

Sorption analysis of ^{137}Cs on Karawang's clay samples

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Abstract – The objective of this work is to characterize the specific of distribution coefficient (Kd) values of ^{137}Cs onto Karawang's clay for radioactive waste disposal facility purpose. Sorption phenomena was affected by contact time, ionic strength and loaded concentration of CsCl. Experiments were done in a batch method, with initial concentration was 10^{-8} M CsCl in the experiments of contact time and ionic strength effects. In the CsCl loading experiment, the concentration was varied from 10^{-8} to 10^{-4} M CsCl and ^{137}Cs radioactive solution was used as a tracer. The solid-liquid ratio is 10^{-2} g/mL. The results shown that obtained Kd values were 21,714 and 4035 mL/g after contacted for 8 days for Sample-1 and 2, respectively. The presence of K^+ and Na^+ ions in solution had reduced the Kd value Cs-137 where the effect of K^+ is greater than Na^+ on decreased the value of Kd. The increasing of CsCl concentrations in solution had reduced the value of Kd. In both samples of clay were closely fit to Freundlich isotherm and pseudo-second order kinetic model. The results are very useful as the input of the safety assessment activity of site candidate for radioactive waste disposal facility in the future.

Key words: ^{137}Cs ; radioactive waste; clay; sorption; disposal.

Introduction

Radionuclide of ^{137}Cs is one of main product of nuclear fission reaction, and together with ^{90}Sr and ^{60}Co , ^{137}Cs is the representative of radioactive waste in low-intermediate level (LLW) with its half-life is 30 years, soluble in water, easy associated with biota in terrestrial and water, mobile in environment and has a similar character with K^+ ion (Volcheck *et.al.*, 2011; Bucur *et.al.*, 2011; Mirkhani *et.al.*, 2010). In general, LLW suggested to be isolated in a near surface facility type disposal facility (IAEA, 2009). Water seepage came from the outside facility can reduce the integrity of waste container, then the water reacts with waste packages containing ^{137}Cs and bring ^{137}Cs out dispersed into environment. Host rock where the disposal facility placed has functioning as the natural barrier system, controlling the flow of all water and retards the possibility of spread of ^{137}Cs contaminants from the facility into the environment (IAEA, 2014).

Clay rock is suitable applied for radioactive waste disposal site especially on the areas that have a high rainfall such as Jawa Island or in Karawang. The clay rock was chosen due to its low permeability, good sorption and their ion exchange character with metal ions or ^{137}Cs , wide availability mainly in the

northern part of Jawa Island (Setiawan, 2013; Yildiz et.al., 2011; Sucipta *et.al.*, 2011). Besides the crystalline and granite rocks, clay rock is also the types of rock are used as the host rock for radioactive waste disposal facility such as those in Mol-Belgium and also in Bure-France (ONDRAF/NIRAS and ANDRA, 2015). Clay rock from Karawang Formation is one of the candidates of potential site for radioactive waste disposal in Jawa Island-Indonesia, where as disposal facility site is expected to provide the safety for environment (Sucipta *et.al.*, 2011). Based on these reason, sorption behavior of ^{137}Cs onto natural clay from Karawang was done, where the contact time, concentration loading, ionic strength, isotherm and kinetic model parameters were applied to estimate the reliability of Karawang Clay planned as the host rock of radioactive waste disposal facility in Indonesia in the future.

The parameter of contact time are intended to acquire the necessary time to reach equilibrium conditions of ^{137}Cs absorbed on clay samples. Ionic strength of the solution which is represented by the presence of K^+ and Na^+ ions in the aqueous solution included in the parameters that can affect the ^{137}Cs sorption onto clay samples (Vejsada *et.al.*, 2005). Effect of concentration of Cs loading on ^{137}Cs sorption onto clay samples were carried out by contacting clay samples with ^{137}Cs with concentration of CsCl were varied from 10^{-8} to 10^{-4} M (Ugur and Sahan, 2012, Setiawan, 2013).

Sorption Cs onto clay sample was approached by using the distribution coefficient (Kd) value, where Kd is the ratio of number of metal ions absorbed in solid phase to the number of metal ions remain in solution (Vejsada, 2005; Missana *et al*, 2008). The objective of this work is to characterize the specific of distribution coefficient (Kd) values of ^{137}Cs onto Karawang's clay for radioactive waste disposal facility purpose. This work was done under the umbrella of 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. Previously, the samples from some areas also have been evaluated [Setiawan, 2011a; 2011b; 2012], and in the end of the program will be selected 2-3 locations of the most feasible site for construction of the disposal facilities.

Materials and Methods

Clay samples were taken from Karawang area in West Java-Indonesia with coordinate of E $107^{\circ} 24'39.91''$; S $106^{\circ} 27'37.36''$ and E $107^{\circ} 24'30.49''$; S $106^{\circ} 27'25.28''$ for sample-1 and sample-2, respectively. After clean-up the samples from roots, leaf and gravels, samples were dried in the oven (105°C , 86 hours), air dried, crushed and sieved to obtain the samples with 100 mesh particle size. The chemical reagent such as CsCl, NaCl and KCl were from *E.Merck production*, however the radioactive solution of ^{137}Cs as a tracer was from *Eckert and Ziegler Isotope Production* with sp. Activity is 3.7 MBq/5 mL.

Batch experiment was applied to determine the Kd value. In 20 mL PE vials, 0.1 g of clay samples were contacted with 10 mL of solution containing CsCl and ^{137}Cs as a tracer. The mixture was gently shaken with a geological roller machine for 12 days. The initial concentration of CsCl was 10^{-8} M. The solid and liquid phases in the vials were separated by using Heraeus Labofuge 400 centrifuge at 2500 rpm and 10 min. The radioactivity in aliquot then are measured with a β -spectrometer Canberra multichannel analyzer completed with 20% eff. HPGc detector at 661.6 keV. The typical counting times were at least about 10 min. Quantification of ^{137}Cs absorbed in clay samples determined by using Kd values,

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

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

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

Where $[C]_0$, $[C]_{\text{solid}}$ and $[C]_{\text{liquid}}$ is the initial concentration of Cs, concentrations of Cs in solid and liquid phases, A_t and A_0 is the activities of ^{137}Cs in initial and final condition of sorption processes, V and M is solution volume and dry mass of sample. The initial of Cs concentration is recognized from the number

of initial concentration of CsCl were given, whereas the final concentration of Cs was calculated by using eq.(2).

For the experiment of ionic strength effect, the initial concentrations of CsCl was set at 10^{-8} M in 0.1; 0.5 and 1.0 M of NaCl or KCl. The solution was contacted with 0.1 g of clay samples. And then the procedures of the experiment similar with the above experiment. The Kd could be calculated by using eq. (1).

In the effect of CsCl concentration loading, the initial concentrations of CsCl were varied from 10^{-8} up to 10^{-4} M, and then the procedures of the experiment similar with the above experiment.

Results and Discussion

Clay sample characteristics

Clay samples were characterized at The Center for forensic lab-Indonesian Police, Jakarta and the Center for integrated lab, Faculty of Science and Technology-State Islamic University Syarif Hidayatullah, Jakarta for XRF and XRD tests. Information of clay content of the samples which was obtained from XRD method analysis have shown that the characteristic peaks of both type of samples in qualitatively have similarity, containing smectite. The results were shown in Table 1.

Table 1. Analytical results of mineral content in Karawang's soil by using XRD method

No.	Minerals	Sample-1	Sample-2
1	<i>Smectite</i>	+++++	+++++
2	<i>Illite</i>		
3	<i>Vermiculite</i>	+	+
4	<i>Quartz</i>	+++	+++
5	<i>Crystoballite</i>		

Note: +++++ predominantly, ++++ dominant, +++ moderate, ++few, + very few

The mineral structure of smectite is composed of 3 layers, 1 octahedral layer was sandwiched with 2 layers of tetrahedral [Das, 2006]. Between the octahedral and tetrahedral layers there are monovalent as well as divalent cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions were exchangeable ions. Silicate tetrahedral bonded with hydrogen bonds between the ends of silica sheets, while Al octahedral bonds in a weak of Van der Waals forces to form the aluminosilicate layers. There is a lack of negative charge in the octahedral layer, thus water and exchangeable ions can enter and separate the layer [Wati *et.al.*, 2011].

Table 2. Chemical composition of Karawang's soil

Elements	Oxides	Sample-1	Sample-2
		Concentration (%)	Concentration (%)
K	K_2O	1,773	1,910
Na	Na_2O	0,026	0,018
Ca	CaO	1,182	1,413
Mg	MgO	0,319	0,290
Al	Al_2O_3	21,629	20,974
Fe	Fe_2O_3	20,075	17,511
Mn	MnO	0,105	0,063
Si	SiO_2	51,381	55,457

Chemical composition of samples was shown in Table 2. The composition assists estimate samples ability to absorb the dissolved radionuclide, especially when associated with ion exchange mechanisms between the metal ions. The number of cation absorbed correspond with the cation exchange capacity of the samples [Missana, *et.al.*, 2008].

Effect of contact time

A typical result of ^{137}Cs sorption into clay samples as a function of contact time was shown in Figure 1. In the early of ^{137}Cs contacting, the sorption rate of samples was fast up to 8 days. After 8 days contact, the increasing of Kd value was slower and then relatively constant. The number of active site in the samples becomes saturated with ^{137}Cs , and equilibrium state of ^{137}Cs sorption was reached [Lujaniene, *et.al.*, 2006]. The obtained Kd values were 21714 and 4035 mL/g in sample-1 and sample-2, respectively. The difference of Kd value of both samples is predicted to be due to differences of chemical contents in the chemical composition of the sample.

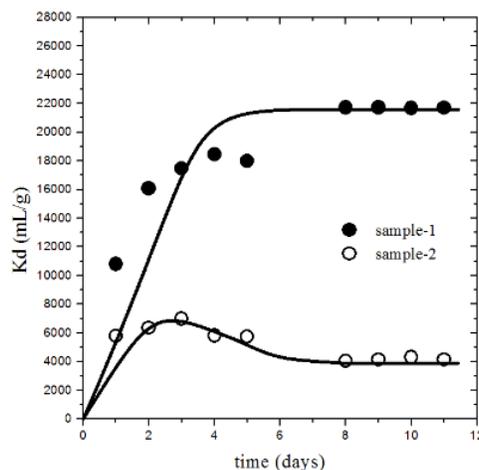


Figure 1. Sorption of ^{137}Cs as a function of time

Effect of ionic strength

Ionic strength of solution was represented by Na^+ and K^+ ions, in the groundwater both ions have enough high concentration so that is expected to affect the ability of sample absorbance to ^{137}Cs . Increasing in Na^+ and K^+ in the solution may block the interaction between ^{137}Cs with samples, and they can reduce the number of ^{137}Cs that was absorbed into the samples as shown in Figure 2. This may be explained by consideration of the structure of the electrical double layer around the samples [Rao, Choppin, 1995]. In the surrounding of samples, a part of the surface charge is neutralized by Na^+ or K^+ ions attracted by ion exchange mechanism with the sample. Therefore the concentration of Cs^+ in the close vicinity of sample is controlled by the competition between Na^+ or K^+ and $^{137}\text{Cs}^+$ to this zone. In other words, some part of formation metal ions-clay sample proceeds *via* an ion exchange between Na^+ or K^+ and the $^{137}\text{Cs}^+$. With similar chemical properties between Cs^+ and K^+ ions in solution causes the Kd values of ^{137}Cs smaller than when the solution is influenced by Na^+ ion.

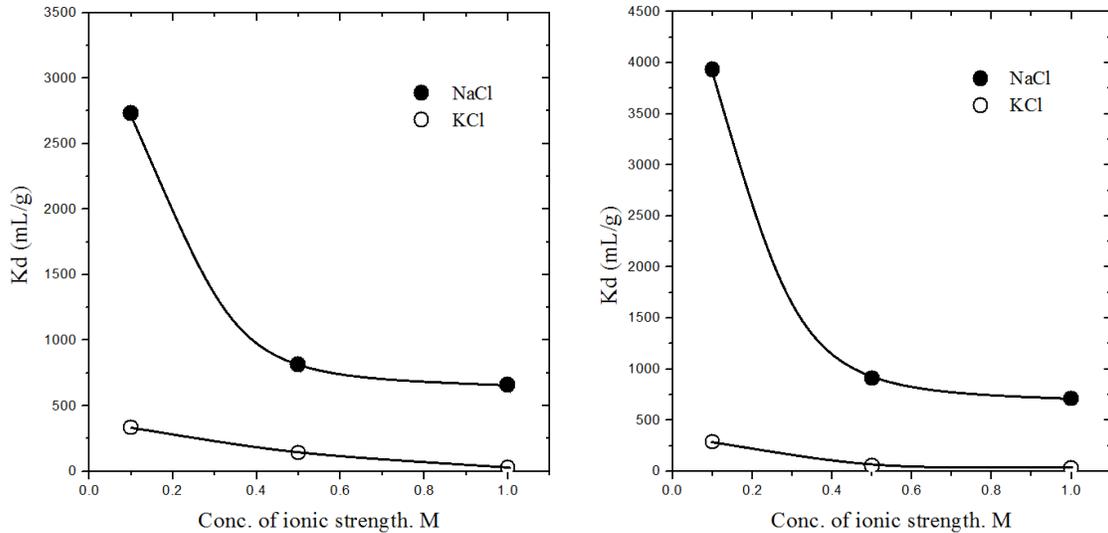


Figure 2. Effect of ionic strength in ^{137}Cs sorption, in sample-1 (left) and sample-2 (right).

Effect of Cs concentrations loading

Figure 3 showed that K_d values decreased with increasing of Cs concentration loading in solution. Significantly the K_d values decreased, it was predicted as the limitation of samples in their exchange capacity to $^{137}\text{Cs}^+$. Increasing the concentrations of Cs^+ ion in solution was not comparable to the sorption capacity of samples, and the K_d values goes to their new saturated level [Staunton and Roubaud, 1997; Vejsada, *et.al.*, 2005].

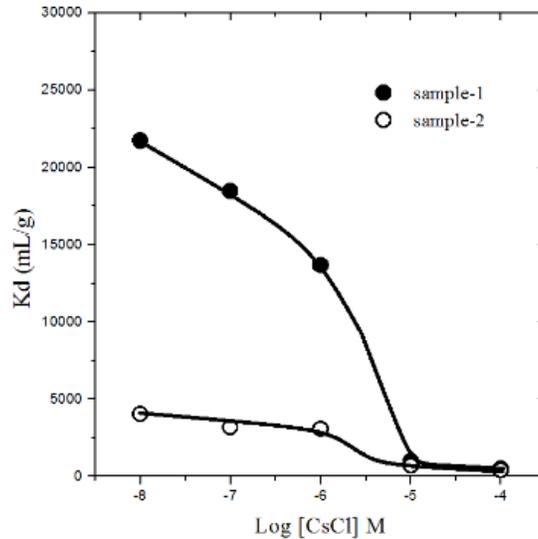


Figure 3. Effect of Cs concentration loading in ^{137}Cs sorption

Isotherm sorption

Sorption isotherm illustrated the number of metal ion distributed among solid and liquid phases when the sorption processes reached equilibrium states. For that purpose, the mixture of solution and samples were contacted in 8 days with initial Cs concentrations were varied. Sorption of ^{137}Cs in both samples of clay were approached with Freundlich isotherm with its equation form as follow,

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

Where $[C]_s$ and $[C]_l$ are the number of Cs absorbed on the solid phase at equilibrium and remains in solution, k is a constant that is related to sorption capacity and n is an empirical parameter that varies with the degree of heterogeneity of the samples. Slope of n is obtained from the interception of plotting of $\log[C]_s$ and $\log[C]_l$ [Yildiz, *et.al.*, 2011]. If the eq. (4) is wrote in a logarithmic model, the equation changed as,

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

In Figure 4 showed that regression determination of linear isotherm was obtained better for sample-2 than for sample-1, and R^2 of sample-1 and 2 were 0.9828 and 0.9924, respectively. The n values of the experiment were 0.671 and 0.779 for sample-1 and sample-2, and a similar result was found in other experiment where $n=0.8285$ on the sorption of Cs on bentonite samples [Yildiz, *et.al.*, 2011]. Sorption capacity (k) of sample-1 and sample-2 were 0.143 and 0.408. Approximation in a linear model could be used as indication in the isotherm sorption of both samples, and the values obtained from linear isotherm are valid only for the concentration range used in the experiment. For the higher concentrations used could overestimate the ^{137}Cs sorption and errors may occur when concentration range were extended over the concentration used. Since the both samples contain smectite, the sorption of ^{137}Cs could occur on ion exchange reactions or in a highly selective sites of fried edge site (FES) [Bucur, *et.al.*, 2011].

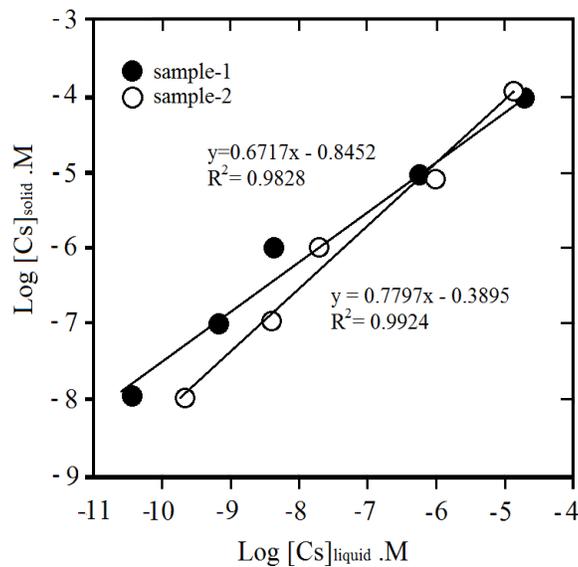


Figure 4. Freundlich sorption isotherm of ^{137}Cs

Kinetic model of sorption

Kinetics of sorption explained the existence of sorption process of absorbate by the absorbent as a function of time. The number of substances that absorbed in a weight of absorbent depends on the concentration of absorbate and the number of absorbent's site vacant.

The results of kinetic model of the sorption processes on the sample were shown in Figure 5. The kinetic model of the experiment result followed the pseudo-second order. The model has been developed by Ho and McKay based on complex reaction occurred in the surface between absorbate and absorbent, and by assuming that sorption capacity of solid phases proportion with the number of active site on the absorbent. Constant of sorption rate determined by the following equation,

$$\frac{dq_t}{dt} = k_2 (q_s - q_t)^2 \quad (6)$$

where k_2 is kinetic constant, q_t and q_e are the number of absorbate absorbed at time t and at equilibrium condition. The result of integration and using of boundary condition $q_t=0$ at $t=0$ and $q_t=q_e$ at $t=t$ gives the result,

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (7)$$

and the eq.(6) could be linear as follow,

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t \quad (8)$$

plotting of t/q_t versus t is a linear curve with slope $1/q_e$ and the intercept is $1/k.q_e^2$ [Ho and McKay, 1999; Zaker, *et.al.*, 2013].

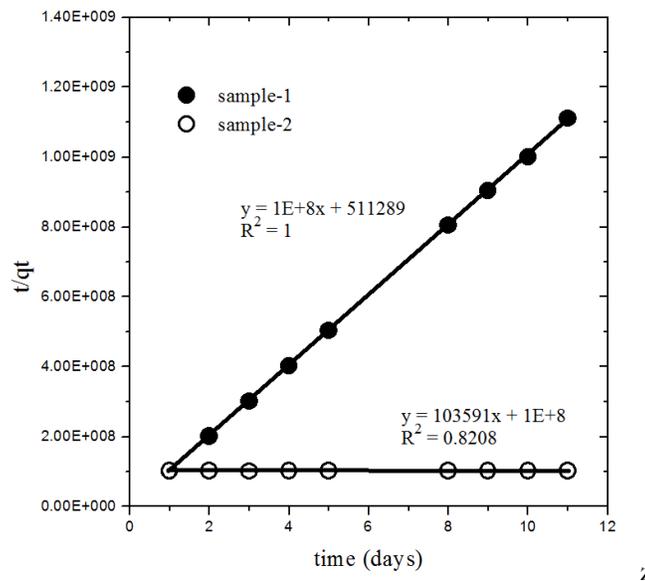


Figure 5. Kinetics model in pseudo-second order

From the Figure 5, sorption of ^{137}Cs probable followed pseudo-second order of kinetic model with relation coefficient values $R^2=1$ and 0.820 . Sorption constant rate (k_2) of sample-1 and sample-2 were 1.9×10^{11} and $1.073 \text{ g.mol}^{-1}.\text{day}^{-1}$ with the number of ^{137}Cs absorbed on clay samples per-unit weight at equilibrium were 1×10^{-8} and $9.6 \times 10^{-5} \text{ mol/g}$, respectively. The k -value is a parameter of kinetics sorption indicates the pace of sorption processes. The larger of k -value, the sorption processes also faster [Sekewael, *et.al.*, 2013]. Other researcher also indicated their sorption mechanism followed pseudo-second order model for Cs sorption behavior on humic acid with initial concentration lower [Celebi, *et.al.*, 2009], and sorption of Cs on cement mortar [Volchek, *et.al.*, 2011]. Specific sorption characteristics are indispensable, and the results will be very useful as the input of the safety assessment activity of the site candidate for radioactive waste disposal facility in the future.

Conclusion

Smectite mineral dominated in clay from Karawang, and 8 days contact time was needed to reach the saturation states of ^{137}Cs onto clay samples with K_d values were 21714 and 4035 mL/g for sample-1 and sample-2, respectively. Any change in the ionic strength of solution has given an effect on the sorption of ^{137}Cs to the sample, due to the competition between K^+ and Na^+ ions to ^{137}Cs , where $\text{K}^+ > \text{Na}^+$ ions. Increasing in the concentration of Cs caused reduce the K_d values of

^{137}Cs on samples. Sorption model of ^{137}Cs onto both clay samples were approached with Freundlich isotherm and pseudo-second order kinetic model. The results will be used as the input on safety assessment activity of candidate site for radioactive waste disposal facility in the future.

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