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Towards a consistent geochemical model for prediction of uranium(VI) removal from groundwater by ferrihydrite

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ABSTRACT

Uranium(VI), which is often elevated in granitoidic groundwaters, is known to adsorb strongly to iron (hydr)oxides under certain conditions. This process can be used in water treatment to remove uranium(VI). To develop a consistent geochemical model for uranium(VI) adsorption to ferrihydrite, batch experiments were performed and previous data sets reviewed to optimize a set of surface complexation constants using the three-plane CD-MUSIC model. To consider the effect of dissolved organic matter (DOM) on uranium(VI) speciation, new parameters for the Stockholm Humic Model (SHM) were optimized using previously published data.

The model, which was constrained from available X-ray absorption fine structure (EXAFS) spectroscopy evidence, fitted the data well when the surface sites were divided into low- and high-affinity binding sites. Application of the model concept to other published data sets revealed differences in the reactivity of different ferrihydrites towards uranium(VI). Use of the optimized SHM parameters for uranium(VI)-DOM complexation showed that this process is important for uranium(VI) speciation at low pH. However in neutral to alkaline waters with substantial carbonate present, Ca-U-CO_3 complexes predominate.

The calibrated geochemical model was used to simulate uranium(VI) adsorption to ferrihydrite for a hypothetical groundwater in the presence of several competitive ions. The results showed that uranium(VI) adsorption was strong between pH 5 and 8. Also near the calcite saturation limit, where uranium(VI) adsorption was weakest according to the model, the adsorption percentage was predicted to be > 80 %. Hence uranium(VI) adsorption to ferrihydrite-containing sorbents may be used as a method to bring down uranium(VI) concentrations to acceptable levels in groundwater.

Keywords: uranium, surface complexation, speciation, dissolved organic matter, ferrihydrite, groundwater

1. Introduction

In recent years it has been revealed that many groundwaters in granitoidic environments contain excessive amounts of dissolved uranium. The recommended guideline value for uranium in groundwater is 15 μg/L (WHO, 2004). In Sweden it has been estimated that about 17 % of all private bedrock wells contain higher concentrations of dissolved uranium (Ek et al., 2007). Also many larger waterworks contain excessive uranium concentrations (Falk et al., 2004) and research into technologies for uranium removal is ongoing. One possible technique could be uranium removal by iron-oxide-coated sand, for which the chemical mechanism is surface complexation of uranium(VI) onto the Fe (hydr)oxides ferrihydrite and goethite (Logue et al., 2004). Of these, ferrihydrite may often be more important because of its much larger surface area and content of reactive surface groups.

To evaluate the possible use of iron-oxide-based sorption media for uranium removal, we need to understand the various mechanisms that affect it. Uranium occurs mostly in the oxidation state (VI) and its uncomplexed aquo ion form is the uranyl cation (UO_2^{2+}); however in certain suboxic environments, uranium is partly reduced to uranium(IV) (Davis et al., 2006). Uranyl can both be hydrolyzed and form a large number of strong complexes with carbonate and with calcium (Guillaumont et al., 2003; Dong and Brooks, 2006). In addition however, uranium forms very stable complexes with dissolved organic matter, DOM (Glaus et al., 1997; Saito et al., 2004). In sediment pore waters, the speciation of dissolved uranium may be dominated by DOM complexation, at least at low pH (Jackson et al., 2005). At higher pH (>7) and at elevated CO_2 pressures, common conditions in many groundwaters, recent research employing flow field flow fractionation found that significant U-DOM complexation was not detected, probably because U-carbonate complexes were more stable (Ranville et al., 2007).

Furthermore, uranium(VI) forms strong surface complexes with ferrihydrite and goethite, when pH > 5 (Hsi and Langmuir, 1985; Waite et al., 1994; Payne, 1999). With time, the adsorbed uranium(VI) can be reduced to poorly soluble uranium(IV) species, which further restricts its bioavailability (Neiss et al., 2007). However, at high pH (> 7-8) surface complexation of uranium(VI) is suppressed in the presence of carbonate (Waite et al., 1994; Wazne et al., 2003; Jang et al., 2007).

Studies employing extended X-ray absorption fine structure (EXAFS) spectroscopy have found that uranium(VI) forms a bidentate complex (corner-sharing or edge-sharing) on the surfaces of ferrihydrite and goethite (Waite et al., 1994; Reich et al., 1998; Sherman et al., 2008). According to the EXAFS evidence, at least one additional bidentate complex appears to be formed when CO_3 is present; this is probably a ternary complex consisting of adsorbed UO_2CO_3 where UO_2 is bound to the Fe (hydr)oxide surface group (Reich et al., 1998; Sherman et al., 2008). On the basis of batch experiment results, Sherman et al. (2008) suggested another ternary complex to be stable at low pH, in which CO_3 is bound to the surface group.

To date, most attempts to model uranium(VI) adsorption to ferrihydrite have used the large data set of Payne (1999), which is partly shown in Waite et al. (1994) and Payne et al. (1996), who used these data to calibrate a surface complexation model based on the DLM (Diffuse Layer Model; Dzombak and Morel, 1990). Although the DLM fits for uranium(VI) were found to be excellent, a drawback with using the DLM is its simple structure, which only allows adsorbing ions to be placed in one single electrostatic surface plane (i.e., at the surface of the solid). This makes the model less likely to perform well in environmentally complex systems compared to, for example, the three-plane CD-MUSIC model (Hiemstra and van Riemsdijk, 1996), which considers the characteristic spatial distribution of the charge of a specific adsorbing ion within the two innermost electrostatic planes; this allows the description of surface complexes to be fine-tuned in line with spectroscopic evidence.

The purpose of this paper is to therefore to review existing data on uranium(VI) adsorption to ferrihydrite as well as uranium(VI) complexation to humic substances, to develop a modelling framework for predictions of uranium(VI) removal by ferrihydrite-containing materials from groundwater. In this work, we provided additional new data on uranium(VI) adsorption to ferrihydrite, and we constrained the reactions in a CD-MUSIC surface complexation model from available EXAFS evidence.

2. Methods

2.1. Batch experiments with ferrihydrite

2-line ferrihydrite was synthesized according to the method of Swedlund and Webster (1999) and Schwertmann and Cornell (2003) by bringing a solution containing 36 mM $Fe(NO_3)_3$ and 12 mM $NaNO_3$ to pH 8.0 through dropwise addition of 4 M NaOH. The resulting suspension was aged for 18-22 h at 20^{o}C (Gustafsson, 2003). This procedure has been shown to produce 2-line ferrihydrite (Swedlund and Webster, 1999; Schwertmann and Cornell, 2003).

Before the batch experiments, the ferrihydrite suspensions were back-titrated to pH 4.6 with 0.1 M HNO_3 and vigorously shaken for 15-30 min. Batch experiment suspensions were prepared by mixing an amount of ferrihydrite suspension with stock solutions of $NaNO_3$, water and with $UO_2(NO_3)_2$ salt to obtain solutions with an ionic strength of 0.01 M (as $NaNO_3$) and with a concentration of 10 μM U(VI). Various amounts of acid (as HNO_3) or base (as NaOH) was added to produce a range of pHs. Uranium(VI) adsorption was studied at two different concentrations of ferrihydrite (0.3 and 3 mM as total Fe). In one set of batch experiment suspensions, 2 mM Na_2CO_3 was also included to investigate the role of carbonate on uranium(VI) adsorption.

After 24 h of equilibration in tightly sealed polypropylene bottles on an end-over-end shaker, the samples were centrifuged for 20 min at about 5000 × *g* and filtered using 0.2-μm Acrodisc PF single-use filters after preconditioning them with the sample to avoid significant uranium(VI) sorption to the filters (Payne, 1999). Polypropylene bottles may also sorb uranium(VI) to some extent at high pH; however this effect is insignificant in systems with sufficient ferrihydrite, which adsorbs uranium(VI) much more strongly (Payne, 1999). After equilibration, the pH was measured on the unfiltered sample, using a Radiometer combination electrode. The filtered samples were acidified (1% HNO_3) and analysed for U (^{238}U) using an ICP-MS (Agilent 4500) in a clean room. External calibration (0.1-100 μg l^{-1}) was applied with ^{103}Rh as internal mass standard. Carbonate alkalinity was measured by titration of 20 ml sample to pH 5.4 with 0.01 M HCl under N_2 bubbling (ISO 9963:2). Preliminary experiments with and without Na_2CO_3 addition at various pHs showed that diffusion of CO_2 into or out from the polypropylene bottles was minimal.

2.2. Model approach

For uranium(VI) the solution complexation reactions of Guillaumont et al. (2003) were used (Table 1), although Ca-U-CO_3 complexes were included, with constants taken from Dong and Brooks (2006). However, mixed UO_2-OH-CO_3 complexes were excluded, as a recent study focusing on the solubility of schoepite concluded that the schoepite solubility data were described most consistently when these complexes were not accounted for (Jang et al., 2006). In our opinion it seems likely that the currently available constants for these complexes are overestimated. All constants were incorporated into the geochemical code Visual MINTEQ, ver. 2.60 (Gustafsson, 2008), which was used in all simulations.

For surface complexation modelling of uranium(VI) to ferrihydrite, we used the three-plane CD-MUSIC model (Hiemstra and van Riemsdijk, 1996) as adapted for ferrihydrite by Gustafsson (2001a). In this approach it is assumed that singly coordinated FeOH groups are the only reactive surface groups and that triply coordinated Fe_3O groups consequently do not contribute appreciably to proton and metal sorption. Some support for this simplifying assumption comes from the observation that the point-of zero charge (PZC) for ferrihydrite (8.1; Dzombak and Morel, 1990) is similar in magnitude to that of singly coordinated FeOH groups in ferrihydrite as estimated by the MUSIC model (7.8; Stachowicz, 2007).

However, the surface charging parameters (Table 2 and Table 3) were modified from the original model of Gustafsson (2001a) to be consistent with the recent revision of the goethite charging parameters (Hiemstra and van Riemsdijk, 2006). We assumed that the Stern layer capacitances and electrolyte ion-pair reaction constants were equal to those of goethite, but we maintained a specific surface area of 750 $m^2 g^{-1}$, as in the original model. The site density was then optimized on the basis of published data sets on surface charging on ferrihydrite, and a value of 6.3 sites nm^{-2} was obtained. As an example, Fig. 1 shows the fit of the model to the surface charging data of Hsi and Langmuir (1985).

Surface complexation reactions for uranium(VI) were constrained from EXAFS evidence showing a predominance of bidentate complexes with uranium(VI) only or with a uranium(VI)-carbonate ternary complex (Table 3). The CD (charge distribution) parameters for these complexes were set so that the charge attribution to the surface was at its maximum value, i.e. so that the surface oxygens were fully neutralized; this generally caused the best fits with the model.

Preliminary model optimizations showed that the model was not able to arrive at acceptable descriptions of uranium(VI) adsorption unless the surface sites were divided into high-affinity and low-affinity sites, similar to what was earlier found to be the case for uranium(VI) (Waite et al., 1994; Davis et al., 2004; Fox et al., 2006) and for other strongly adsorbing metal ions (Dzombak and Morel, 1990). There might be different reasons for this, but since the identity of the high-affinity uranium surface complexes remains unknown, we decided to divide the surface sites into high-affinity sites (which amounted to 1 % of the total number of sites) and low-affinity sites (the remaining 99 %), and to optimize separate surface complexation constants for each.

The Stockholm Humic Model (SHM) (Gustafsson, 2001b) was used to describe uranium(VI) complexation onto humic or fulvic acid. The SHM is similar to Model VI (Tipping, 1998) in many respects, but it has a slightly more advanced electrostatic submodel. The SHM has earlier been used for speciation of a range of trace metals including rare-earth metals (e.g., Gustafsson, 2001b; Rönnback et al., 2008) but previously not for uranium(VI). Therefore previously published data were reviewed to produce a consistent model description of uranium(VI) complexation to humic and fulvic acid.

In the SHM, uranium(VI) is assumed to be bound as monodentate or bidentate complexes, in a similar way as for other divalent metals such as Cu and Pb (Gustafsson, 2001b). The reactions describing monodentate and bidentate uranium(VI) complexation can be written as:

$$R\mathrm{OH} + \mathrm{UO_2}^{2+} \Leftrightarrow R\mathrm{OUO_2}^{+} + \mathrm{H}^{+} \qquad K_{\mathrm{UO2,\,m}} \qquad (1)$$

$$2R\mathrm{OH} + \mathrm{UO_2}^{2+} \Leftrightarrow (R\mathrm{O})_2\mathrm{UO_2}^{0} + 2\mathrm{H}^{+} \qquad K_{\mathrm{UO2,\,b}} \qquad (2)$$

where ROH represents a DOM functional group (carboxylic or phenolic). The equilibrium constants $K_{\mathrm{UO2,\,m}}$ and $K_{\mathrm{UO2,\,b}}$ contain electrostatic (Boltzmann) terms (c.f. Gustafsson, 2001b). To account for heterogeneity of site affinity for metal complexation the parameter ΔLK_2 is used to modify the equilibrium constants:

$$\log K_{\mathrm{UO2,m,x}} = \log K_{\mathrm{UO2m}} + x \cdot \Delta LK_2, \quad x = 0, 1, 2 \tag{3}$$

$$\log K_{\mathrm{UO2,b,x}} = \log K_{\mathrm{UO2b}} + x \cdot \Delta LK_2, \quad x = 0, 1, 2 \tag{4}$$

This allows each site to be subdivided into subsites with differing affinity for metal-humic complexation. Consistent with earlier studies, x was set to 0 for 90.1 % of the sites, 1 for 9 % and 2 for 0.9 %.

In addition, the model also considers weak electrostatic binding of the metals to dissociated acid groups of humic and fulvic acid (Gustafsson, 2001b); however, for a strongly bound metal ion such as uranyl the importance of this mode of binding is calculated to be very small.

Amended database files for Visual MINTEQ and PHREEQC (Parkhurst and Appelo, 2004), with the thermodynamic data used in this work, are available from the senior author on request (note, however, that the SHM reactions are not available for PHREEQC).

2.3. Data sources

For uranium(VI) adsorption to ferrihydrite, full optimization was made not only for the data set of this study, but also for the large data set of Payne (1999). The two optimized models were then used to simulate the results obtained in the studies of Wazne et al. (2003), Jang et al. (2007) and Fox et al. (2006) – all these papers report uranium(VI) sorption to ferrihydrite under various conditions, but the data sets were deemed too small to be used for model optimizations.

Furthermore, before the model was used on systems with both uranium(VI) and CO_3, the model was optimized also for CO_3 (data set of Appelo et al., 2002), and for a range of other adsorbing ions including SO_4 (Davis, 1977), Ca (Cowan et al., 1991), H_4SiO_4 (Swedlund and Webster, 1999) and PO_4 (Gustafsson, 2003). We also determined a surface complexation constant for a ternary UO_2-PO_4 surface complex using the data of Payne (1999). Where appropriate, we used surface reactions and CD values consistent with those recently determined or estimated for goethite (Hiemstra and van Riemsdijk, 2006; Hiemstra et al., 2007; Stachowicz, 2007). For H_4SiO_4, however, we found that the MO/DFT-calculated CD values of Hiemstra et al. (2007) did not fit the data of Swedlund and Webster (1999) well, and therefore these CD values were fitted.

Concerning uranium(VI) complexation to humic and fulvic acid, we used the same data sets as used for the optimization of NICA-Donnan parameters for uranium(VI) (Milne et al., 2003; Table 4), although the more recent data set of Saito et al. (2004) was also included. The data set HUO_2-05 by Glaus et al. (1997) was given a slightly larger weight in the optimizations since this study reported uranium(VI) complexation data for different pH values in a wide range from 5 to 10, whereas most of the other studies only reported uranium(VI) complexation results for one single pH value. In the optimizations we used the generic proton-binding parameters of SHM (Gustafsson, 2008), which, *e.g.,* determine the acidity and abundance of the reactive surface sites for humic and fulvic acid, respectively (*R*OH in equations 1-2). In line with previous work, a common set of complexation constants was assumed to be valid both for humic and fulvic acid (Gustafsson, 2001b).

Optimizations of complexation constants were made by minimizing the root-mean square errors (rmse:s) in adsorbed percentages (for the surface complexation model) or in log bound metal (SHM) using Brent's method.

3. Results

3.1. Surface complexation of uranium(VI) to ferrihydrite

When no carbonate had been added in the batch experiment, uranium(VI) adsorption increased with increasing pH until reaching 100 % at about pH 6, and adsorption remained at 100 % until pH 10 (Fig. 2). In the presence of 2 mM CO_3, adsorption decreased considerably with increasing pH at pH > 7, particularly at the lower ferrihydrite concentration used. These results are consistent with earlier work (Payne, 1999; Wazne et al., 2003). The surface complexation model was able to provide a good fit to these data, with an overall *rmse* value of 0.075. The optimized surface complexation constants are seen in Table 3.

We treated the data of Payne (1999) in the same way (Fig. 3). In this case, the model was able to provide a very good fit (*rmse* = 0.060) across the whole range of surface coverages and CO_2 pressures used. However, as is seen in Table 3, the constants optimized for the data of Payne (1999) were consistently lower than those obtained for the data of the present study. Apparently the ferrihydrite preparation used by Payne (1999) had a lower reactivity towards uranium(VI) than the ferrihydrite we had synthesized. Payne (1999) also reported data for uranium(VI) adsorption in the presence of phosphate, which strongly indicated the existence of a ternary UO_2PO_4 surface complex (these results are discussed also by Payne et al., 1996). With the assumption that this surface complex was bidentate and using the CD values as adjustable parameters in the fitting, we obtained a good fit (*rmse* = 0.087) using log *K* = 24.36 for both low- and high-affinity sites (Table 3).

To find out whether other data sets were consistent with the results of Payne (1999) or with our own results, we used the two optimized models, now in "simulation" mode, to predict the uranium(VI) sorption data obtained in three other studies (Fig. 4). In the work of Jang et al. (2007), uranium(VI) sorption isotherms were produced at three different pH values, in the presence of atmospheric CO_2. In this case, the optimized model for the data set of Payne (1999) fitted the data reasonably well (*rmse* = 0.084), whereas the model optimized for our own data clearly overestimated uranium(VI) adsorption (*rmse* = 0.209). The reverse situation was found to be true for the data of Fox et al. (2006), who determined uranium(VI) adsorption at different CO_2 pressures and Ca concentrations; here the 'Payne model' seriously underestimated uranium(VI) adsorption in most cases (resulting in *rmse* = 0.212), whereas the model for our own data performed considerably better although not perfectly (*rmse* = 0.092). For the data of Wazne et al. (2003), who studied uranium(VI) adsorption at two different CO_3 concentrations, the 'Payne model' was again more successful as evidenced by its better fit (*rmse* = 0.094 as compared to *rmse* = 0.169 for our own model). In other words, in two of three cases the model optimized for the data of Payne (1999) was more successful, whereas in the third case 'our own' model was better.

For environmental simulations it is necessary to arrive at one common set of surface complexation constants. In the light of the above results, it was decided to calculate a set of recommended constants based on a weighted average of the model for Payne's (1999) data and of the model for our own data, where the former was given a weight of 70 % and the latter 30 %. The resulting weighted-average constants are seen in Table 3.

3.2. Uranium(VI) complexation to humic acid and fulvic acid

For all data sets except for one, optimization of the SHM converged to reasonable values. The excluded data set was the one of Borovec et al. (1979); the reason was that very poor fits were obtained with the SHM because the model predicted a much higher uranium(VI) complexation capacity than was observed. Possibly this might be caused by a much lower concentration of reactive surface sites in the study of Borovec et al. (1979) compared to the one given by the generic proton-binding parameters in the SHM. The resulting weighted-average complexation constants and ΔLK_2 value are shown in Table 4. The results indicate a large surface site heterogeneity for uranium(VI) complexation by humic substances, i.e $\Delta LK_2 = 2$. This is larger than has earlier been found for metals such as Cu and Pb (Gustafsson, 2001b) and it indicates that at the low uranium(VI) concentrations usually found in groundwater, complexation to DOM may be very strong. It should be noted that none of the data sets covered a sufficiently large range in pHs and uranium(VI) concentrations to allow simultaneous optimization of log $K_{\mathrm{UO2,\,m}}$ and log $K_{\mathrm{UO2,\,b}}$. This suggests that the optimized weighted-average constants may be rather uncertain.

3.3. Example calculations with the optimized geochemical model

To illustrate the potential use of the model, the uranium(VI) speciation and adsorption for a specific groundwater composition was made as a function of pH. A hypothetical groundwater contained 0.1 mM SO_4, 0.1 mM Cl, 0.2 mM Si, 0.1 μM U(VI), 0.5 μM PO_4 and 2 mg/L DOC, of which 70 % was assumed to be fulvic acid. Dissolved carbonate was given by partial CO_2 pressures (PCO_2) of either 7.6×10^{-4} atm or 7.6×10^{-3} atm, which encompasses a range of typical CO_2 pressures found in groundwater. Dissolved calcium was calculated from charge balance, and the temperature was assumed to be 10°C. The calculated uranium(VI) speciation as a function of pH for this groundwater composition is shown in Fig. 5. The simulated pH dependence is limited upwards by calcite precipitation, which occurs at pH 8.04 at $PCO_2 = 7.6 \times 10^{-4}$ atm, or at pH 7.39 at the higher CO_2 pressure. The model predicts UO_2-DOM complexes to predominate at pH < 7.3 or at pH < 6.6, depending on the CO_2 pressure, whereas Ca-UO_2-CO_3 complexes are dominant at higher pH. The contrasting results for the two CO_2 pressures show that a larger CO_2 pressure limits the window for the UO_2-DOM complexes considerably.

The percentage adsorbed uranium(VI) to ferrihydrite can also be calculated. In this simulation it was assumed that the suspension contained 1 g/L ferrihydrite, and that adsorption of Ca, CO_3, SO_4, PO_4, Si and Cl had already reached steady-state, so that no net adsorption/desorption of these ions occurred during the simulation. For simplicity, the adsorption of DOM to ferrihydrite was not considered, although DOM is likely to promote uranium(VI) adsorption to some extent at pH < 7 (Payne et al., 1996). The model shows that uranium(VI) adsorption is fairly strong over the whole pH range, with a maximum occurring at pH 7.2 or pH 6.6, depending on the CO_2

pressure (Figure 6). At higher pH:s uranium(VI) adsorption gets considerably weaker, which is an effect mainly of Ca-UO_2-CO_3 complexation in solution and to some extent also strong competition from adsorbed Si. However also at calcite saturation (at pH 8.04 when $PCO_2 = 7.6 \times 10^{-4}$ atm and at pH 7.39 when $PCO_2 = 7.6 \times 10^{-3}$ atm), between 85 and 90 % of the added uranium(VI) is predicted to be adsorbed. At pH 5, the ternary $(FeOH)_2UO_2PO_4^{2-}$ surface complex was calculated to account for > 90 % of the adsorbed uranium(VI). The importance of the $(FeOH)_2UO_2CO_3^-$ surface complexes increased with increasing pH and they became dominant within 0.5 pH units below the pH at the calcite saturation limit.

4. Discussion

Inclusion of the EXAFS-derived structures in the CD-MUSIC model allowed for a very good description of the uranium(VI) adsorption data for ferrihydrite. The model fits are comparable in quality to those obtained by Waite et al. (1994) with the DLM. In the model optimization, there was no need to include a second type of UO_2CO_3 surface complex (as suggested by Sherman et al., 2008) since this did not lead to any significant improvement in the model fit. It remains to be investigated to what extent the model is able to describe uranium(VI) adsorption in environmentally complex systems. An intriguing and unresolved issue is why the reactivities of ferrihydrite towards uranium(VI) turned out to be different in different studies; this has potentially large implications for simulations of environmental systems, since we do not know the reactivity of naturally formed ferrihydrite in relation to the synthesized ones that were used in the batch experiments. The simulation results indicated that ternary $(FeOH)_2UO_2PO_4^{2-}$ complexes may be very important for uranium(VI) adsorption when PO_4 is present, at least at low pH. Although the existence of such a surface species has not yet been demonstrated by EXAFS spectroscopy, experimental support for a strong uranium(VI)-PO_4 interaction comes from the observation that PO_4 amendments greatly retarded uranium(VI) transport through a goethite-coated sand column (Cheng et al., 2007).

Concerning uranium(VI) complexation to humic and fulvic acid, the published data were of a lower quality as regards the variation in pH values and uranium(VI) concentrations. As a consequence the optimized complexation constants are probably more uncertain than for ferrihydrite. The optimized SHM parameters predict that uranium(VI) complexation by DOM is important under weakly acid conditions in natural aquatic systems (Fig. 5). However, under neutral to alkaline conditions and in the presence of substantial carbonate, conditions that are typical for many groundwaters, the uranium(VI)-DOM complexes become unimportant as compared to Ca-U-CO_3 complexes. The simulations are qualitatively consistent with the flow field flow fractionation data of Jackson et al. (2005) and Ranville et al. (2007).

Uranium(VI) removal to ferrihydrite is dependent both on solution speciation, on the surface reactivity of ferrihydrite and on competitive interactions with other ions. The calibrated geochemical model suggests that uranium(VI) removal by ferrihydrite-containing sorbents could be an attractive alternative in small-scale systems for drinking-water treatment. Near the calcite saturation limit, however, the uranium(VI) removal may not be very efficient (between 85 and 90 % adsorption as suggested by the simulation in Fig. 6) but nevertheless sufficiently strong to bring down dissolved uranium(VI) concentrations to acceptable levels. The feasibility of this technique was recently shown by Dässman (2008), who used iron oxide-coated olivine to remove uranium(VI) in a water treatment plant near Eskilstuna, Sweden. The iron oxide coating consisted mostly of ferrihydrite. The groundwater at this site had a composition similar to the low-CO_2 water in the previous simulation (Fig. 5 and Fig. 6) and a pH of 8.0 (close to the calcite saturation limit). Uranium(VI) removal was monitored over a period of three months and was found to be > 50 %. The relatively low removal percentage as compared to the simulation result may possibly be explained by substantial channeling occurring in the substrate (Dässman, 2008).

5. Conclusions

Evidence from EXAFS spectroscopy was used to constrain a three-plane CD-MUSIC surface complexation model for uranium(VI) adsorption to ferrihydrite. However, in line with earlier model attempts, the surface sites had to be divided into low- and high-affinity sites to describe the data well. Application of this modelling concept to published data sets revealed that different ferrihydrites appear to have different reactivities towards uranium(VI). Evaluation of uranium(VI) complexation to DOM with the Stockholm Humic model showed that this process is important for uranium(VI) speciation at low pH. However in neutral to alkaline waters, Ca-U-CO_3 solution complexes predominate.

Simulations of the calibrated geochemical model showed that uranium(VI) adsorption to ferrihydrite, in the presence of several common competitive ions, is fairly strong between pH 5 and 8, and that it exceeds 80 % even near the calcite saturation limit, where uranium(VI) adsorption is weakest. This suggests that uranium(VI) adsorption to ferrihydrite-containing sorbents is an attractive alternative for uranium(VI) removal from groundwater.

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REFERENCES

Appelo, C.A.J., van der Weiden, M.J.J., Tournassat, C., Charlet, L. 2002., Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environ. Sci. Technol. 36, 3096-3103.

Borovec, Z., Kribek, B., Tolar, V., 1979. Sorption of uranyl by humic acids. Chem. Geol. 27, 39-46.

Cheng, T., Barnett, M.O., Roden, E.E., Zhuang, J., 2007. Reactive transport of uranium(VI) and phosphate in a goethite-coated sand column: an experimental study. Chemosphere 68, 1218-1223.

Czerwinski, K.R., Buckau, B., Scherbaum, F., Kim, J.I., 1994. Complexation of the uranyl-ion with humic acid. Radiochim. Acta 65(2), 111-119.

Cowan, C.E., Zachara, J.M., Resch, C.T., 1991. Cadmium adsorption on iron oxides in the presence of alkaline-earth elements. Environ. Sci. Technol. 25, 437-446.

Dässman, E., 2008. Avskiljning av uran från dricksvatten med reaktiva filter. MSc Thesis, Department of Soil and Environment, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Davis, J.A., 1977. Adsorption of trace metals and complexing ligands at the oxide/water interface. PhD thesis, Stanford University, CA, USA.

Davis, J.A., Meece, D.E., Kohler, M., Curtis, G.P., 2004. Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments. Geochim. Cosmochim. Acta 68(18), 3621-3641.

Davis, J.A., Curtis, G.P., Wilkins, M.J., Kohler, M., Fox, P., Naftz, D.L., Lloyd, J.R., 2006. Processes affecting transport of uranium in a suboxic aquifer. Phys. Chem. Earth 31(10-14), 548-555.

Dong, W., Brooks, S.C., 2006. Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environ. Sci. Technol. 40, 4689-4695.

Dzombak, D.A., Morel, F.M.M., 1990. Surface complexation modeling : Hydrous ferric oxide. John Wiley & Sons, New York, NY.

Ek, B.M., Thunholm, B., Östergren, I., Falk, R., Mjönes, L., 2007. Naturlig radioaktivitet, uran och andra metaller i dricksvatten. SGU Report 2007:13, Geological Survey of Sweden, Uppsala, Sweden.

Falk, R., Mjönes, L., Appelblad, P., Erlandsson, B., Hedenberg, G., Svensson, K., 2004. Kartläggning av naturligt radioaktiva ämnen i dricksvatten. SSI Report 2004:14, Swedish Radiation Proctection Authority, Stockholm, Sweden.

Fox, P.M., Davis, J.A., Zachara, J.M., 2006. The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. Geochim. Cosmochim. Acta 70, 1379-1387.

Glaus, M.A., Hummel, W., vanLoon, L.R., 1997. Experimental determination and modelling of trace metal-humic interactions: a pragmatic approach for application in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.H., 2003. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. Elsevier, Amsterdam.

Gustafsson, J.P., 2001a. Modelling competitive anion adsorption on oxide minerals and an allophane-containing soil. Eur. J. Soil Sci. 52, 639-653.

Gustafsson, J.P., 2001b. Modeling the acid-base properties and metal complexation of humic substances with the Stockholm Humic Model. J. Colloid Interface Sci. 244, 102-112.

Gustafsson, J.P., 2003. Modelling molybdate and tungstate adsorption to ferrihydrite. Chem. Geol. 200, 105-115.

Gustafsson, J.P., 2008. Visual MINTEQ version 2.60. http://www.lwr.kth.se/English/OurSoftware/vminteq/index.htm. Stockholm, Sweden, October 2008.

Hiemstra, T., van Riemsdijk, W.H., 1996. A surface structural approach to ion adsorption: the charge distribution (CD) model. J. Colloid Interface Sci. 179, 488-508.

Hiemstra, T. van Riemsdijk, W.H., 2006. On the relationship between charge distribution, surface hydration, and the structure of the interface of metal (hydr)oxides. J. Colloid Interface Sci. 301, 1-18.

Hiemstra, T., Barnett, M.O., van Riemsdijk, W.H., 2007. Interaction of silicic acid with goethite. J. Colloid Interface Sci. 310, 8-17.

Hsi, C.D., Langmuir, D., 1985. Adsorption of uranyl onto ferric oxyhydroxides : application of the surface complexation site-binding model. Geochim. Cosmochim. Acta 49, 1931-1941.

Jackson, B.P., Ranville, J.F., Bertsch, P.M., Sowder, A.G., 2005. Characterization of colloidal and humic-bound Ni and U in the “dissolved” fraction of contaminated sediment extracts. Environ. Sci. Technol. 39, 2478-2485.

Jang, J.H., Dempsey, B.A., Burgos, W.D., 2006. Solubility of schoepite: comparison and selection of complexation constants for U(VI). Wat. Res. 40, 2738-2746.

Jang, J.H., Dempsey, B.A., Burgos, W.D., 2007. A model-based evaluation of sorptive reactivities of hydrous ferric oxide and hematite for U(VI). Environ. Sci. Technol. 41, 4305-4310.

Logue, B.A., Smith, R.W., Westall, J.C., 2004. U(VI) adsorption on iron-coated sands: comparison of approaches for modeling adsorption on heterogeneous environmental materials. Appl. Geochem. 19, 1937-1951.

Neiss, J., Stewart, B.D., Nico, P.S., Fendorf, S., 2007. Speciation-dependent microbial reduction of uranium within iron-coated sands. Environ. Sci. Technol. 41, 7343-7348.

Parkhurst, D.L., Appelo, C.A.J., 2004. User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey, Reston, VA.

Payne, T.E., 1999. Uranium(VI) interactions with mineral surfaces: Controlling factors and surface complexation modeling. PhD thesis, University of New South Wales, Australia.

Payne, T.E., Davis, J.A., Waite, T.D., 1996. Uranium adsorption on ferrihydrite – Effects of phosphate and humic acid. Radiochim. Acta 74, 239-243.

Ranville, J.F., Hendry, J.M., Reszat, T.M., Xie, Q., Honeyman, B.D., 2007. Quantifying uranium complexation by groundwater dissolved organic carbon using asymetrical flow field flow fractionation. J. Contam. Hydrol. 91, 233-246.

Reich, T., Moll, H., Arnold, T., Denecke, M.A., Hennig, C., Geipel, G., Bernhard, G., Nitsche, H., Allen, P.G., Bucher, J.J., Edelstein, N.M., Shuh, D.K., 1998. An EXAFS study of uranium(VI) sorption onto silica gel and ferrihydrite. J. Electron Spect. Rel. Phenom. 96, 237-243.

Rönnback, P., Åström, M., Gustafsson, J.P., 2008. Comparison of the behaviour of rare-earth elements in surface waters, overburden groundwaters and bedrock groundwaters in two granitoidic settings, eastern Sweden. Appl. Geochem. 23, 1862-1880.

Saito, T., Koopal, L.K., Nagasaki, S., Tanaka, S., 2004. Application of the NICA-Donnan model for proton, copper and uranyl binding to humic acid. Radiochim. Acta 92, 567-574.

Schwertmann, U., Cornell, R.M., 2000. Iron oxides in the laboratory. Preparation and characterization. Wiley, Weinheim.

Sherman, D.M., Peacock, C.L., Hubbard, C.G., 2008. Surface complexation of U(VI) on goethite (α-FeOOH). Geochim. Cosmochim. Acta 72, 298-310.

Stachowicz, M. 2007. Solubility of arsenic in multicomponent systems. PhD thesis, Wageningen University, Netherlands.

Swedlund, P.J., Webster, J.G., 1999. Adsorption and polymerisation of silicic acid on ferrihydrite, and its effect on arsenic adsorption. Wat. Res. 33, 3413-3422.

Tipping, E. 1998. Humic ion-binding model VI: An improved description of the interactions between protons and metal ions with humic substances. Aquat. Geochem. 4, 3-48.

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A., Xu, N., 1994. Uranium(VI) adsorption to ferrihydrite – application of a surface complexation model. Geochim. Cosmochim. Acta 58, 5465-5478.

Wazne, M., Korfiatis, G.F., Meng, X., 2003. Carbonate effects on hexavalent uranium adsorption by iron oxyhydroxide. Environ. Sci. Technol. 37, 3619-3624.

WHO, 2004. Guidelines for drinking water quality, Third Edition. Volume 1, Recommendations. World Health Organzation, Geneva, Switzerland.

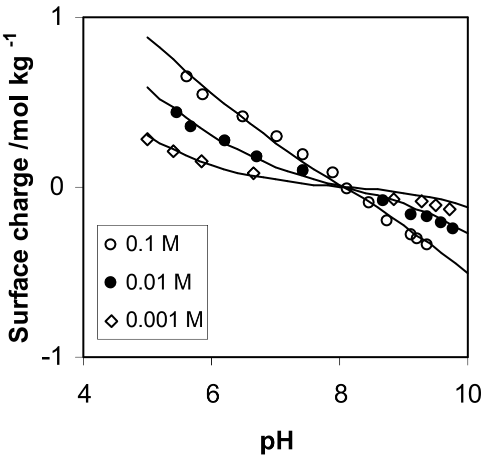

Fig. 1. Surface charge of ferrihydrite at three different ionic strengths (data from Hsi and Langmuir, 1985). The lines are model fits with the surface charging parameters shown in Table 2.

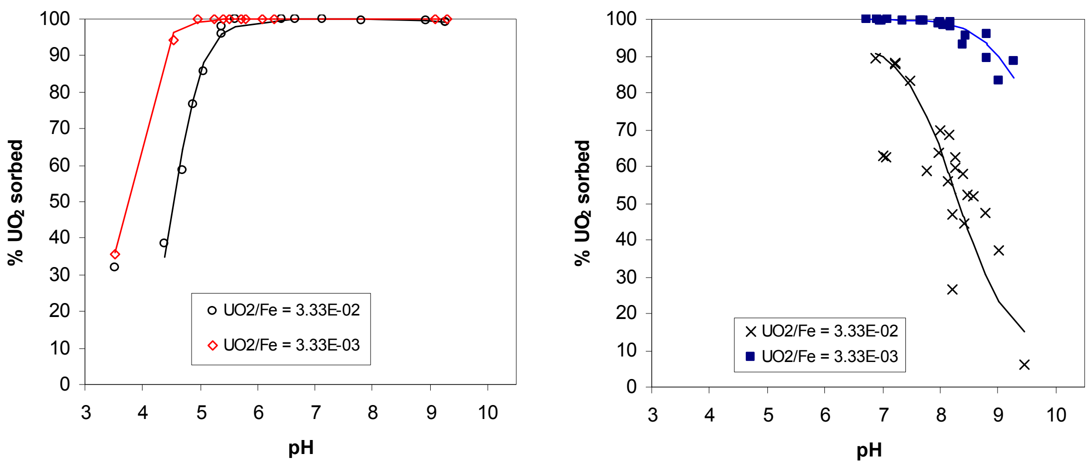

Fig. 2. Percent adsorption of uranium(VI) on ferrihydrite as a function of pH in 0.01 M $NaNO_3$. Solution UO_2/Fe ratios were made up as follows: 3.33E-02: 10 μM UO_2 and 0.3 mM Fe; 3.33E-03: 10 μM UO_2 and 3 mM Fe. Left panel: Systems without CO_3; Right panel: Systems containing 2 mM CO_3. The lines are fits with the optimized surface complexation parameters shown in Table 3.

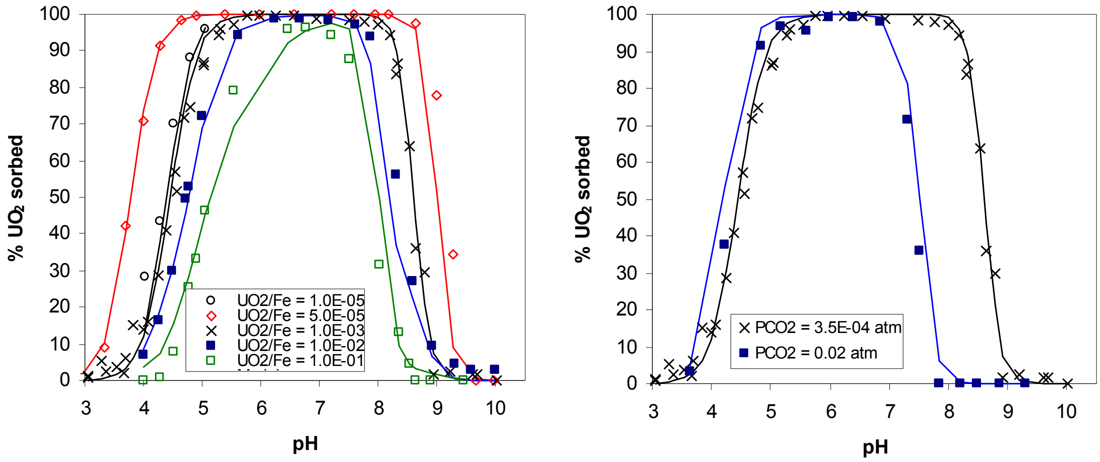

Fig. 3. Percent adsorption of uranium(VI) on ferrihydrite as a function of pH in 0.1 M $NaNO_3$, in the systems of Payne (1999). Solution UO_2/Fe ratios were made up as follows: 1.0E-05: 0.01 μM UO_2 and 1 mM Fe as ferrihydrite; 5.0E-05: 1 μM UO_2 and 20 mM Fe; 1.0E-03: 1 μM UO_2 and 1 mM Fe; 1.0E-02: 10 μM UO_2 and 1 mM Fe; 1.0E-01: 100 μM UO_2 and 1 mM Fe. Left panel: Systems with a constant CO_2 pressure at 3.5×10^{-4} atm. Right panel: uranium(VI) adsorption at two different CO_2 pressures after equilibration with 1 μM UO_2 and 1 mM Fe. The lines are fits with the optimized surface complexation parameters shown in Table 3.

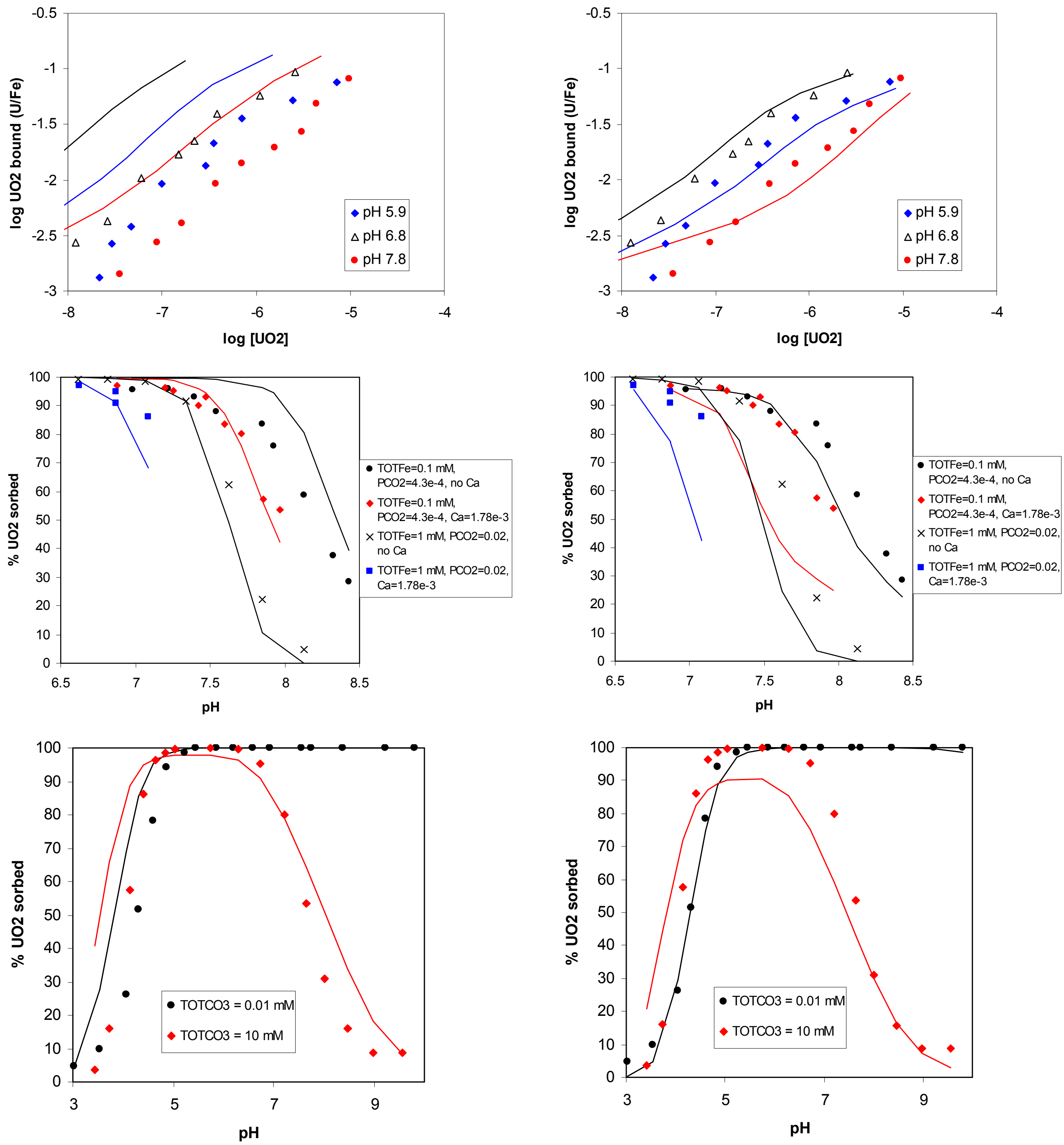

Fig. 4. Adsorption of uranium(VI) on ferrihydrite in the studies of Jang et al. (2007; upper row), Fox et al. (2006; middle row) and Wazne et al. (2003; lower row). The lines are fits with the optimized surface complexation parameters shown in Table 3, for the data of this study (left column) and for the data of Payne (1999; right column). See the cited references for details on experimental conditions.

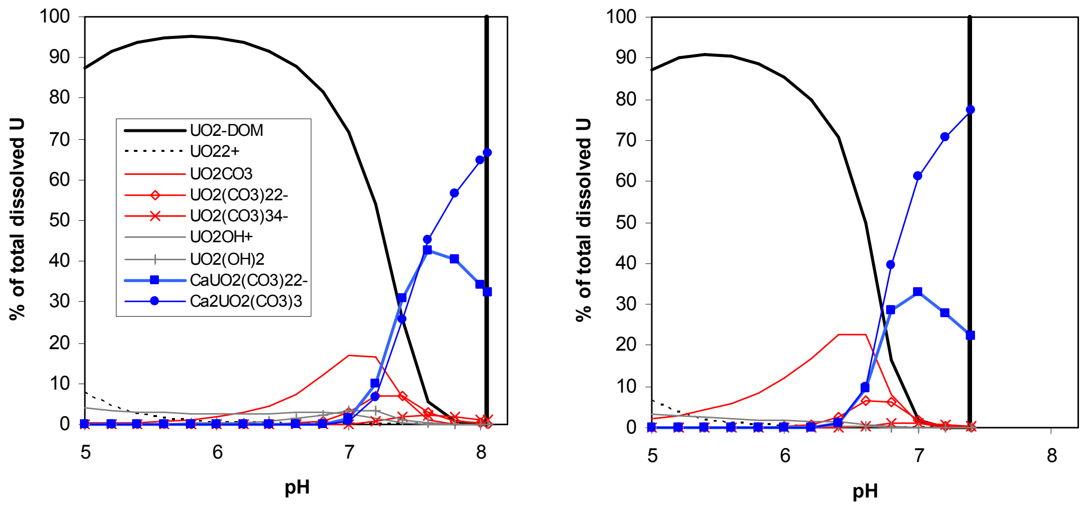

Fig. 5. Simulated uranium(VI) speciation for a groundwater as a function of pH. Left panel: $PCO_2 = 7.6 \times 10^{-4}$ atm; Right panel: $PCO_2 = 7.6 \times 10^{-3}$ atm. The thick vertical line indicates the pH value at which calcite is precipitated. See text for details.

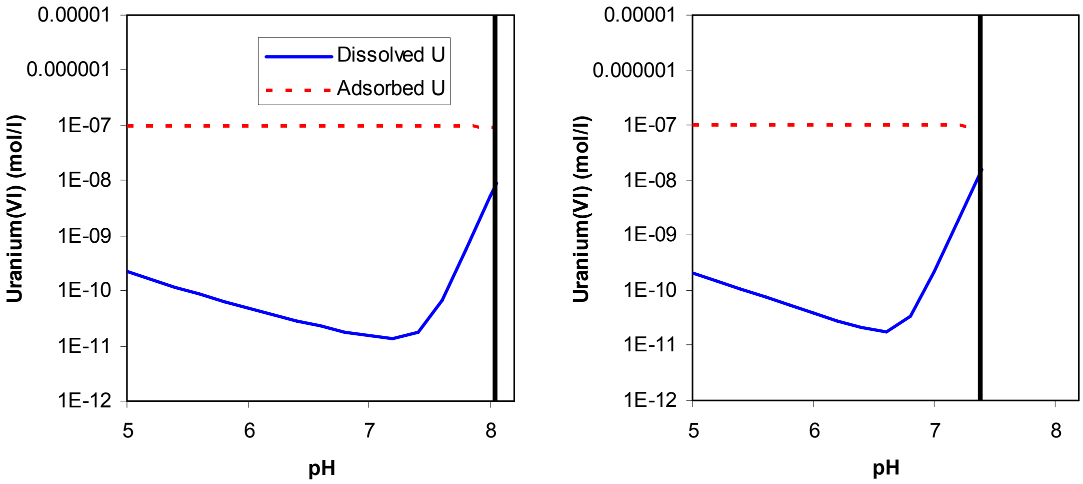

Fig. 6. Simulated partitioning of uranium(VI) between dissolved and adsorbed phases as a function of pH in the groundwater of Fig. 5 in contact with 1 g/L ferrihydrite. Left panel: $PCO_2 = 7.6 \times 10^{-4}$ atm; Right panel: $PCO_2 = 7.6 \times 10^{-3}$ atm. The thick vertical line indicates the pH value at which calcite is precipitated. See text for details.

Table 1

Uranium(VI) complexation constants used in this work[a]

Reaction	log β at 25°C, I = 0	ΔH_r (kJ mol^{-1})
$UO_2^{2+} + H_2O \leftrightarrow UO_2OH^+ + H^+$	-5.25	0.9
$UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)_2^0 + 2H^+$	-12.15	0[b]
$UO_2^{2+} + 3H_2O \leftrightarrow UO_2(OH)_3^- + 3H^+$	-20.25	0[b]
$UO_2^{2+} + 4H_2O \leftrightarrow UO_2(OH)_4^{2-} + 4H^+$	-32.4	0[b]
$2UO_2^{2+} + H_2O \leftrightarrow (UO_2)_2OH^{3+} + H^+$	-2.7	0[b]
$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62	48.9
$3UO_2^{2+} + 4H_2O \leftrightarrow (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.9	0[b]
$3UO_2^{2+} + 5H_2O \leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$	-15.55	123
$3UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_3(OH)_7^- + 7H^+$	-32.2	0[b]
$4UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_4(OH)_7^+ + 7H^+$	-21.9	0[b]
$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2CO_3^0$	9.94	5.0
$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_2^{2-}$	16.61	18.5
$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}$	21.84	39.2

$3UO_2^{2+} + 6CO_3^{2-} \leftrightarrow (UO_2)_3(CO_3)_6^{6-}$	54.0	-62.7
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \leftrightarrow CaUO_2(CO_3)_3^{2-}$	27.18	0[b]
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \leftrightarrow Ca_2UO_2(CO_3)_3^{0}$	30.7	0[b]
$UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2SO_4^{0}$	3.15	19.5
$UO_2^{2+} + NO_3^{-} \leftrightarrow UO_2NO_3^{+}$	0.3	-12
$UO_2^{2+} + Cl^{-} \leftrightarrow UO_2Cl^{+}$	0.17	8.0

[a]All constants are from Guillaumont et al. (2003) except for the two Ca-U-CO_3 complexes, which are from Dong and Brooks (2006).

[b]Not known, a value of 0 was used in the model

Table 2

Model parameters for surface charging of ferrihydrite[a]

	Ferrihydrite
A / m^2 g^{-1}	750[a]
N_s / sites nm^{-2}	6.3
C_1 / F m^{-2}	1[b]
C_2 / F m^{-2}	0.74[b]

[a]From Gustafsson (2001a)

[b]Assumed to be equal to those of goethite (Hiemstra and van Riemsdijk, 2006)

Table 3

Surface complexation reactions

Reaction	$(\Delta z_0, \Delta z_1, \Delta z_2)$[a]	log K[b]	Data source(s)
$FeOH^{½-} + H^+ \leftrightarrow FeOH_2^{½+}$	(1,0,0)	8.1	Dzombak and Morel (1990)
$FeOH^{½-} + Na^+ \leftrightarrow FeOHNa^{½+}$	(0,1,0)	-0.6	Hiemstra and van Riemsdijk (2006)
$FeOH^{½-} + H^+ + NO_3^- \leftrightarrow FeOH_2NO_3^{½-}$	(1,-1,0)	7.42	Hiemstra and van Riemsdijk (2006)
$FeOH^{½-} + H^+ + Cl^- \leftrightarrow FeOH_2Cl^{½-}$	(1,-1,0)	7.65	Hiemstra and van Riemsdijk (2006)
$2FeOH^{½-} + UO_2^{2+} + H_2O \leftrightarrow (FeOH)_2UO_2OH^0 + H^+$	(1,0,0)	3.56, 6.66	This study
		2.69, 5.56	Payne (1999)
		2.95, 5.89	Weighted average
$2FeOH^{½-} + UO_2^{2+} + CO_3^{2-} \leftrightarrow (FeOH)_2UO_2CO_3^-$	(1,-1,0)	17.95, 21.44	This study
		16.44, 20.95	Payne (1999)
		16.89, 21.10	Weighted average
$2FeOH^{½-} + UO_2^{2+} + PO_4^{3-} \leftrightarrow (FeOH)_2UO_2PO_4^{2-}$	(0.25,-1.25,0)	24.36	Payne (1999)
$FeOH^{½-} + H^+ + SO_4^{2-} \leftrightarrow FeOSO_3^{1½-} + H_2O$	(0.5,-1.5,0)	9.23	Davis (1977)
$2FeOH^{½-} + 2H^+ + CO_3^{2-} \leftrightarrow Fe_2O_2CO^- + 2H_2O$	(0.68,-1.68,0)	21.36	Appelo et al. (2002)

$FeOH^{½-} + Ca^{2+} \leftrightarrow FeOHCa^{1½+}$	(0.32,1.68,0)	3.11	Cowan et al. (1991)
$2FeOH^{½-} + H_4SiO_4 \leftrightarrow Fe_2O_2Si(OH)_2^{-} + 2H_2O$	(0.45,-0.45,0)	4.96	Swedlund and Webster (1999)
$2FeOH^{½-} + 4H_4SiO_4 \leftrightarrow Fe_2O_2SiOHOSi_3O(OH)_9^{-} + 4H_2O$	(0.45,-0.45,0)	13.06	“
$2FeOH^{½-} + 4H_4SiO_4 \leftrightarrow Fe_2O_2SiOHOSi_3O_2(OH)_8^{2-} + H^{+} + 4H_2O$	(0.45,-1.45,0)	8.0	“
$2FeOH^{½-} + 2H^{+} + PO_4^{3-} \leftrightarrow Fe_2O_2PO_2^{2-} + 2H_2O$	(0.46,-1.46,0)	27.43	Gustafsson (2003)
$2FeOH^{½-} + 3H^{+} + PO_4^{3-} \leftrightarrow Fe_2O_2POOH^{-} + 2H_2O$	(0.63,-0.63,0)	32.88	“
$FeOH^{½-} + 3H^{+} + PO_4^{3-} \leftrightarrow FeOPO_3H_2^{½-} + H_2O$	(0.5,-0.5,0)	30.54	“

[a]The change of charge in the *o*-, *b*- and *d*-planes respectively.

[b]Two numbers indicate binding to high-affinity sites and low-affinity sites, respectively.

Table 4

Data sets and optimization for uranium(VI) complexation to humic and fulvic acid in the Stockholm Humic Model

Code	Reference	No. of data points	log $K_{UO2, m}$	log $K_{UO2, b}$	ΔLK_2	*rmse*	Weight given
FUO_2-03	Glaus et al. (1997)	259	-	-6.99	2.2	0.37	1
FUO_2-04	Glaus et al. (1997)	34	-	-7.23	2	0.22	1
HUO_2-03	Borovec et al. (1979)	27	-	-	-	-	0[a]
HUO_2-04	Czerwinski et al. (1994)	36	0.59	.	2	0.075	1
HUO_2-05	Glaus et al. (1997)	450	-	-6.68	2	0.33	1.5
HUO_2-06	Saito et al. (2004)	10	0.99	-	2	0.046	1
		Weighted average	**0.79**	**-6.93**	**2**		

[a]Optimization of this data set did not yield meaningful results with the SHM, see text