Applied Geochemistry xxx (2017) 1–6

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Selective and irreversible adsorption mechanism of cesium on illite

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ARTICLE INFO

Article history:
Received 1 December 2016
Received in revised form
11 May 2017
Accepted 12 May 2017
Available online xxx

Keywords:
Cesium
Clay minerals
Illite
FES
Irreversible adsorption
Hydrated-ion size
Hydration energy
Charge density

ABSTRACT

Most of radioactive nuclides emitted into the air eventually fall to the ground, after then 80% of cesium fallout is fixed in soil and the other 20% is mobile as exchangeable fraction. It is most difficult to remove cesium from the soil after contamination because of the strong adsorption onto clay mineral especially illite, compared to other radionuclides and clay minerals. All the experiments were conducted using the 2:1 lattice minerals which as illite, hydrobiotite (vermiculite + biotite) and montmorillonite with 133-cesium chloride. In this study, illite had 0.25 mol/kg of frayed edge site (FES). Furthermore using the TEM-EDS confirmed selective adsorption of cesium. The selective and irreversible adsorption mechanism of cesium on illite was summarized by hydrated ion size, charge density and hydration energy. And the mechanism was proved by using barium. When cesium coexisted with barium, the adsorption efficiency to FES decreases. And when cesium adsorbed on FES was desorbed using various cations, the desorption rate was in order of ammonium > potassium > barium > calcium > magnesium, which follows the hydration energy.

1. Introduction

The importance of nuclear power plants for power generation has steadily increased, which has led to increased leaking of radionuclides in a variety of ways. Among radionuclides, cesium (Cs) is especially troublesome because it has a relatively long half-life of 30 years as well as high solubility and mobility in the water system. In soil environments, Cs cannot be removed from the soil because of its strong affinity; therefore, Cs must be handled with extreme care (Cornell, 1993). Radioactive Cs can be leaked by two different ways: falling out into soil environments after atmospheric diffusion and flowing out into the water system directly. After radioactive Cs is emitted from nuclear power plants, it diffuses into the atmosphere and falls down as particles or in raindrops into the soil. Approximately 80% of radioactive Cs fallout interacts with soil strongly and loses its mobility (Miyazaki, 2012); however, the remaining ~20% moves into the groundwater. After the accident at the Fukushima Daiichi nuclear power plant, Cs was accumulated only at the top soil (0–6 cm) because of its strong affinity with soil (Ohno et al., 2012). It is well known that Cs is adsorbed reversibly and/or irreversibly onto the clay minerals found in soil, and it is usually adsorbed on the surface of minerals via reversible cation exchange (de Koning and Comans, 2004; Dumat et al., 2000). Cs is adsorbed onto most clay minerals reversibly, but it is fixed irreversibly onto illite (Bergaoui et al., 2005; Kim and Kirkpatrick, 1997).

Generally, clay minerals are classified as phyllosilicate minerals. With a basic structural unit containing a silicon tetrahedron and aluminum octahedron, the structure forms tetrahedral and octahedral sheets that are combined with each other. Depending on how many of these sheets are combined to form the lattice and how they combine, clay minerals are categorized as 1:1 lattice or 2:1 lattice clay minerals. Furthermore, there are extra oxygen atoms from the silicon tetrahedral sheets between the lattice when two tetrahedral sheets and one octahedral sheet are combined; these atoms provide repulsive forces, forming an interlayer between the lattice (Brigatti et al., 2006; Sposito et al., 1999). Illite is a 2:1 lattice minerals that possesses potassium (K) that is covalently bonded with oxygen atoms on the interlayer of the lattice; therefore, the interlayer cannot swell, even in the hydrated state. Illite is generated by the weathering of biotite, where the interlayer is fully occupied by K (Jackson, 1962). When the biotite loses K at its edge site during the weathering process, the weathered edge site is referred to as the FES. It is widely accepted that the FES is the major cause for the irreversible adsorption of Cs onto illite, but this mechanism is not currently well understood (Benedicto et al., 2014;

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http://dx.doi.org/10.1016/j.apgeochem.2017.05.019
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Please cite this article in press as: Lee, J., et al., Selective and irreversible adsorption mechanism of cesium on illite, Applied Geochemistry (2017), http://dx.doi.org/10.1016/j.apgeochem.2017.05.019

Okumura et al., 2013). Even though cation exchange is widely accepted to explain the mechanism on irreversible fixation of Cs onto illite, it cannot explain the selective adsorption of Cs in the presence of Ca. Ion size has be used to explain the mechanism, but selective adsorption of Cs in the presence of K could not be well explained. Therefore, the purpose of this study was to investigate the reasonable adsorption mechanisms between Cs and clay minerals to remediate soil that has been contaminated by radio Cs. We also provided information about the selectivity and irreversible adsorption of Cs onto clay minerals, especially onto the FES of illite.

2. Materials and methods

2.1. Materials

All of the experiments were conducted using illite ($K_{0.8-0.9}(Al,Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2$) produced by the *Yong-koong illite* Company, Korea. This mineral was constituted of Al_2O_3, SiO_2, K_2O, Fe_2O_3, MgO, CaO, and Na_2O with some minor components such as Cr (2.8 mg/kg), Cu (8.9 mg/kg), Mn (312.7 mg/kg), and Zn (40.9 mg/kg). The surface area and cation exchange capacity (CEC) of illite were 13 m^2/g and 141.8 meq/kg, respectively. The surface area was analyzed using a methylene blue spot test method (Yukselen-Aksoy and Kaya, 2008). The XRD spectra confirm that the mineral is illite with a d-spacing of 9.3 Å, which corresponds to the 001 plane. It also contains quartz with a d-spacing of 3.34 Å. Hydrobiotite (biotite + vermiculite) and montmorillonite (Sigma Aldrich), which is a 2:1 lattice expanding mineral, were used for comparison. Cs (^{133}Cs) was used for sorption experiments by dissolving CsCl (Sigma Aldrich) in D.I. water; this can be done because the chemical properties of radio Cs and non-radio Cs are the same.

2.2. Methods

2.2.1. XRD analysis

To confirm the effect of the hydrated state on the swelling of the clay mineral's lattice, multi-purpose high-performance X-ray diffractometer (PANalytical, Netherlands) analysis was used from 5 to 50°. Clay minerals were prepared as both dry and wet samples. In particular, wet sample was stirred with D.I. water and filtered, after filtering, the wet sample was analyzed by XRD. The resultant samples were continuously scanned at a speed of 0.02° per 3 s with 40 kV and 30 mA. To calculate the d-spacing (Å), or interlayer distance, of the samples, Bragg's law was used:

$$d\ (\text{Å}) = \frac{n}{2}\cdot\frac{\lambda}{\sin\theta} \qquad (1)$$

here, λ is the wavelength of copper (1.5406 Å), θ is the scattering angle (radians), and n is a constant value.

2.2.2. Radio-cesium interception potential (RIP)

Investigating the RIP provides an analytical method to identify the amount of frayed edge sites (FES); this technique analyzes the irreversible adsorption in the presence of Ca and K (Nakao et al., 2009). 0.1 g of minerals that were put into the cellulose tubular membrane (Membrane Filtration Products, INC., USA) with a MWCO of 5000 Da containing 5 ml of a 0.1 M $CaCl_2$ and 0.5 mM KCl solution. The membrane was then sealed using tubing closures. Then, the bags were put into 250 ml bottles with 200 ml of a 0.1 M $CaCl_2$ and 0.5 mM KCl solution. The solution was replaced periodically with a fresh solution (200 ml of a 0.1 M $CaCl_2$ and 0.5 mM KCl solution) before shaking to maintain equilibration. After 5 days, the dialysis bags were moved to other 250 ml bottles with 200 ml of a 0.1 M $CaCl_2$, 0.5 mM KCl, and CsCl solution, and the samples were shaken for 2 h twice a day. The K and Cs concentrations of every replaced solution were analyzed by ICP-MS (Agilent Technologies).

$$\text{RIP}\left(\text{mol}\ Kg^{-1}\right) = K_d^{Cs}\cdot[\text{mK}] \qquad (2)$$

The value of K_d (l/kg) indicates the solid/liquid distribution coefficient of cesium and mK (mol/l) is the concentration of K in the solution (Absalom et al., 1999; Nakao et al., 2008).

2.2.3. TEM image and EDS analysis

The existence of the FES and structure of the interlayer in illite were analyzed by field emission transmission electron microscope (FE-TEM) measurements (JEOL, USA) at the Korea Basic Science Institute, Korea. To observe the FES visually, all of the samples were weathered with a 0.1 M of $CaCl_2$ solution for a day and dried at 80 °C. After then the sample was mixed with epoxy resin and hardened to observe the cross section of particles (Fuller et al., 2015). To confirm the selectivity and adsorption of cesium on illite, EDS mapping was used. Illite was also weathered using a 0.1 M $CaCl_2$ and 0.5 mM KCl solution and then shaken with a 0.1 M CsCl solution to adsorb Cs onto the illite. In this analysis, Ca^{2+} blocked the planer site where Cs can be adsorbed, and Cs was adsorbed only onto FES (Zachara et al., 2002).

2.2.4. Adsorption mechanism of Cs

To investigate the selective adsorption of Cs on the FES and the extraction of Cs adsorbed on the FES, simple batch tests were conducted. A mass of 1 g of illite was shaken with 20 ml of 0.1 M $CaCl_2$ solution and 0.5 mM CsCl in a centrifuge tube for one day (Rajec and Shaw, 1994). Another test was carried out by shaking in a 0.1 M $BaCl_2$ solution and 0.1 mM CsCl for comparison. Exactly same test was executed using a 0.5 mM CsCl solution instead of 0.1 mM CsCl. The mixtures were then centrifuged at 6000 rpm for 20 min to separate soil from liquid. The supernatant was analyzed to determine the concentration of Cs using ICP-MS and the remaining soil was shaken with 20 ml of a variety of cation chloride solutions (e.g., calcium, barium, ammonium, and potassium). In the solution, the concentration of Cs was measured using ICP-MS, then the desorption efficiency was calculated. The charge density was calculated as follows

$$\textit{Charge density} = \frac{\textit{Total charge}}{\textit{Total volume}} = \frac{\textit{Electric charge}}{\frac{4}{3}\pi R^3} \qquad (3)$$

3. Results and discussion

3.1. Adsorption mechanisms

3.1.1. Swelling of clay minerals

XRD analysis showed that the montmorillonite used in this study had a d-spacing of 1.33 nm in the dried state; however, this was shifted and broadened to 1.96 nm in the wet state. This indicated that the interlayer spacing expanded and that the larger interlayer does not have any limitations in terms of the size for the sorption and desorption of cations. Alternatively, the d-spacing of illite was 1.00 nm; this was not changed even in the wet state, which indicates that illite was not swelled because of K in the interlayer (Nakao et al., 2008). However, the wet status ages the edge site of the interlayer, which might form the frayed edge site.

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