Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 148 (2015) 343–359

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

U(VI) behaviour in hyperalkaline calcite systems

Kurt F. Smith [a,b], Nicholas D. Bryan [b,c], Adam N. Swinburne [c], Pieter Bots [a],
Samuel Shaw [a], Louise S. Natrajan [c], J. Frederick W. Mosselmans [d],
Francis R. Livens [a,c], Katherine Morris [a,*]

[a] *Research Centre for Radwaste Disposal and Williamson Research Centre, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*
[b] *National Nuclear Laboratory, Chadwick House, Risley WA3 6AE, United Kingdom*
[c] *Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*
[d] *Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom*

Received 20 March 2014; accepted in revised form 30 September 2014; available online 13 October 2014

Abstract

The behaviour of U(VI) in hyperalkaline fluid/calcite systems was studied over a range of U(VI) concentrations (5.27×10^{-5} μM to 42.0 μM) and in two high pH systems, young and old synthetic cement leachate in batch sorption experiments. These systems were selected to be representative of young- (pH 13.3) and old-stage (pH 10.5) leachate evolution within a cementitious geological disposal facility. Batch sorption experiments, modelling, extended X-ray absorption fine structure spectroscopy, electron microscopy, small angle X-ray scattering and luminescence spectroscopy were used to define the speciation of U(VI) across the systems of study. At the lowest concentrations (5.27×10^{-5} μM ^{232}U(VI)) significant U removal was observed for both old and young cement leachates, and this was successfully modelled using a first order kinetic adsorption modelling approach. At higher concentrations (>4.20 μM) in the young cement leachate, U(VI) showed no interaction with the calcite surface over an 18 month period. Small angle X-ray scattering techniques indicated that at high U concentrations (42.0 μM) and after 18 months, the U(VI) was present in a colloidal form which had little interaction with the calcite surface and consisted of both primary and aggregated particles with a radius of 7.6 ± 1.1 and 217 ± 24 Å, respectively. In the old cement leachate, luminescence spectroscopy identified two surface binding sites for U(VI) on calcite: in the system with 0.21 μM U(VI), a liebigite-like $Ca_2UO_2(CO_3)_3$ surface complex was identified; at higher U(VI) concentrations (0.42 μM), a second binding site of undetermined coordination was identified. At elevated U(VI) concentrations (>2.10 μM) in old cement leachate, both geochemical data and luminescence spectroscopy suggested that surface mediated precipitation was controlling U(VI) behaviour. A focused ion beam mill was used to create a section across the U(VI) precipitate–calcite interface. Transmission electron microscope images of the section revealed that the calcite surface was coated with a nano crystalline, U containing phase. Selected area electron diffraction images of the U precipitate which was formed at a U(VI) concentration of 4.20 μM were consistent with the formation of calcium uranate. XAS spectroscopy at higher concentrations (⩾21.0 μM) suggested the formation of a second U(VI) phase, possibly a uranyl oxyhydroxide phase.

These results indicated that in the young cement leachate, U(VI) did not react with the calcite surface unless U(VI) concentrations were very low (5.27×10^{-5} μM). At higher concentrations, speciation calculations suggested that U(VI) was significantly oversaturated and experimental observations confirmed it existed in a colloidal form that interacted with the mineral surface only weakly. In the old cement leachate systems at low concentrations batch sorption and luminescence data suggested that U(VI) removal was being driven by a surface complexation mechanism. However, at higher concentrations, spectroscopic methods suggest a combination of both surface complexation and surface mediated precipitation was

---

* Corresponding author.
E-mail address: katherine.morris@manchester.ac.uk (K. Morris).

http://dx.doi.org/10.1016/j.gca.2014.09.043

responsible for the observed removal. Overall, U(VI) behaviour in hyperalkaline calcite systems is distinct from that at circumneutral pH conditions: at high pH and anything but low U(VI) concentrations, a surface mediated precipitation mechanism occurs; this is in contrast to circumneutral pH conditions where U(VI) surface complexation reactions tend to dominate.

---

1. INTRODUCTION

In many countries the long-term management of intermediate level radioactive wastes will be for their final disposal in a deep Geological Disposal Facility (GDF) (NEA, 2004; DEFRA, 2008; Schwyn et al., 2012). The GDF will be designed to isolate radionuclides from the biosphere for sufficient time to allow the majority of the radioactive material to undergo radioactive decay, although for longer lived radionuclides it is clear that transport away from the engineered barrier cannot be ruled out. Once the waste has been packaged, typically by grouting in steel drums, it will be emplaced in the facility and backfilled. Currently it is anticipated that in the UK, the GDF will be backfilled with cementitious material, and engineering cement (e.g. "shotcrete") will be utilised in many designs. This means that consideration of the alkaline conditions that result from cement materials is of wide relevance (Schmidt, 1991; Schwyn et al., 2012). The cementitious environment is expected to remain alkaline (i.e. pH 10.5–13.1) over extended periods and, in the saturated sub-surface, is intended to produce conditions that reduce radionuclide mobility due to formation of insoluble hydrolysis products and increased sorption of cations to negatively charged mineral surfaces (Braney et al., 1993). In a cementitious GDF over time, the portlandite ($Ca(OH)_2$) and calcium silicate hydrate (C–S–H) components of the cement will undergo carbonation via reaction with carbonate in groundwaters to form minerals including calcite ($CaCO_3$; Dow and Glasser, 2003). This will increase the quantity of calcite present in any evolved cementitious GDF. Calcite is also ubiquitous in the natural environment and may well be a component of the host rock environment. Calcite has been shown to sequester metals and radionuclides effectively by adsorption and/or incorporation (Zachara et al., 1991; Geipel et al., 1997; Parkman et al., 1998; Hay et al., 2003; Rihs et al., 2004; Dong et al., 2005; Zavarin et al., 2005; Heberling et al., 2008). Thus, calcite clearly has the potential to be an important reactive mineral phase for radionuclides within the GDF environment.

U(VI) is stable in oxidising environments, readily forms the linear uranyl moiety ($O = U = O$; UO_2^{2+}) and typically has increased mobility compared to U(IV). In addition, under the hyperalkaline to alkaline conditions relevant to this study, U(VI) is expected to remain stable under anoxic and modestly reducing conditions (Gaona et al., 2011). Certain studies concerning U(VI) interactions with calcite have focused on incorporation and coprecipitation (Meece and Benninger, 1993; Curti, 1999; Reeder et al., 2000, 2001; Kelly et al., 2003; Elzinga et al., 2004), whilst others have studied sorption (Carroll et al., 1992; Geipel et al., 1997; Elzinga et al., 2004; Rihs et al., 2004). In an evolving geological disposal facility, the geochemical environment will be dynamic and both sorption and incorporation/coprecipitation reactions with radionuclides are possible.

There is a significant literature on U(VI) calcite interactions at ambient pH, for example, Elzinga et al. (2004) studied the reaction of U(VI) with calcite at pH 7.4 and 8.3 and over the concentration range 5 to 5000 μM using batch sorption experiments, Extended X-ray Absorption Fine Structure (EXAFS) and luminescence spectroscopy. EXAFS analysis of their batch sorption experiments with <500 μM U(VI) produced data consistent with the formation of uranyl triscarbonate surface complexes and suggested that sorption in their systems was taking place via inner sphere complexation, in agreement with Rihs et al. (2004). Unfortunately, their EXAFS analysis could not identify any calcium backscatterers to corroborate the proposed inner sphere bonding, and thus the exact coordination environment of U(VI) in this system remained undetermined. The authors then used luminescence spectroscopy to explore whether different U(VI) surface species were present in their experiments: at <100 μM U(VI) a calcium uranyl triscarbonate complex (in a liebigite-like structure) dominated, whilst for systems in the 100–500 μM range, there was evidence that a different, undetermined uranyl carbonate species became significant. The authors suggested this undetermined phase was likely to be intermediate between the liebigite-like ($Ca_2UO_2(CO_3)_3$) surface complex and U(VI) incorporated into calcite. Indeed, EXAFS and luminescence techniques confirm that when UO_2^{2+} is coprecipitated with calcite, it can exist in multiple coordination environments dependent on the method of precipitation (Reeder et al., 2000, 2001). Furthermore, it has been shown that selective incorporation of UO_2^{2+} during calcite coprecipitation takes place on the '-' steps of the calcite (1 0 4) surface (Reeder et al., 2004; Rihs et al., 2004). Refinement of this concept by Rihs et al. (2004) suggested that the number of binding sites in their experimental system was too low to account for the U(VI) sorption they observed, and that additional sites could be provided by calcium vacancies or "etch pits", which are effectively equivalent to additional '-' steps. Recent computational molecular dynamics simulations (Doudou et al., 2012) support preferential sorption of the $Ca_2UO_2(CO_3)_{3(aq)}$ species onto the '-' steps but also suggest that outer sphere complexation on the calcite terrace should be thermodynamically favourable. In addition to surface complexation and incorporation, calcite has been shown to promote the formation of U(VI) precipitates, such as schoepite ($(UO_2)_8O_2(OH)_{12}\cdot 12H_2O$; Carroll et al., 1992; Geipel et al., 1997; Elzinga et al., 2004; Schindler and Putnis, 2004).