

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/250916325>

Surface complexation modeling of Uranium(VI) sorption on quartz in the presence and absence of alkaline earth metals

Article in *Environmental Earth Sciences* · June 2013

DOI: 10.1007/s12665-013-2579-5

CITATIONS

23

READS

970

3 authors:



Sreejesh M Nair

Technische Universität Bergakademie Freiberg

11 PUBLICATIONS 211 CITATIONS

SEE PROFILE



Lotfollah Karimzadeh

15 PUBLICATIONS 135 CITATIONS

SEE PROFILE



Broder Merkel

Technische Universität Bergakademie Freiberg

342 PUBLICATIONS 4,358 CITATIONS

SEE PROFILE

Surface complexation modeling of Uranium(VI) sorption on quartz in the presence and absence of alkaline earth metals

Sreejesh Nair · Lotfollah Karimzadeh ·
Broder J. Merkel

Received: 13 September 2012 / Accepted: 27 May 2013
© Springer-Verlag Berlin Heidelberg 2013

Abstract Surface complexation models (SCMs) are widely utilized as a tool to study the mobility of radionuclide to the environment. In this study, two SCMs, electrostatic (ES) and non-electrostatic (NES) models are employed in order to simulate the sorption behavior of U(VI) on quartz in the absence of Mg, Ca, and Sr and ES model in the presence of alkaline earth metals. The surface reaction constants ($\log K$) for ES and NES models were fitted to experimental data by coupling PEST with PHREEQC. The SCM prediction of U(VI) sorption on quartz in the absence of alkaline earth metals is in good agreement with the experimental data in the pH range 6.5–9. The estimated $\log K$ values are sensitive to both ES and NES model calculations. In U(VI)-Mg-quartz, U(VI)-Ca-quartz, and U(VI)-Sr-quartz systems, only the ES model shows the general trend of the experimental data. The estimated $\log K$ values are sensitive with respect to the surface reactions. Hence, the ES model is more suitable for model calculations of the U(VI)-Mg-quartz, U(VI)-Ca-quartz, and U(VI)-Sr-quartz systems.

Keywords Uranium · SCM · Alkaline earth uranyl carbonate species · Quartz · Sorption

Introduction

Natural occurrence of uranium in high concentration and its associated environmental contamination is of major

concern in many parts of the world (e.g. Gomes et al. 2011; Kacmaz and Eran Nakoman 2009; Linhoff et al. 2011; Sulekha Rao et al. 2009). Apart from natural occurrence, distribution of uranium to the environment is potentially influenced by human activities such as nuclear industry, uranium mining and milling activities, phosphate fertilizers, coal combustion as well as oil and gas production (Merkel et al. 2002; Merkel and Hasche-Berger 2006, 2008; Campos et al. 2011; Chandrajith et al. 2010; Ricka et al. 2010). Enrichment of radionuclides during certain processes is an important issue and it is known under the term NORM (Naturally Occurring Radioactive Material) (IAEA 2003). One of the important factors which controls the mobility of U(VI) in subsurface is sorption at the solid/solution interface. At circumneutral pH range and in the absence of strong complexing ligands, the mobility of uranium is low due to sorption on mineral surfaces (Barnett et al. 2002; Prikryl et al. 2001; Turner et al. 1996). Batch sorption experiments were widely carried out to study the sorption of U(VI) on different mineral surfaces such as clay minerals (Krepelova et al. 2006; Pabalan and Turner 1996), zeolite (Aytas et al. 2004; Camacho et al. 2010), goethite (Hsi and Langmuir 1985; Missana et al. 2003), TiO_2 (Comarmond et al. 2011; Zhijun et al. 2004), Al_2O_3 (Froideval et al. 2006; Tang and Reeder 2009), etc. under various conditions. Among these, FeOOH is very common in natural sediments and also a very good candidate for sorbing U(VI) for a wide range of pH (Sherman et al. 2008; Guo et al. 2009). Surface complexation models (SCMs) are valuable tools to predict and simulate the sorption behavior and migration of different metal and/or metalloid ions (e.g., Borgnino et al. 2012; Davis et al. 2004; Du et al. 1997). SCM describes a set of adsorption reactions between the aqueous chemical species and the surface of the sorbent, leading to the formation of surface complexes through

S. Nair (✉) · L. Karimzadeh · B. J. Merkel
Department of Hydrogeology, Technical University
Bergakademie Freiberg, Gustav-Zeuner Str. 12,
09599 Freiberg, Germany
e-mail: sreejeshmc@gmail.com

mass action equations and can be readily integrated within reactive transport models (Curtis et al. 2006; Papini et al. 1999). U(VI) sorption on single mineral systems were predicted using SCM giving a good explanation with well-defined systems (Waite et al. 1994, 2000).

Quartz is not a strong sorbent as iron hydroxides, but it is a very common mineral on earth's crust and one of the essential minerals in granite and sandstones. Thus, the sorption on quartz is important to be considered due to its wide occurrence. The sorption of U(VI) on quartz and the importance of SCM have been previously studied (Huber and Lützenkirchen 2009; Prikryl et al. 2001; Stamberg et al. 2003), however, without taking into account the formation of alkaline earth uranyl carbonates. Therefore, more comprehensive studies are needed to understand the sorption behavior of uranium on quartz, especially when rocks such as granite are intended as a host rock for the construction of nuclear waste repositories. Ternary complexes of alkaline earth uranyl carbonates play a significant role in the aqueous speciation of uranium. The formation and existence of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ was first reported by Bernhard et al. (1996). Further studies revealed that alkaline earth metals change the environmental chemistry of uranium at neutral to alkaline pH range by means of complexes such as $\text{M}_2\text{UO}_2(\text{CO}_3)_3^0$ ($\text{M} = \text{Ca}, \text{Ba}$) and $\text{MUO}_2(\text{CO}_3)_3^{2-}$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) (Bernhard et al. 2001; Dong and Brooks 2006, 2008; Geipel et al. 2008; Kalmykov and Choppin 2000).

The focus of our research is to simulate the sorption behavior of U(VI) on quartz using SCM of Dzombak and Morel, a generalized two layer model (GTLM) (Dzombak and Morel 1990) with and without Mg, Ca, and Sr. Two SCMs were employed for the U-quartz system [electrostatic (ES) and non-electrostatic (NES)] and an ES model for U(VI)-Mg-quartz, U(VI)-Ca-quartz, and U(VI)-Sr-quartz systems with smallest possible number of parameters to estimate the surface complexation constants/sorption constants for alkaline earth uranyl carbonate species, which are not published so far.

Materials and methods

Uranium sorption studies

The quartz sand, termed as F32, was used for our experiments and obtained from Quarzwerke Frechen, Germany. The average grain size of the sand is 0.24 mm and a specific surface area of 102 cm²/g. XRD showed that the F32 contains 98.6 ± 0.26 % quartz and 1.4 ± 0.26 % calcite. Further chemical analysis revealed 99.7 % SiO₂, 0.2 % Al₂O₃, and 0.03 % Fe₂O₃. Prior to the experiments, the calcite and iron oxides were removed from quartz sand by

washing with diluted (1:10) 65 % nitric acid for more than a day, then rinsed with deionised water and air-dried. The preparation of reagents and solutions for the U(VI) sorption studies are explained in Nair and Merkel (2011). Five sets of batch experiments were conducted under normal laboratory conditions (temp. 23 ± 1 °C and ambient air) using constant uranium concentration (0.126×10^{-6} M), amount of quartz (10 g) and solution (100 ml) in 150 ml Teflon beakers; (1) only uranium and quartz, (2) uranium, calcium (1×10^{-3} M) and quartz, (3) uranium, strontium (1×10^{-3} M) and quartz, (4) uranium, magnesium (1×10^{-3} M) and quartz, and (5) Only Mg/Ca/Sr (1×10^{-3} M) and quartz. Note that there is no considerable U(VI) sorption on Teflon beakers, which was confirmed by conducting control experiments.

All experiments were conducted with constant ionic strength using 1×10^{-3} M NaHCO₃ and 1.5×10^{-3} M NaCl at a pH range from 6.5 to 9. Low concentration of Mg/Ca/Sr was used to avert the precipitation of mineral phases under alkaline pH conditions. All the experiments were modeled in advance using geochemical speciation code PHREEQC-2 (Parkhurst and Appelo 1999) with the Nuclear Energy Agency thermodynamic database NEA_2007 (Grenthe et al. 2007). The experiments were conducted using a magnetic stirrer (IAK, Germany) for a period of 48 h and samples were collected at constant time intervals to study the kinetics of the U(VI) sorption behavior (data not shown here). Samples were taken after 48 h of the experiment when the sorption of U(VI) on quartz was in equilibrium (Nair and Merkel 2011). The samples were analysed for uranium by differential pulse adsorptive cathodic stripping voltammetry (797 VA Computrace, Metrohm, Switzerland) using a hanging mercury drop electrode (HMDE) as reference electrode (Benedikt 2007). The detection limit of the method is 0.1 µg/L. The percentage of U(VI) sorption on quartz was calculated from the difference between initial and final U(VI) concentration using the Eq. (1):

$$\text{Sorption (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_f are the initial and final U(VI) concentrations in the solution. All the experiments were carried out in duplicates and the percentage of total experimental error is estimated to be less than ±5.

Potentiometric titration

Depending on the pH of the solution, the surface site of the sorbent may exist as protonated (xOH_2^+), deprotonated (xO^-), or neutral (xOH). In order to evaluate the protonation constants for quartz sand F32, acid–base titration was conducted using the instrument “794 Basic Titrino”

(Metrohm AG, Switzerland) with a background of 1.5×10^{-3} M NaCl. A three point calibration was carried out with DIN standard buffer solutions (pH: 4.01, 7.01 and 9.01) before any measurements. The ionic strength of the buffers did not perfectly match the ionic strength of the experiments. But the additional error related to pH measurements as a result of the difference in the ionic strength and the liquid-junction error is likely smaller than other experimental errors. These other errors dominate the uncertainties for the calculated thermodynamic parameters (Illingworth 1981). Thus, standard pH buffers have been used. Initially, the pH of the solution (100 ml) was adjusted to 10 using NaOH (1 M) and adding 10 g of sand to the solution. Titration was performed using HNO₃ (0.01 M) until pH 3 at an interval of 0.5, and a period of 20 min equilibrium time was kept between each pH level. A magnetic stirrer (IAK, Germany) was used to get steady contact of the solution with the solid. The electrodes were checking constantly to avoid the partial clogging of the frit of the electrodes. The surface/sorption reaction constants (log K) for the acid–base reactions was estimated using PHREEQC in combination with the nonlinear parameter estimation programme PEST 11.8 (Doherty 2006).

Model approach and data evaluation

Surface complexation modeling (SCM) has been widely employed (Davis et al. 2004; Stenberg et al. 2003; Zheng et al. 2003) to describe sorption of metals from aqueous solution as a function of pH, solution concentration, ionic strength, etc. It is based on a set of reactions occurring among the aqueous species in the bulk solution and the surface of the sorbent, leading to the formation of surface complexes.

In this study, ES and NES were used as SCM and the surface/sorption constants were derived from the experimental data by coupling PHREEQC with PEST. PEST is commonly used with groundwater flow and transport modeling, and coupling PHREEQC with PEST has been reported by (Appelo et al. 2002; Bachmaf and Merkel 2011; Hull and Schafer 2008). The PHREEQC-PEST approach has the advantage over codes such as FITEQL (Herbelin and Westall 1999) that any number and type of parameters can be optimized as long as the number of parameters to be estimated is less or equal the number of observations. However, in this study only log K values and site density were fitted according to the assumed surface complexation reactions. Quartz is a non-layered and non-porous mineral, and hence the effective surface area is assumed to be equal to the specific surface area. Here, the quartz surface is depicted as single binding site (Q_xOH) and is responsible for all the surface reactions. The log K values for ES and NES models were estimated in the order

of acid–base reactions, U(VI)-quartz system, and U(VI)-Mg/or Ca/or Sr-quartz system. Furthermore, all fitted constants are automatically corrected to zero ionic strength with respect to either ion dissociation theory (e.g., Davies or Wateq–Debye–Hückel equation) or SIT (Specific Interaction Theory). Uncertainties of the estimated constants were not calculated, because the number of observations was not sufficient.

Aqueous speciation calculation of U(VI) was carried out using PHREEQC with NEA_2007 database. In order to calculate the formation of alkaline earth uranyl carbonates, log K values were taken from Dong and Brooks (2006) and added to the NEA_2007 database. Different results can be noticed if the data from Bernhard et al. (2001) and Geipel et al. (2008) are taken in which the formation of zero-valent species for Ca as well as Sr is stated. This issue is discussed in Merkel and Nair (2011). The aforementioned speciation calculation and the log K values are shown in Table 1.

Results and discussion

Aqueous speciation of U(VI)

In the absence of Mg/or Ca/or Sr as well as in equilibrium with the atmospheric CO₂, uranyl carbonate complexes—(UO₂)₂CO₃(OH)₃[−], UO₂(CO₃)₂^{2−} and UO₂(CO₃)₃^{4−}—are the dominant species under neutral to alkaline pH conditions (Fig. 1a). The concentration of U(VI) was kept low (0.126×10^{-6} M), which is comparable to natural conditions, to investigate the impact of alkaline earth elements on the sorption behavior of U(VI). The change in uranium speciation due to Ca, Mg, and Sr is shown in Fig. 1b–e. The effect of Ca on the speciation of U(VI) is illustrated in Fig. 1b, c. Ca₂UO₂(CO₃)₃⁰ as well as CaUO₂(CO₃)₃^{2−} are the most dominant species under alkaline pH conditions and other uranyl carbonate species are less important in this pH range. Here, Fig. 1c depicts the species distribution of U(VI)-Ca system with higher concentration of U(VI)

Table 1 Aqueous speciation of U(VI) with alkaline earth metals and stability constants

Aqueous reactions	log K
1. $2\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$	30.7 ^a
	30.79 ^b
2. $\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{CaUO}_2(\text{CO}_3)_3^{2-}$	27.18 ^a
3. $\text{Mg}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{MgUO}_2(\text{CO}_3)_3^{2-}$	26.11 ^a
4. $\text{Sr}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{SrUO}_2(\text{CO}_3)_3^{2-}$	26.86 ^a
5. $2\text{Sr}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{Sr}_2\text{UO}_2(\text{CO}_3)_3^0$	29.73 ^c

^a Dong and Brooks (2006); ^b Bernhard et al. (2001); ^c Geipel et al. (2008)

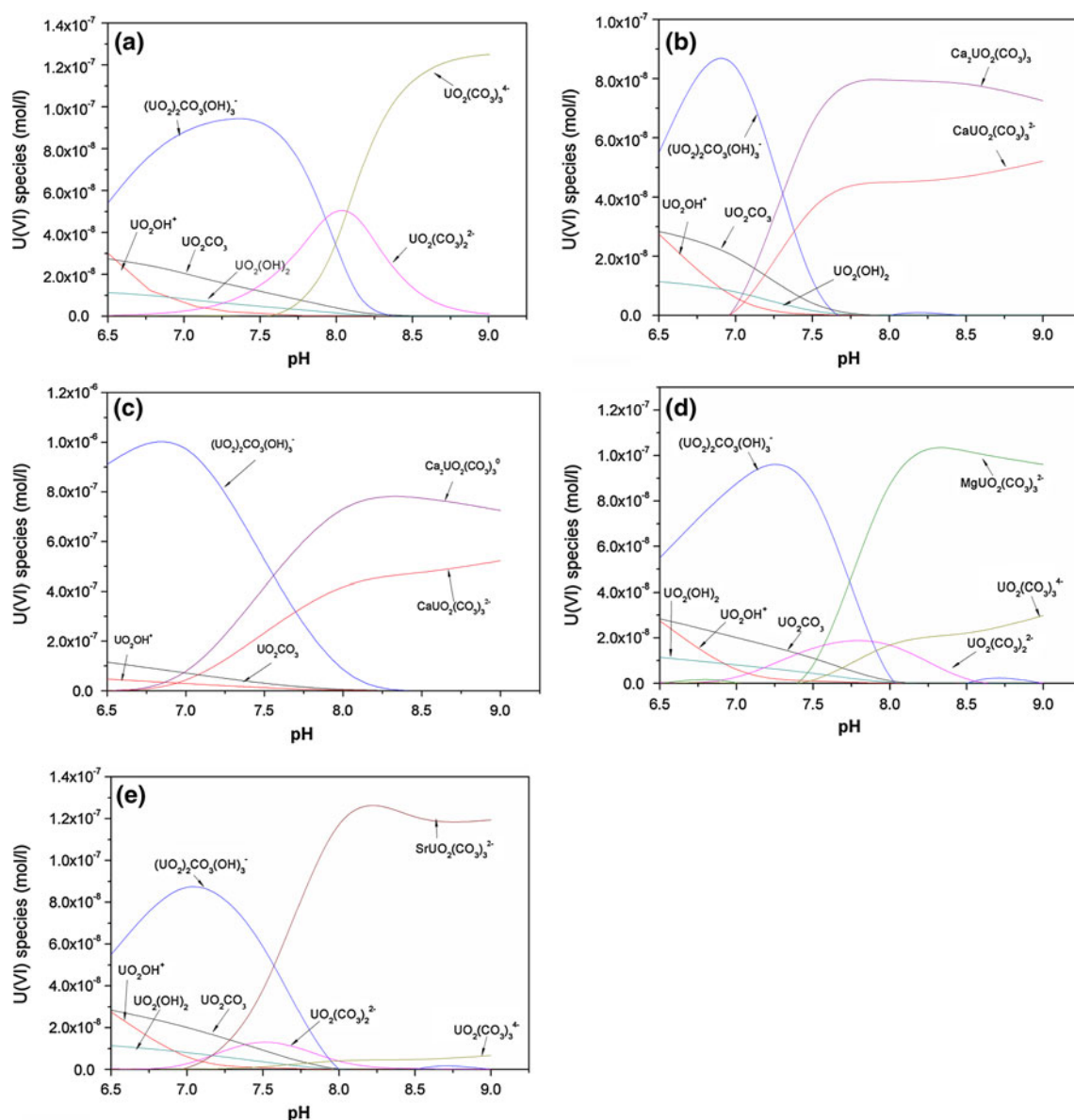


Fig. 1 **a** Calculated U(VI) species distribution (Phreeqc with NEA_2007 data base) in relation to pH (0.126×10^{-6} M U, 1.5×10^{-3} M NaCl, 1×10^{-3} M NaHCO₃, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, after Nair and Merkel 2011), **b** aqueous speciation calculation of Calcium uranyl carbonate species using Phreeqc with NEA_2007 data base and log K from Dong et al. (2006). (0.126×10^{-6} M U, 1×10^{-3} M Ca, 1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, after Nair and Merkel 2011), **c** aqueous speciation calculation of Calcium uranyl carbonate species using Phreeqc with NEA_2007 data base and log K from Dong et al. (2006). (1.26×10^{-6} M U, 1×10^{-3} M Ca,

1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar), **d** aqueous speciation calculation of Magnesium uranyl carbonate species using Phreeqc with NEA_2007 data base and log K from Dong et al. (2006). (0.126×10^{-6} M U, 1×10^{-3} M Mg, 1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, after Nair and Merkel 2011), **e** aqueous speciation calculation of Strontium uranyl carbonate species using Phreeqc with NEA_2007 data base and log K from Dong et al. (2006). (0.126×10^{-6} M U, 1×10^{-3} M Sr, 1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, after Nair and Merkel 2011)

(1.26×10^{-6} M). From Fig. 1d, it is evident that higher concentration, even up to ten times, of U(VI) has not much impact on the speciation of U(VI)-Ca system at alkaline pH range under our experimental conditions. On the other hand, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ is more dominant at near neutral pH condition. Similar observation is found for U(VI)-Mg

and U(VI)-Sr system (data not shown). The change in speciation due to Mg is shown in Fig. 1d. Here, the most dominant species in alkaline pH range is $\text{MgUO}_2(\text{CO}_3)_2^{2-}$. The formation of $\text{Mg}_2\text{UO}_2(\text{CO}_3)_3^0$ was suggested earlier (Dong and Brooks 2006; Geipel et al. 2008), however, without proposing a formation constant. During their

Table 2 Surface reactions of U(VI) species on U(VI)-quartz system and the parameters used for ES model

Surface site density of quartz: 3×10^{-7} mol/m², Surface area: 102 cm² g⁻¹
 Q_{-xOH} silanol surface site

Surface/sorption reactions	log K
1. $Q_{-xOH} = Q_{-xO}^- + H^+$	-6.7
2. $Q_{-xOH} + H^+ = Q_{-xOH_2}^+$	0.4
3. $Q_{-xOH} + UO_2OH^+ = Q_{-xOUO_2OH} + H^+$	1.68
4. $Q_{-xOH} + UO_2(CO_3)_2^{2-} + OH^- = Q_{-xOUO_2(CO_3)_2^{3-}} + H_2O$	20.5
5. $Q_{-xOH} + UO_2(CO_3)_3^{4-} + OH^- = Q_{-xOUO_2(CO_3)_3^{5-}} + H_2O$	25.8
6. $Q_{-xOH} + (UO_2)_2CO_3(OH)_3^- = Q_{-xO(UO_2)_2CO_3(OH)_3^{2-}} + H^+$	5.5
7. $Q_{-xOH} + Na^+ = Q_{-xONa} + H^+$	-9.0

Table 3 Surface reactions of U(VI) species on U(VI)-quartz system and the parameters used for NES model

Surface site density of quartz: 3×10^{-7} mol/m², Surface area: 102 cm² g⁻¹
 Q_{-xOH} silanol surface site

Surface/sorption reactions	log K
1. $Q_{-xOH} = Q_{-xO}^- + H^+$	-5.06
2. $Q_{-xOH} + H^+ = Q_{-xOH_2}^+$	-2.4
3. $Q_{-xOH} + UO_2OH^+ = Q_{-xOUO_2OH} + H^+$	-1.0
4. $Q_{-xOH} + UO_2(CO_3)_2^{2-} + OH^- = Q_{-xOUO_2(CO_3)_2^{3-}} + H_2O$	16.3
5. $Q_{-xOH} + UO_2(CO_3)_3^{4-} + OH^- = Q_{-xOUO_2(CO_3)_3^{5-}} + H_2O$	17.2
6. $Q_{-xOH} + (UO_2)_2CO_3(OH)_3^- = Q_{-xO(UO_2)_2CO_3(OH)_3^{2-}} + H^+$	1.42
7. $Q_{-xOH} + Na^+ = Q_{-xONa} + H^+$	-5.32

investigation, possible mineral precipitation was reported especially at higher concentrations of Mg²⁺ ions. Due to the uncertainty about the existence and the lack of log K, Mg₂UO₂(CO₃)₃⁰ complex was not taken into account for speciation calculation in this study. However, note that the present work gives strong indication for the formation of Mg₂UO₂(CO₃)₃⁰ from the reduction of U(VI) sorption on quartz, i.e., the zero-valent alkaline earth uranyl carbonate species shows less or no sorption on quartz. Figure 1e shows the change in U(VI) speciation by Sr and the most dominant species under neutral to alkaline pH range is SrUO₂(CO₃)₃²⁻ if the proposed Sr₂UO₂(CO₃)₃⁰ is not taken into account.

SCM for U(VI)—quartz system

The GTLM used for U(VI)-quartz system is based on the U(VI) sorption experiments conducted in the absence of alkaline earth elements. Equilibrium constants for acid-base surface reactions of silanol groups for equations 1 and 2 in Tables 2 and 3 were estimated independently for ES as well as NES from the titration data. Further surface reactions and the calculated log K values of ES and NES model for the U(VI)-quartz system are summarized in Tables 2 and 3. The sorption of U(VI) on quartz is independent of pH (6.5–9) and about 90 % of U(VI) is sorbed on quartz. Very low concentration (30 µg/L) of uranium and rather high ratio of anionic uranium species to OH⁻ seem to foster the quartz to sorb nearly all uranium at neutral to alkaline conditions (pH 6.5–9). This corresponds to our observation that considerable U(VI) sorption occurred on both glass

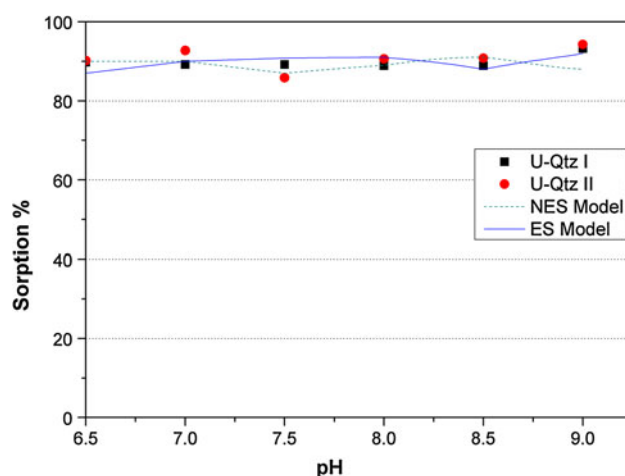


Fig. 2 ES and NES model simulations of U(VI) sorption on quartz as a function of pH (0.126×10^{-6} M U, 1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, U-Qtz I and U-Qtz II refer duplicate measurements)

wares and polyethylene vessels, regardless of pH. On contrary, experiments with 100 µg/L U(VI) and 100 g/L quartz sand for a wider range of pH (data not shown here) revealed a decrease in uranium sorption for pH 8 and 9.

The SCM prediction of U(VI) sorption on quartz in the absence of alkaline earth metals is in good agreement with the experimental data in the pH range 6.5–9 (Fig. 2). In the absence of Mg/Ca/Sr, the most dominant U(VI) species are (UO₂)₂CO₃(OH)₃³⁻, UO₂(CO₃)₂²⁻ as well as UO₂(CO₃)₃⁴⁻, and hence the surface complexation reactions were carried out with respect to the speciation of U(VI) in solution

Table 4 Surface reactions of U(VI) species on U(VI)-Mg-quartz, U(VI)-Ca-quartz, and U(VI)-Sr-quartz systems and the parameters estimated for ES model

Surface/sorption reactions	log K
1. $Q_xOH + Mg^{2+} = Q_xOMg^+ + H^+$	2.6
2. $Q_xOH + MgUO_2(CO_3)_3^{3-} + OH^- = Q_xOMgUO_2(CO_3)_3^{3-} + H_2O$	21.30
3. $Q_xOH + Ca^{2+} = Q_xOCa^+ + H^+$	3.05
4. $Q_xOH + CaUO_2(CO_3)_3^{3-} + OH^- = Q_xOCaUO_2(CO_3)_3^{3-} + H_2O$	22.98
5. $Q_xOH + Sr^{2+} = Q_xOSr^+ + H^+$	1.00
6. $Q_xOH + SrUO_2(CO_3)_3^{3-} + OH^- = Q_xOSrUO_2(CO_3)_3^{3-} + H_2O$	21.70

Surface site density of quartz: 3×10^{-7} mol/m², Surface area: 102 cm² g⁻¹

Q_xOH silanol surface site

(Tables 2 and 3). The estimated sorption reaction constants are with respect to the speciation reactions, which lead to chemical equilibrium model and rely on thermodynamic database used to depict uranium system. Thermodynamic databases can, however, possess uncertainties caused by erroneous derivation of stability constants due to experimental or measurement error. These uncertainties have major impact on model simulations (Meinrath et al. 2004; Nitzsche et al. 2000) and can be predicted using sophisticated program such as LJUNGSKILE (Ekberg et al. 2002; Ödegaard-Jensen et al. 2004). The distribution of U(VI) species depends highly on the thermodynamic database used for calculation. If we consider the ternary $(UO_2)_2CO_3(OH)_3^-$ species as an example, databases such as Minteq.v4.dat and Wateq4f.dat deny the formation of the species whereas NEA_2007.dat, LLNL.dat, etc. show the formation of the same. The uncertainties in the formation of different uranium species and the difference between thermodynamic databases are discussed in Merkel (2011). From Fig. 2, it is evident that both model calculations were distinct and able to represent the U(VI) sorption on quartz. The equilibrium constants (log K) determined by PEST—PHREEQC approach is sensitive with respect to both models, i.e., ES and NES.

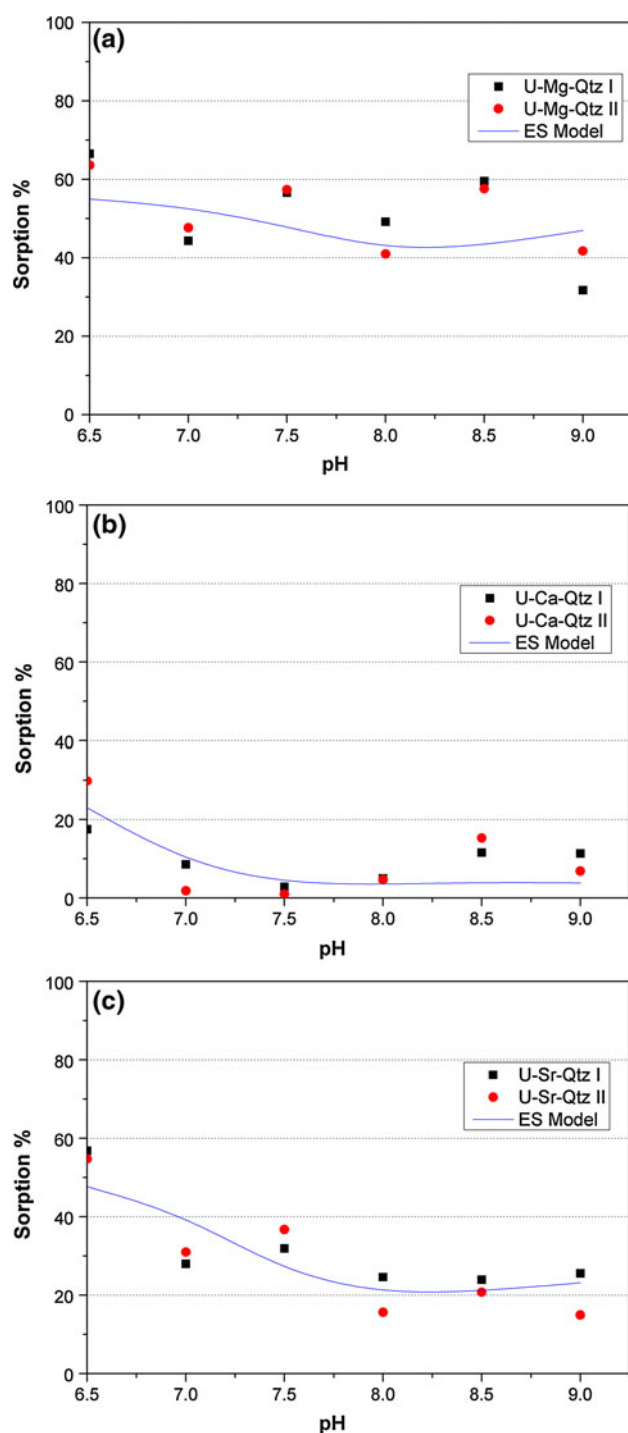
SCM for U(VI)—Mg/or/Ca/or/Sr-Quartz System

ES model is used to simulate the U(VI)—Mg—Quartz, U(VI)—Ca—Quartz, and U(VI)—Sr—Quartz systems, and the respective surface reactions are shown in Tables 2 and 4. During the initial stage of model simulations, all U(VI) species (major and minor) were incorporated within the model. But some of the reactions were not sensitive with respect to the surface reactions. Hence, all nonsensitive reactions were removed from the model. Table 4 represents the calculated log K values for alkaline earth elements as well as for alkaline earth uranyl carbonate species. The role of other main uranyl carbonate species (see “SCM for U(VI)—quartz system”) is particularly predominant in

U(VI)—Mg/or/Sr-Quartz system. These uranyl carbonate species also play a major role in the sorption behavior of U(VI), especially up to pH 7.5. Result of ES model for U(VI) sorption on quartz in the presence of Mg is shown in (Fig. 3a). The model is able to follow the general trend; however, it was not able to follow the oscillations of the experimental data. The estimated log K values for U(VI)—Mg—Quartz are sensitive with respect to the surface reactions under our experimental conditions and are suitable for model calculations. ES model for the U(VI)—Ca—Quartz system is shown in the Fig. 3b. From Fig. 1c, it is evident that most of the uranium in the solution is in the form of zero-valent calcium uranyl carbonate species above pH 7.3 and the ternary species $(UO_2)_2CO_3(OH)_3^-$ below pH 7.3. There is still some doubt in the correctness of certain thermodynamic data of uranium (Grenthe and Lagerman 1991; Merkel 2011). If the log_k of $(UO_2)_2CO_3(OH)_3^-$ is overestimated, then it is likely that the ternary $Me_2UO_2(CO_3)_3^0$ will be dominant over the whole pH range of 6.5–9.0. We do see this effect not only for Ca, but also for Mg and Sr. This is a clear indication that a zero-valent ternary complex is formed for Ca as well as Sr and Mg. The model is showing the general trend of the experimental results, but at pH 7 and 8.5, the residuals are around 10 %. The ES model for the sorption of U(VI) on quartz in the presence of Sr is shown in Fig. 3c. Even though the simulation is in good agreement with the measured data, the coincidence for pH 6.5 and 7.0 could be better. However, the overall average difference between the experimental result and ES model calculation is less than 10 %.

Conclusions

Results of SCMs (ES & NES) are in good agreement with the experimental data for U(VI) sorption on quartz in the absence of alkaline earth metals. The log K values estimated using PEST and PHREEQC are sensitive with respect to both model calculations. The sorption of U(VI)



on quartz in the presence of alkaline earth metals is simulated with ES model. In the presence of Mg, the ES model is able to show the general trend of the experimental data. A similar result was obtained when Mg was replaced with Ca and Sr. Therefore, the ES model is more suitable to model the sorption behavior of U(VI) on quartz in the presence of Mg/Ca and/or Sr. Sorption constants for alkaline earth uranyl carbonates on quartz are not reported in

Fig. 3 a ES model simulation of U(VI) sorption on quartz in the presence of Mg as a function of pH (0.126×10^{-6} M U, 1×10^{-3} M Mg, 1×10^{-3} M NaHCO_3 , 1.5×10^{-3} M NaCl, temp: 23°C , pCO_2 : $10^{-3.5}$ bar, U-Mg-Qtz I and U-Mg-Qtz II refer duplicate measurements), b ES model simulation of U(VI) sorption on quartz in the presence of Ca as a function of pH (0.126×10^{-6} M U, 1×10^{-3} M Ca, 1×10^{-3} M NaHCO_3 , 1.5×10^{-3} M NaCl, temp: 23°C , pCO_2 : $10^{-3.5}$ bar, U-Ca-Qtz I and U-Ca-Qtz II refer duplicate measurements), c ES model simulation of U(VI) sorption on quartz in the presence of Sr as a function of pH (0.126×10^{-6} M U, 1×10^{-3} M Sr, 1×10^{-3} M NaHCO_3 , 1.5×10^{-3} M NaCl, temp: 23°C , pCO_2 : $10^{-3.5}$ bar, U-Sr-Qtz I and U-Sr-Qtz II refer duplicate measurements)

literature so far. Thus, it is important to include the above mentioned sorption constants in reactive transport models to simulate the radionuclide migration in the environment as well as for the performance assessment of nuclear waste disposal sites.

References

- Appelo CAJ, Van der Weiden MJJ, Tournassat C, Charlet L (2002) Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ Sci Technol* 36(14):3096–3103
- Aytas SM, Akyil S, Eral M (2004) Adsorption and thermodynamic behavior of uranium on natural zeolite. *J Radioanal Nucl Chem* 260(1):119–125
- Bachmaf S, Merkel BJ (2011) Sorption of Uranium(VI) at the clay mineral-water interface. *Environ Earth Sci* 63(5):925–934
- Barnett MO, Jardine PM, Brooks SC (2002) U(VI) adsorption to heterogeneous subsurface media: application of a surface complexation model. *Environ Sci Technol* 36(5):937–942
- Benedikt G (2007) 797 VA Computrace—voltammetric trace determination of Uranium(VI) in drinking and mineral water. *Metrohm Information Issue 2/2007*. Metrohm Ltd., CH-9101 Herisau, Switzerland, p 36
- Bernhard G, Geipel G, Brendler V, Nitsche H (1996) Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). *Radiochim Acta* 74:87–91
- Bernhard G, Geipel G, Reich T, Brendler V, Amayri S, Nitsche H (2001) Uranyl(VI) carbonate complex formation: validation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq.) species. *Radiochim Acta* 89(8):511–518
- Borgnino L, Pauli C, Depetris P (2012) Arsenate adsorption at the sediment-water interface: sorption experiments and modelling. *Environ Earth Sci* 65(2):441–451
- Camacho LM, Deng SG, Parra RR (2010) Uranium removal from groundwater by natural clinoptilolite zeolite: effects of pH and initial feed concentration. *J Hazard Mater* 175(1–3):393–398
- Campos M, Azevedo H, Nascimento M, Roque Cu, Rodger S (2011) Environmental assessment of water from a uranium mine (Caldas, Minas Gerais State, Brazil) in a decommissioning operation. *Environ Earth Sci* 62(4):857–863
- Chandrajith R, Seneviratna S, Wickramaarachchi K, Attanayake T, Aturaliya TNC, Dissanayake CB (2010) Natural radionuclides and trace elements in rice field soils in relation to fertilizer application: study of a chronic kidney disease area in Sri Lanka. *Environ Earth Sci* 60(1):193–201

- Comarmond MJ, Payne TE, Harrison JJ, Thiruvoth S, Wong HK, Aughterson RD, Lumpkin GR, Muller K, Foerstendorf H (2011) Uranium sorption on various forms of titanium dioxide— influence of surface area, surface charge, and impurities. *Environ Sci Technol* 45(13):5536–5542
- Curtis GP, Davis JA, Naftz DL (2006) Simulation of reactive transport of Uranium(VI) in groundwater with variable chemical conditions. *Water Res* 42(4). doi:[10.1029/2005WR003979](https://doi.org/10.1029/2005WR003979)
- Davis JA, Meece DE, Kohler M, Curtis GP (2004) Approaches to surface complexation modeling of Uranium(VI) adsorption on aquifer sediments. *Geochim Cosmochim Acta* 68(18):3621–3641
- Doherty J (2006) PEST, Model-Independent Parameter Estimation, User Manual, 5th edn. Watermark Numerical Computing, Brisbane
- Dong WM, Brooks SC (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(15):4689–4695
- Dong WM, Brooks SC (2008) Formation of aqueous $MgUO_2(CO_3)_3^{2-}$ complex and uranium anion exchange mechanism onto an exchange resin. *Environ Sci Technol* 42(6):1979–1983
- Du Q, Sun Z, Forsling W, Tang H (1997) Adsorption of copper at aqueous illite surfaces. *J Colloid Interface Sci* 187(1):232
- Dzombak DA, Morel FM (1990) Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons, New York
- Ekberg C, Ödegaard-Jensen A, Meinrath G (2002) LJUNGSKILE 1.0: A computer program for investigation of uncertainties in chemical speciation. ISRNSKI-R-03/03-SE
- Froideval A, Del Nero M, Gaillard C, Barillon R, Rossini I, Hazemann JL (2006) Uranyl sorption species at low coverage on Al-hydroxide: TRLFS and XAFS studies. *Geochim Cosmochim Acta* 70(21):5270–5284
- Geipel G, Amayri S, Bernhard G (2008) Mixed complexes of alkaline earth uranyl carbonates: a laser-induced time-resolved fluorescence spectroscopic study. *Spectrochim Acta A Mol Biomol Spectrosc* 71(1):53–58
- Gomes MEP, Neves LJPF, Coelho F, Carvalho A, Sousa M, Pereira AJSC (2011) Geochemistry of granites and metasediments of the urban area of Vila Real (northern Portugal) and correlative radon risk. *Environ Earth Sci* 64(2):497–502
- Grenthe I, Lagerman B (1991) Studies on metal carbonate equilibria. 22. A coulometric study of the Uranium(VI)-carbonate system, the composition of the mixed hydroxide carbonate species. *Acta Chem Scand* 45(2):122–128
- Grenthe I, Fuger J, Konings R, Lemire RJ, Muller AB, Wanner J (2007) The Chemical Thermodynamics of Uranium. Elsevier, New York
- Guo ZJ, Li Y, Wu WS (2009) Sorption of U(VI) on goethite: effects of pH, ionic strength, phosphate, carbonate and fulvic acid. *Appl Radiat Isot* 67(6):996–1000
- Herbelin AL, Westall JC (1999) FITEQL 4.0: A computer programme for determination of chemical equilibrium constants from experimental data. Report 99-01. Corvallis, Oregon: Department of Chemistry, Oregon State University
- Hsi CKD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxides: application of the surface complexation site-binding model. *Geochim Cosmochim Acta* 49(9):1931–1941
- Huber F, Lützenkirchen J (2009) Uranyl retention on quartz: new experimental data and blind prediction using an existing surface complexation model. *Aquat Geochem* 15(3):443–456
- Hull LC, Schafer AL (2008) Accelerated transport of Sr-90 following a release of high ionic strength solution in vadose zone sediments. *J Contam Hydrol* 97(3–4):135–157
- IAEA (2003) Radiation protection and the management of radioactive waste in the oil and gas industry. Safety Report Series No 34. International Atomic Energy Agency
- Illingworth JA (1981) A common source of error in pH measurements. *Biochem J* 195(1):259–262
- Kacmaz H, Eran Nakoman M (2009) Hydrochemical characteristics of shallow groundwater in aquifer containing uranyl phosphate minerals, in the Koprubasi (Manisa) area, Turkey. *Environ Earth Sci* 59(2):449–457
- Kalmykov SN, Choppin GR (2000) Mixed $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complex formation at different ionic strengths. *Radiochim Acta* 88(9–11):603–606
- Krepelova A, Sachs S, Bernhard G (2006) Uranium(VI) sorption onto kaolinite in the presence and absence of humic acid. *Radiochim Acta* 94(12):825–833
- Linhoff B, Bennett P, Puntsgag T, Gerel O (2011) Geochemical evolution of uraniferous soda lakes in Eastern Mongolia. *Environ Earth Sci* 62(1):171–183
- Meinrath G, Merkel B, Ödegaard-Jensen A, Ekberg C (2004) Sorption of iron on surfaces: modelling, data evaluation, and measurement uncertainty. *Acta Hydrochim Hydrobiol* 32(2):154
- Merkel BJ (2011) Thermodynamic Data Dilemma. In: Merkel BJ, Schipek M (eds) The New Uranium Mining Boom: Challenge and lessons learned. Springer, Berlin Heidelberg, pp 627–633. doi:[10.1007/978-3-642-22122-4](https://doi.org/10.1007/978-3-642-22122-4)
- Merkel BJ, Hasche-Berger A (2006) Uranium in the environment— mining impact and consequences. Uranium mining and hydrogeology. Springer, Berlin
- Merkel BJ, Hasche-Berger A (2008) Uranium, Mining and Hydrogeology. Fifth International Conference Uranium Mining and Hydrogeology (UMH V). Springer, Berlin
- Merkel BJ, Nair S (2011) Impact of speciation and Sorption on migration of uranium in groundwater. In: Paul M (ed) Nachhaltigkeit und Langzeitaspekte bei der Sanierung von Uranbergbau und Aufbereitungsstandorten. Proceedings des Internationalen Bergbausymposiums WISSYM_2011. Wismut GmbH, Chemnitz, Germany, pp 269–274
- Merkel BJ, Planer-Friedrich B, Wolkersdorfer C (2002) Uranium in the Aquatic Environment. International Conference Uranium Mining and Hydrogeology III and the International Mine Water Association Symposium. Springer, Berlin
- Missana T, Garcia-Gutierrez M, Maffiotte C (2003) Experimental and modeling study of the Uranium(VI) sorption on goethite. *J Colloid Interface Sci* 260(2):291–301
- Nair S, Merkel BJ (2011) Impact of alkaline earth metals on aqueous speciation of Uranium(VI) and sorption on quartz. *Aquat Geochem* 17(3):209–219
- Nitzsche O, Meinrath G, Merkel B (2000) Database uncertainty as a limiting factor in reactive transport prognosis. *J Contam Hydrol* 44(3–4):223
- Ödegaard-Jensen A, Ekberg C, Meinrath G (2004) LJUNGSKILE: a program for assessing uncertainties in speciation calculations. *Talanta* 63(4):907
- Pabalan RT, Turner DR (1996) Uranium(6+) sorption on montmorillonite: experimental and surface complexation modeling study. *Aquat Geochem* 2(3):203–226
- Papini MP, Kahie YD, Troia B, Majone M (1999) Adsorption of lead at variable pH onto a natural porous medium: modeling of batch and column experiments. *Environ Sci Technol* 33(24):4457–4464
- Parkhurst DL, Appelo CA (1999) User's Guide to PHREEQC (version 2). A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculation. USGS, Water Resources Investigation Report pp 99–4259
- Prikryl JD, Jain A, Turner DR, Pabalan RT (2001) Uranium(VI) sorption behavior on silicate mineral mixtures. *J Contam Hydrol* 47(2–4):241–253

- Ricka A, Kuchovsky T, Sracek O, Zeman J (2010) Determination of potential mine water discharge zones in crystalline rocks at Rozna, Czech Republic. *Environ Earth Sci* 60(6):1201–1213
- Sherman DM, Peacock CL, Hubbard CG (2008) Surface complexation of U(VI) on goethite (α -FeOOH). *Geochim Cosmochim Acta* 72(2):298–310
- Stamberg K, Venkatesan KA, Rao PRV (2003) Surface complexation modeling of uranyl ion sorption on mesoporous silica. *Coll Surf A Physicochem Eng Aspects* 221(1–3):149–162
- Sulekha Rao N, Sengupta D, Guin R, Saha SK (2009) Natural radioactivity measurements in beach sand along southern coast of Orissa, eastern India. *Environ Earth Sci* 59(3):593–601
- Tang YZ, Reeder RJ (2009) Uranyl and arsenate co-sorption on aluminum oxide surface. *Geochim Cosmochim Acta* 73(10):2727–2743
- Turner GD, Zachara JM, McKinley JP, Smith SC (1996) Surface-charge properties and UO_2^{2+} adsorption of a subsurface smectite. *Geochim Cosmochim Acta* 60(18):3399–3414
- Waite TD, Davis JA, Payne TE, Waychunas GA, Xu N (1994) Uranium(VI) adsorption to ferrihydrite: application of a surface complexation model. *Geochim Cosmochim Acta* 58(24):5465–5478
- Waite TD, Davis JA, Fenton BR, Payne TE (2000) Approaches to modelling Uranium(VI) adsorption on natural mineral assemblages. *Radiochim Acta* 88(9–11):687–693
- Zheng ZP, Tokunaga TK, Wan JM (2003) Influence of calcium carbonate on U(VI) sorption to soils. *Environ Sci Technol* 37(24):5603–5608
- Zhijun G, Zhaoyun Y, Zuyi T (2004) Sorption of uranyl ions on TiO_2 : effects of contact time, ionic strength, concentration and humic substance. *J Radioanal Nucl Chem* 261(1):157–162