

Sorption Characteristics of ^{137}Cs and ^{90}Sr into Rembang and Sumedang Soils

Budi Setiawan^{1,*}, Yusran Dani², and Nurmaya Arofah²

¹Center for Radioactive Waste Technology - National Nuclear Energy Agency
Kawasan PUSPIPTEK Bld 71, 3rd Floor, Serpong-Tangerang 15310, Indonesia

²Department of Chemistry, Faculty of Science and Technology, State Islamic University Syarif Hidayatullah
Jl. Ir. Haji Juanda No. 95, Ciputat, Tangerang Selatan, Banten 15412, Indonesia

Received February 12, 2016; Accepted April 26, 2016

ABSTRACT

In order to understand the sorption behavior of ^{137}Cs and ^{90}Sr into soil sample from Rembang and Subang, it is important to estimate the effect of contact time, ionic strength and concentration of metal ion in the solution. For this reason, the interaction of ^{137}Cs and ^{90}Sr with soil sample has been examined. The study performed at trace concentration ($\sim 10^{-8}$ M) of CsCl and SrCl₂, and batch method was used. NaCl has been selected as a representative of the ionic strength with 0.1; 0.5 and 1.0 M concentrations. Concentration of $10^{-8}\sim 10^{-4}$ M CsCl and SrCl₂ were used for study the effect of Cs and Sr concentrations in solution. Apparent distribution coefficient was used to predict the sorption behavior. The sorption equilibrium of ^{137}Cs and ^{90}Sr into soil was attained after 5 days contacted with K_d value around 3300-4200 mL/g, where K_d was defined as the ratio of number of radionuclide activity absorbed in solid phase per-unit mass to the number of radionuclide activity remains in solution per-unit volume. Presence of NaCl as background salt in the solution affected K_d values due to competition among metal ions into soil samples. Increase of Cs or Sr concentration in solution made K_d value decreased drastically. This information is expected could provide an important input for the planning and design of radioactive waste disposal system in Java Island in the future.

Keywords: radioactive waste; host rock; cesium; strontium; sorption

ABSTRAK

Dalam rangka memahami sifat sorpsi ^{137}Cs dan ^{90}Sr ke contoh tanah dari Rembang dan Subang, sangatlah penting untuk memperkirakan pengaruh waktu kontak, kekuatan ion dan konsentrasi ion logam di larutan. Dalam hubungan ini, interaksi ^{137}Cs dan ^{90}Sr dengan contoh tanah telah diujikan. Penelitian dilakukan pada kondisi konsentrasi ^{137}Cs and ^{90}Sr kelumit ($\sim 10^{-8}$ M), dan cara batch telah digunakan. NaCl dipilih sebagai representasi kekuatan ionik dengan 0,1; 0,5 dan 1,0 M NaCl. Konsentrasi $10^{-8}\sim 10^{-4}$ M ^{137}Cs and ^{90}Sr digunakan untuk mempelajari pengaruh Cs dan Sr di larutan. Koefisien distribusi digunakan untuk memperkirakan sifat sorpsi. Keseimbangan sorpsi ^{137}Cs and ^{90}Sr ke contoh tanah dicapai setelah 5 hari pengontakkan dengan nilai K_d sekitar 3000-4200 mL/g. Adanya NaCl sebagai garam latar di larutan telah mempengaruhi nilai K_d karena adanya kompetisi diantara ion logam ke contoh tanah. Meningkatnya konsentrasi ^{137}Cs dan ^{90}Sr di larutan telah membuat nilai K_d berkurang secara drastis. Informasi ini akan memberikan masukan yang penting pada perencanaan dan desain sistem disposal limbah radioaktif di pulau Jawa di masa depan.

Kata Kunci: limbah radioaktif; host rock; cesium; stronsium; sorpsi

INTRODUCTION

The first Indonesian nuclear power plant (NPP) will be constructed in Java Island to fulfill the electricity demands in Java and Sumatera Islands in the future. The energy source is planned to contribute to national energy mix system, by at least 5% of the total demand. Consequently, the plant will produce a huge quantity of radioactive waste especially in the form of low-medium level of solid radioactive waste. For example, the waste produced by a 1000 Mwe NPP is predicted to be about

400 drums of 200 L embedded waste annually [1-2]. These embedded waste drums will off course be sources of radiological risk to people and environment.

To minimize those possible risks, waste disposal facilities need to be provided. Therefore, radwaste disposal in Java Island needs to be realized prior the construction of this first NPP. These disposal facilities are expected to be able to reduce or minimize the security risk of waste transportation from waste producing facility to disposal site.

* Corresponding author. Tel/Fax : +62-21-7563142/7560927
Email address : bravo@batan.go.id

The soil in Java Island has a distinctive feature with high cracking due to high intensity of annual rainfall [3]. Rock or soil with low hydraulic conductivity property (10-7 cm/s) such clay is considered to be suitable for the host rock for radioactive waste disposal facility. Such types of rock or soil site are expected to be able to prevent the spread of radionuclides contamination into the environment. From the previous survey, which has been completed based on geological and non-geological criteria, some potential safe areas as the site for waste disposal facilities in Java Island are Rembang and Sumedang that contain appropriate host rock for disposal site [4-6].

To demonstrate the suitability of those two sites, an experiment on the sorption test of radionuclides in solution into the soil samples need to be done. This experiment will be able to indicate the soil ability to retard radioactive contaminants from the radwaste disposal facility spreading in the environment. The sorption mechanisms will be determined through a series of sorption characteristic experiments with some affected parameters.

Cesium (^{137}Cs) and strontium (^{90}Sr) were used in the experiment as the metal ion model due to their existing in the low-level waste inventory, and long half-life. Meanwhile ^{60}Co was used as radionuclide reference to demonstrate the interaction between low-level radioactive waste and rock or soil samples. Furthermore, because ^{137}Cs was easy to be bound to soil, it used to study and predict soil erosion quantitatively by understanding its impact on the action of erosion control [7-8]. The objective of this study is to find the sorption characteristic of radionuclides ^{137}Cs and ^{90}Sr in the Rembang and Sumedang soils. Sorption indicator of ^{137}Cs and ^{90}Sr in the Rembang and Sumedang soils were determined by observing their distribution coefficient (K_d), which was calculated from the initial and final activity of radionuclide remains in the solution using equation (1).

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

where C_0 and C_t are the initial and the final activity of ^{137}Cs or ^{90}Sr in the solution, V is the total volume of the solution in milliliters, m is the dry mass weight of the soil sample in gram and K_d is the distribution coefficient of ^{137}Cs or ^{90}Sr in the soil and the solution in the equilibrium state, respectively.

In this experiments, sorption characteristic of ^{137}Cs and ^{90}Sr has been determined at the trace concentration by evaluating four parameters i.e. contact time, desorption, ionic strength and concentration for both ^{137}Cs and ^{90}Sr in the solution.

EXPERIMENTAL SECTION

Materials

Determination of sampling locations as potential site was obtained from desktop and field works in Java Island geological map of central part section and Indonesian stratigraphic lexicon references [6,9]. Based on the siting criteria, Rembang and Sumedang have been selected to be potential sites. Clay soil from those two candidate sites was sampled and then brought to laboratory to be cleaned and sieved to 100 mesh particle size samples. The samples were then used in the experiment. All chemical reagents (CsCl , SrCl_2 and NaCl) were used in the experiment is from E. Merck production except the radioactive material (^{137}Cs and ^{90}Sr) is from Eckert & Ziegler Isotope Production in 3.7MBq/5 mL sp. activity.

Instrumentation

To weight the soil samples have been used the Mettler series AE200 analytic scale unit. Heraeus Labofuge 400 centrifuge equipment has been used to separate the solid and liquid phases of samples, and Canberra multichannel analyzer (MCA) unit completed with HPGe detector eff. 20% and Perkin Elmer Tri-Carb 2910 TR liquid scintillation counter (LSC) has been used to determine the β - γ activities of radionuclides in the solution.

Procedure

Sorption-desorption

To determine the distribution coefficient (K_d), the experiment was performed in a batch method, in which 0.1 g of soil sample was immersed into a 10 mL demineralized water containing CsCl which labeled with ^{137}Cs or ^{90}Sr in a 20 mL PE vial. Initial concentration of CsCl or SrCl_2 was 1×10^{-8} M and then shakes with geological roller for 12 days. Solid and liquid phases were separated using a centrifuge equipment (2500 rpm, 10 min.). The β and γ -activity remaining in supernatant were measured using LSC and MCA radiometric units. ^{137}Cs was measured at 661.6 keV, which was counted for about 10 min. The coefficient distribution (K_d) was calculated using equation (1). A desorption experiment was conducted by changing the old solution with a fresh demineralized water. The procedure was similar to the previous sorption experiments.

Effects of ionic strength

In the ionic strength experiment, the experiment used the initial concentration of CsCl or SrCl₂ was 1 x 10⁻⁸ M in 0.1 or 1.0 M NaCl solution, which was mixed with 0.1 g of soil samples. The next procedure was similar to the sorption experiments.

Effects of Cs or Sr concentrations

For the effect of CsCl or SrCl₂ concentrations, initial concentrations of CsCl or SrCl₂ was varied from 10⁻⁸ to 10⁻⁴ M. Experiment procedures were performed similar to the previous work [10].

Isotherm sorption

In this study, Freundlich isotherm was applied. This isotherm model is very widely applicable for describing non-linear model of sorption dependence on adsorbate concentration [11]. This model also represents properly the sorption data at low to intermediate concentration on heterogeneous surface of soil samples. The relationship of Freundlich isotherm is exponential and represented in eq. (2),

$$[C]_s = k[C]_i^n \quad (2)$$

where [C]_s is the amount of Cs or Sr sorbed on the solid phase at equilibrium, [C]_i is the concentration of Cs or Sr remain 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 resulted from the interception of plotting log[C]_s and log[C]_i. The eq. (2) could be written in a logarithmic eq. as,

$$\text{Log}[C]_s = \text{log}k + n \text{log}[C]_i \quad (3)$$

All experiments described above were carried out in the Chemistry Laboratory of Disposal Technology Division, Center for Radwaste Technology-National Nuclear Energy Agency of Indonesia in Serpong-Tangerang in year 2012.

RESULT AND DISCUSSION

Sorption-Desorption

Physically, clay samples taken from Rembang area have a brighter color than clay sample from Sumedang area. The mineralogical of the two samples are shown in Table 1. The carbonate, quartz and clay contents of the soil samples were determined qualitatively by X-ray diffraction method in the Directorate of Geology-Bandung.

Sorption kinetics results of ¹³⁷Cs or ⁹⁰Sr by Rembang and Sumedang soil were shown in Fig. 1. Uptake of Cs and Sr ions on soil samples increase sharply in the first 5 days contact and then slow down towards the saturation condition.

Table 1. Chemical mineralogical of the samples

Components	Rembang soil	Sumedang soil
Calcite, CaCO ₃	+++	++++
Quartz, SiO ₂	+++	++
Magnetite, Fe ₃ O ₄		+
Muscovite, KAl(Si ₃ Al)O ₁₀ (OH) ₂	+	
Nontronite, NaO _{0.33} Fe ²⁺ ₃ (SiAl) ₄ O ₁₀ (OH) ₂ .xH ₂ O	+	

Few(+), little bit(++), average(+++), much(++++)

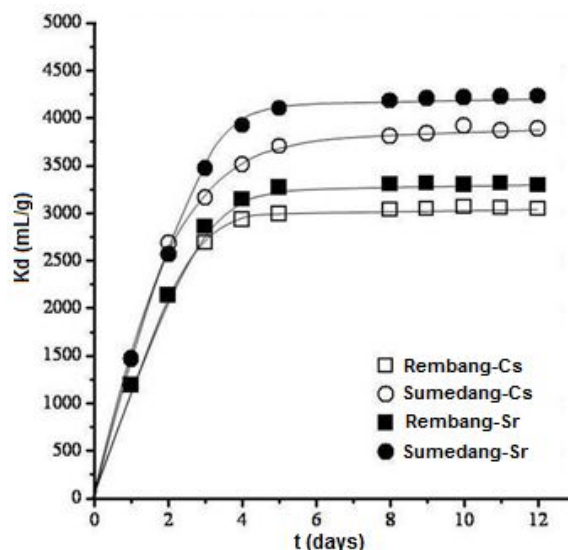


Fig 1. Sorption processes of ¹³⁷Cs or ⁹⁰Sr into Rembang and Sumedang soil

Some parts of ¹³⁷Cs or ⁹⁰Sr from solution were removed by soil samples. The sorption process of radionuclide reached equilibrium state when soil samples become saturated with ¹³⁷Cs or ⁹⁰Sr [12-13]. At the beginning of the reaction, the sorption process of ¹³⁷Cs or ⁹⁰Sr into soil samples was relatively fast due to the domination of the sorption processes to the desorption processes. After 4-5 days of contact, the sorption process slows down and the sorption rate becomes equal to the rate of desorption. This condition is called as a sorption equilibrium condition. Sorption equilibrium of ¹³⁷Cs or ⁹⁰Sr into soil samples was achieved after 5 days of contact with Kd was approximately about 3000-4200 mL/g. However, the result was little bit higher than other references due to the different experiment condition [14-15].

Desorption experiment was done, by replacing the solution containing ¹³⁷Cs or ⁹⁰Sr carrier in PE vials with fresh water and then gently shaking process continued again. The result is shown in Fig. 2.

After 4-5 days contact between soil samples and fresh water, Kd values of ¹³⁷Cs or ⁹⁰Sr decreased and then stable at 3200-1500 mL/g. This is because some parts of ¹³⁷Cs or ⁹⁰Sr, which has been absorbed by soil

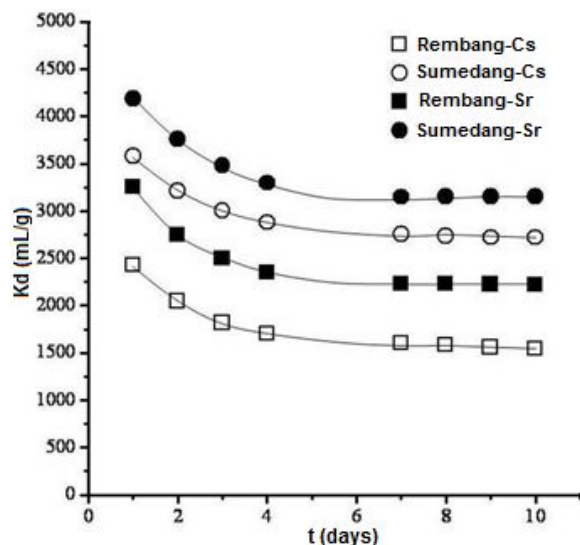


Fig 2. Desorption processes of ^{137}Cs or ^{90}Sr from Rembang and Sumedang soil

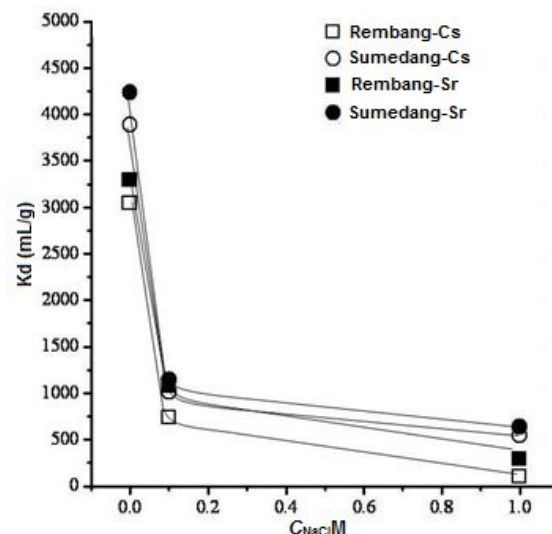


Fig 3. Effect of ionic strength in solution to ^{137}Cs or ^{90}Sr sorption into Rembang and Sumedang soils

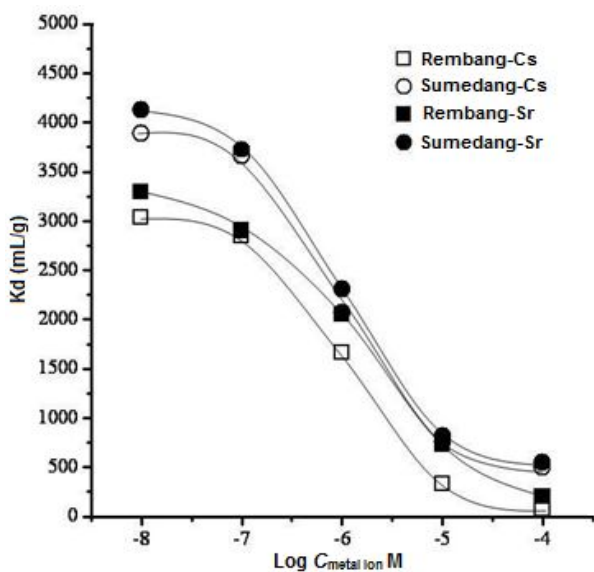


Fig 4. Effect of CsCl or SrCl_2 concentration in solution to ^{137}Cs or ^{90}Sr sorption into Rembang and Sumedang soils

samples, were back into solution again. Concentration of CsCl or SrCl_2 in solution went up and then the sorption reaction in soil sample slowly reached a new equilibrium. The sorption of Cs and Sr ions on soil samples were reversible, suggesting that ^{137}Cs or ^{90}Sr sorption in the soil samples were in a simple bonding mechanism and absorbed in reversible meaning [16].

Cesium and strontium absorbed on the samples is to balance the negative charge on the soil. It is compensated for by counter ions, such as Na^+ , K^+ , Ca^{2+} or Mg^{2+} sorbed on the soil surfaces. These counter ions can be exchanged by cesium and strontium. Calcite and quartz are dominant in both samples. The high

concentration of calcite in Sumedang soil than in the Rembang soil is expected to distinguish the magnitude of Cs and Sr uptake to the soil samples.

Effects of Ionic Strength

Coefficient distribution value of ^{137}Cs or ^{90}Sr in soil sample in the presence of Na^+ ion as background salt in solution was shown in Fig. 3. K_d of ^{137}Cs or ^{90}Sr decreased along with the increase Na^+ concentrations in solution. This was caused by the competition between Cs^+ or Sr^{2+} ions and Na^+ ion around the solid boundary area of the interaction of the soil samples [17-18]. Na^+ concentration was higher than Cs^+ and Sr^{2+} concentration, Na^+ ion was an effective competitor for the high-affinity sites at soil samples [19]. Increasing the Na ion concentration in solution has changed the electrostatic force in the surrounding of the soil samples, and this has led to reduce the metal ion selectivity in exchangeable of soil samples [17].

Effects of Cs or Sr Concentrations

Effect of CsCl or SrCl_2 concentrations in solution to ^{137}Cs or ^{90}Sr sorption in the soil samples were done with initial concentrations were ranged of 10^{-8} to 10^{-4} M, and the result was shown in Fig. 4. Increasing the CsCl or SrCl_2 concentration in the solution decreased the K_d values of ^{137}Cs or ^{90}Sr into Rembang and Sumedang soils. At low concentration, the changing of K_d value was not relatively affected by the concentration of Cs and Sr. However, at higher concentrations, the sorption process was non-linear or the uptake was not proportional to the Cs and Sr concentrations. The non-linear behavior means that the K_d value is only valid for

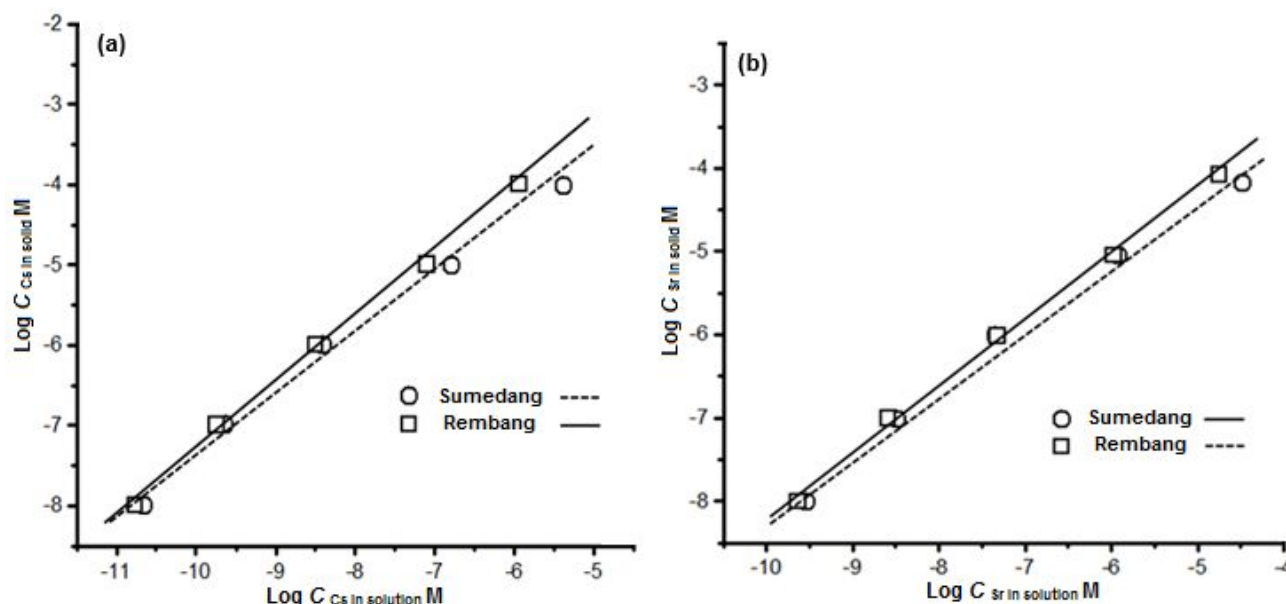


Fig 5. Isotherm sorption of Cs (a) and Sr (b)

one concentration condition of Cs or Sr. This is indicated by the difference of their K_d values. With the increasing of concentration of Cs or Sr in the solution, the K_d value decreased [20-21]. It is clear that the two soil samples have the highest K_d values obtained at lower Cs or Sr concentrations. This suggests that more favorable sites exist in the soil samples with limited sorption capacity.

Isotherm Sorption of Cs and Sr

Sorption process considered involves a solid phase of soil samples and radionuclides (Cs and Sr) solution to be sorbed as a liquid phase. In the sorption isotherm are plotted the uptake the Cs or Sr ions in soil samples and the residual of Cs or Sr in solution.

The typical isotherm sorption results of experiment are shown in Fig. 5 (a) and (b) for Cs and Sr, respectively. In this study, we set the initial Cs and Sr concentrations from 10^{-8} to 10^{-4} M on while $[C]_i$ values in Rembang soil samples decrease to be 2.23×10^{-11} , 2.37×10^{-10} , 3.96×10^{-9} , 1.64×10^{-7} , 4.17×10^{-6} and 3×10^{-10} , 3.3×10^{-9} , 4.6×10^{-8} , 1.2×10^{-6} , 3.3×10^{-5} of Cs and Sr concentration, respectively. In $[C]_s$, the values become 1×10^{-8} , 1×10^{-7} , 1×10^{-6} , 9.8×10^{-6} , 9.6×10^{-5} and 9.7×10^{-9} , 9.7×10^{-8} , 9.5×10^{-7} , 8.8×10^{-6} , 6.7×10^{-5} of Cs and Sr concentration in Rembang soil samples, respectively. The same condition also happens to Sumedang soil samples. That is, increased initial concentration leads to decreased values of $[C]_s$. Analysis of the region of higher saturation yields a slope slightly greater than one for strontium even in Rembang and Sumedang soils. The sorption of cesium tends to be independent of sorption at higher concentration. Those

results suggest that cesium easier dispersed in the environment [22].

The presence of specific information on ^{137}Cs or ^{90}Sr sorption by Rembang and Sumedang soils will be able to give an overview of the ability of the soil from two areas to accommodate the ^{137}Cs or ^{90}Sr in solution, which eventually can be used to assess the level of reliability of soil of both areas against potential radiological risk to humans and the environment.

CONCLUSION

The results showed that sorption equilibrium of ^{137}Cs or ^{90}Sr into Rembang and Sumedang soils achieved after 5 days of the contact time with K_d values were 3000-4200 mL/g. Replacement contaminated solution with fresh distilled water had decreased K_d values of ^{137}Cs or ^{90}Sr into Rembang and Sumedang soils from 4200-3000 mL/g to 3200-1500 mL/g, and the presence of NaCl as background salt in solution also decreased K_d values due to the ionic competition between Na^+ and Cs^+ or Sr^{2+} into soil samples. Increasing CsCl or SrCl_2 concentrations in solution decreased K_d values due to the limitation of sorption capacities of soil samples. The sorption of Cs and Sr ions into soil samples could be more effective when the ionic strength of solution is in a low concentration. All of information obtained from the experiment could give an important input to the decision makers and designer of radwaste disposal system in Java Island in the future.

ACKNOWLEDGEMENT

Thanks are to Mr. Sucipta, M.Si., Teddy Sumantry, B.Sc., and Ms. Wahyu Retno Prihatiningsih, M.Si., of PTLR-BATAN for their assistances in soil sampling, chemical and radioactive materials preparation and also for using the liquid scintillation counter equipment during the experiment. Also to Dr. Julwan Hendry Purba of PTKRN-BATAN for the valuable suggestions.

REFERENCES

1. Anonymous, 2007, *Nuclear Fuel Cycle Simulation System (VISTA)*, IAEA-TECDOC 1535, IAEA-Vienna.
2. Eisenstatt, L.R., Popp, D.M., Vijuk, R.P., and Russ, P.A., 2011, *Process Mass Balance for AP1000 Solid Waste*, Westinghouse Electric Company, Cranberry Township, PA 16066
3. Aryani, D.I., Sasmito, B., and Wijaya, A.P., 2014, *Jurnal Geodesi Undip*, 3 (1), 130–40.
4. Setiawan, B., Sumantry, T., Sriwahyuni, H., Pratama, H.A., Ekaningrum, N.E., Syarmufni, A., Pratomo, B.S., Suganda, D., Waluyo, S., Pudyo, A., Susilowati, D., and Marwoto, 2008, *Siting of Radwaste Disposal in Jawa Island*, Proc. National Seminar on Waste Management Technology, June 24th 2008, BATAN-RISTEK, Serpong-Indonesia;188–194.
5. Sucipta, Setiawan, B., Pratomo B.S., and Suganda, D., 2010, *Jurnal Teknologi Pengelolaan Limbah*, 13 (1), 30–42.
6. Amin, T.C., Ratman, N., and Gafoer, S., 1999, *Geological Map of Jawa Island, Central Section*, scale 1: 500,000, Geology R&D Center, Bandung-Indonesia.
7. Peterson, J., MacDonell, M., Haroun, L., Monette, F., Hildebrand, R.D., and Taboas, A., 2007, *Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas*, Argonne National Laboratory Environmental Science Division, Chicago, IL, USA.
8. Kiziltaş, M.S., Hacıyakupoğlu, S., Gökbülak, F., and Hizal, A., 2009, *Turk. J. Agric. For.*, 33, 295–303.
9. Harahap, B., Bachri, S., Baharuddin, Suwarna, N., Panggabean, H., and Simanjuntak, T.O., 2003, *Stratigraphy Lexicon of Indonesia*, 1st ed., Geology R&D Center, Bandung, Indonesia.
10. Setiawan, B., Mayasari, E., and Meidhika, S., 2015, *Procedia Chem.*, 16, 445–450.
11. Yildiz, N., and Yener, G., 2010, *Ekoloji*, 19 (77), 80–87.
12. Sivaiah, M.V., Kumar, S.S., Venkatesan, K.A., Sasidhar, P., Krishna, R.M., and Murthy, G.S., 2004, *J. Nucl. Radiochem. Sci.*, 5 (2), 33–36.
13. Lujanienė, G., Mažeika, K., Šapolaitė, J., Amulevičius, A., and Motiejūnas, S., 2006, *Lith. J. Phys.*, 46, 375–382.
14. Kearl, P., 2004, *Analysis of Sorption Coefficient (Kd) Values-Supplemental Report for the Tank Farm Facility Preliminary Assessment*, Portage Project No.: 2121.00, Portage Inc.-Idaho.
15. Yang, M.Y., Tian, J.L., and Liu, P.L., 2006, *Soil Tillage Res.*, 87 (2), 186–193.
16. Galunin, E., Chain, P., Alba, M.D., and Vidal, M., 2007, *Sorption-Desorption of Radionuclides and Analogues in Clays Suitable for Barrier*, 3rd Clays in Natural and Engineered Barriers for Radioactive Waste Confinement, Lille-France, 329–330
17. Ding, M., Reimus, P.W., Lukens, W., Chipera, S., and Scism, C., 2006, *Sorption Characteristics of Radionuclides on Clay in Yucca Mountain Alluvium*, Proc. The 11th Int. High Level Radioactive Waste Manag., Conf., IHLRWM, Las Vegas, NV, April 30th–May 4th, 2006, 89–96
18. Mirkhani, R., Roozitalab, M.H., Teimouri, S., and Khaleghpanah, N., 2010, *Soil Sorption of Cesium on Calcareous Soils in Iran*, Proc. 19th World Congress of Soil Science, 1-6 August 2010, Brisbane-Australia; 112–115.
19. Lyklema, J., 2009, *Chem. Phys. Lett.*, 467 (4-6), 217–222.
20. Hakem, N., Al Mahamid, I., Apps, J., and Moridis, G., 2000, *J. Radioanal. Nucl. Chem.*, 246 (2), 275–278.
21. Yildiz, B., Erten, H.N., and Kiş, M., 2011, *J. Radioanal. Nucl. Chem.*, 288 (2), 475–483.
22. Uğur, F.A., and Sahan, H., 2012, *Ekoloji*, 21 (82), 34–40.