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Development of New Formulation of Calcium Aluminate Cement System for Ultrahigh-Temperature Supercritical Geothermal Wells

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ABSTRACT

A national research project on the feasibility of supercritical geothermal power generation and preliminary design of supercritical geothermal exploration wells to be drilled is now in progress in Japan. One of the critical issues in drilling and completing supercritical geothermal wells is long-term integrity of well cement under ultrahigh-temperature conditions. Silica flour blend cement that consists of Portland cement and 30% to 40% BWOC silica flour has been widely used for conventional high-temperature geothermal wells. However, it is known that Portland cement should not be used if the cement will be exposed to temperatures exceeding 400 °C that is the upper limit of stable range of Portland cement. Therefore, calcium aluminate cement, which is a non-Portland cement system, is necessary to be considered for cementing supercritical geothermal wells. In this paper, study on development of a new calcium aluminate cement system is presented. Various compositions of aluminate cements and retarders were tested in laboratory to evaluate the rheological properties and thickening time of cement slurries, and compressive strength of set cement. Based on the test results, optimum formulation of aluminate cement system for supercritical geothermal wells is discussed in consideration of the wellbore temperature conditions during cement placement.

1. INTRODUCTION

Supercritical geothermal systems are very high-temperature geothermal systems that are located at depths near or below the brittle–ductile transition zone in the crust where the reservoir fluid is assumed be in the supercritical state where temperature and pressure are, respectively, in excess of 374 °C and 221 bar. These systems have garnered attention in recent years as a possible type of unconventional geothermal resource because of their very high enthalpy (Reinsch et al., 2017) geothermal fluids. Furthermore, supercritical geothermal systems contribute to energy security and reduction of emission of CO2. A national research project on the feasibility of supercritical geothermal power generation and preliminary design of supercritical geothermal exploration wells to be drilled is now in progress in Japan. One of the critical issues in drilling and completing supercritical geothermal wells is long-term integrity of well cement under ultrahigh-temperature conditions. Silica flour blend cement that consists of Portland (API Class G) cement and 30% to 40% BWOC silica flour blend has been widely used for conventional high-temperature geothermal wells. It is, however, known that Portland cement should not be used if the cement will be exposed to temperatures exceeding 400 °C that is the upper limit of stable range of Portland cement. Therefore, calcium aluminate cement, which is a non-Portland cement system, is necessary to be considered for cementing of supercritical geothermal wells. In addition to this, it was reported that some high-temperature geothermal wells have more sulfide than conventional geothermal wells (Jolie et al., 2018). In the previous study, it was demonstrated that calcium aluminate cement has higher acid resistance and heat resistance so it is expected that well cementing with calcium aluminate cement contributes to long term stability (Pyatina and Sugama, 2016; Sugama and Pyatina, 2017). On the other hand, calcium aluminate cement has the quick hardening property (Rohson, 1962). It is a big problem how to get the sufficient pumping time for deep supercritical geothermal wells. This work presents new cement developed for supercritical geothermal wells with the properties of heat resistance and sufficient pumping time. Some retarders effective up to 150 °C are surveyed and the results of high-temperature setting tests are presented.

2. MATERIALS AND METHODS

2.1 Materials and Samples Preparation

Silica cement

Silica cement is geothermal cement used for comparison in this test is composed API class G Portland cement and 30% to 40% BWOC silica flour to stabilize set cement in high temperature and high pressure environment. The application static temperature range of this cement is 200 °C to 300 °C temperatures.

CAC-1

CAC-1 is composed of Calcium Aluminate Cement, silica and some additives.

2.2 Testing Methods

2. 2. 1 Evaluation of the Rheology

First, water and bentonite were mixed at 500 rpm for 15 minutes, and additional dispersant was added and mixed for another 2 minutes. Second, at 4000 rpm, cement was added to water with bentonite for 15 seconds. Finally, these were mixed at 12000 rpm for

35 seconds. The amount of water was determined to obtain slurry of 1.70 g/cm^3 specific gravity (SG), silica cement was added at 62.2wt% and CAC-1 was added at 55.8wt%.

The plastic viscosity of the above cement slurry was measured by VG meter and its consistency evaluated by the atmospheric pressure consistometer. Consistency was measured for 20 minutes and conformed the max and minimum value.

2. 2. 2. Evaluation of the retarder

The screening of the retarder was done using TAM Air microcalorimeter and oven. The calcium aluminate cement which has high hydration activity was used for this test intentionally. The slurry had SG of 1.85. Pure water and 0 to 1% retarder, 80g calcium aluminate cement were mixed by warring blender. That was mixed by 400 rpm for 15 seconds and then 10000 rpm for 35 seconds. In the cases where the retarders were grain granular, they were grinded.

10 to 20 g of the above slurry was placed into the airtight ampule and the heat release during cement hydration was monitored for 24 hours by the atmospheric isothermal calorimeter set at 85 °C and atmospheric pressure. The other 30 g of the slurry was place into cups and were left under relative humidity of 99+/-1% at 85 °C. The appearance of the slurries in the cups was observed every 30 minutes for hardening. To estimate pumping time, the time slurry became harden was compare with the time of the heat peaks measured by the calorimeter.

Following these tests, thickening time was measured by consistometer to estimate pumping time more accurately. Pressurized consistometer measures the consistency of the slurry under temperature up to 150 °C and pressure up to 12 MPa while the slurry being stirred. The test stopped after the slurry reached 100BC consistency. The slurry was made by the same procedure as the procedure of the evaluation of the rheology. The slurry had the SG of 1.70.

2. 2. 3. Mechanical property

The slurry was made by the same procedure as the evaluation of the rheology. The slurry had the SG of 1.70. The slurry was cured at 250 °C and 17.6 MPa pressure for 72 hours in the curing chamber. After cooling in the apparatus, the samples were submerged into the water, and then, their unconfined compressive strength of some of them were measured. Other samples were additionally heated at 500 °C for 72 hours by the oven at atmospheric condition and their appearance was observed.

3. RESULTS AND DISCUSSION

3.1 Slurry Characterizations

The slurries rheological properties are shown in Table 1. CAC-1 had higher viscosity and consistency than silica cement. This means that CAC-1 needs higher pressure than silica cement to underground during cementing operation. However, difference was very small and it is expected that it was not a serious problem. CAC-1 was stable similarly to the silica cement. CAC-1 dispersed to water smoothly as same as silica cement. These showed that CAC-1 had similar slurry properties to silica cement at SG 1.70.

Table 1: The slurry property of the CAC-1 and silica cement

	silica cement	CAC-1
Slurry gravity	1.70	1.70
Consistency (Bc)	3 - 3	5 - 5
PV (cp)	13	45
YP(lbf/100ft^2)	2	8

Subsequently, the effect of retarder was examined. Generally, calcium aluminate cement has higher activity than Portland cements and is used as early hardening cement. It is the most serious problem in the calcium aluminate cement to keep the working time sufficient to pump and fill the gaps of the annulus between the casing and the formations, and being able to control the pumping time.

The five candidates of retarder from A to E were examined by calorimeter and oven (Table .2). Calorimeter time means the time to start of the heat release. These were known as retarders of Portland cements. Each 1% of candidates was added to the cement slurry of calcium-aluminate cement at 1 % by weight of blend. As a result, retarders A and B have drastically higher performance than the other three candidates. Retarders A and B kept fluidity of the slurries for more than 24 hours. The samples retarded with retarders A or B did not change their viscosity after 24 hours in the oven at 85 °C. In agreement with this result, no hydration peak was detected by calorimeter for these slurries. Retarder C also indicated the retarding effect, however. It was weaker than that of A or B. Retarder D showed very little retarding effect. Retarder E accelerated the hydration but it was too short time to measure the exact time.

As for retarders A, B and C, another experiment was carried out to examine the effect of the amount of retarders on cement hardening time. 0.1, 0.25, 0.50, and 0.75% of retarders were added to the cement slurry and the working time was measured by the same procedure (Figure 1). As a result, the more retarders gave the more long working time in all retarders. The working time increased exponentially with the amount of retarders. Particularly, 1.0 % of retarders A and B showed large effect, over 24 hours, relative to the case of 0.75% added. It was not marked in Figure 1. That great change is not the most suitable condition but it was important that the working time could be changed by the amount of retarders. Retarder C showed the reversing trend at 0.50% and 0.75% cases. It is because retarder C has high viscosity so that the slurry becomes unstable in such small samples.

Table 2: Results of the hardening time with retarders

	Oven	Calorimeter
Non-retarders	≦1 hours	0:45
Retarder A	≧24 hours	≧24:00
Retarder B	≧24 hours	≧24:00
Retarder C	2.5 hours	3:06
Retarder D	0.5 to 1hours	1:06
Retarder E	≦0.5 hours	0:24

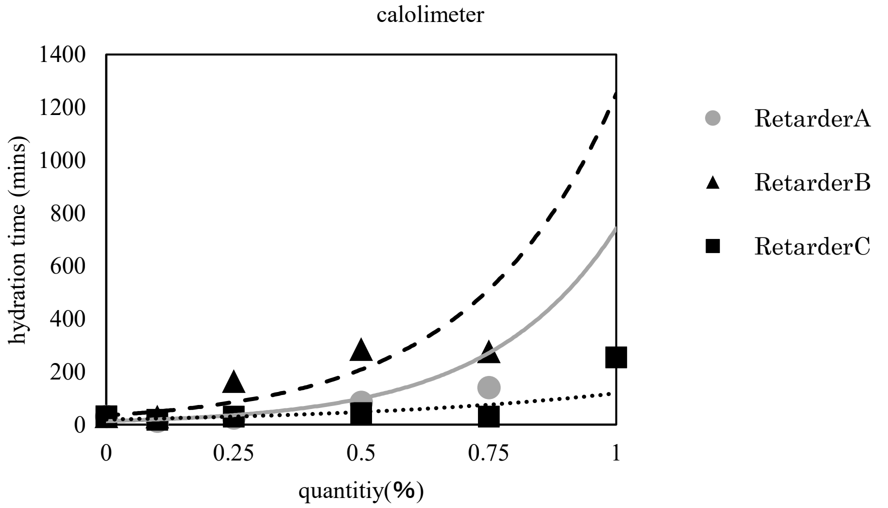

Figure 1: The hardening time depends on the addition amount

Figure 2 represents the measured thickening time curves, which describes pumping time. Without any retarder, CAC-1 showed 1.5 hours thickening time and silica cement showed about 40 minutes thickening time at 150 ℃ temperature. CAC-1 had less activity than silica cement. The thickening time was measured for CAC-1 retarded with retarders A and B respectively. In the case with 2.5 wt% retarder A and 1.0 wt% retarder B indicated that CAC-1 had more than 6 hours thickening time at 150 ℃. Even though it had only 1.5 hours with no retarder, the pressure reached approximately 12 MPa. On the other hand, silica cement had 5 hours thickening time with a retarder. However, CAC-1 with retarder A showed about 3 hours thickening time at 175 ℃ temperature, and about 2 hours at 200 ℃ temperature. It is expected that the retarder was destroyed by high temperature and the cement hydration was strongly accelerated. That is, CAC-1 enhances the sufficient setting time almost equivalent to silica cement at temperatures below 175 ℃.

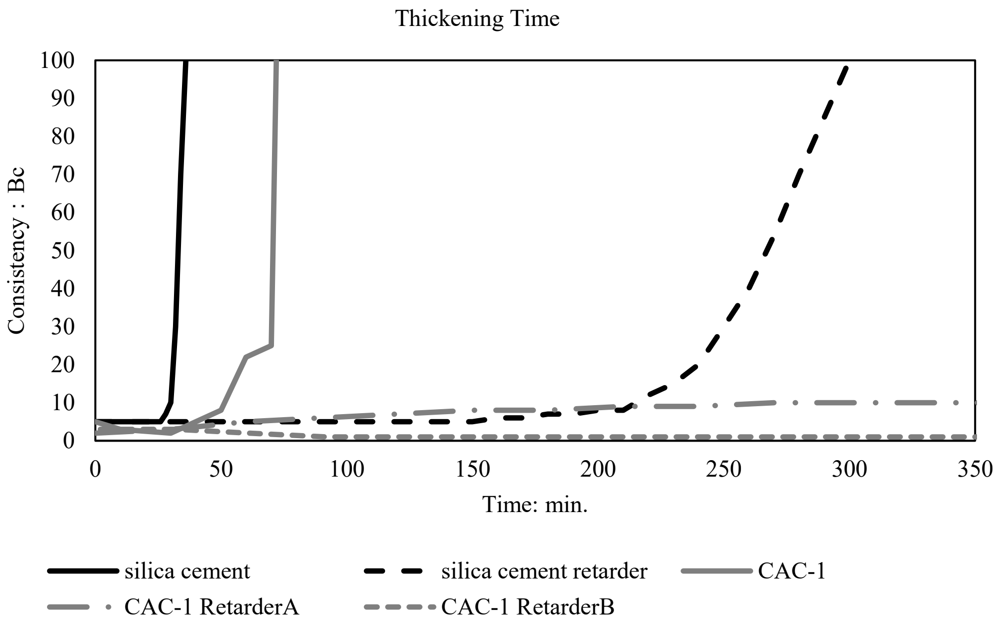

Figure 2: Thickening time of the silica cement and CAC-1 with retarders at 150 °C.

3.2 Mechanical properties

The uniaxial compressive strength of CAC-1 samples was compared against that of silica cement samples. The silica cement and CAC-1 were cured at 250 ℃ and 18.7 MPa for 72 hours. CAC-1 showed 8.1 MPa, it was weaker than silica cement. The little activity of CAC-1 would represent such a negative effect. However, it seems that the strength of 8.1 MPa was enough to support the casing pipes. Cured samples were additionally heated by oven at 500 ℃ for 72 hours. It was not equal to subsurface condition but it gives the measurable estimation. As a result, silica cement was severely broken after the hardening in the oven. On the other hand, CAC-1 had only some little fissures and it was measured as 12.2 MPa of compressive strength. This was only a reference value but it showed that CAC-1 is more heat-resistant than silica cement as was expected at first.

Table 3: Strength of silica cement and CAC-1 after curing and heating.

	silica cement	CAC-1
250 ℃ × 24h curing (MPa)	23	8.1
500 ℃ × 72h heating (MPa)	-	12.2

A) silica cement

B) CAC-1

Figure 3: Appearance after 250 ℃ curing and 500 ℃ heating.

As it was mentioned, some ultrahigh temperature geothermal wells have more sulfide than conventional geothermal wells. It is well known that Calcium Aluminate Cement has higher acid resistance and heat resistance than Portland cement. It is because when $Ca(OH)_2$ is exposed to temperatures greater than 300 ℃, the dehydroxylation of portlandite [$Ca(OH)_2$] formed during Portland cement hydration leads to its conversion into lime (CaO). A major concern regarding the formation of lime is its subsequent hydration in the case of water penetrating through the set cement. Such in-situ portlandite → lime → hydration phase transformation is detrimental to the integrity of the cement as hydration generates expansion-induced cracks in the set cement. In the case of sulfur attack in ordinary Portland cement, the main products of degradation were is gypsum. Sulfur attack caused significant cement expansion, cracking, and loss of concrete. Secondary cementitious materials with calcium aluminate cement reduce the cement's expansion since they do not form expanding reaction products themselves (Pyatina and Sugama, 2016; Bakharev et al., 2002). To use calcium-aluminate cement-based formulations for the supercritical geothermal well, additional tests of acid resistance to estimate long-term durability or ease of variation of slurry gravity for different should be clear. These studies are planned for the future work.

4. CONCLUSION

For supercritical geothermal wells, new cement composed of calcium aluminate cement (CAC-1) was evaluated and some retarders were surveyed to get sufficient pumping time at high temperature. The characterization of CAC-1 was compared with that of conventional Portland cement formulation (silica cement).

・Rheology

CAC-1 represented a little high viscosity but it does not cause a problem.

・Pumping time

CAC-1 with retarder A or B indicated over 6 hours pumping time at 150 ℃.

・Heat resistance

CAC-1 endured the 500 ℃ heating after 250 ℃ curing while silica cement was broken to pieces. This indicates that CAC-1 has higher heat resistance ability than silica cement.

However, additional examination of acid resistance or variation of slurry gravity are necessary for field tests of the CAC-1 blend.

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