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Kinetic evaluation of sorption and desorption

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Abstract Sorption is often quantified by a distribution coefficient, K_d, which is the equilibrium ratio between species sorbed to the rock and species in solution. Traditionally K_d-values are determined in batch experiments from equilibrium concentrations.

In this work we describe an approach to determine rate constants for sorption and desorption from data obtained in ordinary batch sorption experiments. By varying the surface area to solution volume ratio in experiments where the dynamics for sorption equilibration is monitored, the rate constants (and consequently the K_d-value, which is the quota between forward and backward reactions) can be determined.

To demonstrate the method, sorption of strontium to crushed granite was studied. The K_d-value obtained with the kinetic approach was in good agreement with that obtained from equilibrium concentrations.

Keywords Sorption · Kinetics · Cation · Mineral · Sr^{2+} · Granite

1 Introduction

Groundwater mediated transport of metal ions by diffusion or flow in geomedia are the main routes for the spreading of pollutants such as heavy metals and radionuclides. In a deep geological repository for spent nuclear fuel and also in repositories for heavy metals (e.g. mercury), barriers are often used to reduce the probability of transport by flowing groundwater. These barriers also reduce the effective diffusion rate largely due to their high porosity. Sorption of metal ions to the barrier surface will reduce the transport efficiency further and could, in some cases, lead to complete immobilization of the pollutant. As most natural and engineered barriers contain minerals, sorption of cations to mineral surfaces is an important process. Sorption of cation is a fairly complicated process and it is almost always sensitive to the pH and ionic strength of the groundwater. At low pH, protons compete with the metal ions and the effective sorption coefficient for metal ions therefore decreases with increasing acidity. The ionic strength of the groundwater could also influence the sorption coefficient. However, in most cases at higher ion concentrations, the specific sorption of other cations in the groundwater competes with sorption of metal ions. This should not be confused with an ionic strength effect. Cation sorption to mineral surfaces is often discussed in terms of inner- and outer-sphere complexation where the former refers to strong sorption while the latter is usually the case for weakly sorbing cations. The existence of inner- and outer-sphere surface complexes can be verified by X-ray spectroscopy. The thermodynamics of cation sorption to mineral surfaces has been discussed in a series of papers by Sverjensky (Sverjensky and Molling 1992; Sverjensky 1992, 1993). These papers are mainly focused on the impact of mineral surface properties. For the sorbing cations the size and charge appear to govern the energetics of the process, which is analogous to solvation.

In practice, sorption is mostly quantified in terms of partition coefficients, usually referred to as K_d-values. The K_d-value describes the equilibrium constant for the system where the solid material is quantified by its weight rather than surface area or number of sites available for sorption. For this reason, K_d-values should often be considered as operational parameters valid only for the specific surface area

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used in the experiment where the value was determined. As environmental modelling and safety assessment of geological repositories rely on these sorption coefficients, effort should be put into presenting numbers that are not system dependent. Experiments are usually performed using crushed material in order to maximize the solid surface area to solution volume ratio. Freshly crushed material may not have the same surface properties as a material which has been in contact with groundwater for a long time. Furthermore, K_d-values only describe a system in equilibrium, and sometimes even this is questioned. To be able to fully account for competing processes when simulating transport of cations in geomedia, rate constants for sorption and desorption must be known. The rate constants for the forward and reverse process can also be used to calculate the equilibrium constant and thereby checking the internal consistency of available data.

Montes-Hernandez and Rihs (2006) have used kinetic data to obtain some thermodynamic parameters and derived Langmuir-like expressions for the sorption of uranyl ions to birnessite. This approach is applicable when the surface area is rate limiting for the sorption. However, when the dynamics of the process is not limited by the surface area another approach must be applied.

In this work we show a way to determine rate constants for sorption and desorption by varying the solution volume to solid surface area ratio in batch experiments and study the transient part of the sorption. The method is demonstrated in experiments where strontium is sorbed to crushed granite. The obtained sorption and desorption rate constants were verified by comparing with a distribution coefficient (K_d-value) obtained from the equilibrium concentrations.

2 Experimental

The granite was crushed and sieved and the fraction between 118–250 μm was chosen. The granite was washed several times with distilled water using an ultrasonic bath to remove small particles and readily soluble ions that might be released from the granite.

The BET surface area was measured using a Micromeritics Flow Sorb II 2300. Four measurements were performed giving the values 0.40, 0.31, 0.30 and 0.40 m^2/g, resulting in an average value of 0.35 ± 0.05 m^2/g. The sorption experiments were performed as batch experiments. Milli-Q water was used in the experiments.

The experiments were performed in glass vessels with a total solution volume of 100 ml and a $SrCl_2$ (Merck) concentration of 1.0 μM spiked with Sr-85 (PerkinElmer). The gamma activity in the solution was measured and granite was added before the vessels were placed in a cradle. 800 μl samples were taken at different times and measured for gamma activity to quantify concentration in the solution and thus the amount of Sr^{2+} that had sorbed to the granite. Before the gamma measurements, the samples were centrifuged at 6000 rpm for at least 1 minute to remove any particles. Some of the samples taken during the first minutes were not centrifuged. This was to give smaller time intervals between samples. The amount of granite was varied in the experiments; 0.40, 0.60, 0.75, 1.00, 1.20 and 1.25 g (±0.005 g). The pH values of the solutions used were not adjusted and measured to vary between 6 and 7.

3 Data evaluation

Sorption can be described as a second order reversible reaction as reaction (1):

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C \tag{1}$$

where A is the sorbing ion, B is the available surface, C is the ion sorbed to the surface, k_1 is the forward (sorption) rate constant and k_2 is the backward (desorption) rate constant.

The following boundary conditions give (2), which is the rate expression for C:

At time,

$t = 0$: $[A] = a$, $[B] = b$, and $[C] = 0$.
$t = t$: $[A] = a - c$, $[B] = b - c$, $[C] = c$.
$t = \infty$: $[A] = a - c_{eq}$, $[B] = b - c_{eq}$, $[C] = c_{eq}$.

Where c_{eq} is the equilibrium concentration of C.

$$\frac{d[C]}{dt} = -\frac{d[A]}{dt} = \frac{dc}{dt} = k_1 \cdot (a - c) \cdot (b - c) - k_2 \cdot c \tag{2}$$

In order to have consistent units (mol/dm^3), the available surface must be corrected using the cation exchange capacity and the volume used. A cation exchange capacity (CEC) of 0.5 meq/100 g was taken from Lee et al. (2001), who used granite with similar grain size and BET areas. Note that the cation exchange capacity has an impact on only the obtained rate constants, not the distribution factor (K_d-value) which was obtained with this approach.

By adjusting the experimental conditions so that $b \gg c$, (2) can be simplified to:

$$\frac{dc}{dt} = k_1 \cdot b(a - c) - k_2 \cdot c = k_1 \cdot b \cdot a - (k_1 \cdot b + k_2) \cdot c \tag{3}$$

At equilibrium

$$\frac{dc}{dt} = 0 \quad \Rightarrow \quad k_1 \cdot b \cdot a = (k_1 \cdot b + k_2) \cdot c_{eq} \tag{4}$$

Combining (4) and (3) gives

$$\frac{dc}{dt} = (k_1 \cdot b + k_2)(c_{eq} - c) \tag{5}$$

Integration from $t = 0$ ($c = 0$) to $t = t$ ($[C] = c$) gives:

$$\ln\left(\frac{c_{eq}}{c_{eq} - c}\right) = (k_1 \cdot b + k_2)t \tag{6}$$

Plotting $\ln(c_{eq}/[c_{eq} - c])$ for different amounts of mineral versus time gives a straight line with $(k_1 \cdot b + k_2)$ as the slope. The slopes obtained $(k_1 \cdot b + k_2)$ are then plotted versus b resulting in a straight line with the slope k_1 and the intercept k_2.

The sorption and desorption rate constants can then be used to calculate the distribution coefficient:

$$K_{d,s} = \frac{k_1}{k_2} \tag{7}$$

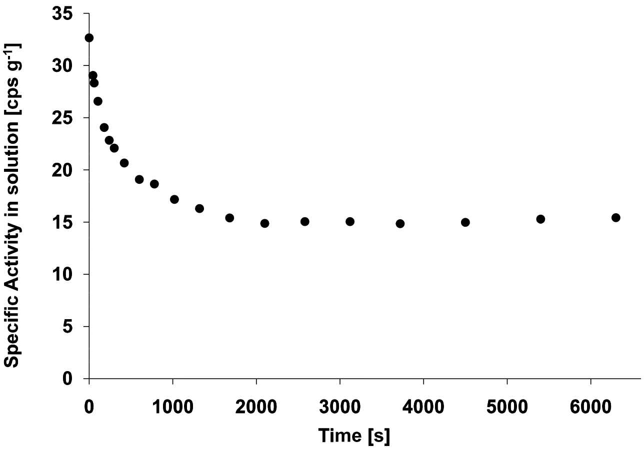

Fig. 1 A typical plot of specific activity in solution as a function of time, this one is for 1.2 gram crushed granite in 100 ml water. As can be seen, equilibrium is reached after 40–60 minutes

4 Results and discussion

In general the equilibrium concentration of Sr^{2+} in solution was reached after approximately an hour. An example is given in Fig. 1.

In Fig. 2 ln $(c_{eq}/[c_{eq} - c])$ versus time is plotted for the different batch sorption experiments and fitted with the least square method. According to (6) a line with the slope $(k_1 \cdot b + k_2)$ is obtained. As can be seen, the slopes increase with increasing available surface.

In Fig. 3 the obtained slopes, $k_1 b + k_2$, are plotted versus available surface area to solution volume ratio. The slope is the sorption rate constant and the intercept with the y-axis the desorption rate constant.

The resulting sorption rate constant is thus 30 $M^{-1}\,s^{-1}$ and the desorption rate constant $5 \times 10^{-4}\ s^{-1}$. The ratio between the rate constants is the equilibrium constant (K_d). The ratio is converted with the CEC to be 0.15 $m^3\,kg^{-1}$. Accounting for the measured BET-area gives a more useful K_d-value of 4.4×10^{-4} m.

To verify the obtained distribution coefficient, a K_d-value was obtained the traditional way from the equilibrium concentrations. The average value was found to be 3.0×10^{-4} m, which is in very good agreement with that obtained using a kinetic approach, confirming that the data for this system is internally consistent.

Furthermore, by rearranging (6) to

$$c = c_{eq}\left(1 - \frac{1}{e^{(k_1 b + k_2)t}}\right) \tag{8}$$

and including the boundary condition $a(t) = a_0 - c(t)$, the concentration of sorbent in solution as a function of time can be calculated and thereby verifying the obtained rate constants. In Fig. 4 two of the experiments are plotted with respective calculated values.

As can be seen, the calculated values fit quite well with the experimental data.

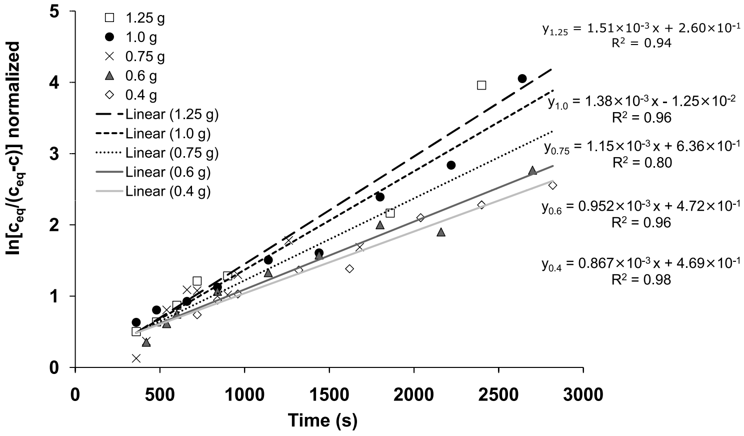

Fig. 2 $\ln(c_{eq}/[c_{eq} - c])$ plotted versus time for the different sorption experiments and fitted to *straight lines* using the least square method. Note that the slope increases with increasing available surface (mass of material). To better illustrate the difference in slopes, the values are normalized to intersect in one point

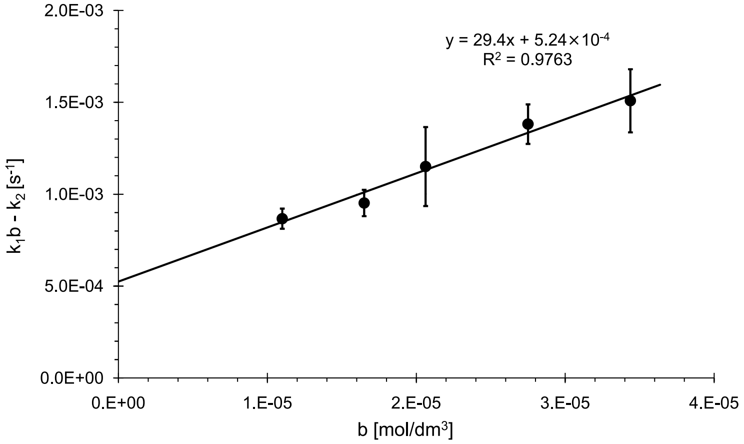

Fig. 3 $k_1 b + k_2$ plotted versus the amount of available surface per volume unit. The data is fitted to a *straight line* using the least square method

From a kinetic point of view it is also interesting to compare the rate constant of sorption to the diffusion limited rate constant of the system. For a heterogeneous system containing particles in the size range of 100–200 µm, the diffusion controlled rate constant based the solid surface area to solution volume ratio is in the order 10^{-4} m s^{-1} (Jonsson 2010). By using the surface site density and the specific surface area of the powder, we calculate the diffusion limited rate constant for the system to be 7×10^3 M^{-1} s^{-1}. We can thus conclude that sorption of Sr^{2+} on granite is activation controlled rather than diffusion controlled. Based on the difference between the experimentally found rate constant for the sorption process and the diffusion controlled rate constant for the system we can estimate the activation energy of the sorption process from the Arrhenius equation to be 13–14 kJ mol^{-1}.

Titanium dioxide and montmorillonite where all exchangeable cation sites were occupied by sodium were also studied using the same approach. It was, however, not possible to achieve sufficient time resolution to capture the dynamics of the sorption process, since it is too fast. The higher apparent reactivity of these materials can mainly be attributed to significantly smaller particle sizes. Even when studying sorption to granite, the amount of reactants needed to be reduced to relatively low concentrations (or surface to volume ratio) in order to achieve proper time resolution.

There are other methods to slow down the rate of sorption. Al-Qunaibit et al. (2005) increased the ionic strength of the solution used considerably to 1 molal when studying sorption of copper to bentonite. Wehrli et al. (1990) lowered the pH when sorption of vanadium and chromium to aluminium oxide was studied. By increasing the H^+ concentration more sorption sites will be protonated and thereby harder to access for the sorbing cation.

Often sorption experiments are performed for long periods of time; months to years (Strawn et al. 1998; Rügner et al. 1999). The reason for this is that after the initial fast sorption a slow decrease in the concentration of sorbing species in solution is observed in some studies. This is often explained by describing the sorption of cations to mineral surfaces as a two step process, one fast and one slow step. The first step is adsorption of the ion to the surface, which is relatively fast, followed by a much slower step. This second step has been reported to be either 1) sorption on sites which have lower affinities for cations, this is often required to model cation adsorption on hydrous ferric oxides (Benjamin and Leckie 1981; Dzombak and Morel 1990), 2) diffusion into the matrix of the sorbent (Strawn et al. 1998; Trivedi and Axe 2000, 2001), 3) slow sorption due to increase in surface charge upon transfer from outer- to inner-sphere complexes (Stumm and Morgan 1996) or 4) surface precipitation (Dzombak and Morel 1990).

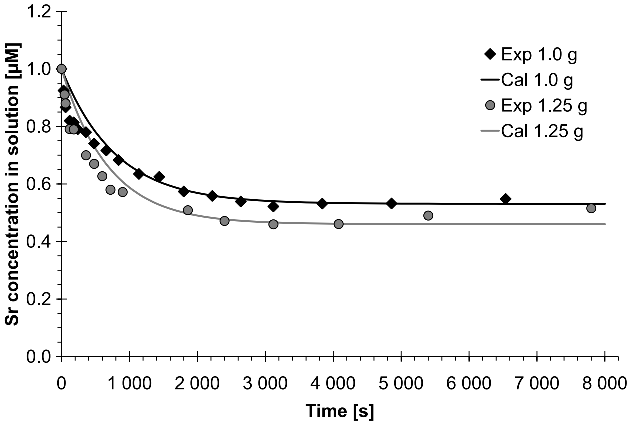

Fig. 4 Experimental data for two of the experiments (1.0 and 1.25 gram crushed granite) and values calculated from the rate constants obtained in this study

In the two latter cases the surface has been somewhat altered and what is observed is sorption to another kind of surface than the original, *i.e.* another sorption process. Matrix diffusion is a well known process. It is often best to study matrix diffusion separately so that this process can be accounted for in the sorption studies.

We observe and describe only one adsorption process in this study. Strontium, the cation used in this study, has a relatively low distribution coefficient compared to most other cations (Crawford et al. 2006), which indicates that the rate of adsorption is relatively slow. Still we needed to use low cation concentrations and available surface areas in order to get sufficient time resolution to capture the kinetics of the adsorption. This implies that the primary adsorption of cations to mineral surfaces is a fast process and equilibrium is reached within hours.

5 Conclusions

Sorption can be regarded as a second order reversible reaction described by three species; (ion) + (surface) $\rightleftharpoons$ (ion sorbed to surface). A number of batch sorption experiments, using strontium as sorbing species, were performed where the surface to volume ratio of granite was varied. In all experiments, equilibrium was reached within hours. The transient part of the equilibration was evaluated and rate constants for the sorption and desorption were obtained. The obtained rate constants were used to calculate the concentration of sorbent in solution as a function of time. The calculated values agreed well with the experimental data.

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