

Ion-Migration Through Bentonite/Zeolite
and Bentonite/Quartz Sand Mixture

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ABSTRACT

In the geological disposal system of the high level radioactive wastes radionuclides begin leaching from the waste form when the canister is degraded by corrosion. The buffer materials, as one of the engineered barriers can retard the migration of the radionuclides to the biosphere. In this study, the diffusivity of radionuclides has been obtained in the compacted clay materials, such as mixtures of bentonite-zeolite, and bentonite-quartz sand for buffer materials. For the bentonite and zeolite mixture, K_d -value for cesium has been increasing with zeolite contents. The increase in the K_d -value has also been obtained for strontium, though the inclination is found to be smaller than that for cesium. In the case of bentonite and quartz sand mixture, the K_d -value has increased with quartz content (up to 70%), though the increasing rate is smaller than that in the zeolite mixture. The purpose of the quartz sand mixing is to improve the thermal conductivity of the buffer materials. It is to be noted that the sorption capability of bentonite and quartz sand mixture is found to be a little bit larger than that of bentonite. As for cesium, the K_d -values obtained in diffusion experiment agree well with those from batch experiments within a factor of 2, while for strontium good agreement has not been obtained.

1. INTRODUCTION

HLWs containing long-lived radionuclides should be isolated from the biosphere in underground repositories. Requirements for the repository include long-term stability of geologic formation, high mechanical strength, lower permeability for the ground water, high thermal conductivity for the decay heat of HLW, and so forth. In order to prevent nuclides from migrating to biosphere, several engineered barriers such as a canister, a backfill, etc. have been investigated in some laboratories.

Among them, the backfill materials play a role of minimizing the migration of ground water between the host rock and the canister and retarding the migration of chemical species (corrosive species & radionuclides), etc.

Bentonite has been chosen as the backfill materials, since it has low permeability, retardation effect, etc. compacted bentonite has been investigated about retardation in some laboratories by the diffusion experiments. It has a disadvantage of lower thermal conductivity, however, the problem can be improved by adding some materials to bentonite.⁶⁾

In this study, quartz sand has been chosen as one of the adding materials. Quartz sand

mixing might cause a decrease of retardation, then ion migrations have been investigated in compacted bentonite-quartz sand mixture beds. On the other hand, in order to improve retardation, zeolite mixing can be effective.⁷⁾ So in this study, cation migrations have been investigated in compacted bentonite-zeolite (mordenite) mixture beds.

At the same time, batch sorption experiments have been made, and the results have been compared with those from the migrations in compacted beds.

2. EXPERIMENTS

2.1. Equipments

Figure 1 shows a schematic diagram of the equipments for migration test and Fig. 2 shows the detail of the diffusion cell. This cell is designed to be used over 250 Kg/cm². The RI containing solution is pressurized by a positive displacement pump to 100Kg/cm². The pressure is kept constant at 100 Kg/cm², by-passing the bulk of the fluid through the pump by the back pressure relief valve. The solution is fed to the diffusion column through pressure transducer to control the feed pressure to the column. SUS 316 piping and joints are used to the high pres-

sure line. The feed pump is KHD-W-52 by Kyowa Seimitsu Co., Ltd. The inner diameter of the diffusion cell is 40 mm ϕ . The bed length has been chosen to be 20 mm throughout the experiments. The upper and lower surfaces are contacted to filters in order to wet the bed surface uniformly and prevent the bentonite from flowing out of the bed. Stainless steel sintered and teflon filters are used for this purpose. The pore size of the stainless filter is $2.0\mu\text{m}$ and that of the teflon filter is $0.1\mu\text{m}$.

2.2 Procedure

The samples examined here are Na-bentonite from Tsukinuno, Yamagata Japan, quartz sand and zeolite from Nimamachi Shimane, Japan. The bentonite and natural zeolite were crushed and sieved to get the particles under #200 Mesh. The grain size of the quartz-sand is between #150 - 200 Mesh. The specific gravities of bentonite, zeolite and quartz sand are 2.67, 2.32 and 2.64g/cm^3 respectively.

In this study, 100% bentonite, the mixture of bentonite-zeolite, and that of bentonite-quartz sand have been packed to beds for the nuclides migration experiments. The ratio of bentonite/zeolite has been chosen to be 80/20, 60/40, 40/60 and that of bentonite/quartz sand to be 70/30, 30/70 respectively. The solutions of CsCl and SrCl_2 diluted with distilled water are fed to the cell respectively. The radio isotope tracers employed are ^{85}Sr and ^{134}Cs . The concentrations of strontium and cesium are chosen at the same value of $\sim 10^{-6}\text{mol/l}$, which is equivalent to the concentration of $\sim 0.3\mu\text{Ci/cc}$.

Before feeding RIs, the beds need to attain saturation with distilled water in order to simulate the repository environment. Feed pressure has been kept constant at the pressure of 100Kg/cm^2 during the saturation process. Observing the swelling pressures and the break through of the feed water at the outlet, it has been concluded that it takes about a week to make the materials saturated with water. Then Sr and Cs solution has been fed to the column for a certain operation time, keeping the feed pressure constant. The flow rate has been evaluated, measuring the out-flowing rate of the solution. The flow rate has been transferred into interstitial velocity, dividing the flow rate by the column cross-section and the bed porosity. Then the feed was stopped and the frange was taken out to push out the bed.

In order to obtain the Sr and Cs concentration profile along the axis of the cylindrical bed, the bed has been sliced perpendicularly to the axis to the thickness of 0.5 to 2mm. The activity of the sliced sample has been measured by γ -counting using a well type NaI scintillation counter. In order to evaluate the water content of the test materials, the sample has been placed in sillicage desiccator for two weeks. The weight loss of dehydration shows the water content in the sample. The activities obtained the nuclides sorbed to the minerals and those soluted to the pore water. The activity in the unit

volume solution can be expressed by the total activity $C_s + C_L$, and activity ratio C_s/C_L in equation (1)

$$\text{where } \frac{C_L}{W_L} = \frac{C_s + C_L}{W_L} / \left(1 + \frac{C_s}{C_L}\right) \quad (1)$$

where

C_s : activity sorbed to the minerals

C_L : activity soluted to the water

W_s : weight of the dry minerals in the sample

W_L : volume of the solution in the sample

If linear sorption isotherm of equation (2) is assumed,

$$k_d = \frac{C_s/W_s}{C_L/W_L} \quad (2)$$

k_d : distribution coefficient

equation (1) can be transformed to equation (3).

$$\frac{C_L}{W_L} = \frac{C_s + C_L}{W_s} / \left(k_d + \frac{W_L}{W_s}\right) \quad (3)$$

When the water content (W_L/W_s) is constant through out the bed, C_L/W_L is proportional to $(C_s + C_L)/W_s$; that is, the relative RI concentration profile in the aqueous phase, can be evaluated by the total activities of $C_s + C_L$ and the sample weight of dry-minerals (W_s).

3. DATA ANALYSIS METHOD

The obtained profiles of the Sr and Cs concentration have been analysed to evaluate the apparent diffusion coefficient in the compacted bed. The well-known convective-diffusion equation (4) taking material balance, in unit bed volume, has been used for analysis²⁾

$$\varepsilon \frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} + \varepsilon V \frac{\partial C}{\partial X} - \varepsilon D \frac{\partial^2 C}{\partial X^2} = 0 \quad (4)$$

where ε : porosity

V : interstitial velocity

D : intrinsic diffusion coefficient

C : ion concentration in aqueous phase

S : ion concentration in solid phase

X : distance from the surface of bed

t : time

When the linear sorption isotherm can be assumed, equation (5) can be introduced

$$S = \rho k_d C \quad (5)$$

where ρ : solid phase density

as shown in Fig. 3 and 4, the equation (4) and dividing the equation by porosity ε , the following equation can be obtained.

$$\left(1 + \frac{\rho \cdot k_d}{\varepsilon}\right) \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial X} - D \frac{\partial^2 C}{\partial X^2} = 0 \quad (6)$$

In equation (6), $1 + \rho k_d/\varepsilon$ is so called retardation factor(R_f).

creep during irradiation. This is illustrated in Figure 9, which shows creep curves for Marlex CL-100 under tensile creep loads of 11.0 and 12.4 MPA (1600 and 1800 psi) at 10-11°C. Curves are shown for unirradiated specimens and for specimens undergoing irradiation at 5 krad/h in IX resin. Similar results are obtained for creep during irradiation in air.

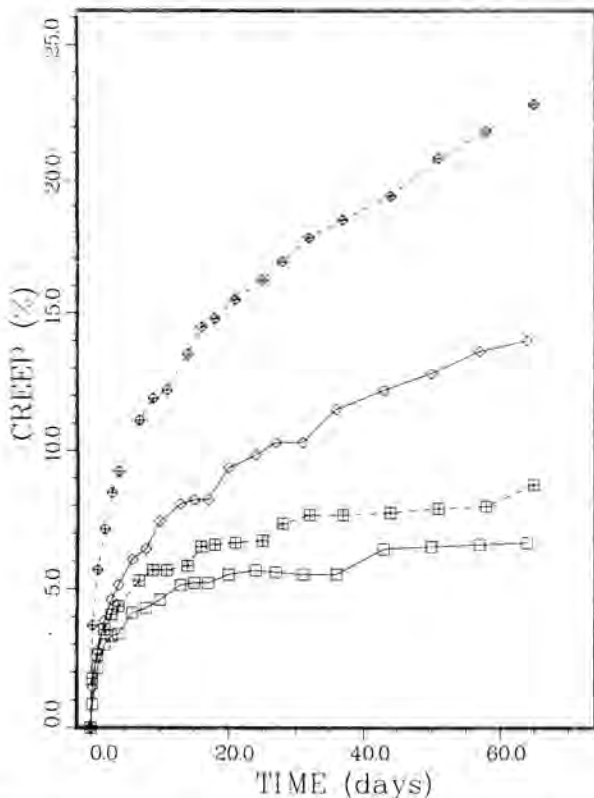


Fig. 9. Creep curves for Marlex CL-100 at 10-11°C under tensile stresses of 11.0 and 12.4 MPA (1600 and 1800 psi). Curves are for unirradiated controls and for specimens undergoing irradiation at 5 krad/h in IX resin. Unirradiated, 11 MPA -□; irradiated 11 MPA -■; unirradiated, 12.4 MPA -◇; irradiated, 12.4 MPA -◆

The data for creep during irradiation for Chemplex (not shown) were similar to the Marlex curves shown in Figure 9. However, there was a significant difference. The Chemplex specimens stressed to 12.4 MPA ruptured about 10 weeks into the test. One specimen irradiated in air ruptured at 71 days and another specimen irradiated in IX resin ruptured at 84 days. This creep rupture during irradiation occurs at approximately half the normal tensile strength of 24.8-25.5 MPA recorded for unirradiated Chemplex from tensile testing in this task. The unirradiated Chemplex controls did not exhibit creep rupture at 12.4 MPA.

CONCLUSIONS

Mechanical testing of HDPE following irradiation at 10-11°C has shown that irradiation resulted in no loss of strength. However, irradiation caused these materials to become less tolerant of deformation. The usual terminology for such changes would be that the material had embrittled. However, since test specimens of these materials irradiated to 50 Mrad tolerated

tensile deformation exceeding 10% and did not break under cyclic bend testing, the term brittle hardly seems appropriate.

The effects of the different irradiation environments (air, soils and IX resins) in modifying the changes in characteristics produced by irradiation were variable. There was some indication that the soils and IX resin moderated attack from air during irradiation to large doses. The effect became noticeable at approximately 50 Mrad in the thinner Chemplex and Marlex non-HIC specimens while it was not observed until 100 Mrad, if at all, in the thicker Marlex HIC specimens.

Marlex became stiffer following irradiation, as indicated in the bend test results. Up to 50 Mrad, Chemplex did not. We do not know whether this difference in the relative stiffness of the two irradiated materials is related to the fact that, before irradiation, the Chemplex is non-cross-linked while the Marlex is highly cross-linked or to the different container fabrication processes or to other factors.

The results of the irradiations conducted at 10-11°C may be explained by radiation-induced cross-linking, except for the environmental effect at large doses discussed two paragraphs previously. In order to accelerate radiation-induced oxidation, irradiations in air at 60-63°C were conducted. (These results were not discussed in this article. They are included in the complete report, including all of the data, for this study.⁽⁸⁾) These higher temperature irradiations resulted in a loss of strength as well as decreases in elongation at yield and elongation at break. The loss of strength appeared to result from degradation of the surface which progressed into the bulk material as the irradiation in air continued. This result is attributable to radiation-induced oxidation. This, combined with the results for irradiation at 10-11°C plus results cited in the literature for irradiations in inert atmosphere,^(1,2) suggest that radiation-induced oxidation may enhance or speed up the decrease in break elongation that results from cross-linking, but does not solely cause this change. Thus, an irradiated HIC may lose much of its ability to tolerate deformation at some radiation dose, which depends on dose rate, before any loss in strength becomes apparent.

Irradiation under tensile stress resulted in increased creep. Under the conditions of these tests (10-11°C and 5 krad/h) the increase in creep did not become significant until stress loads of approximately half the normal tensile strength or greater were applied. The increase in creep during irradiation occurred in both air and IX resin. The Chemplex creep ruptured during irradiation in both air and IX resin.

During irradiation, there is a transition from behavior characteristic of unirradiated material (i.e., necking behavior) to behavior characterized by cracking and breaking without necking. When the type of failure is plotted as a function of dose vs dose rate, the transition from necking to breaking without necking behavior appears linear on a log-log scale. The relationship obtained from these plots for Marlex CL-100 is

$$D_N = 77000 (R)^{0.5}$$

and for Chemplex is

$$D_N = 550000 (R)^{0.3}$$

where D_N is the dose (rad) up to which necking predominates at a dose rate of R (rad/h).

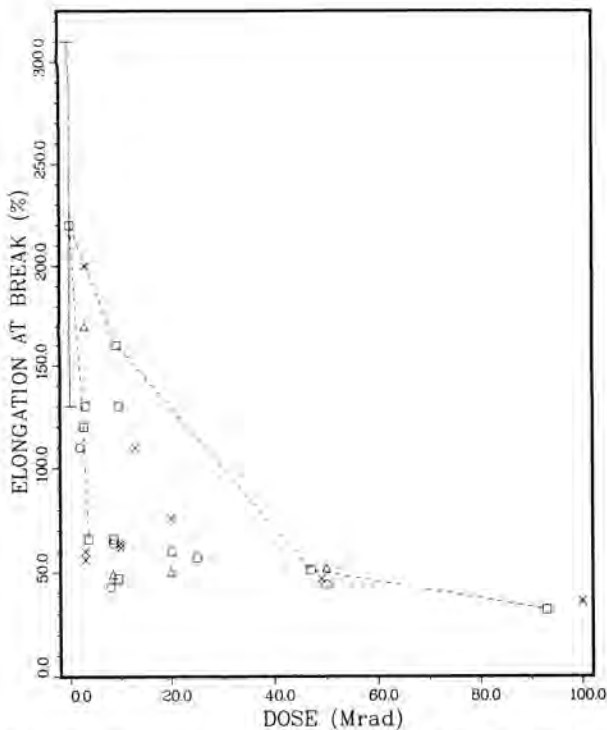


Fig. 6. Elongation at break vs dose of Marlex CL-100 material irradiated at 10-11°C. Symbols indicate irradiation environment: air - □, Barnwell soil - ○, Hanford soil - △, IX resin - X.

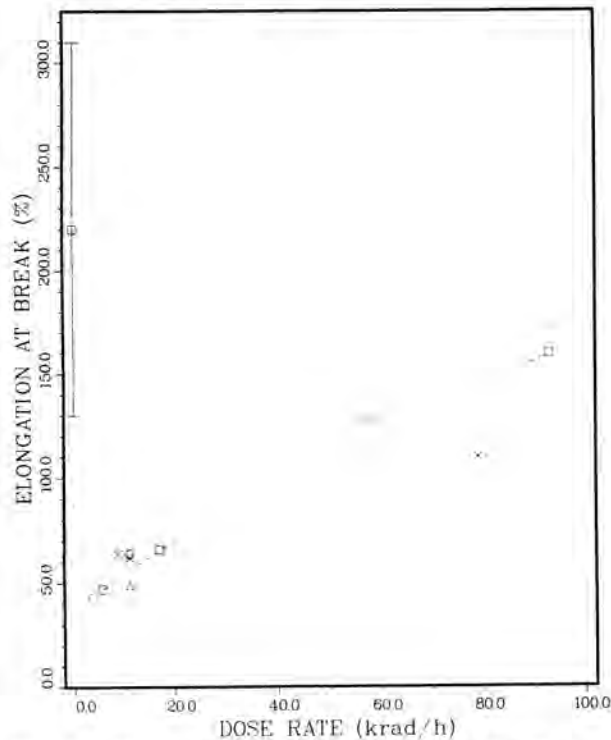


Fig. 7. Elongation at break vs dose rate for Marlex CL-100 HIC material irradiated at 10-11°C for total doses from 8.0 - 13 Mrad. Symbols indicate irradiation environment: air - □, Barnwell soil - ○, Hanford soil - △, IX resin - X.

The two dashed lines in Figure 6 connect air-irradiation points at the highest and lowest dose rates used. The upper line connects points at 93 krad/h, while the lower line, which appears nearly vertical, connects data at 2.5 krad/h. This, plus the data in Figure 7 (see below) shows that break elongation is sensitive to dose rate.

Figure 7 shows that break elongation decreases as the dose rate decreases. This effect occurred in all four irradiation environments and no differences between irradiations in the different irradiation environments were noted. The dashed line connects the air irradiation points in Figure 7.

Bend Testing

The results of bend tests on irradiated Marlex HIC material are illustrated by the curves in Figure 8. These data show that the stiffness of the Marlex HIC material increases significantly upon irradiation. As in the tensile tests the inside surface of this material cracks upon bending. This surface only cracked in tension and not in compression in samples irradiated up to up to 50 Mrad. As in the tensile tests, the onset of cracking in the bend tests was dose and dose rate dependent but was not noticeably affected by the environment (i.e., air, soil, or resin). For specimens irradiated up to 50 Mrad, while cycling in the bend test machine did cause cracks, these cracks did not propagate beyond the surface.

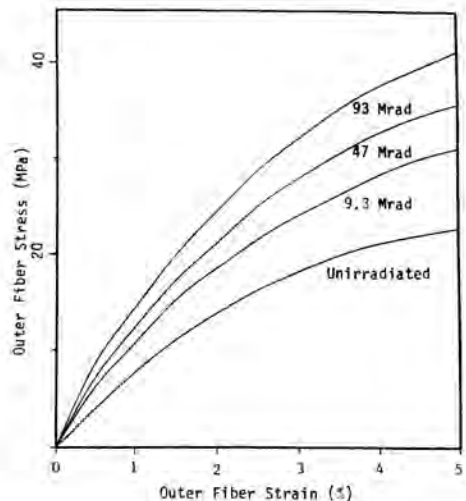


Fig. 8. Bend test curves for irradiated Marlex CL-100 HIC material tested according to ASTM D-790.

The Chemplex behaved differently in the bend testing (data not shown). This material did not get noticeably stiffer following irradiation until doses of approximately 50 Mrad had been attained and, above that dose, the increase in stiffness was smaller than that observed for the Marlex. The Chemplex did not crack in the bend test.

Creep During Irradiation

Creep testing on Type IV tensile specimens of Chemplex and non-HIC Marlex irradiated at 5 krad/h and 10-11°C indicates that the creep rate is faster in the irradiated test samples than in the unirradiated controls. The increase appears to be stress-dependent, i.e., the larger the stress the greater the increase in

Table II Compositions, properties of beds and operation time

Ion	Material	Porosity	Density (g/cm ³)	Interstitial velocity (m/s)	Operation time (s)
Sr	bentonite	0.40	1.6	1.4×10^{-8}	507600
	bentonite 60% zeolite 40%	0.40	1.6	6.4×10^{-8}	337380
	bentonite 40% zeolite 60%	0.37	1.6	4.2×10^{-7}	66600
	bentonite 70% quartz 30%	0.40	1.6	2.7×10^{-8}	415380
	bentonite 30% quartz 70%	0.40	1.6	1.0×10^{-7}	183600
Cs	bentonite	0.40	1.6	1.9×10^{-8}	497340
	bentonite 80% zeolite 20%	0.38	1.6	2.5×10^{-8}	509400
	bentonite 60% zeolite 40 %	0.37	1.6	6.4×10^{-8}	602160
	bentonite 70% quartz 30%	0.40	1.6	2.4×10^{-8}	422400
	bentonite 30% quartz 70%	0.40	1.6	1.5×10^{-7}	152400

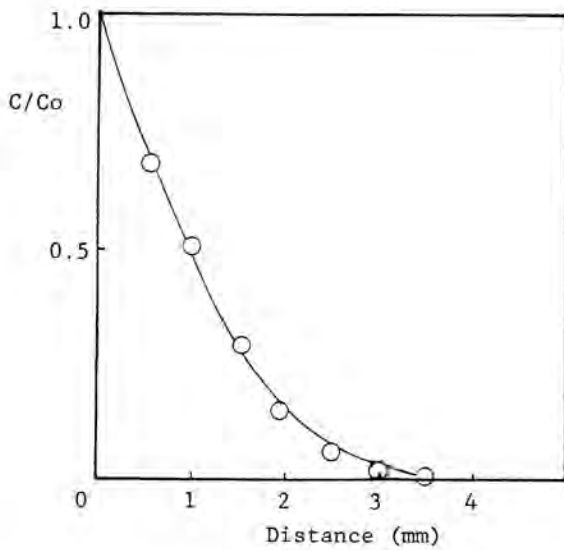


Fig.5 Concentration profile of Cs in the mixture of bentonite 70% & quartz 30%

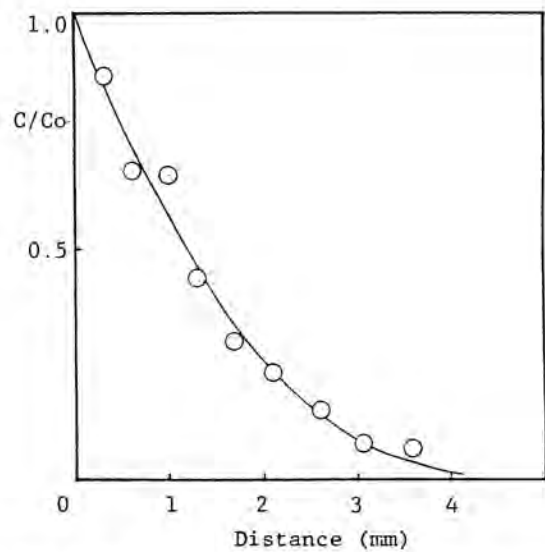


Fig.6 Concentration profile of Sr in the mixture of bentonite 30% & quartz 70%

Table III Observed diffusion coefficients and distribution coefficients obtained by diffusion experiments

Ion	Material	Dobs (m ² /s)	Kd (ml/g)
Sr	bentonite	2.9x10 ⁻¹¹	7.2
	bentonite 60% zeolite 40%	5.8x10 ⁻¹²	34
	bentonite 40% zeolite 60%	5.6x10 ⁻¹²	33
	bentonite 70% quartz 30%	1.9x10 ⁻¹¹	11
	bentonite 30% quartz 70%	7.6x10 ⁻¹²	28
Cs	bentonite	6.1x10 ⁻¹²	56
	bentonite 80% zeolite 20%	2.3x10 ⁻¹²	150
	bentonite 60% zeolite 40%	3.4x10 ⁻¹³	970
	bentonite 70% quartz 30%	2.3x10 ⁻¹²	150
	bentonite 30% quartz 70%	4.5x10 ⁻¹²	79

Table IV Distribution coefficients obtained by batch sorption experiments

Ion	Material	Kd (ml/g)
Sr	bentonite	71
	bentonite 60% zeolite 40%	140
	bentonite 40% zeolite 60%	280
	bentonite 70% quartz 30%	68
	bentonite 30% quartz 70%	70
Cs	bentonite	28
	bentonite 80% zeolite 20%	340
	bentonite 60% zeolite 40%	900
	bentonite 70% quartz 30%	38
	bentonite 30% quartz 70%	59

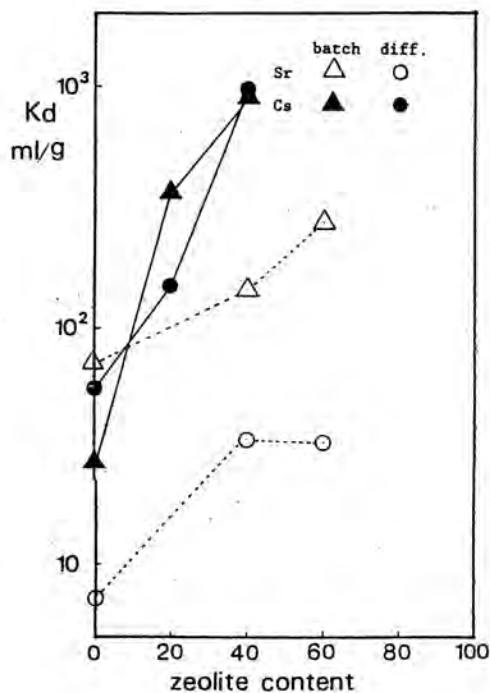


Fig. 7 Kd vs zeolite content

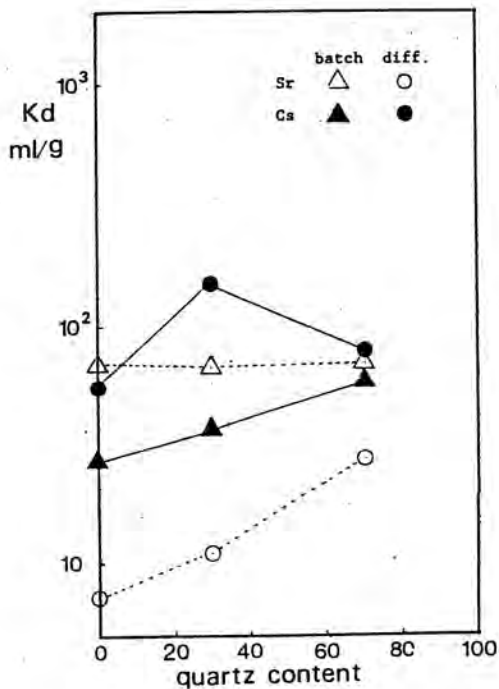


Fig. 8 Kd vs quartz content

As explained before, the sodium concentrations in the contact solution are quite different between in the batch and in the diffusion experiment. Lars Carlsen, Risø National Laboratory in Denmark, has reported the effect of sodium concentration (NaCl) on retention factor ($1/R_f$). It has been observed in chalk that the retention factor for cesium increases from 0.12 to 0.51 as sodium concentration increases from 0.5 M to 4.0 M. On the hand in strontium, the K_d increases from 0.15 to 0.28 at the same rate of sodium concentration increase. Therefore, the increase of sodium concentration causes larger decrease of K_d values for cesium than that for strontium. In Figs. 5 and 6 larger K_d decrease has been observed for cesium than for strontium as increasing the sodium concentration (Na : 8000~20 ppm). Then the higher sensitivity of sodium concentration for Cs than for Sr, agree well to the experiment by Lars Carlsen. In this diffusion experiment the analysis has been made with an assumption of linear sorption. When the equilibrium can not be achieved in the diffusion experiment, the K_d values might be smaller in the diffusion experiment than in the batch experiment. Thus, the ionic strength must be kept at the same level in the diffusion experiment to batch experiment to find whether the sorption equilibrium is attained in the diffusion in the compacted bed column.

5. CONCLUSION

1) Mixing of zeolite to bentonite shows the improvement to retard the migration of strontium and cesium from migration. The effect is much better for cesium than for strontium.

2) Mixing of quartz to bentonite does not decrease the K_d values and even a small increase has been observed.

3) The numerical analysis of the diffusion experiment gives about the same K_d value of Cs as that in batch experiment, though the agreement was very poor for strontium.

4) According to the results, the mixture of zeolite and quartz to bentonite improve the ion sorption characteristics. Though the permeability of ground water is decreased with increasing the mixture content, the zeolite/bentonite and the bentonite/quartz sand mixture might be better than pure bentonite to use for buffer materials, when the content is carefully decided.

5) In order to find whether the linear sorption can be assumed in the compacted bed of water moving condition, the nuclide migration experiment of adjusting the ionic strength to the same as that in the batch experiment has to be investigated to evaluate the K_d values. As for the other nuclides (ie, Am, Eu, Tc), the same evaluation must be made to determine the optimal composition to be adopted at the HLW repository.

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