Retardation behavior of Sr and Cs in Crushed and Intact Rocks: Two potential LLW repository Taiwan host rocks

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Abstract

This study investigates sorption and diffusion of Strontium (Sr) and Cesium (Cs) in two potential host rocks (granite from Kinmen Island and basalt from Penghu Island) by using batch and through-diffusion methods in order to establish a reliable safety assessment methodology. These methods were applied to crushed and intact rock samples to investigate the actual geological environment. According to solid-phase analysis, including X-ray diffraction, elemental analysis, auto radiography, and polar microscopy, the sorption component primarily contained iron–magnesium (Fe–Mg) minerals in basalt and granite. Moreover, the distribution coefficient ($K_d$) of Sr and Cs in various concentrations ($\sim 10^{-2}–10^{-7}$ M) obtained from batch tests indicated a higher sorption capacity in basalt than that in granite because of the 10% Fe–Mg mineral content. The diffusion of Sr and Cs both in crushed granite and basalt reach steady state after 110 days and apparent diffusion coefficient ($D_a$) were $3.29 \times 10^{-11}$ m$^2$/s (for Sr in crushed granite), $4.17 \times 10^{-12}$ m$^2$/s (for Sr in crushed basalt), $2.86 \times 10^{-11}$ m$^2$/s (for Cs in crushed granite), $1.82 \times 10^{-12}$ m$^2$/s (for Cs in crushed basalt), respectively. However, diffusive result ($D_a$) of Sr and Cs in intact rocks was estimated a lower value than those obtained using crushed rocks. According to the diffusive results in crushed and intact rocks, it showed that major retardation of Sr and Cs depended on the microporous structure of tested media, such as decreases of constrictivity ($\delta$) and increases of tortuosity ($\tau$). In fact, the solid/liquid (S/L) ratio decreased as is the case when switching from batch to column experiments and the sorption effect on minerals became even more negligible in retardation of radionuclide migration.

Keyword: Sorption, diffusion, granite, basalt, distribution coefficients ($K_d$), retardation factor ($Rf$)
Introduction

Because of the Fukushima Daiichi nuclear crisis in 2011, the Taiwan Government (Atomic Energy Council) and plant operator (Taipower Company, TPC) announced a permit in November, 2011 for the decommissioning of three nuclear plants (six nuclear units) in Taiwan. The oldest operating nuclear units in Taiwan are the two 604-MW General Electric boiling water reactors at the ChinShan plant, which started commercial operation in 1978 and 1979. Moreover, there are three operating nuclear power plants generating 5144 MW in Taiwan, and two Advanced Boiling Water Reactors (ABWR 1350 MW for one unit) under construction at the LungMen plant that would only be allowed to start up after passing strict safety evaluations both by the government and international nuclear safety organizations.

Nuclear power has the advantage of generating huge volumes of electricity while maintaining its waste in a solid form within the plant. The most contentious waste in terms of safety management is the spent fuel that contains approximately 99% of the radioactivity. Achieving a permanent disposal route for spent fuel is a political challenge that is yet to be fully met in any nuclear-powered country.

Since deep geological disposal is currently the preferred way of disposing nuclear waste, the state-run TPC, owner of three nuclear power plants, initiated a long-term spent-fuel disposal program in the 1980s to prepare a geological repository for operation in 2050. To assess the long-term performance of this repository, it is necessary to deal with the problem of high-level radioactive waste (HLW) considering its long half-life and the associated risk of transporting radionuclides into the environment. Some geological investigations and research and development (R&D) efforts into radionuclide migration have been completed, and the investigations presented in this study are a part of this disposal program [1].
Cesium (Cs) is a high-yield fission product containing up to 6.5% and 6.2% $^{135}$Cs and $^{137}$Cs, respectively [2], and selenium (Se) is also a fission product and have a long half-life $2.95 \times 10^5$ years. Moreover, Se is a natural trace element that is of fundamental importance to human health and Cs is released directly in catastrophic nuclear events and it was reported in Fukushima that Cs resulted in a possible contamination of the ocean environment [3]. In addition to its high generation yield, Cs was considered for this study because of the long half-life of $^{137}$Cs and $^{135}$Cs (30 and $2.35 \times 10^6$ years, respectively), high solubility in water, and chemical properties similar to potassium (K).

The “multi-barrier” concept has been adopted to deal with issues related to nuclear waste repository, such as the use of clays as a buffer/backfill material because of their high sorption capacities. Furthermore, stable and firmly argillaceous formations are suitable as a host rock in the disposal repository. Therefore, granite was initially selected and studied because it is a major host rock on some isolated islands. The sorption and diffusion behavior of Cs on granite, diorite, and mudrock has been studied and reported in literature [4–10].

Batch techniques are frequently used to characterize the sorption of radionuclides in laboratories, and the distribution coefficient ($K_d$) method is widely used for estimating the retardation of radionuclides. However, there are few systematic sorption studies dealing with sorption in host rocks as compared with those related to a bentonite-engineered barrier. The $K_d$ value obtained by the batch method may be too simple to represent the actual system, and it is found that diffusion methods gives more accurate information relating to radionuclides in deep geology [6, 7]. However, some disagreement between $K_d$ and the retardation factor ($R_f$) obtained from the two above-mentioned methods due to differences in the solid/liquid (S/L) ratio has been
reported in literature [11–13]. Moreover, the limitation of one-dimensional diffusion tests is that they may only be demonstrated in the diffusion of Cs and Se compacted in crushed granite with a relatively lower or higher length/diameter ratio (L/D < 0.44 or L/D > 1.78) [9-10]. In a repository environment, sorption often occurs on intact rock or fracture because of the hydraulic-geological conditions. It is found that the sorption of Cs on crushed and intact sedimentary rocks was comparable within an order of magnitude [14].

In this study, batch sorption and column through-diffusion experiments in crushed and intact granite and basalt were performed simultaneously. Moreover, the $K_d$ values were determined using the two methods and their differences are discussed. The purpose of this study is to determine whether it is possible to compare $K_d$ values determined by the batch and static diffusion methods. In fact, such a procedure would be very important in a safety assessment to effectively apply the batch $K_d$ values to describe sorption in an actual environment in a potential repository.
Experimental

Rock samples and solid phase analysis

Rock samples were drilled and collected from Kingman and Penghu Islands, located at latitudes and longitudes of 24°N 118°E and 23°N 119°E, respectively. In terms of geology, seismology, meteorology, hydrology, site geometry, and risk in relation to the local population center, both islands are considered to be a potential repository because of the location of the Taiwan Strait approximately 210 km and 50 km away from Taipei, respectively. The Kingman and Penghu Islands, comprising several discrete islands, are approximately 150 km² and 125 km² in area and are composed of 90% granite and 80% basalt, respectively.

In this study, before use, all rock samples were crushed, sieved, and separated into three size groups: ~20–50 mesh (~0.297–0.833 mm), ~50–100 mesh (~0.149–0.297 mm), and ~200–270 mesh (~0.053–0.074 mm). They were then washed three times using de-ionized water (DIW) and dried at 105 °C for 24 h.

A solid-phase analysis of granite and basalt was performed by powder X-ray diffraction (XRD, D8 Advance, Bruker, Germany) and elemental analysis after sample acid-digestion by inductively coupled plasma–optical emission spectrometry (ICP–OES, JY Ultima-2, France). The major sorption of Cs on both rocks was identified and compared in polar microscopy and autoradiography experiments. The chemical compositions of granite and basalt were listed in Table 1. XRD spectra were compared with those in the International Center for Diffraction Data (JPCDS) database. This showed that major mineral composition of granite (abbreviated as G below) and basalt (abbreviated as B below) included quartz (G & B), biotite (G & B), plagioclase (G & B), feldspar (G & B), goethite (G), and magnetite (B) among other components. The predominant elements of granite and basalt presented as oxides, as
determined by ICP–OES, were SiO$_2$, Al$_2$O$_3$, K$_2$O, Na$_2$O, and Fe$_2$O$_3$.

_Polar-microscopy and auto-radiography experiments_

After pre-treatment by DIW, the crushed samples were sprayed and glued onto a glass plate and then samples were submerged into the stock solution, containing $^{137}$Cs with a specific activity of about 200 Bq/mL. After 7 days of immersion, the samples were taken out and rinsed quickly with DIW to remove excess tracer solution on the sample surface. After drying, the samples were covered with thin transparent films, and then contacted with x-ray films. After exposure for two days, the x-ray films were developed (AGFA, G150, 3-5 min) and fixed (AGFA, G334A.B, 7-10 min). These auto-radiography photos were then compared with the corresponding images from polar-microscopy.

_Batch tests_

Three centrifuge tubes with different particle sizes (~0.297–0.833, ~0.104–0.173, and ~0.053–0.074 mm) were prepared in various Cs concentrations (~$10^{-2}$–$10^{-7}$ M) in order to realize the geometric effect in sorption on rocks. Batch tests reported by ASTM were applied [15], and the solid-to-liquid ratio was 1 g:30 mL. A trace amount of the radiotracer $^{137}$Cs was also added to the liquid with carriers prior to batch tests. After 14 days of shaking, the tubes were centrifuged at 10,380 g (Kokusan H-200, Japan), and the supernatants were radioassayed using an auto-NaI(Tl) gamma detector.
(Packard 5002, US) to determine $^{137}$Cs activity. The pH and $Eh$ values were also measured. The $K_d$ value was calculated by the following formula

$$K_d = \frac{C_0 - C}{C} \cdot \frac{V}{M},$$

where $C$ is the equilibrium concentration of Cs (cpm/mL), $C_0$ is the initial concentration of Cs in solution (cpm/mL), and $V$ and $M$ are liquid volume (mL) and solid mass (g), respectively.

**Through-diffusion tests**

In this study, through-diffusion tests were adopted to determine the diffusion coefficient ($D$) in order to evaluate the transport of radionuclides in compacted media. If $D$ is constant, Fick’s Law may be written as

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right).$$

Furthermore, if the compacted layer of crushed granite is assumed to be homogeneous and isotropic, and the diffusion of the radionuclide occurs only in one dimension, the diffusion equation can be written as

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \quad (D_a = D_e/\alpha, \alpha = \theta + \rho_b K_d),$$

where $\alpha$ is the rock capacity factor. This equation could give a $K_d$ value by bulk density ($\rho_b$) and porosity ($\theta$). $C$ is the concentration of the liquid. The appropriate boundary conditions and initial conditions are given by

$$C(x,0) = 0, \quad 0 < x < L.$$
\[ C(0,t) = C_0, \]
\[ C(L,t) = 0, \]

where \( C_0 \) is the initial Cs concentration at the interface between a tracer-containing reservoir and a slab of rock, and \( L \) is the overall length of the rock slab. The concentration \( C \) of radionuclide can be expressed as a function of \( t \) and \( x \)

\[
\frac{Q_t}{C_0} = \frac{\alpha A}{L} \left[ D_a t - \frac{L^2}{6} - \sum_i \left( \frac{2L^2}{n^2\pi^2} \exp\left(-\frac{D_an^2\pi^2t}{L^2}\right) \right) \right].
\]  

(3)

As \( t \to \infty \), the diffusion process reach equilibrium (steady-state), and the corresponding concentration ratio \( CR(t) \) may be rewritten as

\[
CR(t) = \frac{\sum C_t}{C_0} = \frac{\alpha A}{VL} \left[ D_a t - \frac{L^2}{6} \right],
\]  

(4)

where \( V \) and \( A \) are the volume of the diffusion end and the surface area of the compacted granite powers, respectively. \( CR(t) \) is a straight line with a slope \( m \) and an intersection \( t_x \), in Equation (4). Therefore, a graphical method [16] developed in 1975 by Crank is often employed to determine the apparent diffusion coefficient (\( D_a \)), effective diffusion coefficient (\( D_e \)), retardation factor (\( R_f \)), and distribution coefficients (\( K_d \)) from the values of \( m, V, L, A, t_x, \rho_b, \) and \( \theta \) \([7,16,17]\)

\[
D_a = \frac{L^2}{6t_x}
\]  

(5)

\[
D_e = \frac{m \cdot V \cdot L}{A}
\]  

(6)

\[
R_f = D_e / \theta D_a = 1 + (\rho_b K_d / \theta).
\]  

(7)

After pre-treatment, crushed and intact samples were compacted into independent
columns (four columns in total) with a bulk density \( \rho_b = 1.8 \text{ cm}^3/\text{g} \) and a total porosity \( \theta \) of 0.31 and 0.37 in crushed granite and basalt, respectively. In the through-diffusion experiments shown in Fig 1, total volume (V) of samples in both ends (source and diffusion ends) were removed and collected at a constant frequency in order to detect \(^{137}\text{Cs} \) radioactivity. After removing samples from two diffusion chambers, the same volumes were refilled into two chambers to maintain the initial conditions at boundary \( C(0,t) = C_0 \).

**Results and Discussion**

*Sorption on Cs by PA experiments*

Fig 2 shows photos of the polar microscopy and autoradiography of thin rocks slices (< 10 \( \mu \text{m} \)) after 7 days. In fact, the thin rock samples were submerged into the stock solution containing \(^{137}\text{Cs} \) with a specific activity of 200 Bq/mL. Therefore, the corresponding images of polar microscopy and polar microscopy in Figs 2 and 3 were obtained and compared, respectively. Comparison of the exposure zones shown in Figs 2 and 3 of the mineral components in basalt and granite responsible for the sorption of Cs indicates that biotite is a major mineral content.

*Distribution coefficients \( (K_d) \) from batch tests*

According to the previous studies [8-9], Cs sorption on granite belongs to fast-uptake reaction and reaches equilibrium within 4 hours. After 7 days, the pH of Cs on basalt and granite was recorded as approximately 8.63 ± 0.6 and 7.94 ± 1.0, respectively, and showed a \( Eh \) within the 150–220 mV range in various Cs concentrations (~10^{-2}–10^{-7}M). Fig 4 displays that \( K_d \) in basalt is higher than that in granite at the three sizes (~0.297–0.833, ~0.149–0.297, and ~0.053–0.074 mm). In fact, the specific
surface area (SSA) of crushed basalt and granite by N$_2$-BET increased from 0.61 to 1.96 m$^2$/g as the particle size decreased, and $K_d$ showed a weaker relationship with SSA than the major mineral components. The comparison among crushed basalt, granite, and mudrock [5–7] in different particle sizes shows that the order variance of SSA in mudrock (~14.76–16.69 m$^2$/g) is greater than that in granite and basalt. Therefore, this demonstrates that the major influence on sorption of Cs in basalt and granite is iron–magnesium (Fe-Mg) minerals, with approximately 14.42% Fe$_2$O$_3$ in basalt, such as biotite or magnetite.

Steady-state asymptote

The apparent diffusion coefficient ($D_a$) and effective diffusion coefficient ($D_e$) could only be achieved when the through-diffusion experiments reached steady state. In other words, an important factor, the dimensionless parameter ($t_d = \frac{D_a \cdot t_f}{L^2}$), is introduced here to check whether the diffusion process reaches equilibrium. Crank (1975) [18] stated that the steady state of diffusion is achieved when $t_d$ is higher than 0.45. In this study, the $D_a$, $D_e$, and $t_d$ values of the experimental data shown in Table 2 for basalt and granite are all higher than 0.45, which suggests that the experimental time is sufficiently long to reach steady-state diffusion. Furthermore, a steady-state asymptote calculated only from the slope and interception was carried out in a lower or higher length/diameter ratio (L/D < 0.44 or L/D > 1.78) in the previous studies [9-10]. A non-reactive tracer (HTO) was applied to correct and identify the column geometry or retardation factor ($Rf$) beyond the L/D ratio. In this study, the diffusion length/diameter (L/D) was approximately 0.15 according to the column assembly shown in Fig 1.

Diffusion coefficients ($D_a$ and $D_e$) in basalt and granite
The diffusion parameters calculated from Eqs. (5) and (6) are listed in Table 2, summarizing the through-diffusion experiments on compact basalt and granite. In addition, the accumulative concentration curves for basalt and granite obtained by through-diffusion tests of Cs are shown in Fig 5. This shows that the time lag for the crushed and intact rocks to diffuse out is approximately 15 and 20 days, respectively. The through-diffusion tests showed a high R-square value (> 0.9) in each column and exhibited obvious retardation behavior in crushed and intact rocks. Moreover, Table 2 shows the lowest diffusion coefficients ($D_a = 0.56 \times 10^{-12} \text{ m}^2/\text{s}$ and $D_e = 0.39 \times 10^{-12} \text{ m}^2/\text{s}$) in intact basalt than those in other columns. These results indicate that intact basalt has a higher retardation effect than granite. In fact, in addition to the microporous structure (major sorption minerals), it also showed that the major retardation of Cs depended on porosity of compacted media.

Distribution coefficients and Retardation factors

The results in the batch and column tests are shown in Tables 3 and 4. The $K_d$ values and retardation factor ($R_f$) determined with the two methods are comparable within an order of magnitude. In fact, the S/L ratio decreased as is the case when switching from batch to column experiments, and the sorption effect became negligible. More recent studies [19–22] have reported effective diffusivities, i.e., the diffusivity of the radionuclide in the pore fluid, which should in principle be independent of sorption.

Conclusion

To assess the safety of the planned HLW repository, we need to predict the transport rates of radionuclides through these porous materials. In a preliminary geological
survey, laboratory studies are necessary to realize the diffusive transport of important radionuclides, such as $^{137}\text{Cs}$, through potential waste repository hot rocks. In this study, polar microscopy and autoradiography (PA experiments) and batch tests were very useful and straightforward in understanding the sorption behavior of Cs on biotite. Since diffusion is the dominant transport mechanism in the release of Cs through engineered and natural barriers, it is essential to accurately measure the diffusion coefficients ($D_a$ and $D_e$) for Cs by conducting through-column tests. Granite and basalt were selected and tested in through-diffusion experiments, and both crushed and intact samples were performed in the work to assess the actual geological environment. The observations indicated that intact basalt has a higher retardation effect than granite, and it may play a more suitable role than granite in the site selection for the HLW repository. In addition to the microporous structure (major sorption minerals), this also showed that the major retardation of Cs depended on the porosity of the compacted media. In fact, the S/L ratio decreased as is the case when switching from batch to column experiments and the sorption effect on minerals became negligible in retardation of radionuclide migration.

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References


Figure 1. Schematic plots of diffusion column: (a) crushed rocks; (b) intact rocks; (c) through-diffusion framework after assembly.