

## Applicability of Domestic Bentonite as a Buffer Material of Spent Fuel Repository

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### 사용후핵연료 처분장 완충재로서 국산벤토나이트의 활용성

최종원 · 황주호 · 전관식

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### Abstracts

Four domestic bentonite samples collected from the south-eastern area of Korea were identified as Ca-bentonite by analysing XRD-patterns and chemical compositions. By comparing the surface area, CEC and the swelling rate of these samples, Dong-Hae A was selected as a suitable sample for the investigation of distribution coefficients. Sorption equilibrium of Cs, Co and Am was reached in around 10 days, but that of Sr was found to be much earlier. From the measured distribution coefficients, the domestic bentonite was found to have high sorption capacity. In the effect of varying concentration on the distribution coefficient, the values of radionuclides peaked at about  $10^{-7}$  mol/ℓ of concentration.

### 요 약

국내 남동지역에서 수집된 4가지 벤토나이트 시료를 대상으로 X-선 회절과 화학조성을 분석한 결과 Ca-벤토나이트인 것으로 나타났다. 4가지 시료의 비표면적, 양이온교환능 및 팽윤도를 비교하여, 분배계수 측정을 위한 적절한 재료로서 동해 A 시료를 선택하였다. Cs, Co 및 Am의 흡착평형은 약 10일 정도에서 이루어졌으며, Sr의 경우는 이보다 훨씬 빨리 이루어졌다. 분배계수 측정 결과로부터 국산 벤토나이트가 높은 흡착능을 가지고 있음을 알았으며, 농도변화에 대한 분배계수 값은 약  $10^{-7}$  mol/ℓ의 농도범위에서 최고를 나타내었다.

### 1. Introduction

In the geological disposal system of high level radioactive waste, a waste package as an engineered barrier system conceptually consists of

disposal canister and buffer material surrounding it. In accordance with the regulatory requirements of the U.S. NRC 10CFR part 60.113[1], it was noted that the release rate of any radionuclide from the engineered barrier system following the containment period should not exceed one part in

100,000 per year of the inventory of that radionuclides calculated to be present at 1000 years following permanent closure. In this design criteria of engineered barrier, the function of buffer material is very important from the view point of radiological safety. Its primary functions are to prevent the intrusion of groundwater toward the canister and then, when the canister is breached, to slow the movement of released radionuclides by providing some retardation of radionuclides within the buffer and limiting outward flow. To seek appropriate buffer materials, many studies have been conducted by screening a large number of candidate materials, based on the prerequisites such as low permeability, high sorption capacity and high swelling rate, etc.. As the results of these studies, a kind of clay minerals such as bentonite which satisfies a portion of complicated requirements for buffer material has been proposed [2~4]. But the bentonite samples investigated in those papers are of sodium type whereas in Korea available bentonite is mostly of calcium type, of which the properties are reported to be inferior to those of sodium bentonite for buffer material. It has been reported that the estimated amount of bentonite deposits is about 7 million tons in Korea [5].

This paper presents preliminary results of investigation on the ability of domestic bentonite as a buffer material. Surface area, composition, cation exchange capacity (CEC) and swelling rate of bentonite samples were analysed, and then sorption capacity of the bentonite samples was analysed.

## II. Experimental

### 1. Sample preparation

Four bentonite samples were collected at Yun-il

and Kam-po mining area in the south-east of Korea. Yun-il samples were recommended by a local bentonite marketing company as a representative bentonite in the region (Yun-il mining area 22 and 32) and named Dong-Hae A, Dong-Hae B and Dong-Hae C. Kam-Po sample was named after its location of sampling (Kam-po mining area 35). In addition to those local samples, Wyoming bentonite of which the brand name is MX-80 was used as a reference to compare properties of domestic samples. The samples collected were air dried at room temperature and ground to pass 60 mesh-sieve.

### 2. Material property measurements

The mineralogical analyses of samples were carried out by using X-ray diffractometry and chemical analysis. Specific surface area, CEC and swelling rate were measured and compared by using appropriate methods published [6, 7]. CEC of these samples were measured by using ammonium acetate method.

#### A. Surface area

Two methods were considered for surface area measurement, whose difference lies in soaking materials, polar or non-polar molecules. The Brunauer-Emmet-Teller (BET) method using nitrogen as soaking material is well known as a conventional method for solid particles. For clay minerals, however, nitrogen can not soak into interlayers of particles so that another method using polar molecules, such as ethylene glycol, was suggested. In practice, the results of BET method for montmorillonite was reported to be approximately 13~82 m<sup>2</sup>/g, which was much smaller than the theoretical value, 810 m<sup>2</sup>/g [8].

In this study, ethylene glycol monoethyl ether (EGME) method, one of the methods known to

give results close to the theoretical value, was used to measure the surface area of local samples. EGME method was originally suggested by Carter et al. [6], herein, a few points of experimental procedures were modified from the results of several pre-tests. For time saving, the quantity of soaking material, EGME, was reduced to 2.5 ml. And the  $\text{CaCl}_2$ -saturation procedure was excluded because domestic bentonites were found to be Ca-bentonite.

Each sample was ground to pass a 60-mesh sieve, treated with  $\text{H}_2\text{O}_2$  to decompose organics, and washed with demineralized water. The samples were air-dried and again ground to pass the 60-mesh sieve. One gram of each sample was then placed in shallow aluminum weighing dishes (0.2~0.3g) and dried to a constant weight,  $W_1$ , under  $\text{P}_2\text{O}_5$  desiccant. Approximately 2.5 ml of reagent grade EGME was added to each dried sample. Then the slurry sample was placed in desiccator and evacuated with a vacuum pump to attain a vacuum of  $\sim 33.3$  Pa (250 mtorr) to determine the retention quantity of EGME. The sample was then weighed after evacuation and returned to desiccator, the procedure was repeated until its weight became constant.

If the weight dopped with EGME becomes constant,  $W_2$ , EGME weight,  $W_3$ , retained on the bentonite particles was calculated by subtracting  $W_1$  from  $W_2$ . The surface area was then calculated by dividing  $W_3$  by  $2.86 \times 10^{-4}$  g/m<sup>2</sup> of EGME, which is required to cover one gram of pure montmorillonite [5, 6].

## B. Swelling Rate

The swelling rate of samples was determined by Gibbs and Holtz's method [7] which is to measure the free swelling rate of sample in the uncontrolled volume. Ten grams of air-dried samples were divided into small portions, 0.1~0.2 gram each, and added slowly to the 30 of distilled water

in a 50-ml measuring cylinder, which is to avoid the agglomeration of particles and to reduce the measuring error. After a given time, that the swelling rate was determined by comparing the volume of bentonite gel formed by hydration with the initial volume of air-dried sample using the following relation.

$$\text{Free swelling rate(\%)} =$$

$$\frac{\text{Swelled volume} - \text{Bulk volume of dried sample}}{\text{Bulk volume of dried sample}} \times 100$$

## C. Distribution coefficient

### a) Selection of radionuclides

Radionuclides of Cs-137, Sr-85, Co-60 and Am-241 dissolved in 0.1 N HCl were used as tracers in this study. Cs, Co and Am were purchased from U.S. IPL Co. and Sr were purchased from Du Pont Co.. Comparing the hazard indices of various radionuclides contained in spent fuel with that of uranium ore yielded in nature during the time period required for the safe management of spent fuel,  $\sim 10^5$  yr, these nuclides except Co-60 are found to pose the greatest potential hazard to man after 500 years or longer. Co-60, even with its relative short half-life, was included in this study because it has been generally regarded as an important corrosion product in many cases of spent fuel management.

IAEA and several countries, being the heading groups in radioactive waste management, chose some important radionuclides according to their regulations and safety assessments [9]. Important radionuclides chosen by several countries differ in number and types, depending upon regulation system, safety goal, geological condition and type of reactor, etc. But four nuclides selected in this study were common to them from the view point of radiological safety for several hundred years. The radioisotope which has higher potential hazard is Sr-90, but Sr-85 was used to avoid the

**Table 1. Chemical component of synthetic ground water**

component	concentration (mol/l)	compound used
Na	$3.6 \times 10^{-4}$	NaHCO <sub>3</sub>
K	$9.0 \times 10^{-5}$	KOH, KNO <sub>3</sub> , KF
Mg	$1.4 \times 10^{-4}$	MaSO <sub>4</sub> , MgCl <sub>2</sub>
Ca	$3.2 \times 10^{-4}$	Ca(OH) <sub>2</sub>
Cl	$1.3 \times 10^{-4}$	MgCl <sub>2</sub>
SO <sub>4</sub>	$9.0 \times 10^{-5}$	MgSO <sub>4</sub>
NO <sub>3</sub>	$1.0 \times 10^{-5}$	KNO <sub>3</sub>
F	$1.0 \times 10^{-5}$	KF
pH	$7.0 \pm 0.5$	

difficulties in radiation detection.

#### b) Solution

Synthetic groundwater (SGW) was prepared by using the method suggested by Abry et al. [10]. Chemical components and their concentrations of SGW are listed in Table 1. Each radionuclide was spiked in the solution and the specific activity was adjusted to about 0.1  $\mu\text{Ci/ml}$ .

#### c) Batch experiment

The distribution coefficients of cobalt, cesium, strontium and americium in solution on the bentonite sample, Dong-Hae A, were determined by the batch method [11, 12]. This method has been used widely to assess the sorption or retardation ability of backfill materials. Because the distribution coefficients appear to vary within a wide range depending on given experimental conditions, important factors responsible for the variation must be defined and managed carefully. Through several pre-tests, in this study, it was found that the radioactive tracers were scarcely sorbed by the experimental apparatus, and the experimental procedures were determined as follows. 30 ml of spiked solution whose pH was 6.0 ~ 6.5 was added to 1.0 g of solid sample in

polycarbonate centrifuge tube. The tube was placed on a slow rotating shaker fixed at about 10 rpm to ensure the maximum contact between the solid and the solution and at the same time to keep the solid particles from being ground. After mixing for about 10 days, the sample was centrifuged for thirty minutes at 14,000 rpm (21,000g) to separate solid and liquid phase. About 15 ml of supernatant was filtered through 0.2  $\mu\text{m}$  polycarbonate-membrane filter and the radioactivity of 1 ml of filtrate was measured by a well-type NaI-sintillation detector. Any special attempts were not made for pH adjustment, because the final pH became constant in the range of 8.3~8.8.

The distribution coefficient was calculated by the following relations.

$$K_d = \frac{K-E}{E} \frac{V}{W} [\text{ml/g}],$$

where, W is the solid sample weight, g; V is the volume of spiked solution added, ml; E is the filtrate activity, cpm/ml; B is the initial activity of spiked solution, cpm/ml; and Kd is the distribution coefficient, ml/g.

As mentioned above, distribution coefficient is affected by many factors such as temperature, ion concentration, fluid composition, solid to fluid ratio, pH, redox potential and type of solid material [3, 12]. In this study, at first, the contact time required to reach equilibrium between solid and solution phase was determined to satisfy the conditions for radionuclide sorption isotherms. A distribution coefficient obtained at a specific radionuclide concentration may not be a sufficient one to be applied to the assessment of a realistic disposal system since the radiological source-term released from the waste package has not been clearly defined. Thus, sorption behavior was analyzed within a large range of radionuclide concentration,  $10^{-9} \sim 10^{-1}$  mole/l, which included the various range of concentration used by other researchers [3, 12].

### III. Discussion of results

#### 1. Properties of domestic bentonites

Chemical compositions of four domestic bentonites and MX-80 were given in Table 2. As shown in Table 2, the weight percent of calcium contained in four samples was 2 to 4 times higher than that of sodium, whereas, in the case of MX-80, the former was about 2 times lower than the latter. The amount of sodium in these samples was about 2.5 times smaller than that of MX-80 [13]. The X-ray powder diffraction patterns illus-

trated in figure 1 indicate that our samples mainly contained montmorillonite and a little portion of quartz, feldspar, cristobalite and clinoptilolite. And from the data expressed in numbers in figure 1, the basal-spacing of montmorillonite,  $d(001)$ , was found to be about 15~16 Å, which is the evidence of predominance of Ca-montmorillonite [14].

In Table 3, the specific surface area, CEC and swelling rate of domestic bentonites are listed, which shows that each property of Dong-Hae A is higher than those of other local samples. The reason could be inferred from the results of sur-

Table 2. Chemical composition of domestic bentonites, wt%

Composition	Dong-Hae A	Dong-Hae B	Dong-Hae C	Kam-Pa	MX-80/19/
SiO <sub>2</sub>	59.48	57.72	57.4	61.78	63.00
Al <sub>2</sub> O <sub>3</sub>	18.76	21.61	22.71	20.38	16.10
Fe <sub>2</sub> O <sub>3</sub>	5.94	7.08	6.60	3.42	3.00
FeO	0.85	0.57	0.28	0.18	—
CaO	2.56	2.30	1.42	3.58	1.10
MgO	3.56	1.88	2.15	2.95	1.60
K <sub>2</sub> O	0.76	1.31	0.88	0.37	0.48
Na <sub>2</sub> O	0.78	0.63	0.60	0.91	2.20
Igloss	7.28	6.89	7.95	6.41	—
-H <sub>2</sub> O	7.50	6.73	7.52	8.01	—

Table 3. Surface area, CEC and swelling rates of domestic bentonites

Items	Dong-Hae A	Dong-Hae B	Dong-Hae C	Kam-Po	MX-80
Surface area, m <sup>2</sup> /g	613.34±3.83	422.28±0.84	474.52±5.63	507.60±5.81	600~800
CEC, meq/100g	72.9	55.5	58.3	68.4	75
Swelling rate,	155±7.8	111.0	131.6	143.2	>1200[a] 1200[b]
Particle density g/cm <sup>3</sup>	2.7±0.01	2.58±0.01	2.54±0.01	2.50±0.02	2.70

a) K.H. Head, Manual of soil laboratory testing; Vol. 1, Soil classification and compaction tests, Eng. Lab. Equip. Limited(1980).

b) The measured value in this study.

face area measurement. As mentioned previously, the content of pure montmorillonite contained in domestic bentonite could be calculated from the measured values by dividing by  $810 \text{ m}^2/\text{g}$ . It is expected that the surface areas of quartz and feldspar contained in bentonite as impurities are too small,  $20\sim 25 \text{ m}^2/\text{g}$ , to have influence on the approximation of montmorillonite content. From the results calculated in this way, the montmorillonite content of Dong-Hae A was found to be higher, about 70 %, than those of others. Here, it is no wonder that CEC and swelling rate, general-

ly known as the reactions related with the surface of clay particles, of Dong-Hae A were higher. Consequently, among the samples Dong-Hae A was thought to have more appropriate properties as a buffer material for controlling the intrusion of groundwater and retarding the radionuclide migration. However, the swelling rate of Dong-Hae A was about 12 times lower than that of MX-80 as shown in Table 3, which indicates that the domestic bentonite would be unsatisfactory more or less in the point of achieving a low-permeability as the fluid flow barrier. It could also be deduced

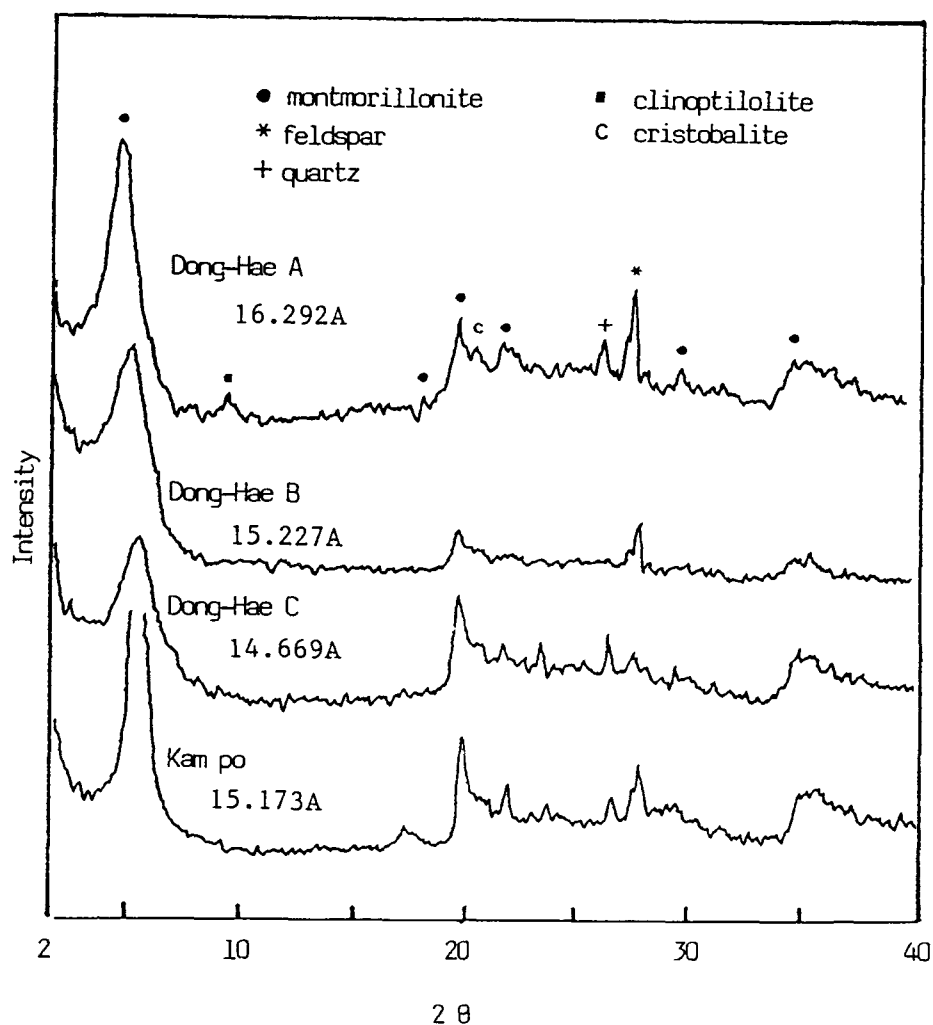


Fig. 1. X-Ray Diffraction Patterns of the Domestic Bentonite.

that a buffer material might be determined by analysing only one of the three properties because they are interrelated.

## 2. Sorption of radionuclides on the material

Figure 2 shows the distribution coefficients with various contacting time between spiked solution and bentonite. As shown in figure 2, it appeared that the equilibrium was reached at about 8 days for Cs, Co and Am, but for Sr it seemed to reach very fast. The contact time used for the remainder of experiments was 10 days, in which the equilibrium would be well established.

In Table 4, the distribution coefficients measured for Cs-137, Co-60, Sr-85 and Am-241 onto Dong-Hae A and the reference data collected from other studies [15~20] were given. This table shows that the distribution coefficients

of each nuclide vary widely with the type of clay mineral used and the results of this study are as high as the reference data. This means that domestic bentonite may have the possibility to be used as a chemical barrier to slow the movement of released radionuclides sufficiently.

The effect of varying concentration on the distribution coefficient is plotted in figure 3. The distribution coefficient of Cs was unaffected by its concentration within the range of  $10^{-9} \sim 10^{-7}$  mol/ℓ. This tendency agreed with Ames's and Salter's results [21, 22]. But in the case of Sr and Co, the distribution coefficients did not vary significantly within the range of  $10^{-7} \sim 10^{-5}$  mol/ℓ and then decreased with increasing concentration. From the results, it seems that there was no more sorption site for Cs in higher concentrations than  $10^{-9}$  mol/ℓ and that there was some surplus sorption sites for Sr and Co in the range of

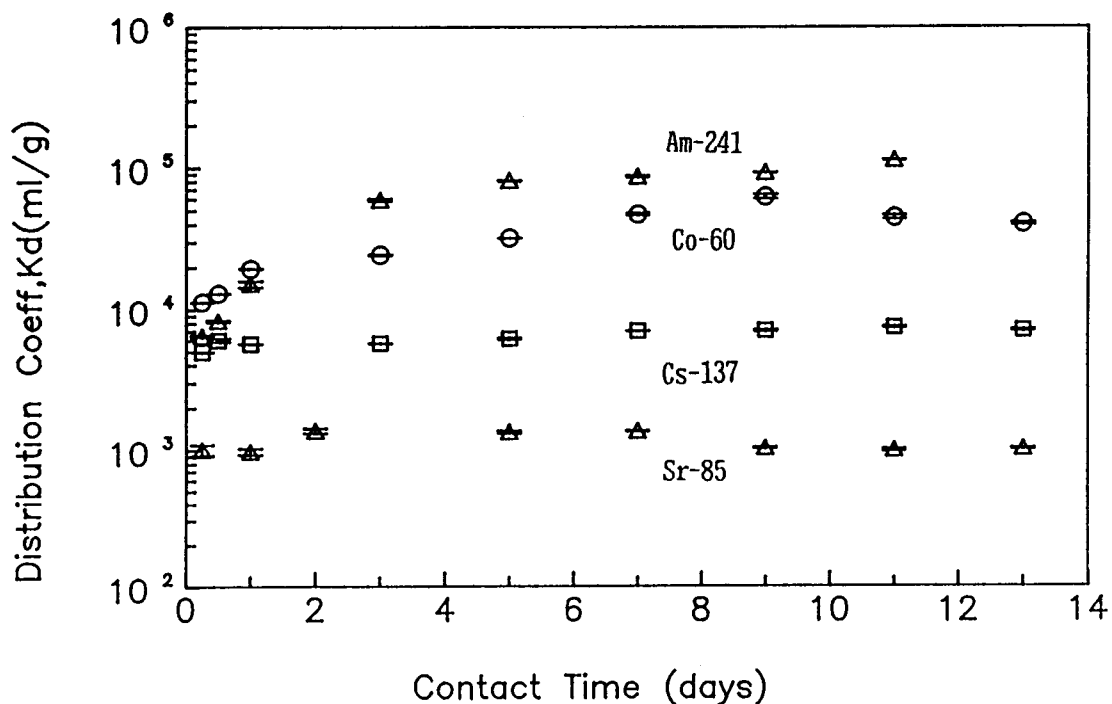


Fig. 2 Effect on the Distribution Coefficient of Varying Contact Time from 0.25–13 Days in Domestic Bentonite (Dong-Hae A) with Synthetic Ground Water (SGW)

Table 4. Distribution coefficients of radionuclides on domestic bentonites

Nuclide	(ml/g)				
	Dong-Hae A <sup>a</sup>	Na-Mont.	Na-Bent.	Ca-Mont.	Ca-Bent.
Cs-137	5920 ± 750	4 ~ 70	1000 ~ 4000	200 ~ 11000	25000 ~ 110000
Sr-85	1345 ± 23	~ 500	~ 6800	~ 50	865 ~ 1200
Co-60	6421 ± 210	8300 <sup>b</sup>	3740		
Am-241	54470 ± 4060		1400		9200
Ref.		15 ~ 18	3, 18	15 ~ 18	3, 18

\*Note ; a : Radionuclides concentration is  $\sim 10^{-7}$  mole/l

b : can not be identified whether it was Na-Mont. or not.

Mont. means montmorillonite and Bent. means bentonite.

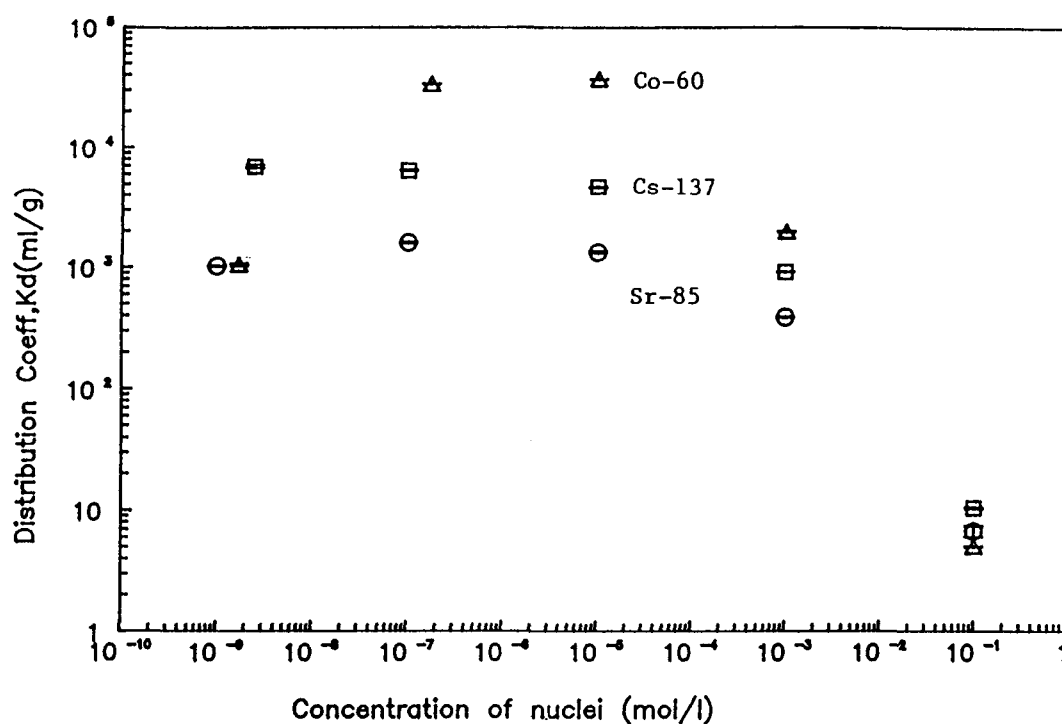


Fig. 3. Effect on the Distribution Coefficient of Varying Concentration from 10 mol/l to 10 mol/l in Domestic Bentonite (Dong-Hae A) Contacted with Synthetic Ground Water (SGW).



$10^{-9}\text{mol}/\ell$  to  $10^{-7}\text{mol}/\ell$ . Thus decrease of distribution coefficients with increasing concentration is probably due to the saturation of sorption sites on the bentonite particles.

#### IV. Conclusion

The local samples were identified as Ca-bentonite. The distribution coefficients of Cs-137, Sr-85, Co-60 and Am-241 on Dong-Hae A sample were measured by batch method. Sorption equilibrium was reached in around 8~10 days, but that of Sr was found to occur very fast. Comparing the results of this study with the reference data, domestic bentonite was found to have high sorption ability. In the effect of varying concentration on the distribution coefficient, the distribution coefficients measured were peaked at  $10^{-9}\sim 10^{-7}\text{mol}/\ell$  of concentration, which was expected to be useful for the radiological safety assessment of disposal system.

These results suggest that the domestic bentonite would be applicable to a chemical barrier material in the repository system. However, since the domestic bentonite was expected to be inferior to Na-bentonite in the point of function to prevent the intrusion of groundwater as a buffer material, an additional study to compensate for this lack seemed to follow. And, at the same time, considering that a large amount of decay heat is generated from spent fuels, a series of study on the thermal stability of domestic bentonite would have to also follow.

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