

Competitive sorption and desorption of arsenate and uranium on bentonite and kaolinite

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Sorption and desorption behavior of U(VI) and As(V) was investigated using twelve glass columns packed either with kaolinite and quartz or with bentonite and quartz applying input solutions containing either U(VI) and As(V) separately or equimolar concentrations of uranium and arsenate at pH 3 and 6.

Breakthrough curves of U(VI) and As(V) showed similar patterns in bentonite packed columns for all solutions applied at pH 3. A slight decline in U(VI) and As(V) retardation in kaolinite packed column was seen in the presence of U(VI) and As(V) in the input solutions at pH 3 due to the competitive effect between U(VI) and As(V) species for adsorption sites on kaolinite (Figure 1A).

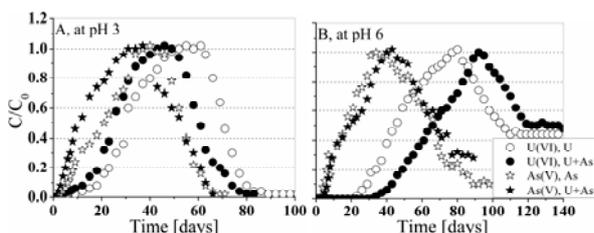


Figure 1: Experimental breakthrough curves of U(VI) and As(V), applying solutions of U(VI) only, As(V) only, U(VI) with As(V) to (A) kaolinite columns at pH 3 (B) bentonite columns at pH 6, [U]= 5×10^{-6} M, [As]= 5×10^{-6} M.

At pH 6, the breakthrough curves of uranium and arsenate were different for all column experiments (Figure 1B). Desorption of U(VI) and As(V) from columns pre-treated with both uranium and arsenate at pH 6 seems to be slower than from those at pH 3. Sorption of U(VI) and As(V) in bentonite packed columns appeared to be irreversible. In contrast, all uranium and arsenate adsorbed to kaolinite packed column was desorbed. The results are explained by two mechanisms: At pH 3, ion exchange was the dominant mechanism. At pH 6, simultaneous ion exchange and surface complexation reactions contributed to the U(VI) and As(V) sorption onto bentonite and kaolinite. This could be mimicked by means of PHREEQC.

Selenite and Selenate Reduction by Siderite: *in situ* and *ex situ* XAS Experiments

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Siderite (FeCO_3) is present in clay rocks and can form in the corrosion layer of steel containers of High-Level nuclear Waste (HLW) in deep geological repositories [1]. Concurrently, ^{79}Se is identified among the largest contributors to the performance assessment associated with HLW since its potential migration is not delayed by sorption onto clay minerals. Selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) anions will interact primarily with the corrosion layers, so understanding the retention of these anions by siderite may improve the performance assessment of HLW.

Sorption experiments were conducted inside an atmosphere-controlled glovebox ($\text{N}_2/\text{H}_2/\text{CO}_2$: 85/5/10). Siderite suspensions (30 g.L^{-1} S) were spiked with selenite or selenate aliquots to obtain total Se concentration of $5 \times$ to 20×10^{-4} M. The concentration of dissolved selenium was monitored vs. time, showing that selenite is completely removed from the supernatant within 10 h whereas only 40 % of selenate was sorbed at the largest sorption time

The Se redox state and molecular environment were probed by X-ray absorption spectroscopy (XAS) *ex-situ* on shock-frozen samples, and *in situ* in a redox-controlling electrochemical cell. *Ex situ* characterizations showed a complete reduction of selenite to amorphous (red) Se(0) within 10 days of reaction time while selenate was only partially reduced. The *in situ* experiment confirmed that selenite full reduction occurred over > 20 h of contact time, demonstrating distinct characteristic times for selenite retention and reduction. These results extend previous studies in which only partial reduction of selenite in presence of siderite was observed [2,3].

DFT-based *ab initio* calculations performed on siderite illustrate the reaction mechanism, with an emphasis on siderite surface reactivity.

- [1] Schlegel *et al.* (2008) *Appl. Geochem.* **23** (9), 2619-2633.
[2] Scheinost & Charlet (2008) *Environ. Sci. Technol.* **42**, 1984-1989. [3] Scheinost *et al.* (2008) *Journal of Contaminant Hydrology* **102**, S1228-245.