

# Uranium Diffusion in Soils and Rocks

Stephanie M. Moore

*Civil and Environmental Engineering, Colorado State University, Fort Collins, Colorado, USA*

Charles D. Shackelford

*Civil and Environmental Engineering, Colorado State University, Fort Collins, Colorado, USA*

## Abstract

The results of a study undertaken to review the process of diffusion of uranium in soils and rocks are presented and discussed. After some background on the geochemistry of uranium and the different definitions for the diffusion coefficient in porous media, i.e.  $D^*$ ,  $D_e$ ,  $D_a$ , values of  $D^*$ ,  $D_e$ , and/or  $D_a$  from the literature are summarized, analyzed and discussed. Diffusion of uranium in compacted bentonite is shown to increase semilog linearly with an increase in porosity (decrease in dry density), and appears to be significantly slower than that in other soils, probably due to the existence of semipermeable membrane behavior and interparticle/intraparticle diffusion as an attenuation mechanism. The effect of attenuation is shown to increase the variability in  $D_a$  relative to that in either  $D^*$  or  $D_e$ , and the variability in  $D^*$ ,  $D_e$ , and  $D_a$  is shown to be greater in compacted bentonite than in unfractured biotitic granite, likely due to a more homogeneous pore structure and a lesser attenuation capacity for the biotitic granite. Overall, the typical preference for reporting only  $D_a$  values is shown to severely restrict the usefulness of the literature on the subject.

## Introduction

Despite the recent nuclear crisis at the Fukushima Dai-ichi nuclear power plant in Japan, interest in the USA in the use of nuclear power as a source of energy to reduce both global greenhouse gas emissions resulting from fossil-fuel generation of electricity and the dependence on the use of imported oil remains strong. As a result, there is renewed interest in uranium mining in the USA as a source of fuel for nuclear power plants as well as several other applications. Also, uranium mining activity remains strong in several other countries, including Canada and Australia, and the potential environmental impact resulting from disposal of uranium based mill tailings and waste rock is an ongoing issue.

Uranium contamination of soil can occur due to natural processes acting on uranium inherently present in soil and rock, or from anthropogenic activities related to the extraction and processing of uranium from soil and rock for industrial applications, e.g. for use as fuel for nuclear power production and as a fissionable material in nuclear weapons. Examples of soil contamination resulting from natural processes include the deposition of uranium originally discharged into the atmosphere via wind erosion and volcanic activity or as a result of water erosion, dissolution, and precipitation. Examples of anthropogenic activities that may result in soil contamination include uranium mining and milling, uranium processing, phosphate mining, heavy metal mining, coal use and inappropriate waste disposal (Gavrilescu et al. 2009). Although soil contamination by uranium from natural processes far exceeds that from anthropogenic activities (Gavrilescu et al. 2009), such activities as mining and milling operations result in potential localized sources of uranium in the forms of waste rock and mill tailings, respectively, that can lead to significant environmental impacts if not contained properly.

Accordingly, a study was undertaken to review the literature pertaining to the diffusion of uranium in soils and rocks. The primary purposes of the study were to evaluate the ranges of diffusion coefficients with respect to uranium diffusion in soils and rocks, to determine any trends in the values, and to identify any missing information for the purpose of directing future research efforts. The study was limited to include only liquid-phase diffusion of uranium through natural soils and rocks or compacted soils used as engineered barriers (e.g. compacted bentonites) and, therefore, does not include gas-phase

diffusion of radon or other decay products of radioactive uranium, nor diffusion coefficients resulting from stabilization/solidification of uranium with pozzolanic materials (e.g. cement).

## **Geochemistry of Uranium**

Uranium (U) is a [metallic chemical element](#) in the [actinide](#) series of the [periodic table](#), with an [atomic number](#) of 92. Uranium occurs naturally in low concentrations of a few [parts per million](#) in soil, rock and water, and is commercially [extracted](#) from uranium-bearing [minerals](#) such as [uraninite](#). Although there are six unstable isotopes (i.e. radioisotopes) of uranium with between 141 and 146 [neutrons](#), only uranium-238 ( $^{238}\text{U}$ ), uranium-235 ( $^{235}\text{U}$ ) and uranium-234 ( $^{234}\text{U}$ ), occur naturally, with  $^{238}\text{U}$  and  $^{235}\text{U}$  being the most abundant at 99.27% and 0.72%, respectively (Gavrilescu et al. 2009). Uranium decays slowly via emission of an alpha particle, such that the half lives of the  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$  are 4.47 billion, 245.5 thousand, and 704 million years, respectively (Gavrilescu et al. 2009).

Uranium in aqueous solutions forms many chemical species as a result of hydrolysis and complexation reactions. These reactions are a function of the chemical conditions, especially the *pH*, oxidation–reduction (redox) potential (*Eh*), and the concentrations of the complexing ligands, such as  $[\text{OH}]^-$ ,  $[\text{HCO}_3]^-$ ,  $[\text{CO}_3]^{2-}$ ,  $[\text{H}_2\text{PO}_4]^-$ ,  $[\text{HPO}_4]^{2-}$ ,  $[\text{PO}_4]^{3-}$ ,  $[\text{SO}_4]^{2-}$ . These reactions control the mobility of uranium in soils, primarily because of the different charges of the various chemical species.

For example, uranium can exist in the +3, +4, +5 and +6 oxidation states, although the +4 (U(IV)) and +6 (U(VI)) oxidation states are the most important because only U(IV) and U(VI) are stable in aqueous solution. Thus, redox reactions that convert soluble U(VI) to insoluble U(IV) and vice versa are particularly important. Also, the formation of negatively charged uranium-ligand complexes, such as the uranium carbonate species (e.g.  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ ), generally decreases the sorption of uranium to soils and, therefore, increases uranium mobility.

Deposits of uranium generally contain relatively insoluble U(IV) in the form of the mineral uraninite,  $\text{UO}_2(\text{c})$ . However, upon exposure of these deposits to water and oxygen during mining activities and deposition of uranium bearing mine wastes, U(IV) is oxidized to U(VI) in the form of the aqueous soluble uranyl cation,  $\text{UO}_2^{2+}$  (Flury & Harsh 2000). Oxidation from U(IV) to U(VI) increases the solubility of the uranium and, therefore, the potential for release of uranium into the environment.

The subsequent fate of U(VI) released from uraninite is governed by precipitation, the formation of solution complexes, and sorption/desorption to/from the solid phase due to surface complexation or ion exchange mechanisms of sorption (Bai et al. 2009). For example, if the *Eh* of the system decreases to a value below about 100 mV, precipitation of highly insoluble U(IV) minerals is possible (Zielinski et al. 1987). Also, uncomplexed  $\text{UO}_2^{2+}$  has a greater tendency to form complexes with organic substances, such as the fulvic and humic acids, than many other metals with a +2 valence (Gavrilescu et al. 2009). Finally, U(VI) is strongly sorbed to mineral constituents, such as iron oxides (e.g. hematite) and ferric oxyhydroxides (e.g. goethite), particularly for *pH* in the range  $5 \leq \text{pH} \leq 8.5$  (e.g. Langmuir 1978, Hsi & Langmuir 1985, Bruno et al. 1995, Duff & Amrhein 1996). However, carbonate complexing of U(VI) can appreciably reduce this adsorption (Gavrilescu et al. 2009).

## **Diffusion**

### **Significance of Diffusion**

Diffusion of contaminants is a significant, if not dominant, contaminant transport process in scenarios where advection (i.e. hydraulically driven transport) is slow or negligible (Shackelford 1988). Such scenarios typically involve low-permeability ( $\leq 10^{-9}$  m/s), fine-grained soils (e.g. clay), and include analyses related to evaluation and design of engineered containment barriers for waste disposal (e.g.

landfills, surface impoundments, etc.), analyses related to the migration of contaminants in low permeability strata (i.e. aquitards and aquicludes), and analyses related to the remediation of existing contaminated soils (Shackelford & Lee 2005). In particular, the process of matrix diffusion, whereby contaminants diffuse from interconnected pores into the surrounding intact clay or rock matrix, may be an important attenuation mechanism when contaminant transport occurs through structured clay and rock formations (e.g. Parker et al. 1994). Finally, Bai et al. (2009) note the importance of intragranular diffusion of U(VI) in sediments from the DOE site at Hanford, WA, and the importance of interparticle diffusion for radionuclide waste disposal at Yucca Mountain, NV, and elsewhere. Thus, knowledge of diffusion of uranium in soils and rocks is important in mining and mine waste scenarios.

## Governing Equations

Diffusion in saturated porous media is governed by Fick's first and second laws. Fick's first law for one-dimensional diffusion may be written as follows (Shackelford & Daniel 1991):

$$J_d = -\varepsilon D^* \frac{\partial c}{\partial x} \quad (1)$$

where  $J_d$  is the diffusive mass flux of the chemical species perpendicular to the total cross-sectional area of the porous medium [ $\text{ML}^{-2}\text{T}^{-1}$ , where M = mass, L = length, and T = time],  $\varepsilon$  is the porosity,  $D^*$  is the effective diffusion coefficient [ $\text{L}^2\text{T}^{-1}$ ],  $c$  is the concentration of the chemical species defined with respect to the volume of pore water [ $\text{ML}^{-3}$ ], and  $x$  is the distance in the direction of diffusion [L]. The effective diffusion coefficient given by Eq. 1 is related to the aqueous-phase or "free-solution" diffusion coefficient for the same chemical species,  $D_o$  [ $\text{L}^2\text{T}^{-1}$ ] as follows:

$$D^* = \tau_a D_o \quad (2)$$

where  $\tau_a$  is the dimensionless apparent tortuosity factor ( $0 < \tau_a < 1$ ) as defined by Shackelford & Daniel (1991). Malusis & Shackelford (2002) further defined  $\tau_a$  as the product of the actual matrix tortuosity factor,  $\tau_m$  ( $0 < \tau_m < 1$ ), which accounts for the reduction in diffusion due to the geometric tortuosity of the network of connected pores that exist within the porous medium, and a restrictive tortuosity factor,  $\tau_r$  ( $0 < \tau_r \leq 1$ ), as follows:

$$\tau_a = \tau_m \tau_r = \tau_m \prod_{i=1}^N \tau_i = \tau_m (\tau_1 \tau_2 \cdots \tau_N) \quad (3)$$

where  $N$  represents the number of all other factors,  $\tau_i$ , that act to reduce or restrict the diffusive solute flux through the porous medium, such as ion exclusion in clays, constrictivity due to non-uniform cross-sectional areas of pores, dead-end or otherwise non interconnected pores, etc. Values of  $\tau_a$  for a given porous medium generally cannot be determined *a priori* and, therefore, must be back calculated by dividing a measured value of  $D^*$  for a given porous medium using a nonreactive tracer, typically an anion (e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ) or radioisotope of water (e.g. tritium or deuterium), by the value of  $D_o$  for the same tracer in accordance with Eq. 2.

The  $\tau_r$  appearing in Eq. 3 also may be considered as the factor by which  $\varepsilon$  is reduced to an effective or through-diffusion porosity,  $\varepsilon_{eff}$ . For example, substitution of Eqs. 2 and 3 into Eq. 1 results in the following alternative form of Fick's first law (e.g. Pearson 1999):

$$J_d = -\varepsilon \tau_a D_o \frac{\partial c}{\partial x} = -\varepsilon \tau_m \tau_r D_o \frac{\partial c}{\partial x} = -(\varepsilon \tau_r) (\tau_m D_o) \frac{\partial c}{\partial x} = -\varepsilon_{eff} D_p \frac{\partial c}{\partial x} \quad (4)$$

where  $\varepsilon_{eff}$  is equal to the product  $\tau_r \varepsilon$ , such that  $\varepsilon_{eff} \leq \varepsilon$ , and  $D_p (= \tau_m D_o)$  is referred to as the "pore diffusion coefficient" (Skagius and Neretnieks 1986). The distinction between Eqs. 1 and 4 is important for two reasons. First, when  $\tau_r < 1$ , the value of  $D^*$  (Eq. 2) will be less than the value of  $D_p$  (Eq. 4). Second, both  $\varepsilon_{eff}$  and  $D_p$  in Eq. 4 are unknown parameters, i.e. since both  $\tau_m$  and  $\tau_r$  generally are not known *a priori*, whereas only  $D^*$  is unknown in Eq. 1, i.e. since  $\varepsilon$  generally is known *a priori*. This second reason is important because  $\varepsilon_{eff}$  often is assumed to be equal to  $\varepsilon$ , such that values of  $D^*$  defined in accordance with Eq. 2 are reported even though Fick's first law has been defined in accordance with Eq. 4. As a result, Fick's first law as given by Eq. 1 was in this study.

An alternative definition of the effective diffusion coefficient commonly encountered is one that includes the porosity, or:

$$D_e = \varepsilon \tau_a D_o = \varepsilon D^* \quad (5)$$

where  $D_e$  is the effective diffusion coefficient. When the effective diffusion coefficient is defined by Eq. 5, Fick's first law for diffusion in saturated porous media must be written as follows:

$$J_d = -D_e \frac{\partial c}{\partial x} \quad (6)$$

In accordance with Eq. 5, since  $\varepsilon < 1$  for porous media,  $D^* > D_e$ . The important difference between Eqs. 1 and 6 is that  $D^*$  is independent of  $\varepsilon$  whereas  $D_e$  is not.

Fick's second law governing transient diffusion of a reactive chemical species subject to sorption and first-order linear decay in porous media may be written as follows:

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 c}{\partial x^2} - \lambda c = \frac{D_e}{\alpha} \frac{\partial^2 c}{\partial x^2} - \lambda c = D_a \frac{\partial^2 c}{\partial x^2} - \lambda c \quad (7)$$

where  $R_d$  is the retardation factor,  $\alpha$  is the rock capacity factor (i.e. Skagius & Neretnieks 1986),  $\lambda$  is the decay constant [ $T^{-1}$ ], and  $D_a$  is the apparent diffusion coefficient. For reactive chemical species subject to linear, reversible, and instantaneous sorption,  $R_d > 1$ , whereas for non-reactive chemical species,  $R_d = 1$ . The rock capacity factor represents the volumetric capacity of the porous medium for the chemical species, and is related to the retardation factor as follows (Pearson 1999):

$$\alpha = \varepsilon R_d \quad (8)$$

Therefore, since  $\varepsilon < 1$ ,  $\alpha < R_d$ . The decay constant,  $\lambda$  [ $T^{-1}$ ], is inversely proportional to the half-life of a given radionuclide such that, for a non-decaying, non-reactive chemical species,  $\lambda = 0$ ,  $R_d = 1$ , and  $\alpha = \varepsilon$ . As previously noted, the half lives of the three dominant radionuclides of uranium, i.e.  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$ , are of such high magnitudes radioactive decay is negligible for most practical time frames.

As is apparent from Eq. 7, the relationship among  $D_a$ ,  $D^*$ , and  $D_e$  is as follows:

$$D_a = \frac{D^*}{R_d} = \frac{D_e}{\alpha} \quad (9)$$

Thus,  $D_a$  represents a lumped effective diffusion coefficient that includes the effect of attenuation via either  $R_d$  or  $\alpha$ . For this reason,  $D_a$  also has been referred to as the effective diffusion coefficient of a reactive chemical species (Shackelford & Daniel 1991). A comparison of Eqs. 2, 5, 8, and 9 reveals that the general order in the magnitudes of  $D_a$ ,  $D^*$ , and  $D_e$  is  $D^* > D_e > D_a$  when  $R_d^{-1} < \varepsilon$  and  $D^* > D_a >$

$D_e$  when  $R_d^{-1} > \epsilon$ . This latter relationship typically governs for diffusion through intact (unfractured) rock where sorption is minimal and the matrix porosity is low (e.g. see Parker et al. 1994).

## RESULTS AND DISCUSSION

### Diffusion of Uranium

The diffusion coefficients for a variety of uranium chemical species diffusing in saturated, compacted specimens of different types of bentonites are summarized in **Table 1**. The focus of the majority of the studies upon which the results in **Table 1** are based has been on the use of compacted bentonites as buffer barriers in containment of high level radioactive waste. The data in **Table 1** (and subsequent tables) are limited in several ways. First, space limitations prevent detailed descriptions of the various bentonites and the methods used to measure the diffusion coefficients, both of which can be found in the references. Second, in some cases, relevant information such as the chemical species, type of bentonite, and/or porosity were not specified in the reference and, therefore, are unknown. Finally, in some cases, values of  $D_e$  and/or  $D^*$  are missing from **Table 1**. These cases generally occur when only  $D_a$  or both  $D_a$  and  $D_e$  values have been reported, but the associated values of  $\epsilon$  and  $R_d$  (or  $\alpha$ ) have not been reported, such that determination of  $D_e$  and/or  $D^*$  is not possible. This relatively common practice of reporting only  $D_a$  limits the usefulness of the data, since the diffusion and attenuation aspects cannot be evaluated independently (Shackelford & Daniel 1991). Also, values of  $D_a$  are not appropriate for use in scenarios involving flux controlled boundary conditions, since diffusive mass flux depends on either  $D^*$  or  $D_e$  (Eqs. 1 or 6), not  $D_a$ . Thus, the practice of reporting only  $D_a$  values should be avoided.

Given the aforementioned limitations, the general ranges of diffusion coefficients are  $1.1 \times 10^{-13} \leq D^* \leq 2.8 \times 10^{-10} \text{ m}^2/\text{s}$ ,  $4.3 \times 10^{-14} \leq D_e \leq 1.8 \times 10^{-10} \text{ m}^2/\text{s}$ , and  $3.1 \times 10^{-14} \leq D_a \leq 4.8 \times 10^{-12} \text{ m}^2/\text{s}$ . Thus,  $D^*$ ,  $D_e$ , and  $D_a$  vary over 3.4, 3.6, and 2.2 orders of magnitude, respectively. Also, the general trend of  $D^* > D_e > D_a$  holds true, but the lower limit on  $D_a$  is only marginally lower than that on  $D_e$  (i.e.  $3.1 \times 10^{-14} \text{ m}^2/\text{s}$  vs.  $4.3 \times 10^{-14} \text{ m}^2/\text{s}$ ), whereas the upper limit on  $D_a$  is 1.6 and 1.8 orders of magnitude lower than that on  $D_e$  and  $D^*$ , respectively. Since the difference between  $D_a$  and  $D^*$  or  $D_e$  primarily reflects the effect of attenuation, the marginal differences between  $D_a$  and  $D^*$  or  $D_e$  values reported in **Table 1** likely reflect, in part, the anionic or neutral forms of the chemical species, such that sorption via cation exchange to the bentonite was limited. Finally, the upper limit on  $D^*$  of  $2.8 \times 10^{-10} \text{ m}^2/\text{s}$  is only slightly lower than the  $D_o$  value of  $3.9\text{--}4.9 \times 10^{-10} \text{ m}^2/\text{s}$  for U(VI) reported by Bai et al. (2009), which is required since  $D^*$  must be less than  $D_o$  if  $\tau_a < 1$  in accordance with Eq. 2.

In terms of a specific type of bentonite, the results from Muurinen (1990) for saturated specimens of compacted MX-80 bentonite are shown in **Figure 1a**. As indicated, both  $D^*$  and  $D_e$  tend to increase semilog linearly with increasing  $\epsilon$  (or decreasing dry density,  $\rho_d$ ), albeit at different slopes, and  $D^* > D_e$  for a given  $\epsilon$ . Of course, in the limit as  $\epsilon$  approaches unity,  $D_e$  must approach  $D^*$ , and both  $D_e$  and  $D^*$  must approach  $D_o$ . The limited number of  $D_a$  values precludes a similar conclusion with respect to the trend in  $D_a$  with  $\epsilon$  (or  $\rho_d$ ). Similar relationships as shown in **Figure 1a** are expected for the other types of bentonites, but the lack of  $D^*$  and  $D_e$  values from the relevant studies precludes such an evaluation. Values of  $\tau_a$  calculated in accordance with Eq. 2 based on the  $D^*$  and  $D_o$  values shown in **Figure 1a** are plotted as a function of  $\epsilon$  in **Figure 1b**. Parker et al. (1994) note that  $\tau_a$  typically is empirically correlated with  $\epsilon$  via a power relationship as follows:

$$\tau_a = a\epsilon^b \quad (10)$$

where  $a = 1$  and  $b$  typically ranges from 1.3 to 5.4, depending on the porous medium. However, as shown in **Figure 1b**, reasonable estimates of  $\tau_a$  for the results based on Muurinen (1990) are obtained

using Eq. 10 with values of  $a$  ranging from 0.150 to 0.188 and a value for  $b$  of 8.18. These values for  $a$  and  $b$  result in significantly lower values of  $\tau_a$  than suggested by Parker et al. (1994), i.e., for the range of  $\varepsilon$  considered, reflecting the significantly increased apparent tortuosity afforded by highly compacted

**Table 1: Diffusion coefficients for uranium (U) chemical species in compacted bentonites<sup>(1)</sup>**

Chemical Species	Type of Bentonite	$\varepsilon$	$\rho_d$ (g/cm <sup>3</sup> )	Diffusion Coefficients (m <sup>2</sup> /s)			Reference
				$D^*$	$D_e$	$D_a$	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	MX-80	0.41 <sup>(2)</sup>	1.6	1.1x10 <sup>-13</sup>	4.3x10 <sup>-14</sup>	NS	Muurinen (1990)
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	MX-80	0.59 <sup>(2)</sup>	1.1	9.4x10 <sup>-13</sup>	4.9x10 <sup>-13</sup>	NS	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	MX-80	0.67 <sup>(2)</sup>	0.9	3.6x10 <sup>-12</sup>	2.1x10 <sup>-12</sup>	8.4x10 <sup>-13</sup>	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	MX-80	0.78 <sup>(2)</sup>	0.6	1.3x10 <sup>-11</sup>	8.9x10 <sup>-12</sup>	4.8x10 <sup>-12</sup>	
UO <sub>2</sub> Cl <sub>2</sub>	MX-80	0.56 <sup>(2)</sup>	1.2	1.4x10 <sup>-13</sup>	6.0x10 <sup>-14</sup>	NS	
UO <sub>2</sub> Cl <sub>2</sub>	MX-80	0.78 <sup>(2)</sup>	0.6	1.1x10 <sup>-11</sup>	7.7x10 <sup>-12</sup>	3.0x10 <sup>-12</sup>	
Dissolved from UO <sub>2</sub>	MX-80	0.67 <sup>(2)</sup>	0.9	2.6x10 <sup>-12</sup>	1.5x10 <sup>-12</sup>	2.6x10 <sup>-12</sup>	
Dissolved from UO <sub>2</sub>	MX-80	0.78 <sup>(2)</sup>	0.6	1.2x10 <sup>-11</sup>	8.3x10 <sup>-12</sup>	2.6x10 <sup>-12</sup>	
NS	NS	NS	1.15	NS	5.7x10 <sup>-11</sup>	7.5x10 <sup>-14</sup>	Yu & Neretnieks (1997)
NS	NS	NS	1.15	NS	5.8x10 <sup>-12</sup>	6.2x10 <sup>-13</sup>	
NS	NS	NS	0.76	NS	1.9x10 <sup>-12</sup>	1.5x10 <sup>-13</sup>	
NS	NS	NS	0.7	NS	1.9x10 <sup>-12</sup>	6.3x10 <sup>-13</sup>	
NS	Kunigel V1	NS	2	NS	NS	4.5x10 <sup>-13</sup>	
NS	Kunigel V1	NS	1.8	NS	NS	4.2x10 <sup>-13</sup>	
NS	Kunigel V1	NS	1.6	NS	NS	8.6x10 <sup>-13</sup>	
NS	Kunigel V1	NS	1.4	NS	NS	1.3x10 <sup>-12</sup>	
NS	Kunigel V1	NS	1.2	NS	NS	1.2x10 <sup>-12</sup>	
NS	Kunigel V1	NS	1	NS	NS	2.2x10 <sup>-12</sup>	
NS	Kunigel V1	NS	2	NS	NS	3.4x10 <sup>-14</sup>	
NS	Kunigel V1	NS	1.8	NS	NS	4.8x10 <sup>-14</sup>	
NS	Kunigel V1	NS	1.6	NS	NS	7.3x10 <sup>-14</sup>	
NS	Kunigel V1	NS	1.4	NS	NS	2.1x10 <sup>-13</sup>	
NS	Kunigel V1	NS	1.2	NS	NS	2.5x10 <sup>-13</sup>	
NS	Kunipia F	NS	1.8	NS	NS	3.1x10 <sup>-14</sup>	
NS	Kunipia F	NS	1.6	NS	NS	4.4x10 <sup>-14</sup>	
NS	Kunipia F	NS	1.4	NS	NS	8.7x10 <sup>-14</sup>	
NS	Kunipia F	NS	1.2	NS	NS	3.3x10 <sup>-13</sup>	
NS	Kunipia F	NS	1	NS	NS	6.9x10 <sup>-13</sup>	

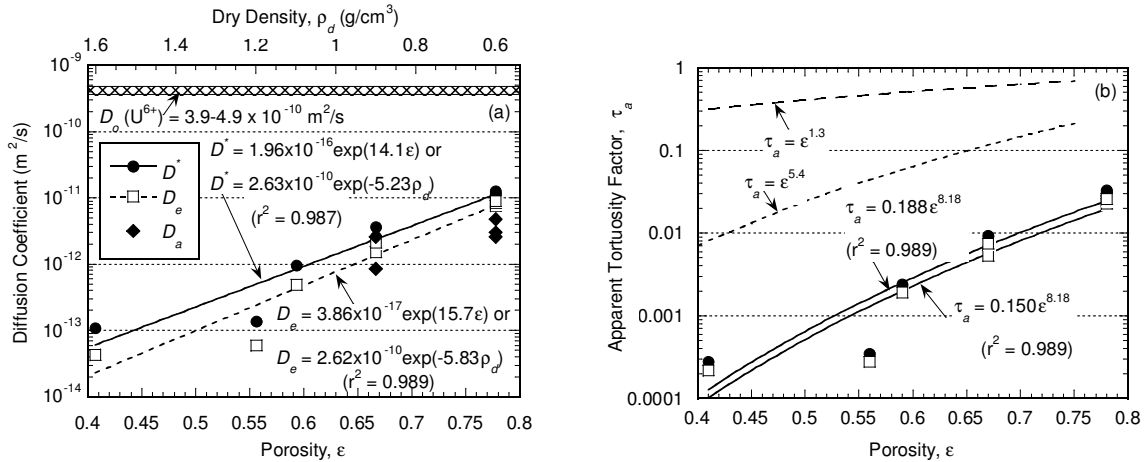
NS	Kunipia F	NS	0.8	NS	NS	$3.7 \times 10^{-12}$
NS	Kunipia F	NS	1.8	NS	NS	$4.3 \times 10^{-14}$
NS	Kunipia F	NS	1.6	NS	NS	$4.5 \times 10^{-14}$
NS	Kunipia F	NS	1.4	NS	NS	$6.5 \times 10^{-14}$
NS	Kunipia F	NS	1.2	NS	NS	$8.8 \times 10^{-14}$
NS	Kunipia F	NS	1	NS	NS	$1.2 \times 10^{-13}$
NS	Kunipia F	NS	0.8	NS	NS	$2.2 \times 10^{-12}$

**Table 1 (continued): Diffusion coefficients for uranium (U) chemical species in compacted bentonites<sup>(1)</sup>**

Chemical Species	Type of Bentonite	$\varepsilon$	$\rho_d$ (g/cm <sup>3</sup> )	Diffusion Coefficients (m <sup>2</sup> /s)			Reference
				$D^*$	$D_e$	$D_a$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.62	0.997	$1.4 \times 10^{-10}$	$8.5 \times 10^{-11}$	$1.9 \times 10^{-12}$	Wang et al. (2005)
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.62	0.996	$1.8 \times 10^{-10}$	$1.1 \times 10^{-10}$	$1.9 \times 10^{-12}$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.63	0.978	$9.5 \times 10^{-11}$	$6.0 \times 10^{-11}$	$1.4 \times 10^{-12}$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.63	0.958	$1.2 \times 10^{-10}$	$7.8 \times 10^{-11}$	$1.2 \times 10^{-12}$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.64	0.953	$2.6 \times 10^{-10}$	$1.6 \times 10^{-10}$	$1.9 \times 10^{-12}$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.64	0.951	$2.8 \times 10^{-10}$	$1.8 \times 10^{-10}$	$2.3 \times 10^{-12}$	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	MX-80	0.64	0.946	$1.3 \times 10^{-10}$	$8.1 \times 10^{-11}$	$1.5 \times 10^{-12}$	

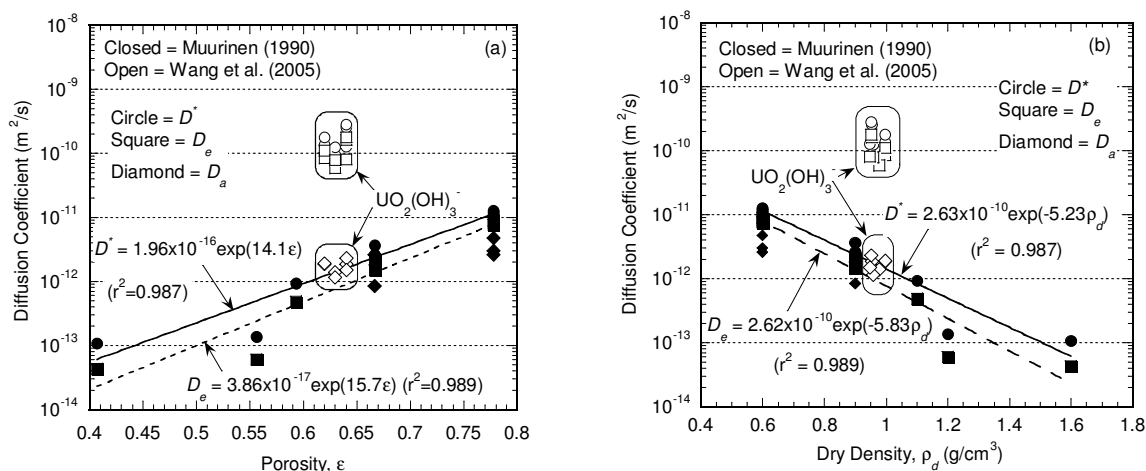
<sup>(1)</sup> NS = not specified;  $\varepsilon$  = porosity;  $\rho_d$  = dry density; <sup>(2)</sup> Based on  $\rho_s = 2.70$  g/cm<sup>3</sup>

bentonites relative to other porous media. Such low  $\tau_a$  values are likely due, in part, to the existence of semipermeable membrane behavior (ion exclusion) in bentonites, which can significantly reduce the magnitude of  $D^*$  in bentonites depending on the porosity of the bentonite and the concentration of the chemical species (Malusis & Shackelford 2002).



**Figure 1: Uranium diffusion through compacted MX-80 bentonite: (a) diffusion coefficient versus porosity; (b) apparent tortuosity factor versus porosity (data from Muurinen 1990)**

The results from Muurinen (1990) for MX-80 bentonite are compared with those reported by Wang et al. (2005) for MX-80 bentonite in **Figure 2**. The comparison reveals that the values of  $D_a$  from Wang et al. (2005) are on the same order of magnitude as those from Muurinen (1990). However, the  $D^*$  and  $D_e$  values from Wang et al. (2005) are significantly higher than those from Muurinen (1990), and the values  $D^*$  and  $D_e$  values from Wang et al. (2005) tend to be only slightly lower than the upper limit given by  $D_o$ . Aside from the differences in the techniques used to measure the diffusion coefficients (i.e. Muurinen (1990) used a through-diffusion technique whereas Wang et al. (2005) used a capillary method), the higher  $D^*$  and  $D_e$  values from Wang et al. (2005) can be attributed, in part, to the anionic complex,  $\text{UO}_2(\text{OH})_3^-$ , evaluated by Wang et al. (2005) versus the neutral species of U(VI) evaluated by Muurinen (1990), since  $\text{UO}_2(\text{OH})_3^-$  presumably is repelled by the negatively charged surfaces of the bentonites particles, thereby facilitating diffusion through the compacted bentonite. Since this explanation excludes cation exchange as an attenuation mechanism, the apparent attenuation of  $\text{UO}_2(\text{OH})_3^-$  as reflected by the significantly lower  $D_a$  values was attributed by Wang et al. (2005) to diffusion of  $\text{UO}_2(\text{OH})_3^-$  into the interlamellar space within the mineral structure of the smectite comprising the bentonite particles. This observation is consistent with the study by Jo et al. (2006) indicating attenuation in granular bentonites due to both interparticle and intraparticle diffusion. Thus, the comparison shown in **Figure 2** illustrates the potential importance on uranium diffusion of both chemical speciation and interparticle/intraparticle diffusion as an attenuation mechanism.



**Figure 2: Effect of chemical speciation on diffusion of uranium through compacted MX-80 bentonite as a function of (a) porosity and (b) dry density.**

The diffusion coefficients for uranium diffusing in saturated specimens of porous media other than solely compacted bentonite are summarized in **Table 2**. The specimens for the study by Alonso et al. (2003) consisted of sheets of granite adjacent to either a solution containing uranium or FEBEX bentonite to evaluate the effect of the bentonite on uranium diffusion in the granite. They found that the presence of the bentonite reduced  $D_a$  about two orders of magnitude, from  $\sim 10^{-13} \text{ m}^2/\text{s}$  to  $\sim 10^{-15} \text{ m}^2/\text{s}$ . The Na-boltwoodite evaluated by Liu et al. (2006) is a uranyl silicate precipitate that was used as a surrogate for precipitated U(VI) resulting from the discharge in 1951 of  $350 \text{ m}^3$  of radioactive waste solution containing 7000 kg of U(VI) at the Hanford site in Washington. The primary purpose of the study by Patra et al. (2011) was to evaluate the influence of distilled water versus 0.1 N  $\text{NaNO}_3$  as solvents on the leaching of uranium from a variety of metallurgical wastes and ore samples. The general characteristics of the other materials noted in **Table 2** should be self evident.

The data in **Table 2** are noteworthy only in terms of the paucity of  $\epsilon$ ,  $D^*$  and  $D_e$  values that have been



reported, which significantly limits any attempt to assess trends in the data. Essentially, the only observation that can be drawn from the data in **Table 2** is that the  $D_a$  values fall within the range  $1.0 \times 10^{-15} \leq D_a \leq 2.8 \times 10^{-10} \text{ m}^2/\text{s}$ , which covers 5.4 orders of magnitude. However, the upper limit  $D_a$  value of  $2.8 \times 10^{-10} \text{ m}^2/\text{s}$  for  $\text{UO}_2^{2+}$  is so close to the aforementioned  $D_o$  value for U(VI) of  $3.9\text{--}4.9 \times 10^{-10} \text{ m}^2/\text{s}$  as to warrant suspicion. Thus, the  $D_a$  values in **Table 2** bentonite-rock and non-bentonite materials are more variable than those in **Table 1** for compacted bentonites.

### Diffusion of Radionuclides of Uranium

The diffusion coefficients for  $^{233}\text{U}$  in the form of several chemical species diffusing in saturated specimens of MX-80 bentonite, sand-bentonite mixtures, and biotitic granite are summarized in **Table 3**. Several observations from the data in **Table 3** are readily apparent. First, the values of  $\varepsilon$  and  $\rho_d$  for

**Table 2: Diffusion coefficients for U chemical species in bentonite-rock and non-bentonite materials<sup>(1)</sup>**

Chemical Species	Material	$\varepsilon$	$\rho_d$ (g/cm <sup>3</sup> )	Diffusion Coefficients (m <sup>2</sup> /s)			Reference
				$D^*$	$D_e$	$D_a$	
$\text{UO}_2(\text{NO}_3)_2$	FEBEX bent. & granite	NS	NS	NS	NS	$1.0 \times 10^{-15}$	Alonso et al. (2003)
$\text{UO}_2^{2+}$	Na-boltwoodite	NS	NS	NS	NS	$2.6 \times 10^{-12}$	Liu et al. (2006)
$\text{UO}_2^{2+}$	Na-boltwoodite	NS	NS	NS	NS	$2.8 \times 10^{-10}$	
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	Silt/clay	0.45	1.48	$1.6 \times 10^{-10}$	$7.2 \times 10^{-11}$	NA	Bai et al. (2009)
NS	Rock	NS	1.37	NS	NS	$2.6 \times 10^{-14}$	Patra et al. (2011)
NS	Rock	NS	1.37	NS	NS	$6.0 \times 10^{-14}$	
NS	U tailings	NS	1.43	NS	NS	$6.6 \times 10^{-15}$	
NS	U tailings	NS	1.43	NS	NS	$4.2 \times 10^{-15}$	
NS	Cu kinker ash	NS	1.33	NS	NS	$2.4 \times 10^{-15}$	
NS	Cu kinker ash	NS	1.33	NS	NS	$6.6 \times 10^{-15}$	
NS	Cu tailings	NS	1.87	NS	NS	$2.6 \times 10^{-14}$	
NS	Cu tailings	NS	1.87	NS	NS	$1.1 \times 10^{-13}$	

<sup>(1)</sup> NS = not specified;  $\varepsilon$  = porosity;  $\rho_d$  = dry density

each of the three types of materials are the same, such that the effect of  $\varepsilon$  or  $\rho_d$  on the measured diffusion coefficients cannot be evaluated. Second, several values of  $D^*$  and  $D_e$  for studies involving compacted MX-80 bentonite could not be ascertained due to the lack of information given in the publications. Third, the  $D^*$  value of  $1.3 \times 10^{-9} \text{ m}^2/\text{s}$  extracted from the information given in the study by Torstenfelt et al. (1983) is greater than the  $D_o$  value for U(VI) of  $3.9\text{--}4.9 \times 10^{-10} \text{ m}^2/\text{s}$  reported by Bai et

al. (2009) and the  $D_o$  value for  $\text{UO}_2(\text{CO}_3)_3^{4-}$  of  $7.2 \times 10^{-10} \text{ m}^2/\text{s}$  reported Yamaguchi & Nakayama (1998) and, therefore, is likely in error. Finally, the  $D_a$  values reported by Yamaguchi & Nakayama (1998) for biotitic granite are greater than the  $D_e$  values (i.e.  $D_a > D_e$ ), which as previously noted is possible when  $\varepsilon < R_d^{-1}$ .

Otherwise, the diffusion coefficients shown in **Table 3** provide an indication of the apparent variability that can exist in the measurement of the diffusion coefficients of  $^{233}\text{U}$  in specific porous media at the given values of  $\varepsilon$  (or  $\rho_d$ ). For example, for compacted MX-80 bentonite (at  $\varepsilon = 0.35$ ), excluding the aforementioned  $D^*$  value of  $1.3 \times 10^{-9} \text{ m}^2/\text{s}$  and the associated  $D_e$  value of  $4.5 \times 10^{-10} \text{ m}^2/\text{s}$ ,  $D^*$  and  $D_e$  vary by a factor of about 3 ( $1.0 \times 10^{-10} \leq D^* \leq 3.1 \times 10^{-10} \text{ m}^2/\text{s}$ ,  $3.7 \times 10^{-11} \leq D_e \leq 1.1 \times 10^{-10} \text{ m}^2/\text{s}$ ), whereas  $D_a$  varies by a factor of about 48 ( $1.2 \times 10^{-14} \leq D_e \leq 5.8 \times 10^{-13} \text{ m}^2/\text{s}$ ). In the case of biotitic granite (at  $\varepsilon = 0.007$ ) for the species  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $D^*$  and  $D_e$  vary by a factor of only about 1.2 ( $1.8 \times 10^{-11} \leq D^* \leq 2.2 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $1.3 \times 10^{-13} \leq D_e \leq 1.6 \times 10^{-13} \text{ m}^2/\text{s}$ ), whereas  $D_a$  varies by a factor of only about 1.7 ( $3.5 \times 10^{-13} \leq D_a \leq 5.9 \times 10^{-13} \text{ m}^2/\text{s}$ ). Thus, the variability in the measured diffusion coefficients is greater in the MX-80 bentonite than in the biotitic granite, and the variability in  $D_a$  is greater than that in  $D^*$  or  $D_e$ . The greater variability in  $D_a$  relative to either  $D^*$  or  $D_e$  can be attributed to the complicating effect of attenuation included in the values of  $D_a$ , and likely reasons for the lesser variability in the diffusion coefficients for the biotitic granite relative to those for the MX-80 bentonite include a more homogeneous pore structure and the lesser attenuation capacity for the biotitic granite.

**Table 3: Diffusion coefficients for  $^{233}\text{U}$  in a variety of porous materials<sup>(1)</sup>**

Species	Material	$\varepsilon$	$\rho_d$ (g/cm <sup>3</sup> )	Diffusion Coefficients (m <sup>2</sup> /s)			Reference
				$D^*$	$D_e$	$D_a$	
NS	MX-80 B	0.35	2.0	$3.1 \times 10^{-10}$	$1.1 \times 10^{-10}$	$5.8 \times 10^{-13}$	Torstenfelt et al. (1983)
NS	MX-80 B	0.35	2.0	$1.0 \times 10^{-10}$	$3.5 \times 10^{-11}$	$1.9 \times 10^{-13}$	
NS	MX-80 B	0.35	2.0	$3.0 \times 10^{-10}$	$1.1 \times 10^{-10}$	$5.7 \times 10^{-13}$	
NS	MX-80 B	0.35	2.0	$1.1 \times 10^{-10}$	$3.7 \times 10^{-11}$	$2.0 \times 10^{-13}$	
NS	MX-80 B	0.35	2.0	$1.3 \times 10^{-9}$	$4.5 \times 10^{-10}$	$4.5 \times 10^{-14}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$3.4 \times 10^{-12}$	Torstenfelt (1986)
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$6.4 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$2.7 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$3.3 \times 10^{-11}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$1.6 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$8.2 \times 10^{-12}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$3.1 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$1.0 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$8.5 \times 10^{-12}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$2.3 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$8.3 \times 10^{-14}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$6.7 \times 10^{-12}$	

$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$6.8 \times 10^{-13}$	
$\text{UO}_2^{2+}$	MX-80 B	0.35	2.0	NS	NS	$2.3 \times 10^{-13}$	
$\text{UO}_2^{2+}$	90% S-10% B	0.13	2.0	$1.7 \times 10^{-10}$	$2.3 \times 10^{-11}$	$1.5 \times 10^{-12}$	
$\text{UO}_2^{2+}$	90% S-10% B	0.13	2.0	$1.7 \times 10^{-10}$	$2.3 \times 10^{-11}$	$1.5 \times 10^{-12}$	Albinsson & Engkvist (1989)
U(IV)	MX-80 B	$0.35^{(2)}$	2.0	NS	NS	$1.2 \times 10^{-14}$	Albinsson et al. (1991)
U(IV)	MX-80 B	$0.35^{(2)}$	2.0	NS	NS	$2.8 \times 10^{-14}$	
U(IV)	MX-80 B	$0.35^{(2)}$	2.0	NS	NS	$1.4 \times 10^{-13}$	
$\text{UO}_2(\text{CO}_3)_3^{4-}$	Biotitic granite	0.007	2.6	$2.2 \times 10^{-11}$	$1.6 \times 10^{-13}$	$5.9 \times 10^{-13}$	Yamaguchi & Nakayama (1998)
	Biotitic granite	0.007	2.6	$2.0 \times 10^{-11}$	$1.4 \times 10^{-13}$	$4.4 \times 10^{-13}$	
	Biotitic granite	0.007	2.6	$1.8 \times 10^{-11}$	$1.3 \times 10^{-13}$	$3.5 \times 10^{-13}$	
$\text{UO}_2^{2+}$	Biotitic granite	0.007	2.6	$5.1 \times 10^{-12}$	$3.6 \times 10^{-14}$	$3.3 \times 10^{-12}$	

<sup>(1)</sup> NS = not specified; B = bentonite; S = sand;  $\epsilon$  = porosity;  $\rho_d$  = dry density; <sup>(2)</sup> Assumed value based on values given by Torstenfelt et al. (1983) and Torstenfelt (1986) for the same bentonite.

Diffusion coefficients for uranium radionuclides other than  $^{233}\text{U}$  also have been reported, but both the number of studies and the results contained in the studies are limited. For example, Sims et al. (2008) report diffusion coefficients ranging from  $3 \times 10^{-14} \text{ m}^2/\text{s}$  to  $1.2 \times 10^{-8} \text{ m}^2/\text{s}$  for  $^{238}\text{U}$  diffusion in an unsaturated prairie soil, but the definition of the diffusion coefficient is not specified. Also, several of the values appear to be exceedingly high so as to approach or exceed a representative  $D_o$  value, which is physically impossible. Sims et al. (2008) also report a single diffusion coefficient for  $^{235}\text{U}$  of  $7 \times 10^{-10} \text{ m}^2/\text{s}$  for the same soil and conditions and with the same limitations. Finally, Rameback et al. (1998) report  $D_a$  values for  $^{236}\text{U}$  diffusing in saturated specimens of compacted MX-80 bentonite ( $\rho_d = 2.00 \text{ g/cm}^3$ ) ranging from  $3.2 \times 10^{-15} \text{ m}^2/\text{s}$  to  $2.2 \times 10^{-13} \text{ m}^2/\text{s}$ .

## Conclusions

A review of the literature on the diffusion of uranium in soils and rocks reveals several conclusions. First, the common practice of reporting only  $D_a$  values as opposed to both  $D_a$  and  $D^*$  and/or  $D_e$  values severely restricts the usefulness of the data and should be avoided in the future. Second, diffusion of uranium in compacted MX-80 bentonite is shown to increase semilog linearly with increasing porosity (or decreasing dry density), and to be potentially significantly affected by chemical speciation. Third, the potential existence of semipermeable membrane behavior in bentonites is a likely reason for the significantly slower rate of uranium diffusion in compacted MX-80 bentonite than would be predicted on the basis of other soils. Fourth, interparticle/intraparticle diffusion can significantly restrict the diffusion of uranium in compacted MX-80 bentonite. Finally, the effect of attenuation is shown to increase the variability in  $D_a$  relative to that in either  $D^*$  or  $D_e$ , and the variability in  $D^*$ ,  $D_e$ , and  $D_a$  is shown to be greater in compacted bentonite than in unfractured biotitic granite, likely due to a more homogeneous pore structure and the lesser attenuation capacity for the biotitic granite.

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