

ALTERATION OF THE CEMENTITIOUS MATERIAL UNDER THE SALINE ENVIRONMENT

H. OWADA, H. ASANO, Y. KUNO*

*EBS Technology Research Project, Radioactive Waste Management Funding and Research Center
2-8-10 Toranomon, Minato-ku, 105-0001 Tokyo, Japan*

H. SAKAMOTO

*Solution Department, Taiheiyō Consultant Co., LTD.
2-4-2 Osaku, Sakura-city, 285-8655 Chiba, Japan.*

S. SHIMODA

*Energy Project and Technology Center, Mitsubishi Materials Corporation.
1-297 Kitabukuro-cho, Oomiya-ku, Saitama-city, 330-8508 Saitama, Japan*

ABSTRACT

Leaching experiment of ordinary and fly ash mixed cement were carried out by using the artificial sea water and deionized water as leachates. The pH values of saline leachates were decreased at the lower solid/liquid ratio in comparison with the case of deionized leachates. $Mg(OH)_2$ and ettringite were observed only in the case of saline water. The results of the geochemical calculation with inputs of $Mg(OH)_2$, ettringite and hydrotalcite well represented in the change of pH value and the mineral-composition with those of the experiment. However, in the latter stage of the fly ash mixed cement case, calculated concentrations of Si and Al of the leachate weren't consistent with the observed values. These results showed that substitution of Mg for Ca and influences of sulfate ion should be considered in the modeling of the cement alteration in the saline water case, and Al-substituted C-S-H might be considered in the alteration of fly ash mixed cement.

1. Introduction

Because candidate site for geological disposal is not yet selected in Japan, the applicability to wide range of disposal environment, such as salinity of the ground water, of every material and those assessment models for EBS system should be demonstrated. Many researches on the alteration of the cementitious material have been carried out and some serviceable alteration models are introduced [1]. Sugiyama's model [2] has been used in the 2nd progress report of TRU-waste disposal in Japan [3]. However, almost of these alteration models are considering only with fresh groundwater but with saline groundwater. Because the alteration of the cementitious material arise the alteration of other barrier such as bentonite buffer and host rock, the validation of the applicability of these alteration models for saline environment is necessary to use the geochemical simulation or performance assessment. However, such a validation of cement alteration for saline environment hadn't been carried out.

Because, from the point of view of the chemical durability, mixed cement such as fly ash mixed cement (FAC) may be used for the construction of the disposal vault as liner, structure, filling material,

*:Present position is Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency

grout and so on, the alteration model for mixed cement is also needed.

In this study, we report the results of a trial to present the applicability of alteration model of ordinary portland cement (OPC) for the geochemical simulation of alteration of FAC and of the batch alteration experiment of OPC and FAC in the artificial sea water (ASW). Results of the geochemical simulation under saline environment reflected the results of the experiment are also reported.

2. Experiment

2.1 Preparation of hydrated cement pastes

Because re-saturation of groundwater will take long time in the actual disposal facility, the cementitious materials will be well hydrated before beginning of the alteration cause by the reaction with groundwater. Therefore, we made well hydrated cement paste by the hot water curing to accelerate the hydration. Because the hydrated minerals in the high temperature are different from those in the lower temperature, the curing temperature was set 323K by following the previous research [4]. Fly ash/OPC ratio in FAC was 30wt%. Cement and water were mixed (water/cement ratio=0.6) and cured for 7 days. The hardened cement were crushed into 5mm or smaller diameter. The crushed cement were dried under vacuum to make easy to fine grinding. The dried crushed cement grinded into 250 μ m. Thereafter, the powdered cement were cured again for 91days with water to hydrate sufficiently. The hydrated cement pastes were dried in vacuum and grinded into 100 μ m.

2.2 Leaching experiment

Immersion experiment [5, 6] and flow-through experiment [7] used to be carried out to evaluate the degradation mechanisms of cementitious materials. We chose the immersion method with various water/solid ratio to identify the minerals in the hydrated and degraded cement in equilibrium with groundwater. Hydrated OPC and FSC pastes were put into PTFE bottles. Deionized water (DIW) or ASW were put into the bottles with water/cement ratio of 10, 100, 200, 1000 and 2000 (cm^3 -water/g-cement). The composition of the ASW is shown in Table 1. These process of immersion were carried out in a globe box of Ar atmosphere and these bottles were stored in the globe box. Immersion period was set 6 months.

species	pH	Na	Ca	K	Mg	Al	C	S	Cl	Si
concentration (mol/litter)	8.2	0.45×10^{-1}	9.4×10^{-3}	1.9×10^{-2}	5.1×10^{-2}	1.8×10^{-6}	2.4×10^{-3}	2.9×10^{-2}	5.3×10^{-1}	N.D.

Table 1: Composition of artificial sea water

2.3 Analyses

Identification of minerals in hydrated and degraded cement pastes was carried out by powder X-ray diffraction method (XRD). The pH values of leachate of every bottle were measured by standard glass electrode. Concentration of Ca, Si, SO_3^{2-} , Mg, Fe, Na and K were measured by ICP method. Before the ICP measurement, the leachate were filtered by using membrane filters of 45 μ m under the Ar atmosphere.

3. Geochemical simulation

3.1 Preconditions

Geochemical calculation to simulate the composition of minerals in the degraded cement and species in the leachate was carried out by using PhreeqC [10]. Thermodynamic data of the primary and secondary minerals was set by JNC-TDB.TRU [11]. Atkinson's alteration model [12] of C-S-H system was selected to calculate C-S-H dissolution[13]. List of the minerals considered in calculation were shown in Table 2.

	Primary minerals	Secondary minerals
All Case	Ca(OH) ₂ , C ₂ AH ₆ , ettringite, C-S-H, Na ₂ O, K ₂ O (Na ₂ O and K ₂ O was considered as the liquidous ion)	C ₃ ASH ₄ , C ₂ ASH ₈ , Caolinite, Pyrophyllite, Monosulfate, Calcite, Analcime, Roemontite
Set in ASW case		Friedel's Salt, Mg(OH) ₂
Set as the parameters for calclations		C ₄ AH ₁₃ , C ₄ AH ₁₉ , Sepiolite, Hydrotalcite

Table 2 List of the minerals considered in the calculation

Liquid/Solid ratio	OPC-DIW					OPC-ASW				
	initial	10	200	1000	2000	initial	10	200	1000	2000
Portlandite						○	○			
Brucite							○	○		
C-S-H gel										
Gypsum										
Ettringite										
Monosulfate										
Katoite	○	○	○	○	○	○	○	△		

Liquid/Solid ratio	FAC-DIW					FAC-ASW				
	initial	10	200	1000	2000	initial	10	200	1000	2000
Portlandite										
Brucite										
C-S-H gel										
Gypsum										
Ettringite										
Monosulfate										
Katoite	○	○	○	○	○	○	○			

Table 3 Results of the XRD experiment

Well Detected Slightly detected Blunk:Not detected

4. Results and discussion

Table 3 shows the dominant results of XRD analyses. In the initial system of FAC, C-S-H gel, monosulfate and katoite were observed as hydrated minerals and mullite and quartz were observed as inert minerals. Because of lower sulfate concentration in the FAC system, monosulfate seemed to be formed instead of ettringite formation. In addition, the minerals in the alteration of FAC were almost the same as those of OPC, except the absence of portlandite and ettringite. This result suggests that the alteration mechanism of FAC might be the same as that of OPC. Precipitation of brucite (Mg(OH)₂) and dissolution of portlandite (Ca(OH)₂) and C-S-H gel were detected in the early stage of the alteration of OPC-ASW case. The color of the cement paste was changed into yellow by the degradation in ASW. Figure 1 shows the change of the pH values of leachates. In the ASW case, the pH value fell under 11 in the small liquid/solid ratio in comparison with IEW case. The value of pH at the equilibrium of brucite is significantly lower than that of portlandite. Figure 2 shows the change of Ca and Mg concentration of the leachate. Ca concentration in the ASW cases were higher than those of DIW cases in all stages of alteration. These result seem to show that Mg substitutes to Ca of portlandite in the hydrated cement

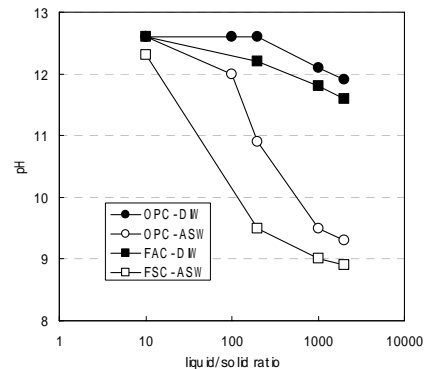


Fig.1 Change of pH of leachate with liquid/solid ratio

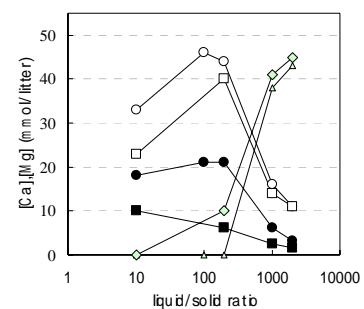
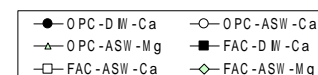


Fig.2 Change of the Ca and Mg concentration of leachate



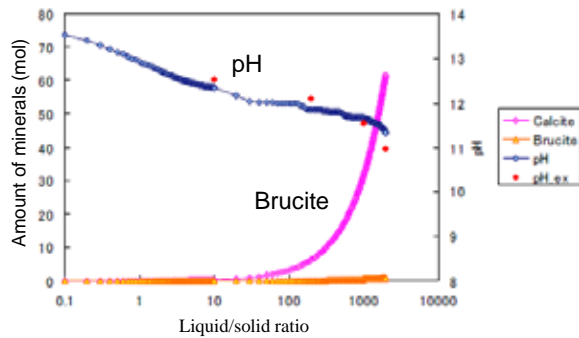


Fig.3 Results of the geochemical simulation of alteration of FAC in DIW

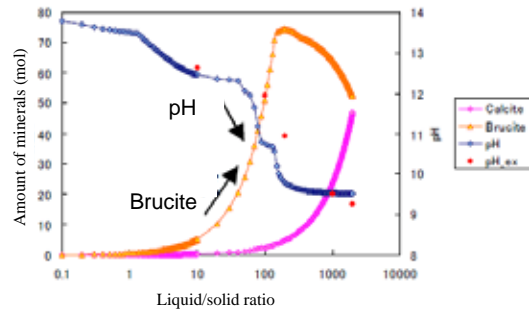


Fig.4 Results of the geochemical simulation of alteration of OPC in ASW

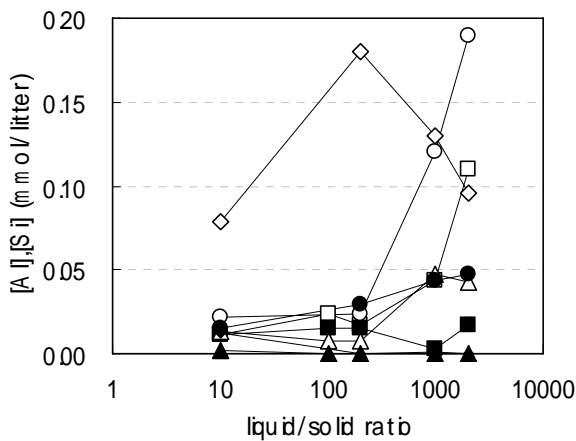


Fig.5 Al and Si concentration of leachate

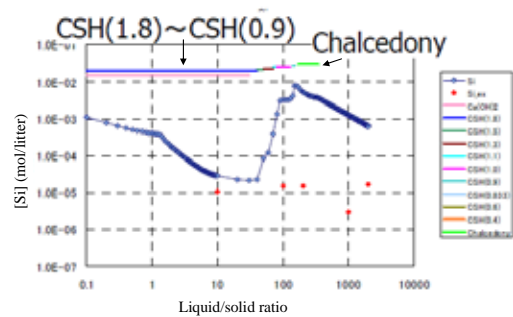
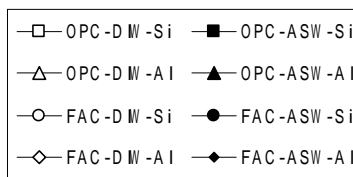


Fig.6 Results of the geochemical simulation of alteration of OPC in ASW (change of Si concentration)

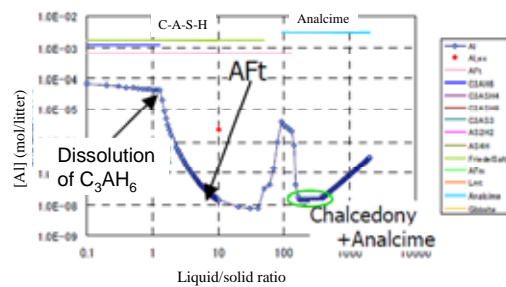


Fig.7 Results of the geochemical simulation of alteration of OPC in ASW (change of Al concentration)

system in early stage of alteration and, in the latter stage, C-S-H gel would be attacked by Mg. Precipitation of gypsum observed in the OPC-ASW might be caused by the SO_4^{2-} released from ettringite by Cl substitution. Figure 3 shows the results of the calculation of the change of pH value in the case of FAC-DIW. In this case, the change of pH value (experimental values were shown as the closed dots in those figures) and the precipitation-dissolution behavior of brucite might be well represented. From this, in the DIW case, the applicability of the alteration model of Ca-Si-H system for OPC is thought to be applicable to the FAC alteration. Figure 4 shows the results of the calculation of pH and Brucite concentration in the OPC-ASW case. These phenomena were also well represented in the ASW case. Figure 5 shows Si and Al concentrations. The increase of the Al concentration in the DIW cases would be due to the dissolution of ettringite. In the ASW case, precipitation of gypsum or other sulfo-aluminate phase might cause the lower concentration of Al. Figures 6 and 7 show the calculation results of Si and Al concentrations in the OPC-ASW case. Calculated values of Si and Al were different from those of experimental values. The difference is thought to be caused by the imperfection of the model for incongruent dissolution of the sulfo-alumino-silicate system such as ettringite, monosulfate, and hydropic acid. In addition, because there are no thermodynamic databases for Al-substituted C-S-H gel, the dissolution of such C-S(A)-H was not considered in these calculations. Therefore, the dissolution behavior of Al and Si in the latter stage, where such C-S(A)-H would dissolve, might not be able to be represented accurately.

5 Conclusions

From the results of the leaching experiment of OPC and FAC using the ASW and DIW and geochemical calculation of cement-water reaction, followings are suggested.

- a. The alteration model of Ca-Si-H system for OPC thought to be applicable to the FAC alteration
- b. In the early stage of the alteration, the alteration calculation considered the Mg containing secondary mineral such as brucite will be applicable.
- c. Thermodynamic data for Al substituted C-S-H gel might be necessary to accurately calculate the latter stage of cement alteration in the saline water.

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