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The effect of EDTA, NTA and picolinic acid on Th(IV) mobility in a ternary system with natural sand

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ABSTRACT

Organic complexing agents, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and picolinic acid, have been widely used at nuclear sites and are therefore found as common co-contaminants in radioactive contaminated land. This study has explored the mechanisms by which these three complexing agents affect the sorption of Th(IV) to pure silica and a natural sand. EDTA, NTA and, to a lesser extent, picolinic acid decreased the sorption of Th to silica, demonstrating the formation and solubility of Th complexes. However, Th sorption to sand was kinetically controlled and complexation enhanced the rate of Th sorption. EDTA and NTA did not sorb significantly to the sand, and metal desorption indicated that the mechanism involved exchange with sand-associated metals. At equilibrium, however, Th sorption was not affected by the presence of the ligands, and modelling suggested that the interaction between Th and the surface binding sites controlled Th sorption thermodynamically.

1. Introduction

Organic complexing agents have been widely used in nuclear waste reprocessing (Baisden and Choppin, 2007) and as degreasing agents, purification and decontamination agents and flocculating agents at nuclear sites (Riley and Zachara, 1992; Toste et al., 1988). Therefore organic complexing agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and picolinic acid have been co-disposed in nuclear waste and are commonly found in radioactive contaminated land (Campbell et al., 1994; Delegard et al., 1984; Killey et al., 1984; McIsaac et al., 1992; Means et al., 1978; Piciulo et al., 1986; Riley and Zachara, 1992; Toste et al., 1988). For example, solutions containing approximately 3.6×10^{-3} M EDTA were periodically disposed of to the process ponds at the US Department of Energy's Hanford Reservation (WA, USA) from 1943 to 1974 (Riley and Zachara, 1992). The analysis of a cladding sludge and a volume reduction slurry waste from these ponds revealed the presence of high solid phase concentrations of EDTA (1.42 and 0.18×10^{-3} mol kg^{-1}), while NTA was present at a much lower concentration (trace and 0.03×10^{-3} mol kg^{-1}) (Toste et al., 1988). Laboratory studies have therefore used concentrations of $11.8–31 \times 10^{-3}$ M (Kocherginsky et al., 2002; Toste et al., 1995; Toste et al., 2005) and 7.3×10^{-3} M (Toste et al., 1995) to simulate EDTA and NTA, respectively, in Hanford wastes. At Oak Ridge National Laboratory (TN, USA), a 3.7×10^{-7} M EDTA concentration was determined in groundwater that had been contaminated from nearby pits and trenches (Riley and Zachara, 1992). The picolinic acid concentration in cement-solidified decontamination waste from FiztPatrick Nuclear Power Station (NY, USA) was determined to be at least 2.2% m/m (McIsaac et al., 1992).

Anthropogenic organic ligands form stable aqueous complexes with many radionuclides and metals and hence may increase their mobility through the environment. EDTA was implicated in the migration of radionuclides, principally ^{60}Co, up to several meters from two radioactive waste burial trenches at Oak Ridge National Laboratory (Killey et al., 1984; McCarthy et al., 1998; Means and Alexander, 1981; Means et al., 1978), and the mobilisation of ^{239}Pu and ^{238}Pu from trench leachates at the Maxey Flats radioactive waste disposal site (KY, USA) was also associated with EDTA complexation (Cleveland and Rees, 1981). EDTA has also been found to actively promote U(VI) migration through intact sandstone cores at pH 5–6 (Read et al., 1998).

Conversely, in other systems, the presence of organic ligands has been found to have either no effect on radionuclide and metal mobility or to enhance sorption. Serne et al. (2002) observed no change in the extent of U(VI) and Th(IV) sorption to a synthetic Fe-coated sand, or to a natural sandy soil, in the presence of equimolar EDTA or picolinic acid (10^{-5} M) over a pH range of 4–10,

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reflecting a lack of significant radionuclide–ligand complex formation. Equimolar NTA (1 μM) did not modify Co sorption to gibbsite at $pH < 7.5$, but at higher pHs a slight increase in sorption suggested the formation of a ternary $CoNTA^-$ surface complex (Girvin et al., 1996). Enhanced sorption to aluminium oxide was also observed for low concentrations (10^{-6} M) of Ni- and Zn-EDTA complexes at $pH < 6$; however, at $pH > 7$, sorption became insignificant and thus complexation increased metal mobility (Bowers and Huang, 1987). The formation of Pb-EDTA (Bowers and Huang, 1987) and Cu-picolinic acid complexes (Davis and Leckie, 1978) has also been reported to prevent the sorption of the divalent metals onto SiO_2 and amorphous iron oxide, respectively, from pH 4–7. Nowack and Sigg (1996) found that EDTA exhibited a pH dependent sorption mechanism onto goethite, and that it had a highly variable influence over di and trivalent metal sorption. Ternary interactions of EDTA-metal complexes with the goethite surface were important for most metals studied.

These contrasting observations reflect the complexity of radionuclide-organic complexing agent interactions and their dependence on the individual characteristics of the system studied (Keith-Roach, 2008). Frequently, the net effect of the complexing agents on radionuclide sorption is reported, rather than the mechanism of the interactions occurring in the system; thus these specific data are difficult to apply in a more general context (Keith-Roach, 2008). Therefore, the aims of this study were to test the hypothesis that the net impact of an organic complexing agent on radionuclide mobility is controlled by competitive interactions between radionuclide and metals associated with the solid phase for both complexing agent and sorption sites on the solid phase, and to define experimentally the mechanisms of these interactions for a natural sand system. In order to achieve these aims, laboratory batch experiments were carried out using two solid phases (pure silica as an artificial solid phase and dune sand as a natural solid phase) and the kinetics of radionuclide sorption, metal desorption and complexing agent sorption processes were quantified with and without the complexing agents being present. The effect of complexing agent concentration and radionuclide complexation was also studied. Thorium was selected as a model tetravalent actinide with a moderate to high affinity for organic ligands, and EDTA, NTA and picolinic acid were included as 3 common organic complexing agents with different denticities (Fig. 1).

2. Materials and methods

2.1. Reagents

All salts used in this study were Analytical Grade Reagents. EDTA sodium salt was purchased from Fisher Scientific (UK) and NTA sodium salt and picolinic acid from Sigma–Aldrich (UK). In order to avoid the abrupt changes in pH that occur if acidified standard solutions of Th are added to environmental matrices, and which could lead to colloid formation, thorium nitrate salt (BDH Chemicals Ltd, England) was used to prepare Th(IV) stock solutions. Anion standards for ion chromatography (IC) analysis were prepared from sodium chloride, sodium nitrate, potassium phosphate monobasic, sodium sulphate and sodium carbonate salts (BDH Chemicals Ltd, England), and copper(II) chloride salt (Fisher Scientific, UK) was used during UV spectrophotometry. All solutions and experiments described in this work were prepared using MilliQ water (Millipore, 18.2 MΩ cm^{-1}) and carried out in an ISO 9001:2000 accredited laboratory.

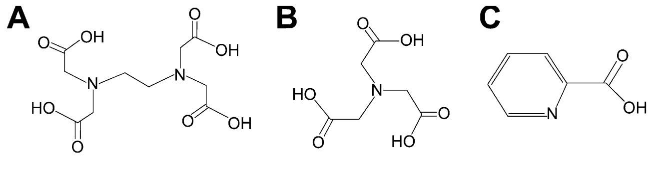

Fig. 1. The chemical structures of A) EDTA, B) NTA and C) picolinic acid showing the potential ligand atoms with electron donor characteristics (i.e. the nitrogen and the deprotonated, negatively charged oxygen of carboxylic acid groups) that are able to bind metal ions, and therefore form highly water soluble metal complexes. Their stability generally increases with the number of donor groups, i.e. with the denticity of the complexing agent.

Dune sand from Drigg Sands in Cumbria (UK) was selected to represent a simple environmental solid phase, as it constitutes a significant fraction of many soil matrices. In addition, this dune sands was chosen because of its location, adjacent to the low-level waste (LLW) repository managed by the British Nuclear Group. The sand was sieved to <2 mm using a plastic sieve (nylon) to remove organic debris and large grains and stored in a plastic container at room temperature until use. To maintain its environmental relevance no further treatments were carried out. Silicon dioxide, crystalline (fine), coating quality, ≥99.9%, 200–700 μm particle size, was obtained from Sigma–Aldrich (UK) and used untreated as an artificial solid phase.

2.2. Batch experiment design

2.2.1. General

All batch sorption experiments were prepared in 50 mL polypropylene centrifuge tubes (Western Laboratory Service, UK). In all experiments, 5 g of solid phase was weighed using a four-figure balance (Salter Electronic Balance ER-182A). Two approaches were taken when the solutions were added: (*a*) the standard approach, involving addition of the stock aliquots directly to the solid phase, always following the same order of addition, MilliQ water, then the Th solution and finally the organic complexing agent solution, and all were added within 2–3 min; and (*b*) the alternative approach, involving pre-equilibrating the solution for 24 h before addition to the solid phase. In (*b*), Th-EDTA and Th-NTA complexes have sufficient time to form (Cartwright et al., 2007) before additional interactions occur. Both approaches resulted in a final solution volume of 10 mL with a final concentration of 5 μM Th and concentrations of organic complexing agents ranging between 5 and 500 μM. The concentrations used throughout this study were up to 3 orders of magnitude lower than those used previously in aqueous complex speciation studies which identified the presence of Th-EDTA and NTA complexes (Cartwright et al., 2007). Moreover, these concentrations are relevant for different contaminated scenarios (Hartman et al., 2009; Riley and Zachara, 1992) and the selected solid: solution ratio (1:2) is relevant for subsurface terrestrial environments.

Procedural blanks and experiments without any solid phase were run to assess potential contamination and sorption to the walls of the vessel, respectively. Neither of these was observed throughout the study. All experiments were carried out in triplicate using an orbital shaker (KS125 basic, JK Ika Labortechnink) and after the required incubation time the experiments were centrifuged at 3500 rpm for 6 min (980 *g* centrifugal force; Legend RT Centrifuge) to centrifuge to <0.2 μm (Gimbert et al., 2005). The pH of the supernatant was measured using a conventional pH meter (Mettler Delta 340) and then sub-samples were diluted and acidified with 2% HNO_3 for inductively coupled plasma – mass spectrometry (ICP-MS) and inductively coupled plasma – optical emission spectrometry (ICP-OES) analyses; whereas for UV spectrometry, the aliquots were diluted with MilliQ water. Finally, undiluted supernatant was taken for ion chromatography (IC) analysis.

2.2.2. Sand system experiments

The effect of 100-fold excess organic complexing agents on the kinetics of Th sorption and metal desorption was investigated using the standard approach (*a*). One hundred μL sub-samples were taken over time (up to 672 h) so that a maximum of 1% of the solution was removed at each time point in any given experiment. The effect of organic complexing agent concentration and solution pre-equilibration were investigated using a 24 h incubation time and following approaches (*a*) and (*b*). Sorption of the organic complexing agents to the sand was monitored in all batch experiments.

2.2.3. Degradation of the complexing agents

MilliQ water was equilibrated with sand in a 5 g: 10 mL solid: solution ratio for 24 h, centrifuged (3500 rpm for 6 min) and the supernatant transferred to a clean centrifuge tube. The supernatant was spiked in triplicate with organic complexing agents to give a range of concentrations between 5 and 200 μM, and sub-samples were taken over time up to 168 h to determine the complexing agent concentration remaining in solution.

2.2.4. Silica system experiments

An incubation time of 168 h was used to study Th sorption, metal desorption and the effect of organic complexing agents in the presence of silica. The experiments were carried out following the standard approach (*a*).

2.3. Analytical methodology

2.3.1. Solid phase characterisation

The particle size distribution of the 2 mm sieved sand was obtained by a laser diffraction method (Malvern Long-bed Mastersizer X with wet sample unit MS17, Malvern Instruments Ltd, UK) following digestion of the organic content with 30% hydrogen peroxide. The N_2-BET specific surface area was obtained using a Gemini 2375 V4.01 Instrument (Micromeritics) and the total C, H and N content was