{HNO}_3$  has not a obvious influence on the leaching concentration and leaching rate except the  $\text{HNO}_3$  concentration =  $0.5 \text{ mol L}^{-1}$ .

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