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Abstract

The effect of humic acid (HA) on the diffusion of Re(VII) was investigated in compacted Gaomiaozi (GMZ) bentonite by the through- and out- diffusion method. The effective diffusion coefficient, De, and accessible porosity, acc, were measured in order to evaluate the impact of humic acid on Re(VII) diffusion. The De value was in the range of (5.2–8.3)$×$10-12 m2/s. The diffusion of Re(VII) was enhanced in the presence of HA, and the De value increased with the increase of ageing time, indicating that the formation of HA-Re complexes was slow. Moreover, the acc was in the range of (0.06– 0.16), which is less than the total porosity. It implies that the HA-Re complexes are anions.

Full Text

Preamble

Effect of Humic Acid Contact Time on the Diffusion of Re(VII) in GMZ Bentonite

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ods. The effective diffusion coefficient (De) and accessible porosity (acc) were measured to evaluate the impact of humic acid on Re(VII) diffusion. The De values ranged from (5.2–8.3)$\times10^{-12}$ m^2/s. Diffusion of Re(VII) was enhanced in the presence of HA, and the De value increased with aging time, indicating that the formation of HA-Re complexes is slow. Moreover, acc ranged from 0.06–0.16, which is less than the total porosity, implying that the HA-Re complexes are anionic species.

Keywords: Diffusion coefficient, Humic acid, Re(VII), Complex, Bentonite
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Introduction

Humic acids (HA) possess a strong ability for metal complexation and can alter the migration of radionuclides in clay environments. Several studies have shown that some radionuclides are strongly retained in humics-rich surface soils [1, 2]. For example, the migration of Eu(III) in bentonite is hindered by HA due to the formation of Eu-HA complexes at the surface of compacted bentonite [1]. In addition, the diffusion of Cu(II) is prevented by humic gels, with the diffusion coefficient in the presence of humic gels being two orders of magnitude lower than that in water [2]. However, humics can also facilitate radionuclide transport through the formation of radionuclide-colloid complexes. Wold et al. [3] found that humics could increase the apparent diffusion coefficient (Da) and decrease the distribution coefficient (Kd) values for both Co(II) and Eu(III) in compacted bentonite.

^{99}Tc is a significant environmental contaminant with a long half-life of 2.1$\times10^{5}$ years, presenting a challenge for cleanup because it is difficult to understand the key processes that affect its mobility in the environment. Tc(VII) is the most stable species in natural oxic environments, with high solubility in water and essentially no absorptive properties toward minerals. In contrast, Tc(IV) is less soluble and can be immobile in groundwater and soils [4–6]. Several researchers have focused on the effect of humic substances (HS) on Tc(IV) mobility [7–9]. For instance, Artinger et al. [7] showed that humic substances enhanced the mobility of Tc(IV) by forming soluble Tc(IV)-HS species. Boggs et al. [9] found that TcO(OH)-HA was the predominant complex under acidic conditions, whereas $TcO(OH)^0$ and $TcO(OH)_2$-HA were the major species under neutral and alkaline conditions, respectively. XANES and EXAFS measurements show that soluble Tc(IV)-HS species are formed through ligand-metal complexation under slightly basic pH and reducing conditions [10]. Moreover, Maes et al. [11] explained the transport of Tc(IV) with organic matter as an organic matter complex/colloid that slowly dissociates. Studies also show that organic ligands like oxalate and acetate increase Tc(IV) solubility [4, 12]. Even in the case of Tc(VII), Maes et al. [13] found that Tc(VII) was reduced to Tc(IV) by the solid Boom clay phase, with the competition effect for Tc(IV) described between the solid phase and dissolved HS.

In the safety assessment of high-level radioactive waste repositories, radionuclide species with high mobility such as $^{99}TcO_4^-$, $^{125}I^-$, $^{36}Cl^-$, and $^{79}SeO_2^-$ are given the most concern in pre-safety assessments [14–17]. The bentonite from Gaomiaozi County, China (GMZ bentonite) has been selected as the backfill material for the high-level radioactive waste repository. The effective/apparent diffusion coefficient (De/Da), porosity (tot), and distribution coefficient (Kd) are fundamental parameters for modeling radionuclide transport behaviors in repository safety assessments [18].

Our recent work showed that EDTA can enhance TcO_4^- transport but does not alter the mobility of ReO_4^- (as an analogue to $^{99}TcO_4^-$) due to the lower reactivity of ReO_4^-. In addition, Liu et al. [19] found that HA has an insignificant effect on the diffusion of Tc(VII) in granite. However, these investigations were performed without considering the effect of HA aging time, and the differences might be obscured by uncertainty or other unknown factors. In this work, the effect of HA on the diffusion of ReO_4^- is studied under different aging time conditions. The De and accessible porosity (acc) were obtained by fitting experimental data from both transient and steady states. The out-diffusion method was employed to clarify whether the interaction between ReO_4^- and HA reached equilibrium.

II. Materials and Methods

A. Material and Experimental Conditions

The experiments were carried out using through- and out-diffusion methods. Table 1 shows the experimental conditions for the diffusion experiments.

The GMZ bentonite was obtained from the Beijing Research Institute of Uranium Geology without further processing. ReO_4^- was prepared in distilled water using NH_4ReO_4 (Alfa Aesar, 99.997%). HA (Sigma-Aldrich) was dissolved by adding a small amount of 0.01 mol/L NaOH.

TABLE 1. Experimental conditions for diffusion experiments

Condition/method	Through- and out-diffusion methods
Bentonite dry density (kg/m^3)	1800
Bentonite type	GMZ (75.4 wt.% montmorillonite)
Temperature (°C)	20 ± 5
Atmosphere	Ambient condition
Saturated solution	Artificial pore water of Gansu Beishan (pH 7.6)
Humic acid (mg/L)	10
pH of tracer solution	2.5–3

B. Data Processing

For through-diffusion, the diffusion parameters De and α were obtained by fitting the following equations based on the initial and boundary conditions:

$$Acum = SLC_0 \left\{ \frac{D_e t}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left[-\frac{D_e n^2 \pi^2 t}{L^2} \right] \right\}$$

with initial and boundary conditions:

$c(x,0) = 0, \quad c(0,t) = C_0, \quad c(L,t) = 0, \quad t = 0; \quad x = 0; \quad x = L; \quad t > 0, \quad t > 0$

where L (m) is the sample thickness; C_0 (µg/m^3) is the initial concentration of the diffusing species; Acum (µg) is the total amount of diffused species through a boundary at x = L at diffusion time t; and S (m^2) is the cross-sectional area of the clay.

The equations for out-diffusion can be described as follows:

$$J(0,t) = \frac{2J_L}{\pi^2} \sum_{n=1}^{\infty} \exp\left[-\frac{D_e n^2 \pi^2 t}{L^2} \right] \quad \text{at } x = 0$$

$$J(L,t) = \frac{2J_L}{\pi^2} \sum_{n=1}^{\infty} (-1)^n \exp\left[-\frac{D_e n^2 \pi^2 t}{L^2} \right] \quad \text{at } x = L$$

where J(0, t) and J(L, t) are fluxes at the high- and low-concentration boundaries, respectively.

The experimental procedure was consistent with the literature [14, 18, 20]. The equilibrium condition was established by contacting artificial pore water containing 10 mg/L humic acid with bentonite for 5 weeks. Aging conditions were created by mixing 10 mg/L humic acid with ReO_4^- in artificial pore water and aging for 0 and 60 days, respectively. The source reservoir was spiked with (0.6–1.6) g/L ReO_4^-. The solutions in the target reservoirs were replaced to keep the concentration of ReO_4^- in this reservoir as low as possible. After completing the through-diffusion experiment, a 10 mL solution without ReO_4^- and HA in both reservoirs was replaced and the out-diffusion experiment was started. Samples were analyzed by ICP-OES (PerkinElmer Optima 2100DV). The experimental and theoretical data processing of the through- and out-diffusion methods have been described previously [14, 21, 22].

The composition of the GMZ bentonite samples was analyzed by powder X-ray diffraction (XRD) using a Model XD-2 (Beijing Purkinje General Instrument Co., Ltd., China) with CuKα radiation at 35 kV/20 mA. The morphology and structure of bentonite were observed using a scanning electron microscope (Hitachi S-3400N).

III. Results and Discussion

The constituent mineral composition of bentonite was determined through X-ray diffraction. Figure 1 Figure 1: see original paper shows scanning electron microscopy (SEM) images of GMZ bentonite. The predominant composition was montmorillonite with characteristic peaks at 2 = 6.14°, 19.9°, 36.7°, and 55.4°. Other minerals such as feldspars, quartz, and Ca-Fe(Ca)CO_3 were also present in GMZ bentonite. The layer structure of GMZ bentonite consisted of one alumina octahedral sheet located between two silica tetrahedral sheets. The same result can be found in other GMZ [23, 24] and MX-80 [25] bentonite research. The results of the analysis by scanning electron microscopy show (Fig. 1(b)) that GMZ bentonite has a multi-layer structure and smoothed shapes.

Figure 2 [Figure 2: see original paper] shows the cumulative amount (Acum) and flux versus time for ReO_4^- under three conditions—HA equilibrium, HA aging 0 days, and aging 60 days—in GMZ bentonite compacted at 1800 kg/m^3 using the through-diffusion method.

Through-diffusion experiments of ReO_4^- in the presence of different HA conditions (HA equilibrium, HA aging 0 days, and aging 60 days) were studied by compacting GMZ bentonite at 1800 kg/m^3. Figure 2 shows the Acum and flux as functions of diffusion time, with diffusion parameters listed in Table 2 . The results show typical diffusion curves, where flux increased dramatically during the transient phase then remained unchanged during the steady phase. The De and rock capacity factor α values were obtained from the steady and transient phases, respectively. α is equal to the accessible porosity acc for anions [20]. The time to reach the steady phase was 5, 8, and 12 days under equilibrium, aging 0-day, and aging 60-day conditions, respectively. The breakthrough curves of flux were almost identical under equilibrium and aging 0-day conditions. Since humic substances can adsorb onto silica sheets of montmorillonite at lower pH [26] and clog bentonite pore space [27], this implies that the interaction between HA and Re(VII) is stronger than that between HA and bentonite. Therefore, Re(VII)-HA complexes can be formed. Moreover, the flux under the aging 60-day condition was higher than the others, indicating that the formation of Re(VII)-HA complexes was slow. Figure 1(b) verified the breakthrough curves of flux, showing that Acum was almost identical under equilibrium and aging 0-day conditions and increased fastest under aging 60-day conditions.

Table 2 shows the measured diffusion parameters for ReO_4^- in GMZ bentonite. The apparent diffusion coefficient (Da) is calculated as follows:

$$D_a = \frac{D_e}{\alpha}$$

The De value under the aging 60-day condition was higher than those under equilibrium and aging 0-day conditions, demonstrating that HA can enhance the mobility of Re(VII). The acc values were less than the total porosity values measured by the HTO through-diffusion method in GMZ bentonite [22], indicating that the Re(VII)-HA complexes are anionic species.

To verify the slow reaction kinetics of Re(VII) and HA, Figure 3 [Figure 3: see original paper] shows the out-diffusion results of Re(VII) diffusion under aging 0-day and 60-day conditions. J(L, t) represents the flux at the target reservoir boundary, and J(0, t) represents the flux at the source reservoir boundary. The curves were calculated using the De and acc values obtained from the through-diffusion experiments (Table 2). The data for Re under the aging 60-day condition at both boundaries (original target and source reservoir) were in good agreement with predictions from the through-diffusion experiment, except for the first three data points. The dead volume was probably the major factor enhancing the mass of Re, especially during short time intervals (from 30 min to a few hours) when the reservoirs were changed.

In contrast, while the J(L, t) values of predicted and measured data agreed with each other, the J(0, t) values were systematically underestimated by model predictions for the diffusion of Re-HA under aging 0-day conditions. This analogous discrepancy at J(0, t) was consistent with Cl^- out-diffusion experiments [17, 28, 29]. J(0, t) showed an exponential decrease with time, which can be explained by heterogeneous porosity distributions being of much less importance for through- and out-diffusion at a low-concentration boundary. However, they significantly influence out-diffusion results at a high-concentration boundary. Figure 3 also shows that the experimental data were identical under 0-day (solid dots) and 60-day (empty dots) conditions. Moreover, the expected curves obtained from aging 60 days provided a better fit than those from aging 0 days. This can be explained by the reaction equilibrium between Re(VII) and HA being achieved when the out-diffusion was started under 0-day conditions.

IV. Conclusion

Diffusion experiments for ReO_4^- in the presence of humic acid under different humic acid conditions (humic acid equilibrium, aged 0 days, and aged 60 days) were investigated using through- and out-diffusion methods. Both De and acc values were obtained by fitting experimental data using a computer code FDP. The De value of Re(VII) under HA aging 60-day condition was larger than that under HA aging 0-day condition. The experimental data were identical under 0-day and 60-day conditions. The results reveal that the interaction between Re(VII) and HA is slow. This study implies the importance of further investigation of the Tc(VII) and HA interaction should consider the aging time.

Note: Figure translations are in progress. See original paper for figures.

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