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Microbial impacts on ^{99m}Tc migration through sandstone under highly alkaline conditions relevant to radioactive waste disposal

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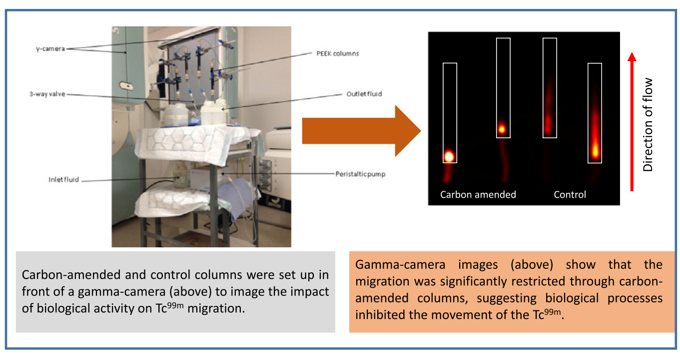
HIGHLIGHTS

- High-pH column experiments assembled representative of aspects of a GDF for ILW
- Biological processes caused restriction of Tc^{99m} migration.
- Gas generation and microbial Fe(III) reduction implicated
- H_2 oxidizers dominate column sediments.
- Implications for geodisposal of intermediate level radioactive waste

GRAPHICAL ABSTRACT



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ABSTRACT

Geological disposal of intermediate level radioactive waste in the UK is planned to involve the use of cementitious materials, facilitating the formation of an alkali-disturbed zone within the host rock. The biogeochemical processes that will occur in this environment, and the extent to which they will impact on radionuclide migration, are currently poorly understood. This study investigates the impact of biogeochemical processes on the mobility of the radionuclide technetium, in column experiments designed to be representative of aspects of the alkali-disturbed zone. Results indicate that microbial processes were capable of inhibiting ^{99m}Tc migration through columns, and X-ray radiography demonstrated that extensive physical changes had occurred to the material within columns where microbiological activity had been stimulated. The utilisation of organic acids under highly alkaline conditions, generating H_2 and CO_2, may represent a mechanism by which microbial processes may alter the hydraulic conductivity of a geological environment. Column sediments were dominated by obligately alkaliphilic H_2-oxidising bacteria, suggesting that the enrichment of these bacteria may have occurred as a result of H_2 generation during organic acid metabolism. The results from these experiments show that microorganisms are able to carry out a number of processes under highly alkaline conditions that could potentially impact on the properties of the host rock surrounding a geological disposal facility for intermediate level radioactive waste.

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1. Introduction

The UK's concept for the disposal of intermediate level radioactive waste (ILW) will involve a deep geological disposal facility (GDF), with numerous engineered barriers potentially containing cementitious materials, as, for example a backfill material (NDA, 2010). Movement of groundwater through a cementitious repository will cause an alkaline plume ($pH \approx 13$) to develop, which will interact with components of the host rock forming an alkali-disturbed zone (ADZ). This ADZ will impact on microbial populations and processes within the host rock; these biogeochemical processes may in turn play a defining role in controlling the migration of key radionuclides through the geosphere, although it is thought that the upper pH limit for microbial activities is approaching pH 12 (Rizoulis et al., 2012). Biofilm formation, for example, may lead to changes in the physical properties of the host rock (Coombs et al., 2010), by causing a decrease in pore volume (Taylor et al., 1990) and therefore retarding radionuclide migration. Most microorganisms are capable of colonising surfaces, with several environmental cues thought to play a role in promoting biofilm formation including oxygen availability and pH (Babauta et al., 2013). Microbial cells secrete extracellular polymeric substances (EPS) comprising polysaccharides, nucleic acids, proteins and lipids which immobilise cells. The composition of the extracellular matrix is influenced by the microbial community composition, shear forces imposed on the biofilm structure, and other environmental factors (Flemming and Wingender, 2010). Microbial mineral precipitation, including microbially induced calcite formation may have similar impacts (DeJong et al., 2006, Cuthbert et al., 2012), particularly under the calcium-rich conditions that will be present in a cementitious repository. These processes may lead to alterations of pore space geometries, altering the hydraulic conductivity of the medium, and potentially resulting in a reduction in flow velocity (Hand et al., 2008).

The mechanisms by which microbial processes may impact on transport pathways in a GDF environment are wide-ranging and will depend on the local conditions. For example, processes that result in gas production, including organic matter utilisation, may cause pressure increases with the potential to damage waste containing barriers (Bonin et al., 2000). Depending on the rate at which gas generation occurs in a GDF, the consequences for fluid transport within a GDF host rock may be varied. Gas accumulation in a porous medium may lead to pore blockages (Taylor et al., 1990); the extent to which microbial gas generation occurs in a GDF host rock will depend on factors such as the availability of cellulose degradation products for microorganisms to metabolize for example. The UK's ILW inventory contains 2800 t of cellulosic materials which will degrade under the hyper-alkaline conditions generated in a GDF (NDA, 2014), although there remain uncertainties regarding the concentrations of cellulose degradation products that will be available in a GDF host rock when the pH conditions are suitable for microbial metabolism (Humphreys et al., 2010).

As well as physically blocking transport pathways, microbial metabolism may also control radionuclide movement through the geosphere via a range of other mechanisms. These include the alteration of mineral surfaces, for example, by forming biofilms that coat grain surfaces decreasing the availability of sorption sites, or by causing mineral dissolution that may impact on the ability of radionuclides to sorb to mineral surfaces (Brookshaw et al., 2012). Microbe-radionuclide interactions may also directly impact on the transport of radionuclides, via mechanisms including biosorption to ligands such as carboxyl, amine and phosphate groups associated with the cell surface, bioaccumulation within cells, and direct redox transformations e.g. bioreduction (Lloyd and Macaskie, 2002). Several Fe(III)-reducing microorganisms have demonstrated the ability to directly reduce redox active radionuclides to insoluble species, for example the reduction of U(VI), Np(V) and Tc(VII) to insoluble tetravalent forms under circum-neutral conditions (Lloyd, 2003). However, few studies have addressed microbial influences on radionuclide mobility under highly alkaline conditions representative of aspects of a GDF for ILW. The work that has been carried out investigating these high pH systems has suggested that microorganisms may play a role in immobilising some radionuclides up to a certain pH limit. As an example, Williamson et al. (2014) demonstrated that microbial U(VI) reduction occurred in microcosm experiments at pH 10.5, with most of the U(IV) formed associated with the solid phase.

Fe(II)-bearing minerals including biogenic siderite and vivianite resulting from the microbial reduction of Fe(III) may reduce radionuclides abiotically (Brookshaw et al., 2012). This mechanism has the potential to retard radionuclide migration through the geosphere, as several radionuclides including Tc are immobile in their reduced state (Lloyd et al., 2000). ^{99}Tc (a fission product of U-235 and Pu-239) is one of the UK's priority radionuclides (Walke et al., 2012) because of its long half-life (2.13×10^5 years; Zachara et al., 2007), and high mobility in its oxidised form [Tc(VII)] (Lear et al., 2010). Previous studies have investigated the mechanisms by which biogenic Fe(II) is capable of reducing Tc(VII) to Tc(IV), forming a poorly soluble precipitate (Zachara et al., 2007, McBeth et al., 2011). However, little is known about this process under the highly alkaline conditions that will be present in a GDF for ILW in the UK. A study carried out by Liu et al. (2008) demonstrated that the rate at which reductive immobilisation of Tc(VII) by Fe(II) occurs becomes slower as pH increases. Thorpe et al. (2014) found similar results when investigating Tc(VII) reduction with pre-reduced Fe(II)-bearing minerals, although a similar rate of Tc(VII) reduction was observed in microcosms at both circum-neutral pH and at pH 9, when Tc(VII) and Fe(III) reduction was concurrent.

This paper presents results of column experiments that aimed to investigate impacts of microbial processes under highly-alkaline conditions relevant to a GDF for ILW on transport in sandstone, and the resulting implications for Tc mobility. As a result of the potential microbial processes in a GDF and their subsequent impacts on transport processes discussed in the previous paragraphs, we hypothesize that in sediment columns incubated at high pH, microbial processes within these columns may inhibit the migration of radionuclides. To investigate these processes, high pH surface waters ($pH \approx 12.1$) were collected from a hyper-alkaline spring which has formed at a legacy lime workings site in the Peak District, UK. This fluid was pumped through sandstone columns with and without acetate and lactate. The impact of microbial colonisation on the mobility of ^{99m}Tc was assessed using a multidisciplinary approach including geochemical, mineralogical and molecular ecological analyses, coupled with radionuclide imaging techniques.

2. Methods

2.1. Field sampling

A hyper-alkaline spring is present at Harpur Hill, Buxton (53.236082° N, −1.9171250° W), which formed as a result of percolation of rainwater though lime kiln waste (Rizoulis et al., 2012). Surface waters ($pH \approx 12.1$, calcium hydroxide dominated) were collected from the hyper-alkaline spring at Harpur Hill, Buxton in sterile bottles. 1 L bottles were filled completely to ensure no headspace remained, and were stored at 4 °C for approximately two weeks.

2.2. Column experiments

Four polyether ether ketone (PEEK) columns (L = 15 cm; ID = 0.75 cm; Applied Research Europe, Berlin, Germany) were packed with approximately 10 g crushed sandstone (grain size < 500 μm). Surface waters collected from the field site were distributed between two sterile polypropylene vessels. Half of the fluid was amended with carbon (5 mM acetate, 5 mM lactate and 50 mgL^{-1} yeast extract). Columns were assembled in duplicate, with two receiving carbon-amended fluid and two receiving unamended fluid. Prior to experiment assembly, all components were sterilised by soaking in Virkon (active ingredients

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