Sorption and Desorption of Uranium(VI) on Clay Minerals

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1 Introduction

The retardation and transport of U(VI) and other contaminants are affected by their sorption/desorption reactions at the water-rock interfaces. Among the more common candidates in this regard are clay minerals which have a very high retention capacity due to (i) their large surface area as well as their osmotic swelling capacity and consequently their plasticity and low permeability, and (ii) the property of these minerals to simultaneously create a permanent negative charge within the structure and a variable charge at the particle edge.

Conventional batch sorption experiments were widely performed to investigate the U(VI) sorption onto clay minerals. However, batch techniques have some severe limitations such as breakdown of soil aggregates, solubilization of soil components due to soil sample agitation, and relatively low solid to solution ratios. Therefore, continuous column experiments were considered as an appropriate technique to study the transport of U(VI) in porous media.

The transport of U(VI) in different with clay minerals packed columns war investigated. The major aim was to verify if the phenomena reported in previous batch experiments are true as well with flow through conditions.

2 Column experiments setup

Column experiments were conducted at room temperature (~295 K) using a total of five PTFE columns of 4 cm inner diameter, 20 cm height, with 0.2µm Teflon filters at both ends of the column to hold the porous media in place. A total mass of 4.00 g of dry clay minerals was mixed well with Teflon stones (grain size: 0.29-0.35 mm) and dry packed to an uniform bulk density of 1.6 g/cm3, with effective porosity of 0.3. The selected clay minerals packed in the columns 1 to 5 were IBECO natural bentonite, STx-1b reference montmorillonite, SWy-2 reference montmorillonite, KGa-1b kaolinite, and KGa-2 kaolinite, respectively. All tools used in column experiments (tubes, collecting bottles, sand, columns) were from PTFE to avoid any surface reaction with uranium at the low concentrations of the experiment. Short tubes with small inner diameter were used to connect the column system to minimize the dead volume. The solutions were pumped from bottom to top at flow rate of 80 µl/min over sorption and desorption periods using a high precision peristaltic pump with planetary drive ISMATEC IPC 24 canals (Ismatec SA, Switzerland). In each column experiment, the column was preconditioned with 0.01M NaCl solution for at least 12h., after which a pulse input of reactant solution was introduced into the column until the breakthrough curves were achieved (after ~ 175, 215, 260, 300, 310 pore volume in columns 1 to 5, respectively). After reaching the breakthrough period, the inlet solution was switched back to a U(VI) free, 10mM NaCl solution in order to investigate the desorption. During the first two weeks of both sorption and desorption experiments daily samples from the outlet were collected. After that, three samples per week were taken. The effluents collected were immediately filtered with 0.2 µm cellulose acetate filters (Membrex, Germany) and analyzed for U(VI), and pH until the uranium concentrations were ~1% of their concentration in the initial input solutions. All reactant solutions had U(VI) concentration of 100 µg/L and 0.01 M NaCl, and were adjusted at pH 6.5. The effluent pH of the columns was fairly constant and close to that of the influent. To test whether some loss of U(VI) onto Teflon stones and the experimental apparatus used occurred, one separate control column (column filled only with cleaned Teflon stone) was used. In that case one day was enough to achieve the breakthrough in the blank column indicating negligible U(VI) retardation in the system itself.

3 Mass balance calculations

In order to examine the fate of uranium (VI) in the column experiments, it is important to account for the amount adsorbed and what is passing through the columns. Any U(VI) not accounted for, could be attributed to removal processes. The mass balance both during loading and eluting the columns was calculated using this equation (1):

$$M = \sum \Delta C \cdot v \cdot \Delta t \qquad (1)$$

Where M is the total mass of U(VI), ΔC is the change of U(VI) concentration between inlet and outlet, and v is the flow rate and Δt is the corresponding time interval.

4 Results and discussion

A flow-through column experiments were performed to evaluate uranium transport behavior and investigate U(VI) sorption/desorption on selected clay minerals.

The influence of the type of packed material on the breakthrough of uranium is illustrated in figure1 There is a significantly higher U(VI) retardation in kaolinite packed columns (columns IV, and V) than smectites packed columns (columns I, II, and III); U(VI) breakthrough was reached after 70, 86, 104, 120, 124 days in columns packed with IBECO, STx-1b, SWy-2, KGa-1b, and KGa-2, respectively. This can be explained by the fact that kaolinite contains more exposed aluminol surface site, which have greater activity toward uranium than silanol sites. Furthermore, column packed with high defect kaolinite demonstrated slightly greater U(VI) retardation than column packed with low defect kaolinite. This phenomenon supports our assumption that most of uranium was adsorbed onto the aluminol sites which is more exposed in the poorly crystallized kaolinite than the well crystallized.

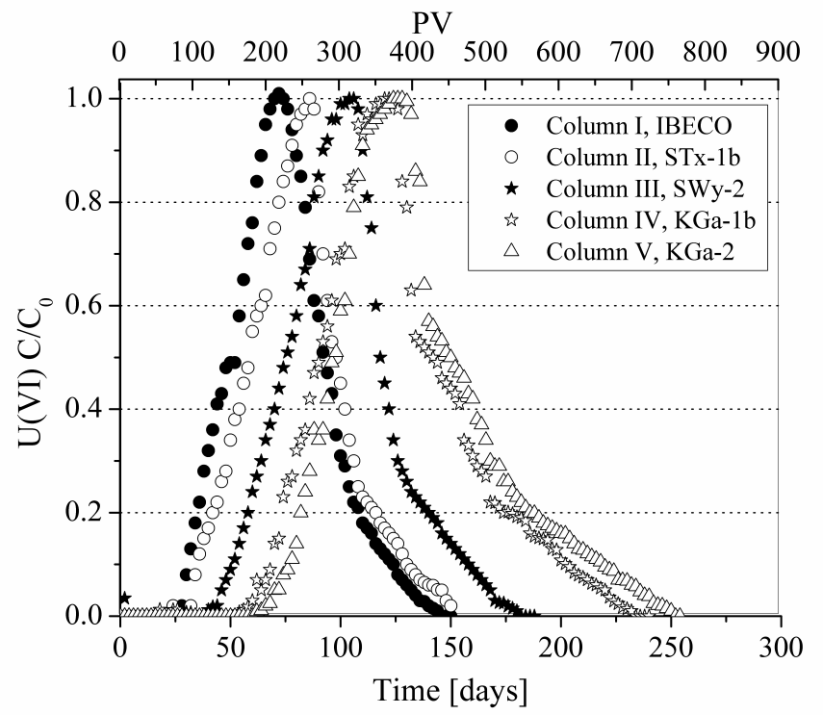

Figure 1.Experimental breakthrough curves (BTCs) of U(VI) flushed into the IBECO bentonite, STx-1b montmorillonite, SWy-2 montmorillonite, KGa1b kaolinite, and KGa-2 kaolinite.[U]=100 µg/L, pH 6.5.

Column experiments can illustrate a phenomenon which is uncovered in the batch experiments; e.g., desorption. In general, columns packed with STx-1b and SWy-2 exhibited irreversible sorption, whereas columns packed with KGa-1b and KGa-2 demonstrated slow desorption, but complete.

The irreversible sorption of U(VI) observed in smectites packed columns can be attributed to high content of iron oxide in the bentonite structure (e.g, 4.3% for SWy-2) comparing to those in the kaolinite structure (e.g., 0.2% for KGa-1b), which has pronounced sorption affinity to uranium (Wazne et

al. 2003). In addition, the presence of the basal plane in (2:1) clay minerals can obviously delay the U(VI) desorption, hence, a slow diffusion of uranium ion from a surface into the interlayer where stable complex might be formed would delay uranium extraction. The mineral composition and the degree of crystallinity can play an important role for governing the sorption and desorption of U(VI).

Quantitative U(VI) recovery rates were obtained from the calculation of mass balance in all columns. U(VI) was totally recovered from kaolinite (although slowly), whereas 53 µg and and 93µg of U(VI) remains in STx-1b and SWy-2 at the end of the experiments, which is an clear indication for irreversible adsorption (Table 1). Incomplete desorption of U(VI) has been reported in some recent works, in both batch experiments (Dong et al. 2005), and in column experiments (Qafoku et al. 2005, Cheng et al. 2007).

On contrary, it is noticeable that the amount of U(VI) desorbed from IBECO was significantly higher than sorbed before. This can be attributed to an amount of uranium released from bentonite structure. This phenomenon was observed in our previous work.

Hence, the U(VI) sorption behavior reported in batch experiments was confirmed in the column experiments, except for bentonite showing a slight release of U(VI) from its structure.

Table 1. Mass balance for the five setups.

	Total U in µg/L	
Columns	**adsorbed**	**desorbed**
IBECO	474	542.1
STx-1b	566	513
SWy-2	724	631
KGa-1b	877	877
KGa-2	939	928

5 References

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