

Effect of pore size on ion adsorption properties of nanoporous silica

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Understanding the ion adsorption on mineral surfaces is of importance in predicting the transport and accumulation of toxic elements and resources. Nanoscale pores (referred to as nanopores) are often seen as the etch pits formed by weathering and hydrothermal alteration and in the aggregates of fine clay or iron (hydro)oxide particles. The behavior of ion adsorption is intimately connected to the structure of the electric double layer which spreads to a distance ($<1 \mu\text{m}$) at a mineral/water interface. However, the distance of electric double layer spreading in a nanopore is expected to be limited to its pore size, and the ion adsorption on the nanopore surfaces may change with pore size. In this study, we evaluated the influence of pore size on the surface charge density and the amount of adsorbed ion.

We used two different nanoporous silica powders (CARiACT Q; Fuji Silysia) with pores of 25 nm radius and 1 nm radius. In order to measure the charge density of nanopore surfaces, the acid/base titration experiment was conducted using the silica powder of each pore radius suspended in a 1 mM solution of NaCl. The surfaces of silica in contact with a neutral or alkaline solution usually have negative charges by the protonation-deprotonation of silanol groups ($>\text{Si-OH} \leftrightarrow >\text{Si-O}^- + \text{H}^+$) and the adsorption-desorption of Na^+ ($>\text{Si-OH} + \text{Na}^+ \leftrightarrow >\text{Si-O}^- \cdots \text{Na}^+ + \text{H}^+$). Comparison of surface charge densities of silica with pores of 25 nm radius and those of 1 nm radius reveals that the surfaces of narrower pores are less negatively charged. This finding means that the surface silanol groups on narrower nanopores less desorb H^+ .

In order to evaluate the effect of pore size on the amount of adsorbed ion, the adsorption experiments for K^+ were performed using silica with different pore sizes. Silica powder was added to a 0.1 mM NaCl solution containing 0.006 mM KCl. The pH of the mixture was adjusted to 4.0, 4.5, 5.6, 6.4, 7.3, 8.2, and then stirred for 30 minutes. The small volume of supernatant was collected and filtered by 0.2 μm membrane filter, and then the concentration of K^+ was measured by a liquid chromatography. The amounts of adsorbed K^+ ion for pores of 1 nm radius was up to more than 50% less than those of 25 nm radius, which is consistent with the result of titration experiments that the surfaces of narrower pores have less negative charges. Our results demonstrate the importance of pore size for a better understanding of the ion adsorption properties.

Keywords: Ion adsorption, Surface charge, Electric double layer, Silica, Nanopore