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Iodine release behavior from iodine-immobilized cement solid under geological disposal conditions

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ABSTRACT

The iodine release behavior from the iodine-immobilized cement was investigated. From the results of immersion tests using ion-exchanged water (IEW) and calculations, the solubility equilibrium model could describe the iodine release behavior. To assess the performance of cement in an actual environment, it is important to confirm that the solubility equilibrium model is applicable to the geological disposal conditions. From immersion tests using simulated ground water, the release of iodine from the cement occurred in a shorter period of time than in the case of IEW, and reactions with CO_3^{2-} and Cl^- , which were contained in the simulated ground water, had an influence on the iodine release behavior. As a result of calculations using the solubility equilibrium model, the liquid-solid ratio at which the iodine was completely released was mostly in agreement with the results of immersion tests. The results show that this model can be applied in a wide range of environments.

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1. Introduction

^{129}I is considered to be the most important radionuclide in the safety evaluation of geological disposal for radioactive waste generated from reprocessing plants (TRU Waste) (FEPC and JAEA, 2007). ^{129}I has a very long half-life (15.7 million years), so it should be immobilized before disposal. Since adsorption to a natural barrier is unlikely (FEPC and JAEA, 2007), it is necessary to immobilize the iodine using waste packages.

The adsorption behavior of iodine to several materials has been investigated (Liu and Gunten, 1988), and it has been reported that iodine adsorption is improved by adding calcium sulfate to aluminate cement (Toyohara et al., 2000). Based on this information, an iodine-immobilized cement solidification process using sulfate-added calcium aluminate cement (S-CAC) was developed (Haruguchi et al., 2013).

Iodine fixing performance is dependent also on the chemical form of iodine, and it has been reported that there is a tendency for the distribution coefficient of IO_3^- to be higher than that of I^-

(Fujihara et al., 1999). Also from a thermodynamic viewpoint, it is shown that calcium aluminate materials in the IO_3^- form are more stable than those in the I^- form (Houtepen and Stein, 1976).

In the S-CAC solidification system, the iodine trapped by a silver adsorbent in the AgI or AgIO_3 form is reduced and eluted by an Na_2S solution. The eluted I^- is oxidized to IO_3^- by using ozone. This solution is condensed to a saturated concentration of NaIO_3 and is solidified using S-CAC.

In the iodine-immobilized cement solid, it is thought that IO_3^- is fixed into oxyanion channels of ettringite (Aft) which is one of the major minerals formed in S-CAC (Haruguchi et al., 2013).

Since the iodine-immobilized cement solid is disposed deep underground, the stability of iodine-containing minerals in a reducing environment is an important issue. In relation to this issue, from the results of investigation of the iodine discharge behavior from the iodine-containing Aft under strong reducing conditions using the electrochemical technique, it was found that the iodine release fraction is small, and it is thought that the Aft is comparatively stable in the reducing environment assumed in final disposal sites (Idemitsu et al., 2013).

The iodine release behavior from iodine-immobilized cement has also been evaluated using experimental and theoretical methods (Haruguchi et al., 2013). As a result, it was shown that it is

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appropriate to describe the iodine release behavior by using the solubility equilibrium model under conditions corresponding to ion-exchanged water (IEW).

In order to actually use this iodine-immobilizing technique, long-term prediction of the iodine release behavior under geological disposal conditions is required. In this study, immersion tests were conducted using simulated ground water, and the iodine release behavior from iodine-immobilized cement under geological disposal conditions was investigated. In this investigation, since it was difficult to maintain reducing atmosphere during the long period, the examination was conducted under the argon atmosphere. The applicability of the solubility equilibrium model under IEW conditions was checked by comparing the results of the model with the results from the immersion tests.

2. Experimental

2.1. Samples

Iodine-containing cement was prepared by mixing 0.4 mol dm⁻³ NaIO₃ solution (specific weight, about 1.07 g cm⁻³) and S-CAC. The S-CAC contained calcium aluminate cement material and CaSO₄·2H₂O in a ratio of 100:15.5 by weight. The solution cement ratio was 0.56. The cement paste was ground, and samples with particle diameters of 250–355 μm were collected.

Fresh ground water (FGW) and saline ground water (SGW) were prepared for the simulated ground water used as the immersion solution. The content of the prepared simulated ground water is shown in Table 1. The SGW solution was diluted two-fold and ten-fold, called 1/2 SGW and 1/10 SGW, respectively. According to the Eh value, FGW and SGW were not in reducing conditions. Since it has been confirmed previously that IO₃⁻ in solution is not reduced to I⁻ easily, the Eh value was not adjusted in these experiments.

2.2. Test procedure

Batch-type immersion tests were conducted. An outline of the immersion test is shown in Fig. 1, and the test conditions and analysis items are shown in Table 2. The sample and immersion solution were put into an immersion container at a given liquid-solid ratio, and the immersion container was kept in a glove box under an inert atmosphere. Once a day, the immersion container was shaken by hand, and the pH of the immersion solution was measured. Immersion process was completed about ten days after no further change in the pH was observed. The immersion container was opened, and the solid phase and the liquid phase were collected.

The concentrations of elements (Ca, Al, I, S, Mg, and Si) contained in each liquid phase were measured by inductively coupled plasma atomic emission spectroscopy. The minerals contained in the solid phase were analyzed by X-ray diffraction analysis qualitatively. The mineral composition of the solid phase in the FGW and non-diluted SGW conditions was analyzed quantitatively by using chemical separation techniques based on Suzuki's method (Suzuki et al., 1990). This method can quantify each mineral by dissolving each mineral by some solvents and measuring the dissolved elements.

Table 1
Composition of immersion solutions.

| Liquid | Concentration of elements/mol dm ⁻³ | | | | | | | | | | |
|--------|--|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | Na | Ca | K | Mg | HCO ₃ | SO ₄ | B | Br | N | Cl | Si |
| FGW | 3.55 × 10 ⁻³ | 1.09 × 10 ⁻⁴ | 6.15 × 10 ⁻⁵ | 5.00 × 10 ⁻⁵ | 3.54 × 10 ⁻³ | 1.11 × 10 ⁻⁴ | 2.93 × 10 ⁻⁴ | 0 | 2.30 × 10 ⁻⁵ | 1.46 × 10 ⁻⁵ | 3.39 × 10 ⁻⁴ |
| SGW | 6.79 × 10 ⁻¹ | 3.30 × 10 ⁻⁴ | 1.10 × 10 ⁻² | 2.50 × 10 ⁻⁴ | 3.50 × 10 ⁻² | 3.00 × 10 ⁻² | 1.70 × 10 ⁻³ | 5.30 × 10 ⁻⁴ | 5.20 × 10 ⁻³ | 5.89 × 10 ⁻¹ | 3.00 × 10 ⁻⁴ |

3. Results and discussion

3.1. Iodine release behavior

The element concentrations of the liquid phase are shown in Table 3. Iodine increased with increasing liquid-solid ratio, and the concentrations of other elements changed. This change was considered to be because of differences in the equilibrium point depending on the mineral phase.

The mineral composition of the solid phase and the relationship between the liquid-solid ratio and the mineral composition are shown in Table 4 and Fig. 2, respectively.

From the results of mineral composition analysis, AFt and AFm decreased with an increase in the liquid-solid ratio, and calcite increased conversely. Although Friedel's salt was generated by Cl⁻ contained in SGW, it disappeared when the liquid-solid ratio became large. From XRD analysis, as shown in Fig. 3, although Friedel's salt was generated and disappeared when the liquid-solid ratio was 10 in the non-diluted SGW case, Friedel's salt was observed also at a high liquid-solid ratio and low Cl⁻ concentration. Since Friedel's salt is a kind of the calcium aluminate mineral contributed to immobilization of iodine, it is necessary to investigate the mechanism based on these results in the future.

Since iodine existed in the AFt, AFm, and HG before immersion, it is thought that the relation between the changes of these minerals and the iodine distribution in these minerals was important. Iodine distribution ratio in the minerals and dissolution fraction at each liquid-solid ratio are shown in Fig. 4.

Much of the iodine presented in the AFt phase, and the iodine was mainly released with the dissolution of AFt. AFm, which is one of the iodine fixing minerals, dissolved at lower liquid-solid ratios than AFt. These results were in agreement with results of tests using IEW (Haruguchi et al., 2013). Moreover, it turned out that iodine does not exist in a secondary mineral phase such as calcite or Friedel's salt. Under SGW conditions, almost all of the iodine was released at liquid-solid ratios between 50 and 150, and under FGW conditions, at liquid-solid ratios between 600 and 900.

Furthermore, not only under IEW conditions but also under typical environmental conditions, it is thought that the dissolution of AFt begins after AFm dissolves. The main iodine fixing mineral is AFt, and the assumption that iodine is released with the dissolution of AFt seems to apply in a wide range of environmental conditions. Additionally, the influence of the environmental conditions on the dissolution of AFt and AFm was more remarkable under SGW condition. It is thought that this is due to the various kinds and amounts of ion components that are contained in SGW.

3.2. Comparison of the immersion test results with the solubility equilibrium model

PHREEQC 2 (Parkhurst and Appelo, 1999) was used for the equilibrium calculations. The initial mineral compositions and iodine distributions in the cement were set based on the results of chemical analysis of the cement, as shown in Table 4. In order to calculate the release of iodine from the minerals containing iodine, the iodine-containing minerals were defined as shown in Table 5 (Haruguchi et al., 2013). IS_AFt means AFt in which half of the

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