

Diffusion of some chemical species through a granite considering their geochemical properties

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Abstract—Through-diffusion experiments for some chemical species onto granite have been carried out to understand their diffusion characteristics according to their geochemical properties. The chemical species used in the experiment were classified into three groups as a nonsorbing tracer, simple cation and multivalent species. The difference in the diffusion process among the nonsorbing tracers was evaluated and discussed in terms of their interactions with the rock's pore surface. The extent of surface diffusion was examined from the view of sorption reversibility for the sorbing cations. For the multivalent species, two kinds of experiments were performed to study the effects of geochemical conditions in acidic and alkaline solutions. Chemical species and sorption properties were also investigated as a function of the pH and carbonates in order to examine the effects of the carbonates on diffusion in alkaline conditions.

Key words: Diffusivity, Surface Diffusion, Carbonate Complex, Granite, Uranium, Thorium, Europium

INTRODUCTION

When toxic wastes are disposed in a deep underground, the rock-mass may act as a natural barrier for a migration of a contaminant. Major water-conducting fractures in a rock mass are considered to form the main transport paths. Sorption onto mineral surfaces and diffusion into the pores in a rock matrix are two main retarding processes along a migration pathway. Thus, it is necessary to understand these diffusion mechanisms and to quantify the diffusion of contaminants into a rock matrix for a safety assessment [1,2].

Since the 1980's, diffusion parameters such as geometric factor ($\delta\tau^2$), effective diffusivity (D_e) or apparent diffusivity (D_a) of radioactive contaminants into geologic media have been measured actively with through-diffusion or in-diffusion setups under well controlled conditions in laboratories [3-5]. A theoretical relationship among various diffusivities was also developed to obtain D_a or D_e from the diffusivity in free-water, D_0 , which are available in the literature without experiments [6,7]. However, it is not convincing because there are more complex interactions among chemical species, solutions, and rock surfaces.

One of the main concerns for the investigators is the interaction between the chemical species and rock surfaces. Both a Knudsen and molecular diffusion involve a migration through a liquid phase within rock pores. There is another possibility for a contribution to a flux from a transport through a sorbed layer on the surface of a pore, a surface diffusion. Several researchers have suggested the contribution of a diffusion of sorbed ions since the measured diffusivities were much higher than the expected ones based on a pore diffusion [7,8]. The idea of sorbed phase diffusion is convincing, but it is not easy to provide sufficient evidence. Although the mobility of a sorbed phase will be smaller than that of a liquid phase, its concentration is much higher; under conditions such that the thick-

ness of the sorbed layer is appreciable, a significant contribution to a flux is possible. Direct measurement of surface diffusion is not feasible since the flux due to a diffusion through a liquid phase is always present in parallel.

Berry and Bond [8] reported that evidence has been obtained for the apparent existence of the process of surface diffusion for the migration of Sr and Am, but not Cs, through clay and sandstone. They explained that the amount of surface diffusion could depend on the strength of the interaction between the surface sites and the nuclides. On the other hand, Skagius and Neretnieks [7] studied cesium and strontium diffusion in a biotite gneiss and found that Cs showed a more obvious existence of a surface diffusion than Sr. Therefore, there would be more complex interactions between the solutes and rock-mass.

Generally, multivalent species are sensitive to geochemical conditions, that is, their chemical species and physico-chemical properties can be changed easily according to the geochemical conditions. Actinides, the representative multivalent species, reveal various chemical species depending on the pH and Eh [9]. And each species has different properties for a sorption and diffusion. Thus, multivalent species reveal a variety of diffusion characteristics along migration paths from a deep underground reducing condition to a surface oxidizing environment.

In relation to a diffusion study, microscopic imaging techniques have been developed: X-ray imaging techniques and autoradiography with microscope images. In the transport model, a rock mass is considered as an infinite medium, thus, whether nuclides diffuse infinitely into a rock mass is another important issue. Polak et al. [10] and Altman et al. [11] introduced X-ray absorption imaging techniques to quantify a diffusion in crystalline rocks. This technique is very effective for examining the extent of diffusion into a matrix without disturbing the system, but it still has somewhat of a range of uncertainties for quantification. Meanwhile, the combination of microscopic images and autoradiography or EPMA (electron probe micro-analyzer) on distribution of tracers on the rock surface can

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give evidence on specific interactions of species with certain minerals in the diffusion process [12].

The objectives of this experiment are as follows: The first is to obtain the diffusivities of some important radioactive nuclides onto domestic granite to provide parametric values for assessing the safety of disposed radioactive wastes in an underground environment. The second is to investigate the surface diffusion effect of the selected nuclides onto granite. And the third is to evaluate the effects of the geochemical conditions on the diffusion of multivalent species onto granite.

DIFFUSIVE TRANSPORT MODEL

When a crystalline rock is kept in contact with a solution, solutes can diffuse through rock pores or sorb onto the rock's surface. If solutes migrate through the rock pores in an aqueous phase at the same time as the sorbed solutes are migrating on the rock surface, the rate of the concentration change in the porous rock is described as [6,7]

$$\varepsilon \frac{\partial C_p}{\partial t} + (1-\varepsilon)\rho \frac{\partial q}{\partial t} = \varepsilon \frac{\delta}{\tau^2} D_v \frac{\partial^2 C_p}{\partial x^2} + (1-\varepsilon)\rho D_s \frac{\partial^2 q}{\partial x^2} \quad (1)$$

where, ε is the porosity of the rock, ρ is the density, δ is the constrictivity, τ^2 is the tortuosity, C_p is the concentration in a rock pore, q is the sorbed concentration on the rock's surface, D_v is the diffusivity in free water, and D_s is the surface diffusivity.

Sorption of solutes onto rock surfaces can be described by the equilibrium distribution coefficient, K_d . When the concentration of the diffusing species is at a tracer level, C_p has a linear sorption relationship with respect to q such as $q = K_d C_p$.

Local chemical equilibrium is assumed in a rock pore. Eq. (1) can be rearranged,

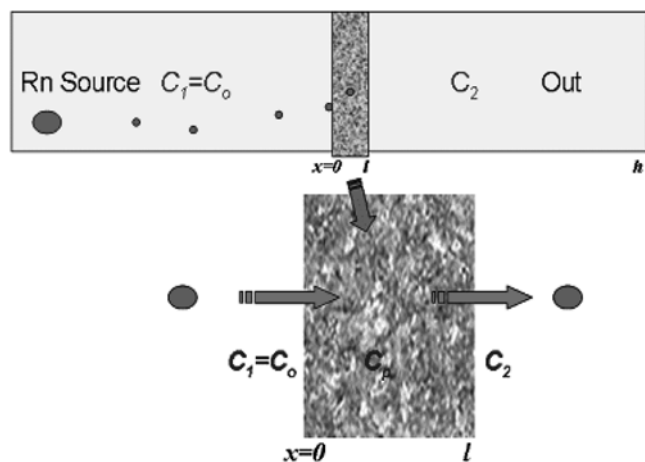


Fig. 1. Schematic diagram of the through-diffusion experiment.

$$\frac{\partial C_p}{\partial t} = D_a \frac{\partial^2 C_p}{\partial x^2} \quad (2)$$

where D_a is the apparent diffusivity and defined by,

$$D_a = \frac{\varepsilon D_p + (1-\varepsilon)\rho K_d D_s}{\varepsilon + (1-\varepsilon)\rho K_d} \quad (3)$$

Initial and boundary conditions in a through-diffusion system are shown in Fig. 1.

$$\begin{aligned} C_1(t=0) &= C_o \\ C_2(t=0) &= 0 \\ C_p(x, 0) &= 0 & 0 \leq x < l \\ C_p(0, t) &= C_o & t \geq 0 \\ C_p(l, t) &= C_2(t) & t \geq 0 \end{aligned}$$

where C_o is the initial concentration, l is the thickness of the rock coupon, and t is elapsed time.

The analytical solution was given by Crank [13]. The total amount of diffusing species at time t , $Q(t)$, which passed through a rock coupon at time t is,

$$\frac{Q}{lC_o} = \frac{D_a t}{l^2} - \frac{R}{6} - \frac{2R}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left[-\frac{D_a n^2 \pi^2 t}{l^2}\right] \quad (4)$$

where R is the rock capacity factor, $R = \varepsilon + (1-\varepsilon)\rho K_d$. As time passes infinity ($t \rightarrow \infty$), Eq. (4) approaches a linear relationship,

$$\frac{C_2(t)}{C_o} = \frac{D_a R}{lh} t - \frac{R}{6h} \quad (5)$$

where h is the container length of the experimental setup in Fig. 1

Obtaining a slope from a curve fitting using Eq. (5), the apparent diffusivity, D_a can be determined. In the case of nonsorbing species, D_a becomes D_p as K_d approaches zero in Eq. (3). Thus, Eq. (4) can be modified for a nonsorbing tracer.

$$\frac{C_2(t)}{C_o} = \frac{D_a t}{lh} - \frac{R}{6h} \quad (6)$$

EXPERIMENTAL

The granite used in this study was sampled from the Hwang-dung quarry in the Chung-Nam province, Korea. The chemical and mineralogical compositions of the granite are arranged in Table 1. The porosity and density were measured with a water saturation method as 0.003 and 2.55 g/cm³, respectively. Before the diffusion experiment, couples of rock coupons were vacuumed to remove the air from the rock pores and placed into a water flask for a month to saturate with water. A schematic diagram of the experimental setup is shown in Fig. 1. A granite coupon was fitted into the central cell, and the space between the rock and acrylate wall was sealed with a

Table 1. Chemical and mineralogical composition of the rock

Element	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	K ₂ O	CaO	Na ₂ O	MnO	P ₂ O ₅
%	74.5	13.5	0.4	3.0	0.9	3.6	2.2	3.3	0.1	0.1
Mineral	Quartz	Albite	Orthoclase	Anorthite	Hematite	Hypersthene				
%	35.8	27.7	21.1	10.5	3.0	2.3				

silicone adhesive.

Three groups of chemical species were used in experiments separately. In nonsorbing tracer test, tritium, chloride, and uranine, an organic dye, were prepared in the forms of tritiated water (THO), KCl, and Na-fluorescein ($C_{20}H_{10}Na_2O_5$) respectively. In a simple cation test, strontium, cobalt, and cesium were prepared in the form of chloride compound such as $SrCl_2$, $CoCl_2$, and $CsCl$. And in a multivalent species test, uranium, thorium and europium were prepared in the form of nitrates such as $UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 5H_2O$, and $Eu(NO_3)_3 \cdot 5H_2O$. The experiments for the multivalent species were designed as two conditions: at pH 4 and at pH 9.5. The test at pH 4 was carried out in a 0.1 M KCl solution, while the test at pH 9.5 was in 0.1 M $NaHCO_3$ [14,15]. The pH was adjusted by adding dilute NaOH or HCl.

The diffusion experiments were started by placing the tracer containing solution into the source reservoir where a blank solution was already placed in both reservoirs for a month. The solutions were stirred mildly with magnetic stirrers. At an appropriate time interval, a 1 ml aliquot was taken from the diffused reservoir to determine the concentration of the tracer. Then the same volume of the solution was replaced to maintain a balance between the two reservoirs.

The concentration of the tritium was analyzed with a Packard liquid scintillation counter, the uranine was analyzed with the HP diode array spectrophotometer at a wavelength of 494 nm, and the other species were analyzed with a Varian ICP-MS (induced coupled plasma - mass spectroscopy).

RESULTS AND DISCUSSION

The method described in Eqs. (5) and (6) was applied to the experimental data. After plotting the concentration of the diffusing species against time, the values of D_e or D_a were obtained from the slopes and arranged in Table 2. The D_v values of the tracers were obtained from the literature [3]. Fig. 2 shows the diffusion curves of the three nonsorbing tracers; tritium, chloride, and uranine. In this calculation, THO was selected as the basic tracer, because it has the same physicochemical properties as water, and groundwater is the main flow medium in a contaminant transport. By definition,

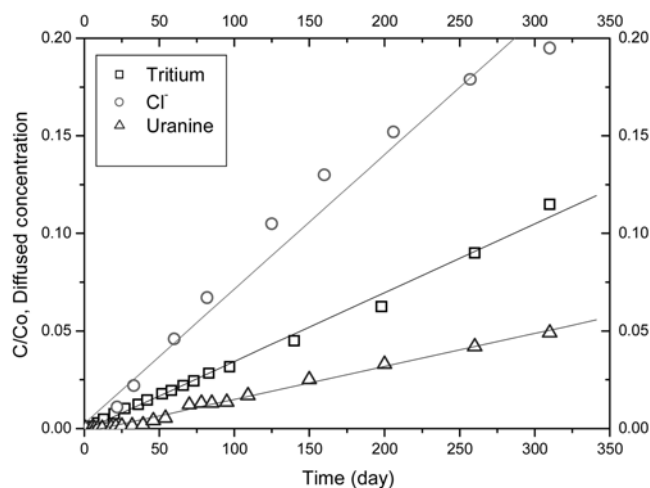


Fig. 2. Diffusion curves of the nonsorbing tracers against the time.

D_e represents the retardation effects from a geometric hindrance when compared to diffusion in free water and is expressed with a geometric factor, δ/τ^2 . It can be written

$$D_e = \epsilon D_p = \epsilon \delta / \tau^2 D_v \quad (7)$$

The geometric factor (δ/τ^2) of the granite is obtained as 0.236 from the tritium data in Table 2. Onto the Swedish granite the D_e of uranine is $2.3 \times 10^{-14} \text{ m}^2/\text{s}$, $\epsilon = 0.002$, and $\delta/\tau^2 = 0.023$ [3], while onto the Japanese granodiorite the D_e of THO is $5.3 \times 10^{-12} \text{ m}^2/\text{s}$, $\epsilon = 0.03$, $\delta/\tau^2 = 0.074$ [16]. Considering this trend, it can be said that the porosity has a great effect not only on the geometric factor but also on diffusivity [2,16]. Chloride diffused faster than tritium. Generally, the surface of a rock pore is charged negatively in most of the neutral and alkaline regions. Thus, anions do not interact with the rock surface and do not penetrate into the micropores of the rock due to the anion exclusion effect. But these anions move fast through macropores. On the other hand, the uranine shows a smaller D_e value than tritium and Cl^- . It can be interpreted that the uranine has difficulty in penetrating micropores due to its large molecular size. Thus, the order of the diffusivity is $Cl^- > \text{tritium} > \text{uranine}$ or in general terms, $\text{anion} > \text{water} > \text{organic dye}$ into the granite. Even though the

Table 2. Diffusivities of the chemical species onto the granite

	K_d (ml/g) % of RS*		D_v ($\times 10^{-9} \text{ m}^2/\text{s}$)	D_e ($10^{-12} \text{ m}^2/\text{s}$)		D_a (m^2/s)		Reference
				Exp.	Cal.	Exp.	Cal. ($D_s=0$) [#]	
THO	0	-	2.4	1.7	-	-	5.7×10^{-10}	16
				5.3	-	2.1×10^{-10}		
Cl^-	0	-	2.0	2.6	-	-	8.7×10^{-10}	
Uranine	0	-	0.45	0.64	-	-	2.1×10^{-10}	6
				0.023				
Sr^{+2}	20	90	0.79	-	0.56	6.4×10^{-14}	1.9×10^{-14}	17
	0.0023			0.2		1×10^{-14}		
Co^{+2}	280	33	0.85	-	0.6	4.8×10^{-16}	8.3×10^{-16}	16
Cs^+	100	35	2.0	-	1.4	7.3×10^{-15}	5.4×10^{-15}	
	0.16			5.1		1.1×10^{-11}		

*% of RS : percentage of reversible sorption [17]

[#]Cal: D_a value calculated when $D_s=0$

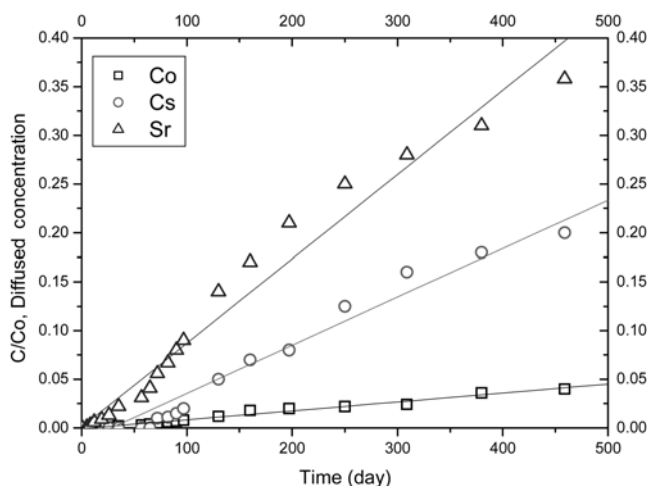


Fig. 3. Diffusion curves of Sr, Co, and Cs against the time.

uranine has been used popularly in hydrodynamic field tests, it is necessary to select an appropriate basic tracer according to its purpose compared to velocity of groundwater.

To express the retardation effects for a sorbing tracer by a geometric hindrance and sorption, the apparent diffusivity, D_a , should be used. However, some researchers calculate the effective diffusivity, D_e of sorbing tracers from experimental diffusion curves [17]. This may evoke confusion for the concept of a diffusion process. For simple sorbing cations such as Sr, Co, and Cs in this experiment, the D_a values are determined from the diffusion curves in Fig. 3 and arranged in Table 2. When surface diffusion does not occur, the apparent diffusivity may turn into a simple form as,

$$D_a = \varepsilon D_p / R \quad (8)$$

For a nonsorbing tracer case, D_a will be equal to D_p .

To check the effect of surface diffusion, D_a is calculated and arranged in Table 2 by assuming there is no surface diffusion by using Eq. (8). The experimental D_a of Co and Cs reveal a similar or smaller value than the simulated, D_a' . It implies a stronger fixation of the species on the rock surface than the expected one. On the while, the experimental D_a of Sr is three times larger than the assumed D_a' . It may imply that a considerable surface diffusion occurred in the case of Sr, while it did not do so in the case of Co and Cs. D_s of Sr is obtained as $5.3 \times 10^{-14} \text{ m}^2/\text{s}$ by Eq. (3).

The apparent diffusivity can be divided into two parts:

$$D_a = \frac{\varepsilon D_p + (1 - \varepsilon) \rho K_d D_s}{\varepsilon + (1 - \varepsilon) \rho K_d} = \frac{\varepsilon}{R} D_p + \frac{(1 - \varepsilon) \rho K_d}{R} D_s \quad (9)$$

The first term in Eq. (9) expresses the retardation effects by a geometric hindrance, and the second term expresses a sorbed phase diffusion. This is a similar expression to the different definition of D_e by Yamaguchi et al. [17]. When surface diffusion is the predominant diffusion process, the obtained D_a is expected to depend on the sorption properties or the rock capacity factor, R , as shown in Eq. (9). The rock capacity factor, R , is about 51 for Sr in this system. Yamaguchi et al. [17] plotted the diffusivities as a function of the sorptivity, ρK_d . This R value is in the sorptive region in Yamaguchi's plot. Thus, the second term of Eq. (9) would be dominant and a surface diffusion acts as the main migration mechanism for Sr in

this system. If R becomes less than 1, it is in a poorly sorptive region: the pore diffusion is dominant corresponding to the first term of Eq. (9). However, this plot is not applicable to all sorbing tracers because there are irreversibly sorbing tracers without surface diffusion like Co and Cs in this system. Therefore, a microscopic explanation is required or another measure to justify surface diffusion. As a measure of diffusion mechanism, Berry and Bond [8] suggested the sorption strength. They explained that a strongly sorbing species has a small surface diffusion contribution, whereas a weakly sorbing species has large one. For Sr, only a limited sorption is seen, suggesting that the interaction between Sr and the surface sites may be weak. The sorbed species is possibly sited predominantly in the outer Helmholtz layer. The Sr may be able to diffuse rapidly through this layer, resulting in the observed surface diffusion term. Cs appears to have a strong interaction with the surface sites, sorbing to a large extent. The sorbed species may well sit in the inner Helmholtz layer and there could be a large resistance to a surface diffusion due to the strength of the Cs/surface forces. This would result in a much smaller surface diffusion term. However, this explanation is not also sufficient to understand the relationship between a sorption and a surface diffusion. As mentioned in the introduction, it is reported that a strongly sorbing Cs moved with a surface diffusion onto a biotite gneiss surface [7].

The mobility related to sorption and diffusion could be quantified by the reversibility of a sorption. A reversibly sorbing species could easily sorb onto the rock surface and rebound again in the solution or move to an adjacent surface, while an irreversible one could hardly do so. Thus, the reversibility of sorption seems to be one of the key factors controlling surface diffusion. It is well reported that Sr sorbs reversibly onto a granite surface by ion exchange and desorbs easily [18]. The measured K_d values and reversibility of a sorption onto the granite are arranged in Table 2. Thus, it is reasonable that Sr moves on the surface of the granite by sorbing and desorbing successively. On the other hand, about 70% of the Co and Cs was fixed strongly onto the granite surface. It is known that Cs and Co sorb preferentially on mica or ferro-manganese oxides of rock surface [18]. Such sorption is a very strong reaction and the sorbed nuclides are hard to move on the sorbed phase. Thus, the reversibility of sorption seems to be one of the key factors controlling surface diffusion.

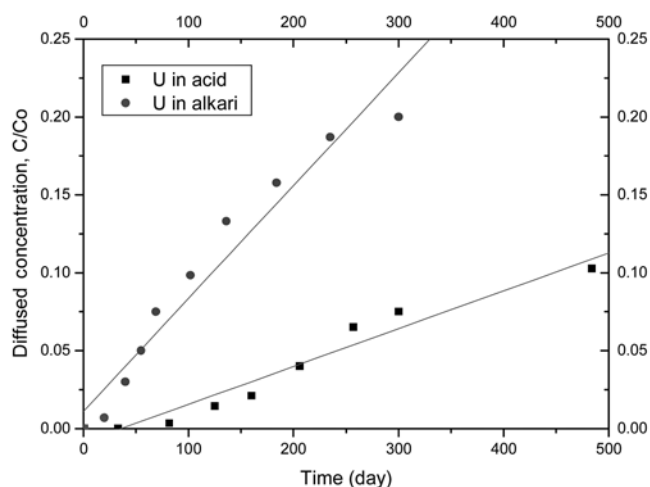


Fig. 4. Diffusion curves of uranium at pH 4 and pH 9.5.

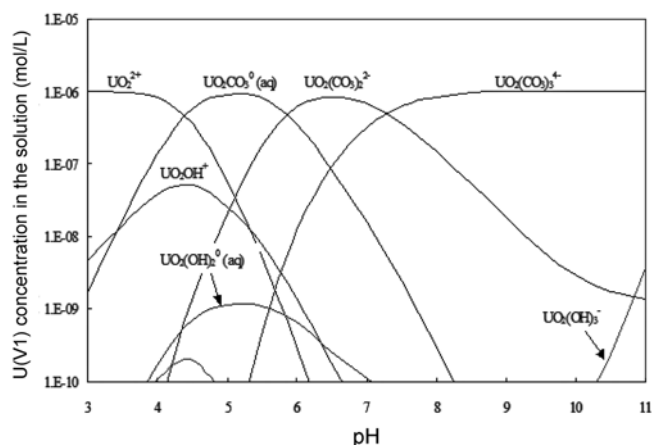


Fig. 5. A typical example of a uranium speciation as a function of the pH [18].

sion. Therefore, if a cation sorbs reversibly, then it may have a chance to move into rock pores by a surface diffusion.

Fig. 4 shows the diffused concentrations of uranium with time at pH 4 and pH 9.5. The D_a value of U at pH 9.5 is about two times larger than that of the uncomplexed uranyl ion at pH 4. It suggests that the chemical properties of the uranium species depend on the pH. Usually, multivalent species have complex speciation and their dominant species are easily transformed into other ones according to the geochemical conditions. Fig. 5 shows a calculated distribution of U species as a function of the pH, which is depicted by Baik et al. [19]. There are some distinctive dominant species at acidic and alkaline conditions regardless of the concentrations of U and carbonates, while many complex species of uranium competitively exist near a neutral condition according to concentrations of U and carbonates as shown in Fig. 5 and other plots [20]. The dominant oxidation state of uranium is hexavalent and the uranyl cation, UO_2^{2+} , is predominant at acidic conditions. Complexation of UO_2^{2+} by chloride, nitrate, or carbonate is negligible. Whereas, more than 99% of the uranium is present as a monomeric tri-carbonate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$ at an alkaline condition around pH 9. It is noteworthy that the diffusivity of the anionic uranium carbonate complex is larger than that of the master cationic species, UO_2^{2+} , both in water and onto the granite. Fig. 6 shows the sorption of uranium onto the crushed granite particles according to the pH and to the carbonate con-

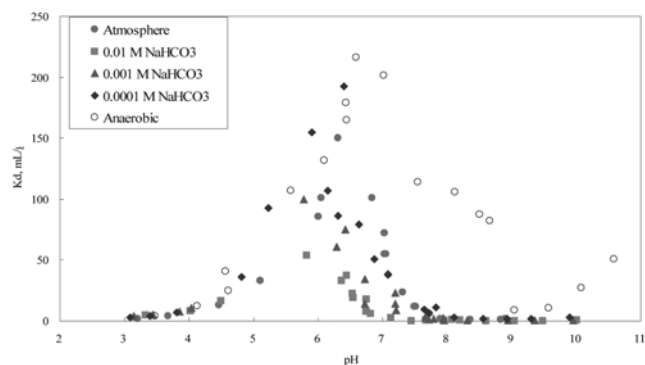


Fig. 6. Sorption profiles of uranium as functions of the pH and carbonates.

centration [19]. The uranium sorbs significantly near a neutral condition, but sorbs very poorly at the acidic and alkaline conditions. And a higher concentration of the carbonates reveals a lower sorption. Because the uranium carbonate complexes are negatively charged, they sorb poorly and diffuse more quickly through rock pores without any interactions than the other multivalent species. Both pore diffusion and surface diffusion might contribute to the diffusion of U in the interconnected pore space of the granite. However, the surface diffusion is only expected to be significant when large amounts of species are sorbed onto the solid. The surface diffusion was less significant from the 0.1 M KCl solution in this system because of the competing effect for the sorption sites by the high concentration of the K^+ ions. The rock capacity factor, R , was therefore very close to the value in Eq. (9), which denotes the poor sorption of uranium onto the rock and a smaller effect of a surface diffusion than that of a pore diffusion.

Yamaguchi et al.'s experimental data for uranium are also arranged in the Table 3 for comparison [14,15]. They obtained K_d values from the diffusion curves, while sorption data were obtained from the batch test in this study. K_d values between two studies show quite different aspects. In this study K_d values of at pH 4 and at pH 9.5 have similar values, while Yamaguchi et al.'s results show about a hundred times difference between pH 4 and pH 9.3. There is the possibility of revealing this distinctive difference in curve fitting to obtain rock capacity factor (R) or K_d . This method may give large errors due to extrapolating of the diffusion curves.

Table 3. Diffusivities of the multivalent species onto the granite

		K_d (ml/g)		D_v ($\times 10^{-9}$ m ² /s)	D_e ($\times 10^{-13}$ m ² /s)		D_a (m ² /s)	
		pH 4	pH 9.5		pH 4	pH 9.5	pH 4	pH 9.5
U	Exp.	4.0	5.6	0.43	-	-	5.4×10^{-14}	1.7×10^{-13}
	*Cal.				3.1	3.1	3.1×10^{-14}	2.2×10^{-14}
	*Yama	0.001	0.11		0.22	1.4	3.5×10^{-12}	4.7×10^{-13}
Th	Exp.	1000	43	0.15	-	-	4.5×10^{-16}	1.1×10^{-14}
	*Cal.				1.1		4.3×10^{-17}	1.0×10^{-15}
Eu	Exp.	150	79	1.0	-	-	3.1×10^{-15}	3.2×10^{-17}
	*Cal.				7.1		1.9×10^{-15}	3.5×10^{-15}

*Cal: D_a value calculated when $D_s=0$

*Yama: Yamaguchi et al.'s experimental data at pH 4 and pH 9.3 conditions [14,15]

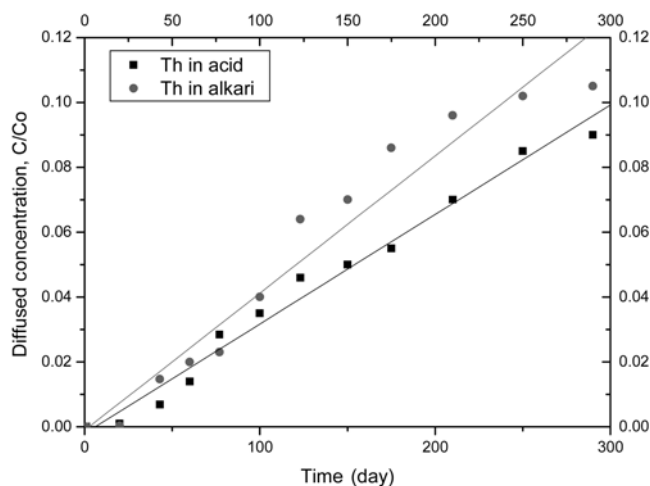


Fig. 7. Diffusion curves of Th at pH 4 and pH 9.5.

Fig. 7 shows the diffusion curves of Th at pH 4 and pH 9.5. The D_a value at pH 9.5 is higher than the D_a at pH 4 as is similar to the U case. The thorium carbonate complex is also negatively charged at pH 9.5 and diffuses faster than the cationic thorium or thorium hydroxides at pH 4. To examine the diffusion modes of thorium, a simulation work is carried out by considering only pore diffusion and arranged together with the experimental results in Table 3. When the experimental data are compared to the simulated one, the former shows about a ten times larger value than the latter. Thus, a surface diffusion has a significant role in the highly sorptive thorium case.

In the case of Eu, the D_a value at pH 4 is two orders larger than D_a at pH 9.5 as shown in Fig. 8. It is the opposite result for the U and Th cases, especially when it comes to compare with the Th cases which have similar geochemical properties. It would be explained by the tendency of forming colloidal materials or of colloidal transport for this diffusive difference between Eu and Th. Even though it may require strict supporting experiments to elucidate the diffusive behavior of Eu. The solubility of Eu and Th is larger than 10^{-4} M at acid solutions, but it becomes about a 10^{-8} M order or less at an alkaline solution [9]. Both nuclides can form carbonate complex at

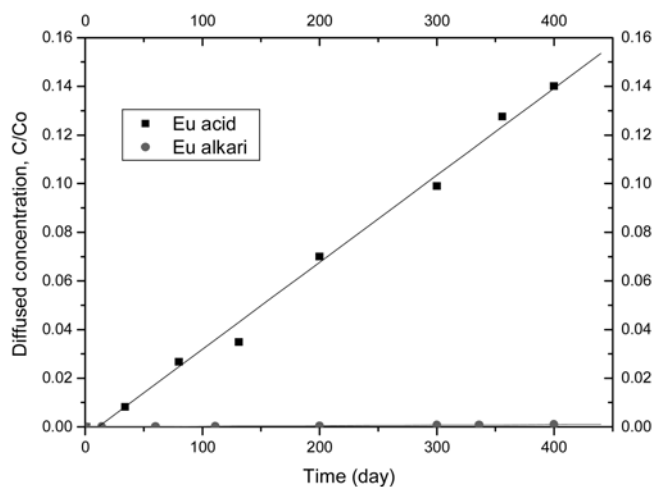


Fig. 8. Diffusion curves of Eu at pH 4 and pH 9.5.

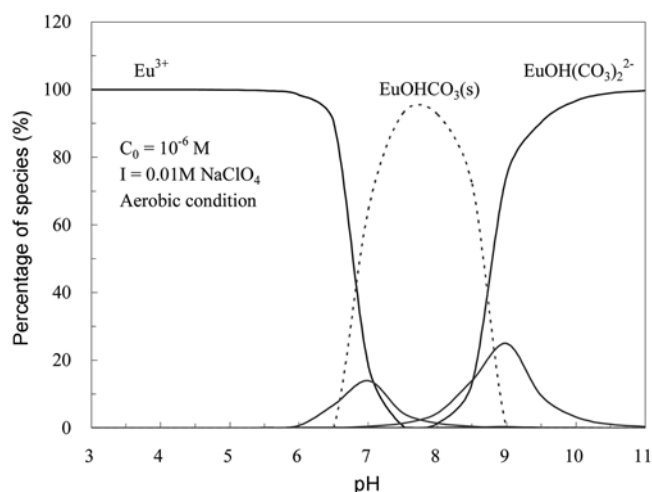


Fig. 9. Eu species as a function of the pH [20].

this experimental alkaline condition as shown in Fig. 10 [21]. Park et al. [23] carried out a migration experiment for U, Eu and Th through the same kind of fractured granite at an alkaline condition. And the result shows Th migrated very poorly but a very little portion of Th moved by colloidal transport, while Eu showed no elution. Thus, such trend can be applied for understanding this diffusion process.

When Eu and Th diffuse through the interconnected pores of the granite at pH 9.5, most of the nuclides sorbs onto the pore surface at first by considering its high K_d value as shown in Table 3. Baik et al. [21] reported that Eu has a stronger affinity to sorb onto granite than that to form carbonate complexes in the solution. Meanwhile at this stage, thorium carbonate complex has less strong affinity with pore surface and better tendency to move through the pore than europium complex. The most diffusible europium carbonate complex shown in Fig. 9 was already in a very low concentration around a 10^{-8} M order at the source diffusing side. As a result, there was no remarkable increase of the Eu concentration with time at the diffused container and it revealed a very low slope of diffusion curves.

Fig. 10 shows the sorption curves of U, Th and Eu as a function of the pH. They show a wide range of K_d values against the pH range. In the whole experimental pH range, U shows the weakest sorption onto the granite, while Th and Eu show high K_d values at the acidic region. At an acidic condition, D_a values of the three multi-

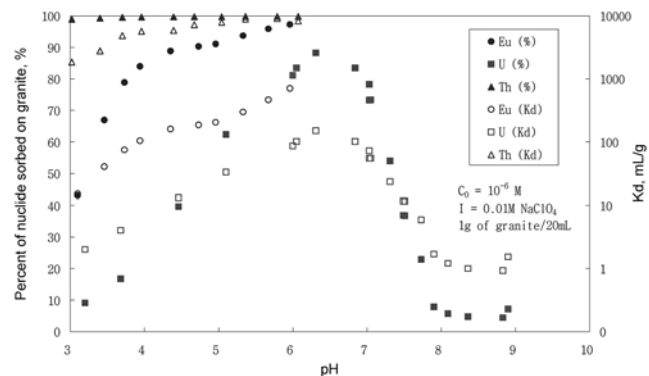


Fig. 10. Sorption profiles of U, Th and Eu as a function of the pH.

valent species are in the order of $U > Eu > Th$, while K_d is $Th > Eu > U$. It means that a weakly sorbing species diffuses easily through the rock. In the alkaline condition, it reveals a high degree of uncertainty when measuring the K_d values of Th and Eu, because their low solubility and their strong sorption result in a very low final concentration. At the alkaline condition, the tendency to form negatively charged carbonate complexes results in a faster diffusion than at the acid condition. However, because Eu has not only a very low solubility, but also a strong sorption affinity resulting in a very poor colloidal movement at the alkaline condition, the D_a of Eu at pH 9.5 is seemingly much lower than D_a at pH 4.

CONCLUSIONS

Diffusive properties of three kinds of chemical species onto granite reveal quite different aspects in the through-diffusion experiments. Among the nonsorbing tracers, chloride diffuses faster than tritium and uranine due to the anion exclusion effects. In the case of simple cations, the sorption reversibility provides a hint of a surface diffusion. The reversibly sorbing species, Sr, has a remarkable surface diffusion contribution, whereas the irreversibly sorbing species like Co and Cs reveals a little contribution. In the case of the multivalent species, the diffusion and sorption of U, Th, and Eu are influenced greatly by the geochemical conditions. Diffusivities at an acidic condition are in the order of $U > Eu > Th$, while K_d is $Th > Eu > U$. That is, a weakly sorbing species diffuses easier than the others. In the alkaline solution, the multivalent species are present as hydroxyl-carbonate complexes and move as an anion. Thus, U and Th reveal a higher diffusivity than the uncomplexed species in the acidic states. However, because Eu has stronger sorption and less forming diffusive complex at the alkaline condition than Th, the diffusivity of Eu at pH 9.5 is seemingly much lower than that at pH 4.

From this experimental result, the following should be considered when assessing the migration of chemical species: diffusion into the rock mass is an important process for nonsorbing species as well as sorbing ones. Diffusive properties of chemical species can be changed significantly according to the changes of geochemical conditions along migration paths.

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NOMENCLATURE

C, C_2 : concentration of a solute in a diffused side [kg/m^3]
 C_o : initial concentration at a source side [kg/m^3]
 C_p : concentration of a solute in a rock pore [kg/m^3]
 D_a : apparent diffusivity [m^2/s]
 D_e : effective diffusivity [m^2/s]
 D_p : pore diffusivity [m^2/s]
 D_s : surface diffusivity [m^2/s]
 D_v : diffusivity in free water [m^2/s]
 K_d : distribution coefficient [l/kg]

l : thickness of the rock coupon [m]
 R : rock capacity factor, $R = \varepsilon + (1 - \varepsilon)\rho K_d$ [-]
 q : sorbed concentration on a solid surface [kg/kg]

Greek Letters

ε : porosity of the rock
 ρ : density
 δ : constrictivity
 τ^2 : tortuosity

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