Research paper

Experimental and modeling investigations of cesium and strontium adsorption onto clay of radioactive waste disposal

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ABSTRACT

Migration of strontium and cesium radionuclide in geohydraulic system is important for safety disposal of radio-active waste containing of these two radionuclides to prevent the migration of radionuclides from the disposal site to provide protection for man and his environment. Geochemical analysis was carried out to investigate the mineral composition of the clay taken from the site to predict the historical and environmental geology of Inshas disposal site. Batch experiments were carried out as a function of pH, solute concentration and under three different temperatures (298°, 313° and 333° K). Sorption capacity of Cs^+ and Sr^{2+} onto clay sample was increased when initial metal ions concentration was increased. Increasing the temperature led to decrease in the sorption of Cs^+ and Sr^{2+} ions. Several kinetic models were used to fit the experimental data and to examine the controlling mechanisms of the sorption processes. The kinetic study showed that sorption followed pseudo-second-order model with a good correlation coefficient ($R^2 = 0.999$) for both studied ions. The experimental sorption data were fitted using Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models. Results showed that the adsorption process was exothermic and favored at low temperature.

1. Introduction

The generated radioactive waste can be divided into liquid, solid and gaseous wastes. Aqueous liquid radioactive waste was generated during research reactor operations and in other operations involving the application of radioisotopes (e.g. medicine, research and education). The type of liquid waste produced depends upon the particular operation being conducted and can vary extensively in both chemical and radio-nuclides content. In a radioactive waste repository, the main protective function provided by natural geological barrier itself, selected in such a way that its impermeability and stability characteristics should prevent contamination to reach to biosphere.

On the other hand, due to the negative evolution of the radioactive waste repository over hundreds or thousands of years, the natural or engineered barriers are deteriorated. As a result many scenarios, which could lead to leak of the radioactive such as intrusion of rain or ground water, leaching of waste containers, etc. are suggested (Alves et al., 2015; Abdel Rahman et al., 2009; Abdel Rahman et al., 2007; Abdel Rahman and Zaki, 2011).

In this regard, a primary concern is the contamination of groundwater that is considered a very important vector of pollution. Any accidental release of aqueous waste solutions containing both cesium and strontium may pose an environmental health risk to the soil/groundwater system (Tianlik et al., 2016). The fate and transport of individual contaminants into an aqueous phase is largely controlled by the degree of contaminant interaction with the surrounding soil materials. Distribution coefficient (K_d) is a parameter was used to present the ratio of ions adsorbed into solid to ions in liquid phase (Kamel and Navratil, 2002) this parameter can be influenced by concentration of the stable elements in soil/aqueous phase.

Clay minerals are important group of minerals because they are among the most common products of chemical weathering of rocks. Clay minerals are important sorbents for radionuclides due to their negative charge, large specific surface area and surface hydroxyl groups. Sorption on clay minerals strongly affects the fate and mobility of radioactive contaminants in the geosphere (Seung and Diwakar, 2012; Zaki et al., 2011). Different clay minerals show different sorption capacities for radionuclides (Deepthi Rani and Sasidhar, 2011). Their high specific surface area allows strong physical and chemical interactions with fluids and dissolved species which are subjected to electrostatic repulsion, sorption or specific cation exchange reactions. These interactions are responsive for the retention in the barrier of leachate components

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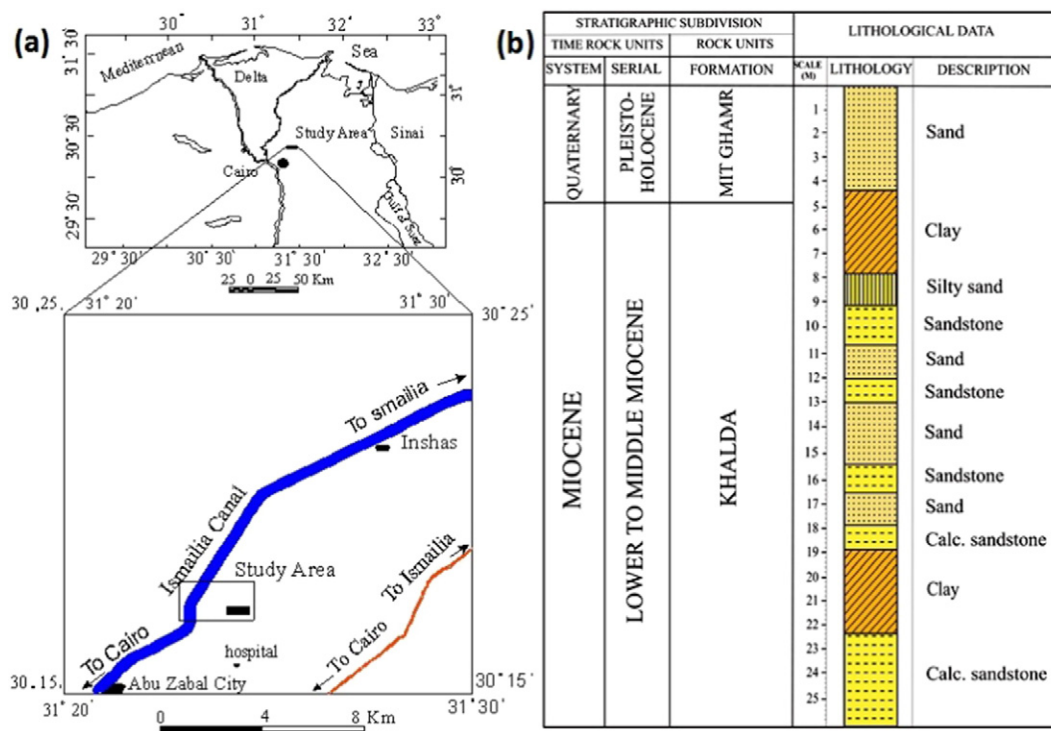(A.-A.M. Abdel-Karim).

Fig. 1. a. Location map and b. Litho-stratigraphic units of borehole B2 of the study area.

such as dangerous metallic cations (Churchman et al., 2006; Sánchez-Jiménez et al., 2012).

Inshas area (Fig. 1a) which is bounded by longitudes 31° 20′ & 31° 40′ E and latitudes 30° 10′ & 30° 25′ N is considered as an important region for the Egyptian Atomic Energy Authority (EAEA). An area of approximately 1 km × 1 km dimensions had been chosen to be exposed to detailed geologic studies. The main purposes of such studies are standing on the lithological succession in the subsurface. The litho-stratigraphy of studied borehole B2 shows a succession of quaternary and tertiary sediments which are arranged from bottom to top (Fig. 1b) into: a) quaternary sediments which is represented by sands, and b) tertiary sediments which are composed of Miocene clays, silty sand, sand, sandstone and calcareous sandstone (Zaki, 2000).

The aim of this work is to study the geochemical and chemical feasibility of the clay as a sorptive barrier towards cesium and strontium ions of Inshas radioactive disposal site.

2. Materials and methods

2.1. Chemicals and reagents

The chemicals and reagents used for cesium and strontium ions were supplied as cesium chloride and strontium chloride, and obtained from Sigma–Aldrich Company. All solutions were prepared using distilled, deionized water (DDW) with a resistivity of 18 MΩ/cm. Stock solutions of the test reagents were prepared by dissolving CsCl and $SrCl_2 \cdot 6H_2O$ in DDW. Clay soil samples were obtained from Inshas disposal site (Fig. 1a).

2.2. Characterization of clay

The clay samples were dried, crushed and sieved through the 38-μm sieve. Clay samples were characterized using X-ray diffractometer; Philips X-ray diffraction equipment model PW 1710 with monochromator, Cu-radiation (λ = 1.542 Å). In order to separate the clay particles

(<2 μm) from the bulk soil sample, the bulk sample was put in a DDW beaker for 7 h, then the supernate was poured in another beaker with 3 glass slides on the bottom and kept for about 24 h. To identify the exact clay minerals in the sample, the above mentioned slides were separately treated. The first slide was kept without any treatment (air dried), whereas the second was heated to 823 K for 2 h and the third was exposed to glycerol vapor in a desiccator for 2 h, then the subsamples were measured by the diffractometer.

Scanning electron microscopy (Philips, XL 30), Fourier transform infrared spectroscopy (BOMEM FTIR, MB-Series) were used to test the function groups and surface formology of the clay sample, respectively. The average particles of the clay samples were ranged from 10 to 35 μm on the basis of SEM results. Moreover, this average attain about 0.001–0.003 mm by using high-magnified polarizing microscope method for comparison. The elemental composition of the clay was measured using an XRF-1800 SHIMADZU sequential XRF spectrometer with a rhodium tube and a 2.5 kW generator. The detection limit was about 0.01 wt.% and analytical precision (relative standard deviation) was $<1\%$ for major elements.

2.3. Batch sorption/desorption studies

A series of batch sorption tests were conducted using clay at pH ranged from 2 to 12. The pH of solutions was adjusted using (0.1 M) of NaOH and HCl. A weighed amount (0.1 g) of the sorbent was introduced into reagent bottles (each containing 10 ml of cesium or strontium ions at 100, 500 or 1000 mg/l concentration). Bottles were shaken at 298°K using a mechanical shaker for 24 h to attain equilibrium. After separating the supernatant liquid by centrifugation at 6000 rpm for 30 min cesium and strontium ions concentration in the supernatant was determined using atomic absorption spectrophotometer (AAS; Buck Scientific, VGP-210). The desorption experiments were conducted at 298°K , where 0.1 g of the loaded clay with Cs^+ or Sr^{2+} were shaken with 10 ml of 0.5 M HCl and centrifuged at 6000 rpm for 30 min and checked at different times using AAS. In all adsorption and