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Cs diffusion in local Taiwan laterite with different solution concentration, pH and packing density

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Abstract

In this work we used an "in-diffusion" method to study the effects of pH, solution concentration and packing density on Cs diffusion by packing local Taiwan laterite (LTL) into modified capillary columns with 5 mm diameter. These packed columns were first pre-equilibrated with synthetic groundwater (GW) for 3 weeks. The diffusion experiments were then carried out at ambient condition for 2 weeks. Our experimental results showed that the Cs diffusion profile fits Fick's second law very well in given experimental conditions, indicating the validity of modified capillary column method. Generally speaking, Cs diffusion in LTL decreases as the pH increases and as Cs concentration decreases. The apparent diffusion coefficient (D_a) increases from 5.52×10^{-12} (10^{-7} M) to 2.18×10^{-11} (10^{-3} M) m^2/s, while the effective diffusion coefficient (D_e) shows slight variation as the Cs concentration changes. Both the derived D_a and D_e values decrease as the pH increases, implying that the diffusion mechanisms of Cs nuclide in alkaline and acid environment are different. In addition, our results show that Cs diffusion is unaffected by the given packing density, indicating the interlaminary space is not the major determinant of Cs adsorption and diffusion in LTL.

Keywords: Diffusion; Capillary column; Radionuclide; Safety assessment; Transport

1. Introduction

The management of radioactive waste is an issue of concern to the public due to the possibility of the long-lived radionuclides releasing via aqueous medium (Vejsada, 2006). These leached radionuclides might enter the environment by transporting through deep geological substances as well as backfill materials such as clay minerals. Clay minerals are considered an important backfill and buffer material due to its large surface area along with high cation exchange capacity. These two characteristics could effectively regulate the concentration of released radionuclides by sorption onto clay mineral surfaces and diffusion into the pores of clay mineral (Wang et al., 2005). As a result, the diffusion of radionuclides in clays attracts a vast amount of studies because it is an important parameter in safety assessment (Johansson et al., 1998; Kozaki et al., 1996, 1999; Montavon et al., 2006; Sato et al., 1992).

The technique of in-diffusion is frequently used to study the diffusion behavior of concerned radionuclide in some geological substances. Generally speaking, utilization of an in-diffusion method might offer many advantages including time saving and taking less laboratory space. Recently, the introduction of the capillary column method, a derivative of the in-diffusion method, makes a remarkable progress in studying the diffusions of concerned radionuclide in compacted bentonite (Wang, 2003; Wang and Liu, 2004; Wang and Tao, 2004; Wang et al., 2003, 2004, 2005; Xu et al., 2006). The small volume of the capillary greatly reduces the space required for experimental apparatus. Also, the amount of experimental solid along with liquid waste is quite decreased in the meantime. This enables the scientists to study these factors (i.e. effects of pH, solution concentration, ionic strength, foreign ions, bulk density) influencing diffusion behavior in an efficient way.

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However, packing a capillary column requires skill since the capillary column is fragile. In addition, packing capillary columns reproducibly is relatively difficult because of the small volume of the column. As a result, we packed several "modified capillary columns" with diameters ranging from 5 to 20 mm and examined their validity by a case study of Cs diffusion in local Taiwan laterite (LTL) in advance (Wang et al., 2007). Our experimental results showed that the diffusion profiles of these modified capillary columns fitted Fick's second law very well. It was indicated that the working diameter of the capillary column could be expanded to at least 20 mm. We filled LTL into modified capillary columns (5 mm in diameter) in this work to study the effects of pH, solution concentration and packing density on Cs diffusion. LTL was selected because it is widely found in northern Taiwan, while Cs is the critical nuclide in performance assessment of radioactive waste repository. Diffusion properties including K_d, apparent (D_a) and effective diffusion coefficients (D_e) are determined by fitting diffusion profiles and compared with one another in this present work.

2. Experimental

2.1. Materials

The LTL was collected from the surface soil with a depth of 2–4 m in Toayuan County, Taiwan. These soils were sieved and the fraction of particles with diameters less than 0.074 mm was collected for characteristic analysis and the diffusion experiment. The specific surface area of LTL is 32.25 m^2/g (N_2-BET) and its cation exchange capacity (CEC) is 14.3 meq/100 g (NaOAc method). The EDS (SEM/EDS, Leo 1530) results showed that the average elemental content on the LTL surface is O (45.81%), Al (15.38%), Si (20.78%), K (2.27%) and Fe (14.12%). Its composition, determined by X-ray diffraction (XRD) (Philips PW1300) is quartz, kaolinite and goethite. In addition, the high surface area associated with high a CEC value implies that some impurity such as smectite is presented in LTL (Miranda-Tervino and Coles, 2003; Shahwan et al., 2005).

2.2. Column fabrication

The modified capillary column is 5 mm in diameter and 40 mm in packing length. The weight of the packed LTL is determined from the mass difference between the filled and empty column. During the packing process, one end of the modified capillary column was sealed with Parafilm to prevent the solid from falling out. These filled columns were then mounted in a polystyrene plate for fixation. After drilling a small pin hole in the Parafilm, these "fixed" columns were placed into polypropylene (PP) tube containing 50 mL of synthesis groundwater for water saturation. After 3 weeks of water saturation, these columns were then transferred to another PP tubes containing 50 mL of ^{137}Cs-spiked groundwater with CsCl carrier. The Cs carrier concentrations of these spiked solutions ranged from 10^{-7} to 10^{-3} M. In addition, the pH of 10^{-7} and 10^{-4} M solutions was adjusted with 0.1 N HCl and NaOH to study the effect of pH on Cs diffusion in LTL. The purpose of using 50 mL of Cs solution is to provide a constant Cs concentration during the entire diffusion period. To minimize the effect of evaporation, the columns were placed in a closed system, in this case, a sealed oven. After 2 weeks of diffusion, these columns were removed from solutions. The packed LTL column was pushed out from modified capillary column and cut into slices with 3 mm of thickness. The radioactivity of each slice was directly measured with an NaI detector and the diffusion profile was determined.

2.3. Mathematical solution

The mathematical solution of the diffusion profile of capillary column is detailed in the literature (Wang, 2003; Wang and Tao, 2004; Wang and Liu, 2004; Wang et al., 2003, 2004, 2005; Xu et al., 2006). Briefly, the diffusion process based on the Fick's second law is described as follows:

$$\frac{\delta C}{\delta t} = D_a \frac{\delta^2 C}{\delta x^2} \tag{1}$$

in which C (mol) is the amount of Cs at distance x (m) from the contacting face of solid and Cs solution at time t (s). By considering the initial and boundary conditions, the solution of Eq. (1) can be expressed as

$$\frac{C}{C_0} = erfc \frac{x}{2\sqrt{D_a t}}, \tag{2}$$

where C_0 is the amount of Cs at the interface between packed solid and solution (in mol). The term C_0 represents the amount of Cs at the interface between packed solid and solution. This value is determined by fitting the exact solution of the diffusion equation rather than using the source solution concentration since it would be a more reasonable approach for determining the true C_0 values from in-diffusion experiments; D_a is the apparent diffusion coefficient (m^2/s), and *erfc*() is the complementary error function

$$erfc(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp(-x^2)\,dx. \tag{3}$$

The relative concentration data (C/C_0) can be plotted by "trial and error" the value of D_a along with C_0. Among these fitting curves, one set of C_0 and D_a values that results in a best fitting is adopted as the C_0 and D_a values of each diffusion experiment. Meanwhile, the quality of curve fitting is controlled by the extent of the root mean square of the fitting (the best fitting). The D_a is thus determined while the C_0, which is obtained as the radioactivity, then is converted into its corresponding amount (mol). In addition, D_e, effective diffusion coefficient, is deduced