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Identification of sorption processes and parameters for radionuclide transport in fractured rock

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SUMMARY

Identification of chemical reaction processes in subsurface environments is a key issue for reactive transport modeling because simulating different processes requires developing different chemical–mathematical models. In this paper, two sorption processes (equilibrium and kinetics) are considered for modeling neptunium and uranium sorption in fractured rock. Based on different conceptualizations of the two processes occurring in fracture and/or matrix media, seven dual-porosity, multi-component reactive transport models are developed. The process models are identified with a stepwise strategy by using multi-tracer concentration data obtained from a series of transport experiments. In the first step, breakthrough data of a conservative tracer (tritium) obtained from four experiments are used to estimate the flow and non-reactive transport parameters (i.e., mean fluid residence time in fracture, fracture aperture, and matrix tortuosity) common to all the reactive transport models. In the second and third steps, by fixing the common non-reactive flow and transport parameters, the sorption parameters (retardation factor, sorption coefficient, and kinetic rate constant) of each model are estimated using the breakthrough data of reactive tracers, neptunium and uranium, respectively. Based on the inverse modeling results, the seven sorption-process models are discriminated using four model discrimination (or selection) criteria, Akaike information criterion (*AIC*), modified Akaike information criterion (*AICc*), Bayesian information criterion (*BIC*) and Kashyap information criterion (*KIC*). These criteria suggest the kinetic sorption process for modeling reactive transport of neptunium and uranium transport in both fracture and matrix. This conclusion is confirmed by two chemical criteria, the half reaction time and Damköhler number criterion.

1. Introduction

In the past decade considerable progress has been made in delineating the physical and chemical processes that govern the fate and transport of metals, radionuclides and other contaminants (Steefel et al., 2005). Sophisticated reactive transport models based on local-equilibrium and kinetic theories have been developed and implemented reflecting the current process understanding (e.g., Dzombak and Morel, 1990; Appelo, 1994; Kohler et al., 1996; Xu et al., 1999; Brun et al., 2001; Dai and Samper, 2004; Ding, 2005; Kwicklis et al., 2006; Samper and Yang, 2006; Scheibe et al., 2006). Geochemical processes and reactive transport parameters in porous media have been studied at various scales from laboratory batch and column experiments to field tracer tests (e.g., Dai et al., 2006; Machado et al., 2008; Matott and Rabideau, 2008; Takeda et al., 2008). In all of these reactive transport models, parameter and process uncertainty is a substantial concern due to intrinsic limitations arising from process model approximations and to uncertainty in model parameters and geochemical processes. To reduce model uncertainty and effectively solve the inverse problem of multi-component reactive solute transport, Dai et al. (2006) developed a mathematical and numerical methodology based on alternative conceptual-geochemical models to evaluate quantitatively plausible geochemical processes. This method has been applied successfully by Yang et al. (2007, 2008) to identify geochemical processes and transport parameters in porous media.

For simulating radionuclide reactive transport in fractured rock systems, we adopt the dual-porosity conceptual model (e.g., Tang et al., 1981; Sudicky and Frind, 1982; Reimus et al., 2003), in which the primary pathway for groundwater flow is through the fractures and the matrix material is saturated with groundwater which is considered immobile. Although the bulk of the water travels through fractures, radionuclides may diffuse into the very large reservoir of water in the matrix and sorb onto immobile minerals, retarding the travel time relative to fracture-only transport. Characterization of radionuclide sorption parameters has been

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addressed by Callahan et al. (2000), Wolfsberg et al. (2002), Reimus et al. (2003), Samper et al. (2006), Reimus and Callahan (2007), Robinson et al. (2007), Dai et al. (2009) and Jakob et al. (2009). These analyses provide extensive information for estimating sorption parameters at various scales. However, there currently is no well-established theory and method for selecting appropriate sorption conceptual models for fractured-rock transport simulations. It has been noted that bias and uncertainty resulting from an inadequate conceptual model are far more detrimental to the model's predictive ability than is a suboptimal set of model parameters (e.g., Carrera and Neuman, 1986; Samper and Neuman, 1989; Neuman, 2003; Ye et al., 2004; Poeter and Anderson, 2005; Refsgaard et al., 2006; Liu and Gupta, 2007; Tsai and Li, 2008; Rojas et al., 2008). Therefore, selecting an appropriate sorption-conceptual model may be more important than, or at least as important as, estimating optimal sorption parameters.

In this study we focus on developing a method to identify the sorption processes (equilibrium or kinetics) and transport parameters for uranium and neptunium transport in laboratory-scale fractured rock. A stepwise inversion strategy is used in this study for designing a list of the scenarios (or steps) and alternative conceptual models which include the most plausible sorption and transport processes, solving scenarios in a stepwise manner and selecting the sorption-conceptual model which provides the best solution to the inverse problem. At each step, the inverse problem is solved with PEST (Doherty, 2006). Modeling different sorption processes involves different numbers of parameters in the inverse models. Usually, with the same observational data, the more parameters involved in the inversion, the better the fit. Therefore, we cannot select the best conceptual model by just checking the goodness of fit or the values of inverse objective functions. To remove the effect of the number of parameters to the solutions of the inverse problems, we use four model identification criteria to select the most likely sorption process in fractures and matrices. These criteria are developed within the context of maximum likelihood theory (Carrera and Neuman, 1986; Samper and Neuman, 1989; Hill, 1998; Poeter and Anderson, 2005; Ye et al., 2005, 2008; Dai et al., 2008). In addition to inversion results, we apply two chemical criteria using the half reaction time and Damköhler number (Hoffman, 1981; Bahr and Rubin, 1987; Domenico and Schwartz, 1990) to confirm the sorption process (equilibrium or kinetics).

2. Transport experiments with fractured tuffaceous rock samples

The transport experiments with fractured tuffaceous rock conducted by Ware et al. (2005) involved six radionuclides (^{14}C, ^{90}Sr, ^{137}Cs, ^{233}U, ^{237}Np, and ^{239}Pu) and a few geologic samples from the tuff confining unit (TCU) in Yucca Flat of the Nevada Test Site, Nevada, USA. Tuffaceous rock samples representing the stratigraphic TCU were selected from boreholes UE-7az and UE-7ba at the United State Geological Survey (USGS) Core Library for the Nevada Test Site in Mercury, Nevada. The samples for fracture transport experiments consisted of competent sections of core (length 13 cm, diameter of 6 cm) with open natural fractures running axially along the length of the section (see Fig. 1 for sample UE-7az-1770). Matrix porosities of the competent cores used in the fracture transport experiments were determined by weighing samples of known volume after oven drying them and again after saturation with natural groundwater from the field boreholes. The difference in weight divided by the product of the water density and sample volume provides a porosity estimate (0.28 for the tuffaceous rock sample in this experiment).

Each radionuclide experiment included two flow rates differing by a factor of four, high (2 mL/h) and low flow (0.5 mL/h). The different flow rates were used to investigate time-dependent transport processes such as rate-controlled sorption or desorption. The tracer injection time was about 23 and 46 h for the high- and low-flow experiments, respectively. The experimental flow system is shown in Fig. 2. The high-flow and least-sorbing-radionuclide experiments were always conducted first for any radionuclide pair to minimize the amount of radionuclides retained in the cores at the start of the subsequent low flow experiments. In all cases, the fractures were flushed until radionuclide concentrations approached background levels prior to initiating a new experiment.

Fig. 1. Photograph of the sections of core (a length of 13 cm and a diameter of 6 cm) with open natural fractures running axially of the sample UE-7az-1770 (modified from Reimus et al. (2006)).

Although the experiments were conducted for several reactive and non-reactive radionuclides and multiple core samples, this study focuses on estimating reaction processes and parameters for neptunium (^{237}Np) and uranium (^{233}U) using the transport experiments for these species and tritium (^{3}H), in the core designated UE-7az-1770. The neptunium (^{237}Np) and uranium (^{233}U) transport experiments were conducted separately with tritium (^{3}H). The radionuclides (such as ^{237}Np) expected to sorb the least were injected before more strongly sorbing radionuclides (such as ^{233}U), thus minimizing radionuclide carryover between experiments and extending the "life" of the fractures for additional transport experiments (Ware et al., 2005).

The core UE-7az-1770 is predominantly non-welded tuff with varying degrees of zeolitization. Quantitative X-ray diffraction mineralogy shows that it contains 69.2% (weight percentage) clinoptilolite, 10.7% K-feldspar, 3.5% cristobalite, 2.6% plagioclase, and the remainder, 14% of smectite, quartz and mica. The thin mineral coatings present on the natural fracture surface are neither sufficiently massive or crystalline to obtain quantitative X-ray diffraction data. Their influence on fluid flow and radionuclide retention is important because of the well-known order-of-magnitude differences in reactivity of fracture coating minerals and core matrix minerals (Grisak and Pickens, 1980; Grisak et al., 1980; Reimus et al., 2006). Therefore, sorption reactions in both matrix and fracture surface are considered in the stepwise inversion processes.

3. Modeling of radionuclide transport in fractured tuffaceous rock

3.1. Forward formulation

The fracture transport experiments were modeled using the one-dimensional advection-dispersion equation with one-dimensional diffusion into the surrounding matrix perpendicular to the

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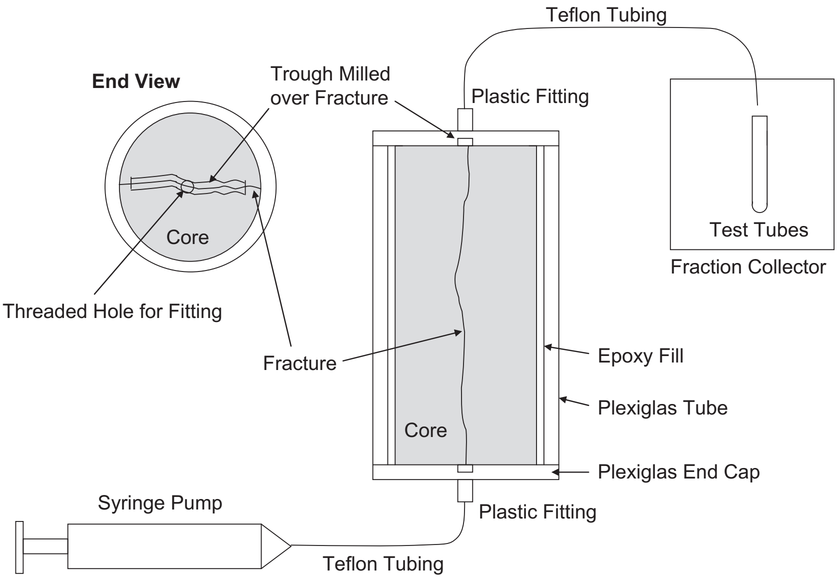

Fig. 2. Schematic illustration of experimental flow system (from Reimus et al. (2006)).

flow direction in fractures (Wu et al., 2010). The semi-analytical model developed by Reimus and Haga (1999) assumes parallel-plate fractures of constant aperture, $2b$, and either constant spacing, L, or infinite spacing (a semi-infinite matrix), no concentration gradients across the fracture aperture, and a steady flow rate in the fractures. Thus, the complexity of the actual fracture geometry and the variable distance between the fracture and the boundary of the cylindrical experimental apparatus are not fully accounted for in the process to estimate effective transport processes and parameters. The equations describing dual-porosity transport under these conditions are based on Maloszewski and Zuber (1985) and Reimus and Haga (1999):

Fracture:

$$R_f \frac{\partial C_f}{\partial t} + v_f \frac{\partial C_f}{\partial x} - D_f \frac{\partial^2 C_f}{\partial x^2} - \frac{\phi D_m}{b\eta} \frac{\partial C_m}{\partial z}\bigg|_{z=b} = 0, \tag{1}$$

Matrix:

$$R_m \frac{\partial C_m}{\partial t} - D_m \frac{\partial^2 C_m}{\partial z^2} = 0, \tag{2}$$

where C_f and C_m are the tracer concentrations in the fracture and matrix (g/cm^3); v_f is the fluid velocity in the fracture (in the x direction, cm/s); D_f is the dispersion coefficient in the fracture (cm^2/s); D_m is the matrix diffusion coefficient (cm^2/s); R_f and R_m are the retardation factors of the fracture and matrix, respectively. For first order kinetic sorption, $R_f = 1 + \frac{k_{ff}\rho_f}{k_{rf}\eta}$ and $R_m = 1 + \frac{k_{fm}\rho_m}{k_{rm}\phi}$, k_{ff} and k_{fm} are the sorption rate constants in fracture and matrix (h^{-1}); k_{rf} and k_{rm} are the desorption rate constants of the fractures and matrix (g/cm^3 h); ρ_f and ρ_m are the bulk density of the fracture and matrix material, respectively (g/cm^3); η and ϕ are the porosity of the fracture and matrix, respectively. For equilibrium sorption, $R_f = 1 + \frac{\rho_f}{\eta} K_{df}$ and $R_m = 1 + \frac{\rho_m}{\phi} K_{dm}$; K_{df} and K_{dm} are the sorption partition coefficients which are expressed as the mass of tracer sorbed per unit mass of material divided by solution concentration of tracer at equilibrium (cm^3/g); and b is the fracture half aperture (cm).

A computer code, RELAP (REactive transport LAPlace transform inversion) was developed by Reimus and Haga (1999) to provide a semi-analytical solution to Eqs. (1) and (2). The code has been applied to interpret various column transport experiments and field tracer tests as reported by Callahan et al. (2000), Reimus et al. (2003) and Reimus and Callahan (2007). The code RELAP is used in this study for the forward simulation of solute transport in the fractured rock. Note that the flow and transport in the fracture-matrix systems may be two- or three-dimensional. However, when the fracture aperture is very small, the fracture faces are uniform and flat, and the permeability in the matrix is close to zero, a one-dimensional approach with double porosity model is reasonable, and the good accuracy of the double porosity model was demonstrated by Wu et al. (2010).

3.2. Inverse modeling and model selection

We use a generalized least square objective function to estimate the parameters for reactive and non-reactive radionuclide transport in the fractured tuffaceous rock. The numerical methodology for estimating these parameters via inversion involves minimizing the objective function (Φ) of multiple experiment data,

$$\begin{aligned} \Phi &= \min \sum_{i=1}^{N} E_i(\boldsymbol{\theta}) \\ E_i(\boldsymbol{\theta}) &= \sum_{l=1}^{L_i} \omega_{il}^2 (\mathbf{u}_{il}(\boldsymbol{\theta}) - \tilde{\mathbf{u}}_{il})^2, \end{aligned} \tag{3}$$

where $E_i(\boldsymbol{\theta})$ is the sub-objective function from experiment i, $\boldsymbol{\theta}$ is the parameters to estimate, N is the number of experiments, $\boldsymbol{\omega}_{il}$ is the weighting coefficient for the lth measurement in the ith experiment, and $\mathbf{u}_{il}$ and $\tilde{\mathbf{u}}_{il}$ are the model outcome and measurement, respectively. The weighting coefficient for each radionuclide is computed from the inverse of the standard deviation of the measurements as explained in Hill and Tiedeman (2007). The following six types of parameters are estimated, in which the first three are common flow and transport parameters which are estimated from tritium experiment data, and the other three are tracer-specific transport and sorption parameters:

(1) mean fluid residence time in fractures (τ), h,
(2) fracture half aperture (b), cm,
(3) Peclet number ($Pe = r_L/\alpha$, where r_L is transport distance, cm, and α is dispersivity, cm),
(4) matrix diffusion coefficient, D_m, cm^2/s,
(5) retardation factor in matrix and fracture, R_m or R_f, and
(6) rate constant for radionuclide sorption to matrix materials and fracture coating minerals, k_{fm} or k_{ff}, h^{-1}.

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4. Model selection criteria

Model parsimony and identification of process-conceptual models can be assessed by model selection criteria as used by Carrera and Neuman (1986) in identifying flow models and by Samper and Neuman (1989) in inferring covariance functions for groundwater quality data. These identification criteria are developed within the context of maximum likelihood theory (Cavanaugh and Neath, 1999 and Ye et al., 2008). Most of them minimize some measure of the closeness between the true (yet unknown) model and the proposed model. The first criterion is the Akaike information criterion (*AIC*) (Akaile, 1974; Poeter and Anderson, 2005).

$$AIC_k = N_z \ln \hat{\sigma}^2_{ML} + 2P_k, \tag{4}$$

where N_z is the number of data used for solving the inverse problem; P_k is the number of estimated parameters; k indicates the kth alternative process-conceptual model, $k = \overline{1,K}$; $N_z \ln \hat{\sigma}^2_{ML}$ is a term obtained from the unbiased least square estimator,

$$\hat{\sigma}^2_{ML} = \left.\frac{\Phi}{N_z}\right|_{\theta_k=\hat{\theta}_k}, \tag{5}$$

where Φ is the generalized or weighted sum of squared residuals yielding a parameter estimate $\hat{\theta}_k$ from minimizing the least square objective function 3 (Ye et al., 2008). The best model is that with the smallest *AIC* value. In order to correct the bias of *AIC* criterion for a small number of calibration data (e.g., $N_z/P_k < 40$), the modified Akaike information criterion (*AICc*) was developed as (Hurvich and Tsai, 1989),

$$AICc_k = N_z \ln \hat{\sigma}^2_{ML} + 2P_k + \frac{2N_z(N_z+1)}{N_z - P_k - 2}. \tag{6}$$

AICc considers the size of the calibration data set and is therefore preferred over the original *AIC*. Schwarz (1978) derived a different criterion in a Bayesian context, called Bayesian information criterion (*BIC*) as defined below,

$$BIC_k = N_z \ln \hat{\sigma}^2_{ML} + P_k \ln N_z. \tag{7}$$

Kashyap (1982) developed another Bayesian model selection criterion, the Kashyap information criterion (*KIC*). According to Ye et al. (2008), *KIC* is defined as

$$KIC_k = N_z \ln \hat{\sigma}^2_{ML} - 2\ln p(\hat{\theta}_k) - P_k \ln 2\pi - \ln|\mathbf{\Sigma}_k|, \tag{8}$$

where $\mathbf{\Sigma}_k$ is the covariance matrix of the estimated parameters for the kth alternative model, and $p(\hat{\theta}_k)$ is the prior probability of the kth alternative model parameter. If the prior information about the model parameters is not available, this prior term can be dropped. As pointed out by Ye et al. (2008, 2010), *KIC* is more accurate than *BIC* because it includes the Fisher information term and accounts for the likelihood of prior parameter estimates (Carrera and Neuman, 1986). *KIC* has the unique ability to select the best models based not only on their goodness of fit to observation data and number of parameters, but also on the quality of the available data and the parameter estimates (Carrera and Neuman, 1986; Ye et al., 2008, 2010). Detailed discussion on Eqs. (4)–(8) can be found in Appendix B of Ye et al. (2008).

Our inverse methodology uses a generalized least-squares objective function (e.g., Dai and Samper, 2004; Doherty, 2006), Φ, which can be used to evaluate Eq. (5) (see Carrera and Neuman, 1986; McLaughlin and Townley, 1996). Values of *AIC*, *AICc*, *BIC* and *KIC* are calculated for all the alternative processes considered for uranium and neptunium transport in laboratory-scale fractured rock.

5. Estimating transport processes and parameters from transport experiments

This study focuses only on the inverse modeling of tritium (^{3}H), neptunium (^{237}Np) and uranium (^{233}U) transport by interpreting multiple experimental data simultaneously. Due to the complexity of the multiple breakthrough concentration curves from multiple transport experiments with different flow rates, we adopt a stepwise strategy from simple to complex inverse models. We first fit the conservative tracer (tritium) breakthrough curves to estimate the common flow and transport parameters (mean residence time, fracture half aperture and matrix tortuosity). Next we couple concentration data from high and low flow neptunium (or uranium) transport experiments into simultaneous inversions, identify sorption processes and transport parameters, and honor the nonvarying components (the common transport parameters) of the experiments for the same tuff column.

5.1. Step 1: Estimating the common transport parameters from four tritium experiments

In the first step, we estimate the common transport parameters, including mean residence time, Peclet number, fracture aperture and matrix diffusion coefficient of tritium by simultaneously fitting the four tritium breakthrough curves from the four experiments on the same column UE-7az-1770. The effective tritium diffusion coefficient is a function of the diffusion coefficients in free solution and the tortuosity of the medium (Rowe et al., 1988). Dai et al. (2007) demonstrated that matrix diffusion coefficients in fractured rocks are scale dependent. Searching the literature to determine the acceptable range of matrix diffusion coefficient for our column experiments, we mainly found values of diffusion coefficients on the column scale (generally 0.01–0.5 m). Reimus and Haga (1999) reported a matrix diffusion coefficient for tritium in the range of 0.5–1.2 × 10^{-5} cm^2/s for a fractured tuffaceous rock. By also considering other published data (e.g. Gillham et al., 1984; Robinson, 1994; Young and Ball, 1998), the tritium diffusion coefficient for this study was constrained between 0.3×10^{-5} cm^2/s and 1.2×10^{-5} cm^2/s. The lower and upper bounds for the Peclet number are between 1 and 100. These limits were imposed in PEST (Doherty, 2006) during the search for possible parameter values. The fracture half aperture is directly related to column length (L), diameter (W), flow rate (Q) and mean residence time (τ) as $b = \frac{Q\tau}{2LW} = \frac{0.5\tau}{2\times13\times6} = 0.0032\tau$. Because τ is a parameter to be estimated, we tie the fracture half aperture to the mean residence time (low flow) with a factor of 0.0032. Therefore, during the inverse process, the fracture half aperture is not estimated but it is calculated every time when a new value of the mean residence time is estimated. Since the four tritium breakthrough curves from two high and two low flow experiments are coupled together to form one inverse problem, the ratio of the mean residence times of the two experiments is constrained to be exactly the inverse of the ratio of flow rates between experiments. The simultaneously-estimated results for the common transport parameters (τ and fracture aperture b) and the tritium diffusion coefficient and Peclet number are presented in Table 1 and Fig. 3. Because the flow rate after 42 h in the tritium/uranium low flow experiment changed greatly, the observed tritium concentrations are not reliable. Therefore, we excluded the tritium observation data of the uranium low flow experiment from inverse modeling (see Fig. 3B).

The estimated mean residence time for low and high flow experiments is 7.05 h and 1.76 h, respectively. The mean Peclet number is 1.25, the mean fracture half aperture is 0.023 cm, and the tritium matrix diffusion coefficient is 6.69×10^{-6} cm^2/s. From a value of 2.44×10^{-5} cm^2/s for tritium diffusion in free solution

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Table 1
Parameter estimates from inverse modeling of four tritium breakthrough curves from four fractured tuffaceous rock experiments (flow rate 0.5 and 2.0 mL/h).

Parameters	Estimated values	95% Confidence intervals	
		Lower bound	Upper bound
τ (LFR) (h)	7.05	5.91	8.19
τ (HFR) (h)	1.76	1.48	2.05
Pe	1.25	0.96	1.55
b (cm)	0.023	0.019	0.026
D_m (cm^2/s)	6.69×10^{-6}	3.99×10^{-6}	9.40×10^{-6}

Note: LFR = low flow rate, HFR = high flow rate, and the fracture half aperture is tied to the estimation of the mean residence time at low flow experiments.

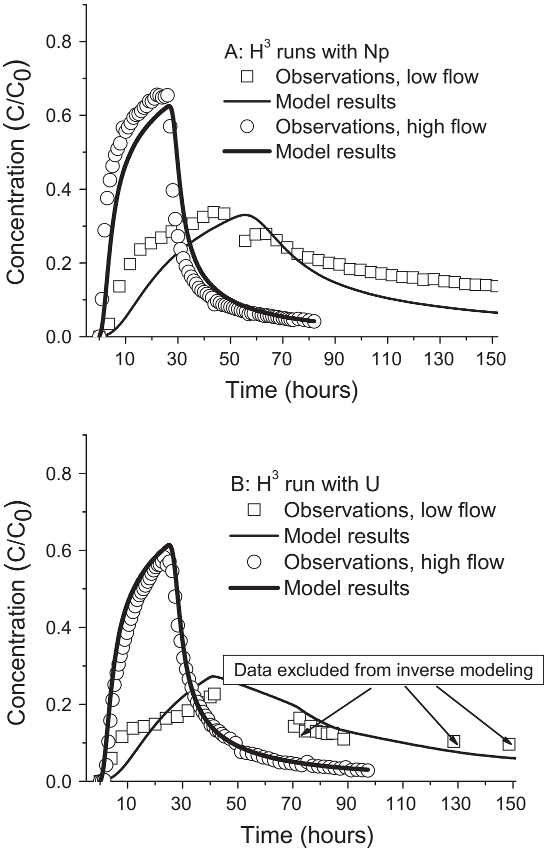

Fig. 3. Fitting four tritium breakthrough curves from four fractured tuffaceous rock experiments.

and an estimated matrix diffusion coefficient of 6.69×10^{-6} cm^2/s, we computed a dimensionless tortuosity factor of 0.274 for this tuffaceous core. Note that the parameters (mean residence time, fracture aperture and tortuosity) estimated from the simultaneous inversion represent some averaged values for these four experiments. These parameters will be used for inversion of neptunium and uranium data and scaling the diffusion coefficients of these two radionuclides.

5.2. Step 2: Identifying neptunium sorption processes and parameters from two experiments

In this step, we fixed the common transport parameters (b and τ, the ratio of τ values being constrained to be exactly the inverse of the ratio of flow rates between experiments) estimated in step 1, and coupled the two neptunium breakthrough curves from high and low flow experiments to estimate the neptunium sorption parameters simultaneously. The relevant field and laboratory values of neptunium sorption parameters published in the literature (e.g. Stumm et al., 1970; Huang and Stumm, 1973; Shackelford, 1991; Williams, 1993; Garcia-Gutiérrez et al., 2001; Reimus et al., 2006) were used to estimate the lower and upper bounds for neptunium retardation factor and kinetic rate constant are (1, 50) and (0.01, 10 h^{-1}), respectively. To explore the relationship between different transport parameters, Reimus et al. (2003) defined a mass transfer coefficient (C_{MT}) as:

$$C_{MT} = \frac{\phi}{b}\sqrt{R_m D_m}. \tag{9}$$

For a given value of the mass transfer coefficient, Eq. (9) shows that there is a perfect negative correlation between retardation factor and matrix diffusion coefficient. Thus, rather than allowing both parameters to vary, we fix the neptunium matrix diffusion coefficient and use inverse models to estimate neptunium retardation factor. From the literature, we find a neptunium diffusion coefficient in free water (D_0) is 1.2×10^{-5} cm^2/s (Reimus et al., 2006). Here, we assume the tortuosity computed for tritium tracer at step one ($\tau_m = 0.274$) can be used for neptunium tracer because the column is the same tuffaceous core with the same pore structure. The neptunium matrix diffusion coefficient is then calculated to be $D_m = \tau_m D_0 = 3.29 \times 10^{-6}$ cm^2/s.

Because neptunium and uranium are sorbing species and have retardation factors much larger than 1, one needs to consider the impact of the sorption reaction on the dispersion in the fracture. Bellin et al. (1993) found that the dispersion process was retarded by strong sorption reactions, which means the dispersivity may be reduced for sorbing tracers. Therefore, the Peclet numbers for neptunium and uranium experiments were not fixed to be equal to that of tritium but were in stead estimated during the inverse process. A lower and upper bounds are set for Peclet number as (0.1, 10). The estimated Peclet number for tritium experiments (1.25) is used as the initial value for inversion of neptunium and uranium experiments.

When estimating neptunium sorption parameters, we need first to select or identify the appropriate neptunium sorption processes (kinetics versus equilibrium), and then solve the inverse problems with corresponding mathematical models. The following alternative sorption-conceptual models are designed for process identification:

(1) Kinetic1 model: An inverse model with kinetically controlled sorption in the matrix in which the sorption retardation factor and rate constant for low flow and high flow are identical. This inverse model implies that the sorption rate constant does not vary with flow velocity, and neptunium sorption onto fracture coating minerals is ignored. There are two sorption parameters (neptunium retardation factor and forward rate constant), plus Peclet number, to be estimated in this inverse model.

(2) Kinetic2 model: An inverse model with kinetically controlled sorption in the matrix in which the sorption rate constants for low and high flow are different and the sorption rate constants vary with flow velocity. The retardation factors for low and high flow are identical. Thus, there are three sorption parameters, plus Peclet number, to be estimated. As in the first conceptual model, we considered neptunium sorption only to matrix minerals, not to fracture coating minerals, so that diffusion would be necessary to bring the reactive solute into contact with reactive surface sites in the matrix.

(3) Kinetic3 model: The third inverse model is designed to test the impact of neptunium sorption onto fracture coating minerals. The kinetic sorption of neptunium onto the fracture surface is added into the previous inverse problem. There

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Table 2
The alternative sorption-conceptual models for neptunium and uranium transport in the fractured rock.

Conceptual models		Kinetic1	Kinetic2	Kinetic3	Kinetic4	Kinetic5	Equilibrium1	Equilibrium2
Np or U	Sorption in matrix	Kinetic	Kinetic	Kinetic	Kinetic	Kinetic	Equilibrium	Equilibrium
	Sorption in fracture	Ignore	Ignore	Kinetic	Kinetic	Kinetic	Ignore	Equilibrium
	Matrix rate constants in high and low flow	Same	Different	Different	Same	Same	Ignore	Ignore
	Fracture rate constants in high and low flow	Ignore	Ignore	Different	Different	Same	Ignore	Ignore
Number of parameters		3	4	7	6	5	2	3

Table 3
Model selection criteria for discriminating neptunium sorption and transport processes.

Criteria	Kinetic1	Kinetic2	Kinetic3	Kinetic4	Kinetic5	Equilibrium1	Equilibrium2
Number of parameters	3	4	7	6	5	2	3
Φ	11.40	10.12	7.97	8.03	8.25	68.87	68.87
AIC	−274.44	−286.76	−309.43	−310.53	−309.34	−60.63	−58.63
AICc	−274.10	−286.23	−308.13	−309.53	−308.59	−60.42	−58.28
BIC	−263.29	−272.83	−287.13	−291.01	−292.61	−52.26	−47.48
KIC	−275.30	−284.50	−309.19	−313.36	−315.58	−68.23	−70.48
Preference	Kinetic5						

are three additional parameters to be estimated, including one retardation factor in the fracture (identical for high flow and low flow), and two sorption rate constants in fracture for low flow and high flow. So, there are a total of seven parameters.

(4) Kinetic4 model: The third inverse model used different forward rate constants of neptunium sorption onto matrix for the high and low flow experiments. The intent of the fourth conceptual model which is based on the Kinetic3 model is to reduce the parameter dimension by using same matrix rate constant for the high and low flow experiments, because the flow rates might have a large impact on rate constants for fracture sorption but not so much on matrix sorption. The other conditions are using the same as those of Kinetic3 model. So, there are a total of six parameters.

(5) Kinetic5 model: In the fifth conceptual model we assume the fracture rate constants for the high and low flow experiments are the same by ignoring the impact of the flow rates

Table 4
Parameter estimates from alternative conceptual models by fitting two neptunium breakthrough curves from two fractured tuffaceous rock experiments (flow rate 0.5 and 2.0 mL/h).

Conceptual model	Parameters	Estimated or calculated values	95% Confidence intervals	
			Lower bound	Upper bound
Kinetic1	Pe	1.53	1.24	1.82
	R_m	16.99	13.66	20.32
	k_{fm} (h^{-1})	0.19	0.14	0.24
Kinetic2	Pe	1.45	1.15	1.76
	R_m	17.73	13.96	21.48
	k_{fm} (LFR) (h^{-1})	0.19	0.13	0.25
	k_{fm} (HFR) (h^{-1})	0.28	0.21	0.35
Kinetic3	Pe	1.25	0.89	1.61
	R_m	18.55	12.18	24.91
	k_{fm} (LFR) (h^{-1})	0.19	0.10	0.28
	k_{fm} (HFR) (h^{-1})	0.16	0.06	0.27
	R_f	5.18	1.0	12.52
	k_{ff} (LFR) (h^{-1})	0.12	0.01	0.30
	k_{ff} (HFR) (h^{-1})	0.25	0.03	0.47
Kinetic4	Pe	1.25	0.96	1.54
	R_m	18.70	13.08	24.33
	k_{fm} (h^{-1})	0.19	0.10	0.28
	R_f	4.42	1.0	9.23
	k_{ff} (LFR) (h^{-1})	0.12	0.01	0.28
	k_{ff} (HFR) (h^{-1})	0.24	0.05	0.42
Kinetic5	Pe	1.25	1.0	1.49
	R_m	19.34	13.76	24.92
	k_{fm} (h^{-1})	0.16	0.01	0.32
	R_f	7.21	1.0	24.37
	k_{ff} (h^{-1})	0.20	0.01	0.42
Equilibrium1	Pe	1.25	0.48	2.02
	R_m	9.81	2.65	16.97
Equilibrium2	Pe	1.25	0.34	2.16
	R_m	9.81	1.75	17.86
	R_f	1.0	1.0	3.47

Note: LFR = low flow rate, HFR = high flow rate.

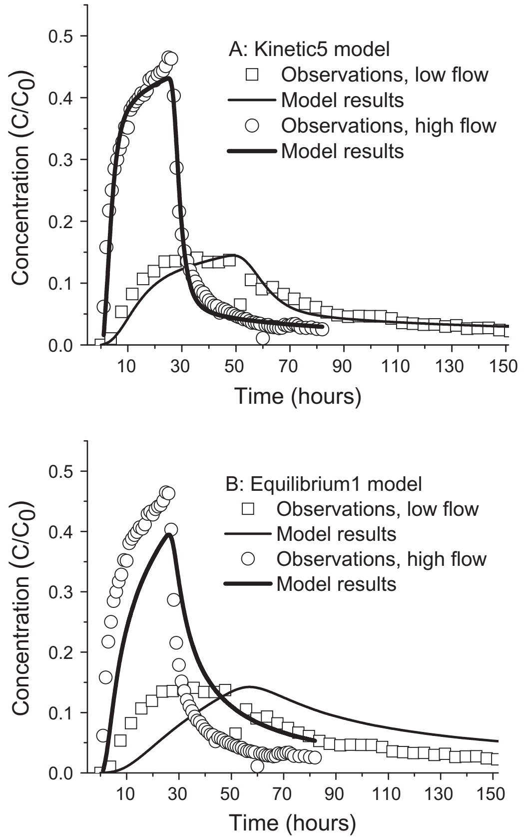

Fig. 4. Fitting two neptunium breakthrough curves from two fractured tuffaceous rock experiments by using Kinetic5 model (A) and Equilibrium1 model (B).

on rate constants for fracture sorption. The other conditions are the same as those of Kinetic4 model. So, there are a total of five parameters to be estimated.

(6) Equilibrium1 model: The sixth inverse model assumes the neptunium sorption is an equilibrium process and only neptunium sorption onto matrix minerals is considered (ignoring its sorption onto the fracture surface). There are two parameters (retardation factor and Peclet number) to be estimated.

(7) Equilibrium2 model: The seventh inverse model considers neptunium equilibrium sorption onto both matrix and fracture surface minerals. There are three parameters (retardation factors for matrix and facture sorption and Peclet number) to be estimated with this model.

A summary of the seven sorption-conceptual models is presented in Table 2.

The estimation results from the above defined seven inverse models are listed in Tables 3 and 4. The Kinetic3 model has the smallest objective function but not the minimum of the four model selection criteria (*AIC*, *AICc*, *BIC* and *KIC*). When the number of parameter dimensions in the Kinetic4 is reduced by using same matrix rate constant for low and high flow experiments, the four model selection criteria also are reduced even though the objective function increases slightly. Furthermore, in the Kinetic5 model, when we assume that the rate constants both in matrix and in fracture are the same for low and high flow experiments, the two model selection criteria *BIC* and *KIC* keep reducing but the other two criteria (*AIC* and *AICc*) increase slightly. As stated by Ye et al. (2008), and Lu et al., (2011), *KIC* is more accurate because it includes the Fished information term and accounts validly for the likelihood of prior parameter estimates. *KIC* has the unique ability to select the best models based not only on their goodness of fit to observation data and number of parameters, but also on the quality of the available data and of the parameter estimates. Because the Kinetic5 model can minimize the *KIC* and *BIC*, we select the Kinetic5 model as the best model.

The curve fitting results from the Kinetic5 and the Equilibrium1 models are plotted in Fig. 4. Because the fitting results from the Kinetic1 to the Kinetic4 are similar to (or worse than) those of the Kinetic5, we do not show the fitting results from the first four models. The Equilibrium2 model has the same value of objective function as that of the Equibrium1 model, but has much higher values for the four model selection criteria (*AIC*, *AICc*, *BIC* and *KIC*) because the Equilibrium2 includes one more parameter in the inversion process. The Equilibrium1 model cannot fit the observational data from either the low or the high flow experiments (Fig. 4B). The objective function value of the Equilibrium1 is about eight times larger than that obtained from the Kinetic5. Sensitivity studies with the Equilibrium1 model indicated that if the early arrivals were properly captured with the Equilibrium1 model by reducing the magnitude of R_m, the peaks would have been much higher than the actually observed concentrations. These results indicate that neptunium sorption is kinetically controlled and the sorption rate constant can be a constant in the low and high flow experiments. The process of neptunium sorption onto fracture surface significantly affects modeling results and it cannot be ignored, even though the fracture coating minerals are not well-developed.

From the Kinetic5 model, the estimated neptunium retardation factor in the matrix is 19.34, which corresponds to a sorption distribution coefficient of 2.05 cm^3/g. The estimated neptunium retardation factor in fracture is 7.21, much smaller than that in matrix. By using the expression of $R_f = 1 + K_a/b$ (Reimus et al., 2003), we can compute the sorption surface area in fracture as $K_a = (R_f - 1)b = 0.14$ cm^3/cm^2. (Here K_a is the surface-area-based distribution coefficient assuming a smooth-walled parallel-plate fracture.) In the matrix the estimated neptunium sorption rate constant is 0.16 h^{-1} versus 0.2 h^{-1} in the fracture.

To confirm the neptunium sorption processes, we use two chemical reaction criteria, the *half time* of the sorption reaction ($t_{1/2}$) and Damköhler number (D_I) computed with Eqs. (10) and (11) (Hoffman, 1981; Domenico and Schwartz, 1990), to test if the sorption can be approximated either as an equilibrium or a kinetic process.

$$t_{1/2} = \frac{\ln 2}{k_f} = \frac{0.693}{k_f}, \tag{10}$$

$$D_I = \frac{\tau}{1/k_f} = k_f \tau. \tag{11}$$

If $\tau \gg t_{1/2}$ in (10), the sorption reaction approaches equilibrium; if $\tau \ll t_{1/2}$, rate-limited kinetic models are necessary to explain the state of the sorption reaction. The Damköhler number in (11) represents the ratio of transport time (residence time) to chemical reaction time. If $D_I \gg 1$, the sorption reaction rate exceeds the transport rate and therefore the reaction can be considered fast enough to be

Table 5
Chemical criteria for confirming the kinetic processes of neptunium sorption onto matrix and fracture coating minerals from Kinetic5 model.

Criteria	Matrix	Fracture
$t_{1/2}$ (h)	4.33	3.47
D_I (LFR)	1.13	1.41
D_I (HFR)	0.28	0.35
Preference	Kinetic	Kinetic

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Table 6
Model selection criteria for discriminating uranium sorption and transport processes.

Criteria	Kinetic1	Kinetic2	Kinetic3	Kinetic4	Kinetic5	Equilibrium1	Equilibrium2
Number of parameters	3	4	7	6	5	2	3
Φ	138.6	126.0	14.15	28.79	88.95	81.85	77.23
AIC	46.85	40.31	−150.53	−88.59	10.94	−2.54	−5.77
AICc	47.32	41.03	−148.76	−87.23	11.95	−2.26	−5.30
BIC	56.85	52.81	−130.53	−71.09	25.94	4.96	4.23
KIC	31.14	29.33	−156.67	−98.13	−17.25	−13.93	−24.93
Preference	Kinetic3						

Table 7
Parameter estimates from alternative conceptual models by fitting two uranium breakthrough curves from two fractured tuffaceous rock experiments (flow rate 0.5 and 2.0 mL/h).

Model	Parameters	Estimated or calculated values	95% confidence intervals	
			Lower bound	Upper bound
Kinetic1	*Pe*	8.0	0.1	17.86
	R_m	25.23	17.08	33.37
	k_{fm} (h^{-1})	1.50	0.41	2.59
Kinetic2	*Pe*	8.0	0.14	15.85
	R_m	27.01	18.47	35.54
	k_{fm} (LFR) (h^{-1})	0.11	0.02	0.21
	k_{fm} (HFR) (h^{-1})	1.10	0.54	1.66
Kinetic3	*Pe*	6.0	3.83	8.17
	R_m	21.5	17.07	25.92
	k_{fm} (LFR) (h^{-1})	0.13	0.08	0.18
	k_{fm} (HFR) (h^{-1})	1.10	0.34	1.86
	R_f	12.66	6.02	19.29
	k_{ff} (LFR) (h^{-1})	0.01	0.01	0.06
	k_{ff} (HFR) (h^{-1})	1.50	0.89	2.11
Kinetic4	*Pe*	7.0	2.02	11.99
	R_m	21.5	1.0	43.54
	k_{fm} (h^{-1})	0.13	0.04	0.21
	R_f	31.43	26.88	35.97
	k_{ff} (LFR) (h^{-1})	0.01	0.01	0.03
	k_{ff} (HFR) (h^{-1})	1.50	1.07	1.93
Kinetic5	*Pe*	9.0	0.1	42.16
	R_m	21.5	8.77	34.23
	k_{fm} (h^{-1})	0.5	0.01	2.63
	R_f	15.83	1.0	53.38
	k_{ff} (h^{-1})	1.50	0.01	4.12
Equilibrium1	*Pe*	2.58	1.02	4.14
	R_m	43.91	25.84	61.97
Equilibrium2	*Pe*	1.01	0.1	2.05
	R_m	73.32	1.0	147.46
	R_f	18.16	1.0	43.08

Note: LFR = low flow rate, HFR = high flow rate.

at equilibrium. Conversely, if $D_I \ll 1$, the reaction is slower than the transport rate and therefore should be described by kinetics.

Table 5 lists the calculated chemical reaction criteria based on the parameters estimated from Kinetic5. In Kinetic5, the estimated k_{fm} in matrix is 0.16 h^{-1} and the mean residence time (τ) is 1.76 and 7.05 h for the high and low flow experiments. Thus, $t_{1/2} = 4.33$ h, which is larger than the mean residence time in the high flow experiment but less than that in the low flow experiment. The computed $D_I = 0.28$ and 1.13 for the high and low flow experiments, respectively. So, the neptunium sorption reaction in the high flow experiment is kinetically controlled but in the low flow experiment it may be close to equilibrium. We still can use the kinetic model to simulate the low flow experiment because the Damköhler number (1.13) is still close to 1. The estimated k_{ff} in fracture is 0.2 h^{-1}. The computed $t_{1/2} = 3.47$ h, which is larger than the mean residence time for the high flow experiment but less than that in the low flow experiment, and $D_I = 0.35$ and 1.41 for the high and low flow experiments, respectively. Thus, neptunium sorption reaction in fracture at the high flow experiment is also kinetically controlled but in the low flow experiment it may be close to equilibrium. Even though the computed half reaction time at the low flow experiment is less than the mean residence time and the Damköhler number is slightly larger than 1, we cannot assert that the sorption onto both the matrix and the facture surface is at equilibrium, because the two chemical reaction criteria (Eqs. (9) and (10)) require that the half reaction time is much less than the mean residence time and the Damköhler number is much larger than 1. Therefore, in the low flow experiment neptunium sorption onto the matrix and the facture surface is likely still kinetically controlled but close to equilibrium. We still need to use a kinetic model to simulate the neptunium sorption processes.

Combining the results of model selection criteria which indicated that the Kinetic5 model fits the observational data much better and that its objective function is about eight times less than that of the Equilibrium1 model, we therefore conclude that neptunium sorption at low and high flow experiments is kinetically

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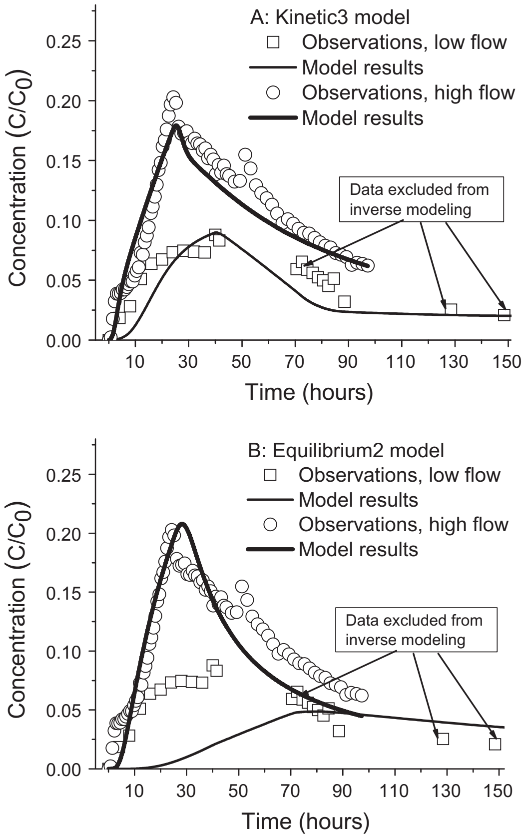

Fig. 5. Fitting two uranium breakthrough curves from two fractured tuffaceous rock experiments by using Kinetic3 model (A) and Equilibrium2 model (B).

controlled. Non-equilibrium neptunium sorption onto matrix and fracture surface is also confirmed based on the two chemical reaction criteria.

5.3. Step 3: Identifying uranium sorption parameters from two experiments

In this step, we used the same method as step 2 by fixing the major common transport parameters (mean residence time, fracture half aperture and matrix tortuosity) and coupling the two uranium breakthrough curves from high and low flow experiments to estimate the uranium sorption parameters simultaneously. Because the flow rate after 42 h in the uranium low-flow experiment changed with time, the observed uranium concentrations are not reliable. Therefore, we excluded the uranium observation data of the low flow experiment after 42 h from inverse modeling.

The relevant field and laboratory values of uranium retardation factors and kinetic rate constants published in the literature (Shackelford, 1991; Williams, 1993; Barnett et al., 2000, 2002; Garcia-Gutiérrez et al., 2001; Reimus et al., 2006) were used to determine the lower and upper bounds to be (10, 100) and (0.01, 10 h^{-1}), respectively. Like the neptunium experiment inversion in step two, the Peclet number for the uranium experiments was not fixed but was in stead estimated during the inverse process. A lower and upper bound is set for Peclet number as (0.1, 10). From the literature, we also find that the uranium diffusion coefficient in free water (D_0) is 1.2×10^{-5} cm^2/s (Reimus et al., 2006). As for the neptunium experiments, we then calculate the uranium matrix diffusion coefficient by $D_m = \tau_m D_0 = 3.29 \times 10^{-6}$ cm^2/s.

To identify the uranium sorption processes, we solved the inverse problem under seven alternative conceptual models similar to those used for neptunium (see Table 2). The resulting estimates from the seven conceptual models are listed in Tables 6 and 7. The Kinetic3 model has the smallest objective function and minimizes all of the four model selection criteria (*AIC*, *AICc*, *BIC* and *KIC*). The simulation results from the Kinetic3 and Equilibrium2 models are plotted with the experimental data in Fig. 5. Because the fits of the Kinetic1, Kinetic2, Kinetic4 and Kinetic5 models are worse than the Kinetic3 model, we do not show the fitting results from the former four models. The Equibrium1 model has a larger value of objective function than the Equibrium2, and it also has slightly higher values for the four model selection criteria (*AIC*, *AICc*, *BIC* and *KIC*). The Kinetic3 model fits the observational data of the low and high flow experiments much better than other four kinetic models. The objective function value of the Equilibrium2 model is about five times larger than that of the Kinetic3 model. These results indicate that uranium sorption process is kinetically controlled; the sorption rate constant varies with flow velocity. We therefore need to apply different rate constants for low and high flow transport experiments. Uranium sorption onto fracture surfaces cannot be ignored, even though the fracture coating minerals are not well-developed.

The estimated Peclet number from the Kinetic3 model is 6 (see Table 7). This Peclet number value is about four times larger than those estimated from tritium experiments. These results imply that the dispersivity of uranium is about four times smaller than that of tritium. The estimated uranium retardation factor in the matrix is 21.5, corresponding to a sorption distribution coefficient of 2.3 cm^3/g. In the fracture the estimated uranium retardation factor is 12.66, corresponding to a surface-area-based sorption distribution coefficient in the fracture of 0.27 cm^3/cm^2. The uranium sorption rate constants in the matrix are varied with flow rate. In the high flow rate experiment, the estimated rate constant is 1.1 h^{-1} versus 0.13 h^{-1} in the low flow experiment. In the fracture, the estimated rate constants are 0.01 and 1.5 h^{-1} for the low and high flow experiments.

To confirm the uranium sorption process, we calculated the two chemical reaction criteria (Eqs. (9) and (10)) based on the parameters estimated from the Kinetic3 models (see Table 8). With the Kinetic3 model, the estimated k_{fm} in the matrix for the high and low flow experiments are 1.1 and 0.13 h^{-1}. The mean residence time (τ) for the high and low flow experiments are 1.76 and 7.05 h. The calculated half reaction time $t_{1/2} = 0.63$ h < τ, and the Damköhler number $D_I = 1.94 > 1$ for the high flow experiment. Even though the computed half reaction time at the high flow experiment is less than the mean residence time and the Damköhler number is slightly greater than 1, we cannot assert the sorption process is at equilibrium as we discussed in step two. Therefore, at the high flow experiment uranium sorption is likely still kinetically controlled but close to equilibrium. For low flow experiment, $t_{1/2} = 5.28$ h < τ and $D_I = 0.92 < 1$. Thus, uranium sorption in the matrix for the low flow experiment is also kinetically controlled. The estimated k_{ff} in fracture for the high and low flow experiments are 1.5 and 0.01 h^{-1}. For high flow experiment, $t_{1/2} = 0.46$ h < τ, and $D_I = 1.58 > 1$. As for uranium sorption in the matrix, uranium sorption reactions in fractures under high flow is still kinetically controlled but close to equilibrium. For the low flow experiment, $t_{1/2} = 47.53$ h > τ, and $D_I = 0.1 < 1$. Thus, uranium sorption in the

Table 8
Chemical criteria for confirming the kinetic processes of uranium sorption onto matrix and fracture coating minerals from Kinetic3 model.

Criteria	In matrix	In fracture
$t_{1/2}$ (LFR) (h)	5.28	47.53
$t_{1/2}$ (HFR) (h)	0.63	0.46
D_I (LFR)	0.92	0.1
D_I (HFR)	1.94	1.58
Preference	Kinetic	Kinetic

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fracture at low flow is kinetically controlled. Finally, based our chemical criteria, together with the superior fit of the Kinetic3 model to the experimental data, we conclude that uranium sorption onto matrix and fracture surface minerals at these low and high flow experiments is still kinetically controlled.

6. Summary and conclusions

The sorption processes of neptunium and uranium are identified in this study based on inverse modeling. Seven alternative sorption models are developed for each radionuclide to reflect different conceptualizations of the sorption processes; the seven models are then calibrated against the flow-through experiments performed on a fractured tuffaceous rock core at two different flow rates. Based on the model calibration results, four model selection criteria are calculated, and the Kinectic5 model for neptunium experiment and the Kinetic3 model for uranium experiment are selected as the best one by the model selection criteria. The major conclusions of this study are as follows:

(1) Stepwise inversion allows estimation of common transport parameters (b, τ and D_m) from conservative tracer (tritium) data, followed by sorption parameters from reactive solute (neptunium and uranium) data. The stepwise method of inverse modeling is able to estimate a large number of optimum parameters for radionuclide transport through the fractured tuffaceous rock: the mean fluid residence time in fractures, fracture aperture, Peclet number, matrix diffusion coefficients for tritium, neptunium and uranium, and retardation factors and kinetic rate constants for neptunium and uranium. These estimated parameter values are valuable for other scientists conducting similar studies, in particular for determining reasonable parameter ranges.

(2) The sorption of neptunium and uranium onto fracture surfaces cannot be ignored, even though the fracture coating minerals are not well-developed. Inclusion of this process in the inverse model significantly reduces the objective function, and all four model selection criteria indicate the benefit of including this process.

(3) The kinetic rate constants of sorption onto fracture surfaces and matrix minerals are constant for the low and high flow neptunium experiments. But, they vary with experimental flow rates for uranium experiments so that we estimated different values of these parameters for the high and low flow rate uranium experiments.

(4) The kinetic transport behavior of neptunium and uranium was clearly demonstrated by the model selection criteria. All the criteria select kinetic models for both neptunium and uranium experiments as the best model, although this model has a large number of model parameters. In other words, improvement of the model fit comes from appropriate sorption-conceptual model, which justifies the increasing number of model parameters (i.e., model complexity).

(5) Preference of the kinetically-controlled sorption process is independently confirmed by the two chemical criteria: the half reaction time and Damköhler number. This is the first time that the chemical criteria are used for cross validation of the model selection results of the four statistical model selection criteria.

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