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Effect of colloids on non-Fickian transport of strontium in sediments elucidated by continuous-time random walk analysis

Dong-Xu Liu a,b, Rui Zuo a,*, Andrey P. Jivkov c, Jin-Sheng Wang a, Li-Tang Hu a, Liu-Xing Huang b

a College of Water Sciences, Beijing Normal University, Engineering Research Center of Groundwater Pollution Control and Remediation, Ministry of Education of China, Beijing 100875, PR China
b Northwest Institute of Nuclear Technology, Xi’an 710024, PR China
c Research Centre for Radwaste & Decommissioning and Modelling & Simulation Centre, Dalton Nuclear Institute, The University of Manchester, Manchester M13 9PL, UK

ABSTRACT

Understanding the influence of colloids on radionuclide migration is of significance to evaluate environmental risks for radioactive waste disposals. In order to formulate an appropriate modelling framework that can quantify and interpret the anomalous transport of Strontium (Sr) in the absence and presence of colloids, the continuous time random walk (CTRW) approach is implemented in this work using available experimental information. The results show that the transport of Sr and its recovery are enhanced in the presence of colloids. The causes can be largely attributed to the trap-release processes, e.g. electrostatic interactions of Sr, colloids and natural sediments, and differences in pore structures, which gave rise to the varying interstitial velocities of dissolved and, if any, colloid-associated Sr. Good agreement between the CTRW simulations and the column-scale observations is demonstrated. Regardless of the presence of colloids, the CTRW modelling captures the characteristics of non-Fickian anomalous transport (0 < β < 2) of Sr. In particular, a range of 0 < β < 1, corresponding to the cases with greater recoveries, reveal strongly non-Fickian transport with distinctive earlier arrivals and tailing effects, likely due to the physicochemical heterogeneities, i.e. the repulsive interactions and/or the macro-pores originating from local heterogeneities. The results imply that colloids can increase the Sr transport as a barrier of Sr sorption onto sediments herein, apart from often being carriers of sorbed radionuclides in aqueous phase. From a modelling perspective, the findings show that the established CTRW model is valid for quantifying the non-Fickian and promoted transport of Sr with colloids.

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1. Introduction

Due to potential radio-ecological impacts and environmental risks to human health, the safe disposal of spent nuclear fuel (SNF), high-level radioactive waste (HLW) and low-and intermediate-level radioactive waste (LLW) in underground geological media is widely recognized as a grand engineering challenge affecting present and future generations (Faybishenko et al., 2016). Fundamental understanding of the transport and fate of radionuclides, including a wide range of actinides (e.g., 238U, 239Pu) and fission products (e.g., 90Sr, 137Cs, 99Tc), in heterogeneous geological formations is one of the key elements required to underpin safety assessment (SA) and/or performance assessment (PA) of nuclear waste repositories (Blechschmidt and Vomvoris, 2010; Fuller et al., 2016; Rumynin, 2011). In the past several decades, it has been repeatedly demonstrated that colloidal particles could facilitate the transport of radionuclides due to their potential to carry species (Kersting, 2012; Kersting et al., 1999; Novikov et al., 2006; Sen and Khilar, 2006). These colloids are generally defined as being between 1 and 1000 nm, e.g. humic substances, clays, metal oxides, and microorganisms (Rumynin, 2011; Simunek et al., 2006). By attaching to mobile colloids, low solubility and/or strongly sorbed radionuclides (e.g. Pu isotopes) can migrate over significant distances in groundwater over time scales of concern (Kersting, 2013). This colloid-mediated process is neither accounted for in classical...
advection-dispersion models based on a constant dispersivity and a linear sorption process (Kersting, 2012; Kosackowski, 2004; Kosackowski and Smith, 2005) nor in thermodynamic methods based on the solubility and attachment potential (Zänker and Hennig, 2014), as they commonly assume that sorbing radionuclides can attach to the stationary solid phase and thus underestimate the transport domain in real scenarios. Thus, further investigations on colloid-facilitated radionuclide transport are being carried out, particularly, for strongly sorbed radioelements. Nevertheless, in the context of colloidal effects, there are few examples that explore the specific mechanisms and modelling strategies for the anomalous migration of Sr with weaker sorption.

Generally, modelling of colloid-facilitated species transport mainly refers to the topics of colloid stability, colloid-species stability, their transports, and various interactions among colloids, species and porous media (Flury and Qiu, 2008; Yuan and Shapiro, 2012; Zänker and Hennig, 2014). It is beyond the scope of this article to give a comprehensive overview and detailed discussion of those topics.

In practice, in conjunction with well-designed column experiments, the colloidal and facilitated species transport has been often studied by modified forms of advection-dispersion equation (ADE) with expressed colloid filtration theory (e.g., physical and/or chemical non-equilibrium models) (Adriani et al., 2018; Bai et al., 2018; Bradford et al., 2003; Chopra et al., 2016; Chrysikopoulos and Katzourakis, 2015; Flury and Qiu, 2008; Liang et al., 2013; Ma et al., 2016; Massoudieh and Ginn, 2007; Moridis et al., 2003; Pang and Simunek, 2006; Rahmatpour et al., 2018; Wang et al., 2013; Wolvesberg et al., 2017; Yao et al., 1971; Yecheskel et al., 2018; Zhang et al., 2017) and by additionally taking advantage of the solution chemistry and interaction energy data (Lov et al., 2018; Makselon et al., 2017). In this line of work, the major mechanisms underlying the transport of colloidal particles in fractured porous media include advection, dispersion, sorption, attachment/detachment, blocking, physical strainaging, size exclusion and aggregation (Babakhani et al., 2017; Molnar et al., 2015; Simunek et al., 2006). While the cited continuum ADE-based models provide significant description of the species migration with colloids, it remains challenging to estimate the required parameters in real scenarios, such as water chemistry, hydrodynamic dispersion and adsorption-desorption rates. It is reported that a primary limitation of the continuum approach lies in the excessive number of parameters involved in various transport mechanisms in real-world scenarios (Babakhani et al., 2017). There are some bottlenecks concerning reliably modelling colloid/nanoparticle migration, such as the challenge of ubiquitous physicochemical heterogeneities, the scale-dependent hydraulic conditions, the absence of reliable measurement techniques and data for relevant systems (Schafer et al., 2012; Zänker and Hennig, 2014). Furthermore, the fickian-based ADE framework, where hydrodynamic dispersion is represented as a diffusion-like process governed by Fick’s Laws, has been shown to be limited, to some extent, for capturing non-fickian or anomalous migration for both solutes and colloids (Edery et al., 2015; Gao et al., 2009; Kosackowski and Smith, 2005). In addition, the conservative tracer parameters fitted from the ADE-based style can be invalid for the sorbed tracer transport (Rubin et al., 2012). Therefore, it is appealing to explore extended modelling framework.

The CTRW framework offers a general representation of dispersive transport with successful applications to a broad range of systems from the pore scale upwards (Berkowitz et al., 2006; Berkowitz et al., 2016; Cortis et al., 2004; Dentsz et al., 2011; Edery et al., 2016; Rubin et al., 2012; Wang and Cardenas, 2017). Together with other well-documented models, e.g., multi-rate mass transfer (MRMT) model, fractional advection-dispersion equation (FADE) model and two-region model, the CTRW model has been shown to evaluate better the full tracer transport behavior, particularly the late-time tailing (Burnell et al., 2017; Chen et al., 2017; Gao et al., 2009; Neuman and Tartakovsky, 2009; Zaheer et al., 2017). Developments of CTRW mainly include: two-scale models to account explicitly for bimodal characteristic (Berkowitz et al., 2008; Bijelic et al., 2011); CTRW-based filtration model employing partial differential equation (PDE) formulation to explain the bio-colloid transport behavior (Cortis et al., 2006); non-Fickian transport based on pore scale images and models (Bijelic and Blunt, 2006; Le Borgne et al., 2011); migration and retention models to quantify the coupled sorption and transport behavior (Liu et al., 2017; Raveh-Rubin et al., 2015; Rubin et al., 2012); reactive transport models of engineered nanoparticles by using particle tracking (PT) formulation (Naftaly et al., 2016). Whereas, the CTRW-based analysis for the non-Fickian and co-transport of Sr with varying colloids remains uncommon.

A major merit of CTRW over ADE-based continuum models can be deduced from these past experiences. The latter models commonly separate mathematical terms to describe transport and chemical reactions, which in turn require identification and, often impractical, experimental estimation of coupling parameters. The former models provide the means to identify the coupling between reaction and migration and to account for the effects of the physicochemical processes on the anomalous transport characteristics of solutes and colloid-size particles (Naftaly et al., 2016; Rubin et al., 2012).

The objectives of this work are: (1) to quantify and interpret the underlying anomalous transport of Sr in the absence and presence of colloids by means of the CTRW model and column experiment data; and (2) to explore the validation of the CTRW strategy when accounting for colloid-mediated and non-Fickian migration of species with weaker sorption - e.g., stable Sr isotope (as an analog for 90Sr) herein. Experiments with natural sediments collected from the Beishan area for HLW geological disposal in China have been conducted. The experimental data is from transport observations of Sr and its co-transport with three types of synthetic colloids: Fe(OH)3 (ferric hydroxide) colloid (FHC), silica colloid (SC), humic acid colloid (HAC). Our analysis advances the understanding of Sr anomalous transport without and with colloids, which is beneficial for environmental modelling and risk evaluations for radionuclide mobility.

2. Materials and methods

2.1. Sediments

Five near-surface (0–10 cm) sediment samples (labeled a–e, respectively) were collected from typical locations in Beishan area, northwest China. The Gobi desert Beishan site was the first suitable candidate for China’s HLW repository and underground research laboratory (URL), where the groundwater was of CI-SO4-Na type with a range of 7–9 in pH (Faybishenko et al., 2016; Wang et al., 2018).

The elemental composition (Table S1) of the sediment samples was measured and estimated by inductively coupled plasmaatomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Furthermore, scanning electron microscopy (SEM) was utilized to extract two-dimensional (2D) images of the microstructure information, such as size and shape of pores and aggregates. Based on the selected SEM images (Fig. S1), the pore size distributions (PSDs) of the samples were estimated (Fig. S2). The results were presented in section 3.1 below.
2.2. Column experiments

Prior to batch experiments and column observations, four groups of stock liquids were prepared: Sr\(^{2+}\) solution; Fe(OH)\(_3\) (ferric hydroxide) colloid (FHC) suspension; silica colloid (SC) suspension; and humic acid colloid (HAC) suspension. Details on the preparation of stock liquids, as well as batch experiments to explore the Sr sorption kinetics (Fig. S3), can be found in the supplementary material.

The column experiments were carried out in five sets (each set includes four columns prepared for four types of input liquids) of plexiglass columns which were placed vertically and packed with the five sediment samples (a, b, c, d, e, respectively). In each column (1.6 cm diameter and 5 cm length), a sediment sample with a density of 1.50 g cm\(^{-3}\) was packed (Fig. S4). For each type of packed medium, four groups of input liquids at pH 7 were supplied to columns as follows: (1) Sr\(^{2+}\) solution (10 mg L\(^{-1}\)); (2) mixture of Sr\(^{2+}\) solution (10 mg L\(^{-1}\)) and FHC suspension (100 mg L\(^{-1}\)); (3) mixture of Sr\(^{2+}\) solution (10 mg L\(^{-1}\)) and SC suspension (100 mg L\(^{-1}\)); (4) mixture of Sr\(^{2+}\) solution (10 mg L\(^{-1}\)) and HAC suspension (100 mg L\(^{-1}\)). Note that, since a fresh column was packed for each column experiment, small altering porosity could give rise to slightly varying interstitial velocities, even for identical flow rates (Chryssikopoulos and Katzourakis, 2015). Consequently, the influence of flow rates on the transport results has not been quantified in this work.

In order to remove trapped air from the packed columns, these were initially saturated with deionized water from bottom to top. Then, the input liquids were applied at the top of the columns at a flow rate, 0.25 mL min\(^{-1}\), by a peristaltic pump. At the bottom of the columns, effluents were monitored over experiments’ durations, where the Sr concentration, \(C_t\), was determined by ICP-AES. Thus, the temporal profile of concentrations was easily obtained.

Denoting the experiment duration by \(T\) and the Sr concentration at the inlet by \(C_0\), at any time \(0 \leq \tau \leq T\) we define a normalized concentration \(c\) by:

\[
c = \frac{C_t}{C_0}
\]

Further, the recovery or cumulatively eluted mass fraction of Sr is calculated by:

\[
R_{Sr} = \frac{\int_0^t Q_{out} C_t dt}{\int_0^t Q_{in} C_0 dt} = \frac{\int_0^t C_t dt}{\int_0^t C_0 dt} = \frac{\int_0^t dt}{\int_0^t dt}
\]

where \(Q_{in}\) and \(Q_{out}\) are the input and effluent volumetric flow rate, respectively. \(Q_{out}\) is equal to \(Q_{in}\) with a breakthrough during the experiment, that is, 0.25 mL min\(^{-1}\) as defined above.

2.3. CTRW-based reactive transport model

The CTRW formalism originates in Einstein’s approach to Brownian motion. In the geological context, CTRW provides a stochastic representation of dispersive transport accounting for the disorder of the system. Species’ longer-scale transport emerges from particle transitions between sites with displacement \(s\) within time \(\tau\). Existing material heterogeneities are captured by the probability of particle transition between sites. This is described by a probability density function (pdf), \(p(s, \tau)\), as detailed in other sources (Ben-Zvi et al., 2018; Berkowitz et al., 2006; Berkowitz et al., 2016; Bijeljic et al., 2011; Dentz et al., 2004; Edery et al., 2014). The formulation allows for both Eulerian (PDE-based) and Lagrangian (PT-based) methods to be used for transport modelling with potential physicochemical processes, i.e. advection, diffusion, hydrodynamic dispersion across various scales, and trap-release (e.g., attachment/detachment, etc.) mechanisms (Berkowitz et al., 2016). This work employs the CTRW-PDE framework, which is explained briefly below for completeness.

The CTRW transport equation with the normalized concentration, \(c\), is formulated in Laplace space and can be given in one dimension form (Cortis and Berkowitz, 2005; Edery et al., 2014; Yuan and Sin, 2011):

\[
uc_{Lap}(x, u) - c_0(x) = -M_{Lap}(u) \left[ \frac{\partial}{\partial x} c_{Lap}(x, u) - D_s \frac{\partial^2}{\partial x^2} c_{Lap}(x, u) \right]
\]

(3)

\[
M_{Lap}(u) = \frac{\psi_{Lap}(u)}{\Gamma(1 - \beta)} \int_{0}^{\infty} \frac{\psi_{Lap}(u)}{1 - \psi_{Lap}(u)} \left( \frac{u}{c_{Lap}(x, u)} \right) dt
\]

(4)

In Eq. (3), \(u\) is the Laplace variable, \(c_0\) is the initial concentration, \(c_{Lap}(x, u)\) is the Laplace-transformed normalized tracer/particle concentration, \(M_{Lap}(u)\) is a memory function that captures the small scale (below the measured resolution level) heterogeneity, and \(\psi_s\) and \(D_s\) are the transport velocity and generalized dispersion coefficient, respectively. In Eq. (4) for the memory function, \(\psi(t)\) is a probability density function (pdf), and \(\psi_{Lap}(u)\) is the Laplace-transformed form of \(\psi(t)\), defined as the probability rate for a transition time \(t\) between transport sites, and \(\Gamma\) is a characteristic time. It is recognized that \(\psi_s\) and \(D_s\) are time-dependent and fundamentally differentiated from the pore water velocity \(v\) and dispersion coefficient \(D\) in the classical ADE framework (Berkowitz et al., 2006).

A key step in the CTRW modelling is the selection of \(\psi_{Lap}(u)\), which needs to capture the nature of migration patterns in geological media. Several forms of \(\psi_{Lap}(u)\) have been proposed in the literature (Berkowitz et al., 2006; Cortis and Berkowitz, 2005). The truncated power law (TPL) has been shown an appropriate selection, as this can quantify a broad range of transport regimes, including the evolution from non-Fickian to Fickian transport (Edery et al., 2014). The TPL Laplace transform for conservative tracer transport reads:

\[
\psi_{Lap}(u) = \left[ 1 + \tau_2 u t_1 \right]^{\beta} \exp \left( t_1 u \right) \Gamma \left( -\beta, \tau_2^{-1} + t_1 u \right) / \Gamma \left( -\beta, \tau_2^{-1} \right) \quad 0 < \beta < 2
\]

(5)

where \(t_1\) is a characteristic transition time marking the onset of the power law region, which can be determined from the transport parameters (Nissan et al., 2017); \(\tau_2 = t_2 / t_1\), where \(t_2\) is a cut-off time marking the onset of Fickian transport; \(\Gamma\) is the incomplete Gamma function; and \(\beta\) is a measure of the degree of dispersive transport and characterizes the relative shapes of the anomalous transport regimes. If \(\beta > 2\), the transport distribution displays Fickian feature; \(1 < \beta < 2\) corresponds to a moderately non-Fickian system, and \(0 < \beta < 1\) reveals highly non-Fickian migration (Berkowitz et al., 2006). Note that \(t_2\) plays only minor role in the transport behavior for \(\beta > 2\). The CTRW equation converges to the classical ADE with \(\psi(t)\) decreasing exponentially.

When reactive species are considered, the adsorption and desorption processes are described with a “sticking” rate and a “sticking time” pdf (Cortis et al., 2006; Margolin et al., 2003). This is achieved by modifying the probability density function \(\psi_{Lap}(u)\). The new transition pdf for reactive species in the Laplace space reads:
ψ_{Lap}(x, u) = \psi_{Lap, 0}(x, u + \Lambda - \Lambda \psi_{Lap}(u)) \tag{6}

where ψ_{Lap, 0} is a known function of a conservative tracer; Λ is the average "sticking" rate; ψ_{Lap}(u) is the single "sticking time" pdf.

Small-scale heterogeneities in physicochemical interactions and the power law tailing can be depicted by ψ_{Lap}(u) (Cortis et al., 2006):

ψ_{Lap}(u) = \frac{1}{1 + u^\mu} \tag{7}

where μ is a parameter to represent the power law tailing degree, 0 < μ < 1.

Arguably, by advancing an irreversible deposition term, Eq. (3) can be extended to quantify the colloidal transport with an attachment-detachment process (Cortis et al., 2006):

u_{C_{Lap}}(x, u) - C_0(x) = -M_{Lap}(u) \left[ k_f \psi_{C_{Lap}}(x, u) + v_x \frac{\partial}{\partial x} C_{Lap}(x, u) \right] - D_f \frac{\partial}{\partial x} C_{Lap}(x, u) \tag{8}

where k_f is an irreversible attachment coefficient accounting for colloid deposition/loss owing to diffusion, interception, and gravitational sedimentation, and is normally estimated using the filtration theory (Simunek et al., 2006).

Note that more information is frequently required to account for the potential mechanisms of colloid-mediated transport (Babakhani et al., 2017). In this study, as no additional experimental evidence to substantiate the relevant mechanisms exists, we do not attempt to introduce a filtration term to the CTRW model for Sr transport with colloids. Since the sorption kinetics of Sr implied weaker interactions between Sr and the selected colloids (Fig. S3), it is expected that the Sr\textsuperscript{2+} would be the dominant species during Sr transport with colloids in aqueous phase. Furthermore, the migration patterns of nanoparticles or colloidal particles can be similar to those of the conservative species due to low attachments or strongly repulsive forces between the particles and the collectors (Kosakowski and Smith, 2005; Naftaly et al., 2016). Accordingly, the CTRW-TPL model with adsorption/desorption above can be employed to quantify the Sr breakthrough curves (BTCs) in the absence and presence of colloids. Arguably, this formulation herein is appropriate for the transport of total aqueous Sr, i.e., dissolved Sr (Sr\textsuperscript{2+}) and colloidal Sr (colloid-Sr complexes).

The CTRW equations can be solved with a set of given boundary conditions. Herein Robin boundary condition (BC) is specified at the column inlet with a step input and Neumann BC is set at the outlet.

### 2.4. CTRW modelling strategy

The experimental breakthrough curves (BTCs) are reproduced by the CTRW simulations conducted through the MATLAB CTRW toolbox (https://www.weizmann.ac.il/EPF/People/Brian/CTRW/software). The inversion of CTRW-TPL model involves six parameters, including v_x, D_f, \beta, t_2, Λ and μ.

Multi-parameter fitting and optimization can be a time-consuming process, requiring sensible selection of initial parameter and evaluation of final results to minimize the potential effect of the intrinsic parameters non-uniqueness (Berkowitz et al., 2016; Hansen and Berkowitz, 2014; Wang and Cardenas, 2017). Therefore, it is advisable to iteratively alter initial guesses according to the sensitivity of the correlated physical parameters. Initial values of v_x and D_f can be estimated by analyzing the experimental information, such as, an analogous-conservative tracer behavior occurred in the promoted transport of Sr with FHC, etc. Further, on the basis of the BTC shapes and β values in published literature, a range of β, from 0.8 to 1.3, is tested. The cut-off time, t_2, is relatively insensitive to the transport and is set to a large initial value, 10^6.

Then, the parameters Λ and μ, which account for the effect of sorption and the power law slope of the BTCs, can be estimated by adjusting the initial values (e.g. 0.01 and 0.02, respectively). The routine to estimate initial values and to adjust inputs using trial and error method, to a great extent, corresponds to the numerical experiments for addressing the effect of various CTRW parameters (Cortis et al., 2006) and the parameter sensitivity analysis in our study (Fig. S5). Thus, good agreement between the CTRW modeling results and column-scale observations can be achieved.

### 3. Results and discussion

#### 3.1. Chemical composition and pore space characteristics of the sediment samples

Samples-a, b, c and e, exhibited approximately equal contents of the main elements, while sample-d exhibited Ca enrichment, 48.77%, on the expense of reduced Al, Fe and Mg (S-1, Table S1). This enrichment is likely to inhibit the sorption of Sr onto material surfaces during transport experiments as Ca is expected to occupy more adsorption sites. The chemical analysis suggests that the natural sediments may contain Al and Fe oxides or hydroxides, as well as some organic-inorganic composite colloids.

Selected SEM images of the sediment samples are shown in Fig. S1. These reveal irregular granular structures with aggregates of different sizes. The complex pore space formed between the aggregates affects strongly the flow and transport behavior (Xiong et al., 2016) including migration studied here, although the packed columns are frequently considered to be homogeneous macroscopically.

The broadly varying pore size distribution (PSD) in heterogeneous media makes the modelling of transport properties at pore scale a challenging problem (Jivkov and Xiong, 2014; Xiong et al., 2015). In order to facilitate future pore-scale modelling efforts and to assess the potential correlation between pore structures and transport characteristics, the PSDs of the samples were quantified (S-1). A well-established algorithm, introduced by Rabbani et al. (2014) and known as the water-shed algorithm, was applied to the SEM images (Fig. S1); see also Rabbani et al. (2017) for the updated version. The average pore radii are approximately 56 μm, 60 μm, 61 μm, 76 μm, and 62 μm, respectively (Fig. S2). It is expected that larger pore size will result in increased water flow rate and decrease the residence time of aqueous Sr, under equal other conditions, e.g. pore connectivity. Hence, it is anticipated that sample-d with the largest average pore radius will provide a more permeable domain compared to the sample-a with the smallest average pore size and to the other samples-b and c with intermediate average pore sizes.

#### 3.2. Breakthrough curves of Sr without colloids

Fig. 1 shows the measured Sr BTCs from column experiments without colloids. For sample-d, the earlier front and peak arrival of Sr suggests the existence of preferential paths and/or weaker interactions between Sr and mineral surfaces. This may be attributed to the larger pore throats and to the competitive sorption of other elements, e.g. Ca, onto minerals, as discussed in relation to the chemical composition. Note that sample-e has similar BTC to sample-d. Despite the average pore size of sample-e being close to that of samples-a, b and c, this is likely because sample-e has a...
number of quite large pores (larger than sample-d even, see Fig. S2) which might produce a relatively loose region of the packing column and have facilitated the transmission significantly.

In contrast, the BTCs of samples-a, b and c appear to give similar behaviors with flatter fronts and delayed tailings, corresponding to longer residence times of Sr. This may be attributed to the narrower pore channels, as well as to the trap-release processes.

On the whole, these observed BTCs from the packed columns can be divided into two groups. The first one includes BTCs of samples-a, b and c with the relatively slow migration features, while the second one consists of ones of columns packed samples-d and e, which indicate earlier breakthrough behaviors. Hence, the following inverse modelling will be just conducted against for samples-b and d, as representatives of the two groups of transport behaviors, respectively.

3.3. CTRW modelling of the transport of Sr without and with colloids

The results of applying the CTRW-TPL model to column experiments with samples-b and d are shown together with experimental ones in Fig. 2. The figure shows clearly that the presence of inorganic colloids (FHC and SC) and organic matter (HAC) increases the transport of strontium and results in stronger recoveries. The recoveries are further illustrated in Fig. 3. Tables 1 and 2 provide the estimations of the parameters used in the CTRW-TPL models and the calculated recoveries for specimens-b and d, respectively.

For sample-b, the transport of Sr was enhanced notably more by FHC than by SC and HAC (Fig. 2A). Specifically, the co-transport of Sr and FHC displays an earlier arrival with a shorter breakthrough time, as well as a greater recovery (R_{Sr} = 81.8%) of Sr (Fig. 3A and Table 1). This can be attributed to a number of factors, such as pore-scale local heterogeneities, differences in colloidal properties (including sizes, specific surface areas, surface energies, etc.) and colloid-surface interactions (Kosakowski and Smith, 2005; Naftaly et al., 2016; Yuan and Shapiro, 2012) specific to FHC. It is likely that the third factor plays the largest role in this case, due to the attachment affinity of positive FHC particles to the negatively charged porous media (S-3). This leads to a reduction of binding sites for Sr on the mineral surfaces. Meanwhile, the repulsive forces between the positively charged FHC particles and Sr^{2+} may produce a greater transport velocity of Sr. Hence, apart from the Sr^{2+} trapped onto mineral surfaces and into dead-end pores, or attached to immobile colloids, the remaining Sr^{2+} and colloidal Sr appear to pass freely through the packing column. Differently, the transport of Sr or its co-transport with SC/HAC in sample-b is characterized by a larger fraction of Sr being immobilized because of trap mechanisms. These include sorption onto minerals, diffusion into stagnant domains, attachment on static colloids due to potential sedimentation and filtration processes.

For sample-d, the BTC features show earlier arrivals and the greater Sr recoveries compared to sample-b (Figs. 2 and 3 and Table 2). As already mentioned, the greater pore throats and more contents of Ca in sample-d are potentially responsible for the typical characteristic of observed BTC of Sr through the column filled with sample-d. Our interpretation of the results is that in addition to the mechanisms operating also in sample-b - colloidal attachment, competitive binding and electrostatic interactions of the charged particles, the presence of local macro-pores contributes substantially to the observed behavior. The macro-pores have less surface area for absorption (per unit material volume) and bind less colloids and dissolved cations. This results in faster interstitial velocities and facilitated transport of dissolved and colloid-
associated strontium. Unlike the results for sample-b, the presence of FHC and SC in sample-d appears to increase the Sr migration. This seems to be a synergetic effect of relatively larger pores and colloidal attachment. However, the presence of HAC leads to significantly larger increase (Fig. 2B and Table 2), which can be attributed to a greater affinity for metal binding of HAC as for sample-b.

The CTRW-TPL modelling results indicate clearly the existence of facilitated-transport and demonstrate the characteristics of non-Fickian transport of Sr, \(0 < \beta < 2\). The latter is observed regardless of the absence or presence of colloids (Tables 1 and 2).

The CTRW-TPL modelling results indicate clearly the existence of facilitated-transport and demonstrate the characteristics of non-Fickian transport of Sr, \(0 < \beta < 2\). The latter is observed regardless of the absence or presence of colloids (Tables 1 and 2).

In the cases with sample-b, the estimated \(0 < \beta < 1\), reveals strongly anomalous transport with much earlier arrivals and tailing effects. Specifically, for FHC with distinct \(v_p\) this is mainly due to reduced binding sites and repulsive interactions between FHC and Sr with positive charges. Contrary to expected, the HAC case with smaller \(\beta\) and greater \(v_p\), shows weaker facilitated-transport behavior with a slightly accelerated transport process and limited recovery. Our explanation is the potential immobilization mechanism and filtration process. These are beyond the capabilities of the present model, but will be a subject of further investigations.

For sample-d, the BTCs for all cases exhibit similar transport features. Specifically, the cases of colloid-free and SC, where \(\beta < 2\), are likely to be trapped onto materials, the calculated \(1 < \beta < 2\) suggest moderate anomalous transport. For the cases of FHC and HAC with distinctive \(v_p\), the calculated \(0 < \beta < 1\) shows a strongly non-Fickian transport. The causes can be attributed to the existence of preferential paths or macro-pores originating from local heterogeneities and other enhanced mechanisms (e.g., competitive binding and/or electrostatic interactions, etc.) leading to breakthroughs in a very short time. This demonstrates further that small-scale local heterogeneities can influence strongly the transport behavior at larger scales (Berkowitz et al., 2006).

Table 1

<table>
<thead>
<tr>
<th>Colloidal properties</th>
<th>(v_p \times 10^{-2}) ((\text{cm min}^{-1}))</th>
<th>(D_p \times 10^{-2}) ((\text{cm}^2 \text{ min}^{-1}))</th>
<th>(\beta)</th>
<th>(t_f) ((\text{min}))</th>
<th>(\Lambda)</th>
<th>(\mu)</th>
<th>(R_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloid-free</td>
<td>0.91</td>
<td>0.23</td>
<td>0.91</td>
<td>(10^{1.22})</td>
<td>5.42E-3</td>
<td>6.95E-5</td>
<td>0.655</td>
</tr>
<tr>
<td>FHC</td>
<td>6.81</td>
<td>3.27</td>
<td>0.89</td>
<td>(10^{2.18})</td>
<td>1.00E-9</td>
<td>1.00E-11</td>
<td>0.818</td>
</tr>
<tr>
<td>SC</td>
<td>2.86</td>
<td>0.99</td>
<td>0.88</td>
<td>(10^{2.58})</td>
<td>1.00E-14</td>
<td>1.00E-15</td>
<td>0.696</td>
</tr>
<tr>
<td>HAC</td>
<td>11.10</td>
<td>2.97</td>
<td>0.62</td>
<td>(10^{2.73})</td>
<td>1.00E-13</td>
<td>1.00E-15</td>
<td>0.707</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Colloidal properties</th>
<th>(v_p \times 10^{-2}) ((\text{cm min}^{-1}))</th>
<th>(D_p \times 10^{-2}) ((\text{cm}^2 \text{ min}^{-1}))</th>
<th>(\beta)</th>
<th>(t_f) ((\text{min}))</th>
<th>(\Lambda)</th>
<th>(\mu)</th>
<th>(R_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloid-free</td>
<td>1.65</td>
<td>0.18</td>
<td>1.28</td>
<td>(10^{2.02})</td>
<td>6.80E-6</td>
<td>6.80E-8</td>
<td>0.876</td>
</tr>
<tr>
<td>FHC</td>
<td>42.25</td>
<td>0.16</td>
<td>0.50</td>
<td>(10^{3.15})</td>
<td>6.80E-6</td>
<td>7.60E-8</td>
<td>0.893</td>
</tr>
<tr>
<td>SC</td>
<td>8.21</td>
<td>2.72</td>
<td>1.08</td>
<td>(10^{4.03})</td>
<td>1.80E-5</td>
<td>7.60E-8</td>
<td>0.904</td>
</tr>
<tr>
<td>HAC</td>
<td>24.40</td>
<td>4.59</td>
<td>0.85</td>
<td>(10^{3.21})</td>
<td>1.80E-6</td>
<td>7.60E-8</td>
<td>0.963</td>
</tr>
</tbody>
</table>

Fig. 3. Estimated recovery (cumulatively eluted mass fraction) of strontium for sample-b (A) and sample-d (B), calculated by Eq. (2), in the absence of colloids and in the presence of three types of synthetic colloids.
3.4. The novelty and limitations of the present modelling approach

The CTRW-based model has been extended as alternative to the traditional description of migration phenomena and has been applied to quantify the anomalous transport of Sr (as a substitute of $^{90}\text{Sr}$), as observed with column scale experiments. The principal novelty of the work is the evaluation of non-Fickian and colloid-mediated transport with the CTRW formulation, as well as the understanding of effects of different mechanisms on Sr transport. It has been shown that the CTRW-TPL model can directly quantify the anomalous Sr transport in the absence and presence of colloids, and this is seen as the method key strength.

Compared to the classical ADE approach, which treats the dispersion process in an overly simplified style (Rubin et al., 2012), the application of CTRW is a step towards greater physical realism in the simulation of the anomalous Sr transport. This work offers a coupled CTRW strategy that can simultaneously simulate the dissolved Sr and the adsorbed one, albeit without distinguishing between colloid and surface adsorption at present. On the other side, the well-documented ADE-based models that distinguish between the adsorptions on the colloidal particles and on the grain surface have been included in the literature (Flury and Qiu, 2008; Šimůnek et al., 2006). In practice, the development of such explicit ADE-based model with applications to Pu transport based on existing experimental information is a subject of ongoing work.

Note that the present CTRW modelling is not accompanied by mechanistic transport simulations on the basis of colloid filtration theory and mass balance information for Sr. One obstacle to perform mechanistic simulations is lacking measurements of colloid transport and Sr retention in solid phase. Even then, based on the information mined from the available data, we emphasize that in this work the CTRW model accounts for the anomalous transport of Sr quantitatively, captures the BTC measurements reasonably well, and allows us to explore the non-Fickian and enhanced Sr transport behavior in the presence of colloids. If the surface/solution interactions were to be interpreted thoroughly, well-designed experiments and more parameters would be required for quantitative analysis. Importantly, the present CTRW formulation is appropriate for capturing migration patterns of weakly sorbed species (e.g., Sr), as well as colloids under unfavorable attachment conditions (e.g. strongly repulsive forces), due to their similar behaviors with those of the conservative tracers.

Overall, from a modelling perspective, the CTRW-based approach can serve as a robust and practical framework to describe this anomalous transport of Sr with colloids. Should sufficient data become available, the current CTRW approach can be extended to include more complex interactions between colloid and dissolved species, reactive transport with intricate trapped kinetics, etc., as suggested in previous works (Berkowitz et al., 2016; Cortis et al., 2006; Shapiro and Yuan, 2013).

4. Conclusions

Our investigation reveals the importance of quantifying non-Fickian processes including the effect of colloids on the Sr migration. The practicability of the established CTRW model to evaluate Sr non-Fickian transport in the absence and presence of colloids has been clearly demonstrated. Additionally, it is implied that, colloids can promote Sr transport as a barrier of $^{90}\text{Sr}$ sorption onto sediment media, i.e., the blocking sorption effect for elements with weaker sorption (Ma et al., 2016), apart from often being carriers of strongly sorbed radionuclides in aqueous phase. Specifically, we conclude that:

(1) Good agreement has been achieved between the CTRW simulations and the experimental data both for samples from the first (sample-b) and the second (sample-d) groups. The presence of colloids (FHC, SC, HAC), has been shown to increase the transport of Sr and to yield higher recoveries to various degrees. The causes for colloid-facilitated transport can be, e.g. the repulsive effect between the positively charged FHC and $^{90}\text{Sr}^{2+}$, together with a reduction of binding sites for $^{90}\text{Sr}^{2+}$ as the affinity of FHC particles to the negatively charged porous media (sample-b), and the existence of greater pore throats leading to the faster interstitial velocities of dissolved and colloid-associated strontium, as well as the potential competitive binding (sample-d).

(2) Regardless of the absence or presence of colloids, the CTRW-TPL modelling has demonstrated the characteristics of non-Fickian transport of Sr. For structures with relatively smaller pores (sample-b) the calculated $0 < \beta < 1$ reveals strongly anomalous transport for all cases with and without colloids. Colloids enhance the anomalous behavior to various degrees, with FHC and HAC showing the prominent effect. For structures with relatively larger pores (sample-d), the moderately anomalous behavior without colloids, $1 < \beta < 2$, can be enhanced by the presence of colloids to strongly anomalous behavior (FHC and HAC, $0 < \beta < 1$).

Conflicts of interest

The authors declare that they have no competing interests.

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Appendix A. Supplementary data

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References


