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Combined electron microscopy and vibrational spectroscopy study of corroded Magnox sludge from a legacy spent nuclear fuel storage pond

Colin R. Gregson [a], David T. Goddard [b], Mark J. Sarsfield [a], Robin J. Taylor [a,*]

[a] National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale CA20 1PG, UK
[b] National Nuclear Laboratory, Preston Laboratory, Springfields, Salwick, Preston PR4 0XJ, UK

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ABSTRACT

Samples of filtered particulates and sludges, formed from corroding magnesium alloy clad uranium metal ("Magnox") fuel elements, collected from one of the legacy nuclear fuel storage ponds located at Sellafield (UK) were investigated by Environmental Scanning Electron Microscopy with Energy Dispersive X-Ray analysis (ESEM/EDX), micro-Raman spectroscopy and Fourier transform infra-red spectroscopy (FT-IR). ESEM imaging confirmed the dominant morphology to be clusters of interlocking platelets typical of brucite ($Mg(OH)_2$). EDX analysis was suggestive of some conversion to the related phase, hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$), due to elevated levels of Al associated with Mg. Other apparent morphologies were less commonly observed including flaky sheets, consistent with earlier stages of Magnox alloy corrosion. In a few specific cases, rods were also observed suggestive of some conversion to Mg-hydroxycarbonate phases. Discrete phases rich in U were also identified. Fluorescence in the Raman spectroscopy also indicated surface coatings of organic macromolecules and iron sulphide on hematite containing particles, attributed to microbial activity within the open air pond. Some specific differences in the solid phases between pond areas with differing conditions were apparent.

1. Introduction

The UK has a number of "legacy" fuel storage ponds and wet silos that date back to the earliest days of the nuclear industry. Some of these facilities contain large inventories of sludge due to the in-pond corrosion of Magnox fuel elements (Mg-based alloy clad U metal fuel used in the UKs first generation of civil nuclear reactors). These sludge beds contain substantial inventories of leached fission products (notably Cs and Sr) and actinides (mainly U, Pu and Am) closely associated with a predominantly brucite ($Mg(OH)_2$: main corrosion product of Magnox alloy) matrix but they can be very heterogeneous in both physical and chemical compositions. This combination of high hazard and heterogeneous nature of the wastes contained within ageing legacy facilities presents enormous engineering and technical challenges for future decommissioning programmes in which these wastes must be safely retrieved and processed into secure wasteforms. Potential sludge components may include corrosion products from pond furniture (fuel skips) and pond infrastructure (concrete degradation products). Since the majority of the fuel storage ponds containing corroded Magnox sludge (CMS) are open to the air then a potential exists for the introduction of additional extraneous materials such as particulates (either wind blown or carried by rainfall), seabird guano and animal remains. Together with CO_2 ingress this encourages the growth of micro-organisms leading to frequent seasonal algae blooms obscuring pond clarity and hampering retrieval operations [1]. The presence of microbial activity is likely to have a significant role in the control of the redox environment within the storage ponds and will affect the environmental behaviour of redox sensitive actinides such as Pu [2–4]. Microbial degradation products such as humic acids and alginates have the potential to reduce or increase actinide mobility depending on local environmental conditions within the ponds [5–9]. The long term ingress of CO_2 into the pond environment may also facilitate the transformation of brucite to various Mg-hydroxycarbonate phases (details given in Table S1) with differing affinities for actinide sorption [10] as well as carbonate complexation of actinide ions in solution [11]. In the course of our work [12] concentrations of Pu were measured in liquor samples from one of the legacy pond facilities at Sellafield and shown to be well above Pu solubility limits due to association with suspended or colloidal materials. Differences in oxidation states of aqueous Pu species were also observed and linked to differing pond environments.

Abbreviations: ATR, attenuated total reflectance; CMS, corroded Magnox sludge; ESEM, environmental scanning electron microscopy; EDX, energy dispersive X-ray analysis; XRD, X-ray diffraction.

* Corresponding author. Tel.: +44 19467 79266; fax: +44 19467 79007.

E-mail addresses: colin.r.gregson@nnl.co.uk (C.R. Gregson), dave.t.goddard@nnl.co.uk (D.T. Goddard), mark.j.sarsfield@nnl.co.uk (M.J. Sarsfield), robin.j.taylor@nnl.co.uk (R.J. Taylor).

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In order to support the retrieval of these sludges, further characterisation work on actual radioactive samples taken from the ponds has now been undertaken, focusing on the solid phases present in both sludge itself and suspended particulates associated with sludge using a combination of microscopy and vibrational spectroscopy. The aim of the current work was thus to investigate the nature of the solid phases, including a comparison of solids obtained from different locations within the pond, in order to understand the influence the solid phases may have on radionuclide release and mobility. Previous powder-X-ray Diffraction (powder-XRD) and electron microscopic studies of simulated sludge, corroded from unirradiated Magnox alloy in the laboratory under conditions thought to be representative of the Sellafield legacy ponds, led to the identification of brucite (platelet morphology) and artinite phases (needles/rods) as the main constituents of the sludge [13].

There is also a much wider interest in the characterisation and conversions of MgO, $Mg(OH)_2$, $MgCO_3$ and intermediate hydroxycarbonate phases due to their uses as backfill material in nuclear waste repositories [14], formation of “moonmilk” mineral deposits [15], CO_2 sequestration [16] and presence in extraterrestrial materials [17].

The liquor and sludge samples available to us were taken from various locations within one of the legacy fuel pond storage facilities at Sellafield. This pond dates from the 1950s and was used for several decades to store and de-can Magnox reactor fuel ready for reprocessing. The liquor samples were taken from (a) a sample point within a highly contaminated isolated Pond Bay within the pond facility complex, (b) from a downstream Holding Tank following liquor transfers from the bay, and (c) from various sample points within the Main Pond area. Sludge samples were taken from the main storage pond complex only [18]. Samples were taken during operational trials involving either sludge transfer or sludge disturbance to assess potential activity release as might occur during future retrieval programmes. Techniques applied to these samples were (i) ESEM/EDX (Environmental Scanning Electron Microscopy/Energy Dispersive X-ray analysis) of filtered particles from liquor and sludge samples, (ii) micro-Raman spectroscopy of filtered particles from liquor and sludge samples and (iii) Fourier transform infra-red spectroscopy (FT-IR) of the sludge samples.

SEM is obviously an excellent means of investigating particle structures particularly when coupled with a technique such as EDX that provides elemental information of individual particles or clusters of particles. However, whilst SEM images of Mg-hydroxycarbonate phases are relatively limited, those of brucite [19], dypingite (flakes [20], “flaky” rosettes, organic coated rosettes, rosettes grown on nesquehonite [21]); nesquehonite (rods [21], platelets [22]); “mouldy” hydromagnesite on fibrous artinite [23] and synthetic hydromagnesite spherical particles with rosette microstructure [24] have been reported.

Raman spectroscopy is a very useful spectroscopic technique capable of determining diagnostic vibrational bands on oxide surfaces and can, therefore, give useful information regarding bond arrangements and crystal structure. Micro-Raman enhances the capability of the technique by allowing the laser source to be focused on discrete solid phases which may exhibit different morphology when examined under an associated optical microscope. In general, Raman studies of Mg-based minerals are rather limited. Frost and co-workers have carried out several studies and reported Raman spectra for nesquehonite [22], artinite, dypingite [25], synthetic Mg/Al, Fe hydrotalcites [26], natural hydrotalcites with sulphate and carbonate in the interlayer [27] and synthesised hydrotalcites with sulphate, molybdate and chromate ions in the interlayer [28]. Some reference spectra have been made available [29].

Infra-red spectroscopy can be used to identify bulk spectral properties of the samples under investigation and in other contexts has been used on various Mg-hydroxycarbonate mineral phases, *e.g.* nesquehonite, artinite and hydromagnesite. For instance, Miyamoto and Kato [30] carried out IR diffuse reflectance measurements of some hydrous magnesium carbonates produced by terrestrial weathering on Martian meteorites and Cloutis et al. [31] analysed a range of hydrous carbonate minerals including artinite, brugnatellite, coalingite, dawsonite, gaylussite, hydromagnesite, hydrotalcite, manasseite, pirssonite, pyroaurite. Frost et al. [32] characterised dypingite and artinite with a hydrotalcite related formulae (partial substitution of Mg by Fe) in relation to their ability to sequester CO_2 using a combination of FT-IR and near Infra Red spectroscopies. Each mineral phase displays specific OH and CO_3^{2-} stretch vibrations, characteristic of the positions of water, OH and CO_3^{2-} groups within the crystal lattice of each mineral [33]. For artinite, which has been observed in CMS simulants [13], the IR spectrum displays two unique features. Firstly, the H_2O bend mode at 1600 cm^{-1} is shifted to a lower frequency of 1575 cm^{-1}, which implies the strong participation of water molecules in inter-chain bonding. Secondly, the carbonate υ_3 stretch modes are split into three components and are shifted to lower frequencies than those of hydromagnesite and nesquehonite indicating that the carbonate groups are more active in bonding within the crystal structure. Nesquehonite also displays a similar spectrum to artinite but with different frequencies for the OH and CO_3^{2-} stretch modes. Hydromagnesite presents a completely different spectrum with sharp and well resolved CO_3^{2-} bands indicating that the carbonate group is not active in bonding.

2. Experimental methods

2.1. Samples analysed

The details of the samples analysed within this project and their origins are listed in Table S2. Briefly, samples denoted P1-3 and HT1-3 were respectively taken from the isolated Pond Bay and downstream Holding Tank during the first two mini- and third full test sludge transfer trials. Samples MP1-4 were liquor samples from the Main Pond area. Samples S1-2 were two sludge samples also recovered from the Main Pond area. Sampling techniques are described in Ref. [18]. Due to various restrictions these samples were significantly aged (10–20 months) before they were characterised. Some liquor samples had experienced a pH drift from the pond pH of 10–11 down to pH $\sim$ 8–9 presumably due to CO_2 adsorption. Whether this storage affected the nature of the particles present is thus uncertain. The CMS simulant used was unirradiated Magnox alloy corroded within our laboratories under conditions similar to Sellafield pond storage. Although, predominantly brucite from Magnox corrosion, powder-XRD has shown the presence of brucite and artinite in one simulant [13]. The morphology of a typical simulant is seen in Fig. 1d.

2.2. ESEM/EDX analysis

Samples (P1-3; HT2-3; MP1-4) were filtered to isolate suspended particulates and the material retained on polycarbonate filter paper (0.2 or 0.08 μm) allowed to air dry. Small sections (roughly 2–4 mm^2) of the filter paper were attached to stubs using carbon adhesive tape. Sludge samples (S1-2) were deposited directly onto stubs covered with carbon adhesive tape as were some large black particulates (0.5–1 mm) isolated from sludge. Examination was undertaken using optical microscopy and ESEM. Samples P1-3 and HT1-3 were examined with an Electroscan 2020 ESEM using secondary electron imaging at a pressure of 3–7 Torr. Samples MP1-4 and S1-2 were examined with an FEI Quanta 200FEG ESEM at low and high vacuum using both secondary and