

Study of Cs sorption on illite

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Radionuclides released from the near-field of a radioactive waste repository will undergo sorption reactions with the minerals in the host rock. The sorption on clay minerals such as smectites, illites and kaolinites may be of particular importance for many of the considered rock types. Performance assessment studies for future nuclear waste disposal requires predictions on sorption properties of the host rock for a wide range of physico-chemical conditions. Such a goal can only be achieved by developing first sorption model that can describe and predict the sorption on pure mineral systems. The aim of the work presented here was to investigate the sorption of Cs(I) on illite from a mechanistic view point. This work is a part of a wider programme which already successfully allows the development of a near-mechanistic understanding and modelling of the sorption on montmorillonite (1,2).

Conditioning and characterization of the sorbent

A natural illite (illite du Puy from France) was initially purified and conditioned to the homo-ionic Na-form. The conditioned Na-illite was then characterized in terms of mineralogy, chemical inventories and surface properties. The accurate mineralogical composition was analysed by means of XRD and FTIR and the structural formula determined by EDS analyses (SEM/TEM) and bulk chemistry. The conditioned Na-illite is composed of 93% very well-crystallized pure illite associated with 7% kaolinite. The illite is highly substituted in Fe and Mg in the octahedral site. Iron and total extraction demonstrates that no other secondary phase is present within the conditioned Na-illite.

The Na-CEC was evaluated to be 12.8 meq/100 g at neutral pH and strongly decreases with pH. The N₂-BET surface area was measured yielding to a value of 125 m²/g.

Finally, the aqueous cations which are released at low and high pH due to the dissolution of illite can sorb competitively with the radionuclides on the surface sites and influence sorption measurements.

Consequently, we investigated the evolution of solution composition in equilibrium with Na-illite as function of pH, time, solid/liquid ratio and ionic strength.

Cs sorption measurements

The sorption data were measured in suspensions of Na-illite in NaClO₄ background electrolyte (0.01, 0.1 or 1 M). Batch experiments were conducted in an inert atmosphere (CO₂ and O₂ ~5 ppm) using ¹³⁴Cs radio-tracer. Short and long-term kinetics at different Cs concentration, sorption edge at Cs trace concentration and different ionic strength, and isotherm data were determined.

The kinetics of Cs sorption depends strongly on the Cs equilibrium aqueous concentration. Sorption at very low concentration (~10⁻⁹ M) is much slower than at higher concentration. The time to reach constant sorption differs from 1 h (high concentration) to 5 days (low concentration).

The Cs sorption is strongly dependent on the NaClO₄ concentration, but only varies slightly with pH, except at low ionic strength (Fig. 1).

Finally, we measured the Cs sorption isotherm at neutral pH, 0.1 M NaClO₄, for a wide range of Cs equilibrium concentration. The whole isotherm is clearly non-linear which is characteristic of a sorption occurring on several site-types (Fig. 2).

Cs sorption 'near-mechanistic' modelling

In principle, sorption measurements combined with physico-chemical characterization data can be interpreted in terms of 'near-mechanistic' sorption models (2). Experimental results of Cs sorption edges reveal a pronounced ionic strength dependency and a slight variation of sorption with pH. This behaviour suggests a cation-exchange mechanism. Cs sorption on Na-illite was hence modelled by assuming sorption by cation exchange. For this purpose, we used the MINSORB geochemical code, which is basically the MINEQL code in which the two sorption mechanisms, cation-exchange and surface

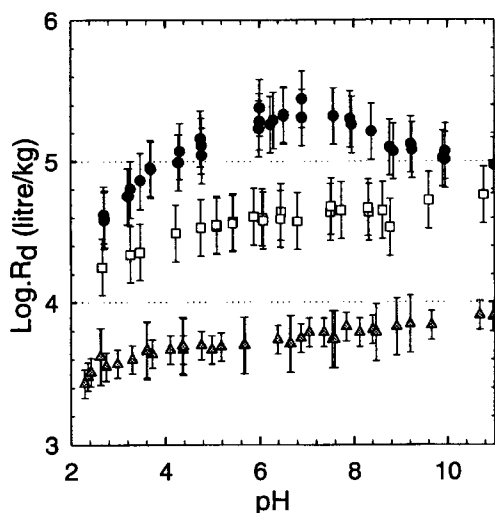


FIG. 1. Cs sorption pH edges at Cs trace concentration on Na-illite at three different NaClO_4 concentration, 0.01 M (black circles), 0.1 M (open squares) and 1 M (grey triangles).

complexation were incorporated (2,3). In a first step, the number of site-types, site-type capacities and selectivity coefficients for the Cs-Na exchange reactions were derived by modelling the isotherm data. We demonstrated that three sites are sufficient to reproduce our whole set of data.

In a second step, we modelled the Cs sorption edges at different ionic strength while accounting for the competing effect of other aqueous cations. In particular, accounting for the competition of protons is of prime importance for understanding the Cs sorption at acid pH.

In conclusion, the study demonstrates that Cs

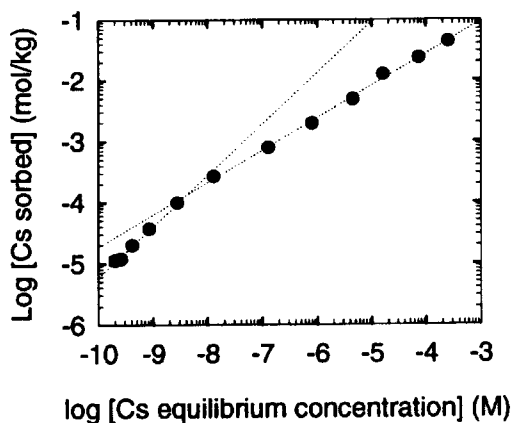


FIG. 2. Cs sorption isotherm on Na-illite at 0.1 M NaClO_4 .

sorption on illite can be successfully and fully modelled with a 3 sites cation exchange model. However, competing cations play a significant role and have to be taken into account for describing the influence of pH, in particular at low ionic strength. A near-mechanistic understanding of Cs sorption on illite has been acquired and will be confronted to other independent set of data.

References

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