Effect of metal ions in groundwater to radiocesium sorption into bentonite mineral from Tasikmalaya

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Abstract. Karawang and Sumedang areas were two of the preferred sites for radioactive waste disposal facilities in the future, and the effect of coexistence ions in their groundwater to radiocesium sorption in bentonite sample has been studied. Bentonite material is placed in the surrounding of disposal facility and usually is used as an engineered barrier to prevent the migration of radiocesium from the facility to the environment by sorption mechanism. The concentration of cation in groundwater such as K+, Na+, Ca2+ and Mg2+ have been obtained from the field work and could many folds higher when compared with the assumed radiocesium concentration releases to the environment. The existed cations in groundwater were predicted to be able affected to the radiocesium sorption into the bentonite sample. Coefficient of distribution (Kd) was used as the indicator of radiocesium sorption into bentonite sample. The result showed that increased in cation concentration in groundwater reduced the Kd value of radiocesium into bentonite samples up to 21 % compared with no cation exists condition in groundwater.

Keywords: radwaste disposal, 137Cs, bentonite, sorption, metal ion.

1. Introduction
One activity on the radioactive waste management is determination of location for radioactive waste disposal facility. Based the previous study [1], Karawang and Sumedang areas were selected as the preferred site for radioactive waste disposal facilities in the future, and later the site character should be investigated in detail such as their geochemical characteristic. Radioactive waste disposal activity is one of the activities on the radioactive waste management. Radioactive waste with radioactive material content should be managed properly and to be processed or immobilized with a cementation method becomes the waste package. Waste packages are then stored safely at the interim storage facility, before being sent to the disposal facility. A final disposal facility is usually equipped with a barrier-lined system, call as the multi-barrier system [2]. One of barrier in the facility as engineered barrier is made from bentonite material.

On the disposal facility, the waste package becomes an interaction target of water or groundwater. Intense contacts with water caused degradation of waste package. As the result of a direct contact between waste matrixes with water causes the soluble radionuclide (such as radiocesium) in a waste package releases with water media through engineered barrier to environment. Released radionuclide with water flow as long the migration pathway in the engineered barrier will cause direct contact with bentonite as one of the engineered barriers, and radiocesium sorption in the barrier/bentonite media could occur. Radiocesium sorption into the solid phase (bentonite) is also highly influenced by the condition of the existing groundwater chemistry in the location which is also affected by the condition
of mineral soil or rocks nearby. The sorption reaction of radiocesium to solid phase in the groundwater system is as a controlling of radiocesium concentrations distribution to the environment [3]. The chemical elements in groundwater such as the major cations (K⁺, Na⁺, Ca²⁺, and Mg²⁺) of groundwater later can act as the competitor ion to the radiocesium sorption into bentonite. Due to the preferred site of disposal facility was planned is at Karawang and Sumedang areas, the data of major cation concentration in groundwater from both sites needs to be analyzed to predict the effect of coexistence ions to the radiocesium sorption into bentonite samples. Major cations in groundwater usually have concentration several times higher than the estimated concentration of radiocesium released into the environment, and it will be predicted to give a greatly influence to the radiocesium sorption into bentonite. As the indicator of radiocesium sorption into bentonite samples, the distribution coefficient has been used.

Radiocesium such as ¹³⁷Cs has long half-live (~30 yr), has chemical properties similar to K⁺ ions are easily assimilated by plants and organism at the aquatic and terrestrial system, mobile on the natural waters system, effectively enter to the food chain system [4]. And also geological availability of Cs⁺ ion in the soil, sediment or in surface water depends on the sorption capacity of solid phase contact —such as bentonite— with radiocesium [5]. Objective of the experiment is to obtain the major cations concentration in the groundwater from Karawang and Sumedang sites and their effects to the sorption of radiocesium into bentonite sample.

2. Methodology

2.1. Materials

Groundwater sample was collected from the residence’s well in the nearby sites (in Karawang and Sumedang), and bentonite sample was taken from Cidadap-Tasikmalaya with composition as listed at Table 1. Non-active solution of CsCl with concentration of 10⁻⁸ M was prepared, and some NaCl, KCl, MgCl₂ and CaCl₂ solutions from Merck KGaA with concentrations of 10⁻⁸, 10⁻⁶ and 10⁻⁴ M were also prepared to be used on the study of the effect of coexistence ions on groundwater to radiocesium sorption into bentonite sample. The ¹³⁷Cs radioactive solution was obtained from Eckert & Ziegler Isotope Production with sp.activity 3.7 MBq/5 mL was used as a tracer.

| Table 1. The composition of bentonite from Tasikmalaya [6] |
|-----------------------------------------------|
| Sample properties | Weight % of sample |
| SiO₂             | 57.22            |
| Al₂O₃            | 29.83            |
| Fe₂O₃            | 0.33             |
| Na₂O             | 0.014            |
| K₂O              | 0.53             |
| CaO              | 0.12             |
| MgO              | < 0.001          |
| MnO              | 0.002            |
| TiO₂             | 0.49             |
| Others           | ~ 11.463         |

2.2. Equipment’s

Portable water checker, geological compass, global positioning system/GPS, roller mixer, centrifuge, multichannel analyzer/MCA unit and glass equipment’s were used in the laboratory. Determination of cations existed in groundwater was done directly by using portable water checker after the well water was settled and cleaned up from the dirty materials by filtering, see Figure 1.
2.3. Sorption procedure
Sorption experiments were performed in a 20 mL PE vials at room temperature. Solid-liquid ratio was setting at 10⁻² g/mL, and batch method was applied for the experiments. The vial containing 10⁻⁸ M CsCl, bentonite samples and cations (K⁺, Na⁺, Ca²⁺, and Mg²⁺) with the variation of cation concentrations (10⁻⁸, 10⁻⁶, 10⁻⁴ M) as well as a ¹³⁷Cs tracer was contacted by using a geological roller apparatus, then separated to the solid and liquid phases by centrifuge equipment (10 min, 2500 rpm). Gamma activity of liquid phase then measures with MCA unit completed with HPGe crystal detector 20% efficiency and analysis software of GENII. Contact times of samples and ¹³⁷Cs were 14 days to reach the equilibrium condition of sorption of ¹³⁷Cs in bentonite sample [7,8].

3. Results and Discussions
The results of major cations measurement on groundwater at the investigated sites (Karawang and Sumedang sites) were shown in Table 2. Seen from Table 2, Na⁺, K⁺, and Mg²⁺ ions as the dominance cations in groundwater were taken out from investigated site. The present of these cations is quite high when they were compared to the initial concentration of CsCl, which was given on the solution in this experiment (10⁻⁸ M). It is found that Ca²⁺ ion in the well water was only present in the solution of sample no 7 that come from Sumedang site. This analysed result could be explained when we referred to the geological map of the Sumedang region of Ujung Jaya Sub-distric area as seen in Figure 2. The possibility is that the groundwater in this area was still hard affected by the presence of widespread of limestone (Tpc) layer as seen in Figure 2 [9]. While in other site, in the area with relatively thick of clay-stone formation, the Na⁺, K⁺, and Mg²⁺ cations dominated the groundwater chemistry composition.

The value of coefficient of distribution (Kd) was used as the indicator of radiocesium sorption into bentonite sample, and was defined as the number of radiocesium absorbed per-unit dry weight of solid phase compared with the number of radiocesium remains in solution per-unit volume of liquid phase. And to be formulated as equation (1),

$$Kd = \frac{C_0 - C_t}{C_t} \times \frac{V}{m}$$

where $C_0$ and $C_t$ are initial and final concentration of ¹³⁷Cs in the solution, $V$ is total volume of the solution (mL), $m$ is dry weight of the sample (g) and Kd is coefficient distribution of ¹³⁷Cs.
Table 2. The results of major cation measurement on groundwater at the sites

| No. | Sample | Coordinate                  | NaCl (M)     | KCl (M)  | CaCl2 (M) | MgCl2 (M) |
|-----|--------|-----------------------------|--------------|----------|-----------|-----------|
|     |        | Karawang site               |              |          |           |           |
| 1.  | S: 107°24’26.7” E: 06°26’34.8” | 1.36×10⁻³   | 0.79×10⁻³ | nd        | 0.86×10⁻³ |
| 2.  | S: 107°24’24.1” E: 06°26’43.5” | 0.64×10⁻³   | 0.79×10⁻³ | nd        | 0.43×10⁻³ |
| 3.  | S: 107°24’26.51” E: 06°27’37.8”| 8.17×10⁻³   | 1.33×10⁻³ | nd        | 1.29×10⁻³ |
| 4.  | S: 107°24’28.5” E: 06°27’32.7” | 3.45×10⁻³   | 1.06×10⁻³ | nd        | 0.65×10⁻³ |
| 5.  | S: 107°24’34.1” E: 06°27’39.8”| 8.17×10⁻³   | 1.59×10⁻³ | nd        | 0.43×10⁻³ |
| 6.  | S: 107°24’36.4” E: 06°28’28.5” | 18.17×10⁻³  | 0.53×10⁻³ | nd        | 0.86×10⁻³ |
|     |        | Sumedang site               |              |          |           |           |
| 7.  | S: 108°07’03.0” E: 06°44’21.3”| 2.72×10⁻³   | 1.06×10⁻³ | 0.77×10⁻³ | 1.29×10⁻³ |
| 8.  | S: 108°08’14.4” E: 06°45’06.1”| 13.62×10⁻³  | 1.06×10⁻³ | nd        | 0.65×10⁻³ |
| 9.  | S: 108°07’25.7” E: 06°44’05.2”| 4.54×10⁻³   | 1.06×10⁻³ | nd        | 0.43×10⁻³ |
| 10. | S: 108°07’19.9” E: 06°43’59.3”| 6.36×10⁻³   | 1.06×10⁻³ | nd        | 0.65×10⁻³ |

nd: not detected

Figure 2. Geological map of Ujung Jaya Sub-district area [9]
The effects of cation in groundwater to radiocesium sorption in the solid phase (bentonite samples) are shown in Figure 3. The number of radiocesium absorbed in the solid phase drastically decreased when the main cations concentration in groundwater increased. In general, there has been obtained an order of competition among main cations present in groundwater affected to the sorption ability of bentonite to radiocesium as Na\(^+\) < K\(^+\) < Ca\(^{2+}\)~ Mg\(^{2+}\).

![Figure 3](image)

**Figure 3.** The effect of cations existing in the groundwater to the radiocesium sorption into bentonite samples

The strong effect of competition of major cations to radiocesium sorption indicated that the complexity electrostatics bond occurred on the outer sphere of solid phase samples [9] affected the sorption ability of bentonite samples. Divalent cations such as Ca\(^{2+}\) and Mg\(^{2+}\) gave larger competition effect compared with the monovalent cations such as Na\(^+\) and K\(^+\). The small monovalent cations such as Na\(^+\) provided the weakest competition compared to all major cations that were given in the experiment. Larger cations such as Cs\(^+\) and K\(^+\) are more polarized and more easily distorted to the hydration surface compared with the small cations such as Na\(^+\) [11,12], and the small cations will be closer to the surface of solid phase, easier and more strong interaction with the surface site of solid phase. The small cations formed a weak bond on the surface of solid phase when they interacted with bentonite sample, in the presence of more concentrated Ca and Mg ions concentration in solution has caused it to be difficult for Cs to interact with the surface of bentonite. From the data of major cation concentrations in groundwater with such condition as shown in Table 2, the Kd values of \(^{137}\)Cs in bentonite samples were predicted reduced the sorption of Cs ion into bentonite sample, and the Kd values of \(^{137}\)Cs into bentonite will be decreased and the ranged becomes 1300 to 2700 mL/g or decreased to 21% of Kd value when no cation exists condition in groundwater.

4. Conclusion

Based on the direct measurement from the investigated sites, the concentration of Na\(^+\), K\(^+\), and Mg\(^{2+}\) ions were dominantly in the groundwater about 10\(^{-2}\) to 10\(^{-3}\) M, due to the claystone formation present at these area. However, for sample number 7, the groundwater was predicted to be affected with limestone formation, and the prediction of Kd values will be in deceased with range in 1300 to 2700 mL/g. To prepare a disposal facility in the both areas is recommended that the facility shall be avoid the area with high concentration of Ca\(^{2+}\) because it can be reduced the Kd value of radiocesium into bentonite samples.
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