Comparative Analysis of Hydration Expansion Performance of Desulfurized gypsum-based α/β Gypsum

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Abstract. Gypsum has micro-expansion characteristic during the process of hydration and solidification, and there are certain differences in the hydration expansion characteristics of different types of hemihydrate gypsum. In this paper, by analysing the gypsum crystal morphology, particle size distribution, hydration heat, dimensional change rate, and morphology change of hydration products in the process of hydration process, the hydration expansion performance of α/β gypsum are compared and discussed. The results indicate there are differences in the hydration swelling mechanism between α-gypsum and β-gypsum. The expansion of gypsum is the result of the combined effect of the crystal transformation and the release hydration heat during the hydration process. The particle size distribution and the amount of hydration water added have a great influence on the expansion performance.

1. Introduction
There are differences in strength and dimensional stability between α-type gypsum and β-type gypsum [1]. α-gypsum has higher strength and hardness, and is mainly used in dental moulds, precision casting moulds, craft moulds, etc. [2-3] Moulds usually require high dimensional accuracy, and the expansion performance of gypsum will affect the dimensional stability of the product. β-type gypsum is mainly used for building materials. If gypsum is used to prepare large-volume products, such as gypsum floors, gypsum blocks, gypsum mould boxes, the hydration expansion properties of α-gypsum and β-gypsum are very important for the fine application of gypsum [4-5]. In this paper, desulfurized gypsum-based α-gypsum and desulfurized gypsum-based β-gypsum are selected as the research objects. By analysing the gypsum crystal morphology, particle size distribution, hydration heat, dimensional change rate, and morphology change of hydration products in the process of hydration process, the hydration expansion performance of α/β gypsum is compared and discussed.

2. Experimental

2.1. Materials
The chemical composition analysis of desulfurized gypsum-based α/β gypsum is shown in Table 1.
Table 1 The chemical analysis of desulfurized gypsum-based α/β gypsum

| Sample  | SO₃   | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | Cr₂O₃ | SrO | Crystal water |
|---------|-------|------|------|-------|-------|------|-----|-------|-----|---------------|
| α-gypsum | 57.57 | 40.31| 1.02 | 0.51  | 0.21  | 0.15 | 0.12| 0.09  | 5.9 | 6.3           |
| β-gypsum | 49.17 | 35.15| 3.21 | 1.64  | 0.74  | 0.35 | 0.35| 0.02  | 5.5 | 5.5           |

2.2. Methods

According to "Dental gypsum products" (ISO/DIS6873) and "αhigh strength gypsum plaster" (JC/T 2038), the expansion performance ofα-gypsum and β-gypsum are determined. The hydration heat is measured by hydration heat analyzer (TAM-air) and its initial temperature is set to 25℃. The adding water values for hydration heat analysis of desulfurized-based α-gypsum, desulfurized-based β-gypsum, naturalα-gypsum and natural β-gypsum are 0.39, 0.9, 0.35 and 0.64, respectively.

3. Result and discussion

3.1. The hydrate expansion rate of desulfurized-based α-gypsum and β-gypsum

![Graph of hydrate expansion rate curves of α-gypsum and β-gypsum](image)

Fig.1 The hydrate expansion rate curves of α-gypsum and β-gypsum

The hydrate expansion rate curves of desulfurized α-gypsum and β-gypsum measured at standard consistency using the standard test method of “α-type high-strength gypsum” are shown in Figure 1. It can be seen from the figure that the hydrate expansion rate of α-gypsum is about 0.41%, and the hydrate expansion rate of β-gypsum is about 0.17%. The results indicate that the hydrate expansion rate of α-gypsum is greater than that of β-gypsum.

3.2. The hydration heat of desulfurized α-gypsum and β-gypsum

The hydration heat flux and cumulative heat release amount of desulfurized α-gypsum and desulfurized β-gypsum are shown in Fig.2 and Fig.3. It can be seen that the hydration heat flux of desulfurized α-gypsum and desulfurized β-gypsum is concentrated between 0 min-60 min. From Fig.2, the heat flux peak of α-gypsum is at 30min. The peak value and the cumulative heat release are 0.048 W/g and 90.278J/g, respectively. From Fig.3, the highest heat flux peak of β-gypsum is at 38min, the peak value is 0.073 W/g, and the cumulative heat release is 89.82J/g. It is noting that there is a weak exothermic peak of β-gypsum which is at 5min. It is mainly because the calcination temperature for the preparation of β-gypsum is difficult to control suitably, especially for the fast burning method of
dihydrate gypsum which inevitably contains a small amount of AIII as by-product. The hydration rate of AIII is extremely fast, and its theoretical hydration heat at 25℃ is (25700±85 J/mol), which is higher than that of α-gypsum (17200±85 J/mol) and β-gypsum (19300±85 J/mol). The hydration heat of desulfurized β-gypsum is mainly concentrated between 20 min~50 min, and the hydration heat of desulfurized α-gypsum is mainly concentrated between 5~50min, indicating that the hydration heat release of desulfurized β-gypsum is more concentrated, resulting in a sharper exothermic peak. Moreover, the cumulative heat release of α-gypsum is slightly higher than that of β-gypsum and this is consistent with the chemical analysis result of the two types of the gypsoms. By comparing the hydrate expansion rate and the hydration heat release of the two gypsoms, it can be seen that the hydrate expansion rate of gypsum mainly occurs in the hydration heat release stage, indicating that the expansion process and the hydration process are almost synchronized.

![Fig.2 The hydration heat curve of α-gypsum](image1)

![Fig.3 The hydration heat curve of β-gypsum](image2)

From Fig.2 and Fig.3, the measured cumulative heat release of desulfurized α-gypsum is 90.278 J/g, and the measured cumulative heat release of desulfurized β-gypsum is 89.82 J/g. The standard consistency water requirement of desulfurization α-gypsum and desulfurization β-gypsum in this experiment is 34.8% and 62.6% respectively. Specific heat of dihydrate gypsum at 25°C is 1.1J/g•K; Specific heat capacity of water is 4.2 J/g•K; Thermal expansion rate of dihydrate gypsum is 32.3×10⁶/K⁻¹.

According to the above conditions, the temperature increase of the hardened body and the thermal expansion values of the two gypsoms can be calculated as follows:

\[ \Delta T_{\alpha} = 90.278 J/g \div (0.162 \times 4.2 J/g \cdot K + 1.1862 \times 1.1 J/g \cdot K) = 45.5K \]

\[ \Delta T_{\beta} = 89.82 J/g \div (0.43979 \times 4.2 J/g \cdot K + 1.1862 \times 1.1 J/g \cdot K) = 28.5K \]

\[ \Delta E_{\alpha} = 32.3 \times 10^6 / K^{-1} \times 45.5K = 0.147\% \]

\[ \Delta E_{\beta} = 32.3 \times 10^6 / K^{-1} \times 28.5K = 0.092\% \]

Compared with the experimental expansion values which are shown in Fig.1, the calculation result also indicate the theoretical thermal expansion value of α-gypsum is obviously higher than that of β-gypsum. However, the theoretical thermal expansion values are lower than the experimental values, which explain the thermal expansion caused by the exothermic heat of hydration is only part of the reason for the expansion of gypsum.

3.3 Crystal form transformation and phase change

The hydration and hardening of hemihydrate gypsum is the process of the continuous growth of gypsum crystals from the supersaturated solution. The higher the degree of super saturation of the gypsum slurry is, the more crystal nuclei are formed. In the process of crystallization, the crystal grains overlap and coexist to form a crystalline structure network. In the process of hemihydrate
hydration, the crystal structure of gypsum is transformed from trigonal crystal system to monoclinic crystal system and its solid phase volume increases by 40.20%; the total volume of solid phase and liquid phase decreases by 7.05%. It can be seen that the hydration of gypsum is a process in which the volume of the solid phase increases continuously, while the total volume of the solid phase and the liquid phase decreases slightly. The schematic diagram of gypsum grains hydration process is shown in Fig.4. It indicates the grains in the gypsum slurry continue to grow as the hydration reaction progresses, approaching each other and the fluidity of the slurry slowly loses to form a plastic body. With the further development of hydration, between the gypsum grains more and more contact points occur. And the plasticity is lost to form a hardened body. During the process of plasticity loss, the internal compressive stress formed by the continuous growth of grains in the hardened body is also increasing. The external appearance is volume expansion during the hydration reaction.

Figure 4 The schematic diagram of gypsum grains hydration process

The morphology structures of α-gypsum and β-gypsum before and after hydration are shown in Fig.5 and Fig.6. It can be seen that the crystal morphology of α-gypsum and β-gypsum changes significantly before and after hydration. The crystals change from short pillars before hydration to laths or rods, and the hydrated grains overlap with each other and are in close contact to form a denser hardened structure, which is an important source of strength of the hardened body. There are also a large number of interconnected pores between the overlapping dihydrate gypsum crystals. And the morphology structure of α-gypsum after hydration is relatively denser than that of β-gypsum. The water requirement for normal consistency of α-gypsum and β-gypsum are 34.8% and 62.6% respectively. In the process of gypsum hydration, approximately 18.6% of the free water is converted into gypsum crystal water, and the remaining unreacted water exists in the pores of the hardened body in the form of attached water. It can be seen that the porosity of the α-gypsum hardened body is lower than that of the β-gypsum, which is the main reason for the difference in strength between the two gypsums. The high porosity of β-gypsum slurry can provide space for the hydrate expansion of gypsum grains and alleviate the mutual squeezing caused by the expansion effect between the grains to a certain extent. Moreover, the high porosity can also reduce the compressive stress formed inside the hardened body. That’s another important reason that the hydration expansion rate of α-gypsum is greater than that of β-gypsum.
4. Conclusions
The results show that the expansion of gypsum is the result of the combined effect of the crystal transformation and the release of heat of hydration during the hydration process. There is a clear difference between the hydration and expansion behaviors of α and β gypsum. The main differences are summarized as follows:

The hydration expansion rate of α-gypsum is significantly higher than that of β-gypsum. The resulting experimental expansion amounts are 0.41% and 0.17%, respectively. The expansion rate curve of gypsum is almost synchronized with the hydration exotherm curve, indicating that the expansion process mainly occurs in the hydration process.

The cumulative heat release of desulfurized α-gypsum and desulfurized β-gypsum is basically the same, but the hydration reaction of desulfurized β-gypsum is more concentrated, and the heat flux peak is higher than that of desulfurized α-gypsum.

α- gypsum and β- gypsum have different body temperature rises and different grain growth spaces during hydration. They are the two main reasons why the expansion rate of α-gypsum is significantly greater than that of β-gypsum.

Acknowledgments
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