Preparation and mechanism of ultra-lightweight ceramics produced from sewage sludge

Yuanfeng Qi, Qinyan Yue*, Shuxin Han, Min Yue, Baoyu Gao, Hui Yu, Tian Shao

Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Shanda South Road No. 27, Jinan, Shandong 250100, China

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ABSTRACT

The preparation, characterization, preheating mechanism and bloating mechanism of ultra-lightweight ceramics (ULWC) manufactured by dehydrated sewage sludge (DSS) and clay were studied. Three experiments were designed to investigate the addition of DSS, the effect of preheating treatment and sintering treatment, respectively, and then the optimum conditions for preparing ULWC were determined. Chemical components, especially ratios of carbon content to iron oxide content (C/Fe-ratios), were used to explain the preheating mechanism; physical forces (surface tension and bloating force) combined with C/Fe-ratios were used to explain the bloating mechanism. The characterizations (physical properties, microstructure properties and toxic metal leaching properties) of ULWC that were prepared under the optimum conditions were tested. The results showed that the optimum addition of DSS was 20–30 wt.%, and the pellets which preheated at 400 °C for 20 min and sintered at 1150 °C for 10 min were beneficial to produce ULWC. Property tests of ULWC showed that ULWC was light (with a bulk density of 330.80 kg m^{-3}), waterproof (with a water absorption of 5.30 wt.%), nontoxic (contents of toxic metal leaching test were all below the detection limit) and suitable for practical civil engineering.

1. Introduction

Sludge, as the by-product of wastewater treatment plants, has become a major concern in China [1,2] due to industrial development. To prevent secondary pollution induced by sludge and convert sludge into useful resources has been widely investigated. Many treatment processes explored to dispose sludge, such as incineration, sanitary landfill, compost, production of activated charcoal, oil and methane [3–8]. Lightweight ceramics (LWC), not only had low density, but also presented some special characteristics, such as high strength, heat insulation and quakeproof property, are widely used in building materials, metallurgy, chemical industry, agriculture and environmental protection. Two kinds of sintering process, the one-stage sintering process and the two-stage sintering process (The one-stage sintering process means the preheating treatment process and sintering treatment process were simultaneous. The two-stage sintering process means the preheating treatment process preceded before the sintering treatment process) commonly applied in ceramic industry. Because of the finiteness of natural resources and the great demand for municipal engineering materials, many researchers have studied sludge for preparing LWC. Merino [9,10] studied the possible utilization of sludge ashes from wastewater treatment plant and developed lightweight ceramics (the true density of sludge ceramics was approximately 2000.00 kg m^{-3}). Cheeseman and Vird [11] developed LWC (with mean bulk densities of 1350.00 kg m^{-3}) in rotary electric tube furnace. Wang et al. [12] developed LWC (with bulk densities of 930.00 kg m^{-3}), and one-stage sintering process was used during the three studies. Mun [13] developed LWC (minimum bulk densities were approximate 600.00 kg m^{-3}) with two-stage sintering process. According to the authors' research, the ultra-lightweight ceramics (ULWC, bulk densities ≤500.00 kg m^{-3} and true densities ≤1000.00 kg m^{-3}) materials were more extensive application in civil engineering compared to LWC [14]. As filler materials for AFBRs (anaerobic fixed bed reactors) used in wastewater treatment [15], the back flushing was easy to proceed. According to our preliminary study of ULWC concrete, ULWC could be applied for building materials: when the water-to-cement mass ratio is 0.50 and the ULWC-to-water volume ratio is 2, the 28d (28d age of concrete) compressive strength and rupture strength of the ULWC concrete is 41.40 and 5.50 MPa, respectively. When the ULWC concrete and ordinary concrete have the close compressive strength, rupture strength and volume, the mass ratio of ULWC concrete to ordinary concrete is 0.30–0.36.

There were few studies about the production process of ULWC from sludge and/or the difference between one-stage and two-stage. In addition, sintering treatment was a complex physical–chemical phenomenon, and many researchers investigated

* Corresponding author. Tel.: +86 531 88365258; fax: +86 531 88364513.
E-mail address: qyyue@sdu.edu.cn (Q. Yue).

bloating mechanism with chemical components of raw materials [16,17,21,22], but few of them explained the bloating phenomenon and the preheating mechanism blending physical forces with chemical compositions. In the present study, the optimum conditions for preparing ULWC from sludge, the preheating mechanism and bloating mechanism was investigated.

2. Materials and methods

2.1. Raw materials

2.1.1. Pretreatment of dehydrated sewage sludge (DSS) and clay

Dehydrated sewage sludge obtained from the Jinan Wastewater Treatment Plant. Clay obtained from a brickfield (in Zibo City, Shandong Province). DSS and clay were dried at 105 °C for 4 h, crushed to pass sieve No. 100 (the diameter of mesh is 0.154 mm), and preserved until being used in polyethylene vessels to avoid humidification.

2.1.2. Chemical analysis

Chemical components of DSS and clay were determined by energy dispersive X-ray fluorescence spectrometer (EDX). DZ10-100 equipment was used during this part.

2.1.3. Thermal analysis

DSS and clay analyzed with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal analysis of DSS and clay conducted in air atmosphere; SDT Q600 equipment applied during this part. The two samples heated at a rhyme of 10 °C/min in the range between room temperature (22 °C) and 1100 °C, respectively. SDT Q600 equipment used to obtain DSC and TGA diagram at the same time.

2.1.4. Toxic metal elements

1000.00 g of DSS was soaked into 1.00 L of hydrochloric acid (0.20 mol L^{-1}; HCl: ρ = 1.19 g mL^{-1} Guaranteed Reagent (GR)) for 24 h. 1.00 mL of leach solution obtained from the supernatant was collected for the toxic metal elements leaching test. Toxic metal elements (Cu, Zn, Pb, Cr, Cd, Hg, Ba, Ni, and As) of 1000.00 g of DSS were determined by ICP-AES (IRIS Intrepid II XSP equipment) and were compared with GB 5085.3-2007 [18].

2.2. Preparation, characterization and laboratory experiments of ULWC

2.2.1. The preparation of ULWC

The raw pellets were thermal treated according to the following four steps as shown in Fig. 1:

Step 1: *Dosage, mixing and drying*. Raw pellets were prepared with DSS and clay. The raw materials (DSS and clay) were completely mixed, then, the mixture was poured into a pelletizer (DZ-20 equipment) to produce pellets (about 7.00 wt.% of water was added). Two sieves (the diameters of meshes were 5.00 mm and 6.00 mm, respectively) were used to sift the pellets, which were selected for the following treatment. Before thermal treatment, raw pellets settled in draught cupboard at room temperature (22 °C) for 24 h.

Step 2: *Preheating treatment*. The dried raw pellets held by porcelainous crucibles were settled in muffle and preheated for 10–30 min at a certain temperature (the preheating temperature and preheating time were different in different experiments).

Step 3: *Sintering treatment*. After preheating treatment, pellets were rapidly shifted into electric tube furnace (the sinter-
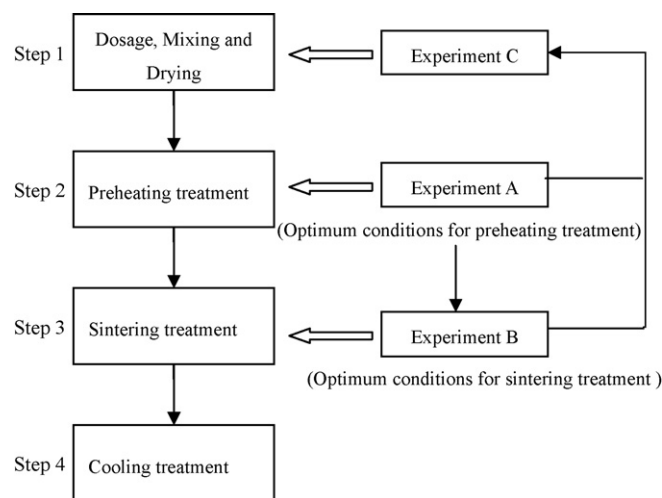

Fig. 1. Flow chart and positions of laboratory experiments.

ing temperature and sintering time may vary in different experiments). The electric tube furnace (SKQ-6 with a maximum temperature of 1600 °C, made in China) was 8 cm in internal diameter and 150 cm long, with a heated zone of 60 cm. The pellets settled just in the center of the heated zone.

Step 4: *Cooling treatment*. After the sintering process, the pellets settled in draught cupboard until they cooled to room temperature (22 °C).

2.2.2. Characterization of ULWC

Water absorption, bulk density and grain density were employed to characterize the quality of the sintered pellets. Mean values of two independent determinations are included.

Water absorption and bulk density were determined according to GB/T 17431.2-1998 [19]. Before the tests, sintered pellets settled into an exsiccator (105 °C) for 4 h. Then 100 g dried pellets were settled into a measuring cylinder (500 mL) and leveled completely. Bulk volume of dried pellets was tested. 200 mL of water was added into the measuring cylinder and covered the pellets completely (if the pellets float on the water, press them down with a piece of iron sheet). After 1 h, a dry towel was used to dry the surface of the wet pellets and 1 h saturated wet pellets were weighed. Water absorption was calculated from Eq. (1), and bulk density was calculated from Eq. (2):

Water absorption

$$= \frac{\text{mass of 1 h saturated wet pellets} - \text{mass of dry pellets}}{\text{mass of dry pellets}} \times 100\% \tag{1}$$

$$\text{Bulk density} = \frac{\text{mass of dry pellets}}{\text{bulk volume of dry pellets}} \text{kg m}^{-3} \tag{2}$$

Grain density was tested by the dry mass (M_{dry}) and the volume of the sintered pellets (V_{grain}). Individual grain density is calculated by the Archimedes' principle.

2.2.3. Laboratory experiments

Three laboratory experiments designed to determine the optimum conditions, and the physical–chemical behaviour and bloating mechanism were investigated at the same time. The position of each experiment is shown in Fig. 1. Definite experiments were:

Experiment A: *Preheating experiment*. Raw pellets were prepared with DSS and clay at a mass ratio of 3:7 according to the bloating effect area [20]. Raw pellets were preheated at 200, 250, 300, 350, 400, 450 and 500 °C. At the selected preheating temperature, raw pellets were preheated for 10, 20 and 30 min, respectively, then were rapidly shifted into the electric tube furnace at sintering temperature of 1150 °C and sintered for 10 min. The scorching hot pellets settled in draught cupboard and cooled down to room temperature (22 °C), then characteristic tests of the sintered pellets were performed, and the optimum preheating temperature and preheating time were determined.

Experiment B: Sintering experiment. Raw pellets were prepared with DSS and clay at a mass ratio of 3:7, and then preheated according to the conditions of experiment A. After the preheating treatment, raw pellets were rapidly sintered at the electric tube furnace at 950, 1000, 1050, 1100, 1150 and 1160 °C. Pellets were sintered for 5, 10, 15 min at each sintering temperature. After the cooling treatment, the characteristic tests of the sintered pellets were performed, and the optimum sintering temperature and sintering time for the preparation of ULWC were determined by the results of water absorption, bulk density and grain density tests.

Experiment C: The addition of DSS. Raw pellets were prepared with DSS and clay at a range of mass ratios: 4:6, 3:7, 2:8, 1:9, 0:10 (as a comparative trial). Conditions for preheated treatment and sintering treatment were selected from experiments A and B. Cooling treatment, characteristic tests of the sintered pellets were performed, the optimum conditions (mass ratio of DSS: clay, preheating temperature and preheating time, sintering temperature and sintering time) for preparing ULWC were determined.

2.3. Properties of ULWC prepared in the optimum conditions

In this part, ULWC were prepared according to the optimum conditions, and some properties (physical properties, microstructure properties and toxic metal elements) were tested, respectively.

Physical properties: Water absorption and bulk density were determined mainly according to GB/T 17431.2-1998 [19] and were calculated from Eqs. (1) and (2). Grain density was determined by measuring M_{dry} and V_{grain}. Individual grain density was calculated by the Archimedes' principle.

Four samples were examined by scanning electron microscopy (Hitachi S-520) both in the surface and in the cross-section (Au coated). The four selected samples were as follows: (1) the raw pellets; (2) pellets which were preheated at 400 °C for 20 min and then sintered at 1050 °C for 10 min; (3) pellets which were preheated at 400 °C for 20 min and then sintered at 1100 °C for 10 min; and (4) pellets which were preheated at 400 °C for 20 min and then sintered at 1150 °C for 10 min.

1000.00 g of ULWC was soaked into 1.00 L hydrochloric acid (0.20 mol L^{-1}; HCl: ρ = 1.19 g mL^{-1} Guaranteed Reagent (GR)) for 24 h. 1.00 mL of leach solution obtained from the supernatant was collected for the toxic metal elements leaching test. Toxic metal elements (Cu, Zn, Pb, Cr, Cd, Hg, Ba, Ni, and As) of 1000.00 g of ULWC were examined by ICP-AES (IRIS Intrepid II XSP equipment) and were compared with GB 5085.3-2007 [18].

3. Results and discussion

3.1. Chemical compositions of DSS and clay

Chemical compositions of DSS and clay are shown in Table 1. The main components of DSS were silicon dioxide, calcium oxide and aluminum oxide, followed by tungsten dioxide, iron oxide and sulfate. The main components of clay were silicon dioxide, aluminum oxide and iron oxide.
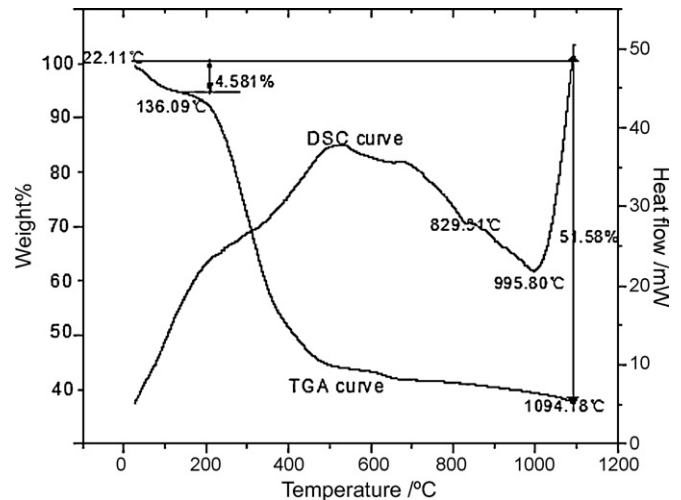
Fig. 2. Thermal analysis (DSC/TGA) of DSS.

3.2. Thermal analysis (DSC/TGA) of DSS and clay

Results of the thermal analysis of DSS up to 1100 °C are shown in Fig. 2. The observations of DSC and TGA, jointly with chemical analysis, showed that during heating treatment, the following phenomena occurred.

From 22 to about 136 °C, 4.58% of weight loss was shown in TGA curve which was caused by the elimination of absorbed water. An inflection was also observed in the DSC curve. This means that DSS has a highly hygroscopic character [9].

From 200 to about 600 °C, about 45.00% of weight loss was shown in TGA curve which should attribute to the elimination of structural water and the combustion of organic matters. An obvious exothermic peak was shown in DSC curve between 200 and 600 °C because of the combustion of the organic matters.

From 600 to about 1094 °C, about 5.00–6.00% of weight loss was shown in TGA curve. Endothermic reaction occurred in DSC curve, which attributed to the elimination of carbon dioxide formed from calcium carbonate and to the loss of sulphur dioxide formed by thermal decomposition.

Results of the thermal analysis (DSC/TGA) of clay up to 1100 °C are shown in Fig. 3, and the following phenomena occurred during heating treatment.
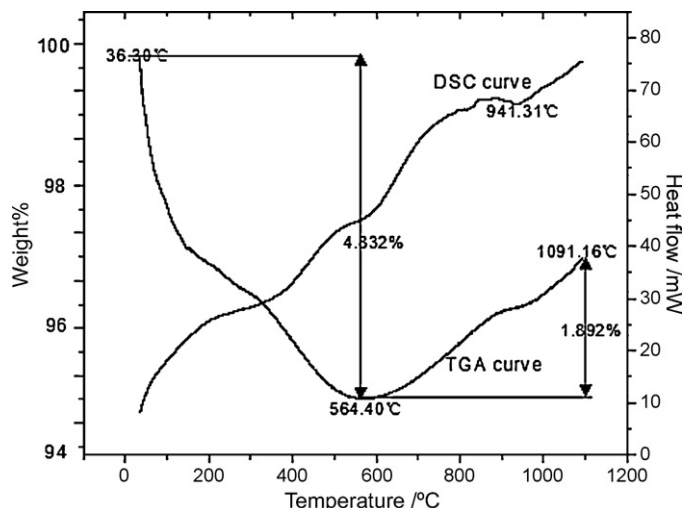
Fig. 3. Thermal analysis (DSC/TGA) of clay.

Table 1
Chemical component of DSS and clay.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	WO_2	Sulfate	Phosphate	Other
DSS	24.90	13.10	9.72	21.35	2.11	–	10.44	9.08	5.62	3.68
Clay	64.36	19.58	6.71	0.87	2.32	2.18	–	–	–	3.98

The important weight loss, which occurred at about 564 °C, was attributable to the elimination of structural water formed from OH^- ions in reticular positions of clay. The curve of DSC detected with an endothermic character and had a small peak a little before 600 °C.

From about 564 to 1091 °C, about 1.89% weight gain was shown in TGA curve. An exothermic phenomenon occurred between 650 and 950 °C, which should attribute to the elimination of carbon dioxide formed from calcium carbonate. An endothermic phenomenon occurred at about 941 °C, and this probably attributed to the fusion of the flux (the mixture of Fe_2O_3, FeO, CaO, MgO, Na_2O and K_2O).

3.3. Toxic metal elements leaching test of DSS

Toxic metal elements leaching test of 1000.00 g of DSS soaked into 1.00 L hydrochloric acid (0.20 mol L^{-1}; HCl: $\rho = 1.19$ g mL^{-1} Guaranteed reagent (GR)) for 24 h is shown in Table 2. The major toxic metals were Cu and Zn (total contents of 39.69 and 23.19 mg kg^{-1} of DSS, respectively), followed by Ba. Concentrations of Cd, Cr, Ni and As were 0.07, 2.59, 0.31 and 0.23 mg kg^{-1} of DSS, respectively. Toxic metal element, Hg, did not exist in DSS, and all the eight kinds of toxic metal elements did not exceed the value of threshold, as prescribed in GB 5085.3-2007 [18]. The concentration of total Pb was 6.07 mg kg^{-1} of DSS, and exceeded the value of threshold (≤ 5.00 mg kg^{-1} of hazardous waste) obviously. High leaching concentration of Pb would be harmful to the groundwater [23,24]. Depending on this case, more attention should be paid to the concentration of Pb in ULWC.

3.4. Results of preheating treatment (experiment A)

Results of preheating treatment are shown in Fig. 4. Raw pellets were preheated at different preheating temperatures and preheating times before sintering at 1150 °C. Fig. 4A shows raw pellets preheated for 10 min at different preheating temperatures. Grain density and bulk density decreased with the increase of preheating temperature before 400 °C, but increased with preheating temperature between 400 and 500 °C. In addition, bulk density and grain density had a minimum density at 400 °C, which was 500.00 and 1001.00 kg m^{-3}, respectively. Fig. 4B shows raw pellets preheated for 20 min at different preheating temperatures. Water absorption, grain density and bulk density all had the same kind of curve, and all decreased with the increase of preheating temperature before 400 °C and then increased with the preheating temperature between 400 and 500 °C. At 400 °C, water absorption, grain density and bulk density had a minimum with 5.7 wt.%, 829.00 and 402.80 kg m^{-3}, respectively. In addition, for practical civil engineering purpose, the general water absorption capacity should be below 15.00 wt.% [19], which was met by all ULWC samples as presented in Fig. 4B. The general bulk density should be below 500.00 kg m^{-3}, which was only met by ULWC samples preheated at 400 °C for 20 min. Fig. 4C showed the results of raw pellets preheated for 30 min at different preheating temperatures. Generally, water absorption, bulk density and grain density had the same results as shown in Fig. 4B.

Considering all the results mentioned above, the optimum preheating temperature and time were 400 °C and 20–30 min.
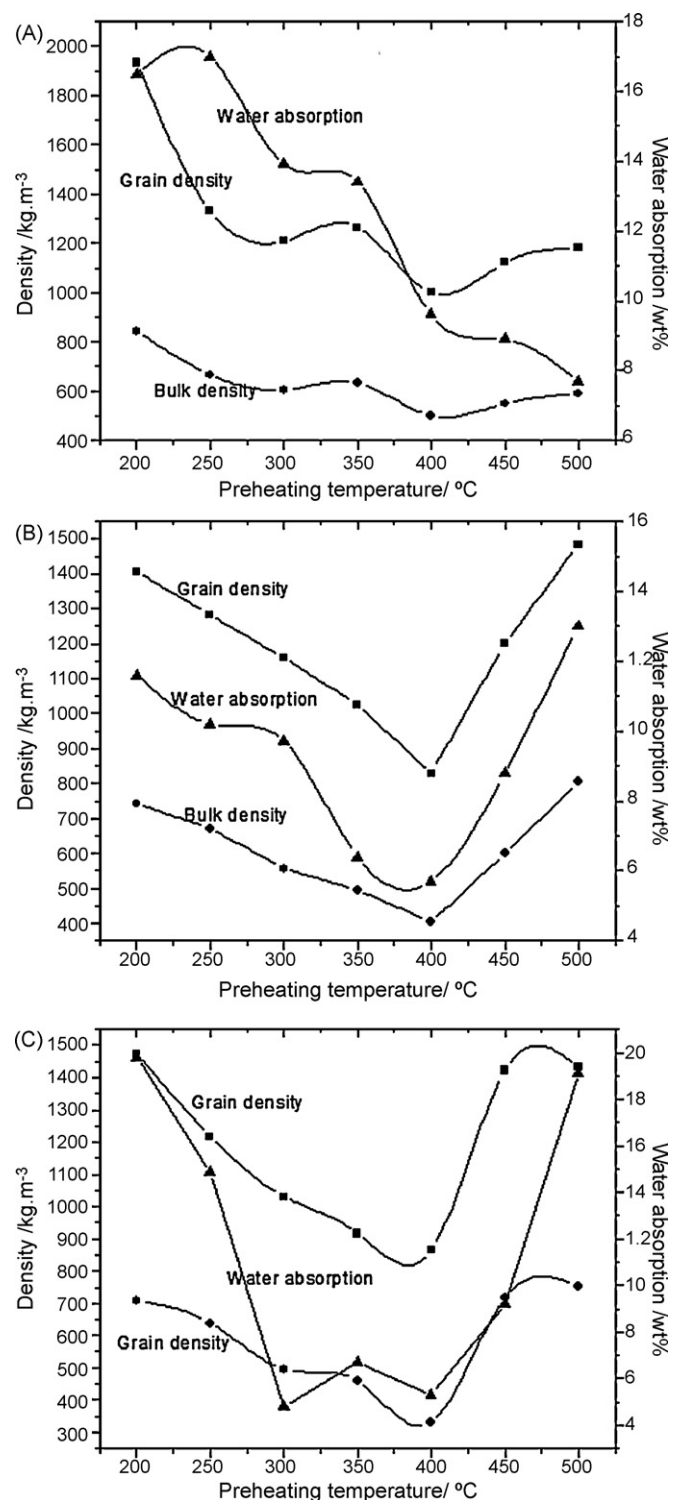

Fig. 4. Effect of preheating treatment (experiment A). (A) Preheated for 10 min; (B) preheated for 20 min and (C) preheated for 30 min

Table 2
Toxic metal elements of DSS.

Toxic metal	Contents (mg kg^{-1} of DSS)	Threshold (mg kg^{-1} of hazardous waste)	Toxic metal	Contents (mg kg^{-1} of DSS)	Threshold (mg kg^{-1} of hazardous waste)
Total Cu	39.59	100.00	Total Hg	ND	0.10
Total Zn	23.19	100.00	Total Ba	11.86	100.00
Total Cd	0.07	1.00	Total Ni	0.31	5.00
Total Cr	2.59	15.00	Total As	0.23	5.00
Total Pb	6.07	5.00			

3.5. Results of sintering treatment (experiment B)

Raw pellets preheated at 400 °C for 20 min, then shifted into electric tube furnace and rapidly sintered. The results of experiment B are shown in Fig. 5. Water absorption had a sharp drop at 1100 °C as the sintering time varied from 5 to 15 min, which changed from 23.80% (Fig. 5A), 22.50% (B) and 22.80% (C) to 12.50% (A), 10.40% (B) and 10.40% (C), respectively. Bulk density did not change before 1100 °C, which were 642.50 (Fig. 5A), 627.50 (B) and 625.00 kg m^{-3} (C), respectively. A sharp drop of bulk density occurred at 1150 °C, which were respectively 481.30, 330.80 and 448.20 kg m^{-3}. In addition, the average bulk density of the pellets sintered at 1150 °C for 10 min (Fig. 5B) were all lower than those sintered at 1150 °C for 5 and 15 min (Fig. 5A and C).

Depending on all the above mentioned, the optimum conditions for sintering process were determined after preheating treatment (preheated at 400 °C for 20 min), pellets were sintered at 1150 °C for 10 min.

3.6. Addition of DSS (experiment C)

Raw pellets were prepared with different mass ratios before preheating treatment (preheated at 400 °C for 20 min) and sintering treatment (sintered at 1150 °C for 10 min). Results of the addition of DSS are shown in Fig. 6. Bulk density was detected to be lower when the addition of DSS was 10–30 wt.% (points A, B and C), which were respectively 405.00, 353.70 and 300.80 kg m^{-3}. Water absorption reached to a maximum (24.60%) when the addition of DSS was 20 wt.% (point A).

3.7. Mechanisms

3.7.1. Preheating mechanism

Generally, two physical–chemical changes occurred during preheating treatment: dehydration and carbonization.

Dehydration: preheating treatment caused the emissions of absorbed water and structural water, and prevented the pellets from breaking at high temperatures.

Carbonization: organic matters existed in DSS converted to carbon, carbon monoxide and carbon dioxide. The generated gases would decrease the grain density preliminarily. Carbon was a kind of flux and reactant (that reacted with oxygen released from iron oxide) during bloating effect.

Ratios of carbon content to iron oxide content, which were called C/Fe-ratios for short in the following sections, were used to explain the preheating mechanism in this section. Iron oxides, specifically Fe_2O_3, released oxygen at 1000–1100 °C [16]. During the preheating treatment which is shown in Section 3.4 (the preheating temperatures were below 500 °C), the iron oxide content was constant, and C/Fe-ratios varied considerably by the carbon content. When the preheating time settled at 10 min (Fig. 4A) carbonization may not be completely finished, and carbon content was at a low ratio that caused C/Fe-ratio at a low level. Bulk density, grain density and water absorption decreased with the increase of preheating temperature. When the preheating time was prolonged to 20–30 min (Fig. 4B and c), minimum bulk density, grain
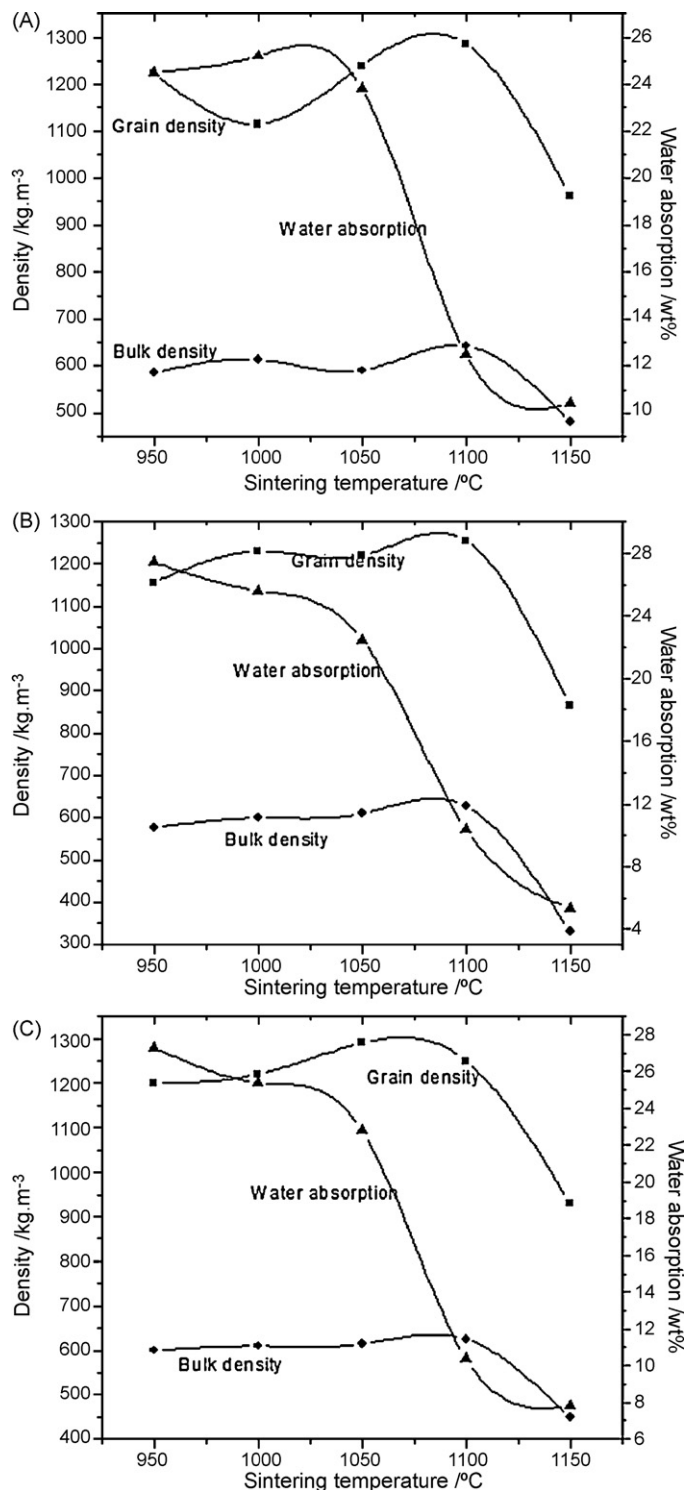

Fig. 5. Effect of sintering treatment process (experiment B). (A) Sintered for 5 min; (B) sintered for 10 min and (C) sintered for 15 min
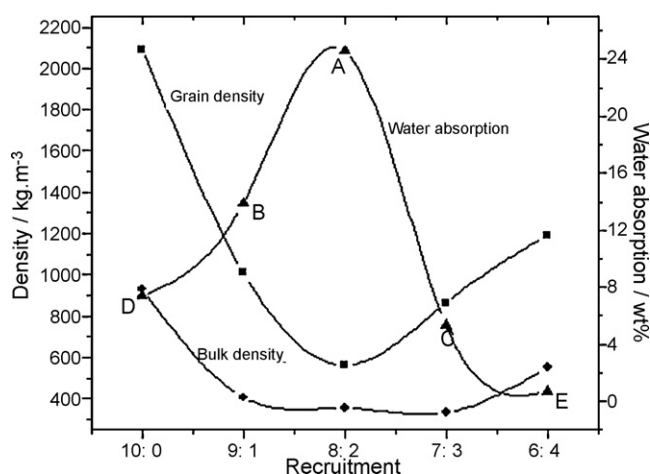
Fig. 6. Recruitment of DSS (experiment C). Addition of DSS: point A 20 wt.%; point B 10 wt.%; point C 30 wt.% point D 0 wt.%; point E 40 wt.%.

density and water absorption were obtained at 400 °C, which meant that the carbon generated from carbonization made the C/Fe-ratios more efficient in bloating the pellets. However, when the preheating temperature was above 400 °C, more carbon was generated from carbonization. The C/Fe-ratios (when the preheating temperature was 450 °C or 500 °C) were at a high level but not so efficient in bloating the pellets. According to all above mentioned, it could be inferred that low content or high content of carbon was not efficient in bloating the pellets. In other words, there existed an optimum C/Fe-ratios, which could bloat the pellets maximally. The most suitable ratios of carbon content to iron oxide content would be the aim of future work.

3.7.2. Bloating mechanism

Bloating was a complex phenomenon combined with physical and chemical changes. Necessary chemical components were required for the ULWC formation, and they could be classified into three groups [16].

Glassy phase, which formed the framework and surface of ceramics, should be in possession of enough viscosity when pellets heated in pre-set high temperatures (about 1150 °C). Major components of the raw materials: Al_2O_3 and SiO_2 belonged to glassy phase.

Gaseous compositions, which generated gaseous bubbles bloating the body of ceramics, included carbon and iron oxide (specifically Fe_2O_3 released oxygen (O_2) at 1000–1100 °C). Carbon rapidly reacted with oxygen to generate carbon monoxide (CO) and carbon dioxide (CO_2). The gas, CO, CO_2 and O_2 (if possible) would inflate the bodies of pellets. Suitable C/Fe-ratios were vitally important for bloating.

Flux, which lowered the melting point of the glassy phase, included CaO, MgO, Na_2O, Fe_2O_3 and carbon.

Two kinds of physical forces were used to explain the bloating phenomenon during this part [21,22].

Surface tension (ST): This kind of physical forces was generated from the viscosity of glassy phase at high temperatures. ST increased with the increase of sintering temperature and then decreased with the increase of sintering temperature.

Bulging force (BF): This kind of physical force was caused by CO, CO_2 and O_2, and bloated the pellets. BF increased with the increase of the sintering temperature and diameters of the pellets, but decreased with the increase of the ratios or the volume of pellets.

Suppose the gas was perfect gas and bodies of pellets were perfect spheres and Clapeyron equation ($pV = nRT$) could be used to deduce relationships of the factors:

$$BF = PS \tag{3}$$

$$pV = \frac{4}{3}\pi r^3 p = \frac{1}{3}rpS = \frac{1}{3}rBF \tag{4}$$

$$BF = \frac{3nRT}{r} \tag{5}$$

where p is for pressures intensity of gas; V is for volume of the pellets; r is for radius of the pellets; n is for molar volume of gas; R is for constant; T is for temperature and S is for the surface of the pellets. The equation showed that BF increased with the increase of the molar volume of gas. As mentioned above, gas has much to do with the C/Fe-ratios.

Generally, when combined both the investigation of Ducman and Mirtic [25] and Fig. 5, the bloating mechanism could be described as follows:

$ST = BF = 0$: as the sintering temperature increased, pellets surface would melt, both of ST and BF were increased. When the sintering temperature was below 1000 °C, glassy phase was not completely melted and gaseous bubbles were not generated (both ST and BF were proximate to zero), and pellets surface was not covered by glassy phase. High water absorption was detected (Fig. 5A–C) before 1000 °C. Both bulk density and grain density changed little during this part.

$ST > BF$: between sintered in 1000–1100 °C, pellets surface began to melt. ST increased to be much powerful than BF, which caused a sharp drop of water absorption but the change of bulk density and grain density was not detectable (Fig. 5A–C).

$ST = BF$: as the sintering temperature rose to 1150 °C (Fig. 5A–C), surface of pellets was melted completely, and gaseous components released enough gaseous bubbles to bloat the pellets. Water absorption, bulk density and grain density all approached to minimum points.

$ST < BF$: as the sintering temperature surpassed 1200 °C, gaseous bubbles passed through the surface of pellets and then bulged the pellets into pieces.

C/Fe-ratios and physical forces (ST and BF) were used to explain the results in Fig. 6.

C/Fe-ratios were the most suitable for bloating at point A (with a 20 wt.% addition of DSS) and released quantities of gaseous bubbles, then pellets would be extremely bloated at this moment. Shells of the pellets surface were unable to cover the gaseous bubbles [25]. Bulk density and grain density detected to be low at this point.

Physical forces (ST and BF) were proximately equal and suitable for shells covering gaseous bubbles at points B and C. Because of the lower C/Fe-ratios, BF was less powerful than that of point A. Water absorptions at points B and C became extremely lower than those at point A.

Contrastive pellets (prepared with clay only) are shown at point D. Because of lower C/Fe-ratios, bodies of the pellets were not bloated, and bulk density was extremely high (930.5 kg m^{-3}). Shells of pellets were melted at high temperatures and then decreased at the water absorptions.

C/Fe-ratios at point E were higher than those were at points A, B, C and D, and BF was higher than ST was, too. Gaseous bubbles, which generated inside the bodies, escaped from the shells, and bulk density and grain density were increased.

Table 3
Physical properties of ULWC prepared in optimum conditions.

	Bulk density (kg m^{-3})	Grain density (kg m^{-3})	Water absorption
Product (ULWC)	330.80	865.30	5.30%
GB/T 17431-1998	<500.00	–	<15.00%

3.8. Properties of ULWC prepared under optimum conditions

3.8.1. Physical properties of ULWC

ULWC were prepared under optimum conditions (addition of DSS was 30%, preheated at 400 °C for 20 min and sintered at 1150 °C for 10 min), and the physical properties (bulk density, water absorption, and grain density) were tested according to GB/T 17431.1-1998 [14]. Results are shown in Table 3. The ULWC pro-

duced in optimum conditions were lighter (with a bulk density of 330.80 kg m^{-3}) and had lower water absorption (5.30 wt.%). This kind of ULWC would be more suitable for practical civil engineering.

3.8.2. Toxic metal leaching test of ULWC

Results of toxic metal leaching tests of 1000.00 g of ULWC soaked into 1.00 L hydrochloric acid (0.20 mol L^{-1}; HCl: $\rho = 1.19$ g mL^{-1} Guaranteed reagent (GR)) for 24 h is shown in Table 4. Contents of
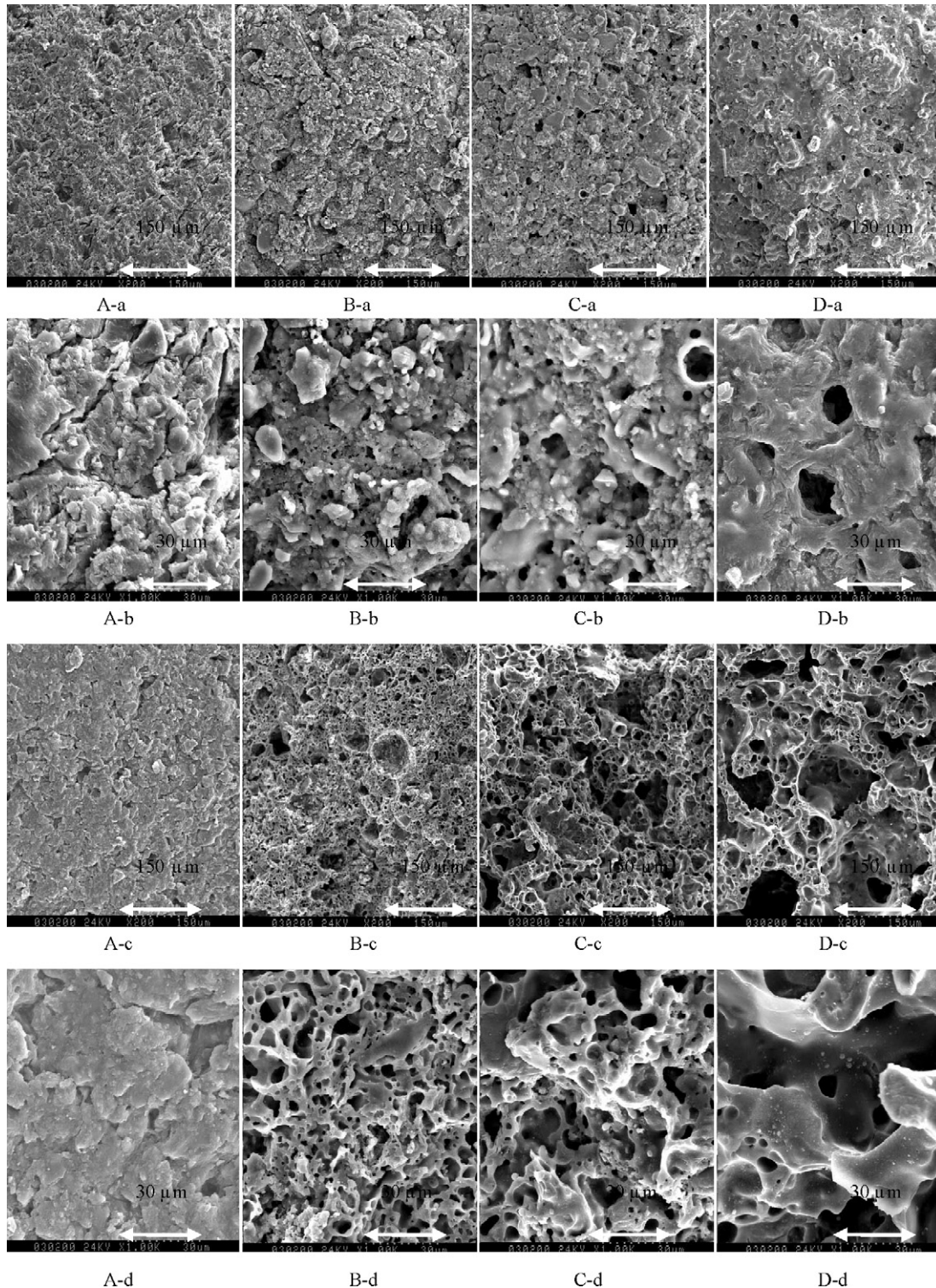

Fig. 7. Microstructure of ULWC (SEM). A-a and b surface of raw pellets (200,1000 times); A-c and d fracture surface of raw pellets (200 and 1000 times); B-a and b surface of pellets sintered at 1050 °C; B-c and d fracture surface of pellets sintered at 1050 °C; C-a and b surface of pellets sintered at 1100 °C; C -c and d fracture surface of pellets sintered at 1100 °C; D -a and b surface of pellets sintered at 1150 °C; D -c and d fracture surface of pellets sintered at 1150 °C.

Table 4
Toxic metal leaching test of ULWC.

Toxic metal	Contents (mg kg^{-1} of ULWC)	Threshold (mg kg^{-1} of hazardous waste)	Toxic metal	Contents (mg kg^{-1} of hazardous waste)	Threshold (mg kg^{-1} of ULWC)
Total Cu	0.04	100.00	Total Hg	ND	0.10
Total Zn	0.02	100.00	Total Ba	0.02	100.00
Total Cd	0.01	1.00	Total Ni	ND	5.00.
Total Pb	0.07	5.00	Total As	0.01	5.00
Total Cr	0.01	15.00			

toxic metal elements, as compared to those of DSS (Table 2), did not exceed the value of threshold as prescribed in GB 5085.3-2007 [18]. In addition, the concentration of total Pb, which was far exceeded the value of threshold in DSS, dropped from 6.07 mg kg^{-1} of DSS to 0.08 mg kg^{-1} of ULWC. Toxic metal elements were involved in ULWC and were harmless to the environment.

3.8.3. Microstructure analysis

Microstructure of raw pellets, ceramics (preheated at 400 °C for 20 min but sintered at 1050 and 1100 °C, respectively) and ULWC is shown in Fig. 7.

Surface figures (A-a and A-b) and fracture surface (A-c and A-d) showed the microstructure of raw pellets, and no aperture could be found neither in surface nor in fracture surface. Amorphous phase existed both in and outside the pellets. Surface figures (B-a and B-b) and fracture surface (B-c and B-d) showed the microstructure of ceramics sintered at 1050 °C for 10 min. Few apertures could be found in B-a. Surface was melted but rough at this temperature (ST > BF, gaseous bubbles were trapped inside), and crystals with diameters between 90 and 120 μm could be found in B-b (accurately quartz). B-c showed that apertures (diameters between 150 and 750 μm) widely existed inside, and frameworks (thickness between 15 and 20 μm) were approximately formed in B-d. Surface figures (C-a and C-b) and fracture surface (C-c and C-d) showed the microstructure of ceramics sintered at 1100 °C for 10 min. A small quantity of aperture could be found in C-a (ST > BF, but BF increased rapidly), and surface was melted fundamentally. The diameters of apertures in surface were 30–60 μm, and crystals with diameters between 60 and 120 μm could be found in C-b. Quantities of apertures (diameters between 150 and 900 μm) were shown in C-c, and frameworks (thickness between 30 and 90 μm) were formed completely in C-d. The fourth column of Fig. 7 shows the microstructure of ULWC. D-a showed the surface was melted completely and smooth (BF = ST). Some apertures that existed in surface (diameters between 30 and 150 μm) could be easily found in Fig. 7C-b. Obvious apertures (diameters were 1600 μm at least) abundantly distributed inside (C-c). Frameworks (diameters between 60 and 180 μm) were thick and formed completely (C-d). Surface of ULWC (D-a) was more smooth and porous than those of raw pellets and other ceramics (A-a, B-a and C-a). As the increase of temperatures, mean diameters, both the apertures inside and outside were also increased (A-b A-c, B-b B-c, C-b C-c and D-b D-c). Frameworks were formed at 1100 °C but were completely formed at 1150 °C (C-d compared with D-d). Because of gaseous bubbles and meltdown of glassy phases, two physical forces (ST and BF) were equivalent at 1150 °C, and then bodies of pellets were bloated at this condition. The results of SEM improved the correctness of the bloating mechanism as proposed in Section 3.7.2.

4. Conclusion

The optimum conditions for preparing ULWC were as follows: the addition of DSS was determined to be 25–35%; raw pellets were preheated at 400 °C for 20 min and then were rapidly shifted into electric tube furnace sintered at 1150 °C for 10 min. Mean bulk density, grain density and water absorption of ULWC prepared in

optimum conditions were separately 330.80, 865.30 kg m^{-3}, and 5.30 wt.%, and all of the characteristics conformed to the standard. Toxic metal leaching test compared with that of DSS showed ULWC were nontoxic. SEM figures showed ULWC were of cellular structure.

Preheating treatment process would increase the quality of ULWC, and two physical and chemical changes occurred during this process: dehydration and carbonization. Experiment A showed that a chemical component, especially C/Fe-ratios, explored the preheating mechanism.

Bloating was a complex phenomenon combined with physical and chemical changes. Suppose if the gas inside the pellets was prefect gas and bodies of pellets were sphere, physical forces (ST and BF) combined with chemical compositions (especially C/Fe-ratios) could explain the bloating phenomenon.

Acknowledgements

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