Conceptual Modeling of the Humic Colloid-Borne Americium(III) Migration by a Kinetic Approach

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The humic colloid-borne Am(III) migration is investigated by laboratory experiment. As the reactions controlling the Am(III) migration are found to be not in equilibrium, the experimental results are interpreted by a kinetic model, i.e., the Kinetically Controlled Availability Model (KICAM). Model parameters determined by fitting experimental data in one groundwater sand system are applied (i) to describe the Am(III) sorption and migration behavior in three other groundwater sand systems with lower humic colloid concentrations and (ii) to calculate the recovery of modified column experiments with different column lengths. Further refinement and applicability of the laboratory calibrated model to a real system is considered briefly.

Introduction
The colloid-borne transport of contaminants has attracted much attention (1-5). The process has to be quantified for the safety assessment of radioactive waste disposal as there is ample evidence for the colloid facilitated mobilization of actinides, both in field studies (6-10) and in laboratory experiments (4, 11-15).

Apart from inorganic minerals, humic substances are major aquatic colloids. The humic colloid concentration in groundwater may increase to more than 100 mg per L in geological formations with a lignite intercalation (16). Multivalent actinides are found to have a strong interaction with humic colloids (17-24).

A number of batch and column experiments have been performed to investigate the influence of humic colloids on the sorption and migration behavior of actinides (11, 12, 15). However, up to now, no consistent description of these experiments is available. Although the numerical tools exist (e.g., TRAPIC (25)), the humic colloid-facilitated transport of actinides cannot be quantified for the safety assessment at the moment, because the basic interaction processes of actinides with humic colloids and sediment surfaces are poorly understood.

Using batch experiments to predict the migration behavior does not yield any satisfactory results. The distribution coefficients ($R_k$ values) can only be used to predict the retention factors ($R_k$ values), if local chemical equilibrium can be assumed. Zeh (26) predicted from these $R_k$ values from batch experiments an Am(III) breakthrough with a retention factor of 250. In contrast to this, the column experiments showed about 70% of Am(III) to be eluted

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colloid/sediment interaction is expected. It could not be
deduced from the experiments to what extent the sediment
surface is coated with humic colloids.

The characteristic parameters of the Am(III) column
experiments are listed in Table 1. The lowest Darcy velocity
of 0.4-45 m s\(^{-1}\) is reported for quartz sand, which is the main component (85\%) of the mineral (11), a
relatively low tendency to sorb humic and fulvic acids in the
pH neutral range is reported (33, 34).

### TABLE 2. System Parameters of the Batch Experiments for Model Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GoHy-2227/BA</th>
<th>GoHy-532/BA</th>
<th>GoHy-182/BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HA], eq dm(^{-3})</td>
<td>7.2E-04</td>
<td>3.5E-04</td>
<td>1.2E-05</td>
</tr>
<tr>
<td>[Surf], eq dm(^{-3})</td>
<td>2.5E-03</td>
<td>5.0E-04</td>
<td>5.0E-07</td>
</tr>
<tr>
<td>[CO(_2)] , mol dm(^{-3})</td>
<td>1.3E-05</td>
<td>3.0E-06</td>
<td>2.6E-06</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.3</td>
<td>6.8</td>
</tr>
<tr>
<td>[Am(_{eq})], mol dm(^{-3})</td>
<td>1.7E-08</td>
<td>1.7E-08</td>
<td>1.7E-08</td>
</tr>
</tbody>
</table>

* The italic portion is used for model calibration. [HA] = humic acid concentration, [Surf] = concentration of surface sorption sites, [Am\(_{eq}\)] = total Am concentration used in the column experiments, \(q\) = groundwater/Am (III) equilibration time prior to the column experiments, \(t_s\) = column length, \(\epsilon\) = effective porosity, \(v_o\) = Darcy velocity, \(R_i\) = retention factor, and \(t_{res}\) = residence time in the column (of Am not interacting with the sediment).

### Model Development

In the following sections, a kinetic model is developed to
describe actinide batch and column experiments. It is an
empirical approach based on association/dissociation kinetics
of actinides with humic colloids and mineral surfaces.
The model is called Kinetically Controlled Availability Model (KICAM).

#### Experimental Implications on the Model Development

Speciation calculations for the systems under investigation (11) show that, at pH of groundwaters, Am(III) is humic
colloid-bound, except for the system with the lowest humic
colloid concentration (GoHy-182), where Am(III) is present
as Am-carbonato-species.

The migration behavior of Am(III) depends on the
kinetically controlled interaction of humic colloid-bound Am
with the sediment surface. The experiments reveal two basic kinetic effects: (i) association kinetics of Am(III) with humic colloids and (ii) dissociation kinetics of Am(III) from humic colloids. Attempts to describe the experimental results with a single kinetically controlled dissociation reaction failed. Therefore, the experiments suggest that the Am humic colloid complexation is at least a two-step process: fast association of Am(III) with humic colloids (\(k_{fast}\approx 10^9 \text{ mol}^{-1} \text{ dm}^3\)) followed by a slow secondary reaction to another Am(III)/
mic colloid binding mode (\(k_{slow}\approx 10^{-3} \text{ mol}^{-1} \text{ dm}^3\)).

The results of the Am recovery in column experiments show
that the dissociation from the primary reaction step is about 2 orders of magnitude faster than the secondary reaction step (\(k_{2nd}\approx 10^{-4} \text{ s}^{-1}\)). Therefore, the two binding modes shall be referred to as “fast” and “slow” in the following sections.

Considering two reaction steps leads to a satisfactory
description of the experiments (11). It cannot be excluded
that more than two dissociation reactions exist, as indicated
by kinetic investigations on Sm(III)/Eu(III) humic acid
dissociation (35). However, no experimental evidence is
known for the existence of different humic colloid-bound
Am(III) species corresponding to the assumed kinetic reactions (e.g., by spectroscopic methods). Furthermore, the
processes causing the observed kinetic phenomena have not
yet been understood. Therefore, only two association/
dissociation reactions are considered to keep the kinetic
model as simple as possible.
TABLE 3. Chemical Reactions Considered in KICAM

| Reaction | Rate Constant
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\text{Am}^{III} + \text{HA} \rightarrow \text{Am}^{III} \text{HA}^{\text{slow}}$</td>
<td>$K^1$</td>
</tr>
<tr>
<td>$\text{Am}^{III} + \text{HA} \rightarrow \text{Am}^{III} \text{HA}^{\text{fast}}$</td>
<td>$K^II$</td>
</tr>
<tr>
<td>$\text{Am}^{III} + \text{Surf} \rightarrow \text{AmSurf}$</td>
<td>$1/K^{III}$</td>
</tr>
</tbody>
</table>

The "slow" reaction may be explained by two different reaction mechanisms: An intermolecular process, i.e., association of the Am(III)–humic colloid complex and another humic colloid, or an intramolecular process, e.g., structural stabilization of the Am(III)–humic colloid complex. The intermolecular formation reaction explicitly depends on the humic colloid concentration, whereas an intramolecular formation reaction does not.

The Am(III) recovery in the column experiments of Artinger et al. (11) increases with increasing the humic colloid concentration and can thus be attributed only to the "slow" binding mode (see supporting information). Therefore, an intermolecular formation process for the "slow" binding mode is more likely than intramolecular binding.

In the column experiments no special attention is given to the surface reaction that results in a retarded Am(III) transport. The surface sorption of Am(III) is regarded as an adsorption onto the sediment without considering specific surface reaction mechanisms such as ion exchange, surface complexation, sorption onto humic substance coatings or surface precipitation, etc. The formation of inorganic Am(III) complexes and mixed humate complexes is shown to be relevant for the systems under investigation (11). In the model development consideration of Am(III) solution speciation leads to a complex system of chemical rate equations. The parameters to be determined for such a system are not unambiguous. Since the complexation reactions of metal ions with inorganic ligands are fast compared to metal ion–humic colloid association/dissociation reactions, all inorganic Am(III) solution species can be subsumed under dissolved inorganic americium (Am$^{III}$) in order to keep the reaction scheme simple and ascertainable.

Rate and equilibrium constants determined using the "species" Am$^{III}$ are operational constants that implicitly contain an inorganic Am complexation. To account for the solution speciation in the kinetic modeling, another set of experiments is required to provide a database for further model refinement.

Description of the Kinetically Controlled Availability Model (KICAM). Figure 1 shows the reaction scheme considered in the KICAM model. The following Am(III) species are taken into consideration: dissolved aquo and other inorganic complexes (e.g., hydroxo or carbonato) of Am(III) (Am$^{III}$), Am(III) sorbed onto the sediment (AmSurf), an inorganic americium (Am$^{III}$) in order to keep the reaction scheme simple and ascertainable.

Parameter Determination. The rate constants $k_1$–$k_5$ controlling the interaction of Am(III) with humic colloids and mineral surfaces are determined from batch and column experiments (Tables 1 and 2, italics) using eqs 4–7 (Table 4). The evaluation of the equations used for parameter determination needs an extended mathematical formalism and is therefore given in the Supporting Information. The derived sets of reaction rates and corresponding equilibrium constants are given in Table 5. In the following chapter the determined set of rate constants is applied to different Am(III) sorption and migration experiments to test KICAM.

Model Test

Figure 2 shows the experimental and calculated $R_S$ values for batch experiments as a function of the reaction time. Experimental and calculated data in all groundwater/sand systems indicate that KICAM is able to describe the dependence of the americium distribution coefficient on the humic colloid concentration. The temporal change of $R_S$ of about 2 orders of magnitude is also reflected by the calculated values. Slight deviations may be due to the incompleteness of the used reaction scheme, e.g., difference in the humic colloid composition or disregard of Am(III) solution speciation in groundwaters.

Table 1 shows the experimental and calculated values for the Am(III) recovery in column experiments. Model results for the GoHy-2227 systems at variable equilibration time agree with experiments. This suggests that the parameterization made in this work appears reasonable. The experimental and calculated Am(III) recoveries also agree for the other three systems. Predictions are made for the Am(III) recovery in migration experiments at variable column length. The predicted Am(III) recoveries fit to the experimental values (Table 1).

Discussion

The model presented in this paper (Kinetically Controlled Availability Model) is an empirical approach based on the kinetically controlled interactions of Am(III) with humic colloids and mineral surfaces. The parameters are determined from experimental data. The model describes well both column and batch experiments under various conditions.

The rate constants for KICAM are determined from batch and column experiments in the system GoHy-2227. To test KICAM, the Am recovery of independent column experiments (not used for parameter determination) in the GoHy-2227 system are calculated. The applicability of KICAM is verified.
for the GoHy-2227 system, since the predicted and experimental data are found to agree with each other.

Applicability of the derived set of rate constants to other systems (with lower humic colloid concentration) is also investigated. Calculation of the Am recovery of column experiments for other systems shows a good agreement with experiments. Slight deviations of the experimental and calculated Am recoveries may be attributed to the simple reaction scheme applied or to the disregard of Am(III) solution speciation in the model.

KICAM provides a tool for modeling the migration of humic colloid-borne actinides (Am(III)), which allows the implementation of kinetically controlled actinide humic colloid interactions. This is a prerequisite for the predictive geochemical modeling of the migration behavior of actinides, and metal ions in general, in an aquifer rich in humic colloids.

KICAM is based on static and dynamic laboratory experiments with a time scale from about minutes up to some thousands of hours. The model describes processes that can be observed within such time scales. Much slower processes that may be relevant for real aquifers, however, cannot be observed experimentally and, hence, cannot be quantified by the model. Therefore, the application of KICAM to predict the influence of humic colloids on the actinide migration in the long-term safety assessment requires critical validation. First steps toward this final goal are made by starting desorption experiments on lanthanides bound to natural humic colloids. These experiments are in progress. They serve to quantify the reversibly and/or irreversibly bound lanthanides in natural humic colloids on a time scale over 1 year.

Acknowledgments

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Supporting Information Available

Evaluation of equations used for parameter determination, fit procedures of reaction rates and corresponding equilibrium constants (Table 6), and recovery vs equilibration time (Figure 3) and $R_e$ vs reaction time (Figure 4). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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