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Interaction of ^{137}Cs with Sumedang Clay as Natural Barrier of Radwaste Disposal

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ABSTRACT

The interaction of ^{137}Cs with Sumedang clay as a natural barrier for radwaste disposal system has been studied. The initial concentration of Cs was 10^{-8} M for the experiments on the contact time and the effect of Na and K concentrations on the sorption of ^{137}Cs; however, the initial concentration ranging from 10^{-8} to 10^{-3} M of CsCl in the solution for the effect of CsCl concentration. The distribution coefficient K_d is used as the indicator of ^{137}Cs sorption into samples. It was found that the K_d values decreased nonlinearly with the concentration of Na and K, and also to the effects of CsCl concentration. A Freundlich isotherm was proposed to explain the sorption phenomena observed in the experiment. Conclusion of the experiments shown that the presence of metal ions such as Na^+ and K^+ and variation of CsCl concentrations in the solution have a significant effect on the sorption of ^{137}Cs to the samples. The results should be taken into account for the assessment or selection of the site of radwaste disposal facility in the future.

INTRODUCTION

Based on the energy assessment report issued by BPPT to fulfill the national energy demand, nuclear energy or nuclear power plants (NPPs) could already be inserted into the national energy mix system by 2030 [1]. The application of nuclear energy to meet the national energy needs should be coupled with the readiness of the management of the radioactive waste (radwaste) that will be produced, and back-end system facilities such as the disposal facility should also be prepared. In addition, in the near future, the National Nuclear Energy Agency (BATAN) will introduce the 10-MW experimental power reactor (EPR) that is the research embryo towards the design of future NPP in Indonesia.

Similarly to the radwaste from NPPs, the radwaste originating from EPR will, after being processed, eventually be placed at a disposal facility. Radwaste disposal in a geologic medium is proposed as a method to isolate the radwaste from the environment for a long period of time. Near-surface disposal is one of the most suitable methods to dispose of radwaste, especially for the low-level radwaste type [2]. Soil as a natural barrier on a disposal system is predicted to be able to prevent the dispersion of radionuclides, and the interaction of radionuclides with soil can directly effect the retardation of nuclides dispersion from the waste package in a disposal facility onto environment by sorption mechanism [3]. The scenario considered was that of radionuclide leaching from a disposal facility through intrusion mechanisms of water into the disposal facility, followed by container corrosion/damage, dissolution of radionuclides from waste matrix, and the dispersion of radionuclides through the engineered or natural materials surrounding the facility. Based on the results of selected scenario, the safety assessment study can be conducted. Radionuclides dispersion into environment can be limited by the presence of sorption ability of soil around the disposal facility.

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The degree of interaction of radionuclide contaminants such as ^{137}Cs with soil materials around the facility controls the occurrence of ^{137}Cs transport in groundwater to environment, and the study of ^{137}Cs sorption by the soil sample becomes an important subject to be studied to control the presence of ^{137}Cs in the liquid phase.

In order to predict the sorption of radionuclides in the soil as natural barrier, the concept of K_d has been proposed. The sorption of ^{137}Cs describes the removal processes of ^{137}Cs from the solution onto the solid phases. Studies on the sorption characteristics of ^{137}Cs in solid-water systems are closely related to the safe near-surface disposal system.

Cesium-137 is one of the predominant radionuclides in a radwaste inventory yielded by nuclear fission in a nuclear power plant operation. With a half-life of about 30 y, high solubility in a solution, and easy association with plants and species in terrestrial and water environment [4], ^{137}Cs is one of the most important radionuclides to be studied in assessing the disposal facility safety. In this study, the sorption characteristics of ^{137}Cs on the Sumedang soil matrix, and the K_d factor that represents it, has been determined. The condition of experiments were taken into account with no variation of pH, and no special pretreatment of the clay samples was given before experiment. The study of the sorption behavior of ^{137}Cs onto Sumedang clay as a function of time, the presence of NaCl and KCl ions, and the CsCl concentration in solution has been done.

The activity of sorption experiment has been performed in our group since 2008 within the framework of radwaste disposal siting activity based on clay-typed soil location in Java Island [5]. Previous studies of ^{137}Cs sorption characteristics onto clay have been carried out from various site candidates (Tuban, Subang, Karawang, and Serpong) for the disposal facility, where clay-typed soils have generally been chosen as candidates for the radwaste disposal in Java Island. [6-9]. The results obtained from these activities are the collection, compilation, and arrangement of the K_d value data as the database of preferred sites for radwaste disposal facility in Java island.

EXPERIMENTAL METHODS

Reagents and materials

The reagents used in the experiments, namely CsCl, KCl, and NaCl, were obtained from E. Merck. Solution of ^{137}Cs was purchased from Eckert & Ziegler Isotope Products as CsCl in 0.1 M HCl with a specific activity 3.7 MBq/5 mL and then diluted to 20 000 Bq/mL in a 200 mL polyethylene (PE) bottle as stock solution. The demineralized water was made by using distillation unit apparatus, filtered with anion and cation filters columns, and then was used to produce the chemical solution.

Clay samples were taken from the candidate site at Sumedang at a 50-75 cm depth from soil surface, and the coordinates of sampling location are shown in Table 1.

Table 1. Location of sampling.

No.	Sample	Coordinate	
		S	E
1.	Sample - A	108° 06’ 58.6”	06° 44’ 40.7”
2.	Sample - B	108° 06’ 58.6”	06° 44’ 41.7”
3.	Sample - C	108° 06’ 59.4"	06° 44’ 40.8”
4.	Sample - D	108° 06’ 57.9”	06° 44’ 39.8”
5.	Sample - E	108° 06’ 57.0”	06° 44’ 40.8”

Apparatus

Clay samples were collected by using an Auger handy sampler. The samples were cleaned up from roots, leaves, and gravel, and then dried, crushed with mortar, and sieved with Fritsch GmbH, BRD-6580 Idar-Oberstein sieves to obtain the 100-mesh particle size clay samples. A Mettler AE 200 analytical balance was used to weigh the samples before contact with the chemical and radioactive solution. A geological roller was used for contacting the mixture of soil-radioactive solution, and to separate liquid and solid phases of mixture a Heraeus Labofuge 400 centrifuge was used. Radiometric measurements of radionuclide aliquot used Canberra MCA equipped with an HPGe detector with an efficiency of 20 %.

Experiments

Static batch method was used at room temperature. A series of five experimental sorption samples were prepared; they are denoted as sample A to sample E. Initial concentration of CsCl was 10^{-8} M for determining the contact time and the effect of NaCl and KCl. However, for experiments on the effect of CsCl concentration, the initial concentration of CsCl was varied in the range of 10^{-8} to 10^{-3} M CsCl. Each sample of each series was then given ^{137}Cs before shaken gently with the roller machine. The solid-liquid ratio in the vial was 10^{-2} g/mL. All samples were mixed in a 20-mL

PE vial. At specified times, the contents of vial containing a mixture of sample and radioactive solution ^{137}Cs was taken out, then the solid-liquid phases were separated with the centrifuge method (2500 rpm, 10 min) and the aliquot was measured using a multichannel analyzer (MCA) [8,9].

All five samples were contacted with ^{137}Cs solution to evaluate the sample's sorption capabilities. From the obtained results, two samples with the best and worst results on sorption were selected as the representatives of the location for further sorption experiments; they were called sample 1 and sample 2. The data range limited by the two values is the range of ^{137}Cs sorption of Sumedang clay samples.

Sorption evaluation

As the indicator of ^{137}Cs sorption into samples, the distribution coefficient of ^{137}Cs is defined as,

$$K_d = \frac{^{137}\text{Cs in solid phase}}{^{137}\text{Cs remains in liquid phase}} = \frac{A_0 - A_t}{A_t} \qquad (1)$$

The concentration of ^{137}Cs in solid and liquid phases after sorption could be calculated from the measured activities of ^{137}Cs as following,

$$C_{\text{liq}} = \frac{A_t}{A_n}\,[C]_0 \qquad (2)$$

$$C_{\text{sol}} = ([C]_0 - C_{\text{liq}})\,\frac{V}{m} \qquad (3)$$

where A_0 and A_t are the initial and final activities of ^{137}Cs (cps) in solution, while $[C]_0$, C_{liq}, and C_{sol} represent concentration of cesium in initial condition and in the liquid and solid phases (M), respectively, while V and m are the volume of solution (mL) and the dry mass of solid (g).

RESULTS AND DISCUSSION

The K_d values as affected by contact time are shown in Fig. 1. The K_d values continuously increased with increasing contact time, and the values became constant after 6 days of contact and reached equilibrium condition, except for the sample-E which took 8 days before equilibrium was achieved. In the initial contact time, the K_d values increased rapidly with time and then gradually slowed down to reach their equilibrium values. Probably, during the first 6 days of contact, the large amount of accessible active site on the surface of sample were present to accept the ^{137}Cs from the solution, and after the 6 days the active sites of the samples became saturated [10]. This observation indicates that the sorption process of ^{137}Cs was relatively rapid. The K_d values of ^{137}Cs were obtained as 7400, 9000, 22 800, 1000, and 3300 mL/g for sample -A, -B, -C, -D, and -E, respectively.

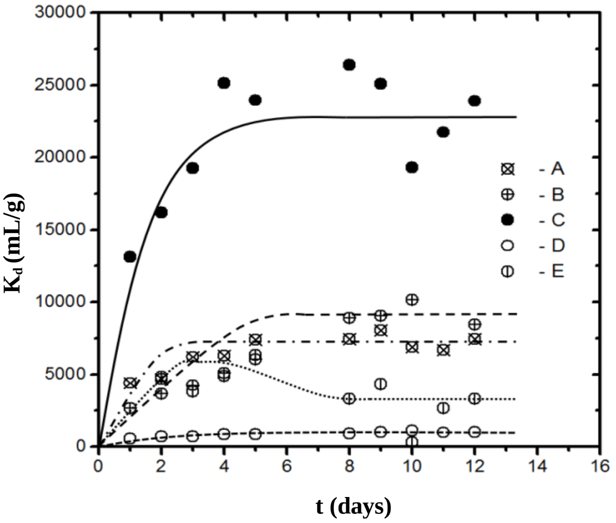

Fig. 1. Effect of contact time on K_d values.

The results were then compared with the previous results as is shown in Table 2.

Table 2. The result of K_d values of previous experiments.

No.	Sample origin	K_d (mL/g)	Ref.
1.	Tuban clay	5000	[6]
2.	Serpong SP-4 soil	3600 – 4700	[7]
3.	Subang clay	5200	[8]
4.	Karawang clay	4000 – 21 700	[9]

The K_d values of samples from Sumedang are rather similar to the K_d values of Karawang clay samples. It is expected that the minerals from both sites (Sumedang dan Karawang) have a common content, smectite [11]. If the resulting K_d values are compared with those of the samples from Tuban, Serpong, and Subang locations, the samples from Sumedang displayed the better K_d values since the samples from Tuban, Serpong, and Subang locations were dominated by kaolinite mineral content [12-14]. Kaolinite mineral has one layer of Si-O and one layer of Al-O bond structures, compared with smectite mineral which has two layers of Si-O and one layer of Al-O bond [15]. The larger number of layers of Al-Si-O structure in smectite than in kaolinite causes the ^{137}Cs sorption capability of smectite to be higher than that of kaolinite [16]. Mukai *et al*. state in their paper that radiocesium is better absorbed in clay minerals such as illite and smectite compared with in other minerals [17]. The aim of the current study was to obtain more detailed data from the preferred locations compared to the previous activity data collection [18], where it was more likely to obtain general sorption data from each surveyed locations.

Other result of ^{137}Cs sorption onto sample experiment can be obtained from Sonderlund *et al.* [19], where Cs sorption was affected by the depth of the sampling site. The value of K_d decreases as a function of the depth of the sampling location. At a depth of about 0.5 m from soil surface, a K_d value of ^{137}Cs of about 7300 mL/g has been obtained. The effect of the difference of grain size distribution from the sample may cause the change of the K_d value of ^{137}Cs, although direct evidence from this experiment is not available because analysis of the grain size distribution of the samples used was not performed. From the results, it can be presumed that the clay that contains smectite or illite can be promoted as the favorable clay type for the host or natural barrier of radwaste disposal facility, especially in the Java Island.

For further discussion, we selected two samples of Sumedang clay that had the best and worst of K_d values, referred to as sample 1 and sample 2, respectively, as representatives of the range of K_d values for the Sumedang sites. The effect of contact time on K_d values is shown in Fig. 2.

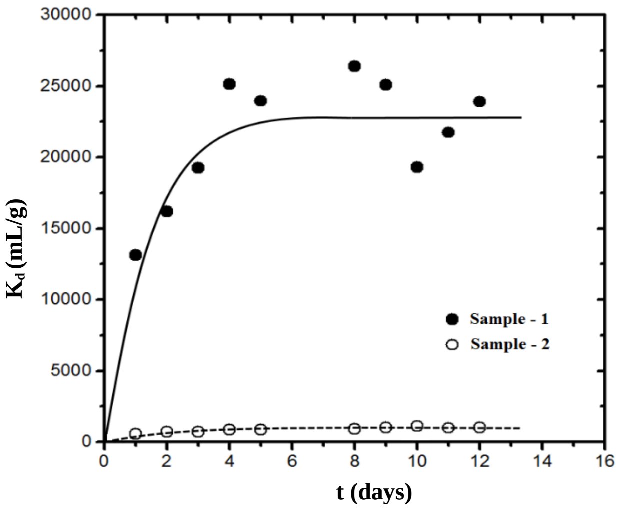

Fig. 2. Effect of contact time on K_d values.

The sorption of metal ion such as ^{137}Cs by clay sample is primarily due to the mineral contents of clay, and the capacity of metal ions to be absorbed is also influenced by the Si/Al ratio of the mineral.

For physicochemical characterization, samples were made in powder form, and the samples were tested by using XRF equipment with soil method to detect the ion elements of soil. The sample characteristics obtained are given in Table 3. The result of XRF testing shows that the Si/Al ratio of sample-1 is lower than that of sample-2. The capacity of metal ion sorption into solid phase is inversely proportional to the Si/Al ratio of the solid phase [20,21], due to O ions' bonding in O_2-Al^{3+}-O_2 framework of mineral in clay sample.

Table 3. Physicochemical characteristics of samples.

Sample properties	Samples (%)	
	Sample-1	Sample-2
Fe_2O_3	22.7	30.1
SiO_2	59.3	53.6
Al_2O_3	12.9	10.8
CEC (meq/100 g)	16.76	13.56

They contribute the negative charge of samples from which the K_d value is derived on minerals for negative electricity. It also can be seen from the value of cation exchange capacity (CEC) of sample-1 is higher than the CEC value of sample -2.

The previous studies [6-9] have shown that the sorption ratio of ^{137}Cs into soil and clay samples are sufficiently high, especially at low concentrations of Cs ion. Cesium sorption on clay sample generally occurs by ion exchange mechanism.

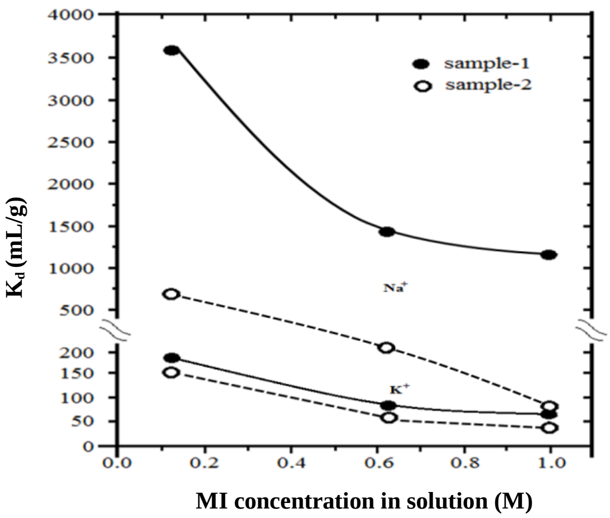

Fig. 3. Effect of metal ion (Na^+, K^+ ions) in solution on K_d values.

The presence of metal ions such as Na^+ and K^+ ions in solution is predicted to affect on K_d value of samples. The result on the effect of Na^+ and K^+ ions in solution on K_d values of ^{137}Cs is shown in Fig. 3.

The effects of metal ions on K_d values can probably be explained by considering the structure of the electrical double layer around the samples [22-24]. Since cationic metal ions are fixed to sample matrix, they potentially give high charge density due to ion exchange processes. The higher negative charge on the sample surface will attract the cations such as Na^+ or K^+ ions from the solution to compensate the charge on the surface of the sample. Thus, in the sample's surrounding, some parts of the surface charge are exchanged with Na^+ and/or K^+ ions. Therefore, the concentration of Cs^+ in the vicinity of the clay samples is controlled by competition between Cs^+ and Na^+ and/or K^+ ions to this zone. In other words, the Cs sorption partly proceeds via an ion exchange between Na^+ and/or K^+ and Cs^+ ions.

The exchange between Cs^+ and Na^+, K^+ ions can easily occur since all of those metals (Na, K, Cs) are in the same group on the periodic table of elements. The K_d value of Cs absorbed on sample give lower value to K^+ ion presence effects compared with Na^+ ion when the both cations make a competition with Cs^+ ion. It can be described that the sorption of metal ions is affected by the ionic radii of the elements. The Na^+ ion has a smaller ionic radius than the K^+ ion, making it harder for it to compete with Cs^+ ion on Cs sorption processes onto sample [25,26]. In addition, the higher concentrations of K^+ and Na^+ ions than Cs^+ ions in the solution also contributes to the competition among the cations present in the solution into sample.

Figure 4 shows that initial concentration of Cs in solution affects K_d values. The data indicates that increasing of Cs concentration in solution decreases the K_d value. The sorption characteristics of Cs into samples indicated that the saturation of Cs in the samples are dependent on the initial Cs concentrations. At low concentrations of Cs, a great number of reaction sites in sample are available for sorption processes, and at higher concentrations, it has been predicted that diffusion of Cs ion to the surface of sample would occur [10,27], or in other words, it can be explained by the limited number of active sites on the surface of the samples [28]. At higher concentration loadings, Cs seems to approach saturation into samples.

The sorption characteristics of samples was described by the Freundlich isotherm equation at the end of contact time, and from the experimental data the isotherms presented in Fig. 5 were obtained.

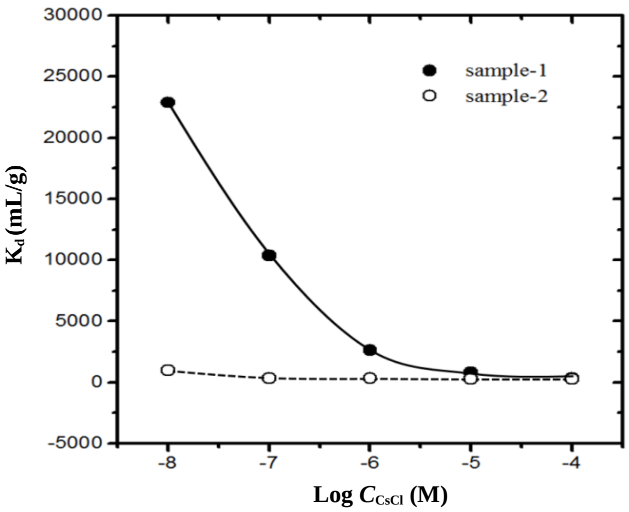

Fig. 4. Effect of initial concentration of CsCl in solution on K_d values.

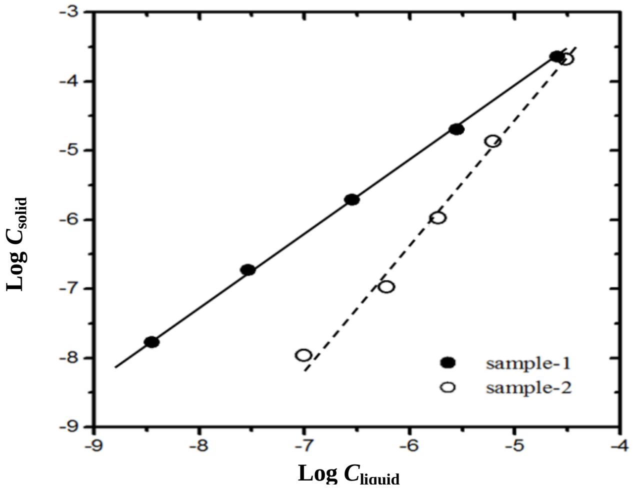

Fig. 5. Isotherm of sorption of ^{137}Cs on clay samples.

The Freundlich sorption isotherm model is expressed as follows:

$$C_{solid} = K_f . C_{liquid}^{\ n} \tag{4}$$

where, C_{solid} is the amount of ^{137}Cs adsorbed per unit mass of solid (meq g^{-1}); C_{liquid} is the equilibrium solution concentration of the ^{137}Cs (meq ml^{-1}); K_f is Freundlich adsorption constant; and n is a constant. By taking the logarithms of both sides, the Freundlich linear isotherm model becomes:

$$\log C_{solid} = \log K_f + n \log C_{liquid} \tag{5}$$

The logarithms of the solid phase (log C_{solid}) and the aqueous phase (log C_{liquid}) were determined at equilibrium condition. Further, log K_f is the intercept, and n is the slope of the Freundlich isotherm. Here, n is an empirical value obtained from the experiment, which may differ from the results of other experiments. In such cases, nonlinear sorption isotherm was observed [29].

Figure 5 shows that the regression of linear isotherm result for sample 1 resulted in a better fit than for sample 2, with R^2 being 0.999 and 0.983 for sample 1 and 2, respectively. The n values of the experiment were 1.065 and 1.736 for sample 1 and sample 2. However, in other experiments, it was found that in the sorption of Cs on clay and montmorillonite samples [11,30] the n values were 0.7797 and 0.903, respectively, indicating that the isotherm of the ^{137}Cs sorption could not be approximated with the linear equation model. The result of isotherm sorption of ^{137}Cs onto samples that was approximated by linear equations only applied to the Cs concentration range used in the experiment. For higher concentrations, the ^{137}Cs sorption may be overestimated and errors may occur when the concentration range is extended beyond the concentrations used.

CONCLUSION

The sorption characteristics of ^{137}Cs in the Sumedang clay samples has been investigated by using batch method. The results show that sample 1 has a better sorption behavior than sample 2, and both samples exhibited rapid sorption rates for ^{137}Cs. Their sorption properties were also influenced by the minerals contained that was indicated by the ratio of Si/Al ratio. The ^{137}Cs sorption into samples depends on the presence of metal ions (such as Na^+ and K^+ ions) and the initial concentration of Cs in solution. The obtained K_d values were higher at lower concentration conditions, and close to saturation condition at higher Cs concentration loading. A Freundlich isotherm was used to explain the sorption phenomenon of ^{137}Cs into clay samples. The results should be taken into account for the assessment or selection of the site of radwaste disposal facility in the future.

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