



Radial diffusion of radiocaesium and radioiodide through cementitious backfill



M. Felipe-Sotelo^{a,*}, J. Hinchliff^a, D. Drury^b, N.D.M. Evans^a, S. Williams^c, D. Read^a

^a Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

^b Golder Associates (UK) Ltd., Browns Lane Business Park, Stanton-on-the-Wolds, Nottingham NG12 5BL, UK

^c Nuclear Decommissioning Authority, Radioactive Waste Management Directorate, Harwell Office, Curie Avenue, Harwell, Oxfordshire OX 11 0RH, UK

ARTICLE INFO

Article history:

Received 30 May 2013

Received in revised form 30 March 2014

Accepted 11 April 2014

Available online 21 April 2014

Keywords:

Caesium

Iodide

Through-diffusion

Cement

Repository backfill

Radioactive waste

ABSTRACT

The function of the backfill material in a geological disposal facility (GDF) is to chemically condition the environment of the near field and thereby chemically retard the transport of the radionuclides present in the waste. This function of the backfill material is usually referred to as chemical containment. Diffusion experiments are being carried out over periods up to four years to assess the diffusion of Cs, Ni, Eu, Th, U and I (as I⁻) through Nirex Reference Vault Backfill (NRVB). The method uses cylinders of NRVB (40 mm diameter, 40–45 mm height) which can be doped via a central well with the radionuclides of interest. Diffusion occurs radially into a surrounding solution already pre-equilibrated with the cement. This paper shows the results obtained during the first two years for experiments undertaken using ¹³⁷Cs and ¹²⁵I⁻ tracers with and without carrier. Comparison is made to tritiated water under identical experimental conditions. Breakthrough of Cs and I⁻ occurred within the first week of the experiments, reaching steady state in the surrounding solution after 20–50 days. The maximum concentrations expected from the original inventories based on a simple dilution calculation have not been reached, indicating that retention in the matrix has occurred; ranging from 10% to 40% for Cs, and up to 50% for I⁻. Corresponding experiments using a solution containing cellulose degradation products (CDP) showed an increased diffusion for both Cs and I. Migration profiles have been obtained and the relative retention of each radionuclide has been confirmed using digital autoradiography. The results indicate that, for both isotopes, migration occurs through the cement matrix rather than through microfissures. However, whereas Cs is homogeneously distributed within the blocks, there is evidence of zones of preferential I⁻ accumulation even where concentrations in solution have reached steady state. Transport modelling using GoldSim has replicated experimental observations, producing comparable partition ratios (R_d) to those reported in the literature.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The present concept for the disposal of intermediate and longer lived low level radioactive waste (ILW and LLW) in the UK is based on a multi-barrier geological disposal facility (GDF). The GDF must fulfil two high-level objectives, which are the isolation of the waste from the biosphere and the containment of the radionuclides present in the waste. The components of the multi-barrier system contribute to achieve these objectives in different ways and over different timescales (Nuclear Decommissioning Authority, 2010a). According to the generic design (Hicks et al., 2008), the waste will be mixed with grout, retained in stainless steel canisters

and placed in an engineered vault at ≥ 200 m depth. After closure, the vault will be backfilled with a material that will contribute to the objectives of containment by a combination of chemical processes, namely solubility limitation, precipitation, co-precipitation and sorption (Nuclear Decommissioning Authority, 2010a,b). One potential formulation for the backfill is the cementitious mixture known as NRVB (Nirex Reference Vault Backfill, from United Kingdom Nirex Limited, 1997). This alkaline grout will serve both as a physical barrier to radionuclide migration and contribute to the chemical containment of the radioactive waste by maintaining the pH of the pore water at high alkalinity. While the mineralogical changes in the first stages of the degradation of the cementitious material are independent of the composition of the groundwater, it will strongly influence the duration of the different stages (Jacques et al., 2010). Reactive transport models performed for a

* Corresponding author. Tel.: +44 1509564108; fax: +44 1509223925.

E-mail address: m.felipe-sotelo@lboro.ac.uk (M. Felipe-Sotelo).

generic groundwater with saline composition flowing through NRVB indicated that the pH of the repository will remain highly alkaline (over pH 11) for thousands and probably hundreds of thousands of years (Nuclear Decommissioning Authority, 2010b). Moreover, the cementitious backfill will also contribute to the containment of the waste by providing a surface for the retention of radionuclides. Consequently, it is important to understand the interaction mechanisms of key radionuclides with the cementitious backfill and to build confidence in the models used to assess the retardation of key radionuclides over extended timescales.

One of the main impacts on the behaviour of some radionuclides in ILW is the degradation of the cellulosic components of the waste, which may include paper, fabrics and wood. These cellulosic materials will degrade under alkaline conditions producing a complex mixture of polyhydroxylic ligands capable of forming strong complexes with transition metals and elements from the actinide and lanthanide series (Glaus and van Loon, 2008). These cellulose degradation products (CDP) may affect mobility of radionuclides either by complexation or by influencing uptake by the cement (Chambers and Williams, 2006). The presence of CDP will modify the ionic strength of the cement pore water, they will complex with metals from the cement, speed up the degradation of the cement (Pointeau et al., 2008) or they may sorb to the solid (Holgersson et al., 1998). Isosaccharinic acid (ISA) is often assumed to be the main component of the mixture (Glaus and van Loon, 2008) in addition to short chain aliphatic acids such as formic, acetic, lactic and threonic acid (Glaus et al., 1999). Previous work (Warwick et al., 2012) has shown that the presence of organic compounds other than ISA had a significant effect on the solubility of radionuclides such as Th, and therefore they should not be neglected from future studies. All these aspects may be acting under repository conditions, and this work attempts to reproduce them by using a mixture of CDP produced in contact with NRVB.

A series of 4-year, radially configured diffusion experiments are being carried out to assess the diffusion of Cs, Ni, Eu, Th, U and I (as I^-) through NRVB. In order to assess the effect of organic ligands on retardation of the radionuclides the experiments are being repeated in the presence of a CDP mixture prepared in the presence of NRVB. This paper describes results obtained after two years for Cs and I^- .

Under the saturated conditions of a deep geological disposal facility, diffusion of radionuclides is the main migration process in engineered barriers unless the permeability is high enough to allow flow and advective transport. Diffusion experiments can provide information to support the performance assessment of a GDF. Results will vary depending on the initial and boundary conditions and whether diffusivity is determined under steady state or non-steady state conditions. Steady state diffusion can be determined by studying mass transport from one solution to another separated by a slice of the solid, whereas non-steady state diffusion can be determined by studying the concentration profile in a solid after contact with a solution containing the species of interest.

Several studies have investigated the immobilisation of Cs and I in cementitious materials using a range of experimental approaches: (i) in-diffusion (Andersson et al., 1981; Albinsson et al., 1996); (ii) through-diffusion (Atkinson and Nickerson, 1984; Johnston and Wilmot, 1992; Sarott et al., 1992; Jakob et al., 1999; Chambers et al., 2006; Chida and Sugiyama, 2009; Bucur et al., 2010) and (iii) out-diffusion or leaching (Mattigod et al., 2001; El-Kamash et al., 2002; Plecas, 2003; Papadokostaki and Savidou, 2009; Sinha et al., 2009; Ojovan et al., 2011).

The experimental approach used in the present work is based on through-diffusion in a radial configuration; the approach has been used successfully to study migration of uranium through granite (e.g. Markovaara-Koivisto et al., 2009). It combines the advantages of a through-diffusion setup where the time of break-

through can be determined by monitoring the tracer receiving solution in contact with the solid and the simplicity of other out- and in-diffusion approaches that avoid the use of specially constructed diffusion cells which are prone to leakage.

The main sorption mechanism of Cs onto cement is incorporation into the structure of the calcium silicate hydrate (CSH) phases, by exchange with the Ca^{2+} cations in the interlayer region of the CSH sheets (Iwaida et al., 2002). Factors that may affect the retention of Cs include the ionic strength of the solution in contact with the cement and the concentration of competing ions (Na, K and Ca) in the cement. Ojovan et al. (2011) reported increased leaching of ^{137}Cs from cement in distilled water in comparison to groundwater of moderate hardness due to partial dissolution of the cement matrix. The same authors also reported twice as much leaching of ^{137}Cs from cement rich in $NaNO_3$ than previously reported for similar specimens prepared with distilled water (Perić et al., 1994). The difference between the leaching rates observed in these two studies could be due to the competition of alkali metal cations with Cs for surface sites, causing a decrease in the partition ratio (R_d) as suggested in batch experiment results reported by Ochs et al. (2006). The same study by Ochs et al. (2006) also concluded that the sorption of Cs is expected to increase with the degradation of the cement pastes as the Ca/Si ratio decreases, and the concentration of Ca in solution drops. The reduction of the Ca/Si ratio causes a change on the surface of the CSH phases; the silanol groups remain deprotonated at high pH increasing the negative charge and the number of strong Cs sorption sites at the same time as Ca competition for these sites decreases. The behaviour of Cs, due to the reduction of Ca/Si ratios and increasing negative charge on the CSH surfaces, is the opposite of the sorption trend for anionic radionuclides such as I^- , observed by Pointeau et al. (2008).

The use of additives in combination with ordinary Portland cement (OPC), such as vermiculite (Sinha et al., 2009), silica fume (Johnston and Wilmot, 1992) or ilmenite ($FeTiO_3$; El-Kamash et al., 2002), may improve retention of Cs within the cements. El-Kamash et al. (2002) attributed the reduction in Cs leaching to a reduction in porosity caused by the silica fume and the ilmenite. Carbonation of the cement can have similar effects on diffusion, as observed for both Cs (Andersson et al., 1981) and I^- , where the rate of diffusion through cement decreased by one order of magnitude as a consequence of the precipitation of $CaCO_3$ (Sarott et al., 1992). For I^- (Atkinson and Nickerson, 1984) and Cs (Atkinson and Nickerson, 1984; Johnston and Wilmot, 1992) the rate of diffusion correlates strongly with the water:cement ratio used when preparing the cement paste. Changes in the water:cement ratio between 0.2 and 0.7 could cause an increase of the diffusivity of Cs and I by up to 4 and 3 orders of magnitude, respectively (Atkinson and Nickerson, 1984). The difference observed in the diffusivity values could not be explained uniquely in terms of porosity changes and the authors suggested that it could be due to constrictivity differences (i.e. the relationship between the diameter of the diffusing ions and the average pore size).

In the case of iodine, one additional aspect that may affect its diffusion is the redox potential of the system. The presence of redox active additives in the cements can cause a change of iodine speciation from reduced to oxidised states or vice versa, with consequent modification of migration behaviour. Thus, Mattigod et al. (2001) reported a reduction in the leachability of iodine in cement blocks that contained steel fibres; the authors postulated the reduction of IO_3^- to I^- by Fe as the cause of the decrease in mobility, however they could not provide data to confirm the changes in the oxidation state. The expected speciation of iodine under the conditions of a cementitious repository is as I^- (Atkins and Glasser, 1992). This is due to the slow kinetics of I^- oxidation to IO_3^- , even in the presence of oxygenated water and secondly, due to the

Download English Version:

<https://daneshyari.com/en/article/4720983>

Download Persian Version:

<https://daneshyari.com/article/4720983>

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