



Transport of low molecular weight organic compounds in compacted illite and kaolinite

Yanhua Chen ^{a, b}, Martin A. Glaus ^{a, *}, Luc R. Van Loon ^a, Urs Mäder ^b

^a Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

^b Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland

HIGHLIGHTS

- Anion sorption and anion exclusion is observed simultaneously.
- Sorption of organic compounds decreases ¹⁴C-borne dose rates.
- Sensitive measuring technique developed (percolation with pulse injection).

ARTICLE INFO

Article history:

Received 21 November 2017

Received in revised form

19 January 2018

Accepted 25 January 2018

Available online 6 February 2018

Handling Editor: I. Cousins

Keywords:

Carboxylates

Alcohols

Illite

Kaolinite

Anion exclusion

Anion sorption

ABSTRACT

¹⁴C-containing dissolved organic compounds may significantly contribute to the calculated annual overall dose emanated from a deep geological repository for radioactive waste. To date, there is a general lack of knowledge concerning the transport behaviour of low molecular weight organic compounds in the geosphere. The present work is aiming at a generic approach to measure weak adsorption of such compounds onto selected clay minerals. Percolation experiments were employed to sensitively measure the retardation of low molecular weight carboxylates and alcohols in compacted illite and kaolinite as a function of the ionic strength. Detection limits of $\sim 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ for the involved sorption distribution coefficients were attained thereby. The adsorption of alcohols on clays was near the detection limit and assumed to occur predominately via H-bonding. The adsorption of organic anions was influenced by several factors such as molecular structure, type of clay surfaces and the chemical composition of the aqueous phase. It was found that the relative position of neighbouring hydroxyl groups strongly influenced the retardation behaviour. Alpha-hydroxylated carboxylates, such as lactate, were found to be most retarded. Ligand exchange at the edge aluminol sites is the most probable explanation for the uptake of the negatively charged organic test compounds by the clay surface. The breakthrough behaviour of organic anions was additionally impacted by anion exclusion in illite. The demonstrated weak retardation of the test compounds can be robustly introduced in transport models, leading thus to a much lower contribution of ¹⁴C to the expected long-term overall dose.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

¹⁴C has been found to be an important contributor to the annually released radioactive dose predicted in performance assessment of a low- and intermediate-level radioactive waste repository (Yim and Caron, 2006). Inorganic and organic ¹⁴C-containing products are formed from the anoxic corrosion of neutron-activated steel (Nagra, 2014; Wieland and Hummel, 2015; Yim and Caron, 2006). The molecular source of ¹⁴C is mainly the neutron

activation of ¹⁴N contained in steel. Inorganic ¹⁴C is assumed to be immobilised by isotopic exchange with CO_3^{2-} in carbonates (e.g. CaCO_3), while the organic ¹⁴C stays mobile. ¹⁴C may thus reach the biosphere predominantly as organic compounds.

Some studies on the chemical form of organic ¹⁴C released from activated steel corrosion were undertaken by Kaneko et al. (2011); Ryota et al. (2014); Yamashita et al. (2014). Reduced hydrocarbons, such as CH_4 , and oxygenated hydrocarbons, in particular carboxylic acids, aldehydes and alcohols were identified. In either case, only low molecular weight (LMW) organic compounds (LMW-OC's) with a maximum chain length of 5 carbon atoms were identified so far (Wieland et al., 2016).

* Corresponding author., OHL0/002, 5232 Villigen PSI, Switzerland.
E-mail address: martin.glaus@psi.ch (M.A. Glaus).

The dose calculation of organic ^{14}C in present performance assessment studies is based on the assumption that the transport of organic ^{14}C is unretarded and that the entire pore space of the host rock is accessible for these compounds. If a weak retardation of the organic ^{14}C can be robustly introduced in the dose calculation models, it would lead to a significant reduction of organic ^{14}C contribution to the overall dose released. Presently, it is not possible to reduce the possible compounds to a manageable list of a few key compounds for which the transport behaviour in clays and clay rocks can be tested.

A broad interest in the fate and reactivity of organic matter in the subsurface can be noted, both regarding natural organic matter (Lehmann and Kleber, 2015) and anthropogenic organic matter. Sorptive stabilisation by soil mineral components governs the availability, turnover rates and toxicity of soil organic matter (Ahrens et al., 2015). Most literature works dealing with the interaction of organic compounds with solids are related to the uptake of compounds of environmental concern (Haderlein et al., 1996; Schwarzenbach et al., 2006; Xiao et al., 2011) or natural organic matter on soils or relevant soil components (Gu et al., 1994; Pignatello and Xing, 1996). There are some studies on the adsorption of LMW organic anions onto oxidic mineral surfaces such as aluminium oxide and aluminium oxide hydroxide using the batch sorption technique (Axe and Persson, 2001; Johnson et al., 2004a, 2004b; Yoon et al., 2004). The type of interaction is assumed to be the formation of inner-sphere complexes (ligand exchange) and/or outer-sphere complexes (hydrogen bonding and/or electrostatic interactions with positively charged sites). However, a generic understanding of uptake of LMW-OC's by clay minerals is currently lacking. Such knowledge would be required to assess the impact of the potential release of unknown mixtures of ^{14}C -bearing compounds from a repository for radioactive waste on the overall dose release curves in performance assessment studies. Studies related to the characterization of dissolved organic matter in argillaceous pore waters indicate that the interaction between LMW-OC's and clays is generally weak (Courdouan et al., 2007).

It is challenging to measure the weak sorption with proper analytical techniques, and it is even more difficult to describe the transport behaviour of LMW-OC's in clay minerals in terms of stoichiometric reactions. Quantitative studies on the sorption of LMW alcohols from aqueous solution by clay minerals are scarce (Brindley, 1966; Theng, 1972). Hydrogen bonding for alcohol adsorption on clay minerals was suggested as the predominant mechanism by Heydemann and Brindley (1968). These studies and the references given therein were mostly referring to solvation of the clays with alcohols. The relevance of the findings gained for aqueous systems, in which water is present in large excess, may be challenged. One dedicated study is concerned with uptake processes for nonylphenol, representing mixtures of rather large molecules with phenolic functional groups (Nagasaki et al., 2003). The R_d 's found therein were of the order of $6 \cdot 10^{-4} \text{ dm}^3 \text{ kg}^{-1}$, confirming thus the assumption of weak interactions. The adsorption of LMW anions onto clay minerals was rarely studied and found to be weak (Lagaly et al., 2006). These studies have all suggested that the adsorption of LMW-OC's on clay minerals is weak, and influenced by many factors such as organic structure, mineral surfaces and solvent properties. A very recent study investigated the uptake of a series of carboxylic acids by Callovian-Oxfordian claystone, which is foreseen as a potential host rock formation in France (Rasamimanana et al., 2017). The compounds investigated exhibit rather strong chelating properties, which may be of less relevance for the compounds expected to be released from the anaerobic corrosion of activated steel.

The general approach of the present study follows a complementary strategy: (i) to develop a methodology to investigate the

transport behaviour of LMW-OC's with a focus on carboxylates and alcohols, (ii) to establish deterministic relationships between structural features of the studied organic compounds and their sorption properties, and (iii) to study the influence of clay surface properties on the transport of LMW-OC's. The percolation technique involving advective flow was tested here to measure the retardation properties. In parallel, diffusion experiments (no advective flow) were carried out for comparison purposes. The work can thus be understood as a first step toward a generic understanding of functional relationships for the uptake of LMW-OC's by clay surfaces. Such knowledge combined with the inventory of the different structural types of organic compounds, might offer a robust predictive tool for assessing the contribution of ^{14}C -compounds to the overall annual dose. Once the key products will have been identified, their transport behaviour in clays and clay rocks can be predicted based on established relationships between structure and retardation behaviours.

It was rarely discussed that anion exclusion effects may simultaneously occur with anion sorption, possibly masking the weak sorption of organic anions onto clay minerals. Therefore, one critical issue in determining the transport properties of LMW-OC's is to develop a model which can describe the anion adsorption behaviour with the existence of anion exclusion effects. Another critical issue is to develop an experimental methodology to measure weak sorption values. For example, it is necessary to minimise potential degradation of these compounds due to chemical and/or microbial activities over the entire experimental and analytical period. In the open literature, sodium azide (NaN_3) has been reported frequently as a biocide inhibiting microbial activities in sorption-desorption experiments, and NaN_3 has been applied at various concentrations ranging from 0.1% to 0.01% (Huang et al., 1998; Sharer et al., 2003; Sijm et al., 1998). However, a few reports have suggested that NaN_3 can react with the organics of interest, therefore the application of NaN_3 as an inhibitor must be carefully evaluated (Chefetz et al., 2006). It is necessary to assess the performance of the selected inhibitor.

2. Materials and methods

2.1. Clay mineral

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-illite has a solid density of 2800 kg m^{-3} . The cation exchange capacity (CEC) determined by the cesium isotope dilution method was $\sim 0.195 \text{ equiv kg}^{-1}$ dry clay (Glaus et al., 2015b). In this Na-ill sample, a $\sim 12\%$ content of sanidine, a K-feldspar, was detected (Bradbury and Baeyens, 2009). Further quantitative information on Na-ill can be found in Montoya et al. (2018). The Na-ill was pre-conditioned in batch suspensions with a NaOH solution to desired pH values, and dried by freeze drying. The kaolinite had $\sim 99\%$ purity and was used as received. The KGa-2 has a solid 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). A detailed characterization of KGa-2 has been given in Van Olphen and Fripiat (1979).

2.2. Reagents, samples and analytical procedures

Reagents of analytical grade or higher quality were obtained from Merck (Dietikon, Switzerland) or Fluka (Buchs, Switzerland). Radioisotopically pure $^{36}\text{Cl}^-$, HTO were obtained from Isotope Products Europe (Blaseg, Germany). De-ionised water (Milli-Q[®])

Download English Version:

<https://daneshyari.com/en/article/8851861>

Download Persian Version:

<https://daneshyari.com/article/8851861>

[Daneshyari.com](https://daneshyari.com)