

Chemical state analysis of cement aggregates deteriorated by

Alkali Silica Reaction by using soft X-ray XAFS

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1. Introduction

The **Alkali-Silica Reaction** (ASR) is known as a reaction which occurs in concrete between the highly alkaline cement paste and reactive silica aggregates and causes serious expansion and cracking in concrete, resulting in critical structural problems. This ASR has been studied intensively with various experimental approaches and several mechanisms have been proposed so far[1,2,3]. However, the detailed microscopic mechanism has not been clarified yet. We investigated the ASR by using the X-ray Absorption Fine Structure (XAFS) spectroscopy, which is a unique technique to reveal the local structure around an x-ray absorbing atom and can be applied to amorphous samples as in the present case.

2. Experimental

Samples were prepared in two different ways.

(1) Sample taken from a real concrete deteriorated by ASR.

Mineral aggregates were andesite from Hokkaido. First, relatively large concrete blocks were samples either by cutting out in water, or by crashing into piece by pressure. ASR should occur exclusively at the surface of the aggregates. Thus, the minerals near the surface and those in the bulk were separately sampled. Reactive and non-reactive parts of the mineral aggregates and cement paste were shaved off and powdered. Powder sample of non-used reactive aggregates were also prepared as a reference. All of these powdered samples were used for the XAFS experiment.

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(2) Virtual ASR using NaOH aqueous solution

To study a well-defined ASR, we prepared fine powdered mineral aggregates, and dipped them in 1 mol/L NaOH aqueous solution at 40 C for 7 days. As a reference, same experiment was done for quartz powder, since quartz is a well-known pure SiO₂, whose XAFS spectra have been extensively studied. To accelerate the reaction, particle size were adjusted to 20 ~ 40 μm.

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

2. Results and Discussion

2.1 Real concrete deteriorated by ASR.

Figure 1 shows the Si K-edge XANES spectra from several parts of a real concrete apparently deteriorated with ASR. They are spectra from the surface and bulk part of reactive aggregates, together with those of reference samples. Unfortunately, however, we cannot find any discrimination among these spectra. This might be due to the fact that the ASR occurs at a very limited surface area and exclusive sampling of the ASR part is too difficult.

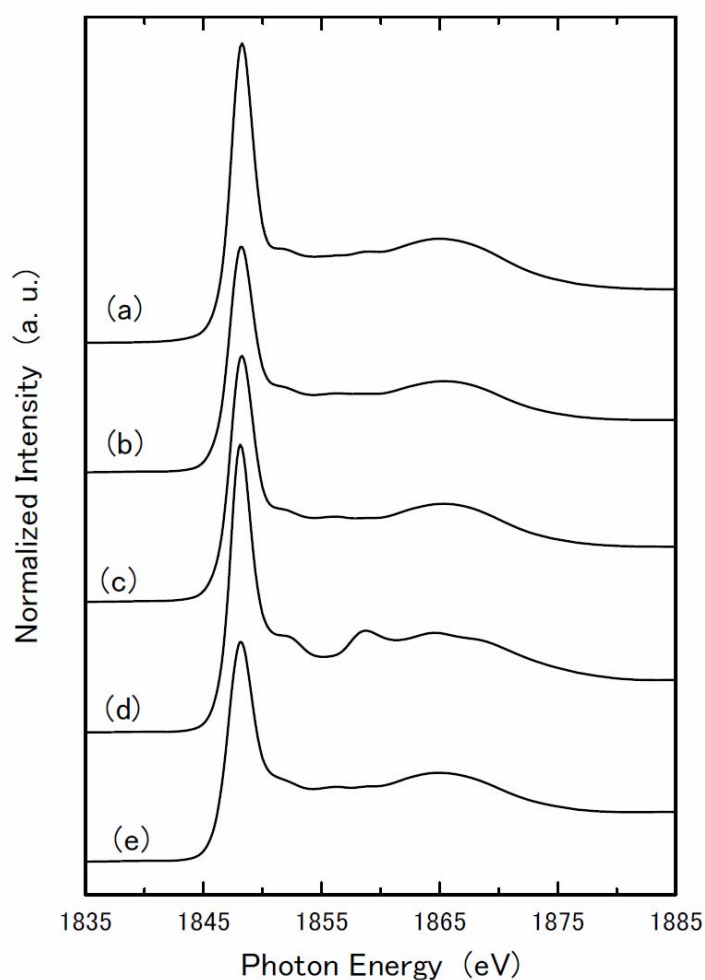


Fig. 1 Si K-edge XANES from reactive aggregates of a real concrete. (a) non-used reactive aggregates, (b) surface part of reactive aggregated, (c) bulk part of reactive aggregates, (d) non-reactive aggregates, and (e) cement paste.

2.2 Virtual ASR using NaOH aqueous solution

Prior to the XAFS experiments, we checked whether the ASR reaction occurred or not with the chemical method (JIS A 1145) and the mortar bar method (JIS A 1146) and obtained the positive result.

Figure 2 shows the Si K-edge XANES spectra from quartz and reactive mineral aggregate powder before and after immersion in 1 mol/L NaOH aqueous solution. Unfortunately, again, 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 dispersed in the aqueous solution. We sampled the supernatant parts both from aqueous solution immersing quartz and reactive mineral aggregates and measured Si K-edge XANES of these liquid under 1 atm He pressure with fluorescence yield mode[3].

Figure 3 shows these spectra together with reference spectra from quartz and wet water glass. Observation of Si K- 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.

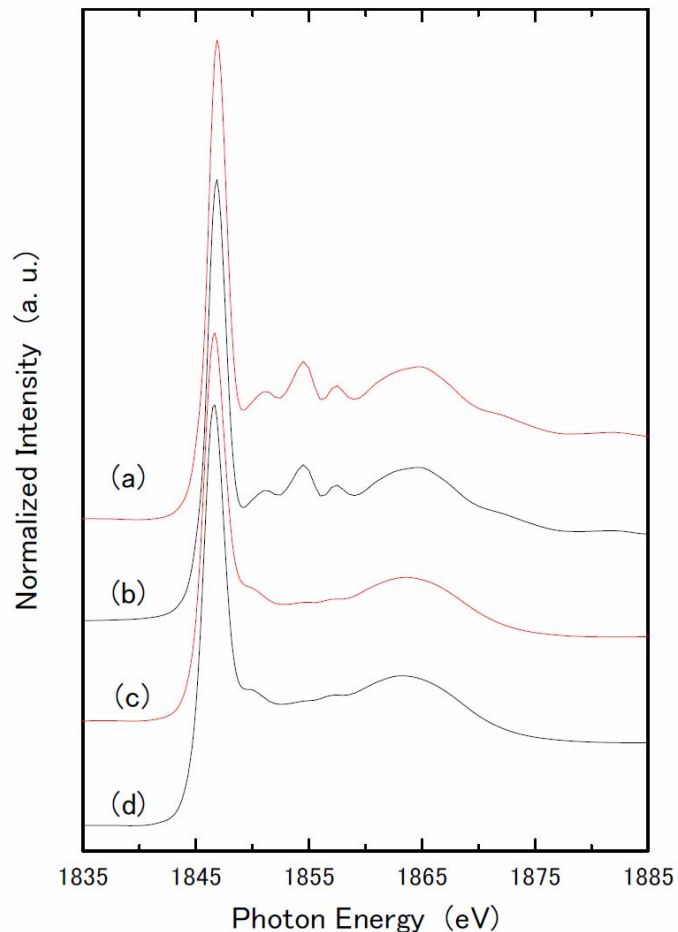


Fig.2 Si K-edge XANES spectra from quartz (a) and (b), the reactive aggregates (c) and (d) Red lines.(a) and (c), black lines (b) and (d) denote before and after immersion in NaOH aq. solution, respectively.

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3. Conclusion

We found the ASR certainly occurs in the NaOH solution by measuring Si K-edge XAFS spectra of the supernatant solution and clarified the chemical state of the ASR product. However, this is the result of an ideal situation. We have to get close to more realistic case, for example, by using water solution from real concrete in which the ASR is supposed to occur.

References

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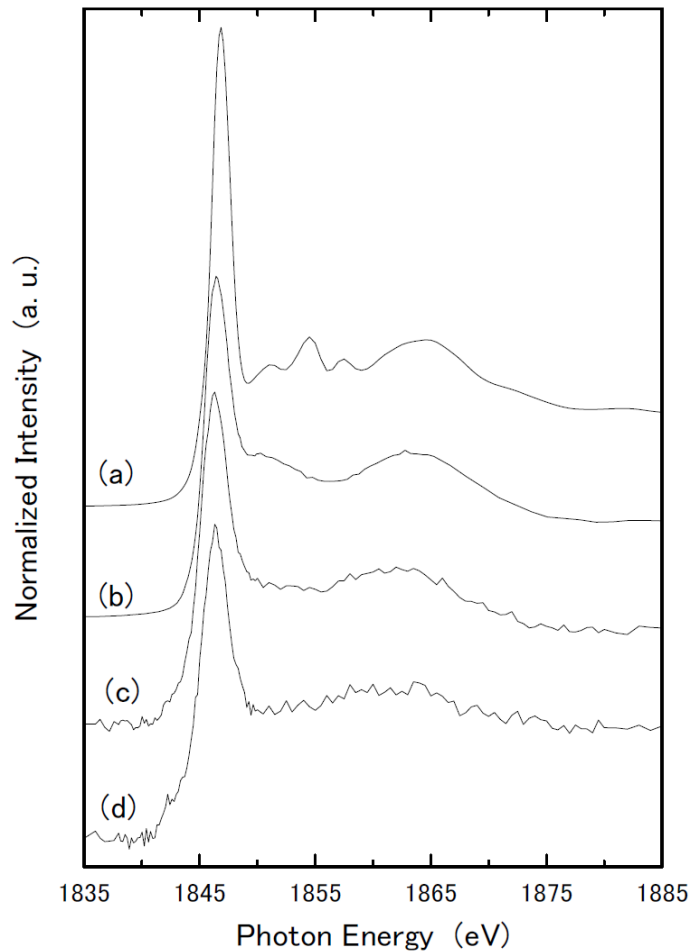


Fig.3 Si K-edge XANES spectra from (a) α -quartz, (b) wet water glass, (c) supernatant NaOH solution of reactive aggregates, and (d) supernatant NaOH solution of quartz.