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Database uncertainty as a limiting factor in reactive transport prognosis

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Abstract

The effect of uncertainties in thermodynamic databases on prediction performances of reactive transport modeling of uranium (VI) is investigated with a Monte Carlo approach using the transport code TReaC. TReaC couples the transport model to the speciation code PHREEQC by a particle tracking method. A speciation example is given to illustrate the effect of uncertainty in thermodynamic data on the predicted solution composition. The transport calculations consequently show the prediction uncertainty resulting from uncertainty in thermodynamic data. A conceptually simple scenario of elution of uranium from a sand column is used as an illustrating example. Two different cases are investigated: a carbonate-enriched drinking water and an acid mine water associated with uranium mine remediation problems. Due to the uncertainty in the relative amount of positively charged and neutral solution species, the uncertainty in the thermodynamic data also infers uncertainty in the retardation behavior. The carbonated water system shows the largest uncertainties in speciation calculation. Therefore, the model predictions of total uranium solubility have a broad range. The effect of data uncertainty in transport prediction is further illustrated by a prediction of the time when eluted uranium from the column exceeds a threshold value. All of these Monte Carlo transport calculations consume large amounts of computing time.

Keywords: Reactive transport modeling; Uncertainty analysis; Thermodynamic database; Uranium; Monte Carlo simulation

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1. Introduction

Understanding of the subsurface geochemical processes is restricted by the generally limited number of available field sites. Usually, the data can be obtained from a limited number of wells or boreholes at locations not chosen according to the needs of the investigator. Prognosis of the future evolvement of the site on the basis of such incomplete and often sparse data requires the generation of a model as close as possible to reality. Environmental prognosis by reactive transport simulation has become a widely accepted tool for the numerical simulation of such processes with the aim of establishing a plausible model for processes involving ground water or ground water/rock interactions.

The rapid increase of cheap computing power has further stimulated this development. Reactive transport modeling is an interdisciplinary activity involving, among others, numerical mathematics, geology, hydrology and chemistry. A reactive transport code accepts field data input from geology and hydrogeology, fundamental thermodynamic data on the relevant chemical transformations and uses numerical algorithms to propose a model that is optimal under the constraints imposed. Deep disposal of nuclear wastes and remediation procedures for sites contaminated by uranium mining activities are examples where reactive transport modeling plays an essential role in performance assessment (Helton, 1994).

Computers produce deterministic results and, hence, some recent concern with computer model-based predictions focuses on the issue of uncertainty. As a matter of fact, a complex computer model is affected by a series of nuisance effects (Ekberg, 1999): numerical problems of the code itself, incomplete understanding of the fundamental physical phenomena, lacking precision or reproducibility of the geological and hydrogeological input data, missing data and experimental uncertainties in the thermodynamic data, etc. On the other hand, computer simulations allow a more detailed understanding of the influences and magnitudes of different nuisance effects.

Quality assessment has become an important aspect in aquatic chemistry and chemical speciation (Szunpar and Lobinski, 1999; Ellison et al., 1997; Cortez, 1995; Staats, 1995). Thermodynamic data is put into databases for geochemical reactive transport modeling and applied under circumstances where a much higher demand for accuracy and precision is needed than is usually intended. It should be noted that thermodynamic data on chemical reactions had been collected in the past with the purpose of revealing relationships among the elements and compounds. These studies had been highly successful — giving rise, for example, to linear free energy relationships (Pettit and Brookes, 1977) or the Pearson concept of hard and soft acids and bases (Pearson, 1973). Application of these data in geochemical databases, however, requires that the data not only indicate a correct relative relationship with other data for similar reactions, but also that the thermodynamic data is as close as possible to the true, but generally unknown value of a certain parameter. The importance of a quantitative estimate of uncertainty in analytical data — including thermodynamic data of aqueous solution species with relevance in geochemical modeling — has resulted in recommendations by international bodies of metrology (ISO/IUPAC/BIPM, 1993).

On the other hand, there is currently relatively little information on the impact of uncertainty in chemical data on the predictive power of a reactive transport model, even though the need for such investigations has become apparent (Ekberg et al., 1997). In the following, we describe an approach to this important aspect of geochemical reactive transport modeling that is made within the frame work of remediation of uranium mining area decontamination (Merkel and Helling, 1998).

2. Methodology

The change of groundwater constituent concentrations during transport in an aquifer may be described by

$$\frac{\partial C_1}{\partial t} = -u\nabla C_i + \nabla(D_\mathrm{d} + D_\mathrm{m})\nabla C_i + R_{C_i}$$

with t = time; D_m = molecular coefficient of diffusion; D_d = hydrodynamic dispersion; C_i = concentration of species i; U = average interstitial velocity; R_{C_i} = source or sink term of species i due to reactions.

This equation turns out to be a partial differential equation of 2nd order. It is inhomogenous and of mixed hyperbolic–parabolic type. Finite difference (FD) and finite element (FE) techniques may be used to solve the equations, although numerical dispersion might be a big problem. Thus, spatial and time discretizations are a big concern (Häfner et al., 1992). In contrast, an algorithm that uses the well-known random walk approach is considerably time-consuming but still more or less free from numerical dispersion. Another advantage of the random walk approach is that water transport and chemical reaction are solved separately and thus standard thermodynamical codes (e.g., PHREEQC) may be used. Using FD or FE techniques, on the contrary, requires that the set of equations be solved once for each species. Reactions of species with other species in the systems are difficult to include.

Following this concept, Walter et al. (1994) developed a two-dimensional model for the simulation of transport of thermodynamically reacting contaminants in groundwater by coupling a proven transport model to a comprehensive geochemical equilibrium model (MINTEQ). Because of the local equilibrium assumption, the coupling between the physical and chemical modules is linear, although the equilibrium chemistry itself is nonlinear. As a result, a fast sequential physical–chemical solution approach can be used.

By a similar concept using the standard software MODFLOW and PHREEQC the code TReaC is created (Nitzsche, 1997). TReaC solves any reactive ground water problem that might be simulated through PHREEQC. In addition, the reactive decay of uranium and its major daughter isotopes is incorporated into TReaC as well as a simple approach to simulate double porosity aquifer materials. Advective steps are computed using the underlying velocity field. The flow field for which the modeling prediction is performed is subdivided into a number of cells. The velocities for particles in a cell are calculated by linear (one-dimensional), bilinear (two-dimensional) or trilinear (three-dimensional) interpolations to the velocities at the nodes. In the subsequent step, dispersion is calculated from a random vector with mean Zero and variances derived from the dispersion tensor. The third step is a speciation step where the chemical reactions are computed from PHREEQC code. Finally, species concentrations for the particles are updated on basis of the speciation step. A similar approach is reported by Fabriol et al. (1993). Verifications of the code are also given in Nitzsche (1997). TReaC is implemented on an IBM Risc 6000 workstation.

Interaction processes with a solid matrix (sorption) are often described by an isotherm where an equilibrium is assumed between the concentration of solute i in solution and the amount of substance i sorbed per unit area of matrix surface. There are both linear (e.g., Henry isotherms) or non-linear isotherms (Freundlich or Langmuir isotherms). Isotherms, however, are lumped-parameter approaches. Surface complexation models are more flexible and, hopefully, closer to the actual physical processes. Nevertheless, surface complexation models consider reversible reactions between surface sites and solutes (Appelo and Postma, 1993; Dzombak and Morel, 1990; Rundberg et al., 1994), while experimental investigations indicate that processes are more complicated and partly irreversible (e.g., (Piriou et al., 1997)). Hence, TReaC accepts the approach implemented in PHREEQC with reactions constants given in the respective default database (Parkhurst, 1995). PHREEQC defines a theoretical 'exchange species' X with a limited exchange capacity. The limit may be set by the user — for example, on the basis of experimentally available site-specific cation exchange capacities (CEC). Since exchange constants may be defined for each solute species with several exchange species, speciation in solution may have a direct influence on exchange behavior prediction. This is particularly so in the change from a predominantly cationic solution species to conditions where neutral species dominate will largely suppress ion exchange and sorption with the solid matrix surface. Therefore, not only ion exchange constants but also thermodynamic formation constants and their uncertainties will influence the transport behavior prediction during simulation.

In the approach we have taken here, the geological setting is kept as simple as possible in order to concentrate on effects from varying thermodynamic data. Hence, transport of uranium through a sand column with a length of 40 cm, a cross-section of 70 cm^2, effective porosity $\eta = 0.32$, a vertical plug flow of 0.14 cm min^{-1} and a dispersivity $\alpha_1 = 1.0$ cm is assumed. Courant number is 0.2. The column is divided into 35 compartments with the total amount of uranium being defined by the capacity of the first compartment, consisting of both uranium in solution and the sorbed uranium. Tests with varying time step widths, compartment numbers and amount of particles were done. The selected conditions are chosen to avoid significant variance contributions from their influence.

The background of this study is given by the requirements for remediation of sites contaminated due to uranium mining activities (Meinrath et al., 1999a; Merkel and Helling, 1998; Schreyer, 1996). Legislation requires that consequences of different remediation strategies are assessed before an action is actually taken (Meinrath et al., 2000a). Hence, uranium has been selected as the element of interest. The WATEQ 4F thermodynamic database which comes with the PHREEQC code has been used with the following modifications. Thermodynamic data of U(VI) hydrolysis, carbonate and sulfate species have been supplemented according to recent chemical investigations

Table 1
Reactions and formations constants for U(VI) hydrolysis and carbonato species at $I = 0$ and 25°C

Reaction	log K	σ	Reference
$UO_2^{2+} + H_2O \Leftrightarrow UO_2OH^+ + H^+$	−5.87	0.08	Choppin and Mathur (1991)
$2\ UO_2^{2+} + 2\ H_2O \Leftrightarrow (UO_2)_2(OH)_2^{2+}$	−5.93	0.05	Meinrath and Schweinberger (1996)
$3\ UO_2^{2+} + 5\ H_2O \Leftrightarrow (UO_2)_3(OH)_5^+ + 5\ H^+$	−16.49	0.12	Meinrath (1997)
$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3^0$	10.27	0.05	Meinrath et al. (1999b)
$UO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$	16.7	0.4	Meinrath et al. (1999b)
$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$	22.9	0.3	Meinrath et al. (1999b)
$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4^0$	2.90	0.1	Burneau et al. (1992)
$UO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$	3.64	0.1	Burneau et al. (1992)

(Choppin and Mathur, 1991; Meinrath and Schweinberger, 1996; Meinrath, 1997; Burneau et al., 1992). Commonly, geochemical transport modeling is based on mean values of thermodynamic data in the geochemical database. However, such mean value-based transport calculations are incorrect. Knowledge of thermodynamic parameters of involved chemical reactions is, by far, less precise than imposed by the use of mere mean values alone (Meinrath, 2000). Like all physical quantities obtained experimentally, a thermodynamic quantity is characterized by its expectation value and its uncertainty, usually given in the form $X \pm y$. It should be noted that this relationship is also a simplification (Donaldson and Schnabel, 1987; Rosenblatt and Spiegelman, 1981; Meinrath et al., 1999b), but will be accepted for the present study. The thermodynamic data, together with its uncertainties σ, are given in Table 1. The data are corrected to zero ionic strength by Davies equation.

Modeling is repeated a large number of times (250–500). In each run, the thermodynamic input data is drawn by a Monte Carlo routine (Box and Muller, 1958) from normal distributions with given mean value and a dispersion set at the specified standard deviation of a thermodynamic constant. The selected data are set at random, while other input data (e.g., pH, formation constants for HCO_3^- and CO_3^{2-} species, etc.) remain fixed. Data files were generated by Pascal code. Resulting datafiles were used for input to PHREEQC runs. For a better performance, PHREEQC source code has been compiled with a 32-bit compiler (Borland C^{++} Builder). The option "SELECTED OUTPUT", available in PHREEQC code, was used to store selected results in order to generate the cumulative probability distributions (cpd). A probabilistic code including database uncertainty into the TReaC code is in progress. From these cpds, the probability distribution functions (pdf) are obtained by numerical differentiation using Savitzky–Golay filters (Savitzky and Golay, 1964).

3. Speciation and thermodynamic equilibrium model

Under conditions of natural aqueous systems, U(VI) is the prevailing redox state (Langmuir, 1998). U(IV) has a high tendency for sorption and a low solubility, but formation of U(IV) requires strongly reducing conditions and/or catalytic activity, for instance by microbial activity. U(V) is stable only in a limited E_H-pH range and has a high tendency for disproportionation. It is not likely to play a role in any aqueous system. The predominant reactions of hexavalent uranium in near neutral aqueous media are complexation by carbonate and hydrolysis (Langmuir, 1998). In areas where high concentrations of sulfate occur due to acidic leaching of uranium-bearing ores and subsequent pyrite oxidation, the complexation of U(VI) by sulfate has to be taken into account. Hydrolytic, carbonate and sulfate solid phases of U(VI) show a comparatively high solubility — in contrast, for example, with phosphates (Vochten et al., 1981, 1992), arsenates (Vochten and Goéminne, 1984) and silicates, three other possible ligands present in natural aqueous systems. Therefore, focus is given to the influence of hydrolysis and complexation by carbonate and sulfate, on the transport behavior of U(VI).

4. Results and discussion

To illustrate the variability in the speciation due to uncertainty in a limited number of thermodynamic data (cf. Table 1), uranium speciation in sea water is modeled. Sea water has quite a constant composition not only with respect to the salt components but also with respect to uranium, that is 3.3 μg l^{-1}. The pH of sea water is 8.22, CO_2 partial pressure is 0.03% and the ionic strength is comparatively high at $I = 0.675$. Under those

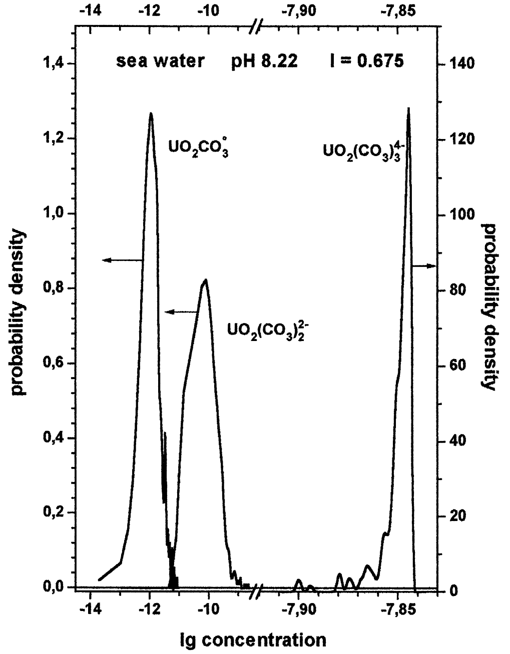

Fig. 1. Distribution functions of probable species concentrations calculated by 250 Monte Carlo cycles for seawater at 25°C. Concentration of dominant species $UO_2(CO_3)_3^{4-}$ is quite narrowly distributed (right scale; please note the change in x-scale also). There is, however, little information on the probable concentrations of the minor species $UO_2CO_3^0$ and $UO_2(CO_3)_2^{2-}$. Their probable concentrations may vary over several orders of magnitude.

conditions, the tricarbonato species, $UO_2(CO_3)_3^{4-}$, is assumed to be the prevailing U(VI) solution species. However, direct methods for verifying this species at this concentration level are not available.

Fig. 1 shows the result of the Monte Carlo simulation. The probability distribution functions are calculated from 250 resampling cycles. The uncertainty in the formation constants does not lead to major uncertainties in the prediction. Please note the change in the abscissa scale. The pdf of the minor species, $UO_2CO_3^0$ and $UO_2(CO_3)_2^{2-}$, is very small due to the width of the probability densities. The area under all probability distribution curves is unity.

5. Acid mine water

A situation like the one shown in Fig. 1 is rather favorable but not typical in most ground water systems. In sea water, concentration of carbonate is high enough to result in the predominant formation of one of the three U(VI) carbonato species. In many systems, especially near neutral ones, however, several species occur with relative concentrations susceptibly depending on ligand concentrations, redox conditions, temperature, etc.

In Table 2, the composition of an acid mine water is considered. The water composition is chosen to be close to the probable water composition of a former uranium sand stone deposit after flooding (Königstein Mine, Germany) (Schreyer, 1996). Due to uranium leaching by sulfuric acid and subsequent pyrite oxidation, sulfate concentrations in the flooded mine are expected to be about 300 mg l^{-1} even after dilution with the flooding water.

The composition, as calculated by the mean values of formation constants given in Table 1, is also given in Table 2. It should be noted that the low pH value of 2.24 prevents the formation of carbonato species ($\log [CO_3^{2-}] < -15$), hence the variations described in the following are due to the small variations within the formation constants of sulfate species. The calculation shows that the species UO_2^{2+} and $UO_2SO_4^0$ have about equal concentrations. The concentration ratio between these species, however, is of considerable importance because the cation UO_2^{2+} will be retarded by sorption, while the neutral species $UO_2SO_4^0$ will be more mobile. Fig. 2 shows the result of a Monte Carlo simulation.

Both the cpd and the pdf are given. The dashed bottom arrows enclose the approximate 95 percentiles that are 38–61% UO_2^{2+}. Since both species account for about 99% of the total U(VI) species in solution, the probability distributions are mirror images and the relative amount in the abscissa holds for both UO_2^{2+} and $UO_2SO_4^0$, respectively.

A consequence of the uncertainty in the solution composition is shown in Fig. 3, where the breakthrough curves of the sand column are simulated, using solutions with the upper and lower 95 percentile composition of Fig. 2. Despite the fact that only two thermodynamic constants are varied, a drastic difference in the breakthrough curves is calculated. It has to be emphasized that this difference is solely a consequence of the calculated difference in the fraction of neutral to positively charged species. All physical and geometric parameters are held constant as well as pH and sulfate concentrations.

Table 2
Composition of acid mine water (simulating Königstein mine flooding) at pH 2.24 ($\log [CO_3^{2-}] < -15$)

Element	UO_2^{2+}	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+
$mg\ l^{-1}$	11.3	301	60.1	14.0	46.0	3.3	1.7	5.4
$mol\ l^{-1}$	4.2×10^{-5}	3.1×10^{-3}	2.22×10^{-4}	2.2×10^{-4}	1.1×10^{-3}	1.4×10^{-5}	4.3×10^{-5}	2.3×10^{-4}

Species	UO_2^{2+} (aq)	UO_2SO_4	UO_2OH^+	UO_2Cl^+	$UO_2(SO_4)_2^{2-}$
$mol\ l^{-1}$ (mean values)	2.080×10^{-5}	2.083×10^{-5}	6.97×10^{-9}	2.93×10^{-8}	3.557×10^{-7}

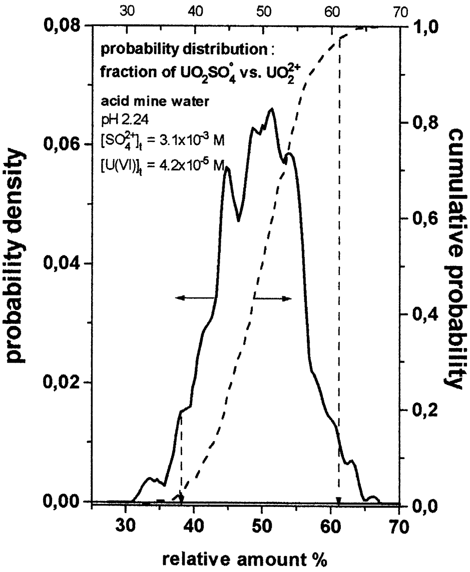

Fig. 2. Probability distribution (left axis) and cumulative probability distribution (dashed curve, right axis) of the UO_2SO_4 fraction in acid mine water. Because $UO_2SO_4^0$ and UO_2^{2+}(aq) contribute about 99% of total species in solution, UO_2^{2+}(aq) fraction distribution is just a mirror image. The 68% confidence limit about median is 43.7–55.3%, while the 95% confidence limit ranges from 37.9% to 61.1%. 95% confidence limits are given in this figure as dashed arrows.

The curve corresponding to the lower 95 percentile has the higher UO_2^{2+} content. Hence, the total uranium concentration that is made up from both the sorbed U(VI) and

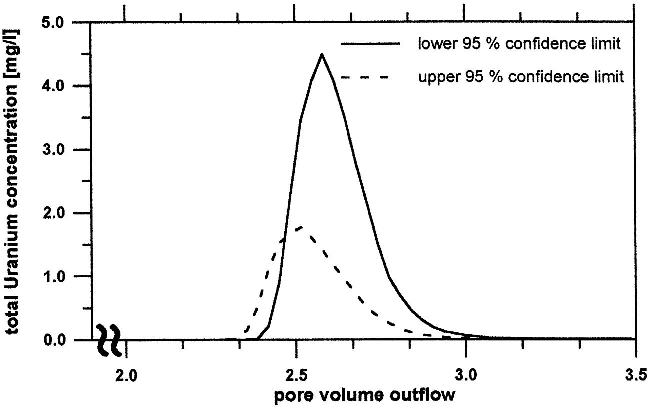

Fig. 3. Column experiment simulated for the upper and lower 95% confidence limit in solution composition (cf. Fig. 2). The higher UO_2^{2+}(aq) concentration delays but enhances (solid line) the breakthrough. Higher concentrations in neutral species $UO_2SO_4^0$ reduces retardation. Because only positively charged ions can exchange with the stationary phase, retardation is stronger for a higher UO_2^{2+} (aq) concentration. The higher total U(VI) concentration calculated for lower 95% confidence limit results from the starting condition of the simulation: eluted is the total amount of uranium in a 'starting' compartment of the column where the higher sorption results in a higher total amount.

Table 3
Chemical composition of calcite-enriched drinking water at pH 6.5

Element	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+
$mg\,l^{-1}$	108.5	53.0	73.5	41.2	16.2	2.1	14.1
$mol\,l^{-1}$	1.8×10^{-3}	1.5×10^{-3}	7.7×10^{-4}	1.0×10^{-3}	6.7×10^{-4}	5.4×10^{-5}	6.1×10^{-4}
Species	UO_2^{2+} (aq)	$UO_2CO_3^0$	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$	$UO_2SO_4^0$		
$mol\,l^{-1}$ (mean values)	6.0×10^{-8}	1.5×10^{-5}	5.6×10^{-5}	1.2×10^{-6}	1.7×10^{-8}		

the solution U(VI) is considerably higher than calculated for the higher 95 percentile, where the higher amount of $UO_2SO_4^0$ reduces the sorbed U(VI) contribution. The higher sorption in a solution with higher UO_2^{2+} amount shows higher retardation, but this effect is weak. This example shows a case where the small variation in one formation constant, here for the species $UO_2SO_4^0$, leads to considerable variation in the calculated properties.

6. Carbonate solutions

It may be expected that variability of properties is even more pronounced for the carbonate system where the given standard deviations are higher than in case of the

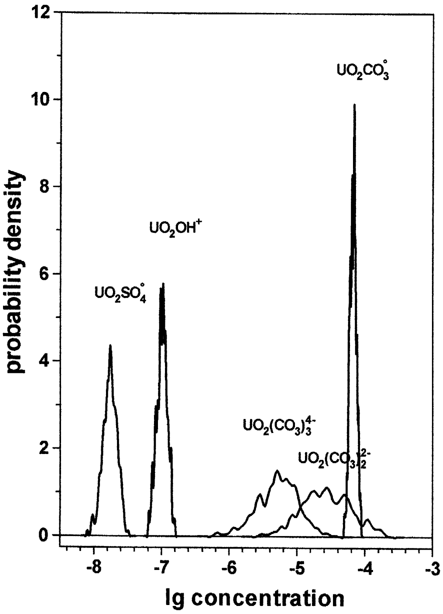

Fig. 4. Probability densities of selected uranium(VI) species in near-neutral carbonate water. Despite the fact that the distribution of prevailing species $UO_2CO_3^0$ is comparatively narrow, the calculation does not allow to predict the dominant species with certainty. There remains the possibility that $UO_2(CO_3)_2^{2-}$ is the dominant species.

sulfate species. The chemical composition of many natural waters is dominated by carbonate rock weathering. Therefore, the solubility of uranium in waters strongly depends on carbonate concentration. For TReaC simulation of uranium transport by carbonate water, a drinking water partly enriched in carbonate by saturation with calcite is considered. Composition of the water is given in Table 3.

For this water, a CO_2 partial pressure of 2% is calculated. The partial pressure is close to the mutual stability limit of the uranium solid phases $UO_2CO_3(s)$ (rutherfordine) and $UO_3 \cdot 2\ H_2O(s)$ (schoepite) (Meinrath and Kimura, 1993). Rutherfordine is assumed as the solubility-limiting solid phase, but calculation shows that schoepite is also close to its saturation limit with a saturation index (SI) varying from $-0.07 < SI < 0.02$. The mean value concentrations of uranium(VI) species in the carbonate water are included into Table 3. The distribution curve for species content is calculated from 500 resampling cycles and given in Fig. 4 for carbonate species, UO_2OH^+ and $UO_2SO_4^0$.

Fig. 4 shows that a prediction of prevailing species is not as straightforward as it had been in the case of the sea water example (cf. Fig. 1) because there is a limited but non-zero probability that $UO_2(CO_3)_2^{2-}$ is the dominant species despite the fact that the pdf of $UO_2CO_3^0$ is much sharper. The total U(VI) concentration in solution is also uncertain due to the fact that equilibrium with a solid phase is considered. Hence, a reservoir is available for uranium, while in the sea water case, the species had to compete for a limited total uranium concentration of 3.3 μg. The pdf of total uranium concentration in the drinking water is shown in Fig. 5 together with its cpd. The effect

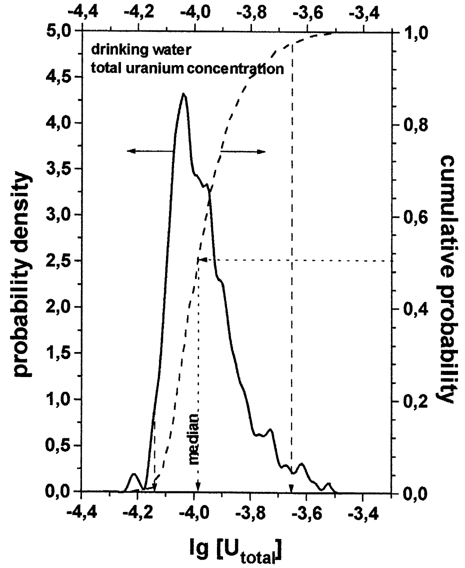

Fig. 5. Probability density (left axis) and cumulative probability (dashed curve, right axis) of total U(VI) concentration in simulated drinking water. The median is at 1.03×10^{-4} M, while upper and lower 68% confidence limits are 1.4×10^{-4} and 8.5×10^{-5} M, respectively. The 95% confidence limits are indicated by dashed arrows and give a concentration range between 2.2×10^{-4} and 7.27×10^{-5} M. Other parameters like pH and dissociation constants of CO_2, etc., are assumed to be known without uncertainty.

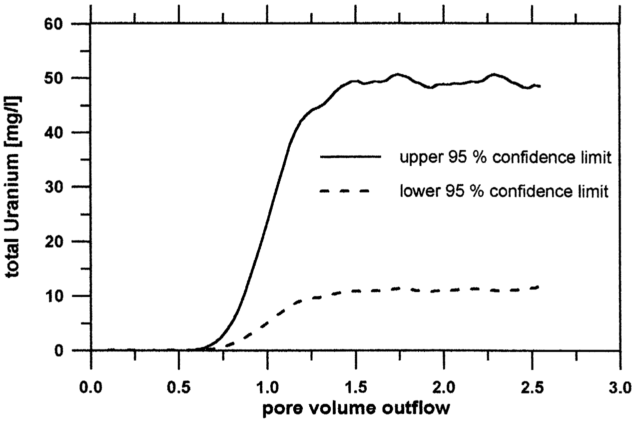

Fig. 6. Breakthrough curves calculated for minimum and maximum total uranium concentration in carbonate containing drinking water at 25°C.

of this uncertainty transfers to the transport prediction, as shown in Fig. 6, where breakthrough curves for the two sets of formation constants are given. These two sets correspond to the upper and lower 95% percentiles, as shown in Fig. 5.

The effect is drastic. Note that there is almost no difference in the retardation because the solution contains mostly neutral and anionic species that effectively reduce sorption

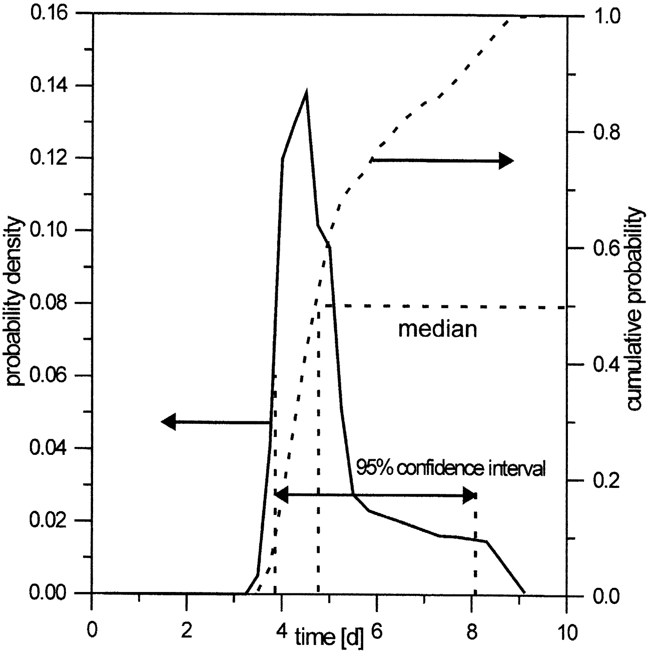

Fig. 7. Estimated distribution of threshold excess (threshold: 10 mg U(VI) l^{-1}) at the column outlet.

and cation exchange within the sand matrix. Hence, the differences in the breakthrough curves are solely due to uncertainty in total uranium concentration.

In most practical cases, the upper and lower 95 percentiles are of mere academic interest. A more interesting question might be, for example, the time a contaminant takes to exceed some threshold contamination at a drinking well downstream of its source. In Fig. 7, the answer is calculated for the sand column and a threshold value of 10 mg l^{-1} ($\cong 4.5 \times 10^{-5}$ M U(VI)) from 350 resampling cycles. The threshold value may be exceeded after only about 3 days, while the maximum probability and the median predict about 4.8 days. The distributions are skewed towards longer times and there is a limited probability that the threshold concentration may be exceeded after almost 10 days.

7. Conclusions

A Monte Carlo study using the code TReaC shows a strong dependence of predictive reactive transport modeling on uncertainties in the thermodynamic database. It should be kept in mind that this study had a rather limited scope. A small number of thermodynamic formation constants in the database have been modified and a simple sand column of 40-cm length has been simulated. No inhomogeneity in the column's properties has been assumed. Two test cases involving transport have been studied. First, an example where the uncertainty in thermodynamic data leads to a range of possible ratios between a cation species, UO_2^{2+}, and a neutral species, $UO_2SO_4^0$, resulting in different retardation properties. Second, uncertainty in the total uranium species concentration results in uncertainty in characteristic properties of the sand column, e.g. breakthrough concentration and the time until a threshold concentration is exceeded.

The effect of uncertainty in geochemical modeling is becoming more widely recognized, with particular focus on uncertainty in mineral solubility is given (Ekberg et al., 1997; Meinrath and Nitzsche, 2000). The foregoing discussion has shown that the influence of uncertainty in the thermodynamic data has to be discussed under a much broader angle, including the effects of chemical speciation on solute mobility. On the other hand, it has to be kept in mind that the majority of thermodynamic constants are not determined for application in geochemical modeling. This is illustrated by the often less-than-rigorous way of analyzing statistical data or the complete lack of uncertainty estimation in the presentation of chemical papers on thermodynamic properties. It must be emphasized that oftentimes, the given figures carry sufficient information for the chemists but are not sufficient with respect to numerical application of the data in geochemical databases (Meinrath et al., 2000a).

Finally, the aspect of processing time has to be discussed. The Monte Carlo approach requires a larger number of repetitive calculations of the same simulation. By large number we mean 250–1000 resampling cycles. These figures present a high demand in CPU time. The sand column simulation for U(VI)-enriched drinking water required more than 120 h. If further parameters had to be considered, for instance, inhomogeneity in the sand column or uncertainty in the carbonate ligand concentration on solubility of calcite, larger number of resampling cycles would have been required. For a three-dimensional real-world problem, a Monte Carlo approach is not feasible. Hence, current work studies applicability of stratified sampling strategies (Williams, 1978; Meinrath et al., 2000b) that require only a few hundred resampling cycles for a fully probabilistic database — instead of several thousands. The more parameters with its associated uncertainty are considered, the wider the resulting prediction uncertainty should be expected. Nevertheless, sorption and kinetics are relevant processes in nature that also have to be included into a code for environmental prediction (Nitzsche et al., 1999). In the above discussion, emphasis was on the effect of the database uncertainty on the modeling output. It has to be concluded that the complexity of a predictive model will be limited by the growing uncertainty with increasing number of uncertainty affected input parameters.

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