Relationship between Crystalline Size, Activity and Expansive Properties of MgO Expansive Agent

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Abstract. The quantitative relationships between the calcination temperature and the crystalline characterization, the activity and the expansive properties of MgO expansive agent were explored through XRD-Scherrer formula, the citric acid method and the length measurement method. The results show that, under the same heat preservation time conditions, there exists exponential relationship between crystalline size and calcination temperature of MgO expansive agent, and exists linear relationship between the activity value of MgO expansive agent and the crystalline size of MgO crystal. Before 28 curing days, the expansion ratios of cement pastes possess logarithmic relationship with the activities of MgO expansive agent, while with the increase of curing age, specimens containing MgO of high activity values show faster increase rates in expansion ratio in 60~180d, and the relationship between the expansion ratio and the activity value of MgO expansive agent becomes more complicated.

Introduction

Using the delayed expansion property of MgO to compensate the temperature shrinkage of concrete has been successfully applied in several mass concrete structures such as dams, diversion tunnels and so on [1,2]. But there still exists many controversies on the expansion properties and stability of MgO expansive agent in the actual use [3-5]. Since the MgO expansive agent is calcined by magnesite, its expansion property is significantly affected by the thermal history in calcination process. Many studies have shown that the calcining temperature is the most important factor influencing the reactivity and expansion property of MgO [6-8], but the specific relationship is still not very clear. In this paper, the quantitative relationships between the calcination temperature and the crystalline characterization, ther activity and the expansive properties of MgO expansive agent were explored, which can provide a reference for the preparation and application of MgO expansive agent.

Raw Materials and experimental Methods

Preparation and basic performance of MgO expansive agent. The MgO expansive agent used here was laboratory-calcined under different calcination temperatures and the same heat preservation time, with the chemical compositions shown in Table 1. As can be seen from Table 1, the chemical compositions of MgO expansive agent under different calcination temperatures are basically the same, with the MgO component accounting for more than 90 %. The particle size distribution tested by the laser particle size analyzer is shown in Fig. 1. As seen from Fig. 1, the particle size distributions of MgO expansive agent under different calcination temperatures are substantially the same.

Testing methods. The activities of MgO expansive agent were tested by the citric acid method according to DL/T 5296-2013 [9], in which, the longer the time represents the lower the activity. The crystalline sizes of MgO were tested by Bruker-AXS D8 DISCOVER X-ray diffractometer equipped with the LynxEye array detector, at a work condition of Cu target, 40kV operating voltage, 35mA

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operating current, 4.0° sola slit, 10-80° 2θ, 0.02° step size and 0.2 sec/step. Compress the powder to a glass sample plate special for the diffractometer, after instrumental parameters being adjusted, insert the glass sample plate into the sample holder and test. Then the crystalline sizes of MgO were calculated by Scherrer formula $D_{hkl}=K\lambda/(\beta_{hkl}\cos\theta_{hkl})$, in which K representing Scherrer constant with the value being 0.89, λ representing the Kα1 wavelength of X-ray being 0.154056nm here; β_{hkl} representing the broadening of (hkl) diffraction peak, in this paper calculated by β=B-b (B being FWHM, half the width of the (hkl) diffraction peak, rad; b being the width of the instrument, here taking 0.140°); θ_{hkl} representing the diffraction angle of (hkl) crystalline faces. The deformation properties of cement pastes mixed with 4% (mass fraction) MgO expansive agent were tested using prism specimens with the size of 25mm×25mm×280mm in which copper head buried at both ends, after pouring the specimens were conserved under (20±1)℃ for (24±2)h with the surface of the specimen covered by PVC plastic film, then removing the mould, and measured the initial length L_0 of each specimen 1h later, after that, the specimens were placed in water under (20±1)℃ and measured the length L_n at each age. Expansion coefficient ε was calculated by the formula $\varepsilon=(L_n-L_0)/L*100\%$, wherein the effective length L=250mm.

Table 1 Chemical compositions of MgO expansive agent under different calcination temperatures. %

Calcination temperature-heat preservation time	MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3
800℃-1h	90.4	4.23	3.01	1.23	0.762
850℃-1h	91.1	3.85	3.01	1.13	0.58
900℃-1h	90.9	4.01	3.03	1.10	0.63
950℃-1h	90.9	4.03	2.98	1.07	0.69
1000℃-1h	91.1	3.88	3.01	1.00	0.36
1050℃-1h	91.0	3.84	3.07	1.13	0.67

Note: Some components of which the content < 0.05% have been discarded.

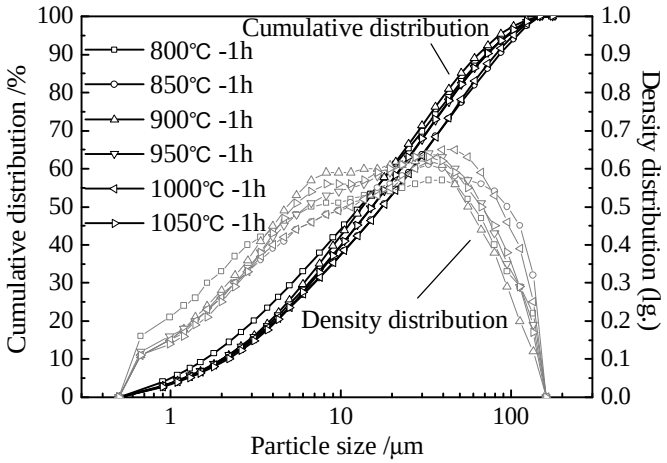

Fig. 1 Cumulative and density distributions of MgO expansive agent.

Results and discussion

The crystalline size of the calcined MgO. The XRD patterns of MgO expansive agent obtained from different calcination temperatures and the same heat preservation time are shown in Fig. 2. As can be seen from Fig. 2, the higher the calcination temperature, the sharper the MgO diffraction peaks, which indicates that the higher the degree of crystallinity. XRD professional analysis software was used to analyze the patterns, and the obtained diffraction angle 2θ and full width at half maximum (FWHM) of

(2 0 0) diffraction peak of MgO are shown in Table 2. Then the crystalline sizes of the calcined MgO were calculated by Scherrer formula and shown in column 5 of Table 2. From Table 2, it can be seen that, the crystalline size of the calcined MgO increases with the increase of the calcination temperature. Meanwhile, the crystalline sizes of the calcined MgO were also calculated using Lorentz formula with the results shown in column 6 of Table 2. From comparison of the calculating results by the two methods, it is found that for MgO expansive agent calcined below 1000℃, the crystalline size obtained by the two methods are basically the same, while for MgO expansive agent calcined under 1050℃, the crystalline size obtained from Lorentz formula is significantly lower than that obtained from the Scherrer formula.

The activity of MgO expansive agents. The activities of MgO expansive agent tested by the citric acid method are shown in Table 3. As can be seen from Table 3 that, under the same heat preservation time conditions, the activity value of MgO expansive agent increases with the increase of the calcination temperature, that is, the hydration activity decreases with the increase of the calcination temperature. It can also be seen from Table 3 that, below 950℃, the calcination temperature has less effect on the activity of MgO; while above 950℃, the calcination temperature plays a greater effect role on the activity of MgO.

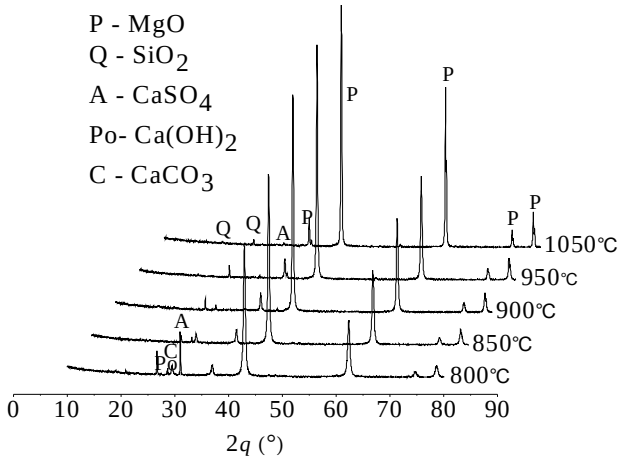

Fig. 2 XRD patterns of MgO expansive agent obtained from different calcination temperatures.

Table 2 Crystalline features of calcined MgO.

Calcination temperature-heat preservation time	(hkl)	2θ (°)	FWHM (°)	D(Scherrer)	D(Lorentz)
800℃-1h	(2 0 0)	42.931	0.410°	31.3	32.0nm
850℃-1h	(2 0 0)	42.951	0.346	41.0	41.7nm
900℃-1h	(2 0 0)	42.951	0.284	58.6	57.3nm
950℃-1h	(2 0 0)	42.931	0.266	67.0	65.5nm
1050℃-1h	(2 0 0)	42.949	0.188	175.9	126.4nm

Table 3 Activity values of MgO expansive agent under different calcination temperatures.

Calcination temperature /℃	800	850	900	950	1000	1050	1200
Activity value /s	50	67	80	104	153	322	360

Expansion properties of cement pastes containing MgO expansive agent. The testing results of deformation properties of cement pastes containing MgO expansive agent are shown in Fig. 3. As can be seen from Fig. 3, the expansion ratios of cement pastes containing MgO expansive agent increase

with the longer of age, while cement pastes containing MgO of different activity values display different expansion development histories. In the early age, expansion ratio of specimens containing MgO under calcination temperature below 1050 ℃ is larger than that of the reference, while expansion ratio of specimens containing MgO under 1200 ℃ is smaller than that of the reference. But in the late age of the testing period (60~180d), the expansion ratio of specimens containing MgO under 1200 ℃ shows a faster increase rate. The test results indicate that by controlling the activity of MgO expansive agent, different final expansion ratio and different expansion development histories can be obtained.

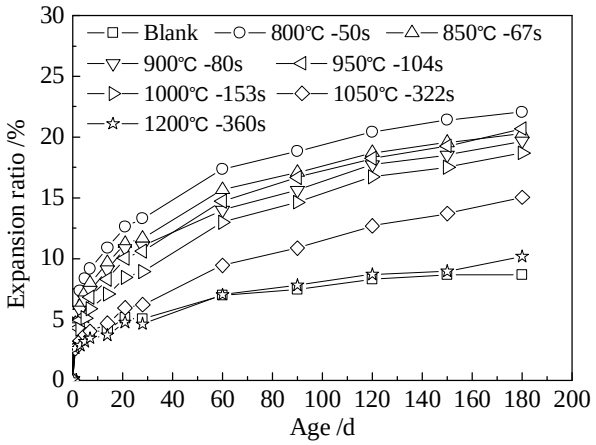

Fig. 3 The expansion curves of cement pastes containing MgO expansive agent.

Relationship between calcination temperature and crystalline size, activity value of MgO expansive agent. Relationships between crystalline size, activity value of MgO expansive agent and calcination temperature are shown in Fig. 4. Relationship between activity value of MgO expansive agent and crystalline size of MgO crystal is shown in Fig. 5. From Fig. 4, it is known that there exist simple exponential relationships between crystalline size, activity value of MgO expansive agent and calcination temperature, with the specific relationship being

$$C=0.00051*\exp (T/83.41998)+26.99701 \quad (1)$$

where C representing calcination temperature and T representing crystalline size of MgO crystal.

As mentioned in section 2.1, the chemical compositions and the particle size distributions of MgO expansive agent used here under different calcination temperatures are basically the same, so it can be considered that the activity of MgO expansive agent relates only to the crystal structure of MgO crystal. And as shown in Fig. 5, there exists simple linear relationship between the activity value of MgO expansive agent and the crystalline size of MgO crystal, with the specific relationship being

$$A=-18.72069+1.91708C \quad (2)$$

where C representing crystalline size of MgO crystal and A representing the activity value of MgO expansive agent.

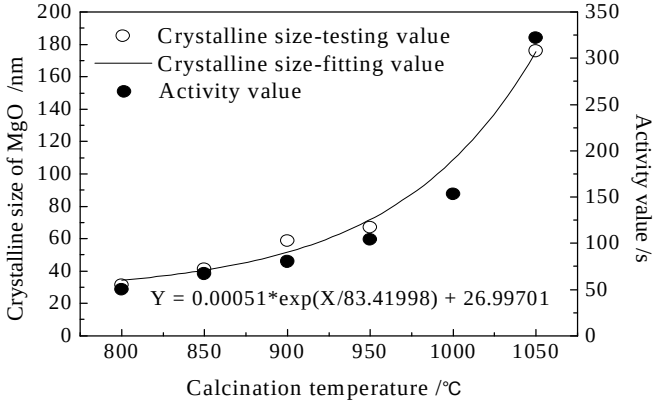

Fig. 4 Relationship between crystalline size, activity value and calcination temperature of MgO expansive agent.

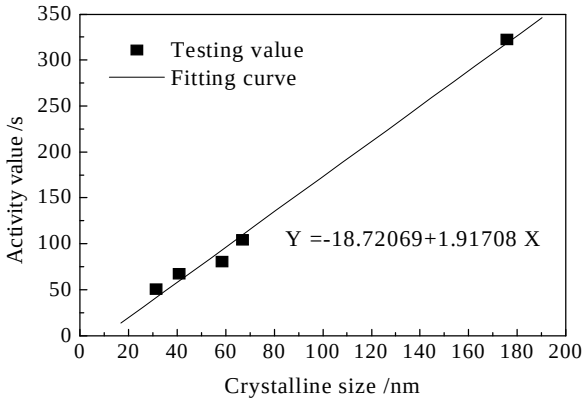

Fig. 5 Relationship between activity value of MgO expansive agent and crystalline size of MgO crystal.

Relationship between activity and expansion property of MgO expansive agent. Relationship curves between activities of MgO expansive agent and expansion ratios of cement pastes containing MgO expansive agent are shown in Fig. 6. As can be seen from Fig. 6, during the early 28 curing days, there exists simple logarithmic relationship between the expansion ratios of cement pastes and the activities of MgO expansive agent, and the absolute value of the slope of the curve gradually increases with the extension of curing age. While with the further extension of curing age, specimens containing MgO of high activity values shows a faster increase rate in expansion ratio in 60~180d, and the relationship between the expansion ratio and the activity value of MgO expansive agent becomes more complicated, which needs to be further analyzed in the later.

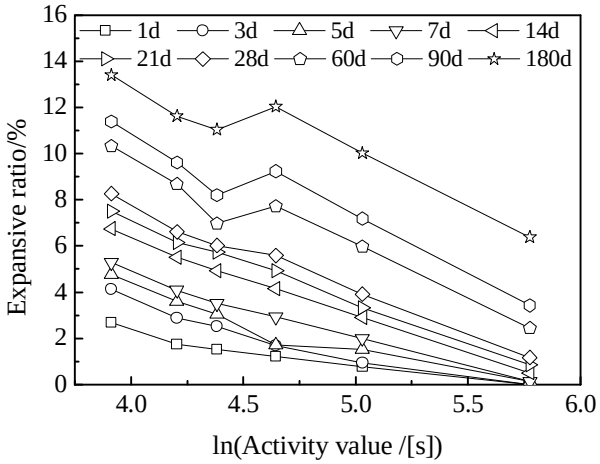

Fig. 6 Relationship curve between activities of MgO expansive agent and expansion ratios of cement pastes.

Conclusion

Under the same heat preservation time conditions, there exist simple exponential relationships between crystalline size, activity value of MgO expansive agent and calcination temperature. Further, controlling the particle size distributions of MgO expansive agent to be basically the same, there exists simple linear relationship between the activity value of MgO expansive agent and the crystalline size of MgO crystal.

There exists simple logarithmic relationship between the expansion ratios of cement pastes before 28 days and the activities of MgO expansive agent, while with the increase of curing age, specimens containing MgO of high activity values show faster increase rates in expansion ratio in 60~180d, and

the relationship between the expansion ratio and the activity value of MgO expansive agent becomes more complicated.

Acknowledgements

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