



Americium and plutonium association with magnesium hydroxide colloids in alkaline nuclear industry process environments



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HIGHLIGHTS

- Am and Pu in Mg-rich alkaline effluents from nuclear fuel storage ponds are mainly associated with colloids.
- In true solution, i.e. material passing through a 1 nm filter, the plutonium appears to be in oxidation state +V.
- In model brucite (magnesium hydroxide) colloid systems, Am(III) is preferentially associated with larger colloids.
- At pH = 10.4, carbonate concentrations >10⁻² M are able to prevent the binding of Am(III) to colloids.

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ABSTRACT

The behaviours of Pu, Am and colloids in feed solutions to the Site Ion-exchange Effluent Plant (SIXEP) at the Sellafield nuclear reprocessing site in the U.K. have been studied. For both Pu and Am, fractions were found to be associated with material in the colloidal size range, with ~50% of the Pu in the range 1–200 nm. The concentration of soluble Pu (<1 nm) was ~1 nM, which is very similar to the solubility limit for Pu(V). The soluble Am concentration was of the order of 10⁻¹¹ M, which was below the solubility limit of americium hydroxide. The size, morphology and elemental composition of the particulates and colloids in the feed solutions were investigated. Magnesium is homogeneously distributed throughout the particles, whereas U, Si, Fe, and Ca were present in localised areas only. Amongst some heterogeneous material, particles were identified that were consistent with hydrotalcite. The distribution of ²⁴¹Am(III) on brucite (magnesium hydroxide) colloids of different sizes was studied under alkaline conditions representative of nuclear fuel storage pond and effluent feed solution conditions. The morphology of the brucite particles in the bulk material observed by ESEM was predominantly hexagonal, while that of the carbonated brucite consisted of hexagonal species mixed with platelets. The association of ²⁴¹Am(III) with the brucite colloids was studied by ultrafiltration coupled with gamma ray-spectrometry. For carbonate concentrations up to 10⁻³ M, the ²⁴¹Am(III) was mainly associated with larger colloids (>300 kDa), and there was a shift from the smaller size fractions to the larger over a period of 6 months. At higher carbonate concentrations (10⁻² M), the Am was predominantly detected in the true solution fraction (<3 kDa) and in smaller size colloidal fractions, in the range 3–100 kDa.

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1. Introduction

The retrieval and processing of significant volumes of legacy

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waste into forms suitable for storage and disposal are among the major challenges in the UK's nuclear clean-up and decommissioning programme. These wastes include large amounts of sludge that have arisen from the corrosion of spent nuclear fuel cladding as well as associated nuclear fuel storage pond liquors. It has been estimated that at Sellafield alone several thousand cubic metres of sludges containing 10^4 TBq of α -particle emitters have to be processed [1,2]. The Magnox spent fuel elements, which were used in the UK's first generation nuclear reactors, comprise a natural uranium metal core, clad by a magnesium-rich alloy. Spent nuclear fuel has been wet stored in dedicated ponds for several decades, and during this period, corrosion of the cladding and fuel has occurred. Several studies on the corrosion of magnesium and magnesium-rich alloys in water have been published, and these indicate that the initial corrosion product is primarily brucite ($\text{Mg}(\text{OH})_2$), formed by the hydration of the MgO layer on the surface of the magnesium metal in the presence of moisture and air [3–5]. Further, it has been shown that colloidal species form in a solution in contact with bulk brucite [6].

Liquid wastes arising from fuel storage ponds and decanning operations typically contain significant amounts of ^{137}Cs , ^{90}Sr and magnesium hydroxide (from the corrosion of fuel cladding in the ponds). At Sellafield, such wastes are treated in the Site Ion-exchange Effluent Plant (SIXEP). Feed solutions to SIXEP that may contain solids are allowed to settle in Bulk Storage Tanks (BST) for times between 10 h and a week, after which the liquor is decanted off and fed into SIXEP. In the plant, the radionuclide contaminants are removed by passing the solution through sand bed filters, followed by a carbonation step that reduces the pH from approximately 11 to neutral. The carbonated solution then passes through ion-exchange clinoptilolite (zeolite) beds, which are selected to remove ^{137}Cs and ^{90}Sr . Gregson et al. [1,7] studied the chemical form of sludges and suspended particles and colloids from an alkaline storage pond at Sellafield. They found that the morphology of the magnesium-containing phases was consistent with brucite, but perhaps with some incorporation of Al to form hydrocalcite-like phases.

Colloids are known as potential controllers of radionuclide speciation and transport due to their small size and high surface area to mass ratio [8,9]. They are capable of binding radionuclides, particularly the actinides, in forms that prevent treatment by the effluent treatment technologies routinely used in the nuclear industry, such as sand bed filtration and ion exchange. Magnesium hydroxide particles have been reported to retain various radionuclides efficiently [10–12]. Therefore, the physical and chemical nature of the solution-borne colloids and their interactions with radionuclides need to be better understood, in order to evaluate the likely challenge to the effluent treatment process and to design improvements [1].

Spent Magnox fuel has numerous radioactive components. However, following irradiation, the majority of fuel by mass will still be uranium. There will also be a range of fission products and minor actinides formed by neutron capture reactions. In the effluents from the storage ponds and silos, the most significant fission products are ^{137}Cs and ^{90}Sr , because of their relatively high solubilities and the high radiotoxicity of ^{90}Sr (they are found exclusively in oxidation states (I) and (II), respectively). Plutonium and americium are significant species in spent nuclear fuel, because they are formed in significant quantities and have high radiotoxicity. In the storage ponds and during effluent treatment, Am would be expected to exist in oxidation state III only, whilst Pu is expected to exist in oxidation states IV and V.

The sorption of Am(III) on various colloids has been investigated in several previous studies [13–16], and it has been shown to associate strongly with colloids. For example, Degueudre et al.

studied the sorption of ^{241}Am ($3 \times 10^{-11} - 3 \times 10^{-10}$ M) onto marl groundwater colloids, with a distribution ratio in the range of $1-3 \times 10^6 \text{ ml g}^{-1}$ [15]. The distribution of Am soluble species was calculated, and approximately 90% of the species were found to be negatively charged. The strong sorption observed onto the negatively charged clay colloids was considered to be due to the formation of a ternary surface complex. Pitois et al. carried out a study of the interaction of $^{152}\text{Eu}(\text{III})$, which was considered as a model for Am(III) behaviour in nuclear fuel storage pond conditions, with brucite bulk solid and colloids at pH 10.4 [6]. In the absence of carbonate, the main $^{152}\text{Eu}(\text{III})$ activity was found to be associated with the bulk solid phase and with colloidal material when the bulk phase was removed. Sorption was found to decrease significantly at a carbonate concentration of 10^{-2} M.

The redox chemistry of Pu is much more complex than that of Am, with several different oxidation states that may coexist, although in the systems studied here, Pu(V) and Pu(IV) would be expected to dominate the speciation [1]. Since Pu(V) exists in aqueous solution as the PuO_2^+ ion, it is less prone to hydrolysis than Pu(IV). Pu(IV) sorption on brucite bulk and colloids has been shown to occur rapidly and completely in alkaline conditions from pH 8 to pH 13, and the interaction is sufficiently strong that it is not affected by the presence of 10^{-3} M citrate (a competing complexing ligand). Additionally, X-ray photoelectron spectroscopy (XPS) results indicate that Pu is incorporated into the brucite subsurface at substantial concentrations and to a depth of at least 50 nm [10,11]. Strontium uptake by naturally occurring and thermally modified brucite has been investigated and high sorption capacity and relatively fast kinetics have been reported, particularly at alkaline pH [12]. Parry et al. studied plutonium behaviour in a model Magnox storage pond liquor containing Pu(IV), corroded Magnox sludge (CMS) simulant, sodium carbonate, polyelectrolyte, and silica [17]. The CMS particles were primarily composed of platy brucite crystals, with a smaller quantity of acicular artinite crystals. In the absence of CMS, 100% of Pu was able to pass a 100 nm filter, but as CMS was added, the Pu was increasingly found in the >200 nm fraction, and for CMS concentrations >10 ppm, virtually all of the Pu was removed by a 200 nm filter. At lower CMS concentrations, the results depended on pH. For example, at 2 ppm of CMS, approximately 25%, 60% and 90% of Pu was in the >200 nm fraction at pH = 10.8, 11 and 11.5, respectively. The presence of carbonate ions (3×10^{-2} M) gave the greatest effect on the system, allowing the majority of Pu to remain in the solution.

In the past, Pu(IV) was presumed as the dominant form of plutonium in the ponds and silos at Sellafield [17]. However, Gregson et al. [1] used analysis of storage pond water samples to show that in certain parts of the pond, the concentrations are better described assuming that Pu(V) dominates, but in other parts, the data were consistent with either Pu(IV) or Pu(V). Although for most samples, the amount in true solution (<1 nm) was less than 1%, for some samples up to 6.8% was observed, which strongly suggested that the Pu was in oxidation state V. For all samples and locations in the pond, they found that most of the Pu (>90%) was associated with large particulates (>200 nm), but there was relatively little Pu in the size range of 1–200 nm, which was interpreted as an absence of intrinsic Pu(IV) oxyhydroxide polymeric or colloidal species.

The first aim of this study was to characterise the colloids in the feed solutions to SIXEP and to study the distribution of Pu and Am in the solutions. The second aim was to study actinide behaviour in a model system (brucite) that is relevant to the SIXEP feed solutions (and the Magnox nuclear fuel storage ponds and silos). Although the SIXEP plant was designed primarily to remove Cs and Sr from effluents, it is also quite effective at removing α -activity in particulate form. Hence, another aim was to attempt to explain this behaviour better. The association of ^{241}Am species with various size

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