Preparation and characteristics of steam-autoclaved bricks produced from electrolytic manganese solid waste

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HIGHLIGHTS

- Producing steam-autoclaved brick utilizing electrolytic manganese solid waste.
- Determination of the most appropriate preparation conditions of the autoclave brick.
- Characterization of the brick, including environmental safe were examined.
- Mechanisms on strength, shrinkage and frost resistance of the brick were discussed.

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ABSTRACT

Electrolytic manganese solid waste (EMSW) is a sort of hydrometallurgical process residue from sulfuric acid leaching for rhodochrosite. The objective of this study was to investigate the feasibility of producing steam-autoclaved bricks with EMSW, and to determine the most appropriate preparation conditions. We tested the compressive strength (CS), dry shrinkage (DS) and frost resistance (FR), using microstructure change analysis combined with component reactions. The crystalline components of raw materials and bricks were examined by X-ray diffraction. Other properties of the brick, including leaching toxicity and radioactivity, were also measured to examine the environmental safety of EMSW steam-autoclaved bricks. The results show that the most appropriate conditions were: EMSW content of 30–40% by mass ratio, cement content of 10.5–12%, formation pressure of 15–20 MPa, W/C ratio of 0.4 and steam pressure of 1.2–1.5 MPa. Under those conditions, the compressive strength can be higher than 15 MPa, dry shrinkage lower than 0.11%, and compressive strength loss and weight loss lower than 10% and 2%, respectively. The compressive strength, leaching toxicity and radioactivity of the brick manufactured under the aforementioned conditions met the standards of GB 11945-1999 MU 15, GB 5085.3-2007 and GB 6566-2010, respectively. The compressive strength mechanism was formed by C-S-H gel and ettringite detected in the brick samples. Dry shrinkage was caused mainly by the removal of gaseous components and the shrinkage of cementitious materials. Frost resistance was influenced mainly by an increase in hydraulic pressure within the pore spaces.

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1. Introduction

As one of the basic material industries, electrolytic manganese metal (EMM) provides products that are widely used in non-ferrous metallurgy, electronics, chemical processing, environmental protection, food hygiene, welding, aerospace and other industries. China is the largest producer, consumer and exporter of EMM in the world. By 2012, the production capacity in China had exceeded 2.11 Mt/a, accounting for 98% of the global annual production [1,2]. As a by-product of EMM, the electrolytic manganese solid waste (EMSW) production ratio is 1:7–10 manganese ore with a

grade of 12–14%, resulting in an annual EMSW production rate of approximately 8–10 Mt.

The current allowable disposal method for EMSW is landfill, which can cause soil contamination, river or groundwater pollution and some other serious environmental pollution [3,4]. Duan et al determined that the main pollutants in the residue were manganese sulfate, ammonia nitrogen and heavy metals, such as cadmium and nickel and also found that 13.7% Mn, 17% Se, 44.09% ammonia and 55.3% SO_4^{2-} from raw materials entered residues [5]. Thus, for environmental protection and sustainable development, utilization of EMSW has become an issue. Many studies engaged in utilization on EMSW including materials of road beds [6], cement retarder [7], or soil fertilizer [8], as well as for building materials [9,10], chemical raw materials [11] and metal recovery

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[12–14]. Few reports on industrial utilization of EMSW were due to low EMSW addition, high cost and process instability. Producing building materials is a ripe technical route for utilizing waste and many methods on this field have been reported.

As for brick, sintered brick, lightweight brick and steam-autoclaved brick are optional. Studies on sintered brick made from municipal solid waste incinerator slag [15,16], red mud [17,18] coal fly ash [19] and river sediment [20] have been reported widely. Utilizing EMSW to make sintered bricks would be unfavorable because calcium sulfate in the EMSW would release SO_2 at 720–980 °C, causing secondary pollution. Producing such lightweight brick requires high loss on ignition and effective organic burn-out to increase porosity and decrease the weight [21]. However, it is difficult to create high porosity by heating the brick because EMSW contains few organics, where as silicon and calcium components are suitable for strength formation under hydrothermal conditions; hence producing steam-autoclaved brick may be more feasible. Extensive research has been conducted on the production of steam-autoclaved bricks from waste materials, such as circulating fluidized bed combustion fly ash (CFBC) [22], Class F fly ash [23], hematite tailings [24] and copper tailings [25]. The production of steam-autoclaved brick requires steam at 120–240 °C, consuming less energy than the sintered method. Furthermore its process is less complicated and raw materials are less expensive, and the consequent lower cost would make it suitable for practical application. With respect to the cost, addition and industrialization prospect, it can be observed that steam-autoclaved brick would be a promising and feasible option. To our knowledge, few studies have been reported on the technology and theory of EMSW autoclave bricks.

The objective of this study was to investigate the feasibility of producing steam-autoclaved bricks with EMSW, and then to determine the most appropriate preparation conditions. Additionally, strength, dry shrinkage and frost resistance are important characteristics which could supply a significant theoretical basis for future research and practical applications for steam-autoclaved bricks. Other properties of the brick, including leaching toxicity and radioactivity, were also measured to examine the environmental safety of EMSW steam-autoclaved bricks.

2. Materials and methods

2.1. Raw materials

Raw materials contained EMSW, cement, quicklime and river sand. The chemical components of the raw materials are shown in Table 1.

EMSW discharged by filtering process employed in the traditional hydrometallurgical process [5] was sampled from the Tianxiong Electrolytic Manganese Company, Chongqing province, China. Each EMSW sample of approximately 500 g was collected from four different corners in a filter cake over a period of 14 days, starting after continuous normal production of 30 days. The samples were sealed for preservation and were desiccated at 60 °C for 7 days, and then crushed to pass through a 100-mesh sieve (0.154 mm) and mixed together for subsequent use.

Commercial P.O. 42.5 Portland cement was used. A ground clinker with a Blaine fineness of 335 m^2/kg was added to prepare the samples.

Lime, purchased in Chongqing, with active CaO of 70.5% was used and its residue on 80 μm sieve is 2.6%.

The river sand (silt content <0.5%), purchased in Chongqing, was used as a fine aggregate. The mass-to-size ratio in size distributions were 9.4%, 68.8% and 21.8%, for >1.25 mm, 1.25–0.125 mm and <0.125 mm, respectively.

2.2. Pretreatment of EMSW

Because of its high concentration of manganese and ammonium sulfate, EMSW must be pretreated before producing bricks for consideration of safety. Quicklime, an alkaline reagent, was used to immobilize the contaminants and remove the NH_4^+-N . This approach is effective and has been verified by other researchers [26,27]. Therefore, EMSW was first agitated with quicklime at a dose of 90 g quicklime per kg of EMSW for 300 s and later air dried for 5 days. Water was added at a liquid-to-solid (L/S) ratio of 0.5.

2.3. Preparation of steam-autoclaved bricks

A total amount of 3.0 kg EMSW, cement and river sand was used to produce each specimen at different weight ratios. Water was added as the water-to-cement (W/C) ratio, then the raw materials were homogenized and formed in a mold with dimensions of 240 × 115 × 53 mm to obtain an early stage samples.

The early samples were then placed in a warm room at 90% relative humidity and 50 °C for 2 h for pre-curing. Then, the samples were transferred into an autoclave with a curing regime of 2-6-3 (digits represent the hours in the heating, holding and dropping stages respectively, i.e., heating 2 h, holding 6 h and dropping 3 h to 25 °C).

2.4. Analysis and methods

2.4.1. Characterization of steam-autoclaved bricks

The compressive strength (CS), dry shrinkage (DS) and frost resistance (FR) were tested to characterize the quality of the steam-autoclaved bricks produced in the experiment in order to determine the most appropriate preparation conditions. Three replicates were carried out in each performance test.

The CS of the specimens kept in a curing box for 28 days was measured by a compression testing device NYL-600 (Jianyi Instruments, Wuxi, China). The CS for the brick specimens was carried out according to GB/T 2542-2003 [28] and DS test procedure was provided elsewhere [29].

Frost resistance refers to the capacity of an object to resist frost-splitting when exposed to a climatic environment [30]. The samples were placed in a galvanized steel container and surrounded by water at all times while in the freeze-thaw apparatus, which could produce freeze-thaw cycles with chamber temperatures in the range of ± 20 °C. The temperature and period in the specimens during a full cycle were from refrigeration at -15 °C for 5 h to heating to 10 °C for 3 h. The frost resistance test contained 15 cycles. The weights and compressive strengths of the samples were determined before and after the frost resistance test. The weight loss (WL) and compressive strength loss (CSL) were calculated as shown by equations below:

$$\text{WL} = (\text{WBF} - \text{WAF}) / \text{WBS} \times 100\% \quad (1)$$

$$\text{CSL} = (\text{CSBF} - \text{CSAF}) / \text{CSBF} \times 100\% \quad (2)$$

where WBF is the weight before frost resistance, WAF is the weight after frost resistance, CSBF is the compressive strength before frost resistance, and CSAF is the compressive strength after frost resistance.

2.4.2. Chemical analysis

The chemical components of the EMSW and other materials were determined by energy dispersive X-ray analysis (EDX) and major and trace element were analyzed with a SHIMADZU XRF-1800 spectrometer.

2.4.3. X-ray diffraction (XRD) analysis

The crystal structure of the EMSW and steam-autoclaved bricks was studied by a Rigaku D/Max-12 kW diffractometer (Rigaku Corporation, Japan) equipped with a graphite monochromator in the diffracted beam. Measurements were performed at 100 mA and 40 kV, with copper $\text{K}\alpha$ radiation from 5° to 70°.

2.4.4. Microstructure analysis

The microstructure of some steam-autoclaved bricks was characterized by using JSM-6301F Scanning Electron Microscope (SEM), to examine the strength formation, dry shrinkage mechanism and frost resistance.

Table 1
Chemical components of raw materials (%).

Index	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na ₂ O	K ₂ O	TiO ₂	V ₂ O ₅	MnO
EMSW	22.03	3.09	8.83	19.16	3.35	31.37	0.237	0.727	0.176	0.39	8.54
Quicklime	4.21	1.933	0.65	72.8	9.3	0.14	0.082	0.014	–	–	–
P.O. cement	17.9	4.84	2.66	68.4	2.92	1.46	0.944	0.753	0.026	–	0.092
River sand	74.4	6.75	3.25	9.89	3.03	0.122	1.25	1.03	0.011	–	–

2.4.5. Leaching toxicity

The heavy metal elements of EMSW and steam-autoclaved bricks were leached by HJ/T 299–2007. The concentrations of heavy metals in the leachates were determined by ICP-AES (Thermo Intrepid II, US). The results were compared with Identification standards for hazardous wastes-Identification for extraction toxicity GB 5085.3–2007 to determine their safety of and applicability for civil engineering.

2.4.6. Radioactivity

To identify the radiation safety of the steam-autoclaved bricks, the internal exposure index (I_{Ra}) and external exposure index (I_r) of the bricks were calculated according to the specific activity of radionuclide of the raw materials. The calculation results were compared with the regulated limit of radionuclides in building materials GB 6566–2010 [31].

3. Results and discussion

3.1. Analysis of EMSW

3.1.1. Chemical analysis

The chemical components of the EMSW are presented in Table 1. It can be observed that silicon, calcium, iron, aluminum and sulfur were the main components of EMSW, while sodium, potassium, magnesium, manganese, titanium and vitriolium were the minor components. K_{alk} , shown in Eq. (3), is usually used to quantitatively depict the property of materials and to determine the acid-base properties of materials for making autoclave bricks. The K_{alk} of EMSW was -0.19 , indicating that the material was characteristically acidic, and that alkaline materials needed to be added to improve the K_{alk} . Consequently, correction materials, like cement and quicklime, are added to adjust the K_{alk} of mixed materials to between 0.8 and 1.2, which is the most appropriate value range for making autoclave bricks [32].

$$K_{alk} = [(CaO + 0.93MgO + 0.6R_2O) - (0.55Al_2O_3 + 0.35Fe_2O_3 + 0.7SO_3)] / 0.93SiO_2 \quad (3)$$

3.1.2. X-ray diffraction (XRD) analysis

The crystalline components of EMSW are given in Fig. 1. The spectra shows a significant amount of crystalline components, predominantly gypsum ($CaSO_4 \cdot 2H_2O$) and quartz (SiO_2), and small amounts of albite ($(Na,Ca)Al(Si,Al)_3O_8$), muscovite ($KAl_2Si_3AlO_{10}(OH)_2$) and ramsdellite (MnO_2). Possible crystalline silicate phases that might be beneficial for generating calcium silicate hydrate (C–S–H) gel or calcium aluminum silicate hydrate (C–A–S–H) were identified, including clinocllore ($(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$) and terranovaite ($NaCaAl_3Si_{17}O_{40} \cdot H_2O$).

3.1.3. Microstructure analysis

The SEM photograph of EMSW in Fig. 2 shows an unequal particle size. Because of their uneven and irregular surfaces, some

Fig. 2. SEM photograph of EMSW.

cylindrical-shaped particles have absorbed many smaller ones. The average particle size was estimated to be $44 \mu m$ (by volume). Because of fine particles of EMSW and high moisture (25–33%), it is difficult for the particles to make dispersion after high-pressure pressed.

3.2. Determination of the most appropriate preparation conditions

3.2.1. Effects of EMSW content and cement content on the brick properties

Two groups of samples with different EMSW and cement contents were prepared. The water-to-cement (W/C) ratio was constant at 0.4 and the cement content was 10% and the formation pressure was 20 MPa. All samples were put through the same 2–6–3 curing regime.

The effect of EMSW content on the properties of the bricks is shown in Fig. 3. The EMSW content had a negative influence on CSL and WL. Given constant conditions, as EMSW content increased, CS obviously decreased from 24.08 to 12.1 MPa, while DS rose from 0.095% to 0.153%. Fig. 3(b) shows that CSL increased from 14.1% to 29.5% while WL increased from 0.85% to 3.85%. The 30–40% EMSW content was used in this demonstration to get high-strength performance bricks. Hence, a 30% EMSW content was adopted in the following experiments.

Using other sample with EMSW content constant at 30% and W/C ratio of 0.4, the effect of cement content on the properties of the steam-autoclaved brick was examined. The effect of cement content on the bricks is depicted in Fig. 4.

The large changes in the values of these performance indices, with the variation in the cement content indicate that cement content was a key factor in making EMSW autoclaved brick. The CS of the brick increased gradually from 14.2 to 23.5 MPa as cement content increased from 6% to 20%. As for DS, its value decreased from 0.143% to 0.065% when cement content increased from 6% to 20%, as Fig. 4(a) shows. The changes in CSL and WL showed the same tendency, and their values decreased with an increase in cement content.

Generally, dry shrinkage increases with increases in cement content. It is conventional caused by shrinkage of C–S–H generated during cement hydration. However, Fig. 4 shows that a decrease in shrinkage with increases in cement content. Shrinkage decreases with an increase in cement content for three reasons: (a) Fine particle size: Waste particles smaller than $74 \mu m$ can delay the setting and hardening of cement [33]. Since the mean particle size of EMSW is $44 \mu m$, particles of less than $45 \mu m$ make up 50% of the volume of the EMSW, adversely affecting hydration. (b) Sulfate content in EMSW: Hydration products of cement will react with

Fig. 1. XRD patterns of EMSW.

Fig. 3. Effects of EMSW content on brick properties: (a) compressive strength and dry shrinkage, (b) compressive strength loss and weight loss.

Fig. 4. Effects of cement content on brick properties: (a) compressive strength and dry shrinkage, (b) compressive strength loss and weight loss.

sulfate to generate Aft and cause volume expansion [34], counteracting the shrinkage caused by C–S–H. (c) Gypsum content in EMSW: It is common knowledge that gypsum will retard the hydration of cement, reacting with C_3A in the cement to form ettringite [35] thereby expanding the volume. XRD analysis has found that EMSW contains 30–45% gypsum. In this study, shrinkage results were measured after curing for 28 days. It is possible that prolonging the curing time would gradually increase the shrinkage as shrinkage tends to be slow in early stages, accelerating as time goes on.

According to the Standard GB 11945-1999, the accepted maximum loss values of CSL and WL are 20% and 2%, respectively. Therefore, to meet such standards, at least 10.5% of cement content has to be added. The K_{alk} value calculated by Eq. (3) was 1.08 when the mass ratio of EMSW, quicklime, cement and river sand in the mixed materials were 30%, 3%, 10.5% and 56.5%, respectively. Similarly, the K_{alk} value was 1.05 when the mass ratio of EMSW was 40%, while the other ratios remained the same. Consequently, the most appropriate proportion for the steam-autoclaved brick are EMSW 30–40%, cement 10.5–12%, river sand 56.5–46.6%.

3.2.2. Effect of formation pressure on brick properties

Under the conditions of 30% EMSW, 10.5% cement, 0.4 W/C ratio and 1.2 MPa steam pressure, mixed materials were separated into 5 groups and subjected to 15, 20, 25, 30 and 35 MPa. The effects of formation pressures on the properties of the brick are shown in Fig. 5. CS climbed as the formation pressures rose to 19.4 MPa and then fell very slightly with higher MPa values, indicating that higher formation pressure could exert an adverse effect on the strength of the brick. There was little effect of formation pressure on DS. A slight variation was from 0.11% to 0.128%, but this was not correlated with either rising or falling MPa values. However,

the variations of CSL and WL were just the opposite, as Fig. 5(b) shows. These values declined with an increasing in formation pressure, with a level off at higher MPa values. Normally, in practice, a favorable formation pressure is between 15 MPa and 20 MPa. High pressure is likely to decrease the life expectancy of the formation machine and lower the strength in later curing. For a good autoclaved brick, formation pressure should better between 15 and 20 MPa.

3.2.3. Effect of W/C ratio on brick properties

Under the conditions of 30% EMSW, 10.5% cement, 20 MPa formation pressure and 1.2 MPa steam pressure, 5 groups bricks were prepared with W/C ratios of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6. The results of the brick properties are shown in Fig. 6. The W/C ratio exerted varying influences on the properties of the brick. As shown in Fig. 6(a), CS reached its peak of 18.6 MPa under the W/C ratio of 0.5. However, as the W/C ratio continued to increase, CS began to decrease. Lower W/C will reduce workability and uniformity in mixing process. However, high water will result in high bleeding rate and more evaporation of the excessive water, leaving large pore and reducing the mechanical strength [36].

In the frost resistance experiment, the influences of CSL and WL were complicated. CSL decreased as W/C ratio increased from 0.1 to 0.3 and then increased as the W/C ratio rose from 0.5 to 0.6. WL decreased as the W/C ratio rose from 0.1 to 0.4, and then increased with the rise from 0.5 to 0.6. Only at the W/C ratios 0.4 and 0.5 are the values of CSL and WL both below the limit values in the Standard GB 11945-1999. In general, the moisture of materials for steam brick production should be low because high moisture could affect the early strength. Hence, the ratio of 0.4 is the most appropriate.

Fig. 5. Effect of formation pressure on the brick properties: (a) compressive strength and dry shrinkage, (b) compressive strength loss and weight loss.

Fig. 6. Effect of W/C ratio on brick properties; (a) compressive strength and dry shrinkage, (b) compressive strength loss and weight loss.

3.2.4. Effect of steam pressure on brick properties

Under the conditions of 30% EMSW, 10.5% cement, 20 MPa forming pressure and 0.4 W/C ratio, the bricks were separated into 5 groups and autoclaved at 0.6, 0.9, 1.2, 1.5 1.8 and 3.0 MPa. The effect of steam pressure on the brick properties is presented in Fig. 7. The results show that raising the steam pressure can enhance the strength of the bricks. Under the different steam pressures, CS increased from 11.4 to 23.7 MPa, while the DS declined from 0.135% to 0.076%, as Fig. 7(a) shows. However, the results also show that the pressure should not be above 2.6 MPa [32] because the crystalline particles of C–S–H would grow and increase their the volume of brick, resulting in a strength decrease, as can be seen in Fig. 7(a). The performances of CSL and WL were similar, as shown in Fig. 7(b), with the values first declining and then rising with the increase in steam pressure. However, the pressures for the minimum values differ: 1.5 MPa for CSL and 1.8 MPa for WL. To some extent, high steam pressure is important for good brick quality, but we cannot ignore the cost of producing steam. Taking

into consideration both the steam production cost and the requirement of the Standard, the most favorable steam pressure was determined to be between 1.2 and 1.5 MPa.

Based on the experimental results above, the most appropriate preparation conditions were determined to be as follows: EMSW content of 30–40%, cement content of 10.5–12%, formation pressure of 15–20 MPa, W/C ratio of 0.4 and steam pressure of 1.2–1.5 MPa. Under those conditions, the CS can be higher than 15 MPa, DS lower than 0.11%, and CSL and WL lower than 10% and 2%, respectively. Consequently, the strength meets the requirements of standard GB 11945-1999 MU 15.

3.3. Steam-autoclaved mechanisms

Steam-autoclaved mechanisms consist of the strength formation mechanism, the dry-shrinkage mechanism and the frost resistance mechanism.

Fig. 7. Effect of steam pressure on the brick properties: (a) compressive strength and dry shrinkage, (b) compressive strength loss and weight loss.

3.3.1. Strength formation mechanism

To determine the factors affecting strength formation, the CS data for the different cement contents were analyzed. As shown in Fig. 3(a), cement content plays an important role in strength formation. We could conclude, therefore, that the microstructure and crystalline components were likely to affect strength formation. SEM photographs of bricks prepared under the conditions of 30% EMSW, 12% cement, W/C ratio 0.4, 20 MPa formation pressure and 1.2 MPa steam pressure are shown in Fig. 8. It can be observed in the pink squares that two different forms existed in the brick: a short stick shape and the other, a small needle shape. The EDX spectrum shows that the main elements for the two substances were Si, Ca, Al, and O; and Ca, Al, O, S and C, respectively. A gross judgment is made that the substance with the short stick shape was probably a sort of C–S–H gel or C–A–S–H gel, and the other, ettringite.

According to XRD analysis as shown in Fig. 9, the main crystalline components of the steam-autoclaved bricks were anhydrite (CaSO_4), albite ($(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$), muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$), quartz (SiO_2) and tobermorite ($\text{Ca}_5\text{Si}_6(\text{O,OH,F})_{18}\cdot 5\text{H}_2\text{O}$). Comparing these results with Fig. 1, it can be observed that gypsum disappeared, and that the presence of ettringite and tobermorite was observed. The disappearance of gypsum is due to its decomposition at the temperature of 180–220 °C in autoclaving. Ettringite, a pozzolanic product of cement hydration, is generated by the active components (mainly C_3S and A_3S) within cement. A high content of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ in EMSW supplies abundant SO_4^{2-} and Ca^{2+} that will react with the primary hydration products and bring about recrystallization to form ettringite [37]. In addition, the presence of tobermorite supplied further proof of the high strength of the brick. The formation of tobermorite is the result of the interaction of SiO_2 with lime at hydrothermal conditions. In the mixed materials, SiO_2 derived mainly from river sand reacts with Ca in the cement and EMSW and generated C–S–H gel under steam autoclaving. As shown in Fig. 8(a), the C–S–H gel was generated at the crust surface of the river sand [38], and its morphology developed quite well; one possible reason for this is that the sand can provide enough silicon to trigger the reaction. Additionally, little C–S–H gel was found at the surface of EMSW particles because the silicon was coated with gypsum, which could inhibit the formation of C–S–H gel. Although EMSW contained both silicon and calcium, which are the main elements required to form C–S–H gel, it would not readily react on its own, because the relatively positive silicon was coated with gypsum or anhydrite, which stopped the hydration action [39]. Therefore, steam-autoclaved bricks could not be produced from EMSW only; and other materials, like cementing materials and aggregates, are also needed.

Fig. 9. XRD patterns of a sample of the steam-autoclaved brick.

3.3.2. Dry shrinkage mechanism

The chemical components of ceramic bodies could commonly be divided into three groups: (a) the aggregate components, which constitute the framework and surfaces of the bodies, consisting mainly of SiO_2 and Al_2O_3 ; (b) the gaseous components, which generate gases or water missed in the autoclaving process at high temperature or in the alkaline background, containing mainly CaCO_3 [18], $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{SO}_4$; and (c) the cementitious materials, which generated cementitious components, such as C–S–H or ettringite, to gel the skeleton and aggregate materials. Unlike ceramics, the dry shrinkage of steam-autoclaved bricks depends on the gaseous components and cementitious materials. The former could release water or gas molecules to bloat pores, where the latter could produce gelation components to compress pore size.

Fig. 10 shows that aggregate materials with different particle sizes combined to form the variable-sized pore structure. It was found that the dry shrinkage varied with capillary tension in inverse proportion to the larger pore size. Water migration in the pore can cause the variation of capillary tension, and consequently, the capillary tension theory can be applied to the dry shrinkage mechanism of EMSW steam-autoclaved bricks.

The shrinkage of autoclave brick is caused by the increasing surface tension of concave menisci in desiccation according to capillary tension theory. The action of this tension would be balanced of the reaction by the shrinkage transformation. As the water evaporated, the process by which increasing tension causes more shrinkage would decrease, ceasing when the water disappeared. For this reason, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ from EMSW would lose water in a 1.5 stoichiometric ratio in desiccation but would also bloat up due to its association with two waters during soaking, as shown in Eqs. (4)–(6). As a result of those reactions, the shrinkage and

Fig. 8. SEM photographs in two different locations with steam-autoclaved bricks.

Fig. 10. SEM photograph of aggregate materials.

bloating would not be in balance, and the continuous shrinkage would occur.

It is noteworthy that $(\text{NH}_4)_2\text{SO}_4$ may have played a role in shrinkage of the brick. Bittner et al. [40] reported that the dry shrinkage of concrete decreased after ammonia removal. Although 90% of the ammonia was removed in the pretreatment of EMSW, the remaining $(\text{NH}_4)_2\text{SO}_4$ reacts with alkaline compounds in cement to form NH_3 as shown in Eq. (7). The reaction accelerates in desiccation because high temperature can release NH_3 and H_2O . Microcosmically, this reaction would result in a proliferation of small pores within the brick, and the volume fraction would increase slightly. The air way would enlarge the capillary, affecting the water surface tension [41]. When the specimens were soaking, the interspaces would be moistened and the reverse reaction of Eq. (7) would occur and decrease the reaction rate. The release of NH_3 would be affected by the cycle of desiccation and soaking in water, which would influence the capillary tension.

The shrinkage may be caused by the large energy gradient triggered by the migration of water in the interlayer of C–S–H to the outside surface, when the relative humidity changes [42]. As soon as the interlayer water content is lower than the relative humidity, shrinkage would begin. Unfortunately, it is difficult to determine the relative humidity and the interlayer water in desiccation or after autoclaving. Thus, there was no way we could compare their contributions to the shrinkage.

3.3.3. Frost resistance mechanism

Frost resistance is the spalling-proof capacity when exposed to changing temperature. It is common knowledge that pure water freezes at 0°C under normal atmospheric pressure. There is a 9% increase in volume when water turns to ice. However, water trapped within the capillary pores does not necessarily freeze at 0°C . The temperature at which water freezes in capillary pores is a function of the size of the pores and the pore chemistry [43]. The steam-autoclaved EMSW is a porous material in which water could be absorbed, reserved and transferred. At the low temperature of -20°C , the water within a diameter of 3.5 nm will freeze

to ice and damage the pores. The freezing of water, however, is not the main contributor to the freezing and thawing deterioration of the brick. The primary damage is caused by the increase in hydraulic pressure within the pore spaces [43]. If the hydraulic pressure could be relieved by allowing the water to escape into an unoccupied void, the frost deterioration would decrease. If the pressure increases and holds steady, the stress may eventually surpass the crush-resistance of the brick and cracking will occur, triggering the compressive strength loss and weight loss. Observing the different frost resistance in the steam-autoclaved bricks as shown in Fig. 11, the pore size and porosity vary with the resistance. The porosity of brick with low frost resistance is higher than the one with high frost resistance. High porosity might be characterized by coarse pores and low compactness [43]. In a brick sample with low frost resistance, the volume increases by freezing, the interspace will be more likely to crack the brick.

Based on the results above, it can be concluded that the correlation between CS and CSL or WL is close. The bricks with low CSL or WL showed high compressive strength and good frost resistance. This result is consistent with the earlier findings referred to in the literature stating that tensile strength was important to bricks' frost resistance [45]. Therefore, an empirical mathematical correlation between frost resistance and compressive strength will be examined in the future. Since both the pore size distribution and porosity can be determined. Consequently, frost resistance can be calculated from these tests.

The component of EMSW is complex because it is often affected by many factors, such as raw materials and process conditions. There is less reports of brick production on such similar material. Unlike fly ash, its autoclaved brick production is common and ripe. And the mechanism analysis of autoclaved brick made from fly ash is becoming deep and thorough. This research on EMSW, however, was limit and some analysis was just conjectural and referred to other bricks from waste materials. Hence, further research and development is needed.

3.4. Environmental safety evaluation

3.4.1. Leaching toxicity

To examine and compare the leaching toxicity of EMSW and its steam-autoclaved bricks prepared under the most appropriate preparation condition, heavy metals like Cd, Pb, Cr, Mn, Cu, Hg and As in the leachates were measured using sulphuric acid and nitric acid leaching methods, and their concentrations are shown in Table 2. Before and after pretreatment of EMSW and its brick, all heavy metals contained in the leachates met the regulatory limit of GB 5085.3-2007; the concentrations of Cr, Pb and Hg were lower than the detection limit. The concentrations of Cd, Mn and As in the EMSW leachate after pretreatment are lower than those of EMSW leachate before pretreatment, indicating that the pretreatment yielded good immobilization of the heavy metals. The concentrations in the leachates of EMSW steam-autoclaved brick were far below the regulatory limit of GB 5085.3-2007, and indicating the brick present no harm to the environment.

3.4.2. Radioactivity

According to national standard GB 6566-2010 [31], ^{226}Ra , ^{232}Th and ^{40}K are used to measure the radiation safety of building materials. The specific activity of ^{226}Ra , ^{232}Th and ^{40}K , internal exposure index (I_{Ra}) and the external exposure index (I_{r}) are presented in Table 3.

The leaching toxicity and radioactivity index of EMSW steam-autoclaved bricks prepared under the most appropriate preparation conditions are all below the standard levels, indicating that they are safe for use as building materials.

Fig. 11. SEM photographs of pore structure of different brick bodies: (a) brick with low frost resistance; (b) brick with high frost resistance.

Table 2

Concentrations of heavy metals in the leachates of EMSW and its steam-autoclaved brick (mg/L).

Heavy metals	Cd	Pb	Cr	Mn	Cu	Hg	As
Concentrations in the leachates of EMSW before pretreatment	0.041	N.D. ^a	N.D.	1680	0.027	N.D.	0.020
Concentrations in the leachates of EMSW after pretreatment	N.D.	N.D.	N.D.	0.036	N.D.	N.D.	N.D.
Concentrations in the leachates of EMSW steam-autoclaved brick	0.010	0.127	N.D.	N.D.	0.015	4.4×10^{-4}	1.23×10^{-3}
Regulatory limit of GB 5085.3-2007	1.0	5.0	15	–	100	0.1	5.0

"–" means there is no threshold value in the standard.

^a N.D. means not detected.

Table 3

Radionuclides in EMSW and its steam-autoclaved brick.

Items	Specific activity (Bq kg ⁻¹)			I_{Ra}	I_r
	²²⁶ Ra	²³² Th	⁴⁰ K		
EMSW	36.9	58.0	631.2	0.2	0.5
EMSW steam-autoclaved brick	29.23	18.41	229.77	0.1	0.2
GB 6566-2010				<1.0	<1.0

4. Conclusions

In this study, the most appropriate condition for preparing EMSW steam-autoclaved bricks was determined to be as follows: EMSW content of 30–40% by mass ratio, cement content 10.5–12%, formation pressure 15–20 MPa, W/C ratio 0.4 and steam pressure 1.2–1.5 MPa. Under those conditions, the CS can be higher than 15 MPa, DS lower than 0.11%, and CSL and WL lower than 10% and 2%, respectively. In the view of strength, the CS, CSL and WL met the requirements of the standard GB 11945-1999 MU 15. According to the results of the toxic metal elements leaching test and the internal and external exposure indices, the EMSW steam-autoclaved bricks present no harm to the environment. Consequently, it is quite feasible to manufacture steam-autoclaved bricks with EMSW.

Comparing the results from experiments and mechanism analysis, it was determined that high compressive strength is generated by C–S–H gel and ettringite formation. Dry shrinkage depends mainly on the removal of gaseous components and the shrinkage of cementitious materials. Frost resistance is primarily influenced by the increase in hydraulic pressure with the pore spaces. An empirical frost resistance number, however, cannot be determined by CSL and WL; further analysis will focus on the pore size distribution and porosity.

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