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Review

The speciation, stability, solubility and biodegradation of organic co-contaminant radionuclide complexes: A review

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ABSTRACT

The potential migration of radionuclides is of concern at contaminated land sites and, in the long term, waste repositories. Pathways of migration need to be characterised on a predictive level so that management decisions can be made with confidence. A pathway that is relatively poorly understood at present is radionuclide solubilisation due to complexation by organic complexing agents that are present in mixed radioactive wastes, and at radioactively contaminated land sites. Interactions of the complexing agents with radionuclides and the host environment, and the response to changes in the physicochemical conditions make their role far from simple to elucidate. In addition, chemical and biodegradation of the organic materials may be important. In this paper, key co-contaminant organics are reviewed with emphasis on their environmental fate and impact on radionuclide migration.

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1. Introduction

Pathways of radionuclide migration need to be understood at radioactively contaminated sites, such as Sellafield in the UK and Oak Ridge in the USA, and those that may become contaminated in the future through surface storage, near surface disposal and deep geological disposal. This encompasses sites with very different physical stresses and biogeochemical conditions. The challenge is to provide a robust understanding of the factors which control migration of radionuclides under these different conditions, and ultimately produce reliable predictions of the functioning of waste management systems.

The role of organic complexing agents in enhancing radionuclide migration is undisputed. A seminal paper (McCarthy et al., 1998) demonstrated that periodic flooding of burial trenches at Oak Ridge National Laboratory has resulted in ^{244}Cm and ^{241}Am migration that far exceeds the original predictions of mobility, due to complexation by natural organic matter. Research has generated a detailed understanding of kinetic, as well as thermodynamic, processes involving complexation of key radionuclides by humic acids, thus humic acids are now included in many models (e.g. Warwick et al., 2000). Anthropogenic organic ligands represent a pool of complexing agents that may be of equal importance in enhancing the redistribution of radionuclides.

The relative importance of anthropogenic organic complexing agents, alongside humic and fulvic acids, within the lifetime of a generic deep geological waste repository has been considered by Evans and Heath (2003). A summary of the timeframes over which complexing agents were categorised as showing significant availability and stability in the zones of the repository is shown in Table 1 (Evans and Heath, 2003). The zones comprise: the near field, high pH, reducing engineered environment; the disturbed zone, formed through the creation of the repository which is also highly alkaline; the host rock, less alkaline but remaining reducing, and; finally the near surface zone which is the only oxidising zone and at environmental pH (pH 4–9). Based on the expected performance of a repository, the study defined that low concentrations of the disposed organic complexing agents would migrate from the engineered environment within the first 100 years post-closure, and only trace concentrations would ever reach the near surface zones. Therefore, as Table 1 shows, humic and fulvic acids were found to be the most important organic complexing agents with respect to the far field of a waste repository. Thus, it is probably reasonable to consider that anthropogenic organic complexing agents act as “shuttles”, transporting radionuclides out of the near field/disturbed rock zone (Evans and Heath, 2003). Of the anthropogenic organic complexing agents, only cement additives reach and persist in the near surface oxidising zone. In cases of contaminated land or release from low-level, surface repositories/storage, the relative importance of the anthropogenic complexing agents in solubilising radionuclides will be site-specific and depend on the source, impacted environment, concentration of the complexing agents and the radionuclides present. Therefore, the impact of these complexing agents on radionuclide solubility must be understood at a fundamental level to allow accurate predictions of behaviour under a wide variety of conditions, and the predicted behaviour must be validated using laboratory experiments or relevant field studies.

In this review, the current understanding of processes affecting solubility, stability and transport of radionuclide-organic complexes will be explored in depth, with relevance to natural and engineered environments. The focus is on anthropogenic organic complexing agents that have been identified as important in Table 1. An overview of the interactions between complexing agents and radionuclides, and the processes affecting the overall solubility of the complexes is given in Fig. 1. Additionally, the analytical and experimental techniques used in the studies discussed are given in Table 2.

Table 1 – Summary of the timeframes (from 0–100 000s years) within which ligands have been identified as having a significant stability and availability within the different zones of a deep geological waste repository (Evans and Heath, 2003)

	Near field	Disturbed zone	Host rock reducing layer	Near surface oxidising layer
ISA	100–1000	100–1000	–	–
Gluconate	–	–	–	–
Authentic cellulose degradation products (ISA-like)	100–1000	100–1000	–	–
Authentic cellulose degradation products (non-ISA)	0–10,000 s	100–1000	–	–
Anion exchange resin degradation products	0–100	0–1000	–	–
Picolinate	0–1000	0–1000	100–1000	–
Cement additives	100–1000	100–1000	–	–
EDTA	0–1000	0–1000	100–1000	–
Humic acids	–	>100,000	Entire period	Entire period
Fulvic acids	Entire period	Entire period	Entire period	Entire period