Sorption Ability of Bentonite Rocks from Yogyakarta to Eliminate the Radiocesium Elements in Solution

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Article Info

Abstract

This activity was to examine the ability of bentonite minerals from Yogyakarta to absorb the radiocesium contained in the solution. The purposes of the experiment were to determine sorption ability of bentonite mineral from Yogyakarta to absorb radiocesium in solution or groundwater and to enrich the Indonesia bentonite capability database to absorb radiocesium. The bentonite material was planned to be used as a buffer material of the engineered barrier system on the radwaste disposal facility in the future. The contact time, the presence of Na and K ions in the solution, as well as the variable of dissolved CsCl concentration were considered as experiment parameters. The value of Kd was also used as the indicator of radiocesium sorption into the bentonite samples. The experiment results shown that the maximum of Kd value was about 6800 mL/g for sample-1, and the presence of dissolved Na and K ions in the solution could reduce the values of Kd which were 800 and 300 mL/g for sample-1, respectively. Determination of isotherm sorption of radiocesium by bentonite from Yogyakarta was approximated by using linear equation or Freundlich law.

1. Introduction

Low-activity radioactive waste in the form of liquid, solid or gas after being processed with cementation method will be changed their forms to a drum-based waste package as well as a concrete shell. After being temporarily stored for some time, then the waste package will be sent to the disposal facility as a final disposal. For wastes that has low activity, the International Atomic Energy Agency has been recommended to be sent to the near surface types of disposal (NSD) facility [1], see Fig.1.

After a long disposal period, there is possibility of the waste packages will be degraded naturally. As a result, water can get into the waste package and there is direct contact with the radioactive waste present in the waste package. Radionuclides present in the waste packages will be dissolved by the water and can come out along the facility with the flow of water towards the water body or aquifer. The release of radionuclides into the environment through groundwater which is a transfer medium to the environment will have undesirable environmental safety consequences, and it should be prevented as far as possible. To anticipate the possibility of radionuclides release from the NSD facility to the environment, the surrounding of NSD facilities will be covered with bentonite material that has low permeability properties [2].

Bentonite minerals have a structure layered of Al-Si-O and changing cations in the tetrahedral of Si sheet so this mineral is expected to be able to absorb well the metal ions or radionuclides dissolved in solution. In addition, bentonite mineral also has a good swelling ability when it made contact with water, so it can be used as a material to fill the cracks in a building structure in the saturation zone [3]. Both of these capabilities are very useful to be used as engineered barrier system (EBS) in a NSD facility [4]. Therefore, it is necessary to conduct the

experiment of radionuclide sorption by using bentonite minerals.
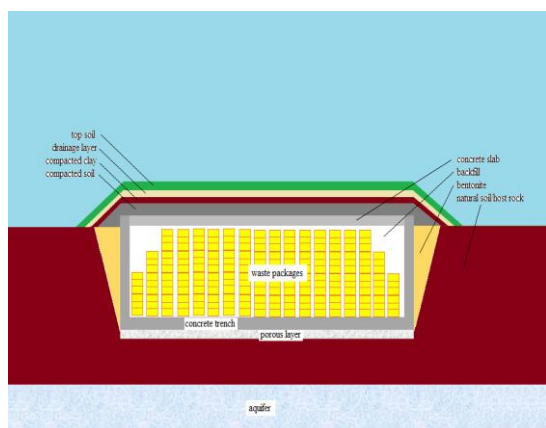
Figure 1. An illustration of near surface disposal facility [5]

Bentonite minerals are quite abundant in Indonesia, for its use as EBS, it is necessary to collect the data of the ability of Indonesian bentonite to absorb the radionuclides when -someday- it is used in an NSD facility. The result of the inventory of the sorption experiment activities is further prepared as a database of the sorption ability of Indonesian bentonite to eliminate the radionuclides such as ^{137}Cs from solution or liquid phase. For that purpose, it was important to examine the sorption ability of bentonite from Yogyakarta region to ^{137}Cs in solution. Bentonite material can also be used to treat the liquid wastewater problems through the adsorption process, such as processing of Rhodamin B dyes [6].

Bentonite absorption ability is usually due to the ion exchange process, where exchange ions presence on the exchange site of bentonite reacted with metal ions in the solution. In addition sorption capability of bentonite was also obtained from Al-Si structures that exist in the bentonite structure, where the structure of Al-O will give the excess of negative charge on bentonite mineral [7]. The metal ions are bound to the structure of Al-O is expected to have a stronger bond than the absorbed via ion exchange process. The illustration of bentonite structure is shown in Figure 2.
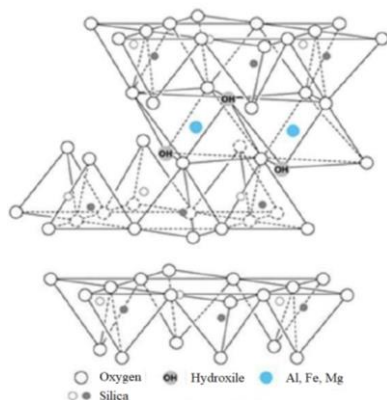
Figure 2. The bentonite structure [3]

Radiocesium is one of the fissions product of nuclear material, when it released into the environment will be able to provide the consequences for the safety of the environment due to the length of its half-life as in ^{137}Cs and 135Cs [8]. The spreading of radiocesium to the environment is strongly influenced by physical and chemical processes such as diffusion and sorption. For that reason, the contact time, the ionic strength and variation of CsCl concentration in solution was used as the parameter that affects the elimination action of radiocesium in solution by mineral bentonite. To determine the number of ^{137}Cs absorbed into bentonite samples, the distribution coefficient (Kd) values was used as the indicator of ^{137}Cs sorption as done on the previous work [9, 10] where Kd is

$$Kd = \frac{number\ of\ ^{137}Cs\ absorbed\ in\ the\ solid\ phase\ per-unit\ mass}{number\ of\ ^{137}Cs\ remains\ in\ the\ liquid\ phase\ per-unit\ volume} \quad (1)$$

$$Kd = \frac{(C_0 - C_t)/M}{(C_t)/V} \quad (2)$$

$$Kd = \frac{(C_0 - C_t)}{C_t} \frac{V}{M} \quad (3)$$

C0 and Ct are the initial and final activities of ^{137}Cs in the solution (Bq), V and M are the volume of used solution (mL) and dry mass of bentonite samples (g).

The purpose of the experiment is to determine sorption ability of bentonite mineral from Yogyakarta to absorb radiocesium in the frame to completing the database of Indonesian bentonite capability to absorb the radiocesium. This work was done under the siting of radioactive waste disposal facilities program in anticipation the introduction of nuclear power plant as one of the energy sources of the future in Indonesia.

2. Methodology

2.1. Materials

Bentonite sample was taken from the bentonite mining located at Nanggulan-Kulon Progo, Yogyakarta in the form of bulk, then brought to the lab for the preparation. Preparation was done in a way cleared of rocks, gravel and plant roots, dried in the oven (100°C, 8 hours). Bentonite was crushed into pieces in a porcelain bowl and then was sieved with sieving tool so that the grain size obtained was about 100 mesh. The chemical reagents such as CsCl, NaCl and KCl were supplied by E-Merck Production. However radioactive solution ^{137}Cs as radiotracer was obtained from Eckert and Ziegler Isotope Production with specific activity was 3.7 MBq/5 mL, purity 99% and then was diluted to 20,000 Bq/mL and kept in a PE bottle as a stock solution [11].

2.2. Equipment

Analytic scale unit Mettler series AE200, Fritsch Gmbh Brd-6580 Idar Oberstein sieving apparatus, Hareus Labofuge 400 centrifuge equipment, gamma spectrometer of Canberra multichannel analyzer (MCA) unit completed with HPGE detector (20% efficiency).

2.3. Procedures

To determine the length of contact time required to reach equilibrium of ^{137}Cs absorbed into the bentonite sample, the bentonite sample was contacted with a solution of 10^{-8} M CsCl and then given ^{137}Cs tracer. Bentonite samples and solution were mixed in a 20 mL PE vial. The solid and liquid ratio is 10^{-2} g/mL. After the vial was sealed, then the vials were inserted into a tin can to be stirred with a roller tool for a certain time. Every day one by one vial was taken out, and then solid and liquid phases were separated using a centrifuge machine. The supernatant was obtained from the solid-liquid phase separation processes, and then measured for its ^{137}Cs activity by using MCA unit. From the results of initial and final activities of ^{137}Cs measurement in the solution, we can then calculate the value of Kd of ^{137}Cs using equation (3).

The influence of ionic strength in solution was represented by the effect of Na and K ions in solution on the sorption of ^{137}Cs into bentonite samples. The solution containing the Na and K ions with varying concentrations (0.1, 0.5 and 1.0 M) was added to the mixture of bentonite samples, 10^{-8} M CsCl solution and then given ^{137}Cs tracer. The contacting method of the effect of ionic strength experiment used the same methods as that of the contact time experiment, as well as its liquid-solid phase separation, the measurement of ^{137}Cs activity and the calculation of the value of Kd of ^{137}Cs.

The effect of concentration CsCl against the ^{137}Cs sorption by bentonite samples were done by varying the initial concentration of CsCl in the solution ranging from $10-8$ to $10-4$ M. The solution was contacted with a bentonite sample and then was given the ^{137}Cs tracer. Further treatment as done similarly in previous experiments and also for the counting of Kd values of ^{137}Cs.

3. Results and Discussion

The samples were taken from Tanjungharjo village, Nanggulan-Kulonprogo, Yogyakarta as the bentonite mining site at 3 sampling points, and then for the experiment materials the samples were called as sample-1, sample-2 and sample-3, respectively. The composition of the sample are given in Table 1.

Table 1. Composition of the samples.

Sample properties	weight %		
	Sample-1	Sample-2	Sample-3
SiO_2	65.86	68.31	69.61
Al_2O_3	13.42	11.72	11.09
Fe_2O_3	4.20	3.22	2.58
Na_2O	0.97	0.15	0.17
K_2O	1.98	1.12	0.39
CaO	2.78	2.02	1.71
MgO	1.51	2.54	2.85

The calculation result of the Kd value against the contact time within 22-day contact period is shown in Figure 3. The equilibrium time has occurred when the sample contacting with ^{137}Cs attains of 18 days of contact time. The equilibrium states reached by all samples were relatively similar time one to another. The ^{137}Cs sorption occurs due to the presence of ionic exchange process between ^{137}Cs with cations present on the part of the active surface of the bentonite sample and the reaction of ^{137}Cs with negative charges in the octahedral framework of bentonite [12].

Bentonite as a 2:1 silicate layer type clay, and is composed of two silica tetrahedral sheets with a central alumina octahedral sheet. Since substitution of alumina for silica in the tetrahedral sheet and iron and magnesium for alumina in the octahedral sheet, the lattice has an unbalanced charge. To balance the charges on the lattice, the presence of cations in solution can neutralize this condition. The bentonite layer also has the interlayer space between two layers and usually the layers are charged. If there any cations present in the interlayer space of bentonite, it could counterbalance this charge in order to constitute a neutral compound. Weak bonds that occur between the layers by means of van der Waals bonds, and both interlayer and surface adsorption takes place with Cs sorption [13].

The Kd values obtained from the experiment for each sample were 6800, 5200, 3700 mL/g for samples-1, 2 and 3. In other studies, the ^{137}Cs Kd value for Na-montmorillonite was about 1000 mL/g [13, 14] The difference in Kd values of ^{137}Cs obtained probably comes from the different composition of the montmorillonite mineral content present in the bentonite sample used [15]. The difference of physicochemical property of samples might cause the different results of sorption capacity, although the quantitatively analysis results of sorption capacity of used samples were not measured.
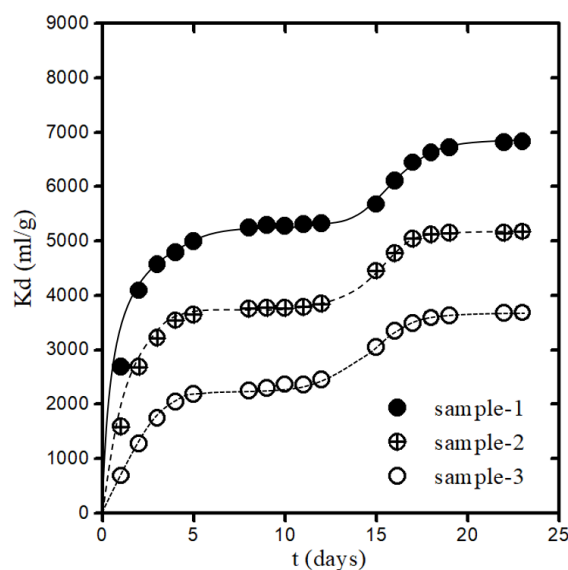

Figure 3. Kd values of ^{137}Cs versus contact time

The presence of ions Na and K in the solution which is the metal ions constituent in ground water can act as a competitor for ^{137}Cs to be absorbed into the sample bentonite. Increased concentrations of metal ions in solution with varying concentrations of 0.1, 0.5 and 1.0 M NaCl and KCl could lower [137]Cs Kd values, as shown in Figure 4.

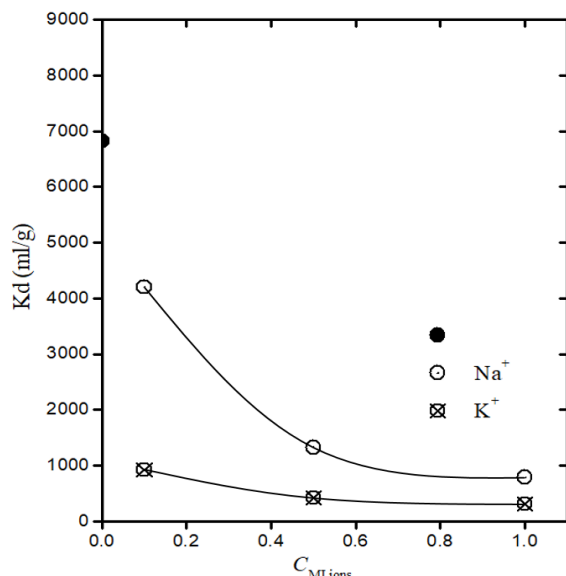**Figure 4.** Effect of Na and K ions to Kd values of ^{137}Cs, at sample-1

Increasing the concentration of metal ions such as Na and K in the solution would increase the competition of sorption between ^{137}Cs and the both of metal ions into bentonite samples. Smaller radius of Na+ ion size than K+ ion made Na+ ion harder to compete with Cs+ ion [16], and to the higher concentration of Na and K ions compared with Cs ion in solution also contributed to reduce the amount of ^{137}Cs absorbed into bentonite samples.

Experiment of the effect of CsCl concentration in the solution in absorbing ^{137}Cs was done by giving the initial CsCl concentration in the solution with range of 10^{-8} to 10^{-4} M. The results indicated that there has been a decrease in the value of Kd ^{137}Cs due to the number of active sites of bentonite which have been controlled by [137]Cs. Increased concentration of CsCl might increase the occupy level of the active site by ^{137}Cs, consequently at high concentrations of CsCl the active site of bentonite was not be able to accommodate of all ^{137}Cs present in the solution, or in other words the limited active site available in the bentonite sample unable to accommodate the amount of ^{137}Cs present in the solution [14]. High Kd ^{137}Cs had been generated from bentonite contacts with low CsCl concentrations, and the value of Kd ^{137}Cs decreased as long as the initial concentration of Cs in the solution was increased.

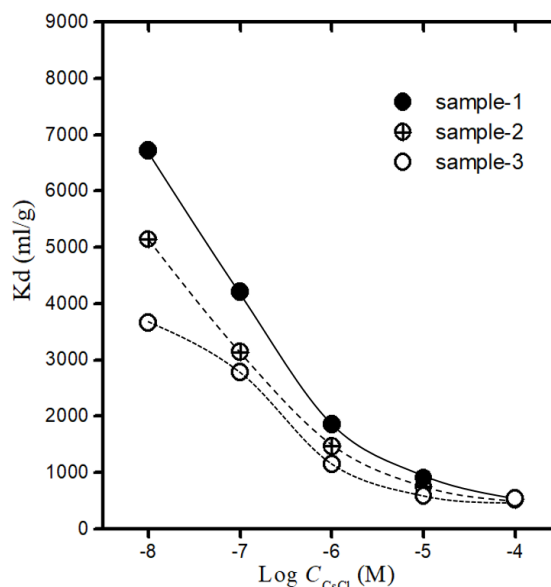**Figure 5.** Effect of CsCl concentrations to Kd values of [137]Cs

Freundlich isotherm is an empirical equation for explaining the metal ion sorption in a sample/material that has a heterogeneous surface with functional group variations on their exchange site surface, such as bentonite mineral. The determination of sorption character of ^{137}Cs by bentonite samples from Yogyakarta and then would be approached by using Freundlich equation as [17],

$$C_{in\ solid\ phase} = K_F . (C_{in\ liquid\ phase})^{1/n} \qquad (4)$$

and then the equation is converted into logarithm form,

$$\log C_{in\ solid\ phase} = \log K_F + \frac{1}{n} \log C_{in\ liquid\ phase} \qquad (5)$$

where $C_{in\ solid\ phase}$ and $C_{in\ liquid\ phase}$ are the number of radiocesium absorbed in the samples (Bq/g) and remaining in the solution (Bq/mL), KF and 1/n are the Freundlich constant and the energy diversity related to sorption processes.

In Figure 6, the data of sorption equilibrium results shown that the linearized isotherm equations followed the Freundlich isotherm model, which have good correlation to coefficient values (R2) of sample-1, 2 and 3 are 0.9997, 0.9995 and 0.9978, respectively. R^2 values give the indication that the sorption isotherm occurred only applies to a certain range of concentration values. Sorption isotherm data have shown that almost all bentonite samples absorb radio cesium provided the linear sorption results, especially at very low concentration ranges. These results indicated that the radiocesium in solution was adsorbed into nonhomogeneous adsorption nature of the bentonite samples [18].

High uptake or elimination of radiocesium from solution by bentonite samples is shown by the wide

concentration of Cs range that was reached, which was indicated by a smaller of 1/n value. The obtained results of 1/n were 0.7791, 0.7979 and 0.8252 for samples 1, 2 and 3, respectively. The concentration ranges of Cs that could be accommodated by each bentonite sample was only as much as the restricted range of Cs concentration remains in solution. A values of 1/n <1 are an indication that a significant adsorption takes place at low concentration and becomes less significant at higher concentration [18]. At the highest CsCl concentration conditions, the sorption isotherm values or results have given the same value.
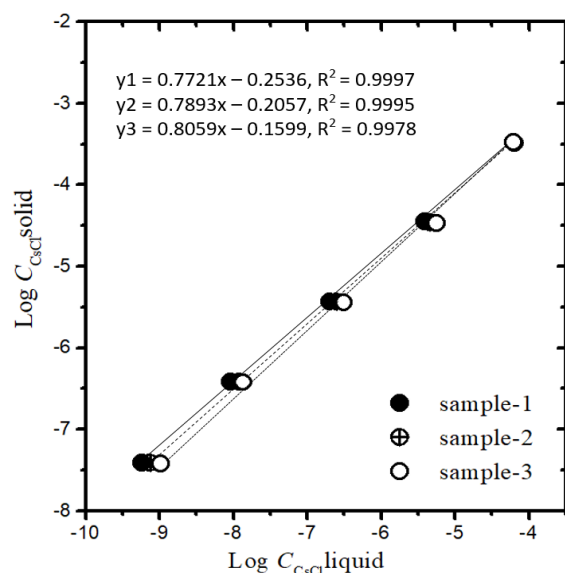

Figure 6. Isotherm results of ^{137}Cs sorption

4. Conclusions

The results are quite hopeful when the bentonite material is later used as a radiocesium adsorbent material. It could be seen from the good adsorption properties of bentonite samples against radiocesium in solution. The results of sorption experiment have provided the Kd value of 6800, 5200, 3700 mL/g for samples 1, 2 and 3, respectively. The results of isotherm sorption from experiments were consistent to Freundlich isotherm models, where the radiocesium to be absorbed on the non-homogeneous surface structure of the bentonite samples. Radiocesium sorption data from bentonite from Yogyakarta which has been obtained will enrich to the database of the ability of local Indonesian natural materials to absorb radiocesium which is being developed by Center for Radioactive Waste Technology. These natural materials will later be used as radioactive waste processing materials or as buffer material on the barrier system of radioactive waste disposal facilities.

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