



Research paper

Transport behaviour of low molecular weight organic compounds in multi-mineral clay systems. A comparison between measured and predicted values

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ARTICLE INFO

Keywords:

Anion exclusion
Anion sorption
Kaolinite
Illite
Opalinus Clay
Organic compounds

ABSTRACT

Determining the retardation properties of argillaceous media for dissolved low molecular weight organic compounds (LMW—OC's) is still an open issue in the assessment of the migration behaviour of ¹⁴C in the near and far field of a deep geological repository of radioactive wastes. Here we report retardation factors of potential carriers of organic ¹⁴C (carboxylates and alcohols) in binary clay mixtures (kaolinite and illite) as well as in Opalinus Clay (OPA), the favoured host rock for the deep geological disposal of radioactive waste in Switzerland. The percolation technique with a pulse injection of the LMW-OC's was used for all measurements. The transferability of sorption values of the LMW-OC's gained on the single-mineral systems (kaolinite and illite, respectively) to the binary clay mixtures and to clay rock (OPA) was tested.

For binary clay mixtures, percolation experiments were carried out using tritiated water and ³⁶Cl⁻ as the reference tracers. The retardation factors predicted by the component additivity approach (CA) were consistent with the measured ones. Deuterated water and bromide were used as reference tracers in experiments with OPA. Complex breakthrough curves of bromide and the test compounds were observed here. Heterogeneities of the pore space are proposed as the main reason to explain the complex structure of breakthrough curve. Additionally, (a)biotic degradation or transformation of the organic compounds over the long experimental duration possibly further added to the complexity of the results in some cases. The derivation of sorption distribution ratios (R_d), determined from the breakthrough curves was therefore inherently associated with large uncertainties. The transferability of retardation data gained on less complex systems to the conditions of OPA was tested using the CA and the global composite (GC) approach. Significant discrepancies were found between the measured values and those predicted by the CA approach. The discrepancies were found to be smaller using the GC approach. In that case, the results obtained for single- and binary clay systems were also used for calibration purposes. Retardation factors of the LMW-OC's in OPA were then predicted based on two empiric relationships. The observed discrepancies are most probably related to the different chemical composition of the aqueous solution (e.g. ionic strength, pH), the various mineralogical features (e.g. compaction), and the different hydraulic conditions within the clay systems (e.g. Darcy flux). The absence of anion-sorption in OPA may be particularly explained by differences in the pH of the OPA pore water and the pore water in compacted kaolinite samples.

1. Introduction

¹⁴C is a dose-limiting radionuclide in the safety assessment for deep geological disposal of radioactive waste envisaged in many countries. The release of ¹⁴C from a repository and the transfer to the surface environment need to be investigated and understood at a process level. ¹⁴C-containing compounds are formed during the anaerobic corrosion of activated steel and may be released as inorganic (CO₃²⁻) or organic compounds. A recent study reported that the key organic compounds

are low molecular weight organic compounds (LMW-OC's) such as aliphatic hydrocarbons, carboxylates and alcohols (Cvetkovic et al., 2017). Clay rocks are being studied in many countries as a potential host rocks for siting deep geological repositories for radioactive waste. In Switzerland, Opalinus Clay (OPA) has been selected as a host rock candidate (Nagra, 2002, 2008). Transport studies of radionuclides have been performed both in the laboratory (Van Loon et al., 2005; Van Loon et al., 2003; Van Loon et al., 2004a), under well-defined conditions and under more realistic situations in field experiments (Gimmi et al., 2014;

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<https://doi.org/10.1016/j.clay.2018.08.004>

Received 13 March 2018; Received in revised form 29 June 2018; Accepted 3 August 2018

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Leupin et al., 2017; Soler et al., 2014; Soler et al., 2008; Van Loon et al., 2004b; Wersin et al., 2008; Yi et al., 2015). The retardation properties, such as the sorption distribution ratio (R_d) of a radionuclide can be very different depending on the mineralogical composition of the clay rock and chemical and physical conditions such as pH, hydraulic properties (e.g. flow conditions in the clay pore water).

No studies on the retardation of organic ^{14}C -containing compounds in OPA are presently available. Transport studies on the LMW-OC's were recently carried out using single-mineral clay systems, illite and kaolinite (Chen et al., 2018). In the present study, sorption properties of selected LMW-OC's were measured in: (i) mixtures of pure clay minerals (kaolinite and illite) and (ii) in an OPA clay rock core using a percolation technique. The decision to use kaolinite and illite was motivated by their importance as argillaceous constituents of OPA (Bossart et al., 2017).

Many investigations were carried out to predict the sorption/retardation properties of radionuclides on single clay minerals. In the open literature, two approaches have been used to transfer the knowledge gained on such model systems to more complex clay rocks consisting of multiple clay minerals (Davis et al., 1998; Payne et al., 2004): (i) the component additivity (CA; bottom-up) approach; and (ii) the global composite (GC; top-down) approach. Both approaches were tested for inorganic species such as Cl^- , Br^- , I^- , Na^+ , Sr^{2+} , Cs^+ , Eu^{3+} and tritiated or deuterated water (HTO or D_2O , respectively). In particular, the CA approach has been successfully applied to predict the surface complexation properties of different metal cations from the transition metal, lanthanide and actinide series to predict their sorption properties in clay rocks based on their sorption behaviour on illite (Bradbury and Baeyens, 2011). All minerals with surface sites available for radionuclide binding were considered and quantitatively assembled in CA modelling. The retardation of radionuclides in a multi-mineral system was then predicted by combining the additivity-based properties according to the fractional contribution of the reactive mineral surfaces and taking into account the chemical composition of the equilibrium pore solution (Alessi and Fein, 2010; Bradbury and Baeyens, 2011; Marques Fernandes et al., 2015). A mechanistic description of the interaction between LMW-OC's and argillaceous media is currently not available. We hypothesised in previous work (Chen et al., 2018) that anion exchange and dipolar interactions are mainly responsible for the uptake observed for carboxylates and alcohols. In view of the broad variety of linear free energy relationships available from the literature for the partitioning of organic compounds of environmental concern (e.g. Abraham et al., 1994; Tülp et al., 2008), such as pesticides and pharmaceuticals, a successful application of the CA approach for LMW-OC's appears at least to be feasible. When the surface composition of the mineral assemblage is too complex to be quantified by adding up individual components, the top-down approach was applied (GC). Although it is accomplished by fitting experimental data, the GC approach requires possible adsorption mechanisms from prior knowledge (Goldberg et al., 2007).

One of the main objectives of the present work is to test these approaches for predicting the retardation behaviour of LMW-OC's in OPA clay rock. A positive result would open the possibility to avoid the laborious and time-consuming measurements on genuine clay rock samples. Percolation measurements using compacted clay mineral systems are much better manageable and offer the possibility of testing parameter variations, such as the variation of pH and ionic strength. Shorter time scales for the measurements are also favourable in the sense of avoiding unwanted microbial deterioration of the test system.

2. Materials and methods

2.1. Clay minerals and reagents

The illite was collected in the region of Le Puy-en-Velay (France) and the kaolinite (KGa-2) was obtained from the Source Clay Minerals

Repository (University of Missouri, Columbia). The illite was purified and conditioned to the Na-form (*Na-ill*) using the methodology given in Glaus et al. (2015b). The purified *Na-ill* has a grain density of 2800 kg m^{-3} . The cation exchange capacity (CEC) determined by the caesium isotope dilution method was $\sim 0.195 \text{ equiv. kg}^{-1}$ dry clay (Glaus et al., 2015a). In this *Na-ill* sample, a $\sim 12\%$ content of sanidine, a K-feldspar, was detected (Bradbury and Baeyens, 2009b). The kaolinite was present at purity of $\sim 99\%$ and it was used as received. The KGa-2 has a grain density of 2650 kg m^{-3} and a comparatively low CEC of $0.03\text{--}0.04 \text{ equiv. kg}^{-1}$ (Glaus et al., 2010).

The OPA sample originated from a geothermal borehole at Schlattigen, Switzerland, from the clay-rich facies at 938 m depth. The bulk dry density was 2412 kg m^{-3} and the porosity 11% (calculated from a grain density of 2710 kg m^{-3}). The clay fraction of the OPA sample was composed of illite ($\sim 43.4 \text{ wt}\%$), illite/smectite mixed layers ($\sim 7 \text{ wt}\%$), kaolinite ($\sim 35.6 \text{ wt}\%$) and chlorite ($\sim 13.8 \text{ wt}\%$) with a total clay content of 83%. Detailed characteristics of the rock sample are summarised in Appendix A2 (Supplementary Information).

Reagents of analytical grade or higher purity were obtained from Merck (Dietikon, Switzerland) or Fluka (Buchs, Switzerland). Radioisotopically pure $^{36}\text{Cl}^-$ and HTO were obtained from Isotope Products Europe (Blaseg, Germany). D_2O ($> 99.8\%$ atom D) was from ARMAR AG (Döttingen, Switzerland). De-ionised water (Milli-Q® water) was used throughout. Helium obtained from Messer (Lenzburg, Switzerland; 5.0; 200 bars) was used to pressurise the percolation solutions.

2.2. Percolation experiments with binary clay samples

The percolation set-up has been described in detail in Chen et al. (2018). Three compacted binary clay samples, named Mix-1, Mix-2 and Mix-3, were prepared from *Na-ill* and *KGa-2* at weight ratios, $\omega(-)$, of 0.25, 1.0 and 4.0, with ω defined as the weight of *Na-ill* (w_{ill} , kg) divided by the weight of *KGa-2* (w_{kaol} , kg; $\omega = w_{\text{ill}}/w_{\text{kaol}}$). The cell lengths were $\sim 1 \text{ cm}$, porosities varied from 0.37 to 0.46, and the measured Darcy fluxes from 1.1×10^{-7} to $2.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. A detailed overview of these samples and those used as pure clay mineral references is given in the Appendix A1 (Supplementary Information), along with a description of porosity calculation.

0.2 M NaCl was used as the percolation solution, and 0.01 mM K_2CrO_4 was applied in all experimental solutions in order to prevent potential microbial activities. A pulse (0.5 cm^3) of HTO tracer and test carboxylates (Table 1) was injected and their breakthrough responses were monitored by sampling and off-line analysis. Additionally, percolation experiments with test alcohols (Table 1) were carried out with sample Mix-2.

2.3. Percolation experiments with the OPA core

The experiments were carried out in a core infiltration apparatus

Table 1
Overview of the LMW-OC's.

| Name | Acronym | Formula |
|---------------------------------------|----------|--|
| Na-propanoate | PRO | $\text{CH}_3\text{CH}_2\text{COONa}$ |
| Na-L-2-hydroxypropanoate ^a | L-2-OH-P | $\text{CH}_3\text{CHOHCOONa}$ |
| Na-butanoate | BUT | $\text{CH}_3(\text{CH}_2)_2\text{COONa}$ |
| Na-DL-3-hydroxybutanoate | 3-OH-B | $\text{CH}_3\text{CHOHCH}_2\text{COONa}$ |
| Methanol | MeOH | CH_3OH |
| Ethanol | EtOH | $\text{CH}_3\text{CH}_2\text{OH}$ |
| 1-propanol | 1-PrOH | $\text{CH}_3(\text{CH}_2)_2\text{OH}$ |
| Ethane-1,2-diol | EG | $(\text{CH}_2\text{OH})_2$ |
| D-Sorbitol | S6OH | $\text{HOCH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ |

^a L-2-OH-P was tested with OPA, and no mass was recovered within the experimental duration, therefore, data not shown.

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