

Binding of multivalent radionuclides to dissolved organic matter – A multi-angle approach

Introduction

Dissolved organic matter (DOM) is the general name which refers to (chemical and/or biological) degradation products of biotic origin ubiquitously present in surface and groundwaters. DOM consists of a heterogeneous continuum of molecules differing in size, chemical properties, functional group types and content (Chin *et al.*, 1994). DOM is known to have a profound impact on contaminant (heavy metals, radionuclides, organic xenobiotics) speciation, mobility and bioavailability in the natural environment. However, due to its ill-defined nature, insight into exact molecular binding mechanisms between DOM and these contaminants is relatively scarce (Aiken *et al.*, 2011).

The Waste&Disposal Expert Group at SCK•CEN have conducted numerous studies in the past which exemplify the strong binding between DOM and multivalent radionuclides (trivalent and tetravalent lanthanides and actinides) (Maes *et al.*, 2006; Liu *et al.*, 2008; Bruggeman *et al.*, 2010). These studies consist mainly of batch-type and transport (percolation) experiments in geochemical conditions representative of Boom Clay, the geological formation which is investigated as a possible host rock for a deep geological repository for radioactive waste. More specifically, it was shown that DOM-associated radionuclide species dominate the aqueous speciation of a broad range of safety-relevant radioisotopes. The strong binding between these isotopes and DOM is equally linked to so-called "colloid-facilitated" transport behaviour observed in long-term transport experiments at lab scale (Maes *et al.*, 2011). Colloid-facilitated transport remains an ill-understood kinetically driven migration pathway in which DOM colloids act as carriers of associated contaminants through the geosphere. Such behaviour has equally been observed by other authors in both lab-scale and field studies (e.g., Artinger *et al.*, 2003). Successful attempts have been made to draft model descriptions of colloid-facilitated transport which simulate concentration changes as a function of time. However, these descriptions are until now not backed up by an understanding of the mechanisms which are responsible for this phenomenon.

Some scarce studies available in scientific literature may point to the fact that conformational changes (folding, charge reorganisation) upon association of multivalent cations with DOM might be responsible for the slow kinetic mechanisms associated with colloid-facilitated transport (Plaschke *et al.*, 2009). However, other studies point to a different type of association behaviour for trivalent and tetravalent metals, respectively. Multivalent metals may also affect the interaction between DOM and solid phases (e.g., Weng *et al.*, 2005). In any case, it is clear that a systematic study providing molecular insight into the interaction of multivalent cations with DOM on short and long-term scale should provide some answers to the open questions existing on this theme.

To this aim, a suite of analytical techniques would have to be investigated for their ability to provide some answers into the different aspects related to metal-DOM uptake (chemical structures formed, conformational changes associated with uptake of metals, changes in

behaviour on different time scales, etc.). These analytical techniques should then be applied to investigate speciation changes of multivalent metals/radionuclides in presence of DOM as a function of time and geochemical parameters (pH, ionic strength, etc.). Such a comprehensive study has, to the author's knowledge, never been undertaken so far.

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Objectives

The objectives of this PhD are:

1. To provide insight into interaction mechanisms of multivalent (trivalent/tetravalent) metals and radionuclides with dissolved organic matter on a molecular scale by means of state-of-the-art analytical techniques, with the focus on slow kinetics observed in batch and transport studies and deemed responsible for colloid-facilitated transport.
2. To show differences and/or parallelism in the interaction of respectively tri- and tetravalent cations with DOM (*i.e.*, to provide evidence of either complexation or colloid-colloid interaction)

In order to reach these objectives, the following strategy is suggested:

1. Cooperation with university labs (K.U.Leuven) and other research institutes (KIT-INE) that specialise in multiscale physicochemical characterisation of the interactions between multivalent metal ions or their clusters and organic ligands or their micellar associations, via complexation, surface adsorption, colloid/colloid or colloid/micelle interaction. Identification of such interaction mechanisms requires a combination of local structure elucidation with meso- and/or macroscale characterisation of the clusters and their behaviour, with techniques such as time-resolved laser fluorescence spectroscopy (TRLFS), diffusion ordered spectroscopy (DOSY) NMR, X-ray and

neutron techniques (SAXS, SANS, XANES, EXAFS, STXM), etc.). At present, the availability of such techniques at SCK•CEN is very limited, if not non-existent.

2. Selection of metals/radionuclides that are both representative for the elements which we like to study and that provide sufficient characteristics which allow good analytical resolution. E.g., Cm³⁺ is known to have strong fluorescent properties which allow identification of a number of aqueous Cm complexes by means of time-resolved laser fluorescence spectroscopy.
3. To follow up the speciation of selected metals/radionuclides with dissolved organic matter as a function of time and geochemical conditions. To this aim, also aqueous solutions stemming from long-running (> 10 y) migration experiments at the Waste&Disposal Expert Group can be used.

The novelty of this research is to be found in the combination of knowledge with respect to colloid-facilitated transport phenomena in batch and transport experiments present at SCK•CEN, and the application of state-of-the-art analytical techniques which highlight (changes in) speciation of the elements in question, present at the research institutes which serve as a partner/promotor to this work.

Promotors

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Prof. Dr. Th. Schäfer (Univ. Berlin – KIT-INE)

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