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Research Progress of the Modification in Sulfur Concrete

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Abstract

Sulfur concrete (SC) is a relatively new type of construction material with advantages of the strong corrosion resistance and quick setting and hardening, which has been applied in construction engineering. SC is brittle with large hardening shrinkage, so it needs to be modified in the process of use. How SC can be modified is a key point of its improvement. In view of the existing research results, the research status of the modification in SC is summarized and concluded in this paper to generate some insights, including the understanding of variations in temperature, effects of molding methods and the addition of fillers and modifiers.

Keywords

Sulfur Concrete, Modification, Molding, Temperature, Filler, Modifier

1. Introduction

Sulfur is a kind of common chemical raw material whose chemical formula is S and it is a light yellow solid as shown in **Figure 1** at room temperature. In **Figure 1**, it can be seen that although the surface of sulfur in the laboratory is slightly dim under the effects of light and ash deposition, it does not affect our conclusion that sulfur is light yellow.

Sulfur has been applied in the fields of agriculture, medicine and rubber products industry [1] [2] [3] [4]. In 1921, it was learned that sulfur can also be used as a binder in construction engineering [5]. In 1924, Kobbe [6] proposed that concrete can be made from sulfur and other mixtures to make sulfur more suitable for conventional construction projects. With the deepening of research, SC is increasingly widely applied in the fields of construction engineering.

Because of its excellent properties, SC has application prospects in many aspects in construction engineering. First of all, with strong corrosion-resistance, SC can resist the invasion of chemical corrosion effectively [7] [8]. Compared with the common Portland cement concrete (PCC), it is more suitable for corrosion-resistant projects of chemical plants and ocean engineering. Secondly, the melting point of sulfur, a kind of cementitious material, is generally not less than 110˚C. After being heated and mixed, with the decrease of the temperature, SC will set and harden, and the speed of setting and hardening is very quick. At room temperature, there is no need to keep the mixture curing to achieve enough compressive strength. Once the temperature is raised to more than the melting point of sulfur, SC is easy to melt and be recycled. Therefore, SC can be applied in some temporary structures like the bridge temporary support, which needs quick installation and removal [9]. It can not only play a supporting role quickly but also directly melt in the heat after use, so as to achieve the result of more convenient removal and collection. In addition, sulfur can be obtained from minerals on the surface of Mars, the moon and other extraterrestrial planets by chemical or physical methods, which reduces the workload and cost of transporting building cementitious materials from the earth to other planets. Therefore, people are paying more attention to SC as the in-situ building materials of extraterrestrial planets [10] [11].

However, the shortcomings of SC in the process of its application have been exposed including brittleness and large hardening shrinkage. Some fatal problems like stress concentration and structural depression will happen in SC-based construction projects due to these defects.

Hence, it is better to modify the SC to avoid its defects. Many relevant researchers in civil engineering are making their constant efforts in this field. But the modification theory is not very perfect. This paper presents the research status of the modification in SC to generate some insights, including the understanding of variations in temperature, effects of molding methods and the addition of fillers and modifiers. Meanwhile, some conclusions are also included in this paper.

2. Study on the Modification

1) Understanding of temperature variation

General forming steps of SC [7] are shown in **Figure 2**. It is showed that sulfur needs to be melted at high temperature, and then mixed with other materials for pouring. Therefore, the better change of sulfur state with temperature variation is the guarantee for the mixture to mix tightly and successful setting and hardening later. At different temperatures, different allotropes appear, and the properties of each allotrope are not the same. With the variation of temperature, the phase changing diagram of sulfur [12] is shown in **Figure 3**, in which each character is expressed as S_α (Orthorhombic sulfur), S_β (Monoclinic sulfur), S_λ (Amorphous sulfur), S_μ (Polymeric sulfur), S_δ (Sulfur vapor).

In order to understand the change of sulfur state and properties at different

Figure 1. Sulfur at room temperature.

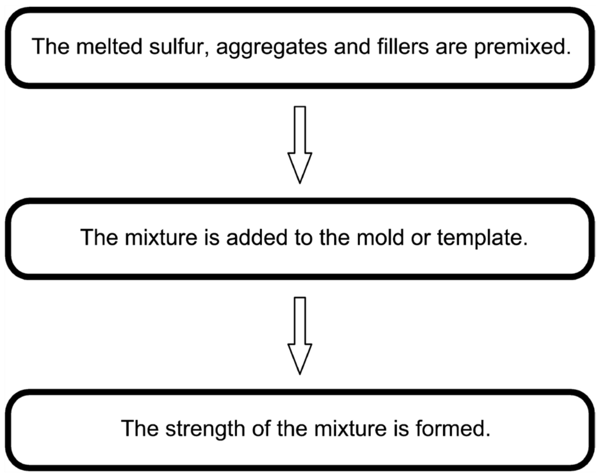

Figure 2. General forming steps of SC [7].

$$S_\alpha \xleftrightarrow{\approx 96^\circ\mathrm{C}} S_\beta \xleftrightarrow{\approx 119^\circ\mathrm{C}} S_\lambda \xleftrightarrow{\approx 159^\circ\mathrm{C}} S_\mu \xleftrightarrow{444.6^\circ\mathrm{C}} S_\delta$$

Figure 3. The phase changing diagram of sulfur [12].

temperatures, researchers have carried out extensive research.

Bacon and Fanelli [13] found that in the temperature from 120˚C to 200˚C, the viscosity of sulfur first decreases, then increases sharply until reaching the peak at near 190˚C, and then decreases. Wang [14] found that when the temperature changes, S_β will change to S_α and during the transformation, due to the change of the crystal lattice, the volume of sulfur will shrink and the shrinkage stress will be formed inside the sulfur. The heat resistance stability and other characteristics of sulfur including bond strength and impact strength will be greatly influenced by the shrinkage stress. Pickard and Xiao [15] concluded that the temperature from 138˚C to 143˚C is suitable for pouring SC without harmful gases generation such as H_2S and SO_2 during the heating process. The temperature range of experiments or construction can be selected in that range. Ksiazek [16] summarized several different properties of the melted sulfur at different temperatures: the melted sulfur at 160˚C, 200˚C to 250˚C, 250˚C and 400˚C is the brown liquid with indication increased viscosity, dark brown liquid with high viscosity, liquid with viscosity decreasing which is trend to depolymerize and very fluid, respectively. From that, an intuitive method to judge the state of the melted sulfur appears.

2) Improvement of molding methods

It is also mentioned above that under the effects of temperature, sulfur will transform from an allotrope to another, and some transformations are unfavorable to the use. There is no doubt that such unfavorable transformations need to be avoided. Ameliorating the molding process of SC can control the temperature variation and the properties of SC will also be improved by better molding process. The properties of SC will be affected by temperature, mixing conditions and pouring methods, and the optimization of the molding process can also be considered in these aspects.

Li [17] reported in the early stage that sillars Co., Ltd. of UK launches a mobile SC production device. From that report [17], the device is used to produce SC with acid resistance and chemical corrosion resistance, whose materials are mixed and poured through high temperature. Mohamed and Gamal [18] developed a sort of SC with low hydraulic conductivity whose internal micropores are not connected and concluded the key points of their molding methods that in the process of adding the modified paste into the molds, the mixture should be compacted in the molds in the vibrator for 10 seconds and after compaction, the mold will be put into the oven with cooling at a rate of 5˚C per minute to prepare. In their results, the proper vibration of mold and the slow cooling of paste can improve the properties of SC. Toutanji *et al.* [19] found that the molding of SC is affected by the temperature vibration and when the sulfur-based mixture comes into contact with the mold with lower temperature, the external cooling of the mixture will accelerate, which will result in the acceleration of the overall shrinkage. Thus, the importance of the proper vibration of mold and slow cooling of paste should be emphasized. Khoshnevis *et al.* [20] introduced a new type of SC mixer, in which heating and mixing materials at suitable temperature are permissible and after more than 500 hours of its work, the durability and stability of the machine and the effect of mixture temperature and sulfur ratio on the final shape of the extrusion were demonstrated. All of the above proves that the properties of SC will be affected by temperature, mixing conditions and pouring methods.

3) Fillers addition

SC generally consists of sulfur and various fillers. Fillers here refer to powder materials with fine particle size, so particle size of them is different from that of aggregates. In the industry, there are many sources of fillers for preparation, mainly including quartz sand, ceramics, and graphite [21]. Conventional Portland cement can also be added into SC as a kind of filler. SC with Portland cement addition will not contain hydration products of Portland cement when there is no water added. Although it seems that fillers whose particle size is relatively fine can be blown away by the breeze at any time, fillers can play an important role of pore filling in SC. From this level, fillers play a certain positive role in improving the later compressive strength and sulfur brittleness. However, fillers and sulfur are two different substances after all. It is still worthy of researchers to make sure the specific function of fillers and the best mixing ratio of various fillers.

Vlahovic *et al.* [22] thought that the selection of fillers is very important, because they form SC together with aggregates wrapped in the sulfur paste, and in the process of forming SC, they provide nucleation sites for crystal formation and growth and fill the voids of aggregates, so as to reduce the sulfur content, control the viscosity of the paste, and reduce the shrinkage during hardening. Bae *et al.* [23] found that compared with PCC, the thermal expansion coefficient of SC is slightly larger and the thermal expansion coefficient of SC will reduce after mixing with mineral fillers. Gwon *et al.* [24] found that the compressive strength of sulfur composites can be improved by replacing sulfur with fly ash and rubber powder which can effectively replace fine aggregates or part of sulfur and compared with sulfur mortar containing a small amount of sand, sulfur composites with the same proportion of rubber powder show higher compressive strength. Obviously, rubber powder and fly ash can also be positive fillers for SC. Gwon *et al.* [25] found that when Portland cement is used as a kind of powder filler, if the cement particles uniformly diffuse in SC and the hydration reaction does not occur in advance, water may invade from the formed cracks and promote the hydration of cement particles and in that opinion, hydration products are likely to fill the cracks that have been generated in the structure and affect the strength of the structure. Gwon and Shin [26] thought that the addition of fly ash as filler significantly enhanced the anti-wear property and the watertightness of SC, which makes the pavement engineering more durable. Szajerski *et al.* [27] summarized that through the compressive strength test, compared with the untreated natural composites, under the condition of high radiation dose, the radiation resistance of SC with fly ash and rubber powder as fillers can be improved. After the tests of the research team of Rasheed [28], it is found that adding fillers can successfully improve the mechanical properties of sulfur polymer mortar and the corresponding conclusion are also came to: by means of reducing the average pore diameter and absorptivity coefficient of composite microstructure, the performance of sulfur polymer mortar can be further improved by micro fillers.

4) Modifiers addition

As mentioned earlier, sulfur, a cementitious material, has exposed its shortcomings as a brittle material in the process of application, which will have a adverse impact on the project. Therefore, if properties of sulfur and modification treatments can be studied and carried out by us, properties of SC may not develop in the original unfavorable direction with the change of environment.

With better modifications in sulfur, some serious brittle failures will not appear in SC. In the use of conventional SC, the main problem is that certain shrinkage stress will be produced in the transformation process of the allotropes in sulfur with the variation of temperature, which is not conducive to the structure [14]. The addition of modifiers in SC can avoid that by reducing the transformation between sulfur allotropes.

Researchers treated SC with different modifiers to find out their effects. Blight *et al.* [29] thought that some modifiers can reduce the brittleness of sulfur like the styrene and dicyclopentadiene which can inhibit the formation of long chain of high molecular sulfur polymer to control the viscosity of liquid sulfur to a certain extent. Wang [30] concluded that polymerized unsaturated hydrocarbons can be used as sulfur modifiers to plasticize sulfur and maintain the stability of crystal form when the temperature changes. Generally speaking, styrene and dicyclopentadiene can be used as representatives of polymerized unsaturated hydrocarbons. Xu [31] believed that one of the reasons why SC has not been successfully popularized and applied is that unpleasant odor will appear in the process of sulfur modification. In the ordinary experiments, it is found that in some process of the conventional modifier modification, unpleasant odor will appear which needs timely ventilation to clean the indoor air. Enayaty-Ahangar and Motahari [32] found that compared with the pure sulfur mortar, the compressive strength and splitting tensile strength of modified sulfur mortar containing 7% by weight of dicyclopentadiene increase by 50.7% and 305.29% respectively, which is considered by them that the allotropic transformation is effectively eliminated after the modification of dicyclopentadiene and the properties of sulfur tends to be more stable. Moon *et al.* [33] have proved that some cheap industrial by-products, such as the industrial by-products of petroleum distillation, can also modify SC to make it possible to compete with the traditional hydraulic cement concrete. It is also an effective solution for promoting the use of green building materials with this cheaper industrial by-product as modifier of SC. Dehestani *et al.* [34] summarized the experimental data of SC modified by styrene and asphalt under different conditions and their control steps for modification are that firstly sulfur is heated to 135˚C，then the styrene or the emulsifier is added. Thus, it needs to be considered whether 135˚C is also a key temperature node of sulfur modification or not. Rasheed *et al.* [28] believed that although the dicyclopentadiene is used to modify sulfur, the transformation between allotropes might still occur with the variation of temperature inevitably, which may cause certain shrinkage cracks in the sulfur polymer. Therefore, sulfur can be modified by modifiers, but the modification may be incomplete.

3. Summary

As a new type of building material, SC has the characteristics of corrosion resistance, quick setting and hardening. In many fields of construction engineering, it can be applied as a substitute for PCC. Even in some fields, SC is more suitable for application than PCC. However, SC is brittle and shrinks greatly in the process of setting and hardening, so it is necessary to modify SC, otherwise fatal problems may appear in major projects.

Temperature is an important factor affecting the application of SC because the transformation between allotropes will accelerate with the variation of temperature, resulting in different states of sulfur. Therefore, in the process of SC mixing, temperature control is particularly important.

The use of SC is greatly affected by temperature. Therefore, in the process of its forming, transportation and pouring, with more mature technology, the problem of imperfect forming of SC will be reduced. At present, many instruments have been developed to assist SC forming in various countries, but there are still few for large-scale buildings, which is worthy of promotion and research.

Some fine powder materials play a filling role as inert fillers in SC. While filling SC micropores, fillers have a certain control effect on the properties of SC. However, the mechanism between different fillers and SC has not been completely clear, so it is worth studying in the future.

Sulfur can be better used in SC after being modified by modifiers. At present, common modifiers are mainly styrene and dicyclopentadiene and so on. Of course, more and more modifiers are appearing, which are also proved to have some modification effects, including various industrial by-products. Therefore, the research on the modification effects of various industrial by-products also has great prospects.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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