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## Evaluation of Radiocesium Sorption in Some Materials as Safety Barrier System of Radioactive Waste Disposal Demonstration Facility

Budi SETIAWAN<sup>a\*</sup>, Elfira MAYASARI<sup>b</sup>, Shely MEIDHIKA<sup>b</sup>

<sup>a</sup>Center for Radioactive Waste Technology-BATAN, Kawasan PUSPIPTEK Bld 71, 3<sup>rd</sup> Floor, Serpong-Tangerang 15310, Indonesia

<sup>b</sup>Dept. of Chemistry, Grad. School, Fac. Of Math. And Science, Andalas University, Limau Manis-Padang 25163, Indonesia

### Abstract

Sorption characteristic study of the prospective barrier materials will be used as safety barrier system on the disposal facilities such as bentonite, kaolinite, and quartz sandy has been done. Such barrier materials were contacted against <sup>137</sup>Cs with affected parameters were the functions of contact time, concentration of CsCl, ionic strength of solution, and the sorption isotherm, and all the experiments were done in batch method. Objective of the research is to obtain a specific sorption character data of radiocesium into some prospective barrier materials for radioactive waste disposal demonstration facility at Serpong. The initial concentration of CsCl being used was 10<sup>-8</sup> M, and 0.1, 0.5, 1.0 M NaCl and also 10<sup>-8</sup>-10<sup>-4</sup> M CsCl for experiments of the effects of shaking time, ionic strength and concentration of CsCl in the solution, respectively. Sorption quantification of <sup>137</sup>Cs was predicted through their distribution coefficient (Kd). Equilibrium state were reached after 7, 5 days and 24 hours shaking time with Kd values 17000; 1100 and 130 mL/g for bentonite, kaolinite and quartz sandy samples, respectively. Increasing of NaCl and CsCl concentrations in solution caused Kd values decreased due to the competition between Na and Cs ions when interacting with the sample, and also due to the limited sorption capacity of the sample to <sup>137</sup>Cs.

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\* Corresponding author. Tel.: +62-21-756-3142; fax: +62-21-756-0927.  
E-mail: [bravo@batan.go.id](mailto:bravo@batan.go.id)

## 1. Introduction

To complete the facility of radioactive waste management coming from the nuclear activities of non-nuclear power plant such as the processing of radwaste and interim storage facilities of waste package at Serpong Nuclear Research Center (SNRC), it is necessary to prepare a disposal facility that serves as an education purpose for the general public and also for demonstrating the ability of mastering nuclear technology in Indonesia. The other benefit of such facility is to reduce the existing of radwaste packages stored in the interim storage facility as a management practicing on the construction project of radwaste disposal facility in the future. The preparation activity of radwaste disposal for demonstration purpose is done in line with the program of radwaste disposal siting in Java Island [1].

To anticipate the safety aspect of such facilities, the study about the materials characteristic that will be used as the safety barrier system of disposal facility is needed to be performed and the results can provide the safety expectation to the community about the safety aspects of radioactive waste management system as a whole. The safety system reliability of disposal facilities could be obtained from the property of the radionuclide sorption on barrier materials candidate to be used. To reduce the possibility of contaminants spreading into the environment, the disposal facilities will be equipped with a prosperous barrier material to absorb the contaminants in the barrier material and radioactive contaminant does not spread out from facility to environment. Based on these reasons, the collection of these important data needs to be obtained. The study of radionuclide sorption in some prospective barrier materials such as local bentonite, kaolinite and quartz sandy has been done in a batch method. Barrier material is generally in the form of local natural minerals that were obtained from the surrounding of disposal facilities, in this case bentonite from West Java, while kaolinite and quartz sandy originating from Bangka and Belitung areas. On the disposal facilities, bentonite and kaolinite materials can act as the buffer material [2] and quartz sandy will serve as the backfill material on the drainage system at the vault part of facilities [3]. By using these materials, it was expected that the spreading of radioactive contaminant from facility to the environment can be controlled well.

Bentonite and kaolinite as buffer material in the disposal facilities has the impermeable property where it plays as an important role to control the groundwater flow and absorb the radionuclide dissolved in the groundwater, to prevent the radionuclide mobility from disposal facility into the environment [4]. In addition quartz sandy materials in addition can be used as a waste package stabilizer in the disposal facilities [5]. All of these materials are used because they are cheap and easy to find in the surrounding of disposal facility.

Radiocesium was used as a representative of the dominant radionuclide in low-activity radioactive waste package [6]. It also has been coming from a nuclear accident such as fall-out processes from nuclear testing into environment. It has quiet long half-life (~ 30 y), high solubility element in solution, has similarity property to  $K^+$  ion, is mobile in many environmental systems and is easy associated with terrestrial and aquatic materials. Radiocesium becomes a reference in the study of low-level radioactive waste interacting with rock or soil [7,8]. For that reason  $^{137}Cs$  radionuclide becomes one of safety concern in the assessment programs for radioactive waste disposal project.

Sorption of radionuclide depends on the concentration of Cs ions in solution [9]. The proportion of soluble Cs concentration changes is predicted by changing the equilibrium of Cs adsorbed in barrier materials as the impact of heterogeneity of the surface in the adsorption sites of material. High-affinity sites of clay are progressively saturated with metal ions and the affinity for Cs on the remaining sites reduced. The effect of ionic strength also has received an attention. This parameter is particularly important in the interpretation of desorption studies [7,11]. Desorption of Cs could be measured in the different ionic strength solutions in which Cs was initially adsorbed. The fraction of Cs adsorbed by a given treatment is often described as irreversibly adsorbed, or fixed. In addition the data of radionuclide sorption potencies on local mineral of Indonesia origin up to now are still very poor. For that reason the interaction data of local natural minerals such as bentonite, kaolinite, and quartz sandy from West Java and Bangka-Belitung areas as barrier materials of disposal systems are very important to be obtained.

The results of the research are important data for the design and engineering activities of the disposal of radioactive waste in Indonesia in the future. Scientific information on the capabilities of the radiocesium sorption by bentonite, kaolinite and quartz sandy from West Java and Bangka-Belitung to retard radionuclide present in the groundwater will enrich the sorption data inventory in Indonesia.

## 2. Experimental

Radiocesium  $^{137}\text{Cs}$  (specific radioactivity 3.7 MBq/5 mL, radionuclide purity 99.00%) obtained from *Eckert & Ziegler Production*, was diluted and kept in a polyethylene bottle as a stock solution. Other chemicals such as NaCl and CsCl were obtained from *E. Merck* and were used without further purification.

Bentonite sample was obtained from Bogor-West Java, while kaolinite and quartz sandy samples were taken from Membalong and Sebagin Bangka-Belitung. The samples in this study were used in their natural state without any treatment, i.e., without saturation with any cation. Samples were cleaned from root, leaf and gravel, dried in the oven (100°C, 7 hr.) then crushed and sieved with *Fritsch GmbH Brd-6580 Idar-Oberstein* sieving apparatus to obtain 100 mesh particle size. Granule samples are then stored on a plastic container prior use in the experiment.

Radiocesium sorption measurement was done in a batch method<sup>12</sup>, where 0.1 g of sample weighted with *Mettler serie AE200* analytic scale unit was contacted with solution containing  $10^{-8}$  M CsCl in a 20 mL polyethylene (PE) vial, and was labelled with radioactive substance  $^{137}\text{Cs}$ . The liquid-solid ratio in the experiment was  $10^{-2}$  g/mL. The vials were capped and shake by using geological roller at room temperature condition. After centrifugation (2500 rpm, 10 min.) with a *Heraeus Labofuge 400* centrifuge machine,  $\gamma$ -activity of 1 mL of the aqueous phase was measured with well-type of *Gamma spectrometer multi channel analyzer (MCA)* unit and was completed with HPGe detector having 20% efficiency and *software Genie 2000*. Quantification of sorption value was done by calculating their distribution coefficient ( $K_d$ ), which is defined as the ratio of concentration of radionuclide in solid and in liquid phases in equilibrium state. The distribution coefficient is,

$$K_d = \frac{C_0 - C_t}{C_t} \frac{V}{m} \quad (1)$$

where  $C_0$  and  $C_t$  are initial and final activity of Cs ion in solution,  $V$  is total volume of solution (mL),  $m$  is dry mass of sample (g) and  $K_d$  is coefficient distribution of  $^{137}\text{Cs}$  in the sample. The effects of ionic strength of solution represented by NaCl solution against the samples were also studied. The samples were mixed with solution containing  $10^{-8}$  M CsCl, variation of NaCl concentrations of 0.1; 0.5 and 1.0 M NaCl and  $^{137}\text{Cs}$  carrier solution in a 20 mL polyethylene. After separation of solid-liquid phases by using centrifugation method the  $\gamma$ -activity of liquid phase solution was measured using similar method. Meanwhile the effect of metal ion concentration of CsCl in the interaction of  $^{137}\text{Cs}$  with the samples was studied by contacting the samples with varying initial concentration of CsCl between  $10^{-8}$  to  $10^{-4}$  M. The procedure of experiment was similar to that of the previous experiment, and the  $K_d$  values was calculated by using Equation (1).

## 3. Results and Discussion

Equilibrium state of nuclides to be absorbed on a geological sample usually takes long period of time, such as in Figure 1 showing the effect of shaking time in the distribution coefficient of cesium in bentonite, kaolinite and quartz sandy samples. The sorption in terms of the distribution coefficient firstly increases with shaking time, and then eventually approaches to an equilibrium value. It can be seen that sorption equilibrium was approximately attained after one to fifteen days of contact. Therefore, a shaking time of two weeks was employed for kaolinite and quartz sandy samples and three weeks for bentonite sample. Blank experiments showed no significantly sorption of  $^{137}\text{Cs}$  on the wall of the PE vial used.

In qualitative point of view, the whole sorption process consists of two distinct steps: an initial step in fast adsorption, and a much slower adsorption. Equilibrium state for quartz sandy is the fastest followed with kaolinite samples, and bentonite is the longest to attain constant values marked by flat graph of  $K_d$  values. The equilibrium state was reached after 7, 5 days and 24 hours of shaking with  $K_d$  values of 17000; 1100 and 130 mL/g for bentonite, kaolinite and quartz sandy samples, respectively. Compared with other similar experiment, the result is rather high due to the different experimental condition<sup>13</sup>.

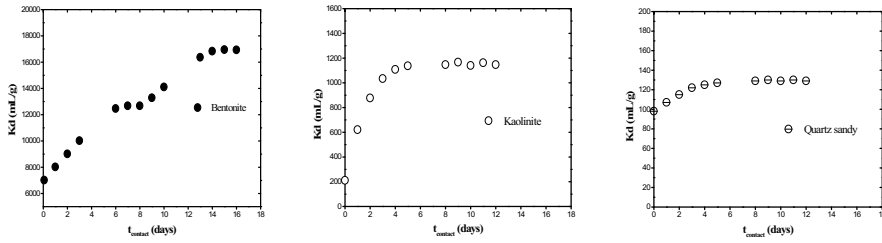


Fig. 1 The effect of shaking time on the Kd values

The presence of Na ion as a representative in the ionic strength experiment is one of major cation in the solution considered to affect the sorption of cesium owing to their competitive reactions. The competitive ions as  $\text{Na}^+$  and  $\text{K}^+$  are present in a concentration of several orders of magnitude higher than that of the radioactive  $\text{Cs}^+$  in waste inventory. At low concentrations,  $\text{Cs}^+$  ion is adsorbed strongly in the frayed edge sites of clay surfaces, and  $\text{Na}^+$  cation in natural systems considered competes effectively with  $\text{Cs}^+$  adsorption for these sites<sup>14,15</sup>. The presence of  $\text{Na}^+$  in solution makes Kd values becomes decreased in all experiments as shown in Fig.2.

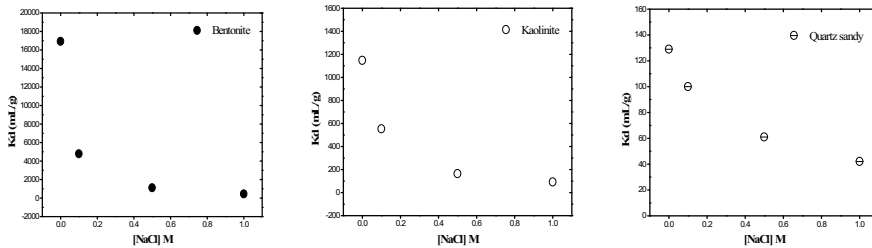


Fig.2 The effect of ionic strength on the Kd values

The effect of the variable concentration of cesium on sorption behaviour was also examined. The distribution coefficients were determined between solid samples and solutions initially containing various concentrations of CsCl from a trace level ( $10^{-8}$ ) up to  $10^{-4}$  M CsCl. The results are shown in Fig. 3.

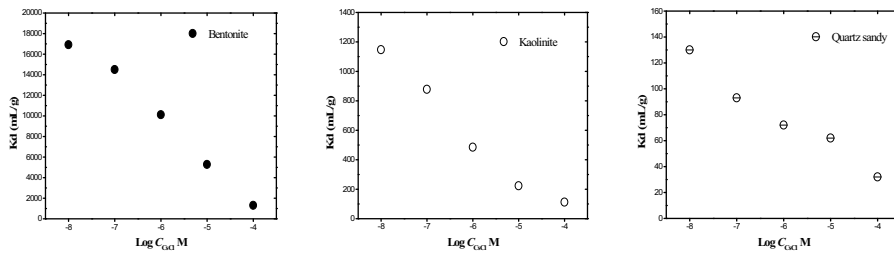


Fig.3 The effect of variable of Cs+ concentrations in solution on the Kd values

The influence of  $Cs^+$  concentration on the Kd values at different initial  $Cs^+$  loadings shows that the  $Cs^+$  uptake is not proportional to  $Cs^+$  concentration in solution. This non-linear behaviour means that energetically less favourable sites become involved with increasing  $Cs^+$  loading, and the value of Kd gradually decreases with an increase in the cesium concentration, and tends to decrease in higher concentration regions<sup>16</sup>. The magnitude of the Kd values is heavily influenced by the sorption capacity of the sample, where the increasing of CsCl concentration provides the remaining concentration of CsCl in the solution rise. This is due to the limited sorption capacity of the sample causing a decrease in the Kd value of  $^{137}Cs$ . Quartz sandy is generally in the form of stable SiO<sub>2</sub> crystal with minimal exchange site, and their sorption of  $^{137}Cs$  provides a minimum values.

By fitting the values of the experimental sorption data to the following linearized isotherm equations as Freundlich isotherm, valuable information can be obtained in the sorption mechanism and properties such as surface heterogeneity of sample. The obtained results from the experiments are shown in Fig. 4. Interpretation of the sorption data to predict contaminant intensity of tested sample surface is expressed through Freundlich isotherm model, where Freundlich constant is determined by using the following equation,

$$C_{solid} = K_F \cdot (C_{solution})^{1/n} \quad (2)$$

whose linearly form is,

$$\log C_{solid} = \log K_F + \frac{1}{n} \log C_{solution} \quad (3)$$

where  $C_{solid}$  is the number of radiocesium absorbed in the sample (Bq/g),  $C_{solution}$  is the number of radiocesium remaining in the solution (Bq/mL),  $K_F$  is the Freundlich constant and  $1/n$  is energy diversity related to sorption processes.

The slopes in linear regression equation of sorption isotherm are 0.77; 0.89 and 1.00 for bentonite, kaolinite and quartz sandy samples, respectively. They indicate that low concentration ranges ( $10^{-10}$  to  $10^{-8}$ ,  $10^{-9}$  to  $10^{-7}$  and  $10^{-8}$  to  $10^{-5}$  M CsCl for bentonite, kaolinite and quartz sandy samples, respectively) give a linear sorption. Different samples used cause the resulted graphs to shift to the right side in accordance with the radiocesium sorption capacity of the samples, and contaminant mobility in high concentration can lead to misinterpretation of the results. The slope ( $1/n$  value) also reflects the heterogeneity in frayed edge site of samples<sup>17</sup>. However, semi-empirically results of Freundlich isotherm do not significantly indicate the sorption mechanism of metal ions or radionuclides into solid samples occurred precisely.

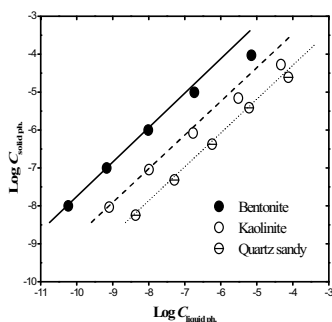


Fig.4 Freundlich isotherm for  $Cs^+$  sorption

## Conclusion

The interaction of radiocesium with prospective barrier materials on the radioactive waste disposal demonstration facility has been studied. The equilibrium states were reached after 7, 5 days and 24 hours shaking time with Kd values of 17000; 1100 and 130 mL/g for bentonite, kaolinite and quartz sandy samples, respectively. Increasing NaCl and CsCl concentrations in solution make Kd values decrease due to the competition between Na and Cs ions when interacting with the sample, and also due to the limited sorption capacity of the sample to  $^{137}Cs$ .

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