

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
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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 HNO_3 (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 CO_2 , uranyl carbonate complexes— $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ —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. $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ as well as $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ 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)

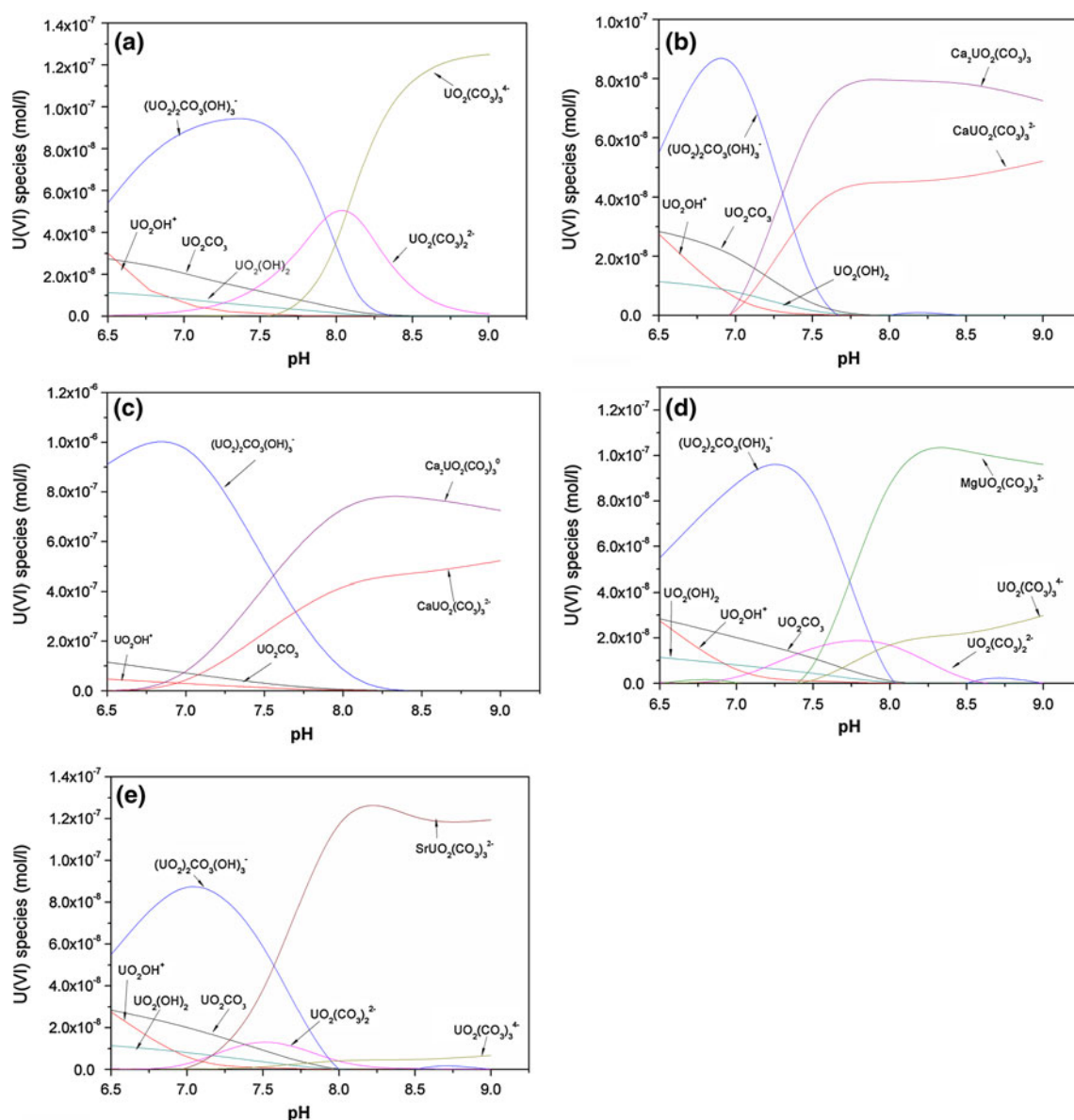


Fig. 1 **a** Calculated U(VI) species distribution (Phreeqc with NEA_2007 data base) in relation to pH (0.126×10^{-6} M U, 1.5×10^{-3} M NaCl, 1×10^{-3} M NaHCO₃, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, after Nair and Merkel 2011), **b** aqueous speciation calculation of Calcium uranyl carbonate species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

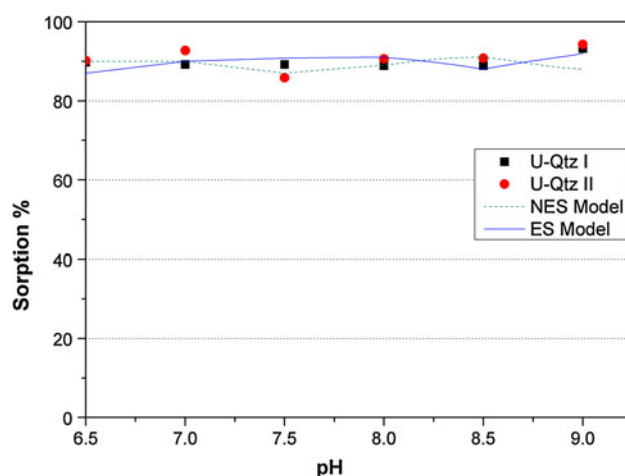


Fig. 2 ES and NES model simulations of U(VI) sorption on quartz as a function of pH (0.126×10^{-6} M U, 1×10^{-3} M NaHCO₃, 1.5×10^{-3} M NaCl, temp: 23 °C, pCO₂: $10^{-3.5}$ bar, U-Qtz I and U-Qtz II refer duplicate measurements)

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.

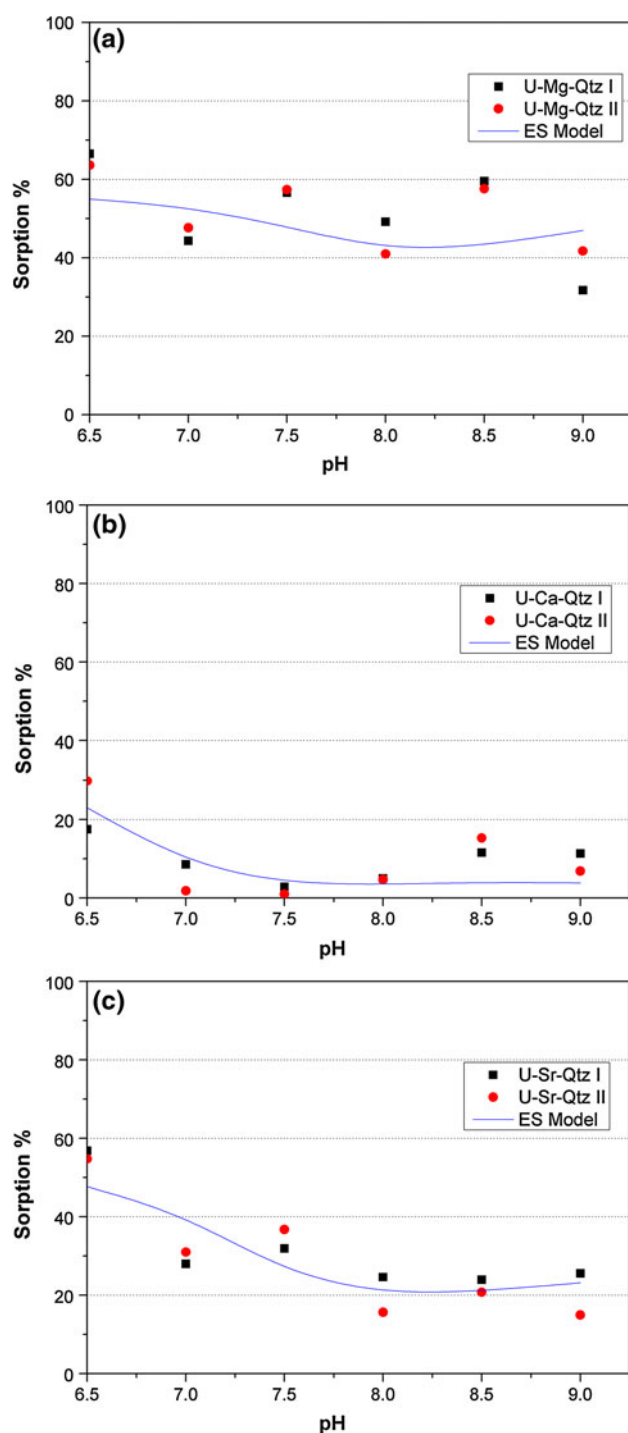
SCM for U(VI)—Mg/or/Ca/or/Sr-Quartz System

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.

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