Sorption and Transport Behavior of ^{137}Cs, ^{90}Sr, and ^{99}Tc on Geological Media in Radioactive Waste Repository, South Korea – 116112a

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ABSTRACT

Sorption experiments and a behavior investigation for the radionuclides ^{137}Cs, ^{90}Sr, and ^{99}Tc were conducted using groundwater and solid materials (mudstone and sandstone) sampled from the Wolsong low- and intermediate-level radioactive waste repository at Gyeongju, Korea. After experiments involving batch sorption, diffusion, and a flow-through column, distribution coefficients (K_d) of the radionuclides were obtained, and sorption properties for each radionuclide were analyzed. Increasing K_d values were observed in the sequence ^{137}Cs, ^{90}Sr, and ^{99}Tc regardless of the geological media tested. For all sorbing radionuclides, K_d values for the mudstone were observed to be higher than those for sandstone regardless of the groundwater. These higher K_d values are the result of higher levels of total organic carbon in the mudstone than were present in the sandstone. In addition, the chlorite, kaolinite, and montmorillonite contents in the mudstone also were higher than in the sandstone. The mineralogical composition of the solid materials was observed to be important in the sorption of sorbing radionuclides.

INTRODUCTION

The presence of radionuclides can affect human health. There are treatment methods for used nuclear fuel; however, a final repository for the radioactive waste still will be required. Construction of the first stage of the Wolsong low- and intermediate-level waste (LILW) repository for disposal of 125,000 drums containing radioactive waste was completed, and construction of the second stage of the near-surface repository for 100,000 drums is planned in Gyeongju, South Korea. The LILW disposal facility is the world's first repository to employ both rock cavern (the first stage) and near-surface (the second stage) repositories on the same site.

With the development of nuclear energy, large amounts of radioactive wastes have been released into the natural environment [1]. Radioactive cesium (^{137}Cs) has a long half-life ($t_{½}$) of 30.17 years. It also is radiologically hazardous, and can be easily assimilated by living organisms [2]. Radioactive strontium (^{90}Sr [II]) with a half-life of 28 years is an important product of the nuclear reactor operations and nuclear explosions by nuclear fission of uranium or plutonium. Accumulation of these radionuclides in the food chain is of great concern, and exposure can lead to various forms of cancer [3]. Technitium-99 (^{99}Tc) is a long-lived ($t_{½} = 2.13 \times 10^5$ years) pure

β-emitter ($E_{\beta max}$ = 292 keV), and is produced as a fission and activation product [4]. It is a health hazard only if it is taken into the body so the main concern is cancer induction from beta particles associated with its radioactive decay [5].

Radionuclides can be released from the drums after long storage periods. The released radionuclides can simultaneously penetrate the artificial barrier of the repository and migrate through groundwater or undergo a diffusion process in the rock [6-7]. Retardation phenomena such as sorption and precipitation also can occur. Therefore, it is important to investigate the sorption characteristics and transport behaviors of radionuclides through geological media and to separate radionuclides from radioactive wastes to assess the safety and long-term performance of a repository. Ion exchange, precipitation, liquid–liquid extraction, and adsorption are traditional methods used to remove radionuclides from liquid wastes, with adsorption being the most effective method [8]. Important work in the safety assessment of a radioactive waste repository involves investigating migration behaviors in radionuclides in groundwater, taking into account the sorption characteristics of various radionuclides onto geological media. This knowledge is needed to measure K_ds, for geological media present at a radioactive waste repository, and to investigate the sorption characteristics of radionuclides.

Therefore, the objective of this work is to investigate the sorption properties including measurements of the K_d values of ^{137}Cs, ^{90}Sr, and ^{99}Tc for mudstone and sandstone sampled at the Wolsong LILW repository. In this paper, we discuss migration of the radionuclides in the environment.

METHODS

Groundwater and Solid materials

To determine the relationship between radionuclide migration and site characteristics, batch sorption, diffusion, and flow-through column experiments for radionuclides such as ^{137}Cs, ^{90}Sr, and ^{99}Tc were conducted using groundwater and solid materials (mudstone and sandstone) sampled from the Wolsong LILW repository. The groundwater was sampled near the site, and the geochemical properties and compositions of the groundwater are shown in Table 1. Solid materials also were sampled near the site, and X-ray diffraction results are shown in Table 2. Total carbon, total organic carbon, and total inorganic carbon contents of the solid materials were calculated, and those results were shown in Table 3.

Table 1 Geochemical properties and compositions of the groundwater used in the experiments

Type	mg/L									
Soil Water	Na	K	Ca	Mg	SiO_2	Cl^-	SO_4^{2-}	NO_3^-	F^-	HCO_3^-
	4.0	4.9	13.4	4.9	N.D.	1.3	9.6	66.1	0.1	5.9
	Sampling depth (m)	Temp. (°C)	pH	Eh (mV)	EC (μS/cm)	DO (mg/L)	COD ppm	DOC ppm	$\delta^{18}O$ (‰)	δD (‰)
	140	16.0	6.9	134.2	206.5	4.7	20.9	3.5	-7.8	-47.7

Table 2 The XRD results of solid materials

	Quartz	K-feldspar	Plagioclase	Mica	Calcite	Amphibole	Actinolite	Epidote
Mud stone	23.3	29.8	18.0	10.4	1.1	2.2	2.6	3.5
Sand stone	19.3	30.0	14.4	5.8	1.8	4.6	0.0	7.3

	Pyrite	Laumonite	Stellerite	Esseneite	Ankerite	Chlorite	Kaolinite	Montmorillonite
Mud stone	1.6	0.0	0.0	0.0	0.0	2.7	3.5	1.2
Sand stone	0.0	0.0	0.0	9.0	1.6	1.5	3.0	1.7

Table 3 Carbon concentrations of solid materials

[mg/Kg]	TC	TOC	TIC
Mud stone	1,916	1,445	471
Sand stone	2,314	558	1,755

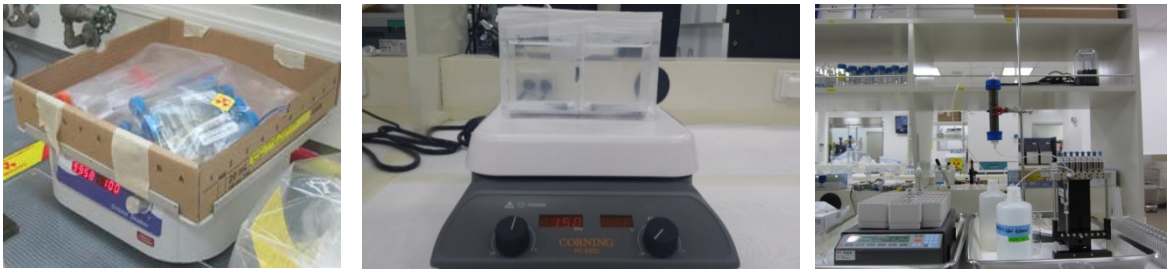
Radionuclides and Analysis

In this work, ^{137}Cs, ^{90}Sr, and ^{99}Tc were the radionuclides studied. Gamma energy analysis (GEA_Canberra GC4020, GC10021) was used to analyze the transport behavior of ^{137}Cs, liquid scintillation analysis (Perkin Elmer 3100 TR) was used for ^{90}Sr, and inductively coupled plasma - mass spectrometry (PerkinElmer, NexION 300D) was used for ^{99}Tc.

Experiments

Five grams of solid material was used in 50 mL of groundwater for the batch sorption experiments. Rock specimen measuring 2.0 cm × 2.0 cm × 0.5 cm were used for the diffusion experiments. For the flow-through column experiments, a 2.5 cm inner

diameter × 5.5 cm long glass column was used. Each experimental setup is shown in Figure 1.



(a) (b) (c)

Figure 1 Experiment for (a) batch sorption, (b) diffusion, and (c) flow-through column.

RESULTS

The sorption capacity was determined experimentally by contacting a solid with a radionuclide solution. The K_d values of the radionuclides were determined, and were observed to decrease in the following order ^{99}Tc, ^{90}Sr, and ^{137}Cs.

The distribution coefficient, K_d (m^3/kg), is defined as:

$$K_d = \frac{(C_0 - C_q)}{C_q} \frac{V}{M} \qquad \text{(Eq. 1)}$$

where C_q is the measured concentration of the radionuclide in the solution phase (Bq/mL), C_0 is the total concentration of the radionuclide (Bq/mL) initially added to the solution, V is the solution volume in contact with the solid (m^3), and M is the amount of solid (kg).

In this study, the batch sorption distribution coefficient of the radionuclide was determined and used to increase our understanding of radionuclide mobility under geological conditions. The K_d values for ^{137}Cs, ^{90}Sr, and ^{99}Tc from our sorption experiments are shown in Table 4.

Tc is present in natural environments as two oxidation states (soluble Tc(VII) and insoluble Tc(IV)) which is dependent on the redox conditions and the pH of the environment. Tc exists in the oxidation state Tc(VII) as pertechnetate TcO_4^- under oxidizing conditions, and in the tetravalent state Tc(IV) as a solid oxide TcO_2(s) under reducing environment in an aqueous solution [9]. In this study, ^{99}Tc will mainly exist as anionic $^{99}TcO_4^-$ because all sorption experiments were carried out in an oxic condition. The K_d for ^{99}Tc show very low values, 2.42 x 10^{-4} m^3/kg for the mud stone and 0 m^3/kg for the sand stone in groundwater sample. This reveals that small

amount of ^{99}Tc was adsorbed onto the solid media in the given groundwater conditions.

In this study, ^{137}Cs was used as a nuclide for sorption of Cs^+ ions in natural water. Measured K_d data show little bit different according to rock type (mud stone and sand stone). The K_d values of ^{137}Cs shown in Table 4 and are relatively high, with 2.24 m^3/kg for mud stone, and 8.16 x 10^{-2} m^3/kg for sand stone in groundwater sample. The K_d values of ^{137}Cs in the mud stone is much higher than sand stone.

In this study, ^{90}Sr was used as a tracer nuclide for the sorption of Sr in natural water.The sorption of ^{90}Sr onto a solid media mainly occurs by an ion exchange similar to the case of ^{137}Cs. The K_d values of ^{90}Sr shown in Table 4 and are relatively smaller than ^{137}Cs due to the low cation exchange capacity compared to ^{137}Cs. The K_d values of ^{90}Sr is 1.06 x 10^{-2} m^3/kg for mud stone and 5.17 x 10^{-3} m^3/kg for sand stone in groundwater sample. The K_d values of ^{90}Sr in the mud stone is much higher than sand stone.

Sorption and diffusion are important retardation processes for radionuclide migration when radionuclides are released from a radioactive waste repository. Thus, sorption and diffusion experimental data for radionuclides, which usually are represented as distribution coefficients and diffusion coefficients, are needed for the safety assessment of a radioactive waste repository. Mudstone in the repository at the Wolsong LILW repository is effective for retarding ^{137}Cs and ^{90}Sr mobility, while ^{99}Tc is expected to be transport as a non-reactive tracer. This study, which is being performed as a part of the site characterization, is investigating migration of released radionuclides through the artificial barrier of the repository and performing a geochemical characterization of the repository. The results of this study will provide basic information and data for the repository safety assessment.

Table 4 The distribution coefficient of radionuclide from sorption experiment

K_d (m^3/kg)	^{137}Cs	^{90}Sr	^{99}Tc
Mud stone	2.24 x 10^{0}	1.06 x 10^{-2}	2.42 x 10^{-4}
Sand stone	8.16 x 10^{-2}	5.17 x 10^{-3}	0.00

Other characteristics including retardation factors and diffusion coefficients will be calculated based on the results of ongoing diffusion and flow-through column experiments.

CONCLUSION

Sorption is one of the important processes for retarding radionuclide migration when radionuclides are released from a radioactive waste repository. Thus, to complete a safety assessment of a waste repository, it is necessary to obtain sorption data for radionuclides. Such data usually are represented as K_d values. In this study, we measured K_d values and investigated sorption characteristics of ^{137}Cs, ^{90}Sr, and ^{99}Tc for mudstone and sandstone sampled at the Wolsong LILW repository.

The K_d values for ^{137}Cs were high for both mudstone and sandstone; however, K_d values for ^{99}Tc were very low for both media forms. The K_d values for ^{90}Sr were found to be at intermediate levels. From the results of our sorption experiments, we also observed that the mineralogical composition of the geological media is an important factor when sorbing radionuclides, especially for strongly sorbing radionuclides. The K_d values were higher for mudstone than for sandstone for all radionuclides studied.

This work involved a geochemical characterization of the Wolsong LILW repository, and was performed as a part of the site characterization effort. The results of ongoing diffusion, and flow-through column experiments will provide basic information and data for the safety assessment of this repository.

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