CHEMICAL STATE ANALYSIS OF ALKALI SILICA GEL BY USING SOFT X-RAY XAFS

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Abstract

The Alkali-Silica Reaction (ASR) is known as a reaction which occurs in concrete between alkali ions from cement and silicate from aggregates. Although the ASR has been studied intensively with a number of experimental approaches, its mechanism has not been completely clarified yet. The aim of this study is to investigate the chemical structure of ASR gel using the X-ray Absorption Fine Structure (XAFS) spectroscopy. The XAFS spectroscopy is a unique technique to reveal the local structure around an X-ray absorbing atom and can be applied to amorphous materials as in this case.

Samples were prepared in three different ways. Those in the first group were directly taken from a reinforced concrete specimen deteriorated by ASR. The specimen was cut out and some powder samples were collected from some portions of the cross section. Those in the second group were prepared in an ideal well-defined ASR process. Fine powdered reactive aggregates were dipped in 1 mol/L NaOH aqueous solution and filtrates were used as the samples. Those of the third group were prepared by an artificial ASR process. First, a block of a hardened cement paste was dipped in distilled water. Then, fine powdered reactive aggregates were immersed in the solution and the supernatant liquid was skimmed off. Both of two types of the sample were prepared in liquid and dried states.

The following is a summary of this study:

(1) Any spectral difference was not observed between the reactive aggregate before and after use and between the surface and bulk regions of the reactive aggregate.
(2) Only difference observed is the Ca content of the non-reactive aggregate, which is more than the reactive aggregate, and Ca exists not as CaO, but CaCO3.
(3) The ASR was confirmed in the artificial condition, and the ASR product was found to be close to water glass.
(4) Since this is the result of an ideal situation, more realistic experiments with more sophisticated methods will be necessary to clarify the mechanism of the ASR.

Keywords: Alkali-Silica Reaction, XAFS, ASR gel, chemical structure
1. INTRODUCTION

The Alkali-Silica Reaction (ASR) is known as a reaction which occurs in concrete between alkali ions provided from cement and silicate from aggregates. The deterioration caused by ASR in concrete structures was discovered in 1983 in Japan and it is now in a more serious situation than expected. While many researches for the ASR were performed [1,2,3], the mechanism of ASR has not been clarified yet. It is probably caused by the diversity of environmental condition on the structures, reactivity and variety of aggregates. This study is the first experiment to investigate a chemical structure of the ASR gel using the XAFS spectroscopy. XAFS is a unique technique to reveal the local structure around an X-ray absorbing atom and can be applied to amorphous materials.

2. EXPERIMENTAL OVERVIEW

2.1 Analytical methods

X-ray Absorption Fine Structure (XAFS) spectroscopy was chosen to analyze an ASR gel in this study. This method has following characteristic and principle. XAFS is an absorption spectroscopy in the X-ray region, which is associated with transitions of core electrons of a specific element to unoccupied states. The spectra, especially, in the near edge region, show characteristic fine structures, depending on the chemical bonding around an X-ray absorbing atom. This is a unique technique to reveal the local structure and can be applied to amorphous materials as in the present case.

Si K-XAFS experiments were performed at the soft X-ray double crystal monochromator beamline, BL-10 of Ritsumeikan SR centre, with the total electron yield and fluorescence yield modes. InSb(111) was used as a monochromatizing crystal.

2.2 Sampling

Samples were prepared in three different ways described as follows. The samples in the first group were directly taken from a concrete deteriorated by ASR. Figure 1 shows a reinforced concrete specimen after a long time exposure. The reactive aggregates were andesite, whose reactivity was positive, confirmed with the chemical method (JIS A 1145) and the mortar bar method (JIS A 1146). The multiple cracks on the surfaces are associated with a severe damage by ASR. It was cut out at the A-A section and some powder samples were collected from each portion of the cross section in Figure 2: (a) reactive aggregate before use, (b) surface of the reactive aggregate, (c) inside of the reactive aggregate, (d) non-reactive aggregate and (e) cement paste.

![Figure 1: Deterioration by ASR](image1.png)

![Figure 2: Sampling](image2.png)
The samples in the second group were prepared in an ideal well-defined ASR process. With reference to the chemical method (JIS A 1145), fine powdered reactive aggregates were dipped in 1 mol/L NaOH aqueous solution at 40°C for 7 days. For comparison, same experiment was done for quartz powder as a well-known pure SiO₂. To accelerate the reaction, these samples were ground into a small size from 20 to 40μm.

The samples in the third group were prepared by an artificial ASR process, as described below. First, a block of hardened cement paste was dipped in distilled water for 2 months. Then, fine powdered reactive aggregates (andesite), whose particle size was adjusted to 20 to 40 μm were immersed in the alkaline aqueous solution for 60 days. The solution was put into a sealed stainless-steel container to keep the temperature and humidity constant, 40°C and 90%, respectively. Finally, the supernatant liquid was skimmed off. Both of liquid and dried states were used as the samples.

3. RESULTS AND DISCUSSION

3.1 Samples from the real ASR process

Prior to the XAFS experiment, the chemical composition of each sample was analyzed by X-ray Photoelectron Spectroscopy (XPS). Figure 3 shows the Al Kα excited XPS spectra from several portions of the reinforced concrete specimen. Chemical composition of the cement paste is well-known and is reflected in the spectrum. All the aggregate samples contain similar elements as the cement paste; calcium Ca, oxygen O, sodium Na, silicon Si, aluminium Al and iron Fe.

It is noted that the non-reactive aggregate contain more Ca than the reactive one. Unfortunately, any significant difference was neither observed between the aggregate before and after use and nor between the surface and bulk of the reactive aggregates. This might be due to the fact that the ASR occurs at a very limited surface area and the composition of the ASR gel changed under the influence of water and heat during the sample treatment.

Figure 4 shows Si K-edge XAFS spectra from the same samples measured by XPS. Spectral profiles resemble each other except that of non-reactive aggregate, which has fine structures, suggesting that the sample has longer range orderings. Ca K-XAFS spectra from these samples were also measured (not shown), which revealed that Ca species of the non-reactive aggregate is likely to be CaCO₃, but others are CaO-like.

![Figure 3: XPS spectra](image)
3.2 Samples from the ideal ASR process

Figure 5 shows the Si K-edge XAFS spectra from quartz and reactive aggregate powder before and after immersion in 1 mol/L NaOH aqueous solution. We cannot find any difference between the spectra before and after immersion of alkaline solution. This result suggests that the product generated by the ASR does not remain on the surface of these powders, but dissolved in the aqueous solution. Next, we sampled the supernatant parts both from aqueous solution immersing quartz and reactive aggregates and measured Si K-edge XAFS of these liquid under 1 atm He pressure with the fluorescence yield mode.
Figure 6: Si K-edge XAFS spectra

Figure 7: Si K-edge XAFS spectra

Figure 6 shows these spectra with reference spectra from quartz and wet water glass. Observation of Si K-edge XAFS spectra from the supernatant part indicates that the alkali silica reaction certainly occurred and some Si-containing water soluble compound exist in the supernatant liquid. The spectra are clearly different from that of quartz, but very close to that of water glass.

3.3 Samples from the artificial ASR process

Considering the former results, an artificial ASR condition was prepared. The way of sampling is indicated in 2.2. In this experiment, the XAFS spectroscopy was performed under
1 atmospheric pressure with the fluorescence yield mode in order to measure a liquid sample. Figure 7 shows the Si K-edge XAFS spectra from a few samples for reference and ASR gel samples in wet and dry conditions. Figure 7 includes spectra from a non-used reactive aggregate and an alkaline aqueous solution. Both ASR gel samples resemble the reference samples. This result shows that the ASR gel is a SiO$_2$-like compound. Since the solution itself does not show any Si K spectrum, it indicates that the alkali silica reaction certainly occurred in the solution and two gel samples are products obtained by the ASR.

4. CONCLUSIONS

- Any spectral difference was not observed between the reactive aggregate before and after use and between the surface and bulk region of the reactive aggregate.
- Only difference observed is the Ca content of the non-reactive aggregate, which is more than the reactive aggregate and Ca exists not as CaO, but CaCO$_3$.
- The ASR was confirmed in the artificial condition, and the ASR product was found to be close to water glass.
- Since this is the result of an ideal situation, more realistic experiments with more sophisticated method will be necessary to clarify the mechanism of the ASR.

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REFERENCES