

Study on the hydration and hardening mechanism of the high-water rapid-setting material

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Abstract. High-water rapid-setting material is a type of cement-based material, which is high water contained, rapid hardening and has early strength. Hydrating and hardening mechanism of this material have been studied by XRD and SEM, the influence of different curing time, gypsum lime content and water-cement ratio on the hydrating and hardening process was explored. The hydration products were measured by XRD. The results show that ettringite is the main product of hydration and hardening. With the increase of curing age, the amount of ettringite increases gradually. The amount of limestone gypsum affects the amount of ettringite. The lower the water-cement ratio is, the more ettringite is formed. SEM analysis shows that hydration reaction will continue with age. The shape of ettringite turns from the acicular to the columnar. Gradually it becomes compact forming network structure. Hydrated calcium aluminate and aluminium hydroxide filled in the network structure which makes the material more compact. Increasing the amount of gypsum within a certain range will promote the formation of ettringite. The lower the water cement ratio is, the more compact the ettringite is and the stronger the material is. Finally, based on the hydration products and microstructure of the material, the hydration reaction equation was established and the growth process of strength was analyzed, and it provides the basis for the study of the durability of the material.

1. Introduction

High-water rapid-setting material [1-3] has been widely used since it was produced due to good material properties [4]. So far, a large number of studies have been carried out on it, mainly reflected in the composition of the material itself, the basic properties of the material, and its hydration and hardening mechanism. In terms of the study on the composition of the material itself, the influence of different admixtures on the material was explored, and the properties of the material was studied and optimized [5, 6]. In the study of basic properties of the material, Liu and Jiang studied their mechanical properties, axial pressure, confining pressure characteristics and creep characteristics [7, 8]. In the study of hydration hardening mechanism [9, 10], Zhou et al studied the hydration hardening products at different ages. Compared with the study on hydration hardening of ordinary concrete and other new cementing materials [11,12], the hydration hardening process and its influencing factors of high water rapid-setting material are relatively few. XRD and SEM were used to analyze hydration



products and microstructure of high-water rapid-setting material [13, 14], exploring the influence of different factors on the hydration hardening process, and then write the chemical reaction equations, explore its reaction process and hardening mechanism.

2. Test plan

2.1. Test materials

The high-water rapid-setting material is composed of material A and material B in the experiment. The composition of material A is sulphoaluminate cement clinker (SAC) and additive (TA), while the composition of material B is gypsum, lime and additive (TB). TA is composed of suspension agent, coagulant and dispersant, and TB is composed of early strength agent and suspension dispersant, etc. Table 1 shows the chemical composition of the remaining components. The sample size is 40mm×40mm×160 mm, and test temperature is 20°C.

Table 1 composition of each material

specimen material	chemical composition /%									
	CaO	Al ₂ O ₃	SiO ₂	SO ₂	TiO ₂	TiO ₂	Fe ₂ O ₃	MgO	K ₂ O	P ₂ O ₅
SAC	41.51	40.05	6.53	7.16	1.69	1.69	1.55	0.79	0.61	0.10
Gypsum	46.61	0.20	1.30	48.34	0.04	0.04	3.46	0.05		
Lime	97.69	0.32	0.51	0.38	0.23	0.23	0.76	0.04	0.07	

2.2. Test equipment and test methods

Referring to “The specification of the cement mortar strength testing method (ISO) law” (GB/T0506-2005), after the test specimen strength, some concretion body hydration products were tested by XRD, and its microstructure was tested by SEM. The measurement values of material compatibility ratio and strength are shown in table 2 and table 3. A, B, C and D were tested in four groups. The influence law of curing age was explored by XRD diffraction patterns and SEM scanning images of group B in different periods. The effects of gypsum lime content in group B and group C were compared. Through group A, C and D experiments, the influence law of water-cement ratio was analyzed.

Table 2 The mix proportion of the materials

Table 3 The compressive strength of thematerials (MPa)

Group	w/b	A material /%				B material /%				Group	Age				
		SAC	TA	G+H	TB	5h	1d	3d	7d		28d				
A	1.0			80+20		A	9.23	13.52	14.12	15.77	18.06				
B	1.5	100	10	80+20	10	B	2.40	5.75	6.05	7.11	7.77				
C	1.5			85+15		C	3.20	5.36	5.65	6.82	10.63				
D	2.5			80+20		D	0.80	2.23	3.05	3.57	4.22				

(annotation: w/b is water cement ratio, SAC represents the clinker of sulphate aluminate cement in material A, TA is the admixture of A, G is gypsum, H is lime, TB is the admixture of B)

3. Microscopic analysis

3.1. Analysis of hydration products

3.1.1. Changes of hydration products with curing age. The XRD pattern of hydration products at different ages in group B specimen was used to explore the variation rule of hydration products with age. As shown in figure1, the hydration products of the 5h are mainly calcite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$), hydrated calcium aluminate sulphate hydrate ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)0.5(\text{OH})\cdot12\text{H}_2\text{O}$) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$). At the age of 3d, hydrated calcium thioaluminate hydrate gradually generates low-sulfur hydrated calcium thioaluminate ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)\cdot14\text{H}_2\text{O}$). Calcium aluminate hydrates into hydrated garnet at an age of 3 to 7 days ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$), and it's not fully reacted; The hydration products at the age of 28d mainly include alunite, calcium sulfate and aluminum glue ($\text{Al}(\text{OH})_3$). The

strongest diffraction peaks of calcite in the XRD pattern of each age are 2332a.u., 2746a.u., 3092a.u., and 4042a.u., respectively, indicating that hydration degree increases with age.

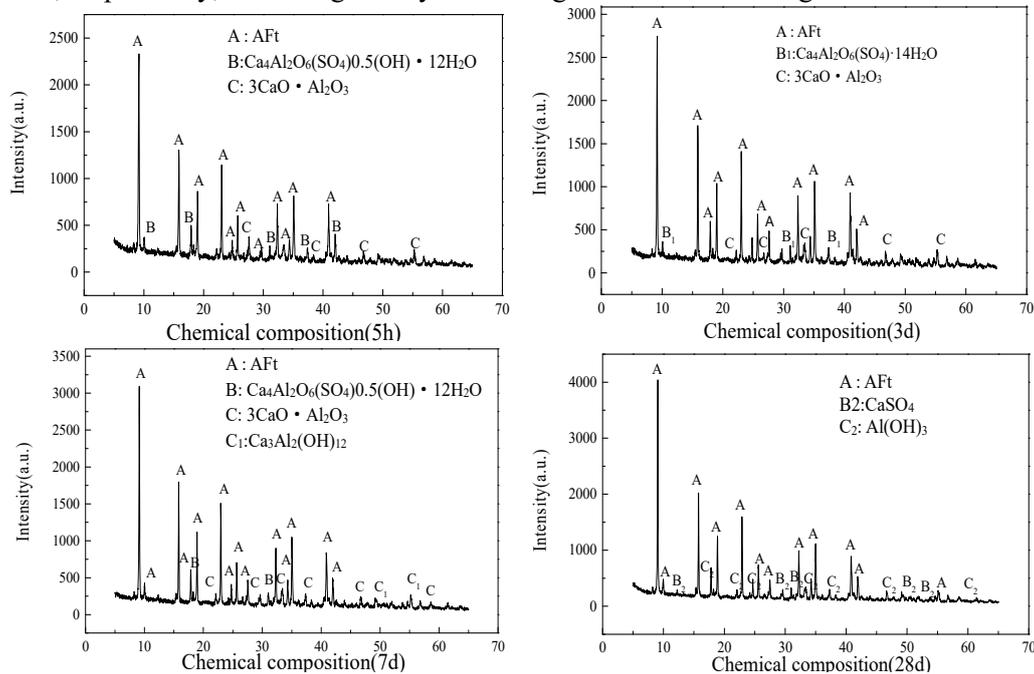


Figure 1. XRD diffraction of hydrated products of group B.

3.1.2. The influence law of gypsum lime content. The effects of gypsum lime content on hydration products were analyzed by XRD diffraction pattern of hydration products of group C for 7d and 28d. As can be seen from figure 2(a), hydration products at an age of 7d mainly include alunite, hydrated calcium aluminate sulphate hydrate and calcium bisulfate ($\text{CaH}_2(\text{SO}_4)_2$), calcium sulfate and calcium aluminate hydrate ($\text{Ca}_4\text{Al}_6\text{O}_{13} \cdot 13\text{H}_2\text{O}$), similar to hydration products of group B at an age of 7d; The hydration products of 28d mainly include alum, hydrated calcium sulfate and water garnet. After 7d, group C materials with high gypsum content continued to hydrate to form calcite, and calcium aluminate hydrate formed hydrogarnet with hydration. The main reason for the increase of compressive strength from 7d to 28d is that alunite is produced by subsequent hydration. As calcium sulfate dihydrate and garnet hydrate can continue to react to produce alum and aluminum glue, the strength of group C materials after 28d can be predicted to increase to a certain extent.

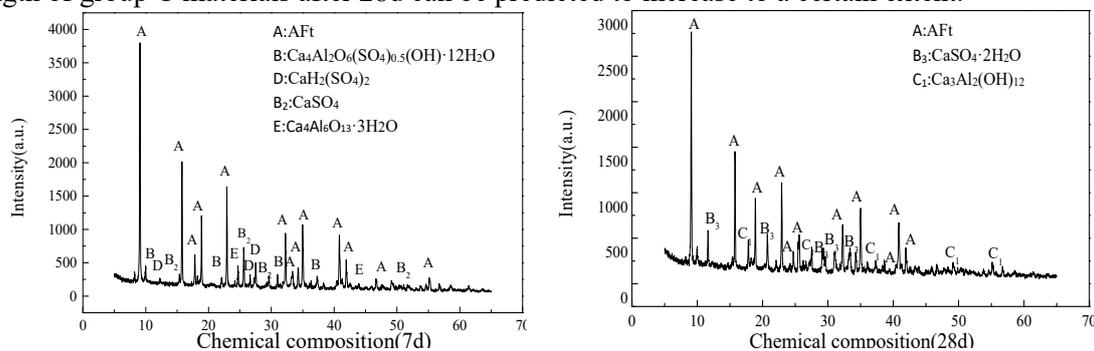


Figure 2. XRD diffraction of hydration products of group C.

3.1.3. The influence law of water-cement ratio. The influence law of water-cement ratio was analyzed by the XRD diffraction pattern of group A, B and D for 7d. From the analysis of the hydration products map of group A, B, D, it is visible that at the water cement ratio of 1.0, 1.5, 2.5, the materials of the 7d hydration products are given priority to ettringite, and the strongest diffraction peak is

respectively 3798 a. u., 3092.a u. and 3496 a. u.. Depending on the type of hydration products, in addition to the main contain of ettringite and low-sulfur hydrated calcium sulphoaluminate, group A (w/b = 1.0) hydration 7d generated water garnet, group B (w/b = 1.5) hydration 7d detection contains water garnet and tricalcium aluminate, group D (w/b = 2.5) hydration 7d detection contains calcium sulfate hydrate and tricalcium aluminate, so in curing 7d, the hydration rate of tricalcium aluminate is $A < B < D$. The hydration reaction rate of the material decreases with the increase of water-cement ratio. Moreover, the crystallinity water of low-sulfur hydrated calcium thioaluminate is related to the water-cement ratio. When the water-cement ratio is 1.0, the chemical formula is $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O}$, and when the chemical formula is higher than 1.0, it is $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 14\text{H}_2\text{O}$.

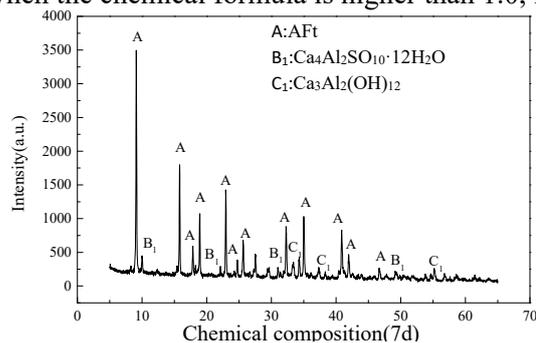


Figure 3. XRD diffraction of hydrated product of group A.

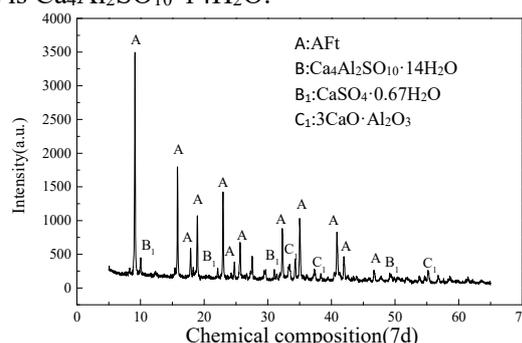


Figure 4. XRD diffraction of hydrated product of group D.

3.2. Microscopic morphological analysis

3.2.1. Effect of curing age. The effects of age on microstructure were analyzed by using SEM images of group B hydrated for 5h, 3d, 7d and 28d. Acicular or columnar calcite crystals are the main products. Figure 5(b) shows that fibrous hydrated silicate gel is formed in the early stage of hydration. Figure 5(a) - (c) shows that the hexagonal laminar substance is low-sulfur hydrated calcium thioaluminate ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)\cdot 14\text{H}_2\text{O}$), $\text{Ca}(\text{OH})_2$. The main reason why the crystal did not precipitate was that $\text{Ca}(\text{OH})_2$, CaSO_4 , $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ were secondary hydrated to form calcite. Figure 5(d) shows that aluminium glue generated at the age of 28d, and it filled with hydration silica gel in the pore of ettringite crystal to make the structure more compact, which is the cause of the material on the compressive strength increases with age gradually.

3.2.2. Effect of gypsum lime content. The effect of gypsum lime content on group B and group C was studied. It can be seen from figure 6 that cubic hydrogarnet appeared in group C after 28 days of hydration, and that the main hydrated product calcite was dense network, and hydrated silicate gel was filled in network pores. In group B aluminum plastic materials generated with hydration, ettringite crystal quantity increased, but mainly ettringite crystal coarsens, grow up, there is still a pore structure, so the strength increased from 7.11MPa to 7.77MPa, slow growth. In group C the compressive strength of the material increase from 6.82MPa to 10.63MPa, grow larger. The main reason is more ettringite formation, and a lot of hydrated silica gel formation which fill in the microstructure, increase the material density, the porosity decreases. It can be seen that changing the amount of gypsum lime in a certain range is conducive to improving the strength of the material.

3.2.3. The influence of water-cement ratio. The influence of water-cement ratio on microstructure was analyzed by an electron microscope scanning graph of group A, B and D for curing 7d, as shown in figure 7 and 8. Comparing with the 1.0 and 1.5, the number and density of albite are different, and the microstructure of crystal is very different. By figure5 shows group B material curing 7d, ettringite is cylindrical cross, structure of the mesh is full of pore. In group A more and more ettringite crystal is overlapping, pore is small and the material is high density. The figure8 group D is acicular ettringite crystal produced by hydration of material, the hydration of fibrous silicate gel packs in ettringite crystal mesh structure, but the material still had a loose structure, pore is more. It can be seen that the

smaller the water-cement ratio, the lower the water content of the high-water rapid-setting material hardening body, the higher the density of the microstructure and the higher the strength.

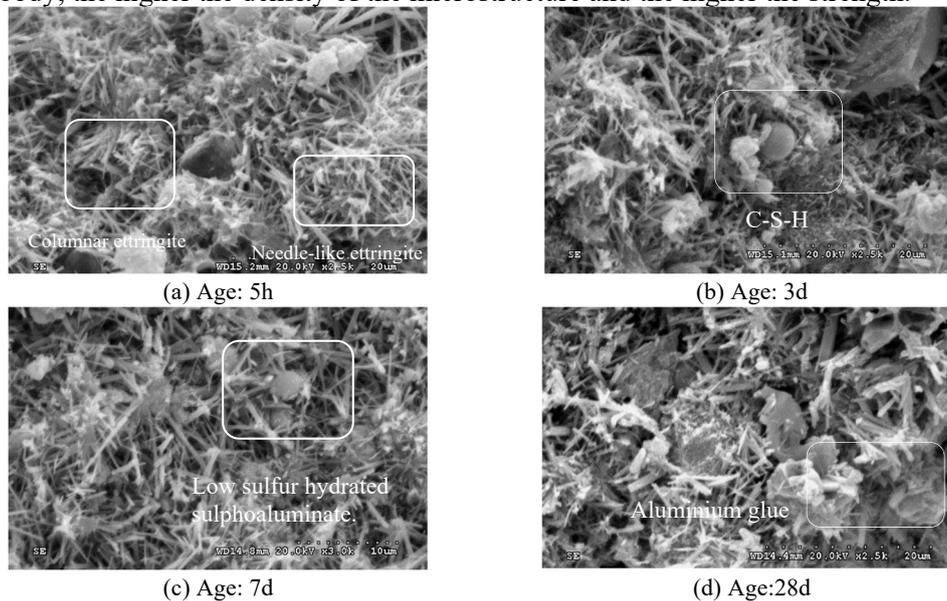


Figure 5. Scanning electron microscope image of group B during hydration process.

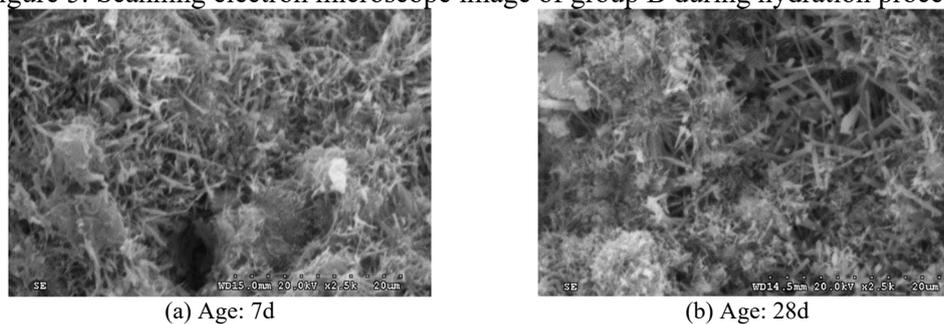


Figure 6. Electron microscope scanning of group C during hydration.

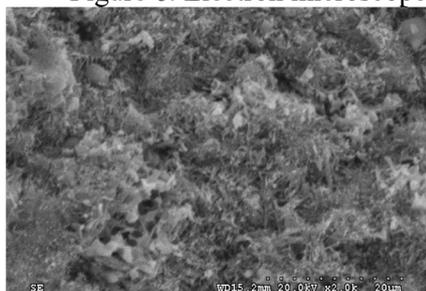


Figure 7. Scanning electron microscope image of group A material hydrated for 7d.

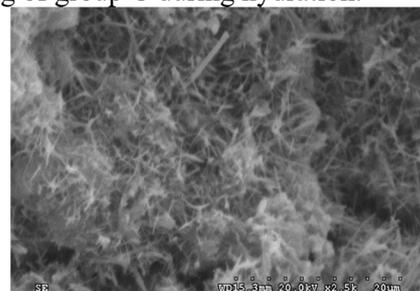
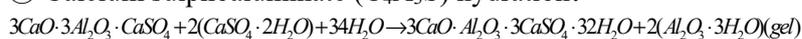


Figure 8. Scanning electron microscope image of group D material hydration for 7d.

4. Analysis of hydration mechanism

From the above test, water cement ratio has great influence on the quantity of ettringite and crystal structure, which affect the dense degree of structure and the strength of materials. According to the mineral composition of the raw materials and the types of hydration products obtained by XRD, it can be seen that the hydration process mainly produces the following chemical reactions:

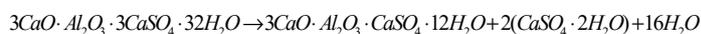
① Calcium sulphoaluminate (C_4A_3S) hydration:



When the content of CaSO_4 is sufficient:



When the content of CaSO_4 is insufficient:



② Dicalcium silicate (C_2S) hydration: $2\text{CaO} \cdot \text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{C} - \text{S} - \text{H} + \text{Ca}(\text{OH})_2$

③ Tricalcium aluminate (C_3A) hydration: $2(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + 27\text{H}_2\text{O} \rightarrow 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O} + 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$

At room temperature, C_4AH_{19} is in a meso-stable state, which tends to transform to C_3AH_6 and other crystals: $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} + 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \rightarrow 2(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}) + 9\text{H}_2\text{O}$

C_3A has large hydration heat, often directly hydration to C_3AH_6 : $3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$

When you have CaSO_4 : $3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

5. Conclusion

The curing age, water cement ratio and gypsum lime content has a great influence on the hydration products and microstructure of high-water rapid-setting material. The mechanism of hydration hardening was studied by XRD and SEM scanning microscopic technology. Conclusions are as follows:

(1) High-water rapid-setting material quickly generates a large number of ettringite at the beginning, with time going on, the formation of ettringite speed slows down. The reason for the increase of main performance is that the ettringite's shape transforms from the needle to the columnar. Hydrated silica gel, such as aluminum plastic gradually generates, and fills in the ettringite connection skeleton, the early strength grows rapidly, the late strength with ettringite volume increases in the number of expansion, and the hydration of tricalcium aluminate slows growth.

(2) When the water cement ratio was small, the amount of alunite produced in the initial stage was large, the hydrated silicate gel was rapidly formed and the material was denser. Water cement ratio is the most important factor affecting hydration in that the water cement ratio will affect the shape of alunite crystal, the porosity of crystal reticular structure and the density of material. The smaller the water cement ratio, the faster the strength growth, and ultimate strength is also the largest.

(3) Increasing the amount of gypsum in a certain range can promote the conversion of intermediate products to calcite, so that the hydration of materials is more sufficient and the strength is continuously enhanced. However, the water cement ratio should not be too large, otherwise, the hydration degree of the material is not high, which will affect the development of strength.

(4) The original strength of the high water material is a certain amount of ettringite generated at first. The hydration is the reaction between mainly mineral composition, dicalcium silicate, calcium sulphoaluminate tricalcium aluminate and gypsum, lime, and calcium sulphoaluminate and dicalcium silicate begins to hydrate at the beginning of the reaction. Tricalcium aluminate gradually generates water garnet, rapidly changing into ettringite crystal when the calcium sulphate is sufficient. As the generation of gelling material and the growth of ettringite, the intensity increases gradually.

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