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XAFS Analysis of the Structure of Ca in Engineered Barrier Materials

Hiroyuki SAKAMOTO[1], Kazuko HAGA[1], Hitoshi OWADA[2], Susumu KUROSAWA[2]
Kiyofumi NITTA[3], Hiroaki NITANI[3], Masaharu NOMURA[3]
[1]Taiheiyo Consultant Co., Ltd., 2-27-8, Higashinihonbashi, Chuo-ku, Tokyo, 103-0004, Japan
[2]RWMC, 1-15-7, Tsukishima, Chuo-ku, Tokyo, 104-0052, Japan
[3]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

Both of bentonite material and cementitious material will be used for the disposal facility of geological disposal of high-level and transuranic radioactive wastes. Although bentonite buffer is expected to have a function to inhibit the migration of radionuclides in geological disposal, bentonite is known to be altered by the attack of alkali and Ca ion from cementitious material. The alteration of the bentonite buffer is thought as a cause of decrease of performance of the disposal facility such as water tightness. Therefore the long-term alteration of bentonite is an important issue in the performance assessment of geological disposal. In this research, quantitative analysis of secondary minerals (C-S-H), generated in the bentonite by the interaction of the cement and bentonite, was conducted by measuring Ca with XAFS.

Experiment

Samples

Altered bentonite and cement-paste samples were quarried out from joined sample of cement-paste and bentonite immersed into deionized water over 5 years under Ar atmosphere.

Calcite, portlandite, hydrogarnet, ettringite, mono-sulfate, mono-carbonate, Friedel's salt and C-S-H were prepared separately as Ca-containing standard minerals.
Simulated altered samples were prepared by mixing C-S-H and Ca-bentonite at several proportions

XAFS Measurements

In order to evaluate C-S-H precipitation at the boundary of the cement and bentonite, Ca *K*-edge (4.04 keV) XAFS measurements were carried out at beamline BL9A with a Si(111) double crystal monochromator at the KEK Photon Factory (Ibaraki, Japan). The measurements were carried out both in transmission mode using ionization chambers, and fluorescence mode using a 19 element Ge detector. Identification of Ca-containing primary and secondary minerals were carried out by using the pattern fitting with Ca-K XANES spectra to those of standard minerals.

Results and Discussion

From results of the measurement of standard minerals and simulated altered samples, the detection limit of secondary C-S-H was confirmed as 1% and C-S-H with various Ca/Si ratio could be discriminated by the pattern fitting.

Results of the pattern fitting of Ca K-XANES spectra of altered bentonite and cement-paste samples indicated that Ca compounds in altered bentonite were C-S-H0.83, C-S-H1.0 and Ca-bentonite and in the altered cement-paste were C-S-H1.4, portlandite and Mono-sulfate.

However, improvement of the discrimination of XANES spectra is necessary to discuss about the Ca/Si distribution of C-S-H in detail. It will be also necessary to improve the spatial resolution to clarify the expansion of the alteration zone such as C-S-H precipitation.

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Table I. Results of pattern-fitting analysis for altered samples immersed in the ion-exchanged water

Ion exchanged water	Cement side (wt %)			Bentonite side (wt %)		
	9-10mm	2-3mm	0-1mm	0-1mm	2-3mm	9-10mm
C-S-H total	88.0	63.3	61.2	100	92.3	90.2
C-S-H0.6	21.1					
C-S-H0.83	66.9			45.6	92.3	90.2
C-S-H1.4		63.3	61.2	54.4		
Calcite			11.3			
Portlandite	12.0	17.9				
Ca type bentonite					7.7	9.8
Friedel's salt		18.8				
Ettringite			27.5			