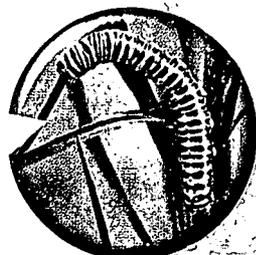
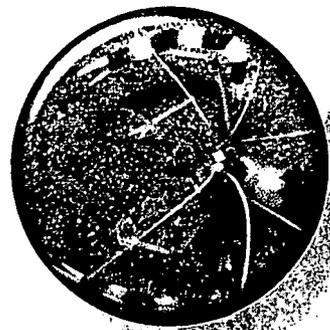


JUNE 15, 2000

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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_s values) can only be used to predict the retention factors (R_f values), if local chemical equilibrium can be assumed. Zeh (26) predicted from these R_s 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

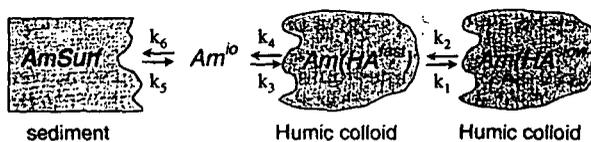


FIGURE 1. Concept of the Kinetically Controlled Availability Model (KICAM) (for details see text).

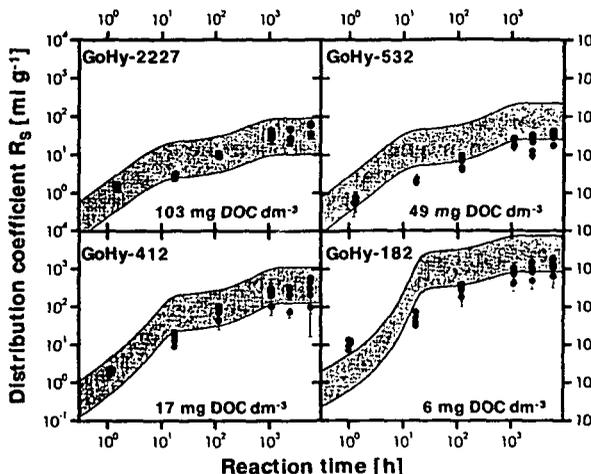


FIGURE 2. Experimental and modeling results for the temporal development of the distribution coefficient in four Gorleben groundwater sand systems. The shaded area corresponds to the model results, taking into account the model uncertainty of a factor of 3.

unretarded ($R_f = 1$). Consequently, Zeh (26) suggested that the kinetically controlled process was involved in Am(III) humic colloid association/dissociation reactions. Other authors also found kinetically controlled metal ion humic acid interactions (27-31). Up to now, however, these findings have not been considered in actinide transport modeling.

The aim of this paper is to develop a model which is capable of quantifying and predicting the actinide sorption and migration behavior in aquifers rich in humic colloids. The applicability of the model developed based on laboratory experiments to real aquifer systems still remains to be examined.

Experimental Basis

The basis of the model development are the experimental findings of Zeh (26) and Artinger et al. (11). Column experiments are performed with varying column lengths, for which the details are given elsewhere (11). The experimental conditions and results are listed in Table 1.

Batch Experiments. Two important observations are made in experiments on the Am(III) sorption (Figure 2, experimental conditions see Table 2) for four groundwater/sand systems: (i) a strong influence of humic colloid concentration on the sorption coefficient and (ii) a continuously increasing sorption coefficient R_s with reaction time, e.g., by about 2 orders of magnitude within 250 days. The first observation underlines the importance of humic colloids for the sorption behavior of Am(III). From the second observation, it becomes evident that kinetic effects need to be included for adequate description of the experiments.

Column Experiments. In the column experiments only the unimpeded transport of Am(III) is investigated. The columns are equilibrated with different groundwaters for 3 months. Therefore, a quasi-equilibrium state of humic

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2

TABLE 1. Relevant Parameters and Experimental and Modeling Results for the Column Experiments^a

Parameter	column experiments											
	GoHy-222/1	GoHy-222/2	GoHy-222/3	GoHy-222/4	GoHy-222/5	GoHy-222/6	GoHy-532/1	GoHy-532/2	GoHy-532/3	GoHy-412/1	GoHy-412/2	GoHy-182/1
[HA], eq dm ⁻³	7.2E-04	7.2E-04	7.2E-04	7.2E-04	7.2E-04	7.2E-04	3.5E-04	3.5E-04	3.5E-04	8.1E-05	8.1E-05	1.2E-05
[Surf], eq dm ⁻³	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02	5.7E-02
[CO ₃ ²⁻], mol dm ⁻³	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	5.0E-06	5.0E-06	5.0E-06	5.0E-07	2.0E-08
pH	7.5	7.5	7.5	7.5	7.5	7.5	7.3	7.3	7.3	6.8	6.8	6.1
[Am ^{tot}], mol dm ⁻³	1.9E-06	1.9E-06	1.9E-06	1.8E-06	1.8E-06	1.8E-06	1.9E-06	1.9E-06	1.9E-06	1.5E-06	1.7E-07	1.8E-06
t ₀ , h	1	168	864	3360	3192	3672	960	240	480	984	624	168
l _s , m	0.5	0.5	0.5	0.25	0.5	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ε, %	31.2	31.3	31.4	31.2	31.5	33.2	32.1	31.6	31.4	32.7	32.6	32.4
v _D , ms ⁻¹	2.9E-06	2.9E-06	3.0E-06	3.0E-06	2.9E-06	3.0E-06	2.4E-07	3.1E-06	2.6E-05	3.0E-06	3.1E-06	3.2E-06
R _f	0.95	0.95	0.96	0.98	0.95	0.98	0.97	0.96	0.95	0.98	0.99	0.98
t _{res} , h	14.2	14.2	14.1	7.1	14.2	22.7	179.6	13.6	1.6	14.7	14.4	13.9
	Recovery											
exp, %	1.9	22.6	35.4	33.5	29.4	28.3	34.0	19.6	6.5	1.6	2.3	0.1
	± 0.2	± 1.1	± 1.8	± 1.7	± 1.5	± 1.4	± 1.7	± 1.0	± 0.3	± 0.2	± 0.8	± 0.2
calc min, %	1.8	13	23	32	24	22	65	9	7	4	4	1.3
calc max, %	2.3	26	40	47	40	38	70	18	14	8	7	1.8

^a The italics portion is used for model calibration. [HA] = humic acid concentration, [Surf] = concentration of surface sorption sites, [Am^{tot}] = total Am concentration used in the column experiments, t₀ = groundwater/Am (III) equilibration time prior to the column experiments, l_s = column length, ε = effective porosity, v_D = Darcy velocity, R_f = retention factor, and t_{res} = residence time in the column (of Am not interacting with the sediment).

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

Parameter	batch experiments			
	GoHy-222/BA	GoHy-532/BA	GoHy-412/BA	GoHy-182/BA
[HA], eq dm ⁻³	7.2E-04	3.5E-04	8.1E-05	1.2E-05
[Surf], eq dm ⁻³	2.5E-03	2.5E-03	2.5E-03	2.5E-03
[CO ₃ ²⁻], mol dm ⁻³	1.3E-05	5.0E-06	5.0E-07	2.0E-08
pH	7.5	7.3	6.8	6.1
[Am ^{tot}], mol dm ⁻³	1.7E-08-1.7E-06			

^a The italics portion is used for the model calibration. [HA] = humic acid concentration, [Surf] = concentration of surface sorption sites, and [Am^{tot}] = total Am concentration used in the batch experiments.

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 8 m a⁻¹ is in the range of flow velocities found in nature (Gorleben site: 0.4-45 m a⁻¹ (32)). The Am(III) recovery increases with (i) increasing flow velocity (10⁻⁷-10⁻⁵ m s⁻¹), (ii) decreasing column length (0.25-0.75 m), (iii) increasing humic colloid concentration (10⁻⁵-10⁻³ eq dm⁻³), and (iv) increasing equilibration time between groundwater (1-10³ h) and Am(III) prior to the injection into the column. The first and second findings can be attributed to the decreasing Am(III) residence time in the column.

Ultrafiltration Experiments. The size distributions of humic colloids and those complexed with Am(III) (AmHA) show a similar pattern. The size distributions of AmHA prior to the injection and after passing the column are found to be unchanged. Therefore, no specific size range of humic colloids is preferably filtered within the column.

The size distribution of AmHA does not change between the injected solution and effluent, although different amounts of Am(III) are recovered in various column experiments. Furthermore, humic colloids are not sorbed considerably by the sediment during equilibration of the system. For quartz 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).

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).

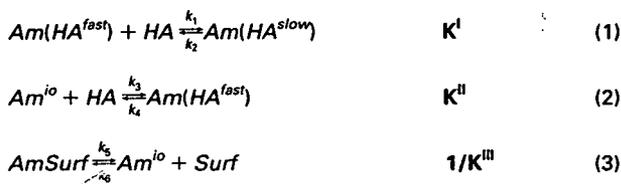
Experimental Implications on the Model Development. Speciation calculations for the systems under investigation (11) show that, at pH of groundwaters, Am(III) is humic colloid-bound, except for the system with the lowest humic colloid concentration (GoHy-182), where Am(III) is present as Am-carbonato-species.

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 ($k_{fast}^{assoc} \approx 10^2 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) followed by a slow secondary reaction to another Am(III)/humic colloid binding mode ($k_{slow}^{assoc} \approx 10^{-3} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$). 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 ($k_{fast}^{dissoc} \approx 10^{-4} \text{ s}^{-1}$, $k_{slow}^{dissoc} \approx 10^{-6} \text{ s}^{-1}$). 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 of 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.

3

TABLE 3. Chemical Reactions Considered in KICAM



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^{io}) in order to keep the reaction scheme simple and ascertainable.

Rate and equilibrium constants determined using the "species" Am^{io} 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^{io}); Am(III) sorbed onto the sediment (AmSurf); and humic colloid-bound Am(III); two binding modes: "fast" ($Am(HA^{fast})$) and "slow" ($Am(HA^{slow})$). Taking into account these species, the KICAM consists of three chemical reactions (Table 3), resulting in four coupled differential equations (Table 4).

Parameter Determination. The rate constants k_1-k_6 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

TABLE 4. Differential Equations for the Am(III) Species Considered in KICAM

$$\frac{d[Am(HA^{slow})]}{dt} = k_1 \cdot [HA] \cdot [Am(HA^{fast})] - k_2 \cdot [Am(HA^{slow})] \quad (4)$$

$$\frac{d[Am(HA^{fast})]}{dt} = k_2 \cdot [Am(HA^{slow})] + k_3 \cdot [HA] \cdot [Am^{io}] - (k_1 \cdot [HA] + k_4) \cdot [Am(HA^{fast})] \quad (5)$$

$$\frac{d[Am^{io}]}{dt} = k_4 \cdot [Am(HA^{fast})] + k_5 \cdot [AmSurf] - (k_3 \cdot [HA] + k_6 \cdot [Surf]) \cdot [Am^{io}] \quad (6)$$

$$\frac{d[AmSurf]}{dt} = k_6 \cdot [Surf] \cdot [Am^{io}] - k_5 \cdot [AmSurf] \quad (7)$$

TABLE 5. Equilibrium and Rate Constants for Am(III) Association/Dissociation Reactions Determined from the GoHy-2227 System Using KICAM

rate constants		equilibrium constants	
$\log(k_1 \cdot s \cdot mol \cdot dm^{-3})$	-3.2 ± 0.2	$\log(K^I \cdot mol \cdot dm^{-3})$	2.8 ± 0.1
$\log(k_2 \cdot s)$	-6.0 ± 0.2	$\log(K^{II} \cdot mol \cdot dm^{-3})$	5.6 ± 0.5
$\log(k_3 \cdot s \cdot mol \cdot dm^{-3})$	1.5 ± 0.5	$\log(K^{III} \cdot mol \cdot dm^{-3})$	6.2 ± 0.5
$\log(k_4 \cdot s)$	-4.1 ± 0.2		
$\log(k_5 \cdot s)$	-3.9 ± 0.5		
$\log(k_6 \cdot s \cdot mol \cdot dm^{-3})$	2.3 ± 0.2		

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 parametrization 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

This manuscript has benefited from comments of two anonymous reviewers; their help is gratefully acknowledged.

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_S vs reaction time (Figure 4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review November 4, 1999. Revised manuscript received February 24, 2000. Accepted March 3, 2000.

ES991246A