Modelling of uranium release from waste rock pile

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Abstract. Uranium release/uptake on material of waste rock pile No. 66 at Schlema-Alberoda (Saxony, Germany) was studied by both static (batch) and dynamic (column) experiments with the aim to obtain input data for modelling of uranium migration in the pile. Most of the experiments were carried out by radiotracer method using ^{233}U as the label. An ambiguous influence of humic acid (concentration 10 and 50 mg/L) on the migration of uranium was observed. The column elution experiments were modelled using PHREEQC that enabled to respect the kinetic character of the desorption process.

Introduction

The study of environmental impact of uranium mining waste rock piles has a large importance as the piles are often situated, e.g. in Germany or in Czech Republic, in urbanized environment. These wastes can also serve as a geological analogue of other kinds of nuclear waste repositories. Understanding of contaminant migration processes at the basic level in a laboratory study can help to develop models, which may be used in transport codes to predict the fate of pollutants on the field scale. An extensive environmental study was performed in the waste rock piles region at Schlema-Alberoda (Saxony, Germany) mainly between 1990-2000 (e.g., Schmeide et al. 2003). Our work performed with waste materials from uranium mining was aimed at better understanding of uranium release/uptake processes and at obtaining suitable input data for modelling of uranium migration.

Waste material from rock pile No. 66 at Schlema-Alberoda was selected for the study. Sampling of the rock material, which included sieving under 1 mm of particle size, and its characterization that comprised mineralogy, granulometric analysis, elemental composition, determination of total carbon, inorganic carbon, specific surface area, and exchangeable uranium was performed (Sachs et al. 2004). Most of sorption/desorption studies by batch and column experiments accomplished in our laboratory were carried out by radiotracer method using ^{233}U as the tracer. Distribution of ^{233}U was measured with liquid scintillation counting. Some evaluations were based on determination of ^{238}U and ^{233}U by means of ICP-MS.

Batch experiments

Determination of exchangeable uranium

The experiments, results of which are presented in this contribution, were performed with the simulated seepage water from the pile No. 66 (0.0175 M $MgSO_4$, 0.0091 M $CaSO_4$, 0.00258 M $NaHCO_3$) aiming to obtain data that could be used in subsequent modelling of uranium migration in near to real conditions.

First experiments aimed at determination of uranium in the rock sample accessible to leaching with natural water and exchangeable with ions in the water. This so called exchangeable or “labile” (Davis and Curtis, 2003) uranium U_{ex} was determined by isotope exchange with ^{233}U in simulated seepage water. In this medium neither changes in concentration in total uranium and ^{233}U nor the change of phase ratio V/m from 20 to 100 mL/g significantly affected the U_{ex} value (20 µg/g, 8.4×10^{-5} mol/kg) that represented approx. 34 % of total uranium in the sample (Sachs et al., 2004). The absence of significant effect was probably due to relative stability of composition of the liquid phase even in changing the phase ratio, as the use of simulated seepage water hindered further leaching of waste rock material.

Sorption/desorption equilibrium and kinetics

Batch experiments carried out with simulated seepage water (pH 8) examined effects of concentration of added uranium and humic acid on uranium distribution and kinetics of uranium sorption and desorption. The near-to-equilibrium distribution data of total uranium (labile + added) corresponded to approximately linear sorption isotherm, K_d = 17 mL/g (Vopalka et al. 2005), with a slight dependence on the volume to mass ratio V/m. Significant increase of equilibrium concentration on the solid phase with the increase of V/m could be explained by the dependence of the exchange between both portions of uranium (added and labile) on the mass ratio. The effect of added Aldrich humic acid (HA, 10 and 50 mg/L) was almost negligible with exception of experiments at higher concentrations of added uranium that caused the increase of sorbed uranium significantly over U_{ex}, in those cases the addition of HA caused an increase of K_d to 25-30 mL/g. The small effect of HA could be explained by saturation of added HA by Ca and Mg present in the simulated seepage water.

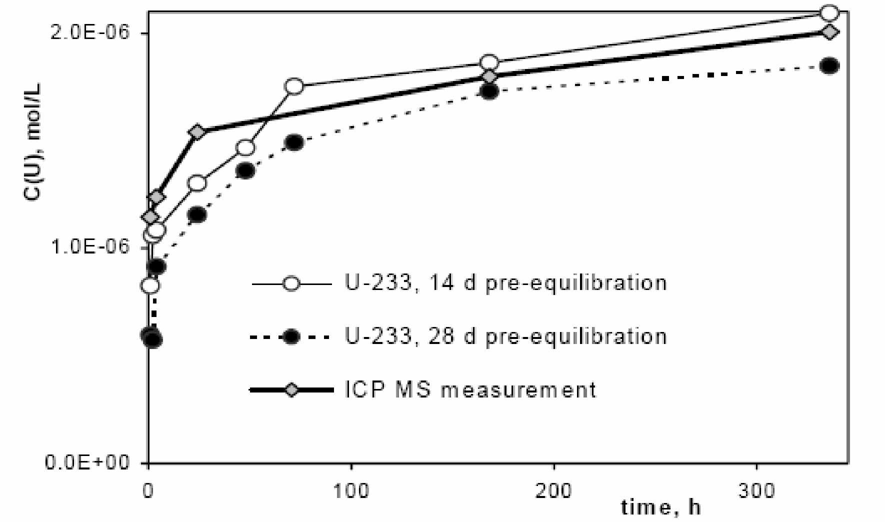

Fig. 1. Kinetics of uranium release from the rock material with simulated natural water at room temperature and *V*/*m* = 20 mL/g – concentration of uranium in water measured by ICP MS or calculated from ^{233}U activity.

Slow kinetics of ^{233}U uptake was found with about two weeks required to obtain a steady-state distribution at *V*/*m* = 10-100 mL/g (Bryan et al., 2004). Rather complicated effects of experimental conditions (total uranium added, *V*/*m*, concentration of HA, the pre-equilibration of phases preceding addition of the spike) on the kinetics were observed. Measured kinetics of ^{233}U uptake always partly represents also isotope exchange ^{233}U–U$_{nat}$, which dominates if the initial concentration of total uranium in liquid phase is near to that in equilibrium with U_{ex}. In the case when the exchangeable amount of the studied contaminant is comparable with the added amount, which is spiked by radioactive tracer, the parameters of the sorption kinetics obtained by evaluation of the uptake of the spike do not describe the kinetic behaviour of the contaminant.

Kinetics of uranium release from the rock material was studied both by radiotracer method and by direct (ICP-MS) measurement of released uranium. In the first case, the material was pre-equilibrated with ^{233}U. In order to avoid premature release of uranium, the pre-equilibration was made with 5.6×10^{-6} M solution of uranium labelled with ^{233}U. This concentration is near to that in equilibrium with U_{ex}. For comparison was the kinetics of uranium release studied also in an experiment, in which no pre-equilibration with ^{233}U was used, and the release of natural uranium was measured (Vopalka et al. 2004). Results of the experiments at *V*/*m* = 20 mL/g are presented in Fig.1. A good agreement between the results of the direct U measurement and of the radiotracer method suggests that the radiotracer method used is suitable for the physical modelling of uranium release from the studied material and for the determination of input data for modelling of uranium release from the pile.

Column experiments

Humic colloid-mediated uranium migration can be studied by column experiments that together with batch experiments might provide an insight into U migration in aquifers. Presence of colloids mostly lowers the retardation quality of porous rock layer (Roy and Dzombak 1998; Warwick et al. 2000) and the kinetic character of interaction of contaminant with natural colloids requires more complicated techniques of migration modelling (e.g., Zurmühl 1998). Preparation and accomplishment of our dynamic experiments aimed at simple modelling of dynamic conditions of uranium leaching and migration in waste rock pile using the method developed with the use of results of batch experiments.

Dynamic experiments were carried out with small columns (inner diameter 0.9 cm, height of rock layer 3 and 5 cm) and linear flow-through velocities between 0.02 and 0.11 m/h. The elution experiments using simulated seepage water that did not contain uranium were preceded by equilibration of the rock sample with uranium solution spiked by ^{233}U directly in the assembled circuit (column and tubings) unless a steady state, characterized by approx. the same values of input and output activities of the spike, was attained (7-10 days). This procedure was based on the results of batch kinetic elution experiments that proved feasibility of this approach. Also here, parallel experiments were run with the non-spiked and non-equilibrated rock and the comparison of results was satisfactory.

The experiments using flow-interruption technique (e.g. Kookana et al. 1994)

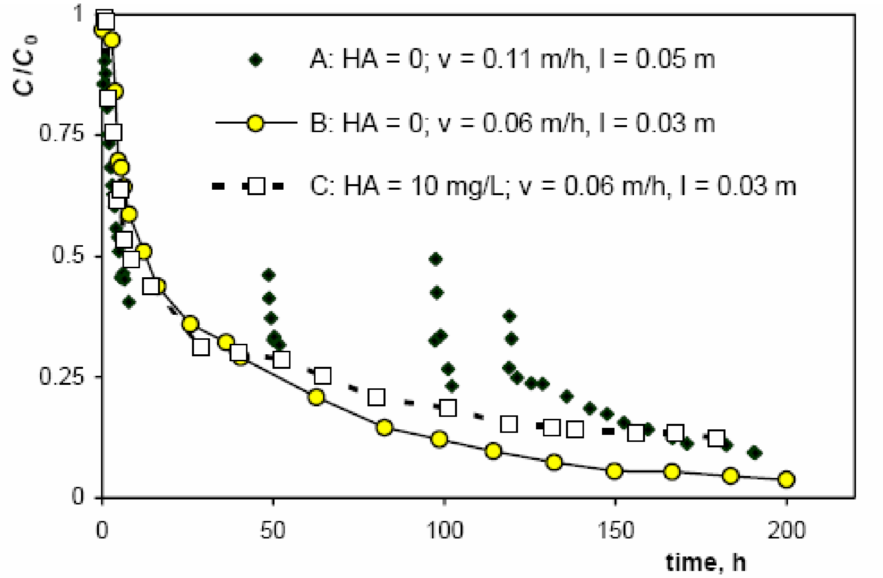

Fig. 2. Dynamics of uranium release from the layer of rock material eluted by simulated seepage water (*l* - height of the sediment layer, *v* - linear flow velocity).

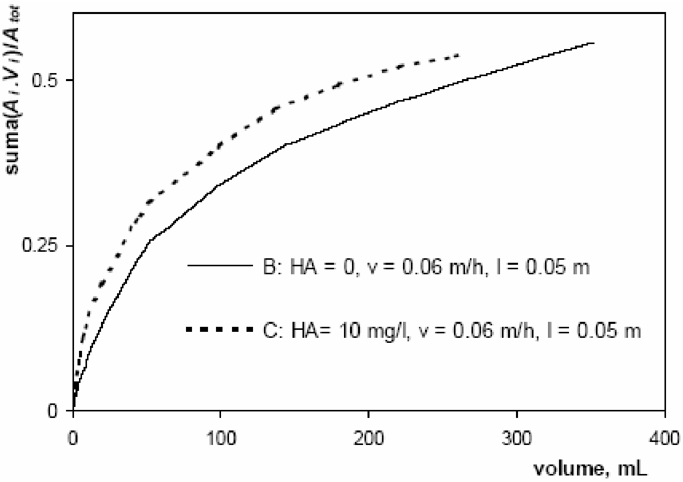

Fig. 3. Influence of the humic acid presence in the water phase on the relative cumulative outflow of uranium from the apparatus (*l* - height of the sediment layer, *v* - linear flow velocity).

showed that non-equilibrium conditions existed during the experiments (Fig.2, curve A). Some of the column experiments confirmed the results of batch experiments that showed only small influence of the presence of HA, e.g. demonstrated by the agreement of the beginning of curves B and C at Fig.2. In contrast to these results, a significant influence of humic acid on U release was observed in other dynamic experiments (see curves B and C on Fig.3). These results, which are presented in the form of relative cumulative activity that is more demonstrative with respect to balance considerations and is also convenient for the calibration of transport models, proved the expected enhancement of uranium transport by complexation with HA. The discrepancy found between the different effects of HA presence was not explained. Large retention of humic acid in the waste rock layer was observed, probably aided by the high content of small particles in the sample (33 wt. % of particles with size under 0.1 mm).

Mathematical modelling

Knowledge of the transport behaviour of uranium in groundwaters is needed for remediation of abandoned milling sites. Parameters necessary for the simulation of uranium migration in real sites could be obtained from evaluation of laboratory experiments that respect the main characteristics of the real system studied. Such laboratory small-scale experiments serve for the development of transport models describing the real situation. The experimental procedure described above represents a physical model of uranium leaching from material coming from waste rock pile near Schlema-Alberoda. The description of experiments aimed at the future extension of the model for field conditions.

The speciation in real water phase, which was modelled using simulated seepage water, is simple: in pH range about 8 predominates a soluble aquo-complex of di-calcium uranyl carbonate $Ca_2[UO_2 (CO_3)_3]_{aq.}$ (Schmeide et al. 2003). According to this simplicity only one uranium species was used for modelling of uranium interaction with the rock surface. The interaction and transport modelling was accomplished in the environment of computer code PHREEQC (Parkhurst and Appelo 1999; Nitzsche and Merkel 1999). The interaction of uranium with the surface was modelled via a formal exchange site, and kinetic character of uranium release recognized in experiments was taken into account.

The model was calibrated by results of one leaching experiment with the simulated seepage water not containing humic acid (see Fig.4. curve B). Validation of the model on results of other experiments was partially successful, in that satisfactory description of the influence of linear flow velocity, which is very important from the point of view of possible spread of uranium in the environment, was achieved (Fig.4).

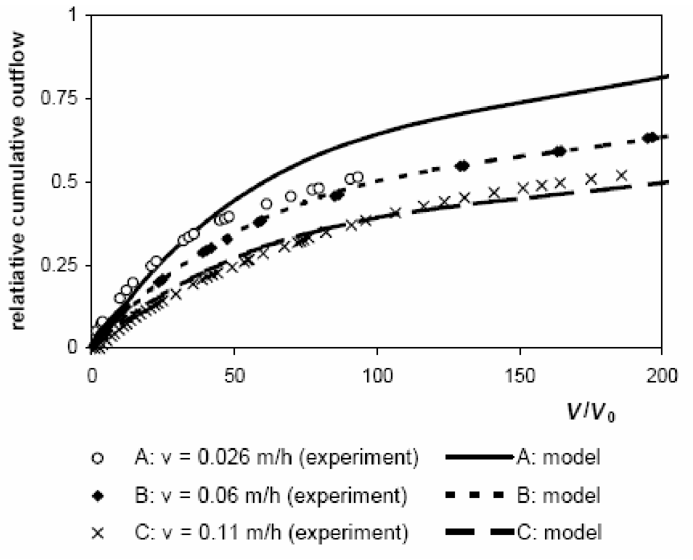

Fig. 4. Influence of the linear flow velocity on the release of uranium from the layer of waste rock material (height 0.05 m, porosity 0.35): comparison of experimental and model results.

Conclusions

The results of batch experiments, which comprised the determination of exchangeable uranium U_{ex} (about 20 µg/g) and of uranium concentration in solution in equilibrium with U_{ex}, enabled the preparation of column experiments using ^{233}U as a tracer that can model real conditions in the waste rock pile. It was found that measured kinetics of ^{233}U uptake does not correspond to kinetics of release/uptake of total uranium (labile + added) due to complications caused by the isotope exchange.

The results of dynamic elution experiments proved the kinetic character of uranium release for experimental conditions used. Substantial release of uranium from the layer of rock pile material in near natural conditions was found: 10 days leaching by simulated seepage water that did not contain uranium released about 50% of accessible uranium. Variable and ambiguous effect of the HA presence on the release rate of uranium from the layer of rock pile material was observed.

Mathematical modelling of the leaching of uranium from the layer of waste rock material was performed by PHREEQC that also enables transport modelling. Satisfactory description of the influence of the flow rate on the uranium release was achieved using model calibrated on one set of experimental data. The model can be recommended for a general modelling of uranium migration in real conditions.

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