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## INVESTIGATION OF ADMIXTURES EFFECT ON DEGRADATION OF CEMENT PASTE IN SAGD AND CCS WELLS

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**Abstract:** In recent years, Steam Assisted Gravity Drainage (SAGD) and Carbon dioxide Capture and Storage (CCS) projects are being developed in oil and gas fields. SAGD is a heavy oil recovery technology to reduce heavy oil viscosity and extract it from underground. CCS is a technology to inject  $CO_2$ , emitted from plants, into a couple of 1000m deep ground through well. The deterioration of well in SAGD and CCS projects may cause leakage of deleterious gas.

In this study, mechanical and chemical degradation of hardened cement paste made of Oil Well Cement (OWC) and Geothermal Well Cement (GWC) containing silica flour in the wells was studied experimentally. In order to imitate the underground condition of SAGD, the cement paste was exposed to the drying and moist sealed condition at 200°C. In addition, the cement paste was exposed to supercritical  $CO_2$  to reproduce the condition to inject  $CO_2$  gas in CCS well. The compressive strength tests after exposure to 200°C and thermal analysis to study carbonation after exposure to supercritical  $CO_2$  suggested that the replacement of silica flour to cement is effective to be applied to both SAGD and CCS injection wells.

**Keywords:** Cement paste, fly ash, polymer, supercritical  $CO_2$ , 200°C steam.

### 1. Introduction

In recent years, Steam Assisted Gravity Drainage (SAGD) and Carbon dioxide Capture and Storage (CCS) projects are being developed in oil and gas field. SAGD is a recovery technology of heavy oil which consists of two horizontal underground wells at depth of a few of 100 m, the injector and the producer as shown in Figure 1. The conventional oil exploration methods is not appropriate to extract heavy oil with high viscosity that is expected as alternative energy source to petroleum. The process of SAGD is to reduce heavy oil viscosity by the injection of hot steam at 200°C thorough the well injector and extract it from underground through the well producer as indicated in Figure 1. CCS is also an underground technology to inject CO<sub>2</sub> emitted from factories into a geological reservoir at more than 1000 m deep underground through the injection well as shown in Figure 2. The injected CO<sub>2</sub> is anticipated to be stored in the reservoir for a long time in order to isolate the  $CO_2$  to be reacted with the mineral. The CCS project has been ongoing in Norway, Canada and Algeria in order to the reduction of









 $CO_2$  emission. In Japan, the survey of possible sites and the demonstration project have been carried out based on the contraction with the Ministry of Economy, Trade and Industry aiming to prevent global warming.

Wells in SAGD and CCS projects are exposed to severe condition in the underground with high temperature, high pressure, and high concentration of CO<sub>2</sub> gas in CCS well. Thus, the wells will be chemically and physically deteriorated during service. If wells are severely deteriorated, the deleterious gas such as high concentration of CO<sub>2</sub> and H<sub>2</sub>S in the underground may be leaked to the ground through the deteriorated well. The prevention from the gas leakage is the most important issue in SAGD and CCS projects because the risk is high to threaten the life of living beings on the ground.

The underground wells consist of steel casing and surrounding cement paste to fill between steel casing and ground. Oil Well Cement (OWC), standardized by the American Petroleum Institute, is generally used for cementing around the casing to be stabilized as well. According to the previous study, the compressive strength of the cement paste with OWC greatly decreases when exposed to moist sealed condition at 200°C, simulating the possible surrounding condition in the SAGD project. In this study, Geothermal Well Cement (GWC) containing silica flour in the OWC is investigated focusing on the strength under SAGD condition and the resistance to high concentration of CO<sub>2</sub> under CCS conditions. In addition, the effect of admixtures such as fly ash and polymer are also examined experimentally.

### 2. Experimental procedure

the experiment, the commercial GWC In manufactured by Japanese cement company was mainly used as the base cement. For the comparison, the OWC was also studied. The effect of fly ash on the cement paste in the well were also examined. The replacement ratio of fly ash to GWC was changed from 10% to 40% with an increment of 10% (named GWCFA10, 20, 30 and 40). In the experiment to simulate CCS condition, the effect of polymer that may be used to increase the bond between cement paste and casing was investigated. The polymer types used in the experiment were polyvinyl emulsion (PVA) and ethylene-vinyl acetate copolymer emulsion (EVA). The polymer mixing ratio was 1% of cement

weight.

In the case of SAGD simulation experiment, the possible extreme surrounding conditions around the cement paste in the injection well during SAGD operation were assumed to be the drying condition at 200°C for dried soil and the moist sealed condition at 200°C for moist soil. The water-to-binder ratio (W/B) of the cement paste was set to 44% because the W/B of about 45% is generally used in oil wells. The specimen size were two types,  $\phi$ 50 x 100 mm cylinder and 20 x 20 x 50 mm rectangular. After 7 days curing under



Figure 3: The exposure method to the moist sealed condition at 200°C



Figure 4: Phase change of the CO<sub>2</sub>



Figure 5: Supercritical CO<sub>2</sub> generator and vessel



Figure 6: Compressive strength test results

sealing condition at 20°C, the specimens were exposed to the dry condition at 200°C or the moist sealed condition at 200°C (Figure 3) for 3 days. After the exposure, the compressive strength test was done using  $\phi$ 50 x 100mm specimens, and the X-ray diffraction analysis and Scanning Electron Microscope (SEM) observation were conducted using crushed 20 x 20 x 50mm specimens.

In the case of CCS simulation experiment, the possible surrounding conditions around the cement paste in the injection well during CCS operation was assumed to be exposure to the supercritical carbon dioxide. The supercritical carbon dioxide is intermediate fluid with characteristics of both liquid and gas (Figure 4). In order to accelerate the carbonation effectively for a short time, very small specimens of  $\phi 4 \ge 4$  mm cylinder were used and the W/B was set to 55 % even though general W/B is about 45 % as explained above. After 7 days curing under sealing condition at 80°C, the specimens were subjected to the supercritical carbon dioxide at 80°C, 14MPa in the vessel for 7 days (Figure 5). Then, specimens were grinded into powder and set in Thermal Gravity-Differential Thermal Analysis (TG-DTA) test machine. The temperature was risen from room temperature to 100°C with 20°C /min, and remained for 10 minutes to evaporate the liquid water in the sample. Then, the temperature was risen to 900 °C with the same temperature rise velocity. The amount of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> due to the dehydrogenation and decarbonized reaction were obtained by the mass loss at 400-500 °C and 600-850 °C, respectively.

## 3. Experimental results

# 3.1 Exposure to dry condition and moist sealed condition at $200^\circ\mathrm{C}$

The compressive strength test results after exposing to drying and moist conditions at 200°C are shown in Figure 6.

In the case of the exposure to the dry condition at 200°C for 3days, the compressive strength was increased, while hydration products of all specimens were not changed due to the exposure as explained later. The reason to increase the compressive strength may be because the severe drying can evaporate the water in fine pores to increase of the solid surface energy of the cement paste and lead to the increase of crack fracture stress based on Griffith crack theory.

In the case of the exposure to the moist sealed exposure at 200°C for 3 days, the compressive strength of GWC was also increased. On the other hand, the compressive strength of cement paste with OWC decreased significantly after exposing to the moist sealed condition at 200°C as shown in Figure 5. Thus, it is suggested that the partial replacement of silica to the oil well cement is effective to improve the compressive strength under moist sealed condition at 200°C. In addition, the compressive strength of GWCFA with fly ash was increased with increase of replacement ratio of fly ash under moist sealed condition at 200°C and then compressive strength of GWCFA30 cement



Figure 7: Hydration products after moist sealed exposure at 200°C

paste was the highest when the replacement ratio was changed from 10 % to 40 %. These results suggest that the compositive replacement of silica and fly ash to the oil well cement can be more effective to improve compressive strength under moist sealed condition at 200°C than sole replacement of them.

X-ray diffraction was carried out to identify hydration products precipitated in the cement paste after the exposure at 200°C. In addition, the hydration products were carefully observed using SEM. The results are shown in Figure 7. According X-ray analysis and SEM observation, Zonotlite was identified in GWC and GWCFA10 and Tobermolite in GWCFA10 and GWCFA20. Both Zonotlite and Tobermolite are calcium silicate hydrate. Then, Tobermolite is plate crystal while Zonotlite is column crystal. The previous studies reported that the cement paste matrix consisting of Tobermolite has higher strength than that with Zonotlite<sup>[3]</sup>. It is attributed to the increase of compressive strength of GWC cement paste with fly ash. On the other hand, Tobermolite and Zonotlite were not found in OWC and granular products such as  $C_5S_2H$  and  $C_5S_2H_6$  were observed after moist sealed exposure at 200°C. The experimental results indicate that the granular

hydration products cannot improve the strength and concludes that the hydration products precipitated by the high temperature exposure affect compressive strength significantly.

## **3.2** Exposure to supercritical carbon dioxide condition

The carbonation of cement paste under the supercritical carbon dioxide is much more progressive than the general carbonation in the atmosphere because supercritical carbon dioxide has high permeability into hardened cement <sup>[4]</sup>. The carbonation is the reaction of main hydration products of Ca(OH)<sub>2</sub> and C-S-H with CO<sub>2</sub> and results in precipitation of CaCO<sub>3</sub> in the cement paste. The reactions are represented below.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
(1)  
C-S-H + CO\_2  $\rightarrow CaCO_3 + H_2O$ (2)

The exposure to the severe supercritical carbon dioxide can promote both reactions simultaneously even though the C-S-H is little carbonated in the normal atmosphere. When the carbonation of C-S-H represented by equation (2) proceeds, pores structure can be coarsened due to the destruction of C-S-H matrix <sup>[5]</sup>. Thus, the understanding of the C-



Figure 10: The difference between molar mass of Ca(OH)<sub>2</sub> before the exposure and molar mass of CaCO<sub>3</sub> after exposure for 7 days

S-H carbonation progress is important to avoid the deleterious gas leakage through the coarse pores.

Figure 8 shows the relationship between  $Ca(OH)_2$ amount variation and square root of exposure days and Figure 9 shows the relationship between  $CaCO_3$  content variation and exposure days.  $Ca(OH)_2$  was not found by thermal analysis after exposure for 3 days because the carbonation progress of  $Ca(OH)_2$  is fast and all of  $Ca(OH)_2$ were carbonated by 3 days exposure. Since the amount of  $CaCO_3$  was still increased even after 3 days exposure, however, the precipitation of  $CaCO_3$  can be ascribed to the carbonation of C-S-H. Hence, the difference between molar mass of  $Ca(OH)_2$  before the exposure and molar mass of  $CaCO_3$  after exposure for 7 days can correspond to the amount of carbonated C-S-H and be used for

the indicator to evaluate the carbonation progress on C-S-H.

Figure 10 shows the difference between molar mass of Ca(OH)<sub>2</sub> before the exposure and molar mass of CaCO<sub>3</sub> after exposure for 7 days. It is found that the difference is almost independent of fly ash replacement. Thus, it is suggested that the fly ash may not affect the C-S-H carbonation progress. In the case of polymer mixing, the carbonation progress of C-S-H are reduced when PVA was used but increased when EVA was used. It deems that the addition of polymer may affects C-S-H carbonation progress depending on the polymer type even if the dosage amount is small. In the case of cement paste with OWC, the difference between molar mass of Ca(OH)<sub>2</sub> before the exposure and molar mass of CaCO<sub>3</sub> after exposure for 7 days was 3.62mol/kg, higher than that when GWC was used. The experimental result indicates that C-S-H of cement paste using GWC may have a higher resistant to the carbonation than that with OWC.

### 4. Conclusions

The conclusion in this study is summarized below.

- (1) The compositive replacement of silica and fly ash to the oil well cement can be more effective to improve compressive strength under moist sealed condition at 200°C than sole replacement of them. The highest compressive strength under moist sealed condition at 200°C was obtained when the replacement ratio of fly ash to GWC with silica is 30 %.
- (2) Under supercritical carbon dioxide condition, the cement paste with GWC had a higher resistance to carbonation than cement paste with OWC did. The replacement of fly ash to OWC was likely to not affect the carbonation by supercritical carbon dioxide
- (3) The addition of polymer may affects C-S-H carbonation progress depending on the polymer type even if the dosage amount is small.

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