Development of High-Temperature Well Cement for Supercritical Geothermal Drilling with Consideration of Set Cement Strength

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ABSTRACT
Supercritical geothermal system has attracted attentions in recent years as next generation of geothermal resource. These systems are located at the depth of 3 to 6 km with the formation temperature and pressure higher than 400°C and of 30 to 60 MPa respectively. Therefore, the heat resistance of the cement materials used for cementing can be considered as a problem during the drilling for the supercritical geothermal wells. The objective of this paper is to evaluate the properties of conventional high-temperature cement and cement under development to improve their thermal resistance through high-pressure and high-temperature (HPHT) curing tests in autoclaves. Moreover, based on the results of these analyses, the applicability of cement materials to supercritical geothermal wells is discussed. The conventional geothermal well cement (GWC) for high-temperature environment used in this study is Portland cement mixed with silica flour, while the cement under development is a modified calcium alminate cement (CAC). In this experiment, all the samples have been cured to get hardened at 250°C for 72 hours as a normal curing. Then, we cured each sample at 300, 350, 400 and 450°C for 24 hours, and for 48 hours and 7 days at 400°C. After the curing, the changes in diameter and length of the samples were checked, and the uniaxial compressive strength and Young’s modulus were measured. Moreover, water permeability of the cement was estimated from measurements using a steady-state gas permeability measurement equipment. As a result, the GWC showed sufficient performance. However, the developing cement which was used for under development had problems such as volume reduction in above 400°C tests.

1. INTRODUCTION
Supercritical geothermal system has attracted attention in recent years as next generation of geothermal resource and various technological developments are necessary for its practical application. One of them is the development of cementing materials that can withstand subsurface HPHT conditions. Supercritical geothermal resources are a geothermal system that utilizes supercritical deep underground reservoir in the Japanese archipelago, which is originated from water contained in the rising asthenosphere and created by the subduction of oceanic plates and squeezed out under HPHT conditions. The development of supercritical geothermal resources to utilize this system is expected to produce energy far beyond the conventional geothermal power generation.

The critical temperature and pressure of pure water are 374°C and 22.1 MPa, while the critical point of formation water containing other components has higher temperature and pressure. Hence, these systems are located at the depth of 3 to 6 km with the formation temperature and pressure higher than 400°C and of 30 to 60 MPa respectively. Examples of drilling that have reached supercritical geothermal systems include the Kakkonda geothermal field in Japan (1995), IDDP-1 (2009), and IDDP-2 in Iceland (2017), etc. In all of these cases, the well temperature where the casing was installed and cemented did not reach 400°C. Accordingly, silica cement for geothermal wells was used. However, Portland cement and silica cement which are conventionally used in geothermal wells cannot be used at temperatures above 400°C because of strength degradation. Therefore, the development of new heat resistance cement material is essential for the development of supercritical geothermal resources. In the present situation, CAC is considered as a cement that can be used at temperatures above 400°C (Walker, 1962). In fact, CAC is usable at temperatures above 400°C and it has been used as cementing material in the DESCRAMBLE project (Martino and Ruch, 2018). However, there is not enough data to evaluate the applicability of CAC for supercritical geothermal wells because the application of CAC is very limited. In addition, curing tests of cement materials under HPHT conditions have been reported a few papers in the past 40 years.

The objective of this paper is to evaluate the properties of conventional high-temperature cement and cement under development to improve their thermal resistance and to clarify the chemical change mechanism through HPHT curing tests. In this study, we developed a new cement material that can be applied to supercritical geothermal wells with the following properties, initial strength of 3.5 MPa or higher in 24 hours, long-term strength of 10 MPa or higher at 450°C and for 28 days, while water permeability is 0.1 mD or less.

2. OUTLINE OF THE EXPERIMENT
2.1 Experimental Materials and Specimen Preparation
The conventional high-temperature cement (GWC) is made from Portland cement mixed with silica flour at a ratio of 7:3, while the cement under development (CAC) is made from calcium alminate cement with finely ground silica. The cement materials were cured under high pressure for 72 hours at 250°C in accordance with API standards using a high-pressure curing chamber. The specific gravity of these slurry was formulated to be 1.85 SG, and cement additives other than dispersant bentonite were not used. The properties of GWC and CAC slurries are shown in Table 1. After making the cement cubes, the GWC and CAC specimens were cored into cylindrical specimens of 15 mm diameter and 30 mm height (Figure 1).
Table 1: Properties of GWC and CAC slurries.

<table>
<thead>
<tr>
<th></th>
<th>GWC</th>
<th>CAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat proof temperature (°C)</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>Specific gravity (SG)</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>C/W, cement to water ratio (kg/L)</td>
<td>100/45.5</td>
<td>100/34.3</td>
</tr>
<tr>
<td>Dispersant (kg)</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Consistency (Bc)</td>
<td>3–5</td>
<td>6–5</td>
</tr>
<tr>
<td>PV/YP (cP / lbf/100ft²)</td>
<td>26/5</td>
<td>34/–4</td>
</tr>
<tr>
<td>Free water (%)</td>
<td>2.1</td>
<td>0</td>
</tr>
<tr>
<td>Yield point (lbf/100ft²)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Thickening time (min)</td>
<td>40 @175°C</td>
<td>40 @150°C</td>
</tr>
</tbody>
</table>

Figure 1: Specimens of GWC (left) and CAC (right).

2.2 HPHT Curing Test

2.2.1 Formation temperature and pressure gradients
According to Naganawa et al. (2017), referring to the formation temperature at Kakkonda WD-1a and IDDP-2, the assumed formation temperature and environment pressure when drilling to the developing supercritical geothermal resources is shown in Figure 2. From the result, up to a depth of 3500 m where the temperature and pressure of the formation water do not reach the critical point (374°C, 22.1 MPa for pure water and 407°C, 29.8 MPa for water with a salinity of 3.2 wt%) is the hydrothermal convection layer, hence the formation temperature and pressure follow saturated vapor pressure curve of the formation water. At the depths deeper than 3500 m, the area becomes a heat conduction area. The figure shows the formation temperature curve assuming a ground temperature gradient of 20°C/100 m and the formation pressure curve assuming a supercritical water density of 100 kg/m³ and 500 kg/m³.

2.2.2 HPHT curing test using autoclave
According to the temperature and pressure shown in Figure 2, HPHT curing was performed using an HPHT curing apparatus with an autoclave (Figure, 3) to reproduce the underground conditions. The autoclave can raise the temperature using the surrounding ceramic heater outside the vessel to reach the target temperature and maintain a constant temperature during the arbitrary time. By adding purified water to inside of the vessel, the wetting and high-pressure conditions of the underground are reproduced. The specimen made in section 2.1 submerged in purified water for 3 days to achieve water saturation. The mass and volume were measured after water saturation. Then, using the autoclave, curing of GWC and CAC at 300, 350, 400 and 450°C for 24 hours, and for 48 hours and 7 days at 400°C were conducted for a total of 36 samples; three specimens for each condition. Finally, the volume and mass after curing were measured to obtain the amount of change.

2.3 Water Permeability
It has been known that the value of water permeability of cement materials used for cementing of drilling should be less than 0.1 mD (API Task Group on Cements for Geothermal Wells, 1985). In this study, the change in water permeability before and after HPHT curing was determined using a steady-state gas permeability measurement system based on Darcy's law using nitrogen gas. We used the conversion formula from gas permeability to water permeability. To measure the water permeability, the specimens had to be in a dry state, therefore they were vacuum dried at 60°C for at least one day. We measured the water permeability before and after curing at HPHT condition and determined the change ratio. We measured the water permeability twice per specimen and obtained the average.
2.4 Uniaxial Compression Test

Based on the field experience that the initial strength and long-term strength of cement materials used for cementing should be at least 3.5 MPa and 10 MPa, respectively, when it stiffened. In this experiment, the specimens were saturated with water and uniaxial compression tests were conducted using precision universal testing machines to reproduce underground conditions. HPHT curing tests were conducted in section 2.2 and after measuring the water permeability in section 2.3, the specimens were again submerged in purified water for 3 days to achieve water saturation. Using these specimens, the uniaxial compression strength was measured. In this test, the loading rate was determined by referring to the API standard.

2.5 DSC Analysis

A possibility of chemical changes of CAC in the high-temperature range was suggested between section 2.1 and 2.4. Therefore, differential scanning calorimetry (DSC) was used to investigate the presence of chemical changes in CAC. In the DSC, a sample and a reference material was placed side by side and measured the temperature difference between the two samples until raising the temperature. The specific heat is calculated from the temperature difference, and the presence of chemical change or phase transformation is examined from the change in the specific heat. In this study, specimens that were not cured at HPHT using an autoclave were heated and examined for chemical changes and phase transformation.

3. RESULTS AND DISCUSSION

3.1 HPHT Curing Test

The volume and mass were measured before and after HPHT curing test, and their variation is shown in Figures 4 and 5. The values of mass and volume of the specimens cured at 250°C for 72 hours and without additional HPHT curing are used as a reference.

The mass increase was observed overall, due to water penetration into the specimen as it is exposed to high-pressure conditions. However, a decrease was observed for the CAC curing at 450°C for 24 hours and 400°C for 7 days. The volume change of GWC is
considered to be a measurement error due to the variation. However, a large volume and mass decrement was observed for curing of CAC at 450°C for 24 hours and at 400°C for 7 days. A significant shrinkage of the CAC volume about 2.5% was observed.

Based on the above results, we discussed the effects on the drilling work. In these results, we focused on the decrease in the volume of CAC. The decrease in the volume of cement suggests the possibility that gaps will be created between the annulus and the casing pipe during the cementing operation. It is possible that the well integrity will not be maintained due to the formation of gaps (micro-annulus) that may prevent the casing pipe from being sufficiently secured, and the passage of gases and liquids through the gaps.

Figure 4. Curing temperature vs. weight and volume change graph.

Figure 5: Curing time vs. weight and volume change graph.

### 3.2 Water Permeability

The results of water permeability measurements are shown in Figure 6. GWC showed a maximum value of 0.26 mD at 7 days curing and remained almost constant from 24 hours to 7 days. CAC showed the most significant increase at 400°C for 7 days curing, reaching 1.37 mD and it increased with temperature. Then both GWC and CAC exceeded the standard value of 0.1 mD. Previous studies have reported that the increase in water permeability is caused by the development of xonotlite which has a needle-like crystalline structure (Pyatina, 2019).

Based on the above results, we discussed the effects on the drilling work. Previous studies by the API Task Group and others have shown that when the water permeability exceeds 0.1 mD, acidic fluids in the formation tend to flow through the cement and contact the casing pipe, resulting in corrosion of the casing pipe will occur. In this experiment, it was thought that the increase in water permeability would affect the long-term integrity of the well due to problems such as corrosion of the casing pipe. In particular, the permeability of CAC largely exceeded the standard value and this is suggesting the need for improvement.
3.3 Uniaxial Compression Test

3.3.1 GWC

The measured results of the uniaxial compression test of the specimens after 24 hours HPHT curing and after long-term HPHT curing test at 400°C are shown in Figure 7. The maximum uniaxial compressive strength at 24 hours curing was 48.7 MPa at 450°C and the minimum value was 33.1 MPa at 250°C without additional curing. It exceeded the target value of 3.5 MPa for initial strength in this study and the target value of 10 MPa for long-term strength in 48 hours and 7 days HPHT curing, therefore showing sufficient performance. Figure 7 shows that the uniaxial compression strength increased as the temperature increased during the 24 hour curing. It is thought that the hydration and pozzolanic reaction progressed. The detailed mechanism of the change in uniaxial compression strength will be discussed later.

3.3.2 CAC

The measured results of the uniaxial compression test of the specimens after 24 hours HPHT curing and after long-term HPHT curing test at 400°C are shown in Figure 8. For 24 hours curing, the lowest uniaxial compression strength was 18.2 MPa at 250°C without additional curing. At 350°C, the maximum uniaxial compression strength of 45.2 MPa was observed. On the other hand, the uniaxial compressive strength decreased at 400°C and 450°C. The increase in mass and strength up to 400°C suggests that the hydration and pozzolanic reactions proceeded as in the same case of GWC. However, a decrease in uniaxial compressive strength was observed at 400°C and 450°C in this experiment. In long-term tests, a significant change in uniaxial compressive strength was not observed. It is thought that the hydration reaction and crystal transformation progressed. The detailed mechanism of the change in uniaxial compressive strength will be discussed later.
3.4 DSC Analysis

The results of DSC analysis are shown in Figure 9. In the first measurement, the value of specific heat changed significantly 2 times between 400°C and 600°C. In the second measurement after cooling, the specific heat showed a lower value compared to the first measurement. However, above 600°C the first and second measured values of specific heat agreed with each other. From this result, CAC happened the chemical change and phase transformation at around 400°C and 550°C.

3.5 Discussion of Chemical Change Mechanism of GWC

In general, the strength of cement is increased by adding of water. This reaction is called the hydration reaction, in which the clinker compound in the cement compounds with water (Takahashi, 2009). Equation 1 shows a typical equation for the hydration reaction. (Japan Cement Association, 2009).

\[
3\text{CaO} \cdot \text{SiO}_2 + 2\text{CaO} \cdot \text{SiO}_2 + \text{H}_2\text{O} \rightarrow n\text{CaO} \cdot \text{SiO}_2 \cdot m\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

\[
\begin{align*}
&n, m: \text{Coefficient}, \\
&3\text{CaO} \cdot \text{SiO}_2: \text{Elite}, \\
&2\text{CaO} \cdot \text{SiO}_2: \text{Belite} \\
&n\text{CaO} \cdot \text{SiO}_2 \cdot m\text{H}_2\text{O}: \text{Calcium silicate hydrate}, \\
&\text{Ca(OH)}_2: \text{Calcium hydrate}
\end{align*}
\]

In addition, the hydration reaction of the aluminate phase and ferrite phase also occurs. Therefore, it is thought that the hydration reaction inside the GWC specimen increased its strength by the penetration of water into the specimen.

Next, we consider the pozzolanic reaction between Portland cement and silica flour. The pozzolanic reaction is a phenomenon in which a glassy substance reacts in cement as the hydration reaction of cement progresses. The dissolved Si and Al are incorporated into the cement hydrate near the fly ash and silica flour particles, resulting in the transformation to the low-Ca type C-S-H phase with
When the pozzolanic reaction is accelerated, calcium silicate hydrate which refractory zonotrite and tobermorite are produced. As a result of the pozzolanic reaction, there is a negative linear correlation between pore volume fraction and compression strength in 20 to 330 nm range. The pore size changes from the range between 20 nm and 330 nm to the range between 3 nm and 20 nm upon heating is known (Yamamoto and Kanazu, 2007). Therefore, it is considered that the uniaxial compressive strength increased due to the microstructural densification caused by the pozzolanic reaction.

3.6 Discussion of Chemical Change Mechanism of CAC
CAC is made from alumina cement with finely ground silica as described in section 2.2. As the crystal hydrate conversion occurs in alumina cement with increasing temperature (Sasakawa et al., 2003). The equation for hydrate crystal transformation in alumina cement is shown in Equations 3 and 4.

\[
3(CaO \cdot Al_2O_3 \cdot 10H_2O) \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2(Al_2O_3 \cdot 3H_2O) + 18H_2O
\]

(3)

\[
3(2CaO \cdot Al_2O_3 \cdot 8H_2O) + 2(3CaO \cdot Al_2O_3 \cdot 6H_2O) + 2(Al_2O_3 \cdot 3H_2O) \rightarrow 9H_2O
\]

(4)

In Equations 3 and 4, “CaO · Al₂O₃ · 10H₂O” and “2CaO · Al₂O₃ · 8H₂O” are metastable crystals, and as the temperature rises the reaction proceeds, and crystal transformation to the stable crystal “3CaO · Al₂O₃ · 6H₂O” occurs. When this crystal transformation occurs, the voids between the crystal particles increase, and the specimen becomes porous, resulting in a decrease in strength. Therefore, this crystal transformation may have caused a decrease in uniaxial compressive strength shown in Figure 8.

4. CONCLUSION
1. The volume of CAC was reduced by about 2.6% at 450°C and 400°C for 7 days HPHT curing, suggesting that the well integrity may not be maintained due to cementing failure.
2. When GWC and CAC were additionally cured at HPHT, the water permeability exceeded 0.1 mD, and CAC showed a remarkable increase of more than 10 times. Therefore, there may be effects such as the promotion of corrosion of the casing pipe.
3. The uniaxial compressive strength of GWC and CAC was confirmed much higher than the target value of 3.5 MPa after 24 hours HPHT curing which is sufficient initial strength.
4. The uniaxial compressive strength of GWC and CAC was confirmed much higher than the target value of 10 MPa after 7 days HPHT curing which is sufficient long-term strength.
5. CAC showed crystal transformation in the high-temperature range, therefore further research and development are needed for new materials.

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REFERENCES


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