Preparation of nano-calcium silicate hydrate and its application in concrete

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Abstract. The calcium silicate hydrate (C-S-H) is the most important hydration product of cement hydration and the most critical source of strength for concrete. In this paper, nano-calcium silicate hydrate was synthesized by sol-gel method. The results show that the nano-calcium silicate hydrate prepared by high-speed stirring and under the action of specific dispersant solution at 40 °C has the smallest particle size and the best dispersion. The early strength of concrete can be improved by adding nano-calcium silicate hydrate as early strength agent. It can reduce its nucleation energy barrier, promote cement hydration, thereby significantly shortening the setting time of concrete, and greatly improving the compressive strength and flexural strength.

1. Introduction
The calcium silicate hydrate (CaO•SiO$_2$•nH$_2$O, C-S-H) is the main hydration product in cement-based materials, accounting for about 70%, and it is one of the main sources of concrete strength improvement. Under different preparation conditions, the morphology of C-S-H also changes, such as semi-crystalline, amorphous and nanocrystalline. With the progress of science and technology, the research of calcium silicate hydrate has gradually developed to nanostructure. The researchers found that the nano-calcium silicate hydrate can effectively promote the hydration of cement, shorten the concrete setting time and improve its early strength.

In this paper, nanoscale calcium silicate hydrate was prepared by sol-gel method. Firstly, the white mud with high calcium content was selected to be used as calcium source after high temperature roasting and pickling treatment. At the same time, silicate was selected as the silicon source to form tiny and dispersed SiO$_2$ particles by hydrolysis and condensation reaction. And it will facilitate the condensation reaction and generate a large amount of Si-OR groups to promote production of SiO$_2$ particles under alkaline conditions.

In addition, polyoxyethylene (5) nonylphenyl ether (Igepal CO-520) was mixed with a cyclohexane solution to form a dispersant, and a large amount of hydrophilic groups was formed on the surface of the sol-gel particles, so that they could be dispersed in solution with a stable way. The products prepared by this process had small particle size, favorable stability, high dispersion, and excellent properties.

2. Experiment
2.1 Materials preparation
2.1.1 The synthetic experimental materials
The white mud that was discarded from papermaking was supplied from the paper mill in Nanping, Fujian, China. The main components of the white mud are listed in Table 1. Nitric acid (HNO\textsubscript{3}, analytical purity), tetraethyl orthosilicate (TEOS, analytical purity), cyclohexane (C\textsubscript{6}H\textsubscript{12}, analytical purity), sodium hydroxide (NaOH, analytical purity), absolute ethanol (C\textsubscript{2}H\textsubscript{5}OH, analytical purity) were all provided by Sinopharm Chemical Reagent Company (China). Polyoxyethylene (5) nonylphenyl ether (Igepal CO-520, Mn=441), cetyltrimethylammonium bromide (CTAB, > 99%) and sodium hexametaphosphate (SHMP, > 96%) were supplied from Sigma-Aldrich Company. All of the above chemicals were used as purchased without any further purification.

| Component | CaO  | MgO  | Fe\textsubscript{2}O\textsubscript{3} | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | LOI  |
|-----------|------|------|-----------------|-----------------|-----------------|------|
| Rate /%   | 51.7 | 1.87 | 0.68            | 5.79            | 2.64            | 35.42|

2.1.2 The performance test material
Cement (C, P. O 42.5, Specific indicators of cement are shown in Table 2); Sand (S, Mx=2.6-2.9); Gravel (G, grain size of 6-20 mm); Mineral powder (P, Level S95); Fly ash (F, Level II); Water(W); Polycarboxylate superplasticizer (Point S, water reduction rate of 30%, solid content of 50%, produced by KZJ New Materials Group Co., Ltd.).

| Compressive strength/MPa | Flexural strength/MPa | Standard consistency water consumption/% | setting time /min | Fineness/% |
|--------------------------|-----------------------|----------------------------------------|------------------|-----------|
| 3 d                      | 28 d                  | 3 d                                    | 28 d             | 141       | 194       | 1.0 |
| 30.3                     | 54.0                  | 7.1                                    | 10.3             |           |           |     |

2.2 Synthesis of nano-calcium silicate hydrate

2.2.1 Preparation of calcium Solution
The white mud that was discarded from papermaking was selected as the calcium source. After crushing, it was raised to 150 °C at a heating rate of 5 °C/min, and then kept at a constant temperature for 30 min. Then, the temperature was raised to 600 °C at a heating rate of 10 °C/min, constant temperature 1 h. Finally, it was raised to 800 °C at a heating rate of 5 °C/min, constant temperature 2 h. After natural cooling, the obtained product was sieved through an 80 μm square sieve and washed repeatedly with distilled water for 3 to 4 times. After soaking in 0.5 mol/L nitric acid solution for 12 h, the impurities were filtered out. The solubility of calcium ion is adjusted to 2 mol/L by adding distilled water to the filtrate. After aging for 10 hours, it can be used as standby calcium solution.

2.2.2 Preparation of Silicon Solution
Tetraethyl orthosilicate (TEOS) was selected as silicon source. The solubility of silicon ion is adjusted to 1 mol/L by adding distilled water, which was used as standby silicon solution.

2.2.3 Preparation of dispersant solution
The dispersant solution was composed of polyoxyethylene (5) nonylphenyl ether (Igepal CO-520) and cyclohexane solution, in which the ratio of Igepal CO-520 and cyclohexane solution was 1:10 (Volume ratio).

2.2.4 Preparation of nano-calcium silicate hydrate
The 150 mL dispersant solution was weighed and placed in a high-speed stirring synthesis device. The stirring speed of 500 rpm was maintained at 40 °C. The calcium solution and silicon solution, prepared by 25 mL were slowly dripped in by peristaltic pump. The molar ratio of calcium to silicon was 2:1 and the dripping time was 2 h. At the same time, 0.5 mol/L sodium hydroxide solution was added to adjust the pH value of the mixed solution to 12, and the stirring speed was maintained at 1000 rpm. The reaction material was
cut, compressed and folded at high speed, so that the raw materials were uniformly mixed and dispersed in a very short time. The white C-S-H gel was obtained by continuously stirring for 3 h.

Finally, the final product of nano-calcium silicate hydrate was obtained by centrifugal washing with 1:1 (volume ratio) ethanol / deionized water solution for four times and then drying in a vacuum drying chamber at 80 °C for 24 h.

2.3 Performance testing and Characterization

2.3.1 Characterization of particle size
The particle size of the nano-calcium silicate hydrate was measured by a laser particle size analyzer Winner 2308C. The laser source was a high performance He-Ne laser with λ = 632.8 nm. A certain amount of calcium silicate hydrate sample particles were dispersed into deionized water, and the sample was uniformly dispersed by ultrasonic oscillation.

2.3.2 Performance test of concrete
The fluidity of cement paste was tested according to GB/T 8077 "Test Method for Homogeneity of Concrete Admixture". The slump, setting time, compressive strength and flexural strength of concrete were tested according to GB/T 8076 "Concrete Admixture".

3. Results and discussion

3.1 Effect of reaction temperature on nano-calcium silicate hydrate
The nano-calcium silicate hydrate was prepared by the sol-gel method. In the synthesis process, the particle size of the calcium silicate hydrate can be adjusted by controlling the reaction temperature, thereby changing the dispersion performance. The experimental synthesis methods of the comparative samples were basically the same, except that the reaction temperature was reduced from 40 °C to 20 °C and increased to 80 °C during the synthesis of the calcium silicate hydrate gel. The particle size of the nano-calcium silicate hydrate particles, prepared at different reaction temperatures, and the fluidity of the cement paste are shown in Table 3.

| Reaction temperature | Particle size /nm | Paste fluidity /mm |
|----------------------|-------------------|--------------------|
| 20 °C                | 210.4             | 220                |
| 40 °C                | 191.7             | 225                |
| 80 °C                | 400.8             | 200                |

As can be seen from Table 3, the calcium silicate hydrate particles was the smallest when the reaction temperature reached to 40 °C. The particle size of calcium silicate hydrate was only 191.7 nm measured by laser particle size analyzer. This result was caused by that the growth process of C-S-H gel will be controlled to avoid agglomeration due to uneven mixing under the action of high-speed agitation and dispersant solution, thereby producing calcium silicate with small particle size and high dispersion.

After the reaction temperature was lowered to 20 °C, the particle size slightly increased to 227.4 nm, which was resulted by the decrease of temperature will affect the growth of C-S-H gel. And the mixing was uneven and the dispersion degree was inhibited, thus increasing the particle size. When the reaction temperature was raised to 80 °C, the particle size increased greatly to 400.8 nm. This was caused by the increased reaction temperature, which will cause serious agglomeration of the calcium silicate hydrate, poor monodispersity, and large particle size during preparation, in turn affected the performance of the paste. When the reaction temperature rose to 80 °C, the particle size increased to 400.8 nm. The calcium silicate hydrate was seriously agglomerated, the monodispersity was deteriorated, and the particle size became large, thereby affecting the performance of the cement paste.

Therefore, the nano-calcium silicate hydrate prepared at 40 °C was incorporated into the cement paste as an early strength agent, which can be filled into smaller gaps. The cement paste had relatively
good flow dispersibility, and there was no undesirable phenomenon such as bleeding in actual operation.

### 3.2 Effect of Dispersant Solution on nano-calcium silicate hydrate

Reasonable dispersant solution has a great influence on the particle size and dispersibility of the nano-calcium silicate hydrate. Among them, the blank group was synthesized by adding distilled water instead of dispersant solution. In the other group, the dispersant was changed to be compounded by cetyltrimethylammonium bromide (CTAB) and sodium hexametaphosphate (SHMP) in a ratio of 4:6. The particle size of the nano-calcium silicate hydrate particles prepared in different dispersant solutions and the fluidity of the cement paste are shown in Table 4.

| Dispersant     | Particle size /nm | Paste fluidity /mm |
|---------------|------------------|-------------------|
| Water         | 433.8            | 200               |
| Igepal CO-520 | 191.7            | 225               |
| CTAB+SHMP     | 284.2            | 215               |

It can be seen from Table 4 that the Igepal CO-520 and cyclohexane solution were compounded as a dispersant, and the prepared nano-calcium silicate hydrate had the smallest particle size and good liquidity of the paste. Because the dispersant can form a large number of hydrophilic groups on the surface of the sol gel particles, so that it can be stably dispersed in the solution during the preparation process. It can well control the growth process of C-S-H sol-gel, and avoid the agglomeration phenomenon due to uneven mixing, thereby preparing a product having small particle size, high stability, good dispersion, and excellent performance.

### 3.3 Application experiment of concrete

In order to illustrate the performance and effect of the nano-calcium silicate hydrate early strength admixture, the slump, setting time, compressive strength and flexural strength of concrete were tested by referring to GB/T 8076 "Concrete admixture" standard. The composition of each component in concrete experiments are shown in Table 5.

| Component | Kg/m³ |
|-----------|-------|
| Cement    | 430   |
| Sand      | 700   |
| Gravel    | 1050  |
| Mineral powder | 30 |
| Fly ash   | 90    |
| Water     | 165   |
| Point S   | 33    |

Among them, the water to binder ratio was 0.3, the content of water reducing admixture was 6.0%. The concrete properties were characterized by changing the content of nano-calcium silicate hydrate (C-S-H) from 0.0% to 1.0% (Table 6).

| C-S-H % | Slump(mm) | Setting time(min) | Compressive strength (KPa) | Flexural strength (KPa) |
|---------|-----------|-------------------|---------------------------|-------------------------|
|         |           | Initial setting   | Final setting             | 12 h | 1 d | 12 h | 1 d |
| 0.0     | 195/450   | 198               | 326                       | 5.2 | 8.9 | 0.7 | 1.8 |
| 0.25    | 205/525   | 132               | 231                       | 12.2 | 20.4 | 2.7 | 5.4 |
| 0.5     | 210/520   | 98                | 187                       | 13.8 | 22.2 | 3.3 | 6.3 |
| 0.75    | 220/525   | 77                | 134                       | 16.3 | 24.4 | 4.2 | 7.9 |
| 1.0     | 220/520   | 85                | 139                       | 15.9 | 23.7 | 4.0 | 7.7 |

From Table 6, it can be seen that the initial slump, setting time, compressive strength and flexural strength of samples without nano-calcium silicate hydrate were the worst. With the addition of early strength agent nano-calcium silicate hydrate, the slumps of concrete were increased, the initial setting time and final setting time were greatly shortened, and the compressive strength and flexural strength were also greatly improved. The effects nano-calcium silicate hydrate with 0.25%, 0.5%, 0.75% and 1.0% content were investigated on the properties of concrete. The results show that the performance of concrete are also improved with the increase of the content of nano-calcium silicate hydrate. Moreover,
it can be clearly found that the performance of concrete with 0.75% content was the best. However, the performance of concrete was reduced as the content continues to increase to 1.0%.

These results prove that the incorporation of nano-calcium silicate hydrate crystal seeds can greatly decrease the nucleation barrier of hydration products, accelerate the hydration process of cement and greatly reduce the setting time due to the dual effects of adsorption and nucleation. Meanwhile, it can not only promotes the formation of hydrated calcium silicate, but the conformation of an appropriate amount of AFt, thereby forming a network structure and filling the pores in the cement stone. And it will further improve the cement stone structure and increase the early strength of the concrete.

4. Conclusion
In this paper, the sol-gel method was used to carry out the synthesis experiment in a high-speed shear stirring device. When the temperature was reached to 40 °C, the growth process of C-S-H gel could be well controlled by high-speed stirring and the dispersant solution formed by Igepal CO-520 combined with a cyclohexane solution, so as to avoid agglomeration due to uneven mixing. The prepared nano-calcium silicate hydrate had the advantages of small particle size, good dispersion and high stability.

The incorporation of nano-calcium silicate hydrate as an early strength agent can improve its early strength with the different content. Among them, the concrete with the content of 0.75% has the best performance. The application of nano-calcium silicate hydrate greatly promotes the hydration of cement, further shortens the setting time of concrete, and greatly improves the compressive strength and flexural strength.

References:
[1] Yang N R 2003 Bull. Chin. Ceramic. Soc. 22(2) 46-52.
[2] Taylor H F W 1993 Adun. Cem. Bas. Mat. 1(1) 38-46.
[3] Richardson I G, Groves G W 1992 Cem. Concr. Res. 22 1001-10.
[4] Taylor H F W 1986 J. Am. Ceram. Soc. 69 464-67.
[5] Cui S P, Guo H X, Wang C 2012 Bull. Chin. Ceramic. Soc. 31(3) 37-40.
[6] Yu L C, Wang W S, Zheng B C 2018 New Build. Mat. 45(10) 35-38.
[7] Wang Z, Yang Y Z, Li J H 2007 Mat. Sci. Techn. 15(6) 789-791.
[8] Zhou D L 2011 Mat. Rev. 25(S1) 480-482.