

Design of CaO-Al₂O₃-SiO₂-H₂O hydrothermal synthesis systems for high temperature and high pressure applications

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ABSTRACT: Hydrothermal synthesis (HS) system is known to have better high temperature resistance than conventional Portland cement-based system. However, there are still many problems with its field application, as thickening time, rheology, and sedimentation stability of HS systems are difficult to tune. In this study, the design of the HS system was optimized in three stages. In the first stage, experiments were conducted to verify the high temperature resistance of the HS system and study the reactivity of different components. In the second stage, experiments were conducted to optimize the engineering performance of the HS system. In the third stage, experiments were conducted to analyze the influence of material ratio, retarder type and alumina on the performance of the HS system. Test results revealed that the AMPS retarder had better performance than tartaric acid at high temperature and all systems had extremely stable physical and mechanical properties.

Keywords: Hydrothermal synthesis system, Retarders, Field application, Mechanical properties.

1 INTRODUCTION

In recent years, deep geothermal resources are one of the focuses of resource development. With the further development of deep geothermal resources, more geothermal wells are drilled with bottom hole static temperatures exceeding 200°C (Gkousis et al., 2022). At downhole temperatures above 110°C, semi-crystalline calcium-silicate-hydrate (C-S-H) produced as hydrated products of Portland cement-based system is gradually converted to crystalline phases, resulting in a decrease of compressive strength and increase of permeability for a set cement (Pang et al., 2021). As the curing temperature further increases, the mechanical properties of the set cement will further deteriorate. This behavior of Portland cement under high temperature is known as cement strength retrogression. In the past, SiO₂-rich materials (mainly silica flour) were often added to the cement slurry to prevent the strength retrogression of set cement under high temperatures. Recent research results show that this method can only mitigate the strength retrogression at relatively short curing time, but cannot completely prevent the long-term strength retrogression (more than 30 days) at 200°C (Pang et al., 2021). Therefore, to improve cementing quality and wellbore integrity of deep wells, it is urgent to find or develop a new material that does not experience strength decline at high temperatures.

The hydrothermal synthesis (HS) systems mainly include CaO-Al₂O₃-SiO₂-H₂O system, CaO-SiO₂-H₂O system and CaO-MgO-SiO₂-H₂O system (Bernard et al., 2021; Dambrauskas & Baltakys, 2014). These systems can react at ultra-high temperatures and have been investigated as a potential cementing compositions for geothermal wells under high temperatures (Blanc et al., 2010). Amorphous calcium aluminate silicate hydrate (C-A-S-H) gels are the main products of the CaO-Al₂O₃-SiO₂-H₂O system with a low CaO to SiO₂ (C/S) ratio under high temperatures, and an increase in the C/S ratio leads to the formation of katoite (Yang et al., 2017). Alumina can improve the crystallinity of tobermorite in hydration products and high temperature stability of set samples (Meller et al., 2007). The hydration products of the HS system with different compositions mainly include gyrolite, jaffeite, tobermorite, xonotlite, etc. (Meller et al., 2007). With the help of these studies, a more comprehensive understanding of the hydration mechanism of HS system can be obtained. However, these studies mainly focused on the effects of calcium-silicon ratio and the reaction temperature on the chemical components of hydration products and did not consider its engineering properties. The objective of this study is to investigate the engineering properties of a new HS system and solve the problems associated with engineering applications of HS systems.

In this study, the formulation optimization of the HS system can be divided into three stages. The first stage of this study mainly focused on verifying whether the system will react in the hydrothermal condition of high temperature and high pressure. The second stage was to optimize the thickening time, fluidity and sedimentation stability of the system. Finer materials were added to the slurries to improve the mechanical properties of the system. The changes in mechanical properties of samples after curing for 2d and 30d were tested to evaluate the high temperature stability of the system. In the third stage, the influence of the proportion of each material and the type of retarder on the system was analyzed in depth.

2 EXPERIMENTAL PROCEDURE

2.1 Raw materials

The bulk materials used in this study include three types of silica flour with different particle sizes (coarse silica flour, general silica flour and fine silica flour, manufactured by Tongbai factory in Henan, China), silica fume (provided by Kuche drilling mud material factory, Xinjiang, China), two types of calcium-rich material (calcium hydroxide flour, calcium oxide flour, purchased from China National Pharmaceutical Group Corporation), and three types of alumina-rich material with different particle sizes (coarse α -alumina, fine α -alumina, and nano activated alumina). Coarse and fine α -alumina were manufactured by Guangdong Senxin Co., Ltd. Nano activated alumina was provided by Hubei Huifu Nanomaterial Co., Ltd. The density and particle size of the powder materials were measured by a pycnometer (model UltraPYC 1200e) and a laser particle analyzer (Malvern Mastersizer 2000), respectively. Detailed information of various bulk materials is shown in Table 1.

Table 1. Detailed information of various bulk materials.

Properties	CSF	GSF	FSF	CHF	COF	SFU	C-A	F-A	N-AA
Purity (%)	95.41	96.8	97.35	98.25	98.02	96.7	99.7	99.8	98.79
Density (g/cm ³)	2.67	2.63	2.44	1.98	3.3	2.39	3.47	3.37	3.301
D50 (μ m)	52.8	15.5	6.1	5.0	6.3	0.4	55.5	9.0	0.013

Note: COF=calcium oxide flour, CHF= calcium hydroxide flour, CSF= coarse silica flour, GSF= general silica flour, FSF= fine silica flour, SFU= silica fume, C-A= coarse α -alumina, F-A= fine α -alumina, N-AA= nano activated alumina.

In order to obtain good slurry properties (such as sedimentation stability, sufficient pre-reaction time, fluid loss control and good mixability), several chemical additives had to be added to the HS system. In this study, synthesized 2-Acrylamido-2-Methyl Propane Sulfonic Acid (AMPS) co-polymer Retarder-H and Retarder-B were used to delay the early hydration of the materials. Tartaric acid is

also evaluated as a potential retarder. Other essential additives consist of fluid loss additive, suspending aid, dispersant, and defoamer.

2.2 Slurry composition design

The study of HS system was divided into three stages. Table 2 shows the detailed composition design of the slurries for different stages. The water to solid ratios (w/s) of all formulations were 0.5. In the first stage, calcium oxide flour, calcium hydroxide flour, coarse silica flour and coarse α -alumina were selected as experimental materials. Five systems with a Ca/Si/Al molar ratio of 1:2:1 were designed. At this time, the thickening time of the system was not concerned. We mainly focused on whether these three materials can react with each other under 240°C, and whether the hydrated system has mechanical strength. In the second stage, coarse silica flour was replaced with fine silica flour and silica fume to increase reactivity of raw materials and mechanical strength of set samples. Five systems with a Ca/Si/Al molar ratio of 1:2:1 were designed. In order to simulate the condition of cementing deep wells and make sure the HS slurry is pumpable during placement, it is necessary to optimize the retarder dosage to adjust the thickening time (use Retarder-H). The thickening time of the HS system was optimized so that all systems reacted under hydrothermal condition of 240°C/50MPa (It took 2.5 hours for the curing autoclave to reach the target curing condition). The mechanical properties and sedimentation stability of all set samples cured under hydrothermal condition of 240°C/50MPa for 2d and 30d were tested. In the third stage, the effect of material ratio, retarder type and alumina on the performance of HS system was analyzed. Three systems with Ca/(Al + Si) molar ratios of 1:3, 1:2 and 1:1 were designed with various dosages of additives.

Table 2. Detailed composition design of the slurries for three stages (% by weight of silica flour).

Formula	Stage 1					Stage 2					Stage 3		
	F1	F2	F3	F4	F5	S1	S2	S3	S4	S5	A1	A2	A3
COF	11.7	0	11.7	0	46.7								
CHF	46.3	61.6	46.3	61.6	0	61.6	68.6	68.6	77.4	77.4	77.4	73.6	158.4
CSF	100	100	100	100	100								
GSF						100	100	100	100	100			
FSF											100	100	100
SFU						0	11.4	11.4	25.6	25.6	25.6	19.3	28.7
C-A	42.6	42.5	42.6	42.5	42.6	42.5	47.3	47.3	53.4	53.4	17.1	0	0
F-A											29.9	0	0
N-AA											6.4	0	0
SA	6	6.1	6	6.1	5.7	12.2	13.6	13.6	15.4	15.4	10.3	7.7	11.5
R-H			10	10.2	9.5	8.2	10.2	12.5	11.5	15.4	20.5*	13.5*	23*
FLA	6	6.1	6	6.1	5.7	6.1	6.8	6.8	7.7	7.7	7.7	5.8	5.6
Dispersant	2	2	2	2	1.9	0.8	0.9	0.9	1.0	1.0	2.6	1.9	2.9
Defoamer	0.7	0.7	0.7	0.7	0.6	0.7	0.8	0.8	0.9	0.9	0.9	0.6	1

Note: COF=calcium oxide flour, CHF= calcium hydroxide flour, CSF= coarse silica flour, GSF= general silica flour, FSF= fine silica flour, SFU= silica fume, C-A= coarse α -alumina, F-A= fine α -alumina, N-AA= nano activated alumina, SA=suspending aid, R-H= Retarder-H, FLA= fluid loss additive. *Optimized value after changing retarder type and dosage

2.3 Optimization of type and dosage of retarder

In the third stage, the type and dosage of retarder were optimized on the basis of formula A1 (see Table 2). In order to scientifically analyze the effects of the dosage of retarders on the slurries, the dosage of retarder referred to the percentage of the total weight of solid materials at this stage (see Figure 3). The slurries with different types and dosage of retarders were tested by a HPHT consistometer (purchased from China Liaoning Bassrett Petroleum Equipment Manufacturing Co., LTD., model: BSRD-8042DG) at 240°C and 120MPa. In this study, it takes about 90 min to ramp up the temperature and pressure from ambient condition to the target curing condition.

2.4 Sample preparation and testing

First, slurries were mixed according to API-10B-2 standards (API Recommended Practice 10B-2, 2013). Secondly, the mixed slurry was poured into steel molds with a length of 65mm and an inner diameter of 25mm. Then, all samples were cured using a curing autoclave under hydrothermal condition of 240°C/50MPa for 2d and 30d. Finally, the set samples were cut and polished into standard cylindrical samples with a diameter of 50 mm and a diameter of 25 mm for various tests. Test conducted include sedimentation stability, water permeability, and uniaxial compression. Detailed test procedure and parameters were the same as our previous studies (Pang et al., 2021).

3 RESULTS AND DISCUSSION

3.1 Test results of the first-stage slurries

During this test series, it was found that mixing calcium oxide and water would generate a large amount of heat. Because slurry F5 contained a large amount of calcium oxide, the heat produced by the reaction caused the slurry to thicken rapidly. Therefore, slurry F5 was excluded first. The macroscopic properties and sedimentation stability test results of the four remaining slurries are presented in Figure 1. It can be seen from Figure 1a that the compressive strength of these slurries after curing was relatively low (between 4MPa and 9MPa), and the water permeability was relatively high (between 0.2mD and 1.25mD). The settlement stability results show that, the maximum density difference of all set samples was less than 0.012 g/cm³, indicating good sedimentation stability (see Figure 2b). These macroscopic properties could not meet the field requirements of cementing operations, but the test results show that these materials could react with each other under 240°C.

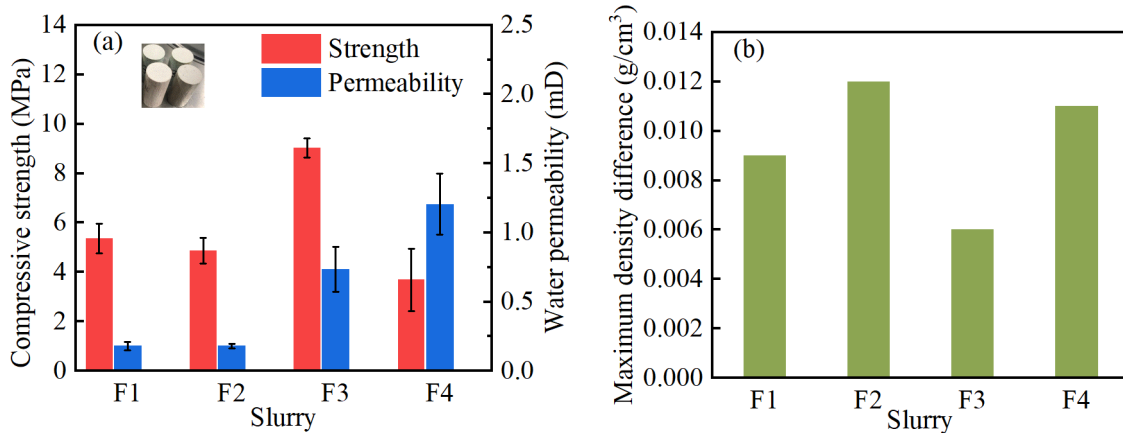


Figure 1. Mechanical properties of the set samples of the first stage (a) Compressive strength and Water permeability (b) Sedimentation stability.

3.2 Test results of the second-stage slurries

The thickening time and macroscopic properties test results of set samples are presented in Figure 2. It can be seen that the addition of finer silica materials led to a significant increase in compressive strength and a dramatic decrease in permeability of all set samples. The compressive strength of all set samples for this stage was doubled compared to those of the first stage (see Figure 1a and Figure 2b). The macroscopic properties of the samples cured for 30 days were not significantly different compared to those cured for two days, indicating excellent stability of the samples at a curing high temperature. The moderate initial consistency of the system (22-26Bc) indicates that this type of system was suitable for pumping in field cementing operations (see Figure 2a). The maximum density difference of all samples was less than 0.011g/cm³, indicating good sedimentation stability.

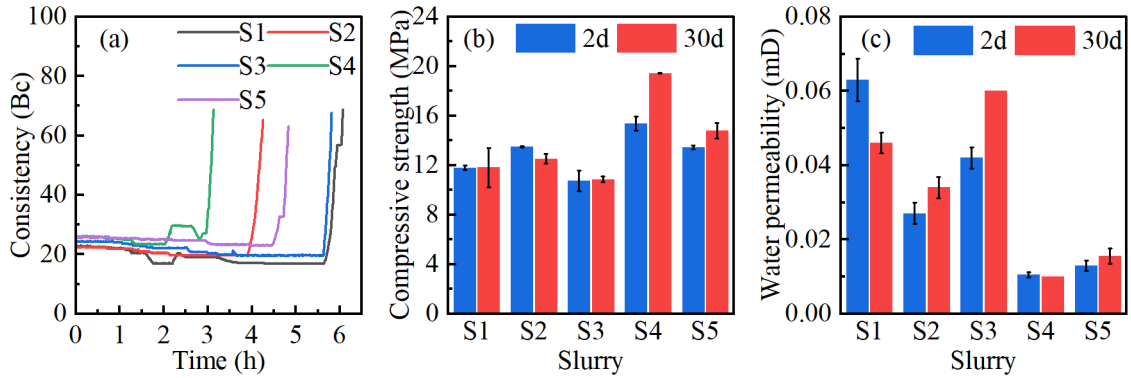


Figure 2. Engineering performance of the slurries and set samples of the second stage (a) Thickening time (b) Compressive strength (c) Water permeability.

3.3 Test results of the third-stage slurries

A previous study has shown that tartrate acid retard cement hydration reaction by chelating calcium ions and forming a semipermeable layer on the hydration particles (Zhang et al., 2016). However, tartaric acid will destroy the sedimentation stability of the slurry, and a small dosage of tartaric acid will lead to the over-retarding phenomenon of the slurry (Gao, 2014). During this stage, it was found that a small amount of tartaric acid would destroy the sedimentation stability of slurry A1. When the addition of tartaric acid was 1%, the slurry was over-retarded and did not set after 10 hours, thus tartaric acid was excluded from the retarders.

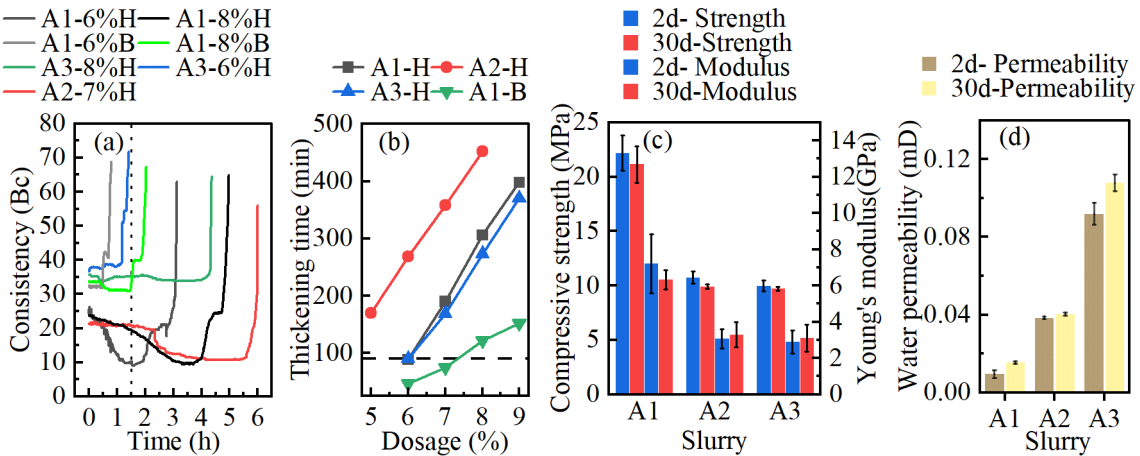


Figure 3. Thickening experiment and performance test of the slurries of the third stage (a) Thickening time (b) Summary of thickening time (c) Compressive strength and Young's modulus (d) Water permeability.

Figure 3b shows that the thickening time of the HS systems increased linearly with the increase of the dosage of other two retarders (H= Retarder-H, B= Retarder-B). It can be seen that Retarder-H has better retarding effect than Retarder-B at the same dosage. Retarder-H is a quaternary copolymerization retarder, while Retarder-B is a ternary copolymerization retarder. Generally, the comprehensive performance of the quaternary copolymer retarder is better than that of the ternary copolymer retarder, including rheology and high temperature resistance (Lu et al., 2016). Indeed, Retarder-H had a better high-temperature retarding effect, and the fluidity of the slurry was better after adding Retarder-H (21-27Bc). Therefore, Retarder-H was the most suitable retarder for the HS system among the three retarders. The optimal dosage of Retarder-H in slurry A1, A2 and A3 is 8%, 7% and 8%, respectively.

The macroscopic physical and mechanical properties of cured samples (slurry A1, A2, and A3) are presented in Figure 3c and Figure 3d. All slurries have stable mechanical properties and

permeability over the 30d curing period. It can be seen that the mechanical properties of the slurries cured for 30d were not much different from those cured for 2d (within the allowable range of error). After 30 days of curing, the increase in permeability of all slurries is also less than that of Portland cement-based system (Pang et al., 2021). These test results show that all formulations of the third stage also have excellent high temperature stability. Slurry A2 and A3 did not contain alumina and had different C/S ratios, but the compressive strengths of the two slurries were almost the same, indicating that the C/S ratio had little effect on the strength of the HS systems. The compressive strength of slurry A1 was much higher than that of slurries A2 and A3. The permeability of slurry A1 was also significantly lower than that of slurries A2 and A3. The difference may be caused by the addition of alumina, but the exact reason needs further investigation.

4 CONCLUSION

The following conclusion can be drawn from this study for hydrothermal synthesis (HS) systems:

- (1) The performance of slurries containing calcium oxide will be seriously affected due to fast reaction rate. Therefore, calcium oxide should be replaced by calcium hydroxide in the HS system.
- (2) AMPS retarder had better retarding effect than tartaric acid at high temperature, and the thickening time of these systems increased linearly with the increase of retarder dosage.
- (3) After several rounds of optimization, the best-performing HS system exhibited a compressive strength of more than 20MPa and water permeability of less than 0.02mD, which stayed stable with time over the 30d curing period evaluated here and could meet the field requirements of cementing operations.

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