MIGRATION OF SR, ND AND CE IN UNSATURATED CHINESE LOESS UNDER ARTIFICIAL SPRINKLING CONDITIONS: A FIELD MIGRATION TEST

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(Received 30 December 2001; accepted 20 May 2004)

Abstract. Double concentration peak phenomenon has been observed in nuclide migration tests in unsaturated Chinese loess during the cooperative research between China Institute for Radiation Protection (CIRP) and Japan Energy Atomic Research Institute (JEARI), and was considered conflicting with traditional theory of solute migration. In order to confirm the existence of this phenomenon and better understand its formation mechanism, we conducted a nuclide migration test that lasted 470 days using Sr, Nd and Ce which are analogues of ^{90} Sr and actinides, with loess and fine arenaceous quartz, respectively, as tracer carriers. In addition, we examined the efficacy of capillary barrier which is constructed by placing fine-grained soil on a layer of course-grained material, according to its influence on nuclide migration. When using loess as tracer carrier, a fraction of Sr migrated downward from the source layer to form a migration peak, and the residual Sr formed another concentration peak which corresponds to the source layer; while Nd and Ce hardly migrated during the 470 day test with only one concentration peak in the source layer. When using fine arenaceous quartz as tracer carrier, double concentration peak phenomenon occurs for all the nuclides examined, with the peaks distributing, respectively, on the upper and lower sides of the source layer. This phenomenon was suggested to result from the very low water containment ability and nuclide retentivity of the source layer arenaceous quartz. Thus, the so called double concentration peak phenomenon is formed by the source and subsequent migration of part of the source. The obviously reduced migration of Sr when taking fine arenaceous quartz as tracer carrier demonstrated significant influence of the capillary barrier formed by the fine arenaceous quartz layer and overlying loess on nuclide migration. Considering that the fine arenaceous quartz layer is very small (7 mm) in thickness and horizontally placed and the small dimension of the test pit, capillary barrier could be an effective way to protect the underlying waste from leaching.

Keywords: capillary barrier, double concentration peaks, nuclide migration

1. Introduction

The safe disposal of radioactive waste is a worldwide environmental concern. Understanding of the migration behavior of radionuclides in aerated zone is very important for shallow land disposal of radioactive wastes. Loess is widely distributed in the semi-arid area of Western China and may probably be used as disposal media of shallow land repository. With the purpose of providing parameters and scientific basis for engineering design and safety assessment of shallow land repository, two phases of six year research cooperation (1988–1993 and 1995–2001, respectively) (Shushen *et al.*, 1993, 2001) between China Institute for Radiation Protection (CIRP) and Japan Energy Atomic Research Institute (JEARI) was implemented on the migration behavior of radionuclides and establishment of methodology for safety assessment in radioactive waste disposal. As a part of the cooperation, two phases of field migration test of nuclides (^{85}Sr, ^{60}Co, ^{137}Cs, ^{237}Np, ^{90}Sr, ^{238}Pu and ^{241}Am) was carried out from May 1989 to August 1991 and from July 1997 to August 2000, respectively, in unsaturated loess under sprinkling conditions, and double peak phenomenon (two concentration peaks in nuclide migration direction) was observed for ^{85}Sr, ^{237}Np, ^{90}Sr, ^{238}Pu and ^{241}Am (Li *et al.,* 1993; Zhao *et al.*, 2001)

According to the traditional theory of solute migration, usually only one concentration peak is expected (Li and Li, 1998). Thus, several hypotheses has been put forward in order to explain the double concentration peaks of ^{85}Sr found in the first phase of cooperative research between CIRP and JEARI. Wang *et al*. (1999) presented a "chemical species" hypothesis that each nuclide may migrate as two important chemical species that have different Kd values and migrate at different speed, but no study was carried out on the nuclide speciation. Li *et al.* (2000) ascribed this phenomenon to competitive adsorption among nuclides on soil surface. They suggested that dissolved nuclides with higher Kd would take up all the adsorption sites available close to the origin, which expels the nuclides with lower Kd values to migrate farther from the origin; while Du (1997) proposed a solubility mechanism which emphasized the influence of solubility on the migration ability of nuclides. Both competitive adsorption and solubility limited migration can only be used to explain the separation of different nuclides in migration direction, but cannot explain the double peak phenomenon. Therefore, the formation mechanism of the observed double peak phenomenon remains unknown. Further, it seemed that one of the aforementioned concentration peak occurred at the origin (corresponding to the source layer), and each nuclide had one migration peak. On the other hand, the nuclide migration experiments conducted in the second phase of corporation between CIRP and JEARI indicate that the difference in media characteristics between the tracer carrier and natural loessmay cause double peak phenomenon (Qian *et al.*, 2002). Hence, one of our purposes of this study was to reveal the influence of tracer carrier characteristics on nuclide migration in loess by using loess and fine arenaceous quartz, respectively, as tracer carrier.

Moreover, the arrangement of fine-grained soil overlying coarse-grained material can divert infiltrating water away from coarser material under unsaturated conditions (Ross, 1990). This kind of structure is called capillary barrier and has widely been used in solid waste including radioactive waste disposal in order to prevent the waste under the coarse grained material from leaching (Schultz *et al.*, 1995; Daniel, 1994). Numerous hydraulic studies have been made on the mechanism, efficacy and numerical simulation of capillary barriers in order to optimize the design (Steenhuis *et al.*, 1991; Stormont, 1995; Porro, 2001; Oldenburg and Pruess, 1993). Perceivably, capillary barrier would reduce the nuclide migration rate. Thus, we look at the function of capillary barrier, in this paper, on the basis of its influence on nuclide migration.

2. *In-situ* Test

2.1. THE CHARACTERISTICS OF THE TEST SITE

The nuclide migration test was carried out at the CIRP's field test site located in Yuci area, Shanxi province. This test site is on a medium cut loess plateau with an elevation of 953 m, an average annual temperature of 9.3 °C, an average annual precipitation of 434 mm and an average annual evaporation of 326 mm. The stable nuclides Sr, Nd and Ce in stead of the radionuclides were taken as tracers in this study. The geochemical behavior of stable nuclide of Sr is almost the same as ^{90}Sr and ^{85}Sr, and REEs are often used as analogues of actinides in nuclide migration studies (Dearlove, 1989; Del Nero *et al*., 1999).

The field test was performed on a platform in the north of the site, where the permeability of the loess layer was lower, and the groundwater table was at a depth of about 31 m. Some background values of the soil and groundwater at the field test site are listed in Tables I and II, respectively. The background content of Sr is 1.07 mg/kg, while Nd and Ce are undetectable in fine arenaceous quartz used in the test. Thus, the effect of the background content of Sr, Nd and Ce on test results could be neglected.

2.2. FIELD TEST

The source layers were obtained by mixing $SrCl_2 \cdot 6H_2O$, $NdCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$, respectively, with loess or fine arenaceous quartz, and the mixtures were well blended with a little water for uniformity. The concentration of tracer

TABLE I

Chemical composition in unsaturated soil (in percent)

SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	Sr, Nd, Ce (mg/kg)
59.9	11.5	3.3	1.25	0.46	0.07	8.9	1.9	2.13	1.54	227.6, 39.8, 60.9

TABLE II

The contents of chemical elements in groundwater (mg/L)

K	Na	Ca	Mg	Al	Fe	Si	Mn	Sr
0.73	80.21	27.54	19.34	0.032	0.032	<0.01	0.027	0.65
Nd	Ce	HCO_3^-	$SO4^{2-}$	NO_3^-	NO_2^-	Cl^-	Br^-	
<0.04	<0.04	317.4	75.48	3.14	13.95	57.97	0.28	

TABLE III

Characteristics of test pit

Tracer	Dimensions	Media	Sprinkling density
Sr, Nd, Ce	20 × 150 × 50 (Depth) cm^3	Natural Loess	20 × 150 cm^2, 5 mm/h, 3h/d
Tracer carrier		Tracer layer	
Fine arenaceous quartz or natural loess		20 × 150 × 0.7(Depth) cm^3	

TABLE IV

Measured concentration of Sr, Nd and Ce in the source layer taking loess as tracer carriers

	Content (mg/kg, dry weight)		
Sample No.	Sr	Nd	Ce
1	20540.7	2727.5	6017.9
2	21103.8	2741.0	5964.2
3	21359.2	2758.6	6168.0
4	21373.7	2760.2	6101.7
5	20962.0	2776.8	6209.9
6	20795.2	2747.9	6039.3
Average value	21022.4	2752.0	6083.5
Standard deviation	325.8	17.1	96.8
Relative standard deviation %	1.55	0.62	1.59

elements in the source layer is listed in Tables IV and V, respectively. Figure 1 shows the sketch of the test pit, the characteristics of which are given in Table III.

A pit was excavated in accordance with designed dimension. The tracer layer was put onto the pit bottom, and then the loess was backfilled into the pit, on top of the source layer. Artificial sprinkling was made to speed up the migration of nuclides. In order to ensure the uniform spatial distribution of tracer material, a PVC frame of 7 mm in thickness with the designed dimension was used in placing the source layer. Briefly, after the pit bottom was shaved as flat as possible, the PVC frame was emplaced at the position for source layer, then the space enclosed by the frame was filled with the tracer material.

A special sampling device (Huang *et al*., 2000) was designed for recovering soil core in order to examine the vertical distribution of nuclides. As shown in Figure 2, the soil core sampling device is composed of a manual screw pressing type sampler, a locating plate and four anchors. Before the emplacement of tracer layer, four anchors were well buried about 60 cm deep into the ground surrounding the pit. Each anchor was connected to a rod reaching up out of the ground to support the locating plate on which there were 6 sampling holes. While sampling, the sampler was pressed downward through one of the sampling holes to recover a soil core.

TABLE V

Measured concentration of Sr, Nd and Ce in the source layer taking fine arenaceous quartz as tracer carriers

	Content (mg/kg, dry weight)		
Sample No.	Sr	Nd	Ce
7	25019.6	3955.8	8135.6
8	22938.1	3818.4	7855.9
9	24173.9	3952.6	8173.7
10	24065.6	3987.5	8221.3
11	26612.0	4032.8	8575.8
12	22868.8	3829.3	8032.3
Average value	24279.7	3929.4	8165.8
Standard deviation	1402.5	86.8	239.2
Relative standard deviation %	5.78	2.21	2.93

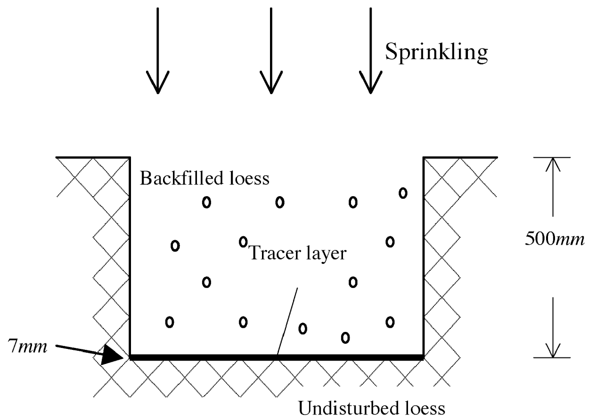

Figure 1. Sketch of the test pit.

In sampling operation, two problems must be considered. One is that the soil core will be compressed while pressing the sampler down and another is that the compressed soil core will fall out of the sampler when retrieving the soil core. Thus, as shown in Figure 2, a negative pressure system was added to the sampling device to overcome these difficulties.

3. Analysis

The field test lasted 470 days. Soil cores were recovered on the 7, 42, 94, 274 and 470th days during the test. Soil cores were sliced into layers of 3 ~ 10 mm thick within 3 days after recovery and ground to 200 mesh size. 0.5 ~ 1.0 g soil sample from each layer were precisely weighed and placed in Taflon beaker. After wetting

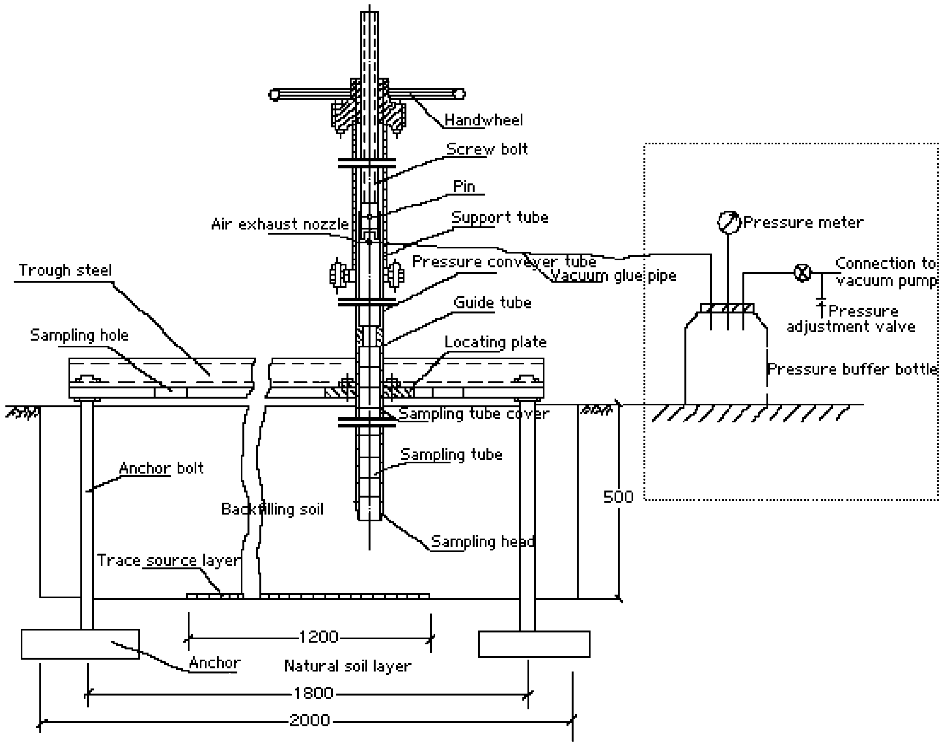

Figure 2. Schematic diagram of soil core sampling device.

with drops of pure water, 10 mL hydrochloric acid was added, and the beaker was placed on a low-temperature electric stove to evaporate the hydrochloric acid to 5 mL. Then, 15 mL concentrated HNO_3 was added and heating was continued until dense viscous material formed in the beaker. Silica was removed by adding 10 mL HF and heating. The silica removing procedure repeated 2–3 times when silica concentration is high. After cooling, 5 mL $HClO_4$ was added, and the sample was digested by heating until the sample was nearly dry and the white smoke disappeared. The sample digesting procedure repeated 2–3 times in case that the concentration of organic matter is high. At this time, the sample residual looks white or primrose yellow (due to its high content of iron). Finally, the inner wall of the beaker was washed using deionized water, and the sample residual was dissolved using hydrochloric acid and diluted to 50 mL. The concentration of Sr, Nd and Ce was determined using ICP-AES.

4. Results and Discussion

Figure 3 shows the vertical underground distribution of adsorbed Sr, Nd and Ce when loess is used as tracer carrier. The results show that there is only one

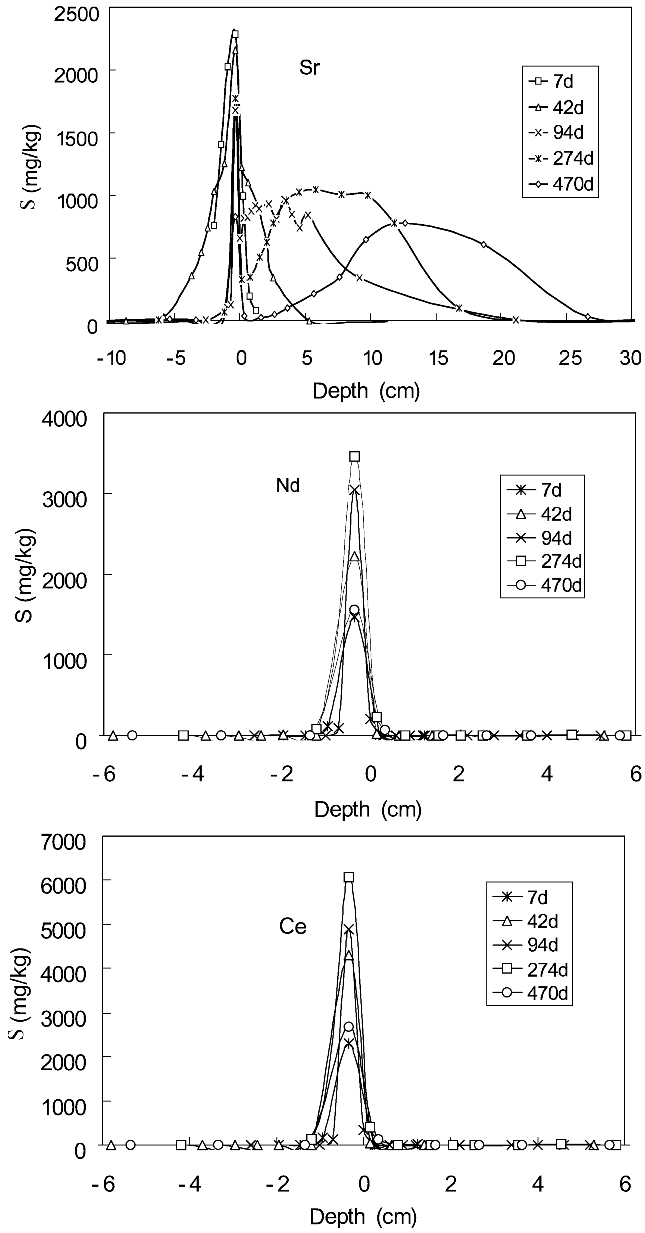

Figure 3. The absorbed concentation of the elements distributed in vertical underground with a trace carrier of natural loess.

concentration peak for Nd and Ce which corresponds to the source layer, but two concentration peaks occur for Sr distribution at each sampling time, of which one corresponds to the source layer and the other is in the loess migration medium. The concentration peak at the origin is formed by the residual nuclide in the source layer, while that in the loess migration medium is generated by nuclide migration and is called "migration peak". According to Liu *et al.* who performed a laboratory experiment with the same loess on adsorption characteristics of Sr, Nd and Ce, the adsorption coefficient of Nd and Ce on loess is much higher than that of Sr, which means that Sr migrates in loess more easily and quickly than Nd and Ce. Our field experiment which lasted 470 days indicates that Nd and Ce could be effectively retarded by loess, while Sr migrates slightly under unsaturated condition in loess.

The vertical underground distribution of Sr, Nd and Ce with fine arenaceous quartz being used as tracer carrier is shown in Figure 4. Similar to those tests for ^{237}Np, ^{90}Sr and ^{238}Pu previously conducted Zhao *et al.* (2001), double concentration peaks occurred obviously close to the source layer for all the nuclide tracers examined. There is little difference between the distributions of Nd and Ce due to their immobility in loess. However, the peaks locate, respectively, on top of and beneath the source layer. Under whatever saturated or unsaturated conditions, flow field is the most important factor governing nuclide migration. Since the matric potential (negative pressure) of fine arenaceous quartz is much lower than that of natural loess Li (2001), the water added while blending the nuclide chemicals with fine arenaceous quartz will move quickly to the natural loess contacting (on top of and beneath) the tracer layer upon the emplacement of tracer layer. Meanwhile, the nuclides are weekly adsorbed by arenaceous quartz and easily migrate with water from the source layer to loess. Thus, the observed double concentration peaks was most probably result from the difference in media characteristics between the tracer carrier (fine arenaceous quartz) and loess, and may initially be generated prior to sprinkling.

From 3 and Figure 4, we can see that, whatever the tracer carrier was used, the migration peaks were significantly broadened and even dome-shaped, and the source peaks were also broadened a little bit. The peak broadening phenomenon was most probably caused by dispersion and diffusion of nuclides which usually ease the nuclide concentration gradient.

Although Nd and Ce migration was not apparent when using loess as tracer carrier, we can find, by comparing Figure 3 with 4, that Sr migrated much faster than taking fine arenaceous quartz as tracer carrier. For example, after 470 days of sprinkling, the concentration peak of strontium taking fine arenaceous quartz as tracer carrier was close to the origin, while using loess as tracer carrier the Sr migration peak was about 13 cm down the source layer! The much reduced Sr migration rate when using fine arenaceous quartz as tracer carrier should be resulted from the effect of capillary barrier that is constructed by placing natural loess overlying fine arenaceous quartz.

According to Ross (1990), the arrangement of unsaturated fine-grained soil overlying unsaturated coarse-grained material forms a capillary barrier which can, under appropriate circumstance, divert infiltrating water away from coarser material. He also pointed out that for a capillary barrier to be effective, special measure must be taken in the design and construction. For instance, the interface between the

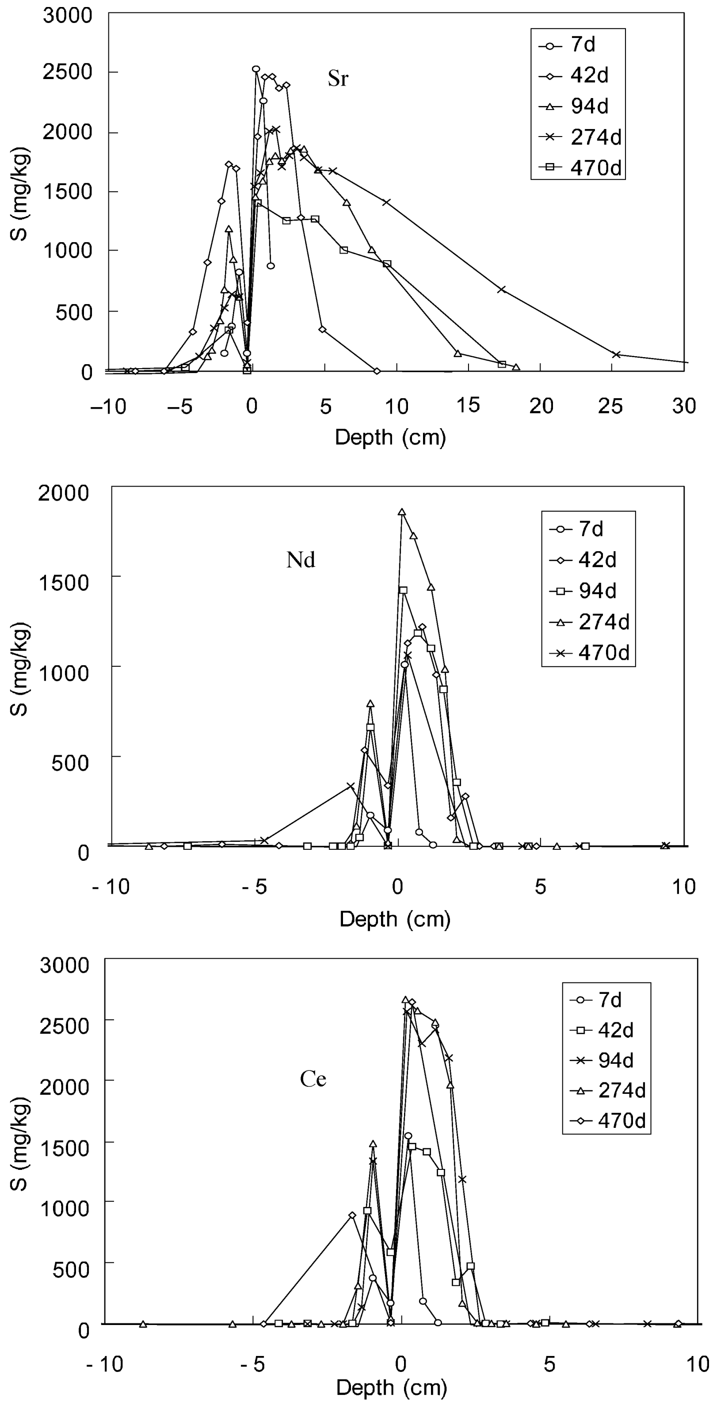

Figure 4. The absorbed concentation of the elements distributed in vertical underground with a tracer carrier of fine arenaceous quartz.

coarse grained layer and the overlying soil should incline outward to form a dome, otherwise water would accumulate at the interface and, finally, invade the coarse grained material, and the coarse grained layer should have a necessary thickness. Laboratory experiments has shown that though the interface between the two layers is deigned horizontally, it could still divert most of the infiltrating water away under certain circumstance such as at low sprinkling density (Wang *et al.*, 2003a, b). In our test, the structure comprising of fine arenaceous quartz and overlying loess worked as a capillary barrier under unsaturated sprinkling conditions, which prevented the fine arenaceous quartz and underlying loess from leaching during sprinkling and, thus, significantly reduced the migration rate of nuclides. Under unsaturated conditions, the water path in the experimental system using fine arenaceous quartz as tracer carrier is schematically shown in Figure 5. Theoretically, the thicker the coarse grained material and the larger the dimension of the capillary barrier, the better the function for the barrier in diverting water would be. However, the fine arenaceous quartz layer in our test was only 7 mm in thickness with a small dimension and placed horizontally. Therefore, capillary barrier could be an effective way in preventing wastes underlying the barrier from leaching.

5. Conclusions

1. Under the springkling density of 5 mm/h, 3h/d, Ce and Nd were effectively retarded by loess and Sr migrated slightly downward during the nuclide migration test which lasted 470 days.

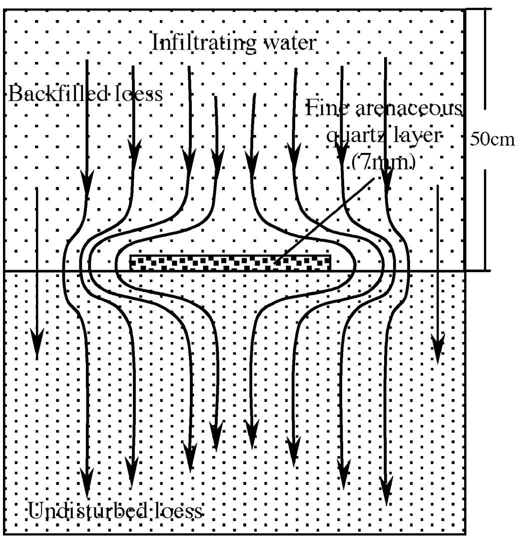

Figure 5. Sketch of the infiltrating water flowing downward when arenaceous quartz layer was taken as tracer carrier.

2. Double concentration peak phenomenon was observed in the field nuclide migration tests of the cooperative research between CIRP and JEARI, which was supposed to conflict with traditional solute migration theory. Our experimental results demonstrated that when using loess as tracer carrier, one of the concentration peaks corresponded to the source layer and was caused by the residual nuclide, and only one migration peak appeared.
3. When using fine arenaceous quartz as tracer carrier, double concentration peaks occurred close to the source layer for all the nuclide tracers examined. This observation is consistent with that in the migration test of ^{237}Np, ^{90}Sr and ^{238}Pu previously conducted with similar tracer carrier. However, one of the peaks appears on top of the source layer, while the other is beneath the source layer. This phenomenon would result from the nuclide migration as the water added in source layer preparation moves quickly to the surrounding loess due to the very low water containment ability and nuclide retentivity of fine arenaceous quartz.
4. Although the source carrying fine arenaceous quartz was only 7 mm in thickness and placed horizontally with a small dimension, the capillary barrier significantly reduced the migration rate of Sr. Thus, capillary barrier could effectively prevent underlying waste from leaching.
5. The broadening phenomenon of nuclide migration peaks observed in the experiments was most probably caused by dispersion and diffusion which usually ease the concentration gradients and could be responsible for the dome-shaped migration profile of strontium.

Acknowledgements

This research was funded by the Hundred Talents Program of Chinese Academy of Sciences ([2000]254), K. C. Wong Education Foundation, Hong Kong, and Chinese Science Fund for Post-Doctorate.

The authors wish to express thanks to the reviewers for the helpful comments and suggestions, which greatly improved the manuscript.

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