

8-11 Prediction of Long-Term Alteration Characteristics of HFSC

— Clarification of Decreasing pH and Development of Alteration Model —

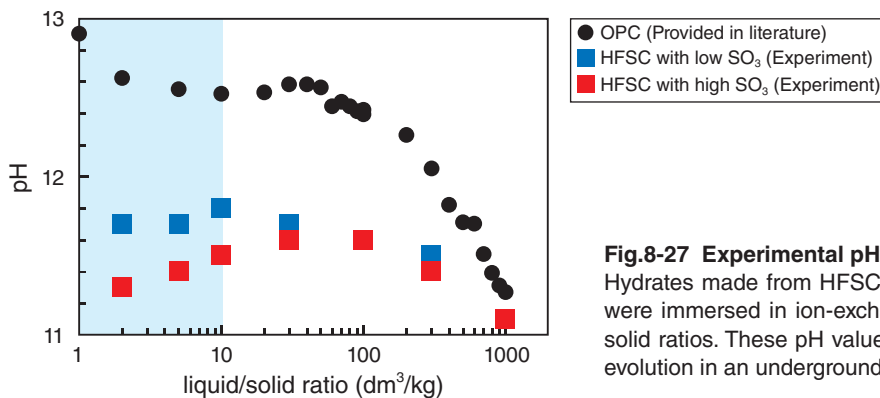
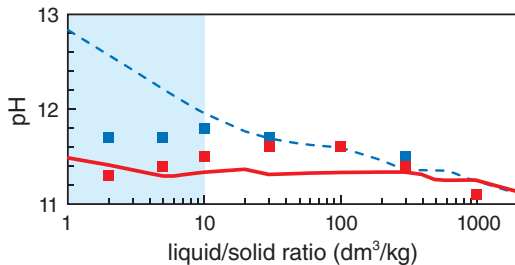


Fig.8-27 Experimental pH value in dissolution experiments
Hydrates made from HFSC containing different amount of SO_3 were immersed in ion-exchanged water with differing liquid-to-solid ratios. These pH values reflect a possible scenario for pH evolution in an underground repository.

(a) Model considers only dissolution and/or precipitation phenomena



(b) Same model as in panel (a), but includes alkali adsorption phenomena

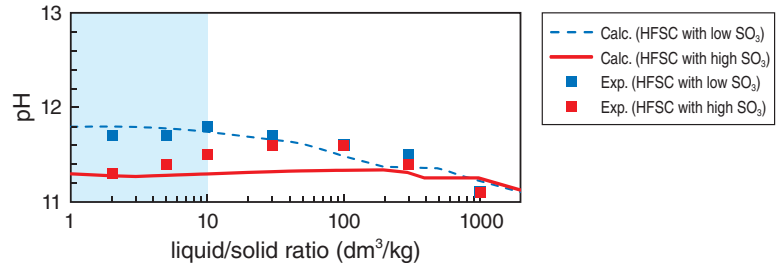


Fig.8-28 Comparison between experimental and calculated pH

Differences between experimental and calculated values (a) can be improved by including alkali adsorption in the model (b).

Cementitious materials are expected to be used to construct an underground repository for the geological disposal of radioactive wastes. Degradation of ordinary Portland cement (OPC) by the ingress of groundwater can generate a high-pH plume (≥ 12.5), which would probably affect the performance of the bentonite buffer used to contain the radioactive wastes and the transport properties of the host rock. Therefore, a new type of high-volume fly ash silica fume cement (HFSC) is being developed that will lead to a lower plume than for OPC.

The long-term alteration characteristics of HFSC need to be predicted to assist in demonstrating the safety of a geological disposal system. The prediction should be made based on an understanding of the mechanisms responsible for alteration phenomena. In this study, dissolution experiments were used with geochemical equilibrium calculations to make a preliminary assessment of the pH-lowering mechanism in HFSC and to predict the long-term alteration characteristics.

These calculations, based on the understanding that pH decreases only when $\text{Ca}(\text{OH})_2$ is absent and the molar Ca/Si ratio in the calcium silicate hydrate (C-S-H) gel is lowered, did not satisfactorily reproduce the experimental results. Dissolution experiments were performed with HFSC containing different amount of SO_3 , with the focus being on SO_4^{2-} as a counter ion and on the response of the alkali

elements (i.e., Na and K). HFSC containing either high or low SO_3 wt% was immersed in ion-exchanged water at various liquid-to-solid ratios, and the resulting pH and liquid composition were measured. At lower liquid-to-solid ratios (≤ 10), the pH was higher for HFSC with low SO_3 than for HFSC with high SO_3 (Fig.8-27). However, the pH calculated with models that only consider dissolution and/or precipitation phenomena differs significantly from the experimental values for HFSC with low SO_3 (Fig.8-28(a)) and so could not be explained by the SO_3 content alone.

An improved chemical equilibrium model was developed by including Na and K adsorption on the C-S-H gel along with the dissolution and/or precipitation phenomena. The pH calculated with the improved model agrees well with the experimental results (Fig.8-28(b)). The model thus developed is expected to help improve our understanding of the mechanisms responsible for lowering pH in HFSC and can be used to predict possible scenarios of pH evolution in a geological disposal system.

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Reference

Hoshino, S., Honda, A. et al., Mechanism of Alkalinity Lowering and Chemical Equilibrium Model of High Fly Ash Silica Fume Cement, Konkurito Kogaku Ronbunshu (Concrete Research and Technology), vol.25, 2014, p.97-107 (in Japanese).