

Experimental Study on Basic Mechanical Properties of Calcium Sulfate Whisker-Reinforced Cement

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Abstract. In order to study the effect of calcium sulfate whisker on the mechanical characteristics of Portland cement, the fluidity, initial setting time, final setting time, flexural strength and compressive strength of calcium sulfate whisker-reinforced cement with 0~1.0% (mass fraction) were studied using experimental method. The results show that calcium sulfate whisker has little effect on the fluidity, initial setting time and final setting time. For the 28-day flexural strength and compressive strength of calcium sulfate whisker-reinforced cement, the optimum whisker content is 0.4% and 1.0% and the corresponding strength is increased by 19.54% and 35.84%, respectively. Compared with calcium carbonate whisker, the reinforcement effect of calcium sulfate whisker on the strength of Portland cement is better.

1. Introduction

Ordinary Portland cement is widely used in civil engineering. However, it has low tensile strength, small tensile strain, easy cracking, low permeability and other shortcomings. Researchers use some fiber materials to improve the performance of cement-based materials, such as steel fiber, carbon fiber, glass fiber, polypropylene fiber and so on [1, 2]. But these fiber materials are not perfect, such as steel fiber is easy to agglomerate in construction, the price of carbon fiber with high tensile strength and elastic modulus is expensive and it has poor dispersion, glass fiber will be eroded by the high alkaline hydration products of Portland cement [3, 4]. Therefore, it is necessary to look for and study a fiber reinforced material with excellent performance, reasonable price and sustainable development.

Calcium sulfate whisker is also called gypsum whisker, which is fibrous single crystal of calcium sulfate. Compared with traditional fibers, it is an ideal fiber substitute. Calcium sulfate whisker has the particle size of granular fillers and the length-diameter ratio of short fibrous fillers, and has the advantages of stable size, high strength, good toughness, high temperature resistance and chemical corrosion resistance [5]. The price of calcium sulfate whiskers is much lower than that of other high performance fibers. Calcium sulfate whiskers are mainly prepared from gypsum. At present, China's proven gypsum reserves are about 100 billion tons, ranking first in the world. In addition, there are other raw materials, such as ammonia alkali waste CaCl_2 , phosphate rock, calcium salts and sulfates, converter slag and tin tailings, rare earth tailings and so on, so sources of raw materials are extensive and using them are conducive to environmental protection and sustainable development [6, 7].

The properties of calcium sulfate whiskers-reinforced cement are studied using experimental method in this paper. Compared with pure cement materials, calcium sulfate whisker has little influence on the working performance of cement-based materials and improves obviously the flexural strength and compressive strength.



2. Working Performance Test

2.1. Test Material and Method

The working performance test of calcium sulfate whisker cement-based material includes fluidity, initial and final setting time. Ordinary Portland cement with strength grade of 42.5 is used. Calcium sulfate whisker (SEM photo as shown in figure 1) is produced by Northeastern University, China and the technical index is shown in table 1.

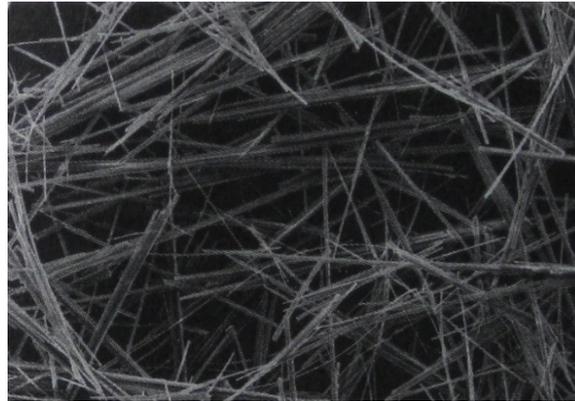


Figure 1. SEM Photograph of CaSO₄ Whiskers

Table 1. The Technical Index of Calcium Sulfate Whisker

Index	Value	Index	Value
Density (g/cm ³)	2.96	Melting point (°C)	1450
Bulk density (g/cm ³)	0.1~0.4	Water-soluble (22°C) (ppm)	<1200
Length (μm)	50~200	Moh's hardness	3~4
Diameter (μm)	0.5~4	CaSO ₄ content (%)	≥96
Tensile strength (GPa)	20.5	Water content (%)	<1.2
Tensile modulus (GPa)	178	pH	7~8

As shown in figure 2, for the measurement of fluidity, the glass plate with the size of 400mm×400mm×5mm is firstly placed on the horizontal position, and the glass plate, agitator, truncated cone die and mixing pot are uniformly rubbed with a wet cloth to make the surface wet without driving water stains. Then put the truncated cone die (upper diameter 36 mm, lower diameter 60 mm, height 60 mm) on the center of the glass plate, and put the mix the cement slurry into the die quickly and flatten it with a scraper. Lift the truncated cone die in the vertical direction and start timing with a stopwatch. When the cement slurry flows for 30 seconds on the glass plate, measure the maximum diameters of the two perpendicular directions of the flowing slurry. Finally, the fluidity of cement slurry is the average value of the two maximum diameters. As shown in figure 3, Vicat apparatus is used to measure the initial setting time (figure 3 (a)) and the final setting time (figure 3 (b)). When the test needle sinks to (4±1) mm from the bottom plate, the cement reaches the initial setting state; when the needle sinks 0.5 mm into the cement body, the cement reaches the final setting state.



(a) Truncated Cone Die

(b) Flowing Cement Slurry

Figure 2. The Test of Fluidity

(a) The Initial Setting Time

(b) The Final Setting Time

Figure 3. The Test of the Initial and Final Setting Time

2.2. Test Results and Analysis

The test results of fluidity and initial and final setting time are shown in table 2.

Table 2. The Test Results of Fluidity and Initial and Final Setting Time

Mixed content (%)	Fluidity (mm)	Initial setting time (min)	Final setting time (min)
0	65.17	270	330
0.2	64.83	270	315
0.4	63.50	270	330
0.6	63.50	270	315
0.8	63.50	265	315
1.0	64.00	275	315

According to the data in table 2, when 0.2%~1.0% (mass fraction) calcium sulfate whisker is added, the fluidity of cement slurry decreases, but the extent of decrease is small. Because calcium sulfate whisker is fibrous single crystal that is a microfiber and has no bending deformation, the phenomenon of agglomeration and winding in steel fiber and polypropylene fiber will not occur when a small amount of calcium sulfate whisker is added [8]. In addition, the diameter of the calcium sulfate whisker is relatively small compared to other fibers, so the cement slurry is not affected by fiber blocking effect [9, 10]. At the same time, mixing 0.2%~1.0% calcium sulfate whisker had little effect on the initial and final setting time of cement slurry.

3. Bending Test

3.1. Test Instrument and Method

YAW-1000 automatic pressure testing machine is used in the test, and the size of test block is 40mm×40mm×160mm, as shown in figure 4. 3-day, 7-day, 14-day and 28-day flexural strength tests are performed on cement samples with calcium sulfate whisker mass fraction of 0, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%, respectively. The loading rate is (50±10) N/s.

The flexural strength R_f is calculated according to the following formula:

$$R_f = 1.5FL / b^3 \quad (1)$$

Where: F is the failure load (N), L is the center distance of the supporting cylinder, $L=100\text{mm}$, and b is the side length of the square section of the test block, $b=40\text{mm}$.

The test results of flexural strength of each group are the arithmetic mean of the measured values of the three test blocks. When any of the three flexural strength values is plus or minus 10% above the mean, this measured data should be eliminated. The final flexural strength test results are averaged with the remaining two flexural strength test values.



(a) Test Instrument



(b) Flexural Test Block

Figure 4. Test Instrument and Flexural Test Block

3.2. Test Results and Analysis

The bending test results are shown in table 3.

Table 3. Flexural Strength of CaSO₄ Whisker Cement-based Materials

Mixed content (%)	Flexural strength (MPa)			
	3 days	7 days	14 days	28 days
0	7.55	11.31	14.24	15.10
0.2	8.20	13.59	14.59	15.40
0.4	6.67	13.23	16.05	18.05
0.6	7.46	12.72	16.11	16.26
0.8	6.31	10.50	16.03	16.20
1.0	7.64	11.83	14.58	15.29

It can be seen from table 3 that the mixture of calcium sulfate whiskers improves the flexural strength of cement materials in general. When the curing time is 3 days and 7 days, the flexural strength is improved less because the properties of cement are more unstable. When curing time is 14 days, the flexural strength of cement test block is maximum with the mass fraction of calcium sulfate

whisker of 0.6%. When curing time is 28 days, the flexural strength of cement test block is maximum (i.e. 18.05 MPa) with the mass fraction of calcium sulfate whisker of 0.4% and is increased by 19.54% compared with ordinary Portland cement test block without calcium sulfate whisker.

4. Compression Test

4.1. Test Method

The compression test blocks are the fractured prismatic blocks in the bending test. The loading rate is (2400±200) N/s and the loading area of the test block is 40mm×40mm. There are 6 test blocks for one group and the test compressive strength of each group is the arithmetic mean of the compressive strength test values of six test blocks in the same group. When one of the six measured compressive strength values in a group is plus or minus 10% above the mean, this measured data should be eliminated. The final compressive strength test results are averaged with the remaining five compressive strength test values. If any of the remaining five compressive strength values is plus or minus 10% above the new mean value, the test results of this group will be invalidated.

4.2. Test Results and Analysis

The compression test results are shown in table 4.

Table 4. Compressive Strength of CaSO₄ Whisker Cement-based Materials

Mixed content (%)	Compressive strength (MPa)			
	3 days	7 days	14 days	28 days
0	49.42	61.16	66.26	72.99
0.2	40.79	64.17	76.02	91.21
0.4	42.61	61.18	73.03	85.87
0.6	42.45	67.77	67.70	78.89
0.8	42.29	66.56	67.34	96.60
1.0	49.47	63.09	68.88	99.15

As can be seen from table 4, the effect of calcium sulfate whisker on early compressive strength of cement-based materials is not obvious. However, with the increase of curing time, the enhancement effect of calcium sulfate whisker increases gradually. When the mass fraction of mixed calcium sulfate whisker is 1.0%, the 28-day compressive strength reaches the maximum value, i.e. 99.15 MPa. Compared with the 28-day compressive strength of pure Portland cement test block, the strength is increased by 35.84%.

5. Comparison of Test Results Between CaSO₄ and CaCO₃ Whisker

According to reference [3], considering the mass fractions of calcium carbonate whisker with 0%, 2%, 3% and 4%, the bending and compressive tests of calcium carbonate whisker cement-based test blocks are carried out, respectively. The comparison test results of cement-based materials with calcium sulfate whisker and calcium carbonate are shown in table 5.

Table 5. Comparison Test Results between Calcium Sulfate Whisker and Calcium Carbonate

Item	CaSO ₄ whisker	CaCO ₃ whisker
Optimum content for flexural strength	0.4%	3.0%
Increased percentage for flexural strength	19.5%	12.1%
Optimum content for compressive strength	1.0%	2.0%
Increased percentage for compressive strength	35.8%	12.5%

Table 5 shows that for the flexural strength and compressive strength of whisker cement-based materials, the optimum content of calcium sulfate whisker is 2/15 and 1/2 of that of calcium carbonate

whisker, respectively. However, the increased percentage for flexural strength and compressive strength of calcium sulfate whisker cement-based material is 1.61 times and 2.86 times than that of calcium carbonate whisker cement-based material, respectively. Therefore, compared with calcium carbonate whisker, calcium sulfate whisker has better enhancement effect on the flexural strength and compressive strength of cement-based materials.

6. Conclusion

When the content of calcium sulfate whisker is 0.2%~1.0%, it has little effect on the fluidity, initial and final setting time of cement slurry.

For the 28-day flexural strength, the optimum fiber content of calcium sulfate whisker is 0.4%, and the flexural strength is increased by 19.54% compared with ordinary Portland cement test block without calcium sulfate whisker.

For the 28-day compressive strength, the optimum fiber content of calcium sulfate whisker is 1.0%, and the compressive strength is increased by 35.84% compared with ordinary Portland cement test block without calcium sulfate whisker.

Compared with calcium carbonate whisker, calcium sulfate whisker has better enhancement effect on the flexural strength and compressive strength of cement-based materials.

7. References

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