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Determination of ^{137}Cs Elimination from Solution By Tasikmalaya Bentonite and Belitung Quartz Sand As Barrier Material Candidate on the Near Surface Disposal Facility

Budi Setiawan, Heru Sriwahyuni

Center for Radioactive Waste Technology, National Nuclear Energy Agency
PUSPIPTEK, 71Bld 3rd Floor, Serpong-Tangerang 15310

Email: bravo@batan.go.id

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Abstract

Batch technique experiment was applied to measure the elimination of ^{137}Cs from solution using bentonite from Tasikmalaya and quartz sand from Belitung. Bentonite material was used as barrier system surrounding on a near surface disposal facility, and quartz sand as backfill material. The distribution coefficient (Kd) of ^{137}Cs on bentonite and quartz sand samples have been measured. Contact time, variation of Na and Cs ion concentrations in solution were applied as the experiment parameters. The Kd values of ^{137}Cs on the samples were 1700 and 3200 mL/g for bentonite and 17 and 37 mL/g for quartz sand samples, respectively. The Na and Cs concentrations in solution affected the Kd values of ^{137}Cs on samples. Isotherm sorption result shown that the interaction of ^{137}Cs onto solid samples was approached with Freundlich model. The data obtained from the experiments and then could be used for radionuclides migration assessment models of disposal facility in the future.

Keywords: Disposal facility, bentonite, quartz sand, ^{137}Cs, sorption.

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1. INTRODUCTION

The results of fall out of nuclear weapons testing in atmosphere in past time, and from the Chernobyl accident in 1986 were recognized as resources of radiocesium which has been introduced into environment in the world presently. Recently, volatile radiocesium also came from radionuclides released from the accident of Fukushima Daiichi Nuclear Power Plant in 2011 (Steinhauser *et al.*, 2014). Radiocesium is the radionuclide which also contained in the aqueous radioactive waste solution, and might release to environment to rise a health risk of the soil or ground water system surrounding the nuclear facility, such as the storage or disposal facilities. The leaching of radiocesium from radioactive waste solution through surrounding barriers of disposal facility into environment is one of the radionuclide migration scenario (Poteri *et al.*, 2014). To retard and control the possibility of radionuclide dispersion in biosphere, various materials (mineral and soil materials) will cover surround the facility, as shown in **Figure 1**.

The experiment of interaction of radiocesium with various mineral or soil samples has been famously studied to show that the radiocesium was becomes one of the most importance radionuclide for the environment safety assessment. Radiocesium nuclide has been known that its easy associated with materials in the aqueous and terrestrial environment and clay mineral is a good material for absorb metal ions in solution such as radiocesium. The clay will play a role to eliminate and immobilize the nuclide from groundwater system, and also to retard the possibility of radionuclide's dispersion from the facility to environment system. Bentonite as one of the representations of clay has a good function as seal material in a disposal facility wall where bentonite will swell when it absorbs the water and then sealing of any cracks in the wall of disposal facility

(Karnland *et al.*, 2006). Water pass through the inter-layer porous of bentonite samples, and then the distance of inter-layer enlarged along with water absorption by mineral. The expanding bentonite then fill the fine holes crack on the concrete wall of disposal trench, causing the water becomes difficult to infiltrate into disposal facility. Quartz sand serves as a backfill material to control the water flow on the cover of facility and inside of the trench (Gorakhi and Bareither, 2017).

One of the safety principles of disposal facility is to prevent the direct contact between the water and waste packages present in the facility. Contact of water flow with waste package will degrade the waste package. Then the packages corrode and water will go into waste package. The direct contact between water and waste packages causes radionuclides dissolution along with water flow. When it happens, the migration of radionuclides into environment will increase. Bentonite mineral can be used for this purpose to retard the migration of radionuclide by sorption mechanism.

The Kd concept was proposed to predict and calculate accurately the interaction or characterize the sorption of radiocesium in the sample materials. This concept is recognized appropriate for disclose the knowledge of sorption equilibrium in the solid-liquid components system. The sorption study of radiocesium by two components system are closely related to the safe of low-level radioactive waste near surface disposal facility. Bentonite is a famous mineral to be used as barrier system in a disposal facility in the world (Savage and Arthur, 2012) also for the future disposal facility in Indonesia. Indonesia has many bentonite mines in Java Island (Sukandarrumidi, 2009) that need to be investigated and developed for use in a nuclear facility such as disposal facility as a potential barrier material. For that purpose, the author has been studied the interaction of radiocesium with bentonite from various location in Indonesia (Setiawan, 2008; Setiawan *et al.*, 2011; Setiawan *et al.*, 2014; Setiawan *et al.*, 2015; Setiawan *et al.*, 2016), and also many authors have been studied the sorption characteristics of ^{137}Cs and also ^{90}Sr as an important radionuclide with different minerals and soils system (Galambos *et al.*, 2012; Ohnuki and Kozai, 2013; Kubota *et al*., 2013; Pendleton, 2014; Tachi and Yotsuji, 2014; Yang *et al*., 2014; Mukai *et al.*, 2015; Setiawan, 2007). With assumption that the first near surface disposal facility will be built in Serpong Nuclear Area-Banten, then the potentially materials required for the construction of facility which was found in the nearby facility need to be investigated including bentonite mineral from Tasikmalaya and quartz sand from Belitung. Objective of the experiment is to study the sorption behavior and character of natural Indonesian minerals such as bentonite and quartz sand as potential barrier material to eliminate ^{137}Cs from solution. In this paper, the Kd values of ^{137}Cs on natural bentonite and quartz sand materials from Tasikmalaya-West Java and Gantung-Bangka Belitung have been measured and discussed.

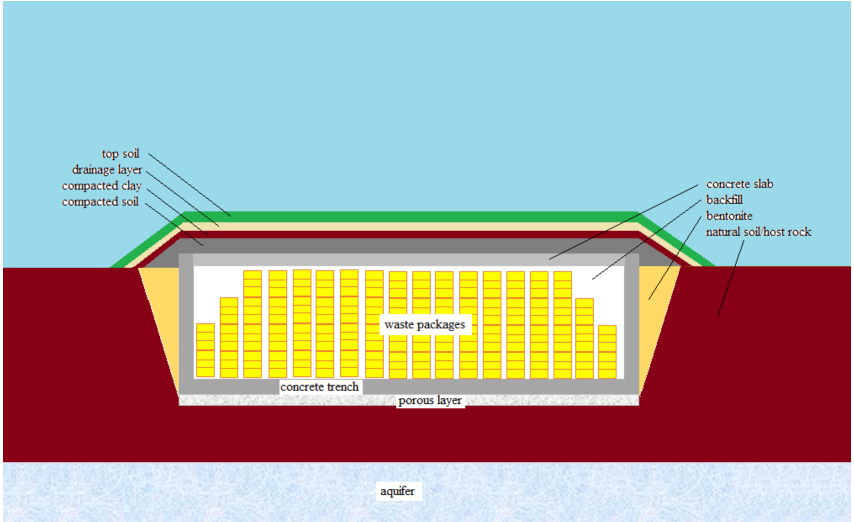

Figure 1. An illustration of the near surface disposal facility, modification from (Bergstrom *et al.*, 2011)

2. Experimental Methods

Materials and Equipments

Sample materials were collected from Pasirhonje village-Tasikmalaya-West Java (S 108°06'10.74''; E 07°35'52.83'') and Gantung-Bangka Belitung (S 108°10'54.7''; E 02°58'14.8'') locations, where in both locations are bentonite and quartz sand mining locations in Tasikmalaya and Gantung. Bentonite mineral was obtained at about 2-7 m depth from the soil surface, while quartz sand was taken from the stockpile of quartz sand mining. The samples for experiment were prepared as follow, were clean-up, oven dried (90 °C, 12 hours), crushed by using an agate mortar and sieved (100 mesh particle size).The chemical reagents (as CsCl, NaCl) were purchased from E.Merck production, and ^{137}Cs as a radioactive solution was purchased from Eckert and Ziegler Isotope Production with specific activity is 3.7 MBq/5 mL.

Mettler series AE200 and Heraeus Labofuge 400 were used as analytic scale unit and centrifuge equipment for weight the samples and separate the solid and liquid phases of the experiment samples. A geological roller also was used to mix the solid phase sample with a solution for contacting the ^{137}Cs in solution with geological samples. To measure the γ-activity of ^{137}Cs in the solution, a Canberra multichannel analyzer (MCA) unit was used completed with 20% eff. HPGe detector and GENII analysis software.

Procedures

Sorption experiment of radio cesium (^{137}Cs) by solid samples (bentonite or quartz sand samples) was conducted by using batch method. 0.1 g of solid samples were weighted and inserted to 20 mL capped PE vials containing 10 mL solution of CsCl with initial concentration was 10^{-8} M and ^{137}Cs with initial γ–activity was 18.000Bq/mL. The vials then were placed in a cylindrical tin container and rolled (155 rpm) by using a geological roller at a certain time. The experiment was performed at room temperature. Supernatant was resulted from separation of solid-liquid phases of sample mixture by using centrifuge machine (2500 rpm, 10 min). Determination of γ–activity of ^{137}Cs radioactive in solution was measured at 661.6 keV channel by using a Canberra MCA radiometric unit, and the distribution coefficient (Kd) of ^{137}Cs as the sorption indicator can be quantified (Setiawan *et al.*, 2016).

$$K_d = \frac{[CsCl\ \ ]_{solid}}{[CsCl\ \ ]_{liquid}} \quad \textbf{(1)}$$

$$[CsCl\ \ ]_{liquid} = \frac{A_t}{A_0}[CsCl\ \ ]_0 \quad \textbf{(2)}$$

$$[CsCl\ \ ]_{solid} = ([CsCl\ \ ]_0 - [CsCl\ \ ]_{liquid})\frac{V}{M} \quad \textbf{(3)}$$

Where $[CsCl]_0$, $[CsCl]_{solid}$ and $[CsCl]_{liquid}$ is the initial, in solid phase and in liquid phase of CsCl concentrations, A_0 and A_t are the condition of initial and final activities of ^{137}Cs at the sorption processes, while V and M are the volume of solution and dry mass sample weight.

Effects of ionic strength of solution experiment to the ^{137}Cs sorption into samples were studied in the condition as follow. Initial concentration of CsCl in the vial was 10^{-8} M in the NaCl solution as ionic strength of solution with various concentrations i.e. 0.1; 0.5 and 1.0 M and then mixed with 0.1 g of solid (bentonite or quartz sand) samples. The similar procedure is applied as in previous experiment, sorption experiment (Setiawan *et al.*, 2016).

Effect of CsCl loading in solution was studied by increasing of initial CsCl concentration loading to the solution. The concentrations of CsCl were ranged from 10^{-8} to 10^{-4} M inserted to vials contained 0.1 g of samples, then ^{137}Cs was poured into samples mixture, capped tightly the vial before putting them in a cylindrical tin for rolling process. After separation of solid-liquid phases, γ–activities of aliquot were measure with MCA detector (Setiawan *et al.*, 2016).

Isotherm study was approached with Freundlich model due to very wide applicable to describe the non-linear model of sorption dependence in the absorbate samples (Yildiz and Yener, 2010). Sorption data at low to intermediate concentrations ranged condition on a heterogeneous surface sample can be properly represented. The Freundlich equation is shown in Eq. 4.

$$[C]_s = k[C]_l^n \quad \textbf{(4)}$$

In a logarithmic model the equation becomes,

$$\mathrm{Log}[C]_s = \log k + n \log[C]_l \quad \textbf{(5)}$$

Where $[C]_s$, and $[C]_l$ is number of Cs ions absorbed on solid phase and remains in solution at equilibrium condition, while k and n is the sorption capacity constant and an empirical number that varies with the degree of samples heterogeneous. Slope n empirically can be obtained from the plotting of $\log[C]_s$ and $\log[C]_l$ interception.

3. RESULTS AND DISCUSSION

A typical sorption of ^{137}Cs results has been obtained from the experiment with time dependency was shown in Figure 2. From this figure can be seen that the sorption of ^{137}Cs was obtained the dependency with contact time. The sorption of ^{137}Cs into samples increased rapidly at the first 100 and 50 min contact for bentonite and quartz sand samples, respectively. It was probably due to the large amount of accessible active site at the samples surface were presence (Konicki *et al.*, 2013). After 400 and 50 min contact timewith bentonite and quartz sand samples, the sorption of ^{137}Cs into samples achieved equilibrium state indicated with the rate of ^{137}Cs sorption process was constantly stable. A huge amount of ^{137}Cs interacted with active site on the samples surface, the condition was indicated with no any change of the ^{137}Cs amount sorbed at samples. The Kd values of ^{137}Cs were 1700 and 3200 mL/g for bentonite-1 and 2 samples, and 17 and 37 mL/g for quartz sand-1 and 2 samples, respectively. Both of bentonite samples are montmorillonite content mineral. The effect of montmorillonite contents may causes the different results of Kd value of ^{137}Cs, although the quantitatively analysis results of montmorillonite contents of samples used were not performed. The Kd value of ^{137}Cs on bentonite samples looks superior when compared to quartz sand, due to the presence of bonding in O_2-Al^{3+}-O_2 framework of mineral in the bentonite samples. This bonding contributed the negative charge on bentonite samples and the negative charge in bentonite samples will interact more with ^{137}Cs in solution, so the obtained Kd values of ^{137}Cs on bentonite samples are also higher than the quartz sand samples (Khalili *et al.*, 2013; Wang and Staunton, 2010).

Kd values obtained from this experiment if compared to the previous results is seen to give a smaller value, see Table 1, predicted due to the differences in mineral constituents and genes of samples.

Table 1. Kd value results from the previous experiments

No.	Materials	Kd values	Ref
1.	Bentonite Trenggalek	7500	Setiawan, 2008
2.	Bentonite Bogor	17000	Setiawan, 2011
3.	Bentonite Cidadap	10600	Setiawan *et al.*, 2014
4.	Clay Smectite Rembang	3000	Setiawan *et al.*, 2016a
5.	Clay Calcite Karawang	4035	Setiawan *et al.*, 2016b

The effect of ionic strength in solution to ^{137}Cs sorption was observed on Figure 3, the results demonstrated the values of Kd decreased with increasing the NaCl in solution. Na ions from NaCl salt will neutralize the negative charges of the sample surface, and the sorption of ^{137}Cs into samples was controlled with the cationic competition between Na ions and ^{137}Cs into the sample surface. Konicki *et al.*, (2013) described that sorption capacity of adsorbate decreased when ionic strength (concentration of NaCl) in solution increased, it was due to occurred the attractive of electrostatic interaction between adsorbate and adsorbent (Konicki *et al.*, 2013; Khalili *et al.*, 2013).

To evaluate sorption capacity of adsorbents (solid samples) in a wide range concentration condition, the initial concentration of CsCl was varied in range of 10^{-8} to 10^{-4} M and the changing of Kd values were determined. The results were shown in Figure 4. It was found that increasing in CsCl concentrations in solution caused the Kd value of ^{137}Cs decreased. The highest of Kd value was found at lowest condition of CsCl concentration, and then decreased when the loading of CsCl concentration in solution increases (Sonderlund *et al*., 2014). At low concentration of CsCl, all of Cs ions in solution can be accommodated by solid samples. With increasing of Cs concentration in the solution caused the active site in the solid sample were occupied by Cs ions, and the excess of Cs ions in solution that were not absorbed by the sample remains in the solution becomes increase.

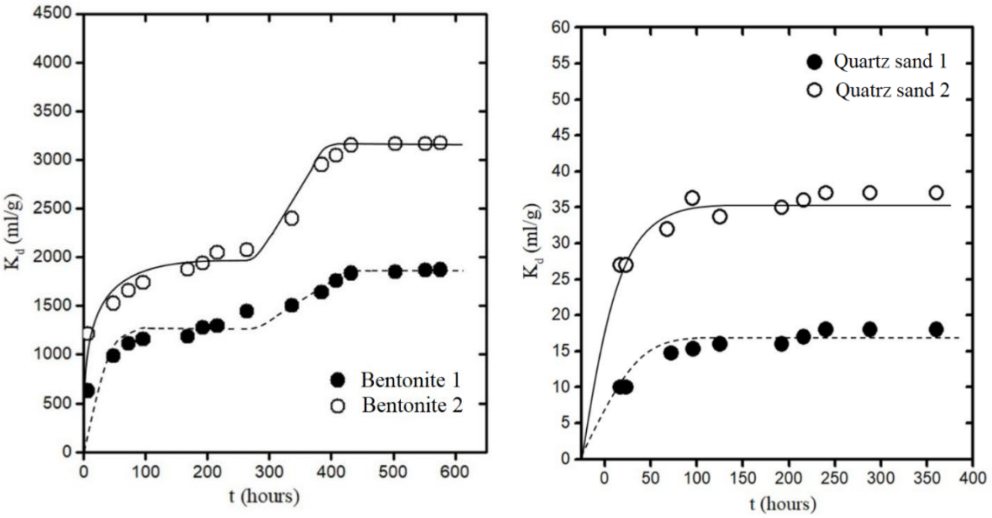

Figure 2. Kd values of ^{137}Cs on samples as time dependency Bentonite-1 and 2 are from Tasikmalaya, and quartz sand-1 and 2 are from Belitung

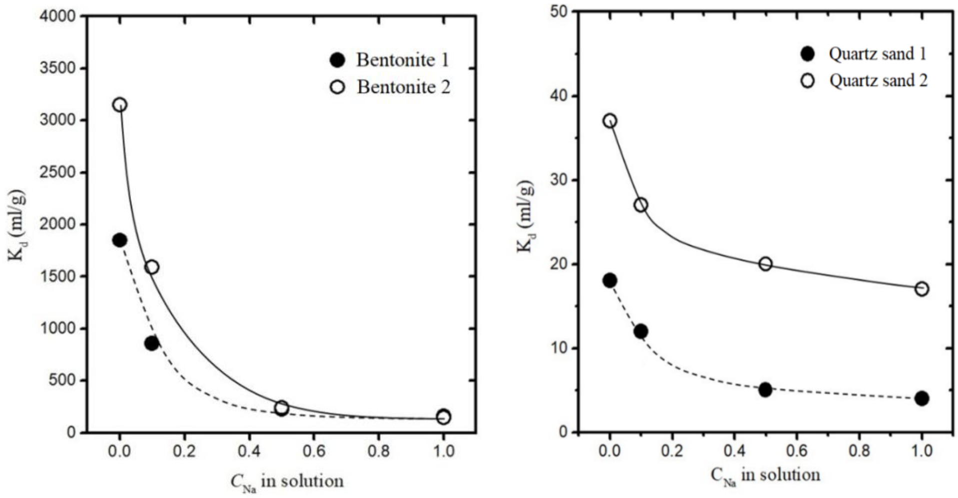

Figure 3. Effect of ionic strength on the ^{137}Cs sorption of solid samples Bentonite-1 and 2 are from Tasikmalaya, and quartz sand-1 and 2 are from Belitung

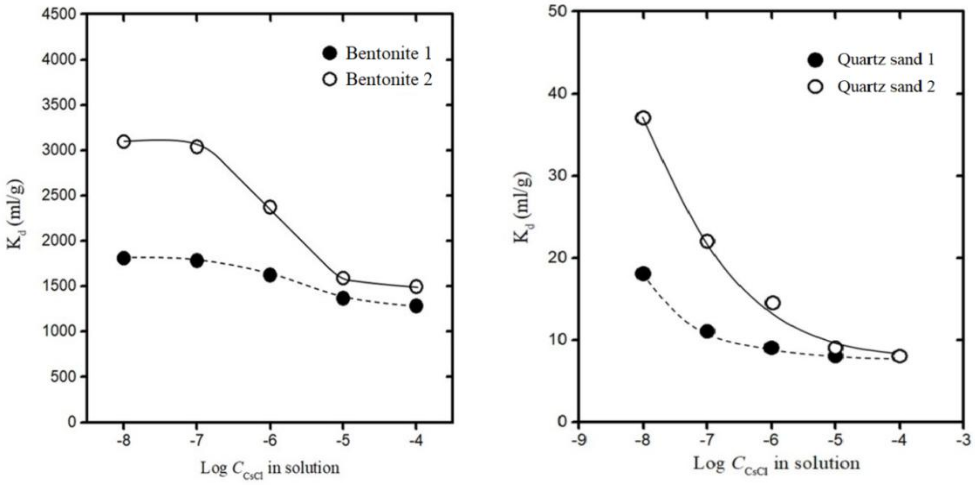

Figure 4. Effect of variation of initial Cs concentration loading in solution on the ^{137}Cs sorption

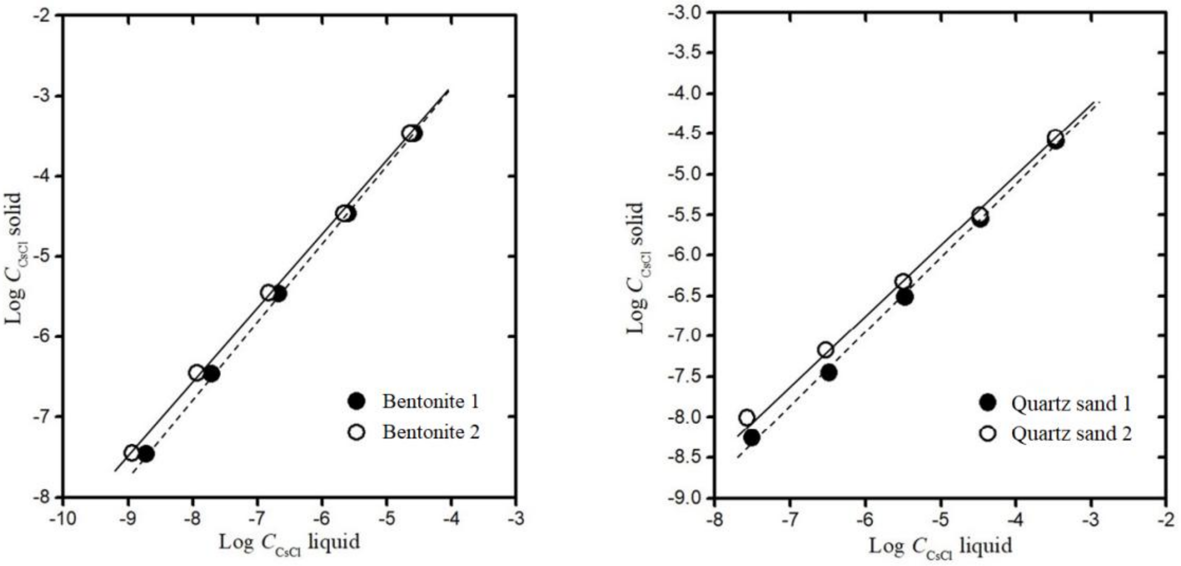

Figure 5. The curve of Freundlich isotherm for ^{137}Cs sorption on solid samples

To investigate the characteristic of interaction between ^{137}Cs in solution with solid samples, an isotherm study was done. Relationship between the numbers of ^{137}Cs left in the liquid phase *versus* the number of ^{137}Cs being absorbed in solid phase was described by sorption isotherm study. For that purpose, the sorption isotherm study was approximated by the Freundlich model due to this model is excellent for explaining the absorption of single component on a heterogeneous surface with the ion-exchangeable ions on their surface. The result was shown in Figure 5.

From the obtained data, we got a linear equation for bentonite-1, bentonite-2, quartz-1 and quartz-2 as follows,Y = 0.9599 x + 0.9251; y = 0.9153 x + 0.7681; y = 0.9499 x – 1.3004 ; y = 0.8596 x – 1.5658, respectively. With n slope and R^2 values were 0.9599, 0.9153, 0.9499, 0.8596 and 0.999, 0.9994, 1.0, 1.0 for bentonite-1, bentonite-2, quartz-1 and quartz-2 samples, respectively. These results showed that the ^{137}Cs sorption onto solid samples had a good agreement with Freundlich isotherm, and suggested that ^{137}Cs was absorbed on the samples surface with heterogeneous of active site (Yildiz *et al.*, 2011).

At low concentration range, the values of experimental sorption data fit in the linearized isotherm equations. The valuable information obtained from the results of Freundlich isotherm that the sorption mechanism of ^{137}Cs onto solid samples occurred at the solid sample with heterogeneous surface. In high concentration of CsCl, the interpretation of sorption data may cause the explanation to be unclear. However, semi-empirically results of Freundlich isotherm do not significantly indicate the occurred sorption mechanism of metal ions or radionuclides into solid samples precisely (Bucur *et al.*, 2011). Similar results have been observed from the previous isotherm experiments, where the samples having heterogeneous surfaces would be more suited to be approximated by the Freundlich equation (Setiawan *et al.*, 2015; Setiawan *et al.*, 2016a; Setiawan *et al.*, 2016b).

4. CONCLUSIONS

From the results of the study, it can be observed that bentonite minerals from Tasikmalaya can be used to eliminate ^{137}Cs from solution. While quartz sand does not provide a good Kd value, so this material will be better when used as drainage of water flow on cover cap layer and in the trench of disposal facility.The obtained results indicated that the bentonite samples have good enough of sorption capacity for radiocesium, however for quartz sand sample the sorption result gave a less value of Kd. The obtained Kd values of ^{137}Cs were 1700 and 3200 mL/g for bentonite samples, and 17 and 37 mL/g for quartz sand samples, respectively. The presence of Na ions in the solution has a significant effect on the elimination of Cs from the solution by the sample. Interaction of ^{137}Cs with solid samples can be approximated by the Freundlich model due to the presence of heterogeneous active site on the solid surface of the sample.

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