

Full Length Research Paper

A research on ceramsite obtained from blast furnace slag and sewage sludge

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In order to solve disposal problem of solid waste, blast furnace slag (BFS) and sewage sludge (SS) were tested as components for producing ceramsite. This study investigated the feasibility of that at different preheating and sintering temperature and duration and different mass ratios (BFS: SS: clay). The results show that the optimal preheating temperature and duration were 400 °C and 20 min and that of sintering were 1000 °C and 20 min. When the content of BFS increased and that of SS declined, the bulk and apparent density gradually increased while the 1 h water adsorption rate relatively decreased. The ceramsite produced had very good characteristics of solidifying heavy metal and the values of Cd, Cr and Sn met China national standard (GB5085.3-2007); the leaching dose of heavy metals reached minimum at 1100 °C. With the increasing of sintering temperature and duration, the gas was gradually released from the ceramsite to form many pores and the glass phase and smooth surface appeared in the ceramsite. The turning point of sintering temperature and duration were 1000 °C and 20 min. The conclusions reveal that it is feasible to produce ceramsite by using blast furnace slag and sewage sludge.

Key words: Ceramsite, blast furnace slag, sewage sludge, preheating process, sintering process.

INTRODUCTION

With the urbanization and industrialization of modern society, large amounts of solid wastes as by-products of manufacture and life are produced every year in the world. In general, the types of solid waste are classified as follows: industrial waste, municipal waste and agricultural waste. Most solid wastes especially industrial waste have one or several kinds of hazardous elements, such as heavy metal, organic matter, bacteria, etc, which are harmful for human health and are discarded by landfill and incineration. At present, research on the cyclic utilization and management of solid waste has been conducted in many countries and regions (Huabo et al., 2008; Nguyen et al., 2010; Alexandre et al., 2006; Maria, 2003; Tumpa and Goel, 2009; Virendra and Pandey, 2005). In this paper, two types of solid waste: blast furnace slag (BFS) and sewage sludge (SS), were adopted for producing ceramsite to observe its characteristics.

Blast furnace slag (BFS) comes from the by-products of the manufacture of pig iron from iron ore, limestone and

coke and is a complex $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system containing 27 to 40% SiO_2 , 30 to 50% CaO , 5 to 15% Al_2O_3 , and 1 to 10% MgO (Bellmann and Stark, 2009). Owing to its alkaline and acidic oxides components and porous structure, study on the application of BFS has been carried out at different fields in recent years. Ensar (2004) research indicates that BFS can be used as a sorbent of phosphate from water solution and the effect factors of adsorption behavior included pH, temperature, agitation rate and BFS dosage by conducting a series of batch adsorption experiments. The characteristics of Kinetic sorption on heavy metal and PO_4^{3-} by BFS are also extensively explored by Nehrenheim and Gustafsson (2008) and Ensar (2005) respectively. Meanwhile, with the purpose of solid wastes recycling, BFS can be mixed with other solid wastes, such as clay (Syamal et al., 2002), lime (Guozhuo et al., 2009), fly ash (Gengying and Xiaohua, 2003; Halit et al., 2008) to produce ceramic tile, concrete or as sorbent to get rid of hazardous matter.

Sewage sludge (SS) which contains the following

Table 1. Elements analyses.

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

components: heavy metal, organic matter and alkaline and acidic oxides are mainly produced from municipal and industrial wastewater treatment plant. In contrast to BFS, research on the application of SS is more in different countries and regions and different fields at present. SS or SS plus other solid wastes can also be used as sorbent or biosorbent on heavy metal (Rozada et al., 2008), phenol (Usarat and Kesinee, 2007) and dyeing pollution (Rozada et al., 2007). According to its characteristics including organic matter, containing high fertility, the general application of SS is as additive to the different soils, such as turgrass (Hefa et al., 2007) and agriculture (Dai et al., 2009; Carbonell et al., 2006). The same as BFS, SS also can be used to produce ceramsite (Xu et al., 2008, 2010) or combined with others waste, for example, fly ash (González- Corrochano et al., 2009), coal ash (Xingrun et al., 2009), discarded tyres (Rozada et al., 2007) to manufacture lightweight aggregate or as packing in fixed-bed system.

The objective of this study was to examine the feasibility of ceramsite produced from blast furnace slag and sewage sludge at different sintering technology and mass ratios (BFS: SS: clay). Meanwhile, the leaching behavior of heavy metals and SEM observation are also included in this paper to discuss environmental safety and microstructure of ceramsite products, respectively.

MATERIALS AND METHODS

BFS in this study was obtained from the energy factory of MA STEEL GROUP, MaAnShan, China. BFS is a type of granular residue which is produced by water quick cooling in the process of steelmaking in blast furnace.

Sewage sludge was produced from dewatering workshop of Jiangxinzhou Wastewater Treatment Plant, Nanjing, China. In this plant, wastewater treatment technology is made up 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 was obtained from the work site in the 3rd Bridge of Yangtze River, Nanjing, China, and the plasticity index of clay was over 17. The chemical compositions of three raw materials aforementioned are shown in Table 1.

The raw materials were ground by SF-130C pulverizer (made in China) at sizes below 100 mm so that they are sufficiently fine to be mixed homogeneously. Five different dry weight ratios of slag: sludge: clay was evaluated in the following experiments as shown in Table 2. Every sort of ratio was defined as SSA, SSB, SSC, SSD, SSE, respectively.

The raw materials were mixed and used by DZ-60 pelletizing machine (made in China) to pelletize ceramsite with particle sizes of 4 to 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. In this study, different samples were heated (preheating) to 300, 400, 500, 600°C and sintered at 900, 1000, 1050 and 1100°C at a rate of 9/min in a muffle furnace and duration was 10, 20 and 30 min, respectively. The values of 1 h water absorption rate, bulk density and apparent density are as follows (GB/T 17431.2-1998, in China):

One hour water absorption rate = 100×1 h saturated weight of ceramic bodies - dry weight of ceramic bodies / dry weight of ceramsite.

Bulk density = dry weight of ceramic bodies / bulk volume of ceramsite.

Apparent density = dry weight of ceramic bodies / volume of ceramsite (only including the watertight internal pores).

The chemical compositions of the raw materials were measured by electron energy disperse spectroscopy (INCA 250 EDS, UK). The concentration of heavy metals which were leached from ceramsite to the water solution were measured by plasma spectrometer (J-A1100, US). The microstructures of the sintered products were measured by Scanning Electron Microscope (CUANTA 200, Holland).

RESULTS AND DISCUSSION

Effect of sintering technology on sintering products

Preheating temperature and duration

To evaluate the effect of various raw materials in different preheating temperature and duration on the physical characteristics of ceramsite, the experiment on SSE chosen as sample was conducted at the following conditions: preheating temperature 300, 400, 500 and 600°C, duration 10, 20 and 30 min to observe the variation of bulk density, apparent density, 1 h water adsorption rate, finally optimizing optimal preheating temperature and duration. The result is as follows in Figure 1a and b.

As shown in Figure 1a, with the temperature increasing, the bulk density slowly decreased before 500°C and then sharply declined to about $700 \text{ kg} \cdot \text{m}^{-3}$ from 500°C to 600°C at different preheating duration, while gradually increased when preheating duration varied from 30 to 10 min. The reason for the phenomenon was that when the preheating temperature and duration increased, the water molecule especially bound water was gradually evaporated at 500°C from the ceramsite and meanwhile, the organic matter started combusting and was carbonized to form carbon oxides which volatilized from the porous structure of the ceramsite. The dual effect of water

Table 2. Content of percentage of three raw materials.

Sort of ceramsite	BFS (w-%)	SS (w-%)	Clay (w-%)
SSA	0	70	30
SSB	5	65	30
SSC	10	60	30
SSD	15	55	30
SSE	20	50	30

BSF, Blast furnace slag; SS, sewage sludge.

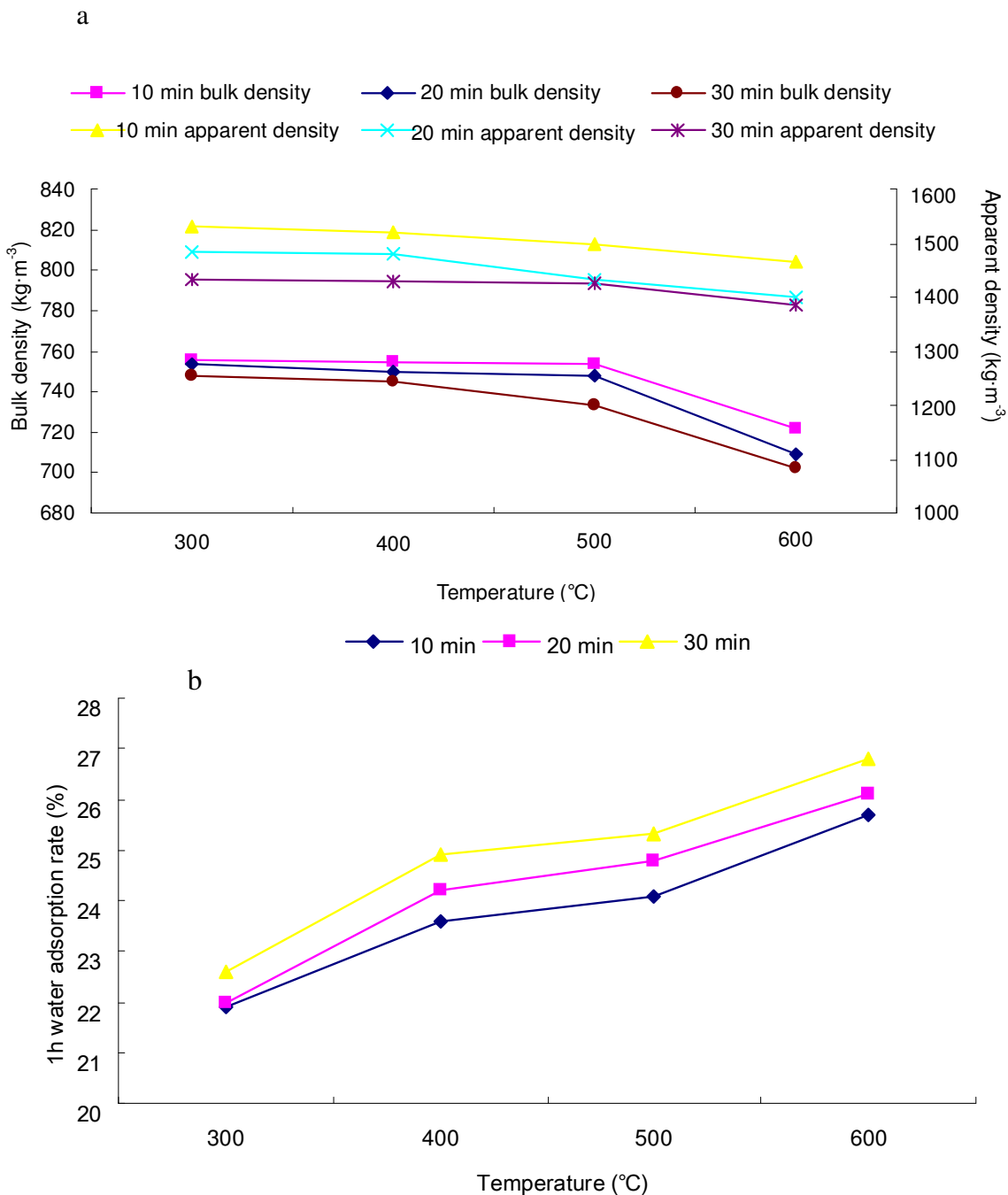


Figure 1. (a) Effect of preheating temperature and duration on the bulk and apparent density of ceramsite SSE. (b) Effect of preheating temperature and duration on the 1h water adsorption rate of ceramsite SSE.

molecule evaporated and organic matter carbonized resulted in the sudden dropping of the bulk density of ceramsite from 500 to 600°C, which indicated that the preheating of the ceramsite was completely finished. Comparing with the bulk density, the apparent density showed the same changes except no sharp declining from 500 to 600°C. The reason was that the pore of the ceramsite included watertight pore and non-watertight pore and when the preheating temperature and duration increased, the water molecule and organic matter firstly were evaporated and carbonized in the non-watertight pore, while finally varied in the watertight pore.

The 1 h water adsorption rate steadily rose from less than 22 to over 26% when the preheating temperature and duration increased in Figure 1b, which corresponded to the variation of the bulk and apparent density in Figure 1a. The result reveals that when density decreased, the inner pore in the ceramsite increased, which resulted from the preheating technology of sintering ceramsite and meanwhile, the 1 h water adsorption rate also gradually increased owing to the increasing inner pore under the dual effect of water molecule evaporated and organic matter carbonized.

According to the 1 h water adsorption rate and the bulk and apparent density, the result mentioned earlier displayed that though the preheating temperature and duration is higher, more effect on the preheating process and the preheating of ceramsite was completely finished at 600°C, the feasibility of economy, namely taking energy was considered to choose the 400 and 20 min as the optimal preheating temperature and duration in the following experiments.

Sintering temperature and duration

The same as preheating temperature and duration, to evaluate the effect of sintering temperature and duration on the physical characteristics of the ceramsite, under the preheating condition of 400°C and 20 min, the experiment on SSE chosen as sample was carried out at the following conditions: sintering temperature 900, 1000, 1050 and 1100°C, with duration 10, 20 and 30 min to observe the variation of bulk and apparent density and 1 h water adsorption rate, finally optimizing optimal sintering temperature and duration. The result is as follows in Figure 2a and b.

It can be seen from Figure 2a that the bulk density of ceramsite slowly increased when the sintering temperature increased from 900 to 1000°C and decreased when sintering duration increased from 10 to 30 min and then sharply increased when from 1000 to 1100°C and from 20 to 30 min, and the variation of the bulk density of ceramsite had little change only on 10 min. The explanation of the phenomenon was that the crystal formed by the complicated compound was decomposed to gas, such as CO₂, CO volatilizing from the porous

structure of the ceramsite when sintering temperature and duration increased from 900°C and 10 min, respectively after the adequate preheating; the porous structure of the ceramsite was melted to be connected with each other from 1000°C and from 20 to 30 min and therefore, the bulk density of the ceramsite dramatically increased; the melting of the porous structure was not conducted on 10 min at different sintering temperature. Comparing to the bulk density, the variation of the apparent density indicated the same trend, which revealed that the inner non-watertight pore and outside pore all had been melted, which was not the same as the preheating technology.

As shown in Figure 2b, the 1 h water adsorption rate of ceramsite gradually decreased with the sintering temperature increasing from 900 to 1000°C and duration declining, and dramatically decreased from 1000 to 1100°C and from 20 to 30 min, while up to 1100, steadily increased when from 30 to 10 min, which corresponded to the variation of the bulk and apparent density in Figure 2a. The reason is that the 1 h water adsorption rate increased when the bulk and apparent density decreased, while decreased with the density increasing; the variation of the density is relative to the quantity of the inner and outside pore of ceramite.

Owing to the regular pore structure (no melted) of ceramsite being considered in BFS and SS content, 1000°C and 20 min were chosen (改为chosen) as the optimal sintering temperature and duration.

BFS and SS content

To examine the effect of the BFS and SS content on the physical characteristics of ceramsite, the SSA, SSB, SSC, SSD and SSE were chosen as samples to observe the variation of bulk and apparent density and 1 h water adsorption rate under the optimal preheating and sintering temperature and duration mentioned above. The result is as follows in Figure 3a to b.

It can be seen from Figure 3a that both the bulk and apparent density increased when the sort of ceramsite varied from SSA to SSE, which indicated that two sorts density increased when the content of SS decreased from 70 to 50% and the content of BFS increased from 0 to 20%. As mentioned in preheating temperature and duration, the bulk density was relative to the content of water molecule and organic matter and inversely proportional to the pore volume of ceramsite, which steadily increased when the organic matter of SS was carbonized to volatilize from the inner structure of ceramsite; the effect of the volatilized organic matter was over that of the decreased water molecule when the content of SS decreased; the crystal formed by the complicated compound was decomposed to gas, such as CO₂, CO escaping from the ceramsite, which caused the increasing of the apparent density; therefore, the

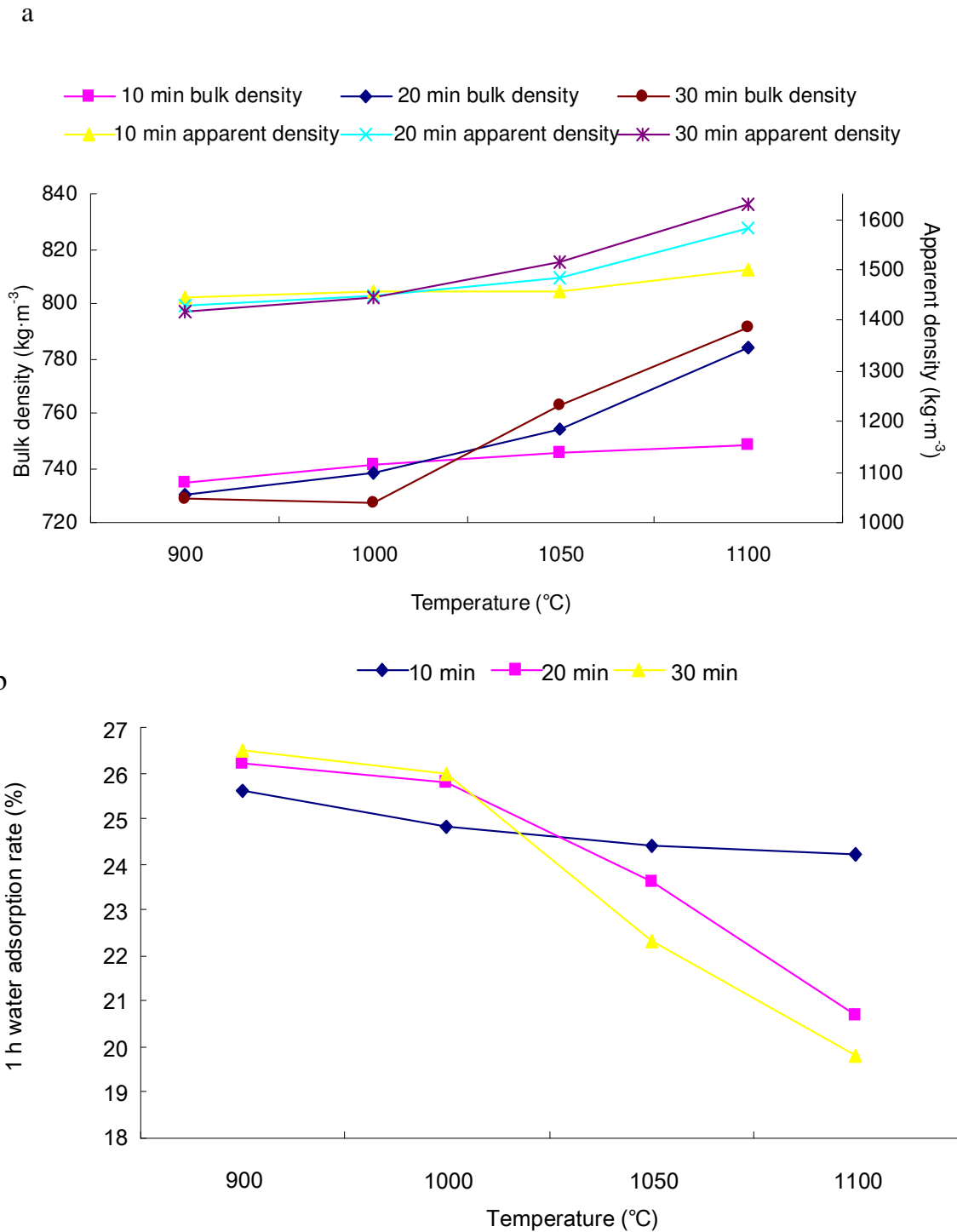


Figure 2. (a) Effect of different sintering temperature and duration on the bulk and apparent density of ceramsite SSE. (b) Effect of different sintering temperature and duration on the 1h water adsorption rate of ceramsite SSE.

phenomenon in Figure 3a could be explained by the cause aforementioned. Corresponding to the variation of the bulk and apparent density in Figure 3a, the 1 h water adsorption rate gradually decreased when both densities

increased and the sort of ceramsite varied from SSA to SSE. The explanation of the trend was identical to that of preheating temperature and duration and sintering temperature and duration.

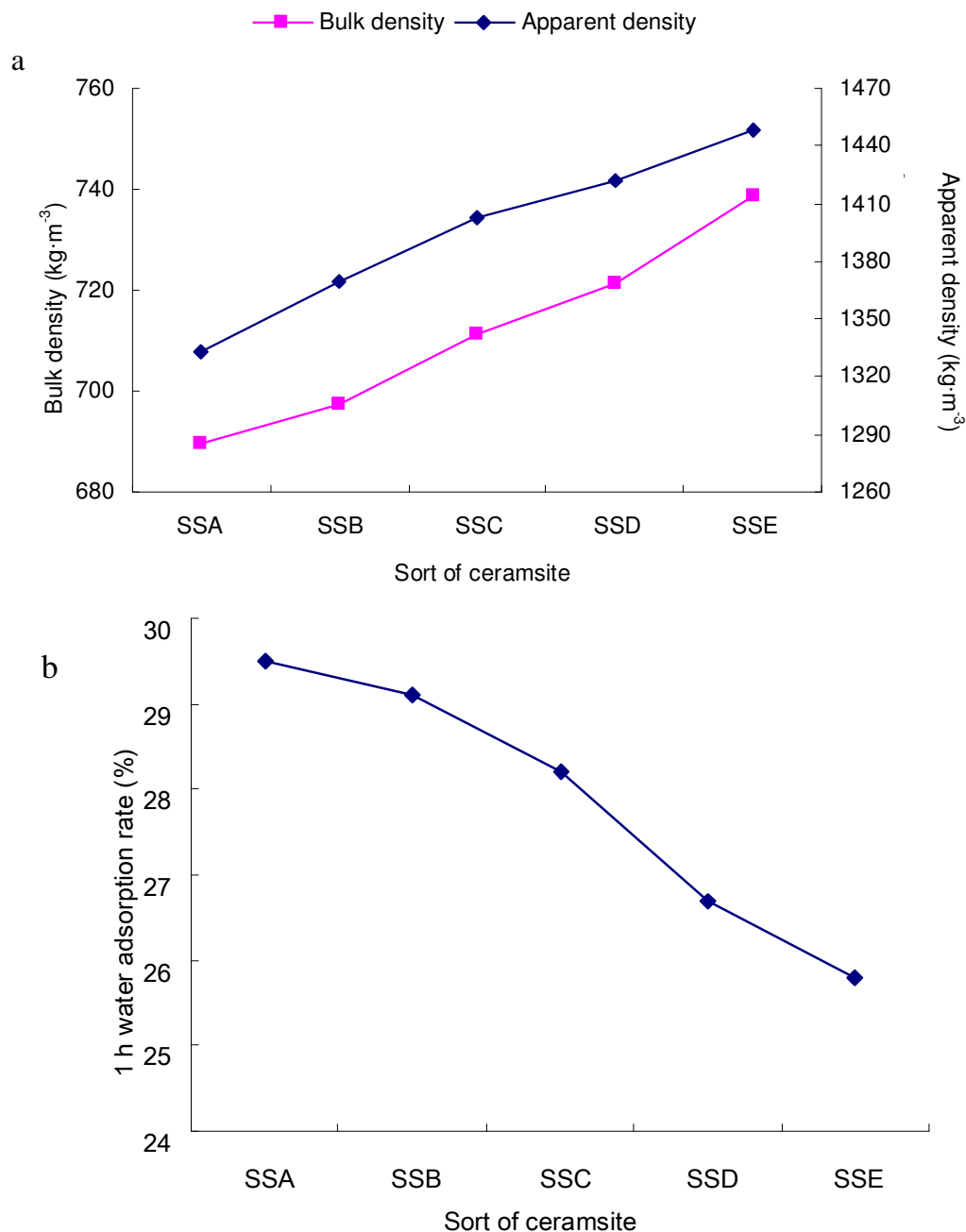


Figure 3. (a) Effect of sort of ceramsite on the bulk and apparent density (b) Effect of sort of ceramsite on the 1h water adsorption rate.

Leaching characteristics of heavy metals

In order to examine the leaching characteristics of heavy metals from ceramsite, the example of SSE was sintered at the following conditions: temperature 900, 1000, 1050 and 1100°C, with the duration 10, 20 min, and the method of leaching experiment was adopted according to China national standard (HJ557-2010). The result is in Table 3.

It can be seen from Table 3 that the values of Cd, Cr and Sn meet China national standard(GB5085.3-2007), which has no requirement on the other heavy metals; when the sintering duration was 10 min, the values of Cr and Sr dramatically decreased while that of V had no change at 1100°C; when the sintering duration was 20 min, the value of V sharply decreased while the changes of Cr and Sr were the same as 10 min, which indicated that the effects of sintering temperature before 1050°C

Table 3. Content of heavy metals leached from ceramsite (mg/L).

Time (min)	Temperature (°C)	Cd	Cr	Pd	Sb	Se	Sn	Sr	Ti	V
10	900	<0.001	0.027	<0.05	<0.05	<0.05	<0.05	0.40	<0.002	0.63
	1000	<0.001	0.028	<0.05	<0.05	<0.05	<0.05	0.57	<0.002	0.40
	1050	<0.001	0.029	<0.05	<0.05	<0.05	<0.05	0.78	<0.002	0.41
	1100	<0.001	0.015	<0.05	<0.05	<0.05	<0.05	0.04	<0.002	0.43
20	900	<0.001	0.026	<0.05	<0.05	<0.05	<0.05	0.46	<0.002	0.57
	1000	<0.001	0.036	<0.05	<0.05	<0.05	<0.05	0.91	<0.002	0.51
	1050	<0.001	0.028	<0.05	<0.05	<0.05	<0.05	0.19	<0.002	0.48
	1100	<0.001	0.005	<0.05	<0.05	<0.05	<0.05	0.04	<0.002	0.21
National standards		<1	<15	-	-	<1	-	-	-	-

and sintering duration 10 min, 20 min on the values of Cr, Sr and V had little changes, which had reverse changes at 1100°C. It is explained that when the sintering temperature was very high especially at 1100°C, the reaction between the heavy metals and silicates which were formed by the minerals in ceramsite happened to form the no melting solid such as aluminosilicate and it was easy for the heavy metals to be fixed in the matrix of that observed the SEM microstructure of sintered products from Figure 4g to h, the ceramsite was completely melted to form glass phase and smooth surface, which limited the release of hazardous gas and heavy metals from the ceramsite.

SEM microstructure observation of sintered products

In order to evaluate the effect of sintering temperature and duration on the microstructure of ceramsite, the SSE chosen as example was sintered at the following conditions: temperature 900, 1000, 1050 and 1100°C, duration 10 and 20 min, and the cross section of ceramsite was observed by SEM. The result is as follows in Figure 4a to h.

Figure 4a and b shows that the inner structure of ceramsite had a lot of irregular grains and maintains natural characteristic, which indicated that the sintering temperature and duration, namely 900°C and 10, 20 min, had no effect on the microstructure of ceramsite. Figure 4c started to have several little pores, which became larger and more in Figure 4d to f. The reason was that there was some gas bubbles to be released from the reaction of the decomposition of organic (sewage sludge contained in raw materials) or inorganic matters and the quantity of gas bubbles gradually increased until the larger pores were formed in the ceramsite. Figure 4f shows that although the larger pores were formed, the melting of ceramsite started and the phenomenon of melting became more serious in Figure 4(h). It was explained that the alkaline compounds such as MgO, Na₂O, etc, were as the flux of melting of ceramsite and the glass phase appeared to form the densified and

smooth structure in the ceramsite. Therefore, it could be concluded from Figure 4a to h that the sintering temperature and duration had prominent effect on the microstructure of ceramsite and the optimal sintering temperature and duration were 1000 and 20 min, which explained the phenomenon in sintering temperature and duration.

Conclusions

Based on the results obtained in this study, the conclusions are drawn as follows:

1. With the increasing preheating temperature and duration, the bulk and apparent density gradually decreased while the 1 h water adsorption rate relatively increased and the optimal preheating temperature and duration were 400°C and 20 min.
2. When the sintering temperature increased and duration decreased, the bulk and apparent density increased before 1000°C, but decreased with duration increasing after 1000°C. The variation of 1 h water adsorption rate was corresponding to the bulk and apparent density. The optimal sintering temperature and duration were 1000°C and 20 min.
3. When the content of BFS increased and that of SS declined, the bulk and apparent density gradually increased while the 1 h water adsorption rate relatively decreased.
4. The ceramsite produced had very good characteristics of solidifying heavy metal and the values of Cd, Cr and Sn met China national standard (GB5085.3-2007). The effects of sintering temperature before 1050°C and sintering duration 10, 20 min on the values of Cr, Sr and V had little changes while that suddenly became small at 1100°C except that of V at 1100°C and 10 min.
5. With the increasing of sintering temperature and duration, the gas was gradually released from the ceramsite to form many pores and finally the glass phase and smooth surface appeared in the ceramsite. The turning point of sintering temperature and duration were

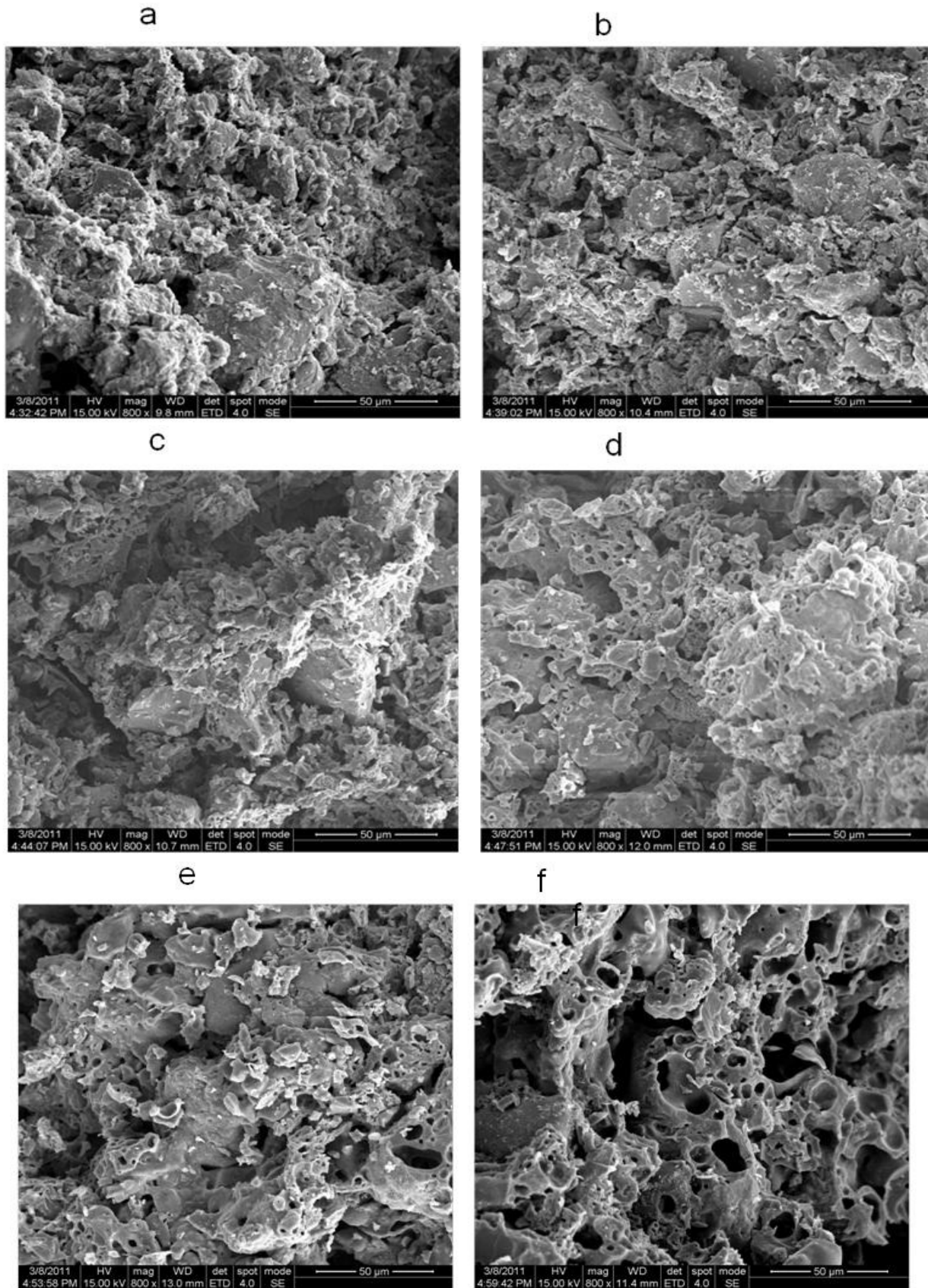


Figure 4. SEM micrographs of sintered products at 900 to 1100°C for 10 and 20 min. (a) 900°C - 10 min (b) 900°C - 20 min, (c) 1000°C - 10 min, (d) 1000°C - 20 min, (e) 1050°C - 10 min, (f) 1050°C - 20 min, (g) 1100°C - 10 min, (h) 1100°C - 20 min.

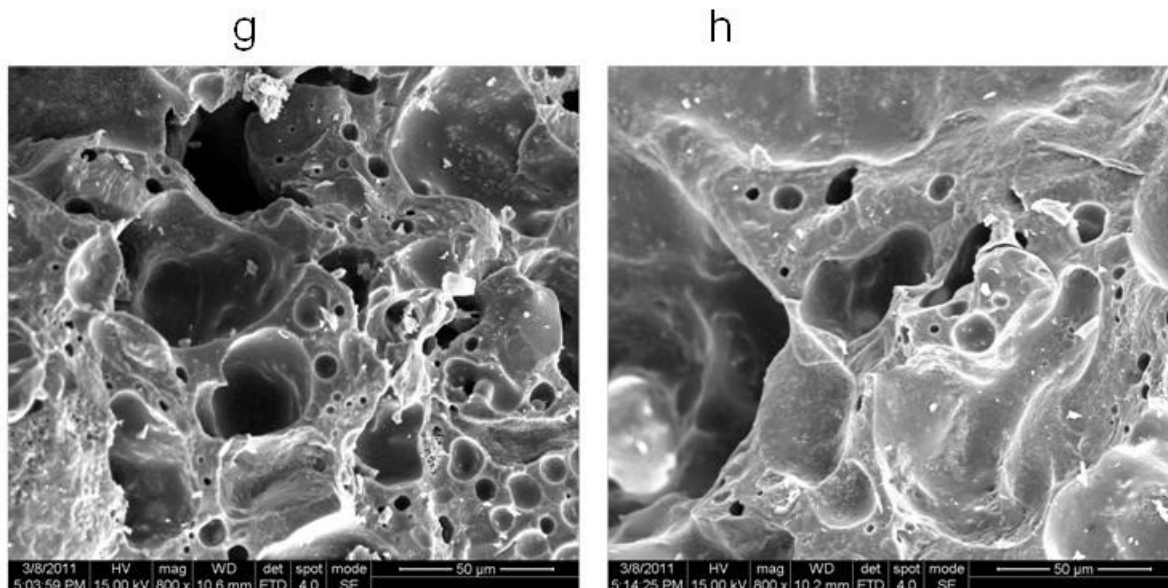


Figure 4. Contd.

1000 °C and 20 min, which was corresponding to 2.

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