Preparation and properties of waste-solid based foam concrete energy-saving materials

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Abstract: In this paper, foam concrete is prepared from industrial waste such as steel slag (SS), blast furnace slag (BFS), flue gas desulfurization (FGD). By studying the stability of foaming agent, the specific surface area of cementing material and curing temperature, the insulation performance of foamed concrete can be improved. The test results show that the HT composite foaming agent has good stability at a high temperature and can be used as a foaming agent for waste-solid based foam concrete. Increasing the specific surface area of the material and increasing the curing temperature of the material can reduce the thermal conductivity of foam concrete. The thermal conductivity of the cementitious materials prepared by the A350 and A500 two-layer cementitious materials at 70 °C are: 0.083 W/(m∙k) and 0.078 W/(m∙k), respectively, which all have a good heat preservation effect. As the coefficient gap between the two is not large. In order to reduce the energy consumption caused by grinding, the A350 material can be used for exterior wall insulation.

1. Introduction
As the urbanization process continues to accelerate, the building area continues to increase, and the proportion of building energy consumption is increasing. According to statistics: from 1980 to 2012, the proportion of building energy consumption to terminal energy consumption increased from 10% to 20%, and by 2030 it will reach 23.1%. In order to achieve maximum resource conservation, environmental protection and pollution reduction, external wall insulation materials are constantly being promoted and used[1]. New building insulation materials such as polyurethane foam, phenolic resin sheets, extruded sheets and other porous materials are widely used in the field of building energy conservation. However, the flammability of organic insulation materials has led to frequent fire incidents in high-rise buildings. The Ministry of Public Security issued a policy of requiring materials for civil building exterior insulation materials to use Class A materials (Fire control bureau of the ministry of public security [2011] No. 65). Such regulations have led to the mainstream practice of the building insulation market. The expansion of the polystyrene board thin plastering exterior insulation system has also to stop construction. Foamed concrete contains a large number of pores, and has a low density, high thermal insulation performance, and a burning grade of A-class non-combustible performance has become the development trend of building energy-saving insulation [2].

At present, the cementitious material generally used for foam concrete is ordinary Portland cement. The production of cement is a high energy consumption process, which consumes energy a lot and
also produces a lot of solid waste and carbon dioxide [3]. At the same time, China is a large country in steel production. With the continuous increase in steel production, the contradiction between resources, energy and solid waste has become increasingly prominent. In 2016, the output of steel slag is about 0.65-1.20 billion tons, while the utilization rate of steel slag in China is less than 30%, which is quite different from the utilization rate of 65% in developed countries in Europe [4-5]. Such a large amount of industrial solid waste is not only occupied by land resources, but also has potential threat to the environment, polluting groundwater, generating dust, etc., so it is very urgent to make rational use of it.

Industrial waste such as steel slag, mine slag, fly ash and other industrial wastes have similar composition of cement. Using solid waste like that to prepare foam concrete can not only reduce the energy consumption of cement production, but also eliminate a large amount of tailings and reduce the pollution of solid waste, and can be used for energy-saving insulation, which is of great significance for energy-saving emission reduction and sustainable development of resources [6], and has a bright prospects.

The key to the preparation of foam concrete is whether the foam stability and the initial setting time of the cementitious material are compatible. Compared with Portland cement, steel slag, mine slag, desulfurization gypsum cementitious material has the disadvantage of slow early hydration rate, and the condensation time is too long, which will cause the foam to melt and collapse. At present, the research on the improvement of foam concrete for industrial solid waste is mainly reflected in the aspects of admixture, specific surface area and curing temperature of cementing materials, but the research factors are relatively simple, and the comprehensive effect of temperature on industrial solid waste cementing materials and foaming agents has not been reported yet.

In terms of foam stability: Ailar Hajimohammadi [7] studied the effect of xanthan gum on improving the pore structure of foam concrete and prepared an insulation material with a density of 700 kg/m$^3$ and a thermal conductivity of 0.25 W/(m·K). Studies have shown that the addition of 0.45% xanthan gum to each of 50% fly ash and blast furnace slag as a cementitious material can increase its 28-day strength by 34%. Mohd Mustafa Al Bakri Abdullah [8] uses sodium hydroxide Alkali activator, preparation of fly ash foam polymer curing at 60 °C, greatly shortening the initial setting time, the strength of 1 day can reach 11.03MPa. J. Sathya Narayanan [9] studied the effects of calcium chloride, calcium nitrate and alum on the setting time of foam concrete with a density of 800-1200m$^3$/kg. The study concluded that although calcium chloride and calcium nitrate can reduce the initial setting time of foam concrete, to reduce foam stability, alum can reduce concrete setting time to 140-85 minutes. Christina Kramer studied the preparation of ultra-high strength foam concrete by adding nano-silica three-phase foam, carbon nanotubes and betaine reinforcing materials to foam concrete [10].

In terms of cementitious materials: Si Caiqin of Anhui University of Technology [11] studied the influence of specific surface area of steel slag, steel slag content and foaming agent on thermal conductivity of foam concrete, and analyzed by orthogonal test: foaming agent content to the thermal conductivity of foam concrete has the greatest influence, followed by steel slag, and the steel slag particle size has the least influence on the thermal conductivity of foam concrete. The steel slag foaming agent has a ratio of 0.07%, steel slag content of 10%, and steel slag particle size of 1.18mm. The foamed concrete has a lower thermal conductivity and can be used as exterior wall insulation material. Abdelkader Bougara research shows that slag substitute cement has good strength properties, especially under 40 °C curing conditions, slag heat activation is the best [12]. Cui Xiaoyu [13] studied the hydration mechanism of steel slag, slag and desulfurization gypsum to prepare solid waste high strength concrete. The research shows that the hydration products are ettringite and CSH gel when the amount of steel slag is less than 40%. This theory provides a theoretical basis for the preparation of foam concrete from industrial solid waste.

In terms of curing temperature: J.-K Kim [14] studied the effect of early curing temperature on the strength of cement materials. The study concluded that the increase in temperature caused a rapid increase in hydration rate and concrete strength. However, due to the non-uniform diffusion of hydration products and the difference in thermal expansion coefficient of concrete components, the
porosity in the cement slurry increases, and the microcracks develop, eventually leading to a decrease in strength in the later stage. Due to the different hydration mechanisms of the solid waste system and the cement system, the influence of the curing temperature on its strength needs further study.

In this paper, foam concrete was prepared based on steel slag, slag and desulfurization gypsum. The stability of the foaming agent, the specific surface area of the material and the influence of curing temperature on the thermal conductivity of foam concrete were studied. In order to explore the possibility of replacing solid waste materials such as steel slag and slag, the three kinds of cement materials, such as steel slag, slag and desulfurization gypsum, were ground to a specific surface area of 350 m²/kg and 500 m²/kg, respectively.

2. Experiment

2.1. Experiment material

The steel slag used in the test is steel slag produced by Hebei Yuhua Iron and Steel Co., Ltd., the slag is the slag of Xingtai Iron and Steel Plant, and the desulfurized gypsum is the desulfurized gypsum produced by Beijing Gypsum Factory. By doing XRF analysis (Table 1), it can be known that the material composition of steel slag and slag contains a large amount of silica and calcium oxide, and has the potential to prepare a cementitious material. The foaming agent used in the experiment is: plant-type foaming agent LC produced by foaming agent for foam concrete and fermenting energy-saving building materials Co., Ltd., animal type foaming agent WZ produced by Jinan Wenzhu Co., Ltd., and Henan Huatai Building Material Co., Ltd. The compound foaming agent produced, code HT.

Table 1. Chemical composition of raw materials (% mass fraction)

| Material       | SiO₂  | Al₂O₃ | CaO  | Fe₂O₃ | MgO  | MnO  | K₂O  | SO₃  |
|----------------|-------|-------|------|-------|------|------|------|------|
| Blast furnace slag | 16.79 | 3.61  | 46.08| 8.56  | 8.07 | 1.79 | 0.075| <0.01|
| Steel slag     | 34.65 | 12.2  | 40.02| 0.13  | 10.04| 11.44| 0.44 | <0.01|
| Desulfurized gypsum | 1.08 | 0.11  | 32.17| 0.16  | 0.23 | 0.01 | <0.01| 46.02|

2.2. Experiment method and test results

2.2.1. Foam stability study

Foam is the basis for the formation of foam concrete vents. To obtain high quality foam concrete, it is necessary to have a foam that meets the technical requirements. China's research on foaming agent for foam concrete started late. With the increasing application range of foaming agent, the technical specification of foaming agent JC/T 2199-2013 was introduced in 2013: 1 h foam settlement distance is not more than 10mm, The amount of bleeding is not more than 80ml, but the index of foam at high temperature has not been specified, and the stability of foaming agent in Japan is evaluated by the percentage of time away from liquid. The liquid discharge cylinder discharged from the foam, whose discharge liquid accounts for 50% of the total mass, is called the 50% liquid discharge time [15], and has a larger application range than the domestic standard. In this experiment, the foam bleeding measuring equipment was used to investigate the effect of temperature on the 1h foam bleeding, sedimentation distance and 50% liquid deposition time of LC, WZ and HT foaming agents. The results are as follows:

1) The effect of the concentration of foaming agent on the amount of bleeding
It can be seen from Figure 1 that the amount of bleeding of various foaming agents increases first and then increases with the increase of the dilution water. WX type foaming agent is 30 times and 40 times of dilution ratio is lower and close, and the bleeding volume is 62mm and 60mm respectively. Considering the production cost of foaming agent, the dilution ratio can be 30 times for foam concrete preparation. The optimum dilution ratio for both LC and HT foams is 40 times. Composite foaming agent (HT) has lower bleeding rate than animal protein type (WZ) and vegetable protein type (LC) foaming agent at the same foam multiple, and can be as low as 50ml, which is lower than other two foaming agents. 16.67%. It can be seen that the composite foaming agent has the best foam stability at a dilution ratio of 40 times.

From the above analysis, it is shown that the stability of the foam is greatly affected by the concentration of the foam. This is because: the foaming agent contains a large amount of amphiphilic surfactant. When it is diluted, its monomer is aligned on the surface of water, the hydrophobic base extends to the air, and the hydrophilic base extends to the water to form two dimensional monolayer; as the concentration of the foaming agent increases, the surfactant molecules self-polymerize inside the solution, and when it reaches (critical micelle concentration), micelles having a three-dimensional spherical structure are formed; the surface tension of the solution is reduced to a minimum, the stability of the foam is the highest. Then, as the concentration of the foaming agent increases, the micelles will grow from a globular structure to a stick-like micelle, and the surface tension of the solution will increase.

Fig1. Effect of dilution multiple on bleeding volume

2) Effect of temperature on foam stability

It can be seen from Figure 2 that the sedimentation distance of the foam increases first and then decreases as the concentration of the foaming agent decreases. The liquid discharging rate can be explained by the Reynolds equation:

\[ v = \frac{2h^3}{3\mu R^2} \left( \frac{2\delta}{R} + \frac{A(h)}{6\pi h^2} \right) \]

Where \( v \) is the discharge rate, \( h \) is the foam film thickness, \( u \) is the bulk solution viscosity, and \( R \) is the bubble radius as a function of the intermolecular interaction. It can be seen from the Reynolds formula that the liquid loss rate foaming agent concentration and the square of the foam radius are inversely proportional. For small-scale foams, the foam diameter has the greatest impact on the discharge rate [16].

As the temperature rises, the ablation occurs after the bubble first expands, because the foam gas begins to expand thermally, the film becomes thinner, and the Marangoni effect is affected, and no
drainage occurs [17-18]. As the temperature continues to increase, the amount of foaming agent on the surface decreases, the molecular exclusive area increases, the surface viscosity decreases, the "repair" effect of surface tension is weakened, and the surface elasticity is lowered, resulting in a decrease in foam stability, and a bubble burst occurred [19]. When the temperature is high, the foam bursts from the top. The acceleration of liquid film discharge and the increase of boundary pressure under the action of gravity are the main causes of foam rupture.

Fig2. Relation curve between dilution water multiple and settling distance at 45°C

In this test, the 50% liquid separation time of LC, WZ and HT foaming agents was measured by the foam bleeding measuring equipment. The results are shown in Figure 3. Compared with 20°C, LC, WZ and HT foaming agents are at 45°C. The 50% liquid precipitation time of the foam was reduced in the environment: 42.65%, 50.62%, 52.23%, among which the foam stability of the HT type foaming agent was the best, and the 50% liquid deposition time at 20 °C was 67 minutes, while the ordinary Portland cement The initial setting time is generally about 40 minutes, and it has good adaptability to Portland cement. The 50-column time at 45°C is 32 minutes and has excellent foam stability. It is consistent with the domestic evaluation of foaming agent quality through the amount of bleeding and settlement.
2.2.2. Study properties of waste-solid based foam concrete

Through the above analysis, it can be known that the HT type foaming agent has good stability, and it is diluted by 1:30, and the steel slag, slag and desulfurized gypsum are divided into two groups according to specific surface areas of 350 m²/kg and 500 m²/kg. Recorded as A350 and A500. According to the following Table 2, mix in a blender for 30 seconds, add water and stir for 60 seconds, then add foam, stir for 15 seconds, and quickly put the slurry into the mold, respectively, at 20 °C, 45 °C, 70 °C under maintenance. The water-to-binder ratio of the entire system gelling system was 0.45.

Table 2. Material composition and curing temperatures of the cementitious materials

| Num  | SS (w%) | BFS (w%) | FGD (w%) | Curing temperature (℃) |
|------|---------|----------|----------|------------------------|
| A500 | 38      | 60       | 12       | 20                     |
| A500 | 38      | 60       | 12       | 45                     |
| A500 | 38      | 60       | 12       | 70                     |
| A350 | 38      | 60       | 12       | 20                     |
| A350 | 28      | 60       | 12       | 45                     |
| A350 | 28      | 60       | 12       | 70                     |

3. Test results and discussion

3.1. Effect of curing temperature on thermal conductivity of foam concrete

The heat transfer coefficient of the sample after three days of curing was measured by the flat plate method. As shown in Figure 4, the thermal conductivity of both foam concretes decreased as the curing temperature increased. This is because thermal curing is conducive to the unstable gas-liquid-solid three-phase slurry to a stable gas-solid two-phase system, the bubbles become pores, the temperature rises, the hydration rate increases, the pores become larger, and become deeper. As
shown in Figure 5, the porosity increases, the longer the heat propagation path, and the more energy is lost. It can be seen that the thermal curing is beneficial to the formation of the porous structure of the cementitious material and reduces the thermal conductivity of the cementitious material. For the A350 and A500 cementitious materials: at the same temperature, the larger the specific surface area, the smaller the thermal conductivity of the material, which is related to its early hydration rate [20-21]. For the early hydration heat analysis of commercially available Portland cement, A350 and A500 cementitious materials, as shown in Figure 6, it can be seen that the early hydration rate of A500 has a peak of bulging and a faster hydration rate, which is beneficial to solidifying pores. A350, A500 two kinds of cementitious materials and Portland cement compared to the early hydration rate, it can be seen that the ratio of foam concrete is feasible.

![Graph showing thermal conductivity variation with curing temperatures](image)

**Fig4.** Normal temperature thermal conductivity variation with curing temperatures

![SEM images on microstructures of aerated concretes at different temperatures](image)

**Fig5.** SEM images on microstructures of aerated concretes at different temperatures
4. Mechanism analysis of solid waste-based foam concrete
From the above discussion, it can be seen that steel slag, mine slag, desulfurized gypsum-based foam concrete has the potential to replace Portland cement, which may be related to its specific surface area and its hydration products of cementitious materials. Laser particle size analysis of A500 cementitious material is shown in Figure 7: its average particle size is about 5-8um, which is much lower than that of ordinary Portland cement. As the particle size of the cementitious material becomes smaller and the specific surface area increases, the optimized micro-level matching state is more obvious, the activity of the gelling material is enhanced, and the hydration reaction is more thorough [22]. Its many micron-sized particles form a coating layer on the surface of the foam, and rapidly participate in the hydration reaction on the foam wall. The rapidly initial slurry has a large restraint and fixation effect on the bubble, which is beneficial to maintain the pore stability.

5. Conclusion
1. Compared with the three foaming agent foams of LC, WZ and HT, the composite foam of HT composite foam has the best performance.
2. Foam stability is affected by concentration and temperature: foam stability of high-concentration foam follows the Reynolds equation. The foam stability is mainly manifested by
gas diffusion between foams at low temperatures, and Marangoni effect and gravity drainage at high temperatures.

3. Increasing the specific surface area of cementitious materials and increasing the curing temperature are the key to the preparation of foam concrete by industrial solid waste. Industrial production can be effectively selected according to actual conditions.

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