Journal of Hazardous Materials 160 (2008) 489–494

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A research on sintering characteristics and mechanisms of dried sewage sludge

Xingrun Wang, Yiying Jin*, Zhingyu Wang, Rasool Bux Mahar, Yongfeng Nie

Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 11 April 2007
Received in revised form
21 November 2007
Accepted 7 March 2008
Available online 20 March 2008

Keywords:
Dried sewage sludge
Sintering process
Sintering mechanism

ABSTRACT

This study investigates the sintering behavior of dried sewage sludge and the related sintering mechanisms, considering sintering temperature and sintering time. Experimental results indicate that the characteristics are primarily influenced by sintering temperature. When the sintering temperature is increased from 1020 to 1050 °C, the specimens' compressive strength and bulk density increase significantly, while water absorption decreases obviously, indicating an improvement of densification due to sintering. However, the compressive strength cannot meet the requirement for traditional ceramic products due to the release of organic matters and the formation of big pores in the products. Phosphorus in sewage sludge initially takes reactions with the formation of calcium magnesium phosphate and aluminum phosphate during sintering, which are helpful for enhancing the compressive strength. So, some materials with high contents of Al could be used to enhance the compressive strength of products. Heavy metals are fixed primarily inside the sintered specimens, with the As, Pb, Cd, Cr, Ni, Cu, Zn concentrations in the leachate found to be in the range of China regulatory requirements. These results reveal the feasibility of recycling dried sewage sludge by sintering as a construction material.

1. Introduction

Increasing urbanization and industrialization have resulted in an enormous increase in the volume of wastewater throughout the world. There was about 42,840 million tons of wastewater generated in China in 2005, which is still increasing by an average rate of 5% every year. Due to a strong growth of the output of wastewater and the increased requirement on water treatment, sewage sludge, as an inevitable by-product of the treatment process of wastewater, is increasing very fast and becomes an important environmental issue.

So far, sewage sludge has been disposed off mainly by three methods, such as landfilling, sea dumping and soil application [1,2]. Difficulties for landfilling come from the high moisture state and large content of volatile solids in the sludge [2,3]. For soil application, heavy metals, which cause a problem of human toxicity as well as aquatic and terrestrial ecotoxicity, are released from the sludge [4]. While sea dumping causes ocean pollution and does harm to the ocean biology. Therefore, it is imperative to investigate new environmentally sustainable applications for this type of waste.

Ceramic, as a kind of lightweight aggregate, can be used to produce concrete mixtures. Using clay to produce ceramic is very common nowadays [5,6], but this method requires too much natural resources. Sewage sludge as a possible substitute of clay can be used to slow down the consumption of resources and to solve the environmental problems caused by this waste.

Earlier studies on making lightweight aggregate from sewage sludge focused mainly on the usage of sewage sludge as an additive material to clay [7–11]. These raw materials were dried, ground, finely mixed, shaped into balls with the aid of water and then sintered at 1000–1200 °C. In order to get qualified products, the proportion of sewage sludge was controlled to be less than 30%, which cannot satisfy the requirement of the quickly increasing output of sewage sludge. If the sludge proportion is too high, the products are found to be porous and loose due to the release of water and organic matters. Therefore, how to improve the weight percentage of sewage sludge added is the main problem at present.

On the other hand, during sintering many reactions and transformations happen in the phyllosilicates and the accompanying minerals, like quartz, calcite, feldspar, hematite and dolomite, which result in the formation of various crystalline phases. All these transformations and products play an important role on the final properties of the ceramic products [5,12]. Many studies have been carried out on clay sintering [13,14], but little is particularly devoted to the sintering of dried sewage sludge and the related mechanisms, while which is very helpful for further research on improving the proportion of sewage sludge in ceramic products.

The aim of this work is to study the sintering characteristics under varying sintering temperature and sintering time, such as compressive strength, bulk density and water absorption. Fixed

* Corresponding author. Tel.: +86 10 62782029; fax: +86 10 62789748.
E-mail address: Jinyy@mail.tsinghua.edu.cn (Y. Jin).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2008.03.054

rate and leaching behavior of heavy metals are also included in this paper to discuss environmental safety of products. Besides, sintering mechanism is researched by mineralogy and microstructure of sintered products.

2. Materials and methods

2.1. Sintering ceramic product

Sewage sludge used in this study was obtained from a municipal wastewater treatment plant in Beijing. The sludge was dewatered mechanically via belt presses, dried in stove at a temperature of 105 °C for 24 h and then pulverized with a ball mill until it could pass through a 45 mm sieve. Cylindrical specimens with a diameter of 20.4 mm and a height of 14 mm were prepared by uniaxial pressing and subsequently sintered in a electric kiln with sintering temperatures ranging from 950 to 1080 °C for 15, 30 and 45 min, respectively. A ramp rate of 9 °C/min and a temperature holding at 420 °C for 20 min were used.

2.2. Characterization

Dried sewage sludge samples were analyzed using standardized methods for fuel analyses, including fractions of ash, and total organic matter, contents of carbon, hydrogen, nitrogen and sulfur, as well as calorific heating values.

The major chemical compositions in sewage sludge, including P, Si, Ca, Mg, Fe, Al, K, Na and S, were analyzed by X-ray fluorescence (XRF) spectrometer (Shimadzu Lab Center XRF-1700, Japan) after combustion at 600 °C for 3 h, and expressed in the form of oxides.

A large number of trace elements, including As, Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge and in sintered products, were determined according to an ASTM method after the samples were digested [15]. The elements were measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer Elan 6000, USA) [16].

Fixed rate of heavy metals was defined as a ratio of the weight of heavy metals in products before sintering to that after sintering.

Standard method for leaching toxicity of solid wastes by horizontal vibration extraction procedure (HVEP) was used for heavy metal determination [17].

Mechanical quality of the sintered products was estimated by testing compressive strength, bulk density and 1 h water absorption rate. In compressive strength test, the single sintered product was pressed down by a steel puncheon until the sintered product was crushed. The compressive strength was calculated as the ratio between the load and the surface area of the sintered product, in stress units. The values of 1 h water absorption and bulk density were obtained as follows [18]:

$$\text{1 h water abosorption rate} = 100 \times \frac{\text{1 h saturated surface} - \text{dry weight of ceramic bodies} - \text{dry weight of ceramic bodies}}{\text{dry weight of ceramic bodies}} \quad (1)$$

$$\text{bulk density} = \frac{\text{weight of ceramic bodies}}{\text{volume of ceramic bodies}} \quad (2)$$

X-ray diffraction (XRD, Seimens O8DISCOVER) using 40 mA and 40 kV Cu Kα radiation was used for the research of crystalline phases in sintered products. The crystalline phases were identified by comparing the intensities and the positions of the Bragg peaks with the data files of the Joint Committee on Powder Diffraction Standards (JCPDS).

A JSM-6460LV scanning electron microscope was used for SEM observation.

3. Results and discussion

3.1. Properties of dried sewage sludge

Results of fuel analysis of dried sewage sludge are shown in Table 1. The heating value is very high, being nearly to peat, which is widely used as a support fuel in the power plants of the mills; therefore, using sewage sludge to produce ceramic products can cut down the cost of additional energy. The total organic matter content is quite high, which means the density of ceramic products will be low due to the release of organic matters. The sulfur content is relatively high and a sulfur removal procedure in flue gas cleanup process is needed.

Table 2 shows the chemical composition of sewage sludge ash determined by XRF after combustion at 600 °C for 3 h. The ash contains large amounts of P_2O_5 and SiO_2, with concentrations of 32.98% and 24.37%. The secondary components are CaO (10.69%), MgO (10.68%), Al_2O_3 (7.95%), Fe_2O_3 (6.09%) and K_2O (5.33%). The contents of other oxides are all less than 1%.

Table 3 shows the trace elements in the dried sewage sludge sample determined by ICP-MS. The major heavy metals identified are Pb and Zn, with concentrations of 1079.6 and 400.8 mg/kg, while the other heavy metals are all less than 100 mg/kg. So, more attention should be paid to Pb and Zn. The first line of Table 4 gives the HVEP results of heavy metals. As shown in this line, they are all

Table 1
Fuel analyses of dried sludge (all on dry basis)

Ash (wt%(dry))	27.15
Total organic matter (wt%(dry))	65.36
Carbon (wt%(dry))	28.06
Hydrogen (wt%(dry))	4.20
Nitrogen (wt%(dry))	3.64
Sulfur (wt%(dry))	1.72
Calorific heating value (kcal/kg(dry))	3609.21

Table 2
Chemical composition of sewage sludge

	Composition (wt%)
P_2O_5	32.98
SiO_2	24.37
Al_2O_3	7.95
CaO	10.69
MgO	10.68
Fe_2O_3	6.09
K_2O	5.33
Na_2O	0.34
TiO_2	0.73
SO_3	0.22
MnO	0.11

Table 3
Concentrations of heavy metals in sewage sludge

Heavy metals	Content of trace elements (mg/kg)
As	21.4
Cd	3.4
Cr	16
Cu	84.56
Ni	13.32
Pb	1079.6
Zn	400.8

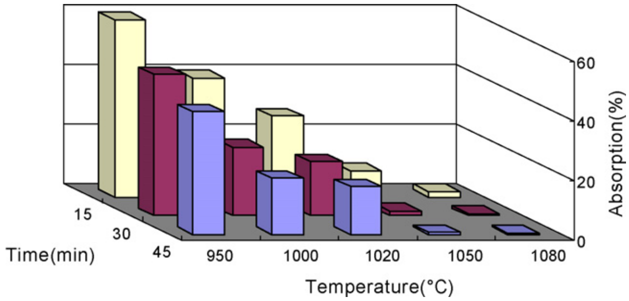


Fig. 1. Changes in water absorption rate for sintered products.

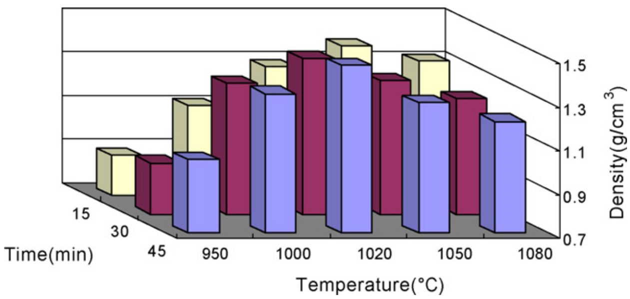


Fig. 2. Changes in bulk density for sintered products.

in the range of China Identification Standard for hazardous wastes [19], but exceed China Environmental Quality Standards for surface water [20].

3.2. Properties of sintered products

3.2.1. Water absorption of sintered products

The water absorption is defined as the ratio of the weight of water in the pores to the sintered product's weight. The quality of sintered products has an fundamental relationship with the water absorption, which is also a function of compressive strength and bulk density of the sintered products [21]. Fig. 1 shows that the rate decreases with increasing sintering temperature. When the sintering temperature is below 1020 °C, the rate ranges from 48% to 17%, which cannot meet the requirement for ceramic products. However, the rate decreases significantly to less than 2% when the sintering temperature reaches 1050 °C, for the reason that densification and melting occur and some of the open pores are closed. Fig. 1 also reveals that water absorption rate decreases by 11% when sintering time is increased from 15 to 30 min at 1050 °C, which is only 0.3% from 30 to 45 min. Sintering time has little effects on water absorption rate when sintering time is more than 30 min. So, some studies are based on the condition of 30 min in the following text.

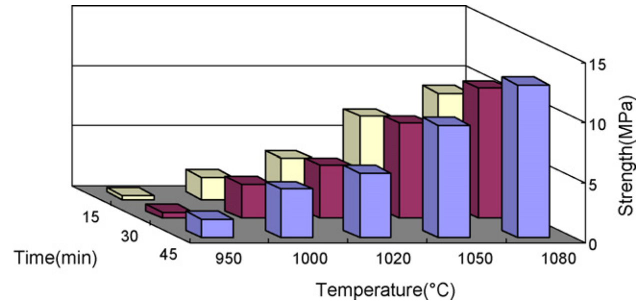


Fig. 3. Changes in compressive strength for sintered products.

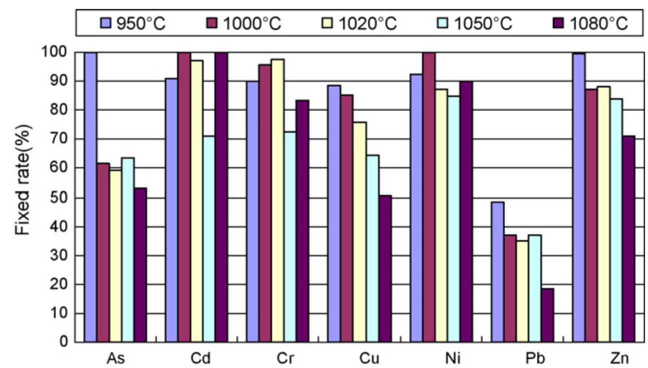


Fig. 4. Changes in fixed rate of heavy metals for sintered products.

3.2.2. Bulk density of sintered products

The bulk density is defined as the ratio of the weight to the total volume of the mass and the open pores. Fig. 2 shows that for 30 min of sintering time, the bulk density increases from 0.93 to 1.41 g/cm^3 with increasing sintering temperature from 950 to 1020 °C, indicating that densification caused by elevated temperatures shrinks the sample, as well as decreases the open pore volume and increases the closed pore volume, eventually causing an increase in bulk density. The effect is most intense at 1020 °C. However, at higher temperature, the surface sintering effect provides a much more closed pore volume, which decreases the bulk density by counter balancing part of the effect of expansion. Fig. 2 also reveals that the products sintered for 15 min have a maximum density at 1050 °C, which is achieved at 1020 °C for the products sintered for 30 min. It is concluded that a longer sintering time degrades the sintering temperature required. The effects are less for longer than 30 min as shown in the comparison between 30 and 45 min.

3.2.3. Compressive strength of sintered products

Compressive strength is a prerequisite for sewage sludge to be recycled as ceramic products. The strength test results are shown in Fig. 3. Sintering temperature is the determinative factor for the compressive strength. Between 1020 and 1050 °C, the strength of

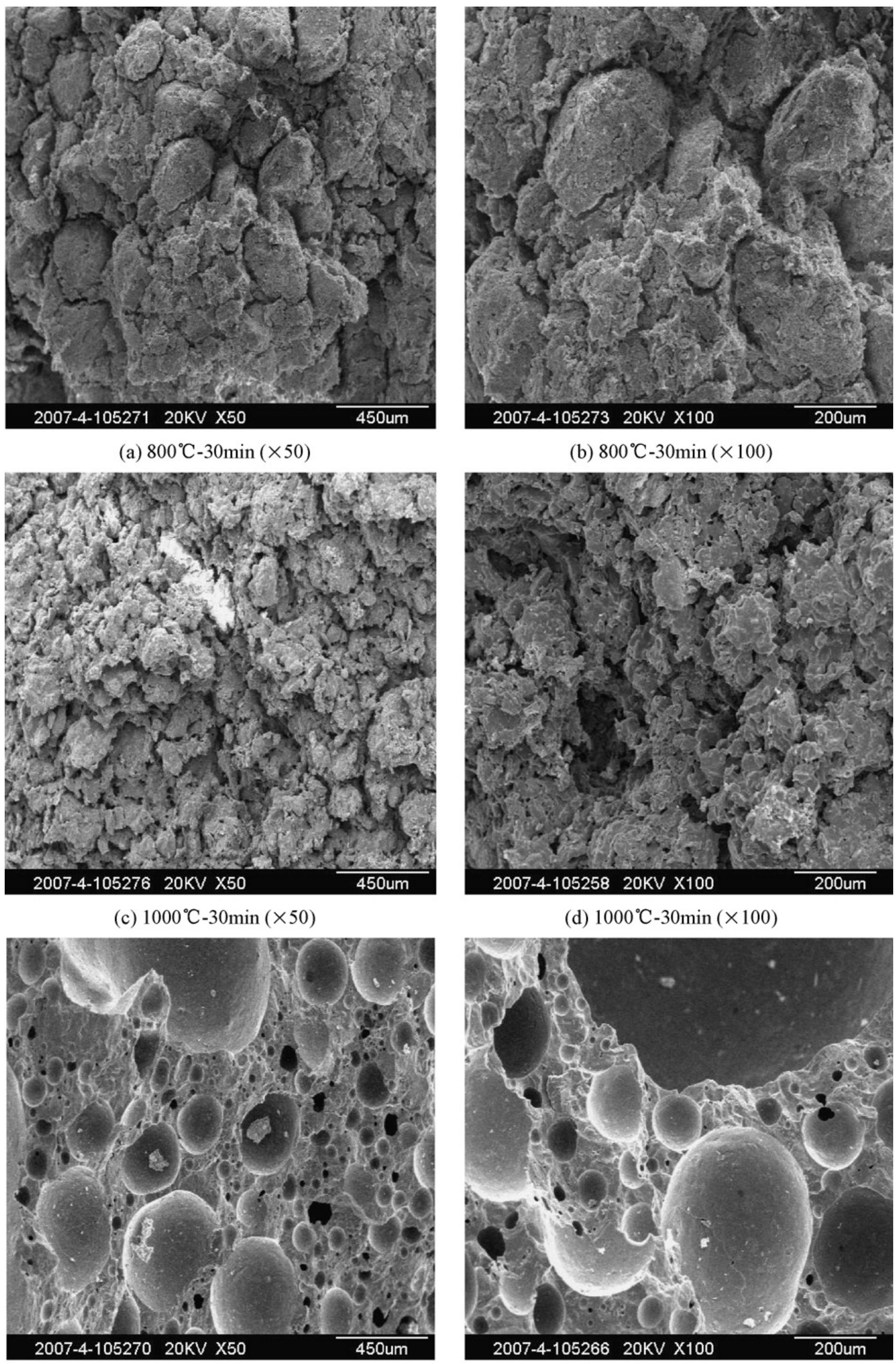
Table 4
HVEP-results of heavy metals in sewage sludge and sintered products

Sintered temperature (°C)	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)
20	0.0564	0.0034	0.3204	0.1582	0.0243	0.0873	1.8928
950	0.0220	0.0001	0.1077	0.0062	0.0065	n.d.	0.1638
1000	0.0249	n.d.	0.0479	0.0057	0.0070	n.d.	0.0449
1020	0.0156	0.0015	0.0352	0.0082	0.0071	0.0453	0.1238
1050	0.0013	0.0002	0.0226	0.0179	0.0088	n.d.	0.1019
1080	n.d.	0.0004	0.0151	0.0132	0.0076	n.d.	0.0451
Identification Standard for hazardous wastes (GB5085.3-1996)	≤1.5	≤0.3	≤10	≤50	≤10	≤3	≤50
Environmental Quality Standards for surface water III (GB3838-2002)	≤0.05	≤0.005	≤0.05	≤1	≤0.02	≤0.05	≤1

sintered products was enhanced significantly from 4.4 up to 10 MPa, revealing an improvement in densification and melting because of sintering, but it can still not fulfill the 15 MPa code requirement with respect to ceramic products due to the high organic matter content and the formation of big pores in the products. Therefore, some additive materials are needed to minimize size of pores and enhance the compressive strength of ceramic products.

3.2.4. Fixed rate of heavy metals

Fig. 4 shows the fixed rates of heavy metals after sintering at different temperatures for 30 min. Cd, Cr, Ni and Zn, with high boiling points are volatilized little in the sintering process, and the fixed rates are all higher than 70%. While the fixed rate of Cu decreases from 88.7% to 50.6% when the sintering temperature increases from 950 to 1080 °C. Pb and As are volatile, even the fixed rate of Pb drops to 18.6% or lower during sintering. At the same time, Pb is the pri-

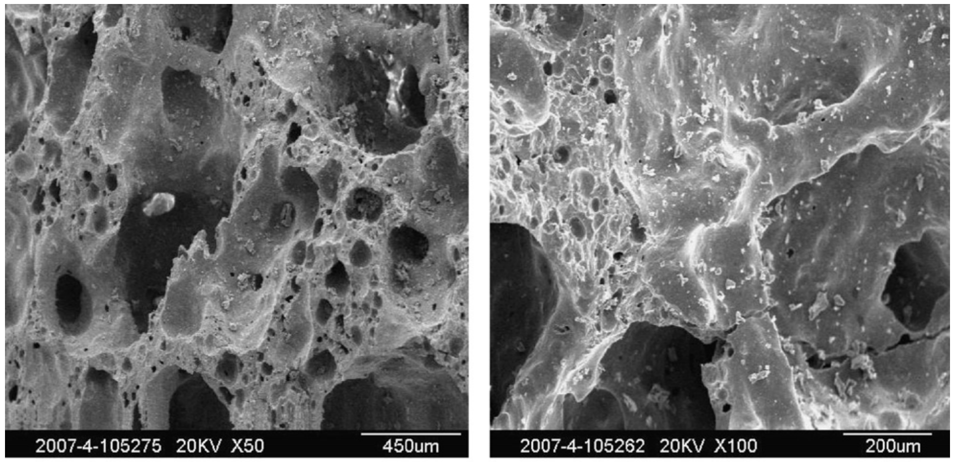


(a) 800℃-30min (×50) (b) 800℃-30min (×100)

(c) 1000℃-30min (×50) (d) 1000℃-30min (×100)

(e) 1050℃-30min (×50) (f) 1050℃-30min (×100)

Fig. 5. SEM micrographs of sintered products at 800–1080 °C for 30 min.



(g) 1080℃-30min (×50)   (h) 1080℃-30min (×100)

Fig. 5. (*Continued*).

mary heavy metal in sewage sludge as discussed in Section 3.1, therefore, some actions must be taken to control Pb volatilization in sintering progress.

3.2.5. Leaching characteristics of heavy metals

HVEP results of As, Cd, Cr, Cu, Ni, Pb and Zn for ceramic products sintered at 950–1080 °C for 30 min are listed in Table 4. The relationship between sintering temperature and leaching behavior mainly depends on the types of heavy metals and/or their compounds formed at that temperature [21,22]. As shown in Table 4, the leaching concentrations of As, Cd and Cr decrease with elevated sintering temperature; while Cu reveals an ascending tendency and Ni, Pb and Zn do not have obvious relationship with sintering temperature. However, all of them are in compliance with China Identification Standard for hazardous wastes and China Environmental Quality Standards for surface water when sintering temperature is higher than 1000 °C.

3.3. SEM microstructure observation of sintered products

Fig. 5 shows the microstructure of sintered products after sintering at 800, 1000, 1050 and 1080 °C, respectively, for 30 min examined by SEM (scanning electron microscope). Fig. 5(a)–(d) shows clearly the particulate nature of the sewage sludge particles at 800 and 1000 °C. Whereas at 1050 °C, melting occurs and the surface of sintered products appears to become sintered bonding and expansive, with a few openings caused by the penetration of bubbles (Fig. 5(e) and (f)). Such bloating effects cause the lightweight property of the aggregates. It is concluded that sewage sludge has lower melting temperature compared with clay and shale, which can effectively lower the sintering temperature and save energy. When the sintering temperature is 1080 °C, more bubbles are generated and busted with the appearance of prominent apertures. The SEM observations are in general agreement with the trends shown by the products properties data above.

3.4. Structural characterization

Fig. 6 gives the XRD data of sintered products sintered at different temperatures for 30 min. Quartz (SiO_2), calcite ($CaCO_3$), phosphorus pentoxide (P_2O_5), hematite (Fe_2O_3) and anhydrite ($CaSO_4$) are detected originally in the sintered products produced at 800 °C. In comparison, the intensities of the peaks associated with phosphorus pentoxide, calcite and anhydrite decrease as sintering temperature increases. At the same time, gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$), calcium magnesium phosphate ($7CaO{\cdot}2MgO{\cdot}3P_2O_5$) and aluminum phosphate ($AlPO_4$) are generated. It is suggested that when the sintering temperature increases from 800 to 1000 °C, several reactions, as follows, take place.

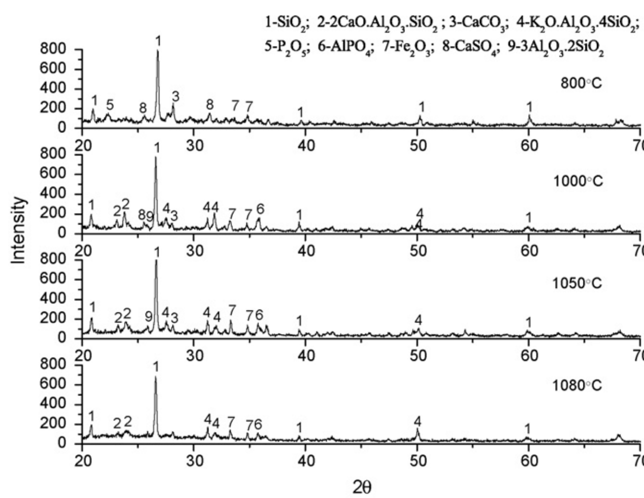


Fig. 6. X-ray diffraction of sintered products at 800–1080 °C for 30 min.

Recycling of sewage sludge as lightweight aggregates involves mechanisms of sintering and bloating in the sintering treatment process. Mechanism of sintering can improve the compressive strength of sintered products significantly, and generation of gehlenite, calcium magnesium phosphate and aluminum phosphate indicates sintering mechanism happens. Melting with generation of glassy phase appears at 1050–1080 °C indicates that sludge ceramic products require relatively lower sintering temperatures than products made from clay or shale, which is up to 1300 °C, and consequently energy is saved. Hematite changes little between 800 and 1000 °C, and decreases significantly when the sintering temperature is higher. In view of the decrease of bulk density in higher heating temperatures (see Section 3.2.2), the reaction that hematite decomposes into FeO and O_2 may happen at 1000–1080 °C:

$$CaCO_3 \overset{780\text{–}900\,^{\circ}C}{\longrightarrow} CaO + H_2O\uparrow \quad (3)$$

$$CaSO_4 \overset{800\text{–}1000\,^{\circ}C}{\longrightarrow} CaO + SO_2\uparrow \quad (4)$$

$$2CaO + Al_2O_3 + SiO_2 \overset{800-1000\,^{\circ}C}{\longrightarrow} 2CaO \cdot Al_2O_3 \cdot SiO_2 \quad (5)$$

$$7CaO + 2MgO + 3P_2O_5 \overset{800-1000\,^{\circ}C}{\longrightarrow} 7CaO \cdot 2MgO \cdot 3P_2O_5 \quad (6)$$

$$Al_2O_3 + P_2O_5 \overset{800-1000\,^{\circ}C}{\longrightarrow} 2AlPO_4 \quad (7)$$

4. Conclusions

Based on the results obtained in this paper, the following conclusions are drawn:

1. Sintering at a high temperature enhances the densification, closes some of the open pores, and causes water absorption rate to decrease, while the bulk density and the compressive strength increase, especially when the sintering temperature reaches 1050 °C. These characteristics are prerequisites for sewage sludge to be recycled as ceramic products.
2. When sintering time increases in the range of 30 min, the water absorption rate decreases while the bulk density increases, but the effect is negligible when sintering time is more than 30 min.
3. The sintered products sintered at 1050 °C exhibited a compressive strength ranging from 9 to 11 MPa. However, it cannot meet the requirement for traditional ceramic products due to the formation of big pores in ceramic products. Therefore, some additive materials are needed to minimize size of pores and enhance the compressive strength of ceramic products.
4. With regard to heavy metals, the fixed rates are very high except Pb. However, Pb is the major heavy metal in sewage sludge, so some actions should be taken to avoid Pb emission. The leaching concentrations of the sintered products are all in compliance with China Identification Standard for hazardous wastes and China Environmental Quality Standards for surface water.
5. XRD results show that phosphorus in sewage sludge initially will take reactions, and calcium magnesium phosphate and aluminum phosphate are formed when sintering, which are helpful for enhancing the compressive strength. So, some materials with high contents of Al could be used to enhance the compressive strength of products.
6. Glassy phase appears simultaneously with decomposition of hematite at 1050–1080 °C.

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