

# Article Preparation and Characteristics of the Fired Bricks Produced from Polyaluminum Chloride Slag and Glass Powder

Fuqian Hei<sup>1,2</sup>, Qing Liu<sup>1,2,\*</sup>, Guodong Zhao<sup>3</sup>, Jinchen Ou<sup>1,2</sup> and Fei Xu<sup>1,2</sup>

- <sup>1</sup> School of Civil Engineering, University of South China, Hengyang 421001, China
- <sup>2</sup> Hunan Provincial Key Laboratory of High Performance Special Concrete, Hengyang 421001, China
- <sup>3</sup> School of Resourse Environment and Safety Engineering, University of South China, Hengyang 421000, China
- Correspondence: liuqing197901@163.com

Abstract: Polyaluminum chloride slag produced in the production of water treatment agents pollutes the environment and wastes land resources in the process of landfill and waste. In order to solve the resource waste of researching polyaluminum chloride slag, it was used to prepare sintered bricks. In this study, sintered bricks were prepared from polyaluminum chloride slag and glass powder. Taking compressive strength, water absorption, linear shrinkage and bulk density as measurement indexes, the effects of the glass powder content (0-10 wt), molding moisture (10-20), molding pressure (15-27.5 MPa), heating method (heat preservation at 400 °C and 1000 °C for 2 h, heat preservation at 500 °C and 1000 °C for 2 h, and heat preservation at 1000 °C for 2 h), heating rate (2–10 °C/min) and sintering temperature (900-1100 °C) on the performance of sintered brick and the conditions for meeting Chinese standards were studied. Then, the sintered bricks prepared at different temperatures were characterized by X-ray diffraction and scanning electron microscopy. The results show that the compressive strength (bulk density) increases and the water absorption decreases with the increase of the glass powder content, molding pressure, molding moisture and sintering temperature. Moreover, the linear shrinkage increases with the increase of the molding pressure, molding moisture and sintering temperature, but decreases with the increase of the glass powder content. When the glass powder content of the sintered brick is 10 wt%, with molding moisture of 20 wt%, molding pressure of 25 MPa, heating mode to directly raise the temperature to the target temperature, heating speed of 10 °C/min and sintering temperature of 1100 °C, the properties, pH value and leaching toxicity of sintered bricks meet the requirements of Chinese standard brick MU15. XRD and SEM analyses showed that with the increase of the sintering temperature, new albite and amphibole phases were formed in the structure, and quartz and other silicate minerals melted to form a liquid phase, making the structure more compact and the performance better. The research results provide a reference for the comprehensive utilization of polyaluminum chloride slag.

**Keywords:** polyaluminum chloride slag; glass powder; fired brick; forming conditions; microscopic characteristics

# 1. Introduction

The water purifying agent polyaluminum chloride occupies a dominant position in the market of drinking water coagulants [1]. According to relevant statistics, in 2015, there were more than 300 water purification agent enterprises in China, and the market demand for water purification agents was 4.176 million tons. Each ton of polyaluminum chloride will produce 15 wt% of polyaluminum chloride slag, and the annual production of wet-based polyaluminum chloride slag will reach more than one million tons [2]. Chlorine salt contained in polyaluminum chloride slag brings some difficulties to the treatment process. At present, the commonly used disposal methods of polyaluminum chloride slag are landfill and discarding, which not only pollutes the environment, but also wastes land resources. Recycling is an ideal solution for solid waste residue. In order to solve



Citation: Hei, F.; Liu, Q.; Zhao, G.; Ou, J.; Xu, F. Preparation and Characteristics of the Fired Bricks Produced from Polyaluminum Chloride Slag and Glass Powder. *Appl. Sci.* 2023, *13*, 1989. https:// doi.org/10.3390/app13031989

Academic Editors: Myoung-Gyu Lee, Filippo Berto and Heng Li

Received: 23 December 2022 Revised: 27 January 2023 Accepted: 31 January 2023 Published: 3 February 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).



the resource utilization of polyaluminum chloride slag, various researchers use harmless polyaluminum chloride slag to produce cement, filler, adsorbent, clay, concrete and other products, but the utilization rate of these products is low and the consumption is small [3–7]. The main components of polyaluminum chloride slag are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which are similar to those of clay and have the conditions for preparing sintered bricks.

With the prohibition of sintered clay bricks, the preparation of sintered bricks from industrial solid wastes is an effective way to solve the problem of bulk solid wastes. The use of industrial solid wastes, such as coal gangue, agro-industrial wastes, alkaline-activated slag, fly ash and pyrite cinder, instead of clay to prepare building materials conforms to the sustainable development method [8–14].

Maryam Achik showed that by using pyrrhotite and yellow clay to burn sintered bricks at 1000 °C, the utilization rate of pyrrhotite can reach 30% [15]. Fly ash is used to replace clay to prepare sintered bricks. The highly doped fly ash sintered bricks have higher compressive strength and lower water absorption [16]. Adding solid waste to clay bricks can also improve the properties of fired bricks, such as light weight, good thermal insulation and high strength [17–21]. Glass powder is a commonly used additive in the preparation of sintered bricks [22,23]. Adding glass powder as a flux can reduce the sintering temperature of sintered bricks, improve the compressive strength of sintered bricks and reduce the water absorption and linear shrinkage [24,25]. Research by Umme Sarmeen Akhtar shows that adding glass powder to sintered clay bricks can reduce the sintering temperature to 650 °C and improve the compressive strength of sintered bricks [26]. A series of studies have been carried out on the application of glass powder to sintered bricks, but few reports have been made on the preparation of sintered bricks using polyaluminum chloride slag and glass powder.

In this study, firstly, quicklime was used to neutralize polyaluminum chloride slag. Then, fired brick was prepared by adding glass powder to polyaluminum chloride slag. The effects of the glass powder content, molding moisture, molding pressure, heating mode, heating rate and sintering temperature on the properties (compressive strength, water absorption, bulk density and linear shrinkage) of fired brick were systematically studied. After obtaining the best technological parameters for preparing sintered bricks, XRD and SEM analysis were carried out for sintered bricks at different temperatures. The research results provide a reference for the preparation of sintered bricks from polyaluminum chloride slag.

## 2. Experimental

#### 2.1. Raw Materials

The polyaluminum chloride slag is taken from the filter press slag produced by Hengyang Jianheng Industrial Co., Ltd. (Hengyang, China). Its water content is more than 35%, and it is a yellow-brown cake with weak acidity. The glass powder is made by grinding waste glass.

## 2.2. Performance Characterization

The raw materials were dried in a vacuum oven at 105 °C for 16 h and ground in a small jaw crusher to a grain size smaller than 0.5 mm. The particle size distribution of raw materials were measured by the laser particle size analyzer on an LS-609 instrument. For the microstructure of the raw materials and sintered bricks, scanning electron microscopy (QUANTA FEG 450, FEI, USA) was used to take sectional images under the accelerated voltage of 20 kV. The chemical composition of the raw materials was analyzed by X-ray fluorescence (zetium, PANalytical Axios Advanced, The Netherlands). The X-ray diffraction (XRD) analysis was performed on the BRUKER D8 Advance, with the scanning angle range from 10° to 90° and step size of 0.02. The mass and energy transitions of the raw materials during the sintering process were tested by the TG-DTG, using a NETZSCH STA 449F3 (TG-DTG, NETZSCH, Germany) thermogravimetric analyzer. The polyaluminum chloride

slag was heated from room temperature (30 °C) to 1000 °C at a rate of 10 °C/min in a nitrogen atmosphere.

# 2.3. Leaching Toxicity

The concentrations of hazardous heavy metal ions in the polyaluminum chloride slag, sintered bricks and its leachate were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent720, USA). The polyaluminum chloride slag was digested with aqua regia and hydrofluoric acid. The results are compared with the 5085.3-2007 [27] to evaluate the hazards of polyaluminum chloride slag. The leaching solution of polyaluminum chloride slag and sintered brick was prepared by the "Toxic Leaching Method of Solid Waste Leaching-Horizontal Oscillation Method" (HJ 557-2010) [28]. The concentration of pollutants and pH in the leaching solution was determined. The results were compared with the Chinese standard GB 8978-1996 [29] to measure the pollution of sintered brick of polyaluminum chloride slag in its usage.

# 2.4. The Preparation of Sintered Brick

Firstly, 2.5% CaO was added to the raw slag of polyaluminium chloride, stirred well with a geotechnical knife, cured for 24 h and then dried in a constant temperature drying oven (105  $^{\circ}$ C) for 16 h. The dried slag was ground in a small jaw crusher and passed through a sieve of 0.5 mm.

The pretreated polyaluminium chloride slag and glass powder were stirred in a cement mortar mixer for 2 min, different masses of distilled water were added and mixed well, then the mixture was sealed and aged for 24 h. The aged material was put into a customized mold and pressed on a microcomputer-controlled electro-hydraulic servo universal testing machine (WAW-EY1000C) by different pressures to produce cylindrical bricks with diameter =  $50 \pm 2$  mm and height =  $50 \pm 3$  mm. The bricks were dried in a constant temperature drying oven to remove the moisture from the bricks. Next, the dried bricks were placed in a muffle furnace (HR-B1600) and heated to different temperatures (900, 950, 1000, 1050, and 1100 °C) at different heating rates, held for 2 h, and then cooled to room temperature for performance testing. The preparation procedure of sintered brick is shown in Figure 1.



Figure 1. Preparation process of sintered brick.

# 2.5. Characterization of Sintered Bricks

The compressive strength, water absorption, bulk density and linear shrinkage are used as indicators to measure the quality of sintered bricks and determine the optimum preparation conditions. Because the sample is smaller than the standard ordinary brick, the compressive strength of the sintered brick, which was measured via a TYE-600E automatic pressure testing machine, was obtained from Equation (1). The water absorption of the sintered brick was obtained from Equation (2). The bulk density of the sintered brick was obtained from Equation (3). The linear shrinkage of the sintered brick was obtained from Equation (4).

$$P = \frac{F}{A}$$
(1)

where P is for compressive strength, MPa; F is for the force of breaking specimens, kN; and A is for the force area of specimens, mm<sup>2</sup>.

$$W = \frac{m_2 - m_1}{m_1} \times 100\%$$
 (2)

where W is for water absorption, %;  $m_2$  is for the weight of specimens after soaking in water for 24 h, g; and  $m_1$  is for the weight of specimens before soaking in water, g.

ρ

$$=\frac{m}{V}$$
 (3)

where  $\rho$  is for bulk density, g/cm<sup>3</sup>; m is for the mass of specimens after sintering, g; and V is for the volume of specimens, cm<sup>3</sup>.

$$S = \frac{D_1 - D_2}{D_1} \times 100\%$$
 (4)

where S is for linear shrinkage, %; D<sub>1</sub> is for the diameter of specimens before sintering, mm; and D<sub>2</sub> is for the diameter of specimens after sintering, mm.

## 3. Results and Discussion

# 3.1. Physico-Chemical Properties of the Raw Materials

3.1.1. Particle Size and Morphology of the Raw Materials

The particle size of the polyaluminum chloride slag and glass powder is shown in Figure 2. It can be seen that the median particle size (D50) of the polyaluminum chloride slag and glass powder is 30  $\mu$ m and 100  $\mu$ m. The polyaluminum chloride slag particles and glass powder are fine and have good fluidity. During the extrusion process, the fine particles can fill the pores formed by the coarse particles, making the structure denser.



Figure 2. Particle size distribution curve of polyaluminum chloride slag and glass powder.

The microstructure of the polyaluminum chloride slag and glass powder is shown in Figure 3. The particle size of the aluminum polychloride slag and glass powder is irregular, and there are sheet substances on the surface of the polyaluminum polychloride slag adhered to the large particles, resulting in loose structure.



Figure 3. SEM image of raw materials: (a) polyaluminum chloride slag; (b) glass powder.

3.1.2. Chemical and Mineral Composition of Raw Materials

The chemical composition of the polyaluminum chloride slag and glass powder is presented in Table 1. The polyaluminum chloride slag has a high content of  $SiO_2$  and  $Al_2O_3$ , which combine to form aluminosilicate at high temperature to modify the mechanical properties of the sintered bricks. However, the chlorine salt contained in the polyaluminum chloride slag will affect the performance of the sintered brick, and the content of chloride ion should be considered when preparing sintered brick. The glass powder is mainly composed of  $SiO_2$ ,  $Na_2O$ , CaO and other chemical compositions.  $Na_2O$  and CaO are the melting aids in the material, which can enhance the glass phase in the sintered brick.

**Table 1.** The chemical composition of raw materials (wt/%).

Samples	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	Cl	LOI
polyaluminum chloride slag	51.2	27.4	3.85	3.48	0.62	5.9	3.8	0.1	0.3	2.6	11.31
glass powder	70.2	1.4	7.9	4.2	0.1	0.1	0.3	15.2	0.3	0.1	-

Figure 4 presents the results of the XRD analysis of the raw materials. The main phase of polyaluminum chloride slag is silicate minerals, including quartz, spinel, gibbsite, perovskite and kaolin. The main phase of glass powder is amorphous phase, which forms more liquid phase under high temperature [25].



Figure 4. XRD patterns of raw materials: (a) polyaluminum chloride slag; (b) glass powder.

Therefore, the mixture of polyaluminum chloride slag and glass powder can be used as the raw material of sintered bricks.

In order to understand the quality change of the polyaluminum chloride slag at different temperatures, the TG-DTG analysis of the polyaluminum chloride slag was carried out and shown in Figure 5. From the TG-DTG curve, it can be seen that the mass loss of polyaluminum chloride slag is relatively uniform during the sintering process and will not cause internal cracking of the brick due to the instantaneous discharge of a large amount of gas. The overall mass loss is 12.24%. The weight loss at 112.99 °C is due to the discharge of residual free water and adsorbed water. The weight loss at 268.01 °C is due to the discharge of crystal water, and the weight loss at 484.55 °C is due to the discharge of structural water. When the temperature reaches 869 °C, the mass loss of polyaluminum chloride slag is the largest at this time [30]. If the slag is heated continuously, the mass will increase slightly, about 0.1%. This indicates that the amorphous substances formed after the destruction of the mineral crystalline phase begin to form new phases at this time and enter the sintering stage.



Figure 5. Thermal analysis of the polyaluminum chloride slag.

#### 3.1.4. Extraction Toxicity Analysis

The leaching of harmful components contained in solid waste will have a certain impact on the environment, so it is necessary to evaluate the safety of the polyaluminum chloride slag. It can be seen from Table 2 that the leaching toxicity of heavy metals from the polyaluminum chloride residue is far lower than the limit value of hazardous waste in the Chinese standard (GB 5085.3-2007) [27]. It can be seen from Table 3 that the index pH in the leaching solution of the polyaluminum chloride residue does not meet the limit value of the Class II standard in the Integrated Wastewater Discharge Standard (GB 8978-1996) [29], so it needs to be treated to avoid secondary pollution to the environment. According to the above analysis, polyaluminum chloride slag belongs to common industrial waste and can be recycled after neutralization treatment.

Table 2. Mass concentration of heavy metal leaching from polyaluminum chloride residue (mg/L).

Toxic Metal Elements	Cu	Pb	Cr	Zn	Cd	Ba	As	Mn
polyaluminum chloride slag	0.65	<0.02	1.52	<0.02	<0.02	2.6	<0.02	1.26
GB5085.3-2007	100	5	15	100	1	100	5	

Element	pН	Cl (mg/L)	Pb (mg/L)	Cr (mg/L)	Cd (mg/L)	Cu (mg/L)	Mn (mg/L)	Zn (mg/L)
polyaluminum chloride slag	3.5	1671.3	<0.02	0.05	<0.02	0.96	2.7	0.61
GB8978-1996	6–9	-	1.0	1.5	0.1	1.0	5.0	5.0

**Table 3.** pH and mass concentration of pollutants in leaching solution of polyaluminum chloride residue.

# 3.2. Neutralization Modification of Polyaluminum Chloride Slag

Polyaluminum chloride slag has weak acidity, so it needs to be neutralized first to prepare sintered bricks [31]. CaO is cheap, which can not only adjust the pH of polyaluminum chloride slag, but also play a certain role in curing. It can be seen from Table 4 that when the addition amount of CaO is 2.5–3 wt% of the polyaluminum chloride slag, the pH value of the polyaluminum chloride slag is close to neutral. The curing reaction is shown in Equation (5).

$$CaO + H_2O = Ca(OH)_2$$
(5)

Therefore, the subsequently used polyaluminum chloride slag is added with CaO for pretreatment.

Table 4. Effect of quicklime addition on pH value of polyaluminum chloride slag.

CaO/%	0	0.5	1	1.5	2	2.5	3
pН	3.3	3.7	3.9	4.1	4.6	6.6	7.8

#### 3.3. Effect of Different Factors on Properties of Fired Bricks

The initial setting is that the molding moisture is 15%, the molding pressure is 20 MPa, 400 °C and 1000 °C are kept for 2 h, the heating rate is 4 °C/min and the sintering temperature is 1000 °C. The effects of glass powder content, molding pressure, molding moisture, heating mode, heating rate and sintering temperature on the properties of sintered brick were studied.

## 3.3.1. Glass Powder Content

The addition of glass powder can promote vitrification and, thus, improve the performance of sintered bricks [25]. Figure 6a indicates the influence of glass powder content between 0 wt% and 10 wt% on the compressive strength and water absorption of sintered brick. The compressive strength of sintered brick increases with the increasing addition of glass powder. When the content of glass powder is increased from 0 wt% to 10 wt%, the compressive strength is increased by 56.8%. An increase in compressive strength was due to the addition of glass powder, which promotes the vitrification of the sintered brick. At the same time, the glass phase can fill the internal pores of the sintered brick, enhance the connectivity between particles and improve the compressive strength of the sintered brick [24]. The water absorption of sintered bricks decreases with the increasing glass powder content. When the content of glass powder was 10 wt%, the water absorption decreased to 23.64%. At this stage, the water absorption is higher than 19% of the Chinese standard. This is because the water absorption of the sintered brick is related to the size of the pores. The sintered brick combined with glass powder will form more glass phase to seal the internal pores at high temperatures, reduce the porosity and lead to the decrease of the water absorption [32].



**Figure 6.** Effect of glass powder content on the characteristics of sintered brick: (**a**) compressive strength and water absorption; (**b**) bulk density and sintering shrinkage.

The linear shrinkage is related to the properties of the materials. Excessive linear shrinkage will lead to the deformation of the sintered bricks, so the linear shrinkage should be controlled. In general, the linear shrinkage of fired bricks is lower than 8% [33]. The influence of glass powder on the linear shrinkage and bulk density of sintered bricks is shown in Figure 6b. The linear shrinkage of sintered brick decreases with the increasing glass powder content. When the content of glass powder reaches 10 wt%, the linear shrinkage decreased to 4.44%. This is as a result of the fact that the shrinkage is related to the loss of water between the particles. The more the content of glass powder, the less the mass of the polyaluminum chloride slag will be. The less the loss of water during sintering, the lower the shrinkage. The bulk density of sintered bricks is in direct proportion to the content of glass powder. As the addition of glass powder increases from 0 wt% to 10 wt%, the bulk density of the fired brick increases from 1.56 g/cm<sup>3</sup> to 1.61 g/cm<sup>3</sup>.

Considering that the water absorption of sintered brick does not meet the Chinese standard, the glass powder content is determined as 10 wt% for further research.

# 3.3.2. Molding Moisture

Proper molding moisture can improve the plasticity of the mixture and the performance of sintered brick [34]. Figure 7 indicates the influence of molding moisture between 10 wt% and 20 wt% on the compressive strength and water absorption of sintered brick. When the molding moisture is 20%, the compressive strength is increased by 26.5%. The compressive strength increases the molding moisture. The reason is that the forming moisture increases the cohesion between materials, making the structure more compact, thus increasing the compressive strength of sintered bricks made of polyaluminum chloride slag [35]. The greater the molding moisture, the lower the water absorption. Because of the more water, the greater the cohesion between the structures, which will reduce the porosity, thus reducing the water absorption.

The bulk density and linear shrinkage of sintered bricks are positively related to the molding moisture (Figure 7b). With the increase of molding moisture, the more sintered bricks are sintered because of the water evaporation and gas discharge, and the higher-temperature sintering makes the particles in the structure rearrange, making the structure denser and, thus, having higher bulk density and linear shrinkage [36].

Based on the above research, the higher the moisture content of sintered brick, the lower the water absorption. The molding moisture of sintered bricks made of polyaluminum chloride slag is determined as 20 wt% for further research.



**Figure 7.** Effect of molding moisture on the characteristics of sintered brick: (**a**) compressive strength and water absorption; (**b**) bulk density and sintering shrinkage.

# 3.3.3. Molding Pressure

The proper molding pressure can improve the molding quality of brick [37]. The influence of forming pressure between 15 MPa and 20 Mpa on the compressive strength and water absorption of sintered bricks made of polyaluminum chloride slag is shown in Figure 8a. When the forming pressure is 15–25 Mpa, the compressive strength increases with the increase of the forming pressure. This is because as the forming pressure increases, the greater the impact generated by the forming pressure between the raw material particles, which reduces the diffusion resistance, and the migration distance of the particles decreases and the structure becomes denser, thus increasing the compressive strength of the sintered brick [38,39]. When the forming pressure exceeds 25 MPa, the compressive strength decreases to 9.91 MPa. With the further increase of the forming pressure during the pressing process, the water slurry inside the brick blank is squeezed out, which makes the surface layer of the brick blank more water, leading to the reduction of the strength of the sintered brick [31]. The water absorption rate decreases with the increase of forming pressure. This is because the greater the forming pressure is, the more the pores between particles are compressed, and the porosity is reduced, resulting in the decrease of the water absorption rate [40].



**Figure 8.** Effect of molding pressure on the characteristics of sintered brick: (**a**) compressive strength and water absorption; (**b**) bulk density and sintering shrinkage.

The influence of the forming pressure on the bulk density and linear shrinkage of sintered bricks made of polyaluminum chloride slag is shown in Figure 8b. The bulk density and linear shrinkage increase with the increase of the molding pressure. When the molding pressure was 27.5 MPa, the bulk density and linear shrinkage reached the maximum of  $1.65 \text{ g/cm}^3$  and 4.63%, respectively. The greater the forming pressure, the closer the particles are, which increases the bulk density.

In order to make the compressive strength and water absorption meet the Chinese standard, the forming pressure is determined as 25 MPa for further research.

#### 3.3.4. Heating Mode

In order to avoid the cracking of fired bricks due to the burning of organic matter or the decomposition of minerals during the sintering process, a proper sintering method shall be selected when preparing fired bricks [30]. Under the same other conditions, the effects of three heating methods on the properties of fired bricks were discussed, namely, 400 and 1000 °C for 2 h, 1000 °C for 2 h, and 500 and 1000 °C for 2 h. The results are shown in Table 5. The compressive strength of sintered bricks made of polyaluminum chloride slag is the highest when the sintering process is heat preservation at 1000 °C for 2 h, while the water absorption, bulk density and linear shrinkage do not change much under different heating modes. This is because the weight loss of the materials is relatively uniform during the high-temperature firing process, and the bricks will not crack due to sudden heat release or a large amount of gas emission. Therefore, the fired bricks made of polyaluminum chloride slag will directly rise to the target temperature during the firing process. When there is no need for thermal insulation before the target temperature, the fired bricks have the best performance.

Heating Mode	Compressive Strength/MPa	Water Absorption/%	Bulk Density/(g/cm <sup>3</sup> )	Shrinkage/%
Heat preservation at 400 and 1000 °C for 2 h	12.86	21.61	1.64	4.60
Heat preservation at 1000 °C for 2 h	15.11	21.40	1.62	4.28
Heat preservation at 500 and 1000 °C for 2 h	12.40	21.30	1.58	4.44

Table 5. Effect of heating mode on properties of sintered bricks.

#### 3.3.5. Heating Rate

If the heating rate is too fast, the reaction of the fired brick will be uneven and cracks will occur, which will affect the quality of the fired brick [30]. Therefore, the proper heating rate shall be controlled. See Table 6 for the influence of the heating rate on the properties of sintered bricks made of polyaluminum chloride slag. When the heating rate is  $10 \,^{\circ}C/min$ , the comprehensive properties of sintered brick are the best. There is no obvious rule that the properties of fired bricks increase with the heating rate, but the overall performance changes little. Therefore, in the subsequent study, the heating rate is determined to be  $10 \,^{\circ}C/min$ .

**Table 6.** Effect of heating rate on the properties of fired bricks.

Heating Rate/(°C/min)	Compressive Strength/MPa	Water Absorption/%	Bulk Density/(g/cm <sup>3</sup> )	Shrinkage/%
4 °C/min	15.11	21.40	1.62	4.28
6 °C/min	14.00	22.41	1.63	4.54
8 °C/min	13.70	22.14	1.61	4.00
10 °C/min	16.90	21.22	1.60	4.19

# 3.3.6. Sintering Temperature

The sintering temperature ensures the quality of fired bricks [41]. The influence of firing temperatures between 900 °C and 1100 °C on the compressive strength and water absorption of sintered bricks is shown in Figure 9a. With the increase of sintering temperature, the compressive strength of sintered bricks also increases. When the temperature rises from 900 °C to 950 °C, the compressive strength does not increase significantly, which is due to the lower sintering degree of the brick. When the temperature rises to 1100 °C, the compressive strength is 19.6 MPa, 72.5% higher than that at 900 °C. The water absorption decreases with the increase of the sintering temperature, from 22.8% at 900 °C to 18.6% at 1100 °C. This is because at a higher sintering temperature, glass powder and other fluxes will form more liquid phase to fill the pores in the structure, making the structure more compact and reducing the porosity, thus increasing the compressive strength and reducing the water absorption [42].



**Figure 9.** Effect of sintering temperature on the characteristics of sintered brick: (**a**) compressive strength and water absorption; (**b**) bulk density and sintering shrinkage.

The influence of sintering temperature on the bulk density and linear shrinkage of sintered bricks is shown in Figure 9b. The results indicate that with an increase of sintering temperature, the bulk density and linear shrinkage also increase. When the firing temperature reached 1100 °C, the bulk density and linear shrinkage reached 1.64 g/cm<sup>3</sup> and 5.14% respectively.

Considering the performance of sintered brick, when the glass powder content is 10 wt%, the molding moisture is 20%, the molding pressure is 25 MPa, the heating mode is heat preservation at 1100 °C for 2 h, the heating rate is 10 °C/min and the firing temperature is 1100 °C, the sintered brick has the optimal performance. Under this condition, the compressive strength is 19.6 MPa, and the water absorption rate is 18.62%, which meets the MU15 grade requirements of Chinese Standards (GB 5101-2017) [43] (compressive strength > 15 MPa and water absorption < 19%). The linear shrinkage is 5.14%, and the bulk density is 1.64 g/cm<sup>3</sup>, which also meet the general requirements.

## 3.4. The Leaching Toxicity of Sintered Bricks

To ensure the environmental safety of the fired bricks, the pollutant concentration in the water-leaching solution of fired bricks prepared under optimal conditions was measured. The results are shown in Table 7. It can be seen from Table 7 that the concentration and pH of heavy metals in the water leaching solution of sintered bricks meet the discharge limits of the Integrated Wastewater Discharge Standard (GB 8978-1996) [29]. Among them, the concentration of Cl<sup>-</sup> decreases significantly, and the concentration of Cl<sup>-</sup> in the leaching solution is 7.1 mg/L, which is almost completely removed. This is consistent with the

research of Zhang [44]. High-temperature sintering can effectively remove chloride ions. The improvement of the pH of sintered brick is due to the neutralization reaction of CaO. Therefore, for the perspective of environmental safety, the sintered bricks prepared with polyaluminum chloride slag are safe and pollution-free.

**Table 7.** pH value of pollutants, mass concentration of Cl<sup>-</sup> and heavy metals in sintered brick leaching solution.

Project	рН	Cl- (mg/L)	Pb (mg/L)	Cr (mg/L)	Cd (mg/L)	Cu (mg/L)	Mn (mg/L)	Zn (mg/L)
Sintered brick	8.2	7.1	0.0003	0.0231	$\begin{array}{c} 0.0008\\ 0.1 \end{array}$	0.0088	0.021	0.0176
GB8978-1996	6–9	-	1.0	1.5		1.0	5.0	5.0

3.5. Analysis of Sintering Mechanism

In order to analyze the phase transformation of sintered bricks during sintering, the phase composition of sintered bricks at different temperatures was analyzed, and the results are shown in Figure 10. When the sintering temperature is 900 °C, the diffraction peaks of gibbsite and kaolinite in the structure disappear, and the diffraction peaks of quartz, spinel, perovskite, etc. become weak, indicating that these phases decompose when calcined at 900 °C, but no new phases are formed at this time. When the sintering temperature is 1100 °C, the diffraction peaks of perovskite, part of spinel and anatase in the structure disappear. Quartz and other silicates melt to form new phases, albite and amphibole, and albite has been proved to improve the strength of sintered bricks [45,46].



Figure 10. XRD spectrum of sintered bricks at different temperatures.

Figure 11 demonstrates the SEM micrographs of sintered bricks at different temperatures. Unburned brick particles of polyaluminum chloride slag are arranged in a disorderly fashion (Figure 11a) and are consolidated by physical action at this time. When the temperature reaches 900 °C (Figure 11b), the sintered brick just reacts and the debris structure on the particles gradually disappears. When the temperature reaches 1100 °C (Figure 11c), more molten-liquid phase is formed in the structure to make the particles more closely connected, which improves the compactness of the sintered brick, thus improving the performance of the sintered brick.



(a) unburned (b) 900°C (b) 1100°C

Figure 11. SEM spectrum of sintered bricks at different temperatures (3 µm).

# 4. Conclusions

Through the study on the preparation and performance of sintered bricks made of polyaluminum chloride slag and glass powder, the following conclusions can be drawn:

(1) It is feasible to prepare sintered bricks by using polyaluminum chloride slag and glass powder, and products with good properties can be obtained. When the mass ratio of polymeric aluminum chloride slag to glass powder to quicklime is 100:10:2.5, molding moisture is 20%, molding pressure is 25 MPa, heating speed is  $10^{\circ}$ C/min, sintering temperature is 1100 °C and insulation time is 2 h at 1100 °C, we can obtain a bulk density of 1.64 g/cm<sup>3</sup>, sintering shrinkage of 5.14%, water absorption of 18.62% and compressive strength of 19.6 MPa of the fired brick. The polymeric aluminum chloride slag contains 2.59% chloride salt, and after high-temperature sintering, the leaching concentration of the chloride ions of the sintered brick with polyaluminum chloride slag is 7.1 mg/L. The pH value and heavy metals meet the discharge requirements of the Comprehensive Discharge Standard for Wastewater (GB8978-1996).

(2) With the increase of glass powder content, molding pressure, molding moisture and sintering temperature, the compressive strength of sintered bricks can be improved and the water absorption can be reduced.

(3) XRD and SEM results show that the phase of sintered brick at 1100 °C is mainly composed of quartz, spinel, albite and other phases. With the increase of temperature, more liquid-filled pores are formed inside the sintered brick, which makes the structure more compact. The compact internal structure and reasonable crystal phase composition make the sintered brick have excellent performance.

**Author Contributions:** Writing—original draft preparation, F.H.; writing—review and editing, F.X.; visualization, J.O.; supervision, G.Z.; project administration, Q.L.; funding acquisition, Q.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by [The key scientific research project of the Education Bureau of Hunan Province] grant number [21A0286] And [The Hunan Provincial University Innovation Platform Development Fund Project] grant number [20K111].

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

**Acknowledgments:** The authors thank for the test instruments and equipment provided by Hunan Provincial Key Laboratory of High Performance Special Concrete.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. Li, F.T.; Li, J.; Wang, Y.; Zhang, Y.X. Implementation of new standard of polyaluminum chloride for drinking water treatment and its industrial impact analysis. *China Water Wastewater* **2022**, *38*, 33–37.
- Li, Q.T.; Zhang, C.Z.; Zhou, J.Z.; Lu, Y.S.; Lu, T.Y.; Gu, Y.F.; Min, J.J. Improvement of sludge dewatering capability with modified polyaluminium chloride residue. *Ind. Water Treat.* 2019, 39, 79–81.
- He, Q.F.; Zeng, L.Q.; He, Z.H.; Liu, X.F.; Zou, J.J. Study on effect of fineness and dosage of PAC waste residue on cement per-formance. *Inorg. Chem. Ind.* 2020, 52, 84–87.
- Li, Q.; Zhang, J.S.; Gao, J.Q.; Huang, Z.Z.; Zhou, H.X.; Duan, H.Y.; Zhang, Z.H. Preparation of a novel non-burning polyaluminum chloride residue(PACR) compound filler and its phosphate removal mechanisms. *Environ. Sci. Pollut. Res. Int.* 2021, 29, 1532–1545. [CrossRef]
- 5. Han, X.G.; Liu, Z.N.; Lu, T.Y.; Gu, L.L.; Gu, Y.F. Preparation of modified polyaluminium chloride residue and its phosphorus removal performance. *Inorg. Chem. Ind.* **2019**, *51*, 59–62.
- Jiao, M.; Jiao, T.W.; Liu, S.T. A Method of Producing Ceramsite from Waste Residue of Water Treatment Agent Polyaluminum Chloride. CN 109437960B, 8 February 2022.
- 7. Xu, P.; Yang, H.; Dong, H.; Ding, Y.; Yuhao, C. The effects of polyaluminium chloride (PAC) slag On the properties of recycled concrete. *Ceram.-Silikáty* **2022**, *66*, 419–427. [CrossRef]
- Xu, H.; Song, W.; Cao, W.; Shao, G.; Lu, H.; Yang, D.; Chen, D.; Zhang, R. Utilization of coal gangue for the production of brick. J. Mater. Cycles Waste Manag. 2017, 19, 1270–1278. [CrossRef]
- 9. He, H.; Yue, Q.; Su, Y.; Gao, B.; Gao, Y.; Wang, J.; Yu, H. Preparation and mechanismof the sintered bricks produced from Yelow River silt and red mud. *J. Hazard. Mater.* 2012, 203, 53–61. [CrossRef]
- 10. Sun, P.; Sun, D.; Wang, A.; Ge, W.; Liu, X. Preparation and properties of sintered brick based on coal gangue and fly ash. *Asian J. Chem.* **2014**, *26*, 1517–1520. [CrossRef]
- 11. Leiva, C.; Rodriguez-Galán, M.; Arenas, C.; Alonso-Fariñas, B.; Peceño, B. A mechanical, leaching and radiological assessment of fired bricks with a high content of fly ash. *Ceram. Int.* **2018**, *44*, 13313–13319. [CrossRef]
- 12. Chin, W.Q.; Lee, Y.H.; Amran, M.; Fediuk, R.; Vatin, N.; Kueh, A.B.H.; Lee, Y.Y. A Sustainable Reuse of Agro-Industrial Wastes intoGreen Cement Bricks. *Materials* **2022**, *15*, 1713. [CrossRef]
- 13. Lau, Z.Y.; Lee, S.L.; Mannan, M.A.; Slavcheva, G.S.; Oucif, C. Performance of polymer grouts made from wastes for permeable rigid pavement connections. *J. Civ. Eng. Sci. Technol.* **2022**, *13*, 150–159. [CrossRef]
- 14. Tang, Y.X.; Lee, Y.H.; Amran, M.; Fediuk, R.; Vatin, N.; Kueh, A.B.H.; Lee, Y.Y. Artificial Neural Network-Forecasted Compression Strength of Alkaline-Activated Slag Concretes. *Sustainability* **2022**, *14*, 5214. [CrossRef]
- Achik, M.; Benmoussa, H.; Oulmekki, A.; Mustapha, M.; Noureddine, E.M.; Touache, A.; Alvaro, G.G.; Rivera, F.G.; Infantes-Molina, A.; Eliche-Quesada, D.; et al. Evaluation of technological properties of fired clay bricks containing pyrrhotite ash. *Constr. Build. Mater.* 2021, 269, 121312. [CrossRef]
- 16. Leiva, C.; Arenas, C.; Alonso-Fariñas, B.; Vilches, L.F.; Peceño, B.; Rodriguez-Galán, M.; Baena, F. Characteristics offired bricks with co-combustionfly ashes. *J. Build. Eng.* **2016**, *5*, 114–118. [CrossRef]
- 17. Hu, H.; Deng, Q.; Li, C.; Xie, Y.; Dong, Z.; Zhang, W. The recovery of Zn and Pb and the manufacture of lightweight bricks from zinc smelting slag and clay. *J. Hazard. Mater.* **2014**, *271*, 220–227. [CrossRef]
- 18. Chiang, K.-Y.; Chou, P.-H.; Hua, C.-R.; Chien, K.-L.; Cheeseman, C. Lightweight bricks manufactured from water treatment sludge and rice husks. *J. Hazard. Mater.* **2009**, *171*, 76–82. [CrossRef]
- 19. Yüksel, A.; Mehmet, A.Y.; Sadrettin, Z.; Ahmet AliK, M.K. Using phosphogypsume and boron concentrator wastes in light brick production. *Constr. Build. Mater.* 2007, 21, 52–56.
- 20. Vishakha, V.S.; Rahul, V.R. Development and investigation of cellular light weight bio-briquette ash bricks. *Clean Technol. Environ. Policy* **2017**, *19*, 235–242.
- 21. Sasaki, N.; Okuno, M. Control of diatomaceous earth insulating brick shrinkage when firing by addition of calcium sources. *J. Ceram. Soc. Jpn.* **2020**, *128*, 936–944. [CrossRef]
- Arulrajah, A.; Disfani, M.M.; Maghoolpilehrood, F.; Horpibulsuk, S.; Udonchai, A.; Imteaz, M.; Du, Y.-J. Engineering and environmental properties of foamed recycled glass as a lightweight engineering material. *J. Clean. Prod.* 2015, 94, 369–375. [CrossRef]
- Ponsot, I.; Bernardo, E. Self glazed glass ceramic foams from metallurgical slag and recycled glass. J. Clean. Prod. 2013, 59, 245–250. [CrossRef]
- 24. Nonthaphong, P.; Siwadol, K.; Prinya, C. Utilization of waste glass to enhance physicalemechanical properties of fired clay brick. *J. Clean. Prod.* **2016**, *112*, 3057–3062.
- 25. Ismail, D. Reuse of waste glass in building brick production. Waste Manag. Res. 2009, 27, 572–577.
- 26. Umme, S.A.; Mohammad, M.Z.; Md, S.I.; Farah, N.; Md, K.H. Effect of different types of glasses as fluxing agent on the sintering temperature of bricks. *Trans. Indian Ceram. Soc.* **2017**, *76*, 128–132.
- 27. *GB* 5085.3-2007; State Environmental Protection Administration of China, Identification Standards for Hazardous Wastes-Identification for Extraction Toxicity. China Environmental Science Press: Beijing, China, 2007.
- 28. *HJ* 557-2010; State Environmental Protection Administration of China, Solid Waste-Extraction Procedure for Leaching Toxicity-Horizontal Vibration Method. China Environmental Science Press: Beijing, China, 2010.

- 29. *GB 8978-1996*; State Environmental Protection Administration of China, Integrated Wastewater Discharge Standard. Standards Press of China: Beijing, China, 1996.
- Chen, Y.L. Preparation and Mechanism of Fired Bricks and Tiles with Low-Silicon Iron Tailings from Western Hubei. Ph.D. Thesis, Wuhan University of Science and Technology, Wuhan, China, 2012.
- Li, N.; Xiang, H.; Lu, Y.J.; Chen, J.M.; Du, D.Y. treatment and utilization of waste residue produced from polyaluminium chloride process. CIESC J. 2011, 62, 1441–1447.
- 32. Hasan, M.R.; Siddika, A.; Akanda, M.P.A.; Islam, M.R. Effects of waste glass addition on the physical and mechanical properties of brick. *Innov. Infrastruct. Solut.* **2021**, *6*, 36. [CrossRef]
- Baskar, R.; Begum, K.; Sundaram, S. Characterization and reuse of textile effluent treatment plant waste sludge in clay bricks. J. Univ. Chem. Technol. Met. 2006, 3, 473–478.
- 34. Gupta, V.; Siddique, S.; Chaudhary, S. Optimum mixing sequence and moisture content for hydrated lime fly ash bricks. *J. Clean. Prod.* **2020**, *285*, 124859. [CrossRef]
- Huang, J.; Wang, X.; Xu, M.T. Influence of formation condition to the performance of molybdenum tailing coal ash sintering brick. *Min. Eng.* 2022, 20, 51–54.
- Zhao, S.Y.; Liu, W.D.; Lu, M.R. Experimental study on preparation of sintered brick from municipal sludge. *New Build. Mater.* 2022, 49, 92–95.
- Luo, L.Q.; Li, K.Y.; Fu, W.; Liu, C.; Yang, S.Y. Preparation, characteristics and mechanisms of the composite sintered bricks produced from shale, sewage sludge, coal gangue powder and ironore tailings. *Constr. Build. Mater.* 2020, 232, 117250. [CrossRef]
- 38. Raju, G.B.; Basu, B. Densification, sintering reactions, and properties of titanium diboride with titanium disilicide as a sintering aid. *J. Am. Ceram. Soc.* 2007, *90*, 3415–3423. [CrossRef]
- 39. Song, J.G.; Wang, F.; Bai, X.B.; Dua, D.M.; Jua, Y.Y.; Xua, M.H.; Ji, G.C. Effect of the sintering technology on the properties of fired brick from quartz sands. *J. Ceram. Process. Res.* **2011**, *12*, 357–360.
- 40. Zhang, Y.; Ni, H.J.; Lv, S.S.; Wang, X.X.; Li, S.Y.; Zhang, J.Q. Preparation of sintered brick with aluminum dross and optimization of process parameters. *Coating* **2021**, *11*, 1039. [CrossRef]
- Karaman, S.; Ersahin, S.; Gunal, H. Firing temperature and firing time influence on mechanical and physical properties of clay bricks. J. Sci. Ind. Res. 2006, 65, 153–159.
- 42. Chindaprasirt, P.; Srisuwan, A.; Saengthong, C.; Lawanwadeekul, S.; Phonphuakd, N. Synergistic effect of fly ash and glass cullet additive on properties of fire clay bricks. *J. Build. Eng.* **2021**, *44*, 102942. [CrossRef]
- GB 5101-2017; General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Fired Common Bricks. Standards Press of China: Beijing, China, 2017.
- 44. Zhang, S.G.; Liu, J.P. Experimental research on chlorine-ion removal from fly ash by water-washing and sintering method. *Environ. Sanit. Eng.* **2014**, *22*, 13–15.
- 45. Jin, B.; Zhao, L.; Wang, X.; Zhao, K.J.; Zhang, J.W.; Zhang, X.T.; Yang, L.S. Preparation of Sintered Brick with Sludge, Shale and Gangue. *Non-Met. Mines* **2021**, *44*, 39–41.
- Dana, K.; Dey, J.; Das, S.K. Synergistic effect offly ash and blast furnace slag on the mechanical strength of traditional porcelain tiles. *Ceram. Int.* 2015, 31, 147–152. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.