

# Evaluation Of The Self-healing Bio-assisted Cement-treated Clay With XAFS

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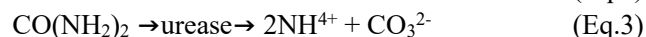
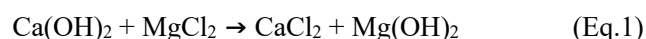
## 1. Introduction

Cement is one of the most widely used materials for ground improvement. Recently, there has been increasing interest in the durability / robustness of cement-treated soil. In the marine environment, cement-treated soil is deteriorated by the percolation of salt from seawater [1].

As a countermeasure to this phenomenon, self-mediated cement treated clay with biomineralization is proposed to enhance the durability of cement-treated clay against seawater [2]. In this study, the morphology were of the cement-treated soil with biomineralization based self-healing cement treated clay was analyzed using X-ray absorption fine structure (XAFS).

## 2. Chemical reaction for deterioration mitigation

Calcium hydroxide, an important cementation component of cement-treated soil, reacts with magnesium salts in seawater to form highly water-soluble calcium salts, which are leached into seawater (Eq.1-2) [1]. In cement-treated soil with Bacteria and urea, urea is hydrolyzed to produce carbonate ions by bacterial function (Eq.3) [2]. The calcium ions resulting from the deterioration are reacted with the carbonate ions derived from urea, and they are reprecipitated as calcium carbonate (Eq.4) [2]. The above chemical reaction equation is described below.



## 3. Experimental method

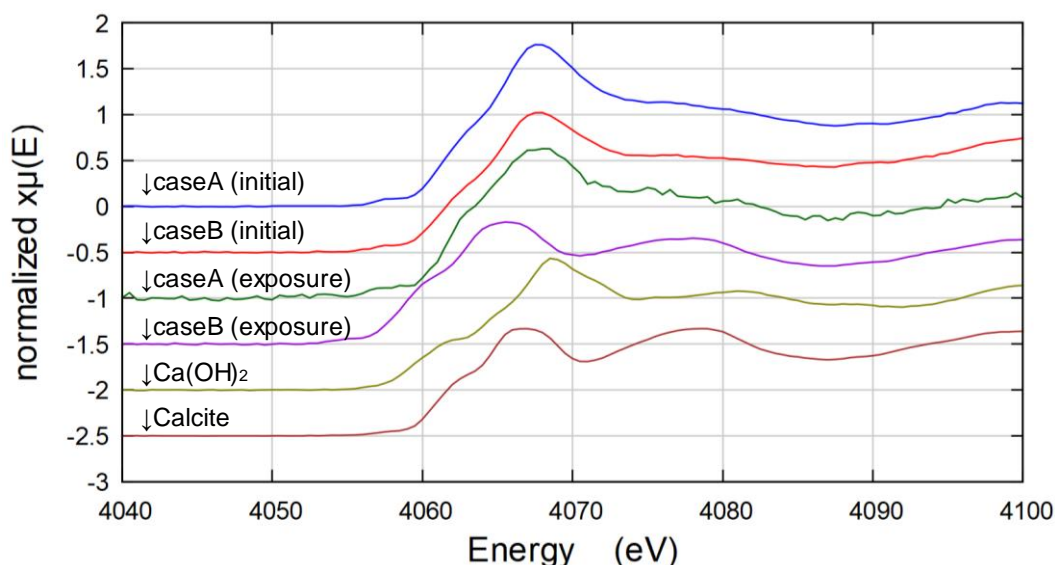
Ordinary Portland cement was added to the marine clay and mixed. This sample was named "Sample A". "Sample B" was prepared by mixing urease-producing bacteria (*Sporosarcina aquimarina*) and urea to mixtures produced similarly to sample A. The samples at this point were used as the initial samples. These samples were filled into a mold and cured under sealed conditions. After curing, the specimens were exposed to 150 mL of artificial seawater for 196 days with only the top surface open. A sample of 5 mm was taken from the exposed surface of the specimen after exposure. The samples were dried in an oven at 105°C until there was no change in mass, and then finely ground using a mortar. In addition, samples of special reagent grade were prepared to simulate calcium hydroxide which are important cementation components of cement-treated soil and bacterial calcium carbonate, respectively.

XAFS measurements were performed at BL-11 of the Hiroshima Synchrotron Radiation Center (HiSOR) with the conventional transmission mode without calibrating the incident X-ray energy.

#### 4. Results and discussion

FIGURE 1 shows the XAFS spectra of samples and reference materials. Focusing on the reference samples, the peak of calcium hydroxide was observed at 4068 keV. Calcium carbonate (calcite), however, showed two peaks at 4066 keV and 4078 keV.

Both the initial samples showed peaks at 4068 keV, and the waveform was similar to that of the calcium hydroxide standard. For sample A (exposure), the peak was identified at 4068 keV, which was similar to that of initial sample. In sample B, a spectrum similar to calcite was obtained after exposure.



**FIGURE 1** Calcium K-edge XAFS spectra of samples and reference materials

Based on these results, fractions of calcium hydroxide and calcite in the samples A and B were calculated using the spectra sum of reference materials. TABLE 1 shows the calculated results at the initial and the exposure stages. Before the exposure, both samples were found to be mainly composed of calcium hydroxide. After the exposure, sample B was almost completely converted to calcite. Calcium carbonate shows different structures depending on the type of urease-producing bacteria used as biocatalysts. Previous study where TG-DTA analysis was used, has shown that the calcium carbonate precipitated by *Sporosarcina aquimarina* is mainly calcite based, and our results strengthen the results of previous study [3].

**TABLE 1** Calculated fractions of calcium hydroxide and calcite in unknown samples.

Sample name	Ca(OH) <sub>2</sub>	CaCO <sub>3</sub> (Calcite)
Sample A(initial)	0.756	0.244
Sample A(exposure)	0.541	0.459
Sample B(initial)	0.751	0.249
Sample B(exposure)	0.190	0.810

#### 5. Conclusion

In this study, the authors used XAFS analysis to investigate the structure of the crystals formed in cement-treated clay mixed with urease-producing bacteria when it comes into contact with seawater. The results showed that most of the calcium hydroxide was converted to calcium carbonate by the microbial function in the sample exposed to seawater, while the calcium hydroxide was the main component in the sample before exposure. Moreover, calcium carbonate turned out to be calcite.

#### REFERENCES

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