

## Research Article

# A Novel Approach to Fabricate Foam Ceramics from Steel Slag

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Received 20 September 2019; Revised 25 February 2020; Accepted 2 March 2020; Published 26 March 2020

Academic Editor: Francesco Ruffino

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A novel approach is used for fabricating steel slag foam ceramics based on the particle-stabilized foaming method. In this work, steel slag was used as the raw material and propyl gallate (PG) was used as the surface modifier. For the first time, steel slag ceramic foams were successfully fabricated based on particle-stabilized foams. The results show that the stability of the ceramic foams was closely related to the pH value and PG concentration. The porosity and compressive strength could be controlled by changing the solid loading of steel slag and sintering temperature. The porosity of steel slag foam ceramics ranged from 85.6% to 62.53%, and the compressive strength was from 1.74 MPa to 10.42 MPa. The thermal conductivity of steel slag foam ceramics was only 0.067 W (m·K)<sup>-1</sup>, which shows that it could be used as a thermal insulation material.

## 1. Introduction

Foam ceramics play an important role in high-technology fields and cellular structures composed of three-dimensional networks. The physical and chemical properties of foam ceramics can be adjusted by changing phase composition, the proportion of gas-solid phase, and the sintering temperature. Foam ceramics display low bulk density, excellent thermal conductive and acoustic insulation, high specific area, and excellent resistance [1]. Based on these properties, foam ceramics can be extensively applied in different fields, such as catalysis carriers, filtration material, biomaterials, thermal insulators, thermal barrier coatings, and soundproof materials [2–6]. Dickinson et al. [7] reported stabilized air bubbles prepared by direct foaming. Tang et al. [8] prepared well-defined porous ceramics with controllable pore size and porosity by burnout of fugitive pore formers. Wang et al. [9] and Deng et al. [10] prepared porous ceramics by particle stacking. Rainer et al. [11] reported the application of in situ foaming technique for the preparation of foam ceramics.

The direct foaming method is a simple and convenient route for the preparation of high-porosity ceramics with open or closed pores [12], by leading air in suspensions. As a promising direct foaming method, granular stabilized foam

[13–17] provides many advantages for the preparation foam ceramic materials, especially that there is no need to add organic or inorganic binders since the potential barrier assembled by ceramic particles has good gas-liquid interface stability.

With the development of industry, a large amount of industrial wastes not only pollute the environment but also occupy a large number of land. Many countries have realized that this phenomenon is an urgent problem to be solved. Steel slag is a by-product of steelmaking process and common industrial waste. In 2018, China's crude steel production was 928 million tons; however, the recycling rate was about 30%. Therefore, this problem has attracted much attention during the past years and has been explored in many fields [18, 19]. In the field of steel and metallurgy, steel slag can be used in metal recovery [20] and to prepare compound desulfurase [21]. In the field of construction, steel slag can be used as a cement raw meal [22–24] and subgrade backfill material [25]. In the field of agriculture, fertilizers [26] and soil improvers [12] can be prepared by using steel slag. In the field of environmental protection, steel slag can be used as raw materials to synthesize products which are applied in wastewater treatment [27].

In addition, glass ceramics can also be fabricated by using steel slag [1]. Some reports have carried out study on glass-ceramics [24, 25], including  $\text{CaSiO}_3$ ,  $\text{CaMgSi}_2\text{O}_6$ , and plagioclase systems [12, 26, 27]. However, there are few reports on the preparation of ceramics from steel slag. Thus, we propose a convenient, low-cost, and ecofriendly method to fabricate foam ceramic, which uses recycled steel slag powder as raw materials and is based on particle-stabilized foams theory [28, 29]. Our work provides an effective approach to improve the utilization rate of steel slag and broadens the application field of solid waste resources. This is very beneficial to environmental protection and economy.

## 2. Experimental Procedure

**2.1. Experimental Materials.** The steel slag was provided by Chengde Iron and Steel Group Co., Ltd., Chengde, China. The element compositions of steel slag are listed in Table 1. Propyl gallate (PG) was purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China.

**2.2. Preparation of Steel Slag Foam Ceramics.** Homogenization of aqueous steel slag suspensions was performed by ball-mixing of aqueous suspensions consisting of deionized water and steel slag particles for 48 h, and the steel slag has an average particle size of  $1.62\ \mu\text{m}$ . Figure 1 shows the SEM picture of steel slag after ball-mixing. PG (the addition amount was in terms of the total suspension quantity) was added to the suspensions, followed by ultrasonic dispersion for 5 min and tuning the pH value. The suspension was preliminarily agitated using a stirrer at the speed of 500 r/min for 3 min and subsequently agitated at the speed of 1800 r/min for 10 minutes to obtain uniform wet foams. The wet foams were dried at room temperature. The dried green body was sintered at  $1150^\circ\text{C}$ – $1250^\circ\text{C}$  with a heating rate of  $3^\circ\text{C}/\text{min}$  and holding time of 2 h. Figure 2 shows the preparation process of steel slag foam ceramics.

**2.3. Characterization.** The Archimedes method was employed to measure apparent porosity and bulk density of fired samples. Microstructures of the samples were characterized using scanning electron microscopy (SEM, MERLIN VP Compact, Carl Zeiss, Jena, Germany). Compressive strength of glass foams was measured with a crosshead speed of 1 mm/min using a versatile material testing machine (AG2000G; Shimadzu, Kyoto, Japan). Three specimens were measured to obtain average values of bulk density and compressive strength. The grain size and pore size of steel slag foam ceramics were assessed by SEM images using “Nano Measurer” software (exploited by Fudan University, Shanghai, China). At least 300 pores and grains were counted to obtain average values and size distributions.

## 3. Results and Discussion

**3.1. Fabrication of Stable Foam Steel Slag Suspension.** The surface of ceramic powder particles was usually modified by using special organic water-soluble molecules. The water-

soluble molecules adsorb on the surface of the oxide to reduce the particle's affinity for water molecules [30, 31]. Experiments show that PG can make steel slag powder hydrophobic and enable the attachment of steel slag particles to the air/water interfaces. Similar to most oxide ceramic powders, they generate hydroxyl groups on the surface of particles; steel slag particles allow the formation of hydroxyl groups due to the unsaturated bonds of oxygen atoms exposed on the surface of steel slag particles, providing a large number of anchoring groups for the adsorption of PG. Figure 3(a) shows the sample of steel slag foam slurry after demolding. The sample can keep its shape without adding auxiliary materials. After 48 h of sample preparation, there is a small amount of drainage from steel slag wet foams (Figure 3(b)). Steel slag particles are closely arranged on the gas/liquid interface due to van der Waals force, which forms the uniform stomatal wall, and the thickness is  $1$ – $1.5\ \mu\text{m}$  (Figure 3(c)). Figure 3(d) shows a process how the steel slag suspension develops into foams. After mechanical foaming, the liquid film separated the air in the suspension. Short-chain amphiphile PG is attached around the steel slag particles; the steel slag particles are closely aggregated at the air/liquid interfaces closely and form the dense particle layers around the bubbles to obtain stable wet foams. The foam loses water at normal temperature and pressure and eventually develops into dry foams. Steel slag particles pack at the air/liquid interfaces and form thin cell walls in the dried foams. At the same sintering temperature, the steel slag particles are densified and the pore structure remains spherical.

**3.2. Influence of PG and pH on Stability of Steel Slag Foam Ceramics.** A large number of experimental results demonstrate that the stability of steel slag foams depends on pH value and PG concentration, as shown in Figure 4. For particle-stabilized foam, pH is a key factor in determining the chemical state of the particle surface. It not only determines the adsorption behavior of the modifier on the particle surface but also determines the stability of the foam suspension. The stabilized foam is prepared in the range of pH 5.0 to pH 10.0. No matter how much PG is added, the wet steel slag foam cannot maintain long-term stability outside the pH range. The stability of wet foam mainly depends on the hydrophobicity of steel slag particles, which is mainly affected by the adsorption of the modifier (PG) on steel slag particles. The stability behavior with different pH values can be explained by the ligand exchange model [32]. When PG is dissolved in water, it first ionized by itself and then exchanged ligands with particles. The ionization of PG is greatly affected by the pH value, and the ionization degree of the PG increases as the pH value increases. The higher the degree of the pg ionization, the higher the degree of ligand exchange reaction. When the pH value is too low ( $\text{pH} < 5.0$ ), the degree of ionization of PG is low and the hydrophilicity is weak. The partial PG aggregated under the action of hydrophobization. PG is seriously inhibited, and a very small amount of PG can be adsorbed on the surface of steel slag particles. When the pH value is too high ( $\text{pH} > 10.0$ ), there

TABLE 1: Composition of steel slag.

Composition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O
Steel slag	40.18	19.1	10.3	8.25	4.90	4.78	4.51	2.62

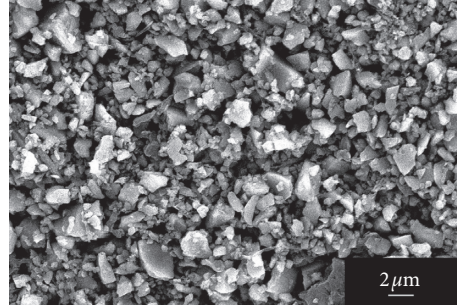


FIGURE 1: SEM images of steel slag particles after ball-mixing.

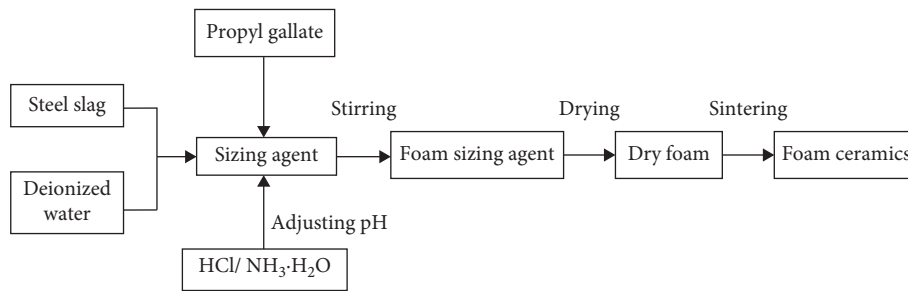
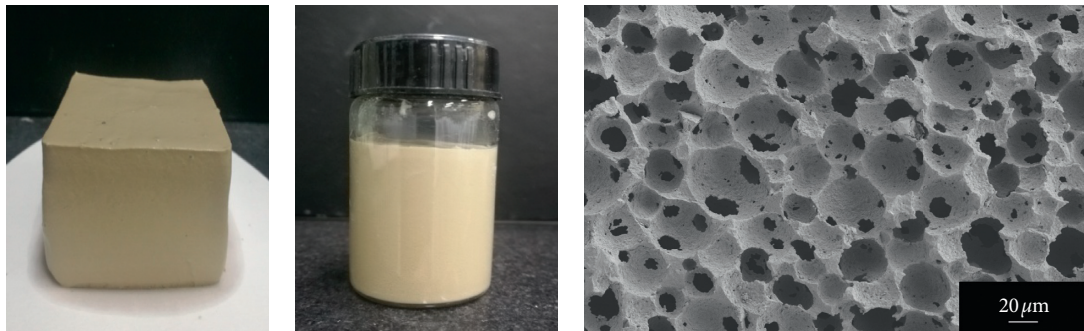


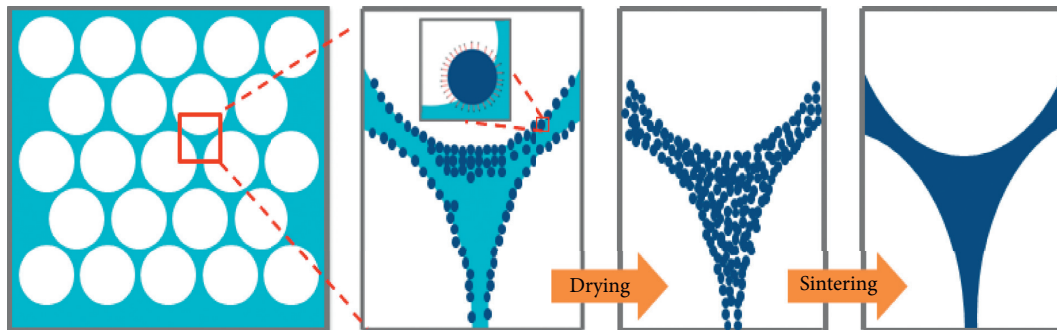
FIGURE 2: Preparation process of steel slag foam ceramics.



(a)

(b)

(c)



(d)

FIGURE 3: (a) Steel slag foam ceramics after demoulding. (b) Steel slag stabilized foams (the photo was taken 48 h after frothing). (c) Microstructure of steel slag foam ceramics. (d) Schematic diagram of ceramic foams with spherical pore structure.

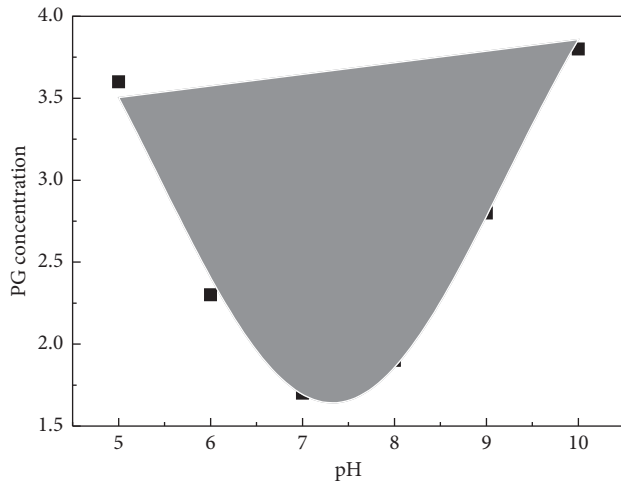


FIGURE 4: Dependence of foam stability on pH value and PG concentration (30 wt.% solid loading).

are less available sites (namely,  $-\text{OH}_2^+$ ) for the adsorption of propyl gallate onto the steel slag surface since protonation of the particle surface is inhibited. In addition, at a high pH value, the negatively charged steel slag particles may be disadvantageous to deproton and PG adsorption due to electrostatic repulsion. Above all, if the pH value is lower than 5.0 or higher than 10.0, the adsorption of PG on steel slag particles is seriously inhibited, resulting in the inability of steel slag particles to achieve adequate hydrophobicity, leading to the instability of steel slag foams.

When the pH value is 5.0–10.0, different PG concentrations are required to prepare stable wet steel slag foams. When pH ranges from 7.0 to 8.0, only a small amount of PG is needed to stabilize the wet foams of steel slag. When the pH range is 5–7 or 8–10, a relatively large amount of PG is needed to obtain the stable wet foam of steel slag, indicating that a large amount of PG can make up for the influence brought by the pH value.

**3.3. Influence of Solid Loading on the Properties of Steel Slag Foam Ceramics.** Solid loading is closely related to the stability of wet foam and the properties of foam ceramics. The experimental results show that when the solid content of steel slag is less than 20 wt.%, the stable foamed ceramics cannot be prepared. The previous literature has suggested that to ensure the stability of foam suspensions, particles should be covered at the air/liquid interface [33]. With the increase of steel slag solid loading, the porosity of foam ceramics decreases from 85.6% to 68.4% and the compressive strength increases from 1.74 MPa to 2.93 MPa (Figure 5). Low solid loading leads to low viscosity of suspension, which is conducive to the incorporation of more air into the ceramic slurry during agitation [34, 35]. Therefore, as the solid content of the steel slag increases, the porosity of foam ceramics decreases and the compressive strength increases, which can be explained by the model of Gibson and Ashby [36]. The porosity and compressive strength of steel slag foams prepared with 30 wt.% of the

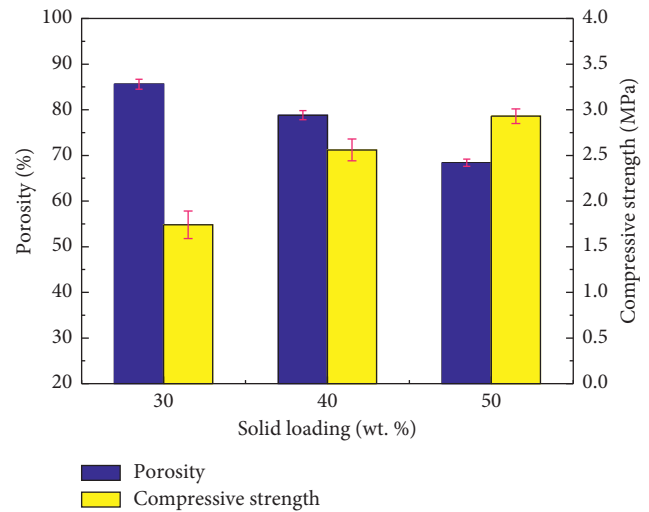


FIGURE 5: Effect of solid loading on properties of steel slag foam ceramics.

solid loading are, respectively,  $85 \pm 1.1\%$  and  $1.74 \pm 0.15$  MPa. The strength of steel slag foam ceramics can be employed in some fields.

**3.4. Influence of Sintering Temperature on the Properties of Steel Slag Foam Ceramics.** The SEM images of steel slag foam ceramics sintered at different temperatures are shown in Figure 6. At  $1150^\circ\text{C}$ , the porosity diameter of foam ceramics is larger than  $1200^\circ\text{C}$  and  $1250^\circ\text{C}$  due to insufficient sintering densification. With the increase in sintering temperature, the sintered steel slag ceramic foams exhibit well distribution as shown in Figures 6(b) and 6(c). When the sintering temperature reaches  $1250^\circ\text{C}$ , the multistage pore structure is stable and the pores are highly connected, which is conducive to thermal insulation performance.

The porosity of steel slag ceramic foams sintered at different temperatures is shown in Figure 7. As shown in Figure 7, the porosity of steel slag foam ceramics at different sintering temperatures decreases with the increase in temperature, which is similar to previous results [29]. This can be explained by the grain growth with the increase in sintering temperature, accompanying with the thickening of wall and decrease in pore size. In addition, it is noted that the porosity of ceramic foam of steel slag decreased more significantly (from 84.86% to 52.17% with increasing sintering temperature from  $1150^\circ\text{C}$  to  $1200^\circ\text{C}$ ) when compared to that at sintering temperature from  $1200^\circ\text{C}$  to  $1250^\circ\text{C}$  (from 52.17% to 46.12%).

As sintering temperature increases, the porosity decreases accompanied by the increase in the compressive strength. More shrinkage occurs at higher sintering temperature. Therefore, the strut wall prepared at higher sintering temperature is thicker [37]. The thickening has a positive effect on the compressive strength but results in lower porosity. Compressive strength increased from  $2.56 \pm 0.06$  MPa to  $10.42 \pm 0.09$  MPa when the sintering

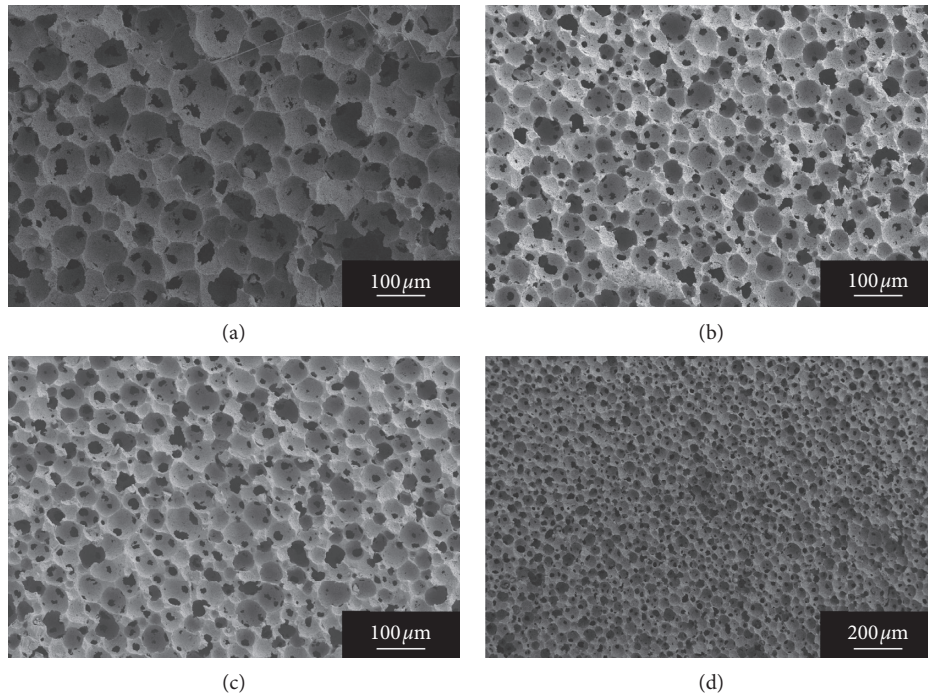


FIGURE 6: SEM images of cell wall of steel slag foams fabricated with 40 wt.% solid loading sintered at (a) 1150, (b) 1200°C, and at (c) (d) 1250°C.

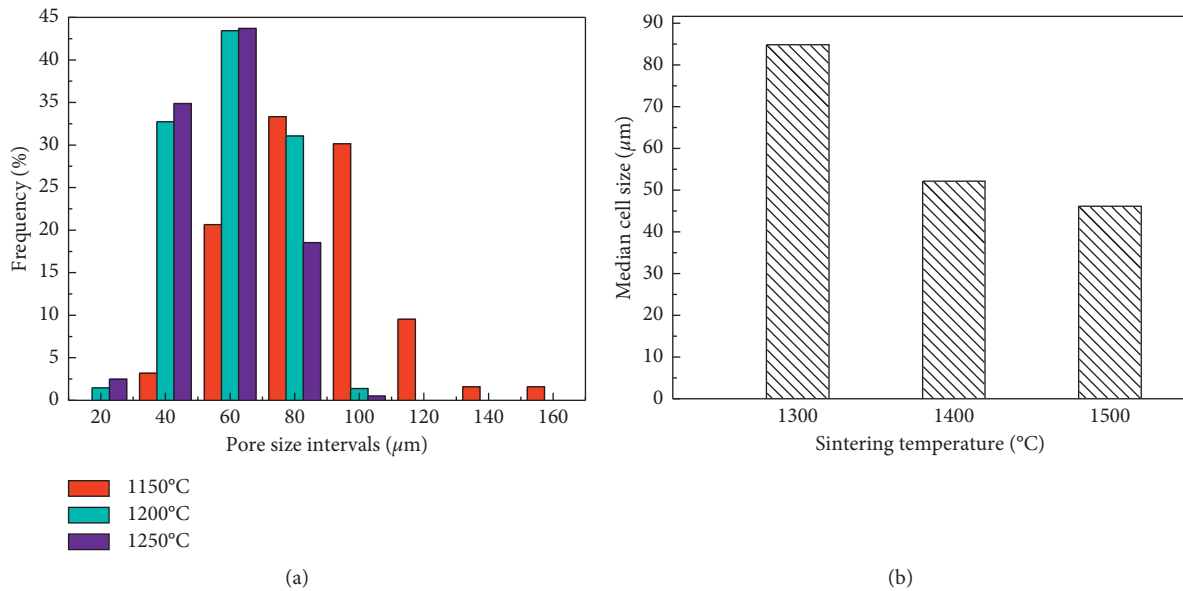


FIGURE 7: Pore size distribution of steel slag foam ceramics sintered at 1150°C, 1200°C, and 1250°C (a) and mean pore size of steel slag foam ceramics sintered at different temperatures (b) (40 wt.% solid loading).

TABLE 2: Porosity and compressive strength as a function of sintering temperature (prepared from 40 wt.% solid loading).

Sintering temperature (°C)	Porosity (%)	Compressive strength (MPa)
1150	84.78 ± 0.04	2.56 ± 0.06
1200	70.61 ± 0.06	9.08 ± 0.03
1250	62.53 ± 0.11	10.42 ± 0.09

temperature increased from 1150°C to 1250°C, along with decrease in porosity from 84.78% to 62.53% (Table 2).

It is reported that the thermal conductivity of most foam ceramics approaches a lower limit of 0.1 W (m·K)<sup>-1</sup> [38]. It is fascinating to note that thermal conductivity of steel slag foams with a porosity of 85.6% is 0.067 W (m K)<sup>-1</sup>, which is lower than that of most foam ceramics. Therefore, steel slag

foam ceramics can be used to prepare thermal insulation materials.

#### 4. Conclusion

Steel slag foam ceramics are prepared by the particle-stabilized direct foaming method. The hydrophobicity of steel slag particles is improved by in situ adsorption of PG. The steel slag foams show strong foam ability and stability. It is a facile and low-cost method to fabricate steel slag foams with porosity in the range of 85.6%–62.53% and with high compressive strength in the range of 1.74–10.42 MPa. The steel slag foams with high porosity and low thermal conductivity could be applied in thermal insulation and other potential fields.

#### Data Availability

The data generated and analyzed in this manuscript are available from the corresponding author on reasonable request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant no. 51772139).

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