Application of a magnetic extraction technique to assess radionuclide–mineral association in Cumbrian shoreline sediments

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Abstract

An assessment has been made of the association of $^{239+240}$Pu, ^{241}Am and ^{210}Po (in secular equilibrium with ^{210}Pb) with iron minerals using a magnetic extraction technique. Grab samples of beach sand from the Cumbrian (UK) coastline were subjected to successive extractions with a ~0.1 T ferrite magnet and a ~0.3 T rare-earth magnet procedure to separate magnetic iron oxide minerals. Radionuclide concentrations in the magnetic extracts were enhanced (by ~4–6-fold) relative to the residue. Those in the ~0.1 T magnet extracts were broadly similar to those in the antiferromagnetic material extracted by the ~0.3 T magnet, despite the very large differences in magnetic property values between the two fractions (one to two orders of magnitude). The percentage of magnetic material in terms of mass was small and therefore, the majority of these radionuclides (on average 88%) were associated with the residue. Removal of stable Fe was incomplete. Given that the radionuclides may also bind to paramagnetic (nonmagnetic) Fe minerals, the data were extrapolated by normalising the results to quantitative Fe removal. This yielded average values of 37%, 45% and 46% for $^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb), respectively, as upper limits for the fraction associated with magnetic + nonmagnetic Fe minerals. There are significant uncertainties inherent in quantifying data from this extraction technique. Nevertheless, it seems reasonable to conclude that radionuclide association with Fe minerals is unlikely to have a significant impact upon the physical dispersion of sediment contaminated by Sellafield discharges in the Irish

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Sea. However, it may be an important factor in governing Pu redox and redissolution behaviour.

1. Introduction

The Irish Sea sediments have been contaminated by the legacy of large discharges in the 1970s from the British Nuclear Fuels (BNF) Sellafield reprocessing plant (Cumbria, UK). Consequently, the seabed sediments contain a substantial repository of long-lived α-emitting radionuclides including ^{239}Pu ($t^{1/2} \sim$ 24,100 years), ^{240}Pu ($t^{1/2} \sim 6550$ years) and ^{241}Am ($t^{1/2} \sim 430$ years). The most recent survey (May, 1995) indicated that the inventory of $^{239+240}$Pu and ^{241}Am in the sub-tidal sediments was in the order of 360 TBq (~108 kg) and 545 TBq (~4.3 kg), respectively (Kershaw et al., 1999). Significant quantities of the natural series radionuclides were also discharged into the eastern Irish Sea at Saltom Bay (near Whitehaven) from the Rhodia Consumer Specialities Ltd. (formerly Albright and Wilson) phosphoric acid production plant between 1954 and 1992 (Poole et al., 1995). These discharges included the β-emitting radionuclide ^{210}Pb ($t^{1/2} \sim$ 22.3 years) that decays to the short-lived α-emitting radionuclide ^{210}Po ($t^{1/2} \sim$ 138 days). $^{239+240}$Pu, ^{241}Am and ^{210}Po (in secular equilibrium with ^{210}Pb) provide the major contribution towards the total α-activity of sub-tidal and inter-tidal sediments along the Cumbrian coastline.

In common with $^{239+240}$Pu and ^{241}Am, ^{210}Pb and ^{210}Po are highly particle reactive. During the peak discharges from Sellafield in the 1970s it was observed that $^{239+240}$Pu and ^{241}Am were rapidly removed from the water column to the seabed close to the outfall as a result of sorption to suspended particulate material (Hetherington et al., 1975). It was estimated that about 85% of the total Irish Sea inventory of $^{239+240}$Pu and ^{241}Am was contained in the fine-grained sediments of a relatively narrow coastal strip about 30 km wide, from Kirkcudbright Bay in the north to the Ribble estuary in the south (Pentreath et al., 1984). The reservoir of contaminated sediment has subsequently been dispersed, to some extent, by general sediment transport processes. Some sediment has moved shoreward in association with the prevailing currents in the eastern Irish Sea (Burrows, 1986) and has resulted in deposition of Sellafield derived radionuclides in inter-tidal and floodplain environments of this area (Aston and Stanners, 1981; MacKenzie et al., 1987 1994). Despite the elapsed time since the peak discharges, the inter-tidal sediments of the eastern Irish Sea continue to remain a potentially important source of radionuclides to surrounding coastal areas (Kershaw et al., 1999).

Resuspension of radionuclide-bearing particles by wind or water is one of the key physical redistribution processes controlling the movement of contaminated sediment. Resuspension is dependent upon particle size and particle density as

observed, for example, by the concentration of heavy mineral particles into placer deposits. Origins of iron-rich heavy mineral particles in the eastern Irish Sea include natural geological sources and industrially derived debris, including blast furnace slag. The coastal sediments close to Sellafield consist of Permo-Triassic desertic sand, with iron oxides occurring both as coatings on quartz grains and as discrete particles of magnetite and haematite (Hamilton, 1999). Other minor sources include the glacial tills and volcanic rocks of the Cumbrian region. Knowledge of the radionuclide distribution with respect to mineral and particle-size association in both shoreline and offshore sediments is important towards making an assessment of their long-term fate that will, in turn, have an impact on the dose commitment. From studies using an autoradiographic (CR39 dielectric detector) technique, it has been suggested that most of the α-activity associated with the surface of Irish Sea sediments is found on iron-rich heavy minerals and hot particles (Hamilton, 1996). However, information concerning the distribution of the individual radionuclides contributing the majority of the total α-activity ($^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb)) in this area is sparse.

Spectroscopic techniques have been applied to directly examine Pu speciation on artificially labelled solids in laboratory experiments (Duff et al., 1999). Although levels of α-emitting radionuclides in sediments along the Cumbrian coastline have been enhanced by the Sellafield discharges (e.g. typically in the order of 10^2 Bq/kg $^{239+240}$Pu and ^{241}Am in sandy material), the concentrations in terms of mass remain low (in the order of μg/kg and ng/kg for $^{239+240}$Pu and ^{241}Am, respectively). To date, spectroscopic techniques lack the sensitivity required for successful application to environmental samples. Instead, studies have been carried out using operationally defined procedures such as the Tessier selective leaching scheme (Hetherington, 1978; Aston and Stanners, 1981; Malcolm et al., 1990) or derivatives of a scheme to assess copper bioavailability in soil (Pulford et al., 1998; McDonald et al., 2001).

The selective leaching data appear to yield conflicting evidence concerning the association of ^{239,240}Pu and ^{241}Am with iron oxide minerals in Irish Sea sediments (Malcolm et al., 1990). For example, the proportion of ^{239,240}Pu reported to be associated with the Fe/Mn oxide phase of Esk estuary sediment ranges from 25% (Hetherington, 1978) up to 75–100% (Aston and Stanners, 1981). ^{241}Am has variously been reported to be predominantly associated with Fe/Mn oxide phases (Malcolm et al., 1990) or distributed between carbonate and organic fractions (McDonald et al., 2001). One reason for the variable data is that these schemes do not give results that directly relate to defined geochemical fractions. The selectivity problems associated with sequential extraction procedures are now widely acknowledged (e.g. Rapin et al., 1986; Marty and Jenkins, 2000).

In the present study, an alternative technique (magnetic extraction) was applied to beach sand samples obtained from sites along the Cumbrian (UK) coastline close to the BNF reprocessing plant at Sellafield and the former Albright and Wilson phosphoric acid plant near Whitehaven. These were subjected to successive extractions with a ~0.1 T ferrite magnet and a ~0.3 T rare-earth magnet, in an

attempt to assess radionuclide association with iron minerals. The extraction efficiency was quantified using magnetic measurements before and after the procedure. In a previous (preliminary) study, a limited amount of information was obtained by gross extraction of magnetic minerals from a single sand sample using the ~0.3 T rare-earth magnet (McCubbin et al., 2000). Radionuclide concentrations on the magnetic extract were significantly enhanced relative to weakly magnetic material. However, it was not possible to use the data to assess association with nonmagnetic Fe oxide phases. A significantly larger dataset is now available. This, together with complementary results for stable Fe in bulk samples and surficial Fe on individual particles, affords the opportunity to extrapolate the data to obtain further insights into radionuclide association with Fe minerals.

2. Materials and methods

Grab samples of shoreline sand were collected, in locations between high and low water, from the beaches at Seascale, St Bees and Allonby (Fig. 1) in May 1997. A second sand sample was collected from Seascale, together with material from the Outer Harbour at Whitehaven, in November 1997. Results for the first (May, 1997) Seascale sand sample have been reported elsewhere (McCubbin et al., 2000), but are included here for completeness.

Grain-size separations were carried out in the laboratory by wet sieving through nylon mesh sieves. Successive extractions of magnetic material from wet sand samples (~20–30 g) were carried out using a ~0.1 T ferrite magnet and a ~0.3 T rare-earth magnet sealed in a polythene bag and swirled in amongst a seawater–sediment suspension. Iron oxides can be divided into ferrimagnetic (magnetite and maghaematite), imperfect antiferromagnetic (haematite and goethite) and paramagnetic (lepidocrocite and ferrihydrite) minerals (Thompson and Oldfield, 1986). Despite its trace level, magnetite generally dominates the magnetic properties of sediment in many environments. The ~0.1 T magnet was used to extract strongly magnetic (magnetite-dominated) grains, and the ~0.3 T rare-earth magnet to extract any remaining weakly magnetic (antiferromagnetic) grains. Extractions were repeated ~30 times until removal of further material was minimal. The yield of material in terms of mass was small (~0.04–0.3 and ~0.2–1 g using the ~0.1 and ~0.3 T magnets, respectively). All fractions (magnetic extracts and residue) were dried and weighed prior to analysis.

Samples were stored for 1 year to allow approximate secular equilibrium to be attained between the parent ^{210}Pb and daughter ^{210}Po radionuclides. Concentrations of ^{210}Po (supported by ^{210}Pb), $^{239+240}$Pu and ^{241}Am were determined by alpha counting on silicon surface-barrier detectors, following chemical separation from all radiometric and gravimetric interference in the presence of ^{209}Po, ^{242}Pu and ^{243}Am yield tracers (Baker, 1984; Lovett et al., 1990). Sources were counted as long as necessary in order to achieve 1 σ counting errors typically better than $\pm 5\%$ for assay of $^{239+240}$Pu and ^{241}Am and better than $\pm 10\%$ for ^{210}Po(^{210}Pb). Selected samples were analysed for total Fe by ICP-OES following leaching with aqua regia
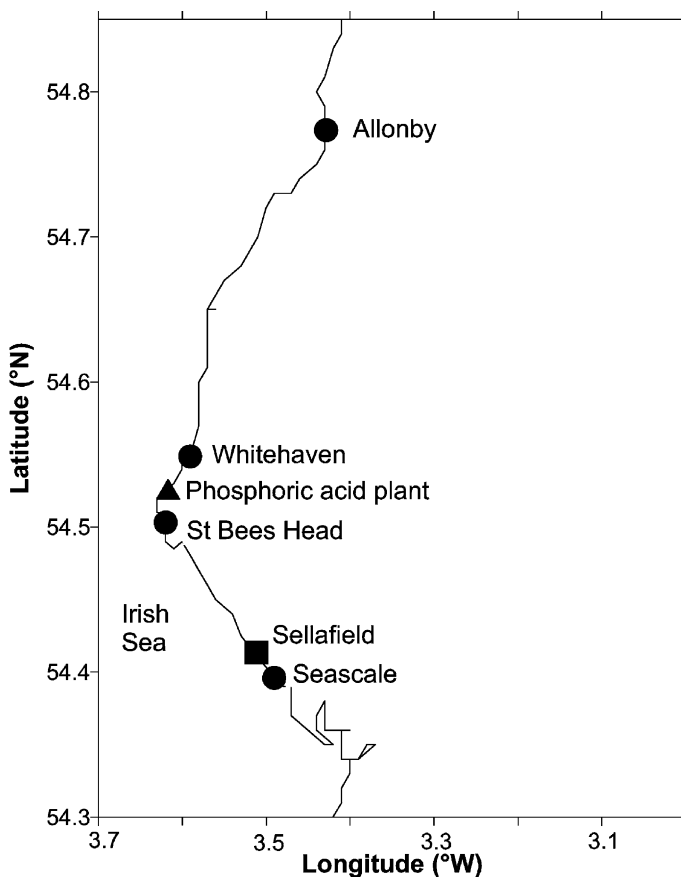
Fig. 1. Map of Cumbrian coastline showing study area. Phosphoric acid plant refers to the Rhodia Consumer Specialities Ltd. (formerly Albright and Wilson) facility.

(Jones and Laslett, 1994). The percentage of the total iron associated with the combined magnetic extracts ('magnetic iron') was calculated by difference between the iron content of the unfractionated (bulk) sand and the residue material (Eq. 1):

$$\text{Magnetic Fe}(\%) = \left[\text{Fe}_{\text{bulk sand}} - \text{Fe}_{\text{magnetic reside}})/\text{Fe}_{\text{bulk sand}}\right]100 \tag{1}$$

In turn, results for the fraction of 'magnetic iron' were used to normalise the radionuclide data (Eq. 2):

$$\text{Norm.extract}(\%) = [\text{rad.}_{0.1\ \text{T}}(\%) + \text{rad.}_{0.3\ \text{T}}(\%)][100/\text{magnetic Fe (\%)}] \tag{2}$$

where norm. extract (%) is the percentage of radionuclide in the combined magnetic extracts normalised to quantitative extraction of total Fe. $\text{Rad.}_{0.1\ \text{T}}$ (%) and $\text{rad.}_{0.3\ \text{T}}$ (%) are the percentages of radionuclide extracted using the 0.1 and 0.3 T magnets, respectively.

Surficial Fe on individual particles was analysed using a JEOL JSM-5900 LV scanning electron microscope (SEM) combined with an energy-dispersive spectrometer (EDS). Samples were mounted onto an SEM stub (1 cm disk) by sprinkling onto double sided carbon tape and examined directly in low vacuum mode without carbon coating. A semi-quantitative analysis of Fe on 100 randomly selected particles was achieved by counting for 100 s, using an acceleration voltage of 20 kV.

Magnetic measurements were made on dried subsamples packed into 10 cm^3 styrene pots. Due to the small quantities of magnetic extract materials available for analysis, these subsamples were dispersed in a nonmagnetic matrix (AnalaR grade calcium fluoride), following the procedure described by Maher (1988). All samples were immobilised by packing any unoccupied volume with clean cotton wool. To characterise the mineralogy and concentration of magnetic minerals within individual samples, the following magnetic measurements were undertaken: low field susceptibility (χ_{LF}) at 0.46 kHz using a Bartington meter; and isothermal remanent magnetisation (IRM) at 300 and 1000 mT using a Molspin fluxgate magnetometer, Molyneux pulse magnetiser and Newport electromagnet. The magnetic susceptibility (χ_{LF}) data provide an indication of the concentration within the sample of strongly magnetic ferrimagnets, such as magnetite. The saturation isothermal remanent magnetisation (SIRM) is operationally defined as that imparted by the 1000 mT field. SIRM values reflect contributions from all remanence-carrying minerals, including the ferrimagnets and also weakly magnetic minerals such as haematite and goethite. The magnetically 'hard' remanence (HIRM), i.e. that acquired at high magnetic fields (between 300 and 1000 mT), reflects the concentration of these weaker magnetic minerals.

3. Results

3.1. Magnetic properties, radionuclide and iron content of magnetic extract fractions

Data for the magnetic properties and radionuclide content of individual magnetic extract fractions are given in Figs. 2a,b. The χ_{LF} and SIRM values of the residue materials were in the range 3–15% of the bulk (Fig. 2a). Those for the ~0.1 T magnet extracts were roughly three orders of magnitude greater than the residue material, and more than one order of magnitude greater than that in antiferromagnetic material extracted using the ~0.3 T rare-earth magnet. The properties of synthetic magnetite are dependent upon grain size. Within the range 10–200 μm, reported values for χ_{LF} range from 4.8 to 6.1×10^{-4} m^3 kg^{-1} (Maher, 1988). Therefore, the susceptibility of the ~0.1 T magnet extracts (average value was 1.2×10^{-4} m^3 kg^{-1}; range was 0.4–2.7 1×10^{-4} m^3 kg^{-1}) was consistent with impure magnetite. The susceptibility of the antiferromagnetic material extracted using the ~0.3 T rare-earth magnet (average value of 400×10^{-8} m^3 kg^{-1}) was of magnitude similar to that reported for goethite and haematite (χ_{LF} = 60–70 $\times 10^{-8}$m^3 kg^{-1}; Thompson and Oldfield, 1986). Finally, the susceptibility
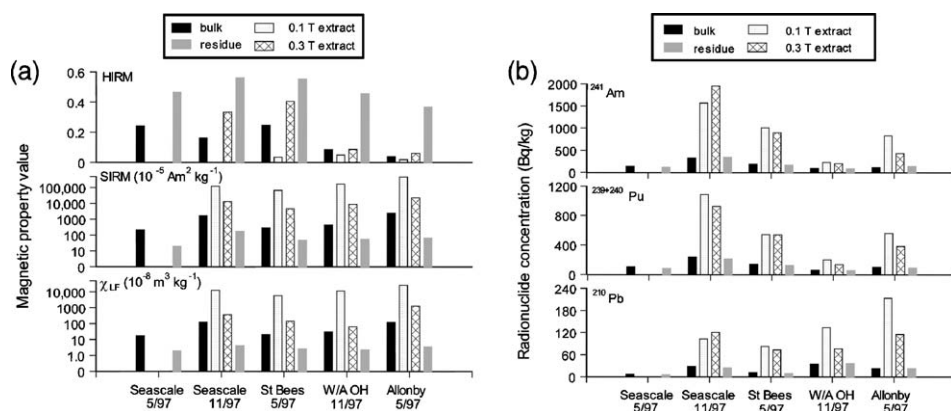
Fig. 2. Magnetic property values and radionuclide concentrations of individual magnetic fractions extracted from Cumbrian shoreline sands. Whitehaven Outer Harbour abbreviated to W/A OH. The figures 5/97 and 11/97 denote samples collected in May 1997 and November 1997, respectively. (a) Magnetic susceptibility (χ_{LF}), saturation isothermal remanent magnetisation (SIRM) and 'hard' IRM (HIRM) component ((SIRM–IRM$_{300mT}$) /SIRM), (b) ^{210}Po(^{210}Pb), $^{239+240}$Pu and ^{241}Am concentration.

of the residue material at each location was remarkably similar (average value of 3.0×10^{-8} m^3 kg^{-1}). Nevertheless, this value is greater than those expected for quartz or feldspar which are diamagnetic ($\chi_{LF} = -0.5 \times 10^{-8}$ m^3 kg^{-1}; Thompson and Oldfield, 1986).

The total iron content of the residue material ranged from ~1.2 up to ~2.4% (Table 1). These values compare with a range of ~1.4–4.8% in unfractionated sand samples. A semi-quantitative analysis of surficial iron on individual sand particles from bulk November 1997 Seascale sand and its magnetic residue was achieved using SEM–EDS. The results (Fig. 3) indicated that the distribution in bulk sand and magnetic residue material was very similar, despite the fact that 50% of the total Fe was extracted from this sample. In both fractions, the majority of particles (~60%) contained <0.5% Fe and a few (~10%) iron-rich particles contained more than half of the total surficial Fe.

The radionuclide data (Fig. 2b) indicate that the concentrations in the residue material were slightly less (average of ~10%) compared with those in unfractionated sand. There was a significant enhancement (average of 4-, 5- and 6-fold for

Table 1
Stable iron (%) in bulk sand and magnetic residue samples of Cumbrian shoreline sands

Site	Collection date	Bulk sand	Magnetic residue	Magnetic Fe (%)
Allonby	May 1997	1.45	1.16	20
St Bees	May 1997	1.62	1.19	27
Seascale	Nov 1997	4.78	2.40	50
W/A OH	Nov 1997	1.92	1.57	18

Whitehaven Outer Harbour abbreviated to W/A OH. Proportion of magnetic Fe calculated using Eq. (1).
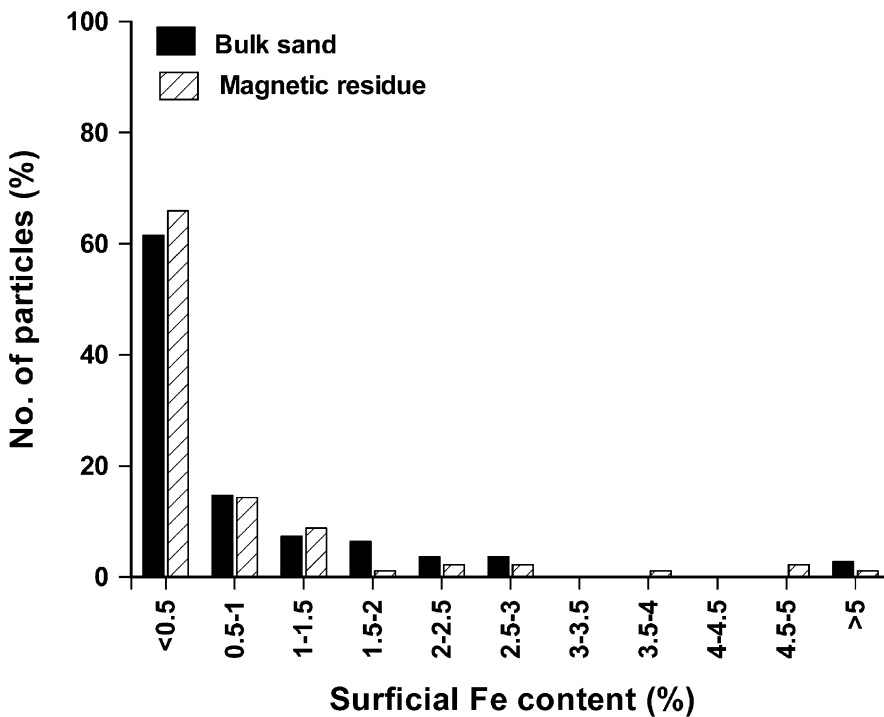
Fig. 3. Distribution of surficial Fe between individual sand particles of bulk Seascale 11/97 sand and magnetic residue. Results derived from individual analyses of 100 particles achieved using SEM–EDS.

$^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb), respectively) of levels in both magnetic extracts relative to residue material in all four samples. Levels in the Seascale and St Bees ~0.1 T magnet extracts were remarkably similar to those in the antiferromagnetic material extracted by the ~0.3 T rare-earth magnet, despite the very large differences in magnetic property values between the two fractions (one to two orders of magnitude). Although levels in the ~0.1 T magnet extracts from Whitehaven Outer Harbour and Allonby sand were measurably enhanced relative to the anti-ferromagnetic material, the difference was <2-fold. Therefore, variations in the magnetic mineralogy (i.e. ratio antiferromagnetic:magnetite dominated grains) of the heavy mineral suite were probably not significant towards binding of all three radionuclides.

The relative importance of individual extract fractions towards bulk properties is determined not only by magnetic or radionuclide concentrations, but also by the percentage of the total mass of sediment each fraction represents. Data for the percentage of material extracted using the ~0.1 and ~0.3 T magnets are given in Fig. 4a. The parameters from Figs. 2a,b and 4a are combined in Fig. 4b,c to show the contribution of the individual extract fractions towards magnetic properties and radionuclide activity, respectively. The percentage contribution was calculated
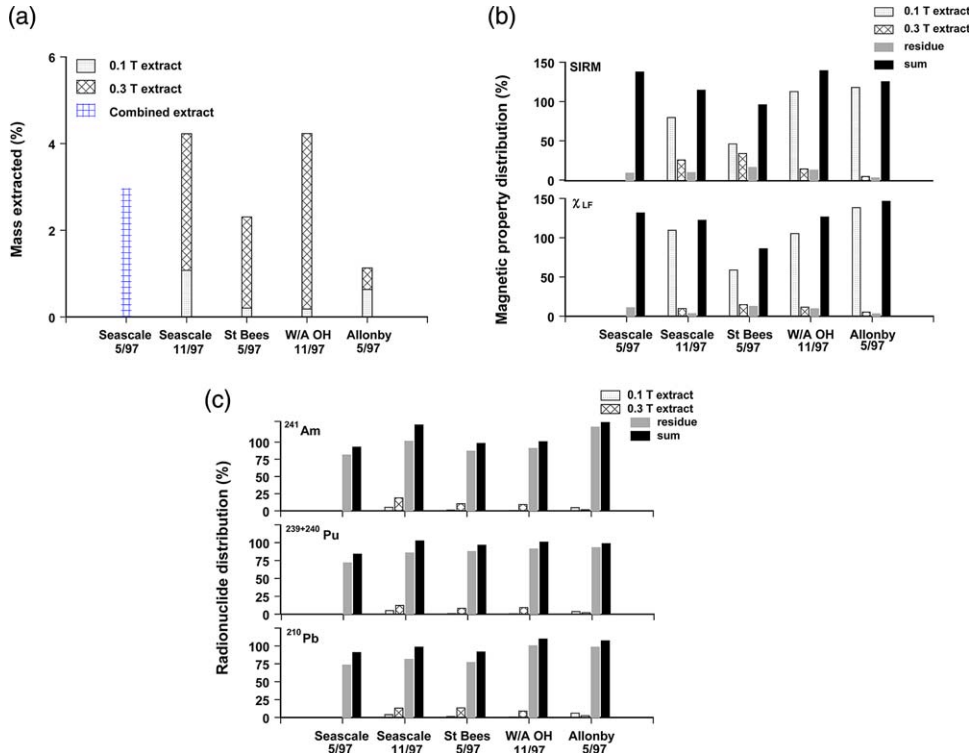
Fig. 4. Contribution from individual magnetic fractions towards properties of bulk sand samples. White-haven Outer Harbour abbreviated to W/A OH. The figures 5/97 and 11/97 denote samples collected in May 1997 and November 1997, respectively. The 5/97 Seascale sand was only extracted using a ~0.3 T rare-earth magnet. (a) Percentage of material extracted using ~0.1 and ~0.3 T magnets, (b) magnetic properties, (c) radionuclide content.

using Eq. (3):

$$\text{Contribution} = (P_\text{f} \times \text{fraction}(\%))/P_\text{bulk} \qquad (3)$$

where P_f and P_bulk are the magnetic property (i.e. χ_LF or SIRM) or radionuclide concentration of the individual extract fraction and unfractionated (bulk) sand, respectively. The sum of the percentage contribution from the individual fractions indicates the extent to which mass balance (i.e. recovery) was achieved during the separation procedure. These data are also given in Fig. 4b,c.

The data in Fig. 4a indicate that the percentage of material extracted by the ~0.1 T ferrite magnet in terms of mass was small (~0.2–1.1%). The quantities extracted by the more powerful ~0.3 T magnet were variable, ranging from ~0.5 to 4%. For most coastal regions, the percentage of heavy minerals in terms of mass is 1% or less, although local concentrations may be considerably higher (up to several tens of percent; De Meijer, 1998). Assuming that data for the magnetic mineral

assemblage provide a reasonable representation of the heavy mineral suite, heavy mineral concentrations in these samples were somewhat greater than most coastal sands.

Data for the mass balance of the magnetic properties (Fig. 4b) indicate that most of the signal was associated with the ~0.1 T magnet extract (average of 79%) with a small but measurable amount (average of 8%) in the residue material. There was an apparent gain in magnetic property values during the extraction of magnetic material from bulk sand (range of recovery values was 86–146 %, with an average gain of 23%). Property measurements on the extracts were carried out using relatively small quantities of material, particularly ~0.1 T magnet extracts where subsample sizes ranged from ~0.02 up to ~0.08 (because the ~0.1 T magnet extracts constituted <1% of the bulk sediment mass). The range in recovery values presumably provides an indication of the experimental error ensuing from sub-sampling small quantities of material from an inhomogeneous sample.

Similar mass balance considerations for radionuclide properties (Fig. 4c) indicate that most of the α-activity was associated with the residue material (average of 88%). The percentages of $^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb) associated with the combined magnetic extracts were in the range 6–17, 7–24 and 9–17%, respectively. Although differences in behaviour were noticeable between the individual radionuclides, the greater variability occurred between samples from different sites. The average percentage of radionuclide activity associated with the combined magnetic extracts ranged from ~7% at Allonby to ~19% in the November 1997 Seascale sand sample. The percentage of the total iron associated with the combined magnetic extracts was calculated using Eq. (1). The results indicate that the proportion of 'magnetic' iron ranged from ~20% in the May 1997 Allonby sample up to ~50% in the November 1997 Seascale sand sample (Table 1). Finally, the data in Fig. 4c indicate that the recovery of α-activity during the extraction of magnetic material from bulk sand was essentially quantitative (range of recovery values was 84–128%).

3.2. Magnetic properties and radionuclide content of individual grain-size fractions

To assess the influence of particle size upon the extraction of magnetic minerals, the bulk sand samples were separated into individual grain-size fractions by wet sieving. They consisted almost entirely (>94%) of material with mean particle diameter in the range 100–500 μm (Fig. 5a). The material from Allonby and Whitehaven Outer Harbour was somewhat finer than that from Seascale and St Bees (most particles <200 μm from Allonby and Whitehaven Outer Harbour and >200 μm from Seascale and St Bees). Given that sediment grain-size distribution may vary markedly along a beach profile both spatially and temporally (Medina et al., 1994), the differences could be specific to these particular grab samples.

The data for magnetic property values in Fig. 5b indicate that a significant variation in χ_{LF} and SIRM values (by one to two orders of magnitude) was observed between the grain-size fractions for all four samples. The finest-grained material (<100 μm) exhibited both the highest χ_{LF} and SIRM values, indicating that the
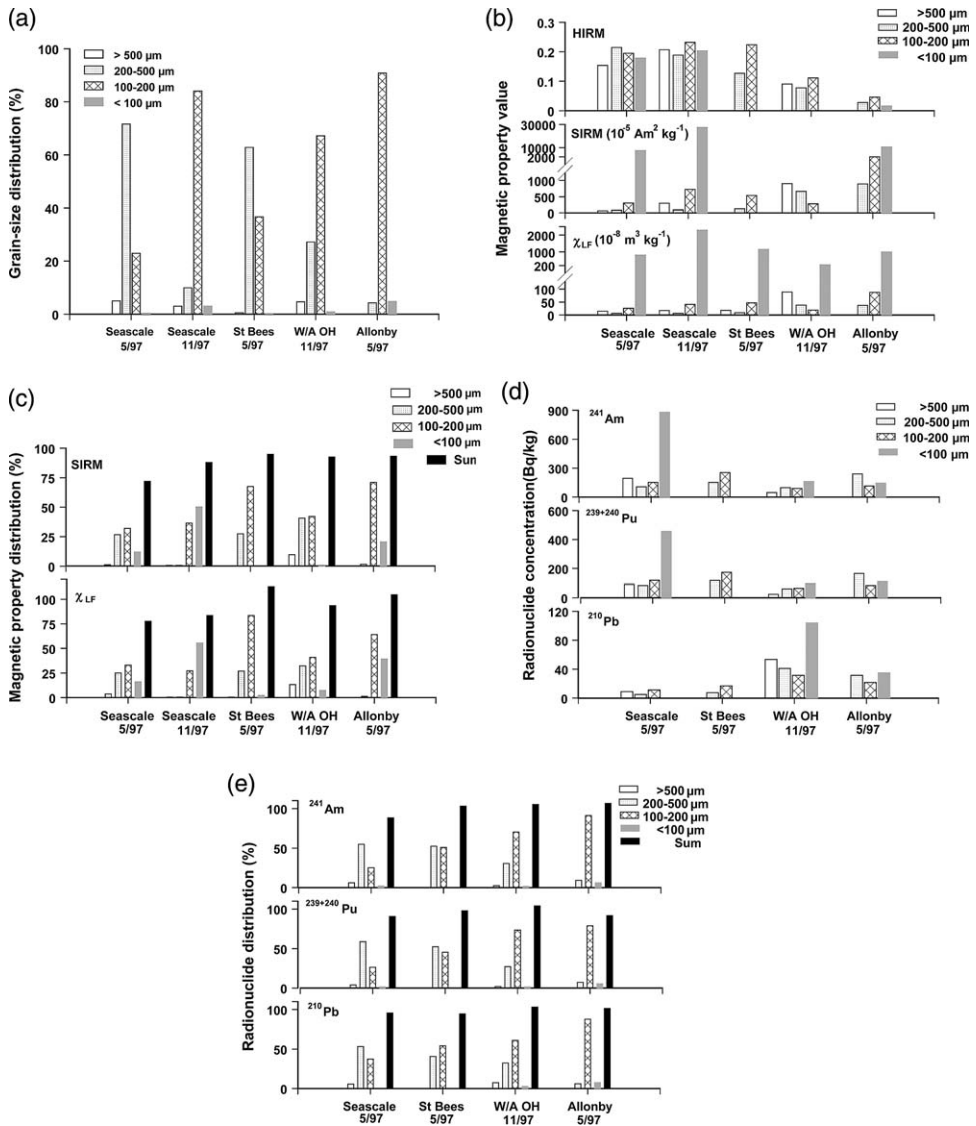
Fig. 5. Magnetic properties and radionuclide content of individual grain-size fractions separated from Cumbrian shoreline sands. Whitehaven Outer Harbour abbreviated to W/A OH. The figures 5/97 and 11/97 denote samples collected in May 1997 and November 1997, respectively. (a) Grain-size distribution, (b) Magnetic susceptibility (χ_{LF}), saturation isothermal remanent magnetisation (SIRM) and 'hard' IRM (HIRM) component ((SIRM–IRM$_{300mT}$) /SIRM), (c) contribution of individual grain-size fractions towards magnetic properties, (d) ^{210}Po(^{210}Pb), $^{239+240}$Pu and ^{241}Am concentration, (e) contribution of individual grain-size fractions towards radionuclide content.

magnetic mineral content was significantly greater than that in the coarser sand fractions. The magnetic property values of the >500 and 200–500 μm fractions

from Seascale and St Bees were markedly less (by ~6 fold) compared with those from Whitehaven and Allonby. Presumably, this is due to the presence of significantly greater amounts of coarse-grained magnetic material in the sunken areas of beach sand sampled at Whitehaven and Allonby. Indeed, a source of such material appears to be abundant on the small beach immediately to the south of Whitehaven Harbour. A sample of coarse-grained sediment obtained here in July 2002 had a χ_{LF} value of 658×10^{-8} m^3 kg^{-1} (i.e. greater than White haven outer Harbour sand by ~20-fold).

The relative importance of individual grain-size fractions is determined not only by magnetic property values but also by the percentage of the total mass of sediment each fraction represents (Fig. 5a). These parameters are combined in Fig. 5c, which shows the contribution of the individual grain-size fractions for both magnetic properties. The percentage contribution was calculated using Eq. 4:

$$\text{Contribution} = \left(P_{gs} \times \text{grain-size}(\%)\right)/P_{bulk} \tag{4}$$

where P_{gs} and P_{bulk} are the magnetic property (i.e. χ_{LF} or SIRM) or radionuclide concentration of the individual grain-size fraction and unfractionated (bulk) sand, respectively. The sum of the percentage contribution from the individual grain-size fractions indicates the extent to which mass balance (i.e. recovery) was achieved during the separation procedure. These data are also given in Fig. 5c. At all locations more than half the magnetic signal was carried in the particle fractions finer than 200 μm. Assessment of mass balances of both magnetic properties (χ_{LF} and SIRM) indicates that the average loss of magnetic minerals during the grain-size separation of the bulk sand was 9% (range of recoveries was 72–113%). It is most likely that incomplete recoveries were due to removal of iron oxide coatings from quartz grains, as a result of abrasion during sieving and shaking of sediment in seawater. Once again, an additional source of uncertainty arises from the fact that the magnetic measurements were carried out using relatively small quantities of material (subsample sizes ranged from ~0.1 up to ~13 g dependent upon availability). The range in recovery values is, therefore, attributed to errors arising from subsampling an inhomogeneous material.

The $^{239+240}$Pu and ^{241}Am data (Fig. 5d) indicate a complicated pattern of behaviour with a notable disparity between the distribution of the Allonby and Seascale samples. The Seascale results indicate that by far the greatest concentration was observed in the finest material (levels in <100 μm fraction were greater by ~5- and ~7- fold compared with that observed in the 100–200 and 200–500 μm fraction, respectively). In contrast, the Allonby data show that the greatest concentration was observed in the coarsest material (levels in the 200–500 μm fraction were roughly double of those observed in the 100–200 and <100 μm fractions). The limited amount of ^{210}Po(^{210}Pb) data also indicates a complicated and variable grain-size distribution pattern. For example, results for the Whitehaven Outer Harbour sand sample indicate a bimodal distribution of ^{210}Po(^{210}Pb) concentrations in the different size fractions. The highest concentration (104 Bq/kg) was observed in the finest-grain fraction (<100 μm) and the lowest (32 Bq/kg) in the 100–200 μm fraction. A relatively high concentration (53 Bq/kg) was also observed in the >500 μm

fraction. The magnitude of variation in ^{210}Po(^{210}Pb) values between the individual grain-size fractions (<4-fold) was considerably less than that observed for the χ_{LF} values (one to two orders of magnitude). In contrast, ^{210}Po(^{210}Pb) levels in all three fractions of the Allonby sample were broadly similar (in the range 22–35 Bq/kg) whereas concentrations in the 100–200 μm fraction from St Bees and Seascale were roughly double of those in the 200–500 μm fraction. It is apparent, therefore, that the enhanced radionuclide concentrations in magnetic extract materials were not simply a function of particle size.

The particularly complex distribution pattern of ^{210}Po(^{210}Pb) is perhaps not surprising as it has multiple sources. These include: (i) formation as a decay product of ^{226}Ra within mineral grains; (ii) surface sorption following aerial deposition; and (iii) as a legacy of discharges from the former Albright and Wilson phosphoric acid plant. Effects influencing levels of ^{210}Po(^{210}Pb) supported by ^{226}Ra within mineral grains could conceivably work in a direction opposite to those influencing surface sorption of unsupported ^{210}Po(^{210}Pb).

Data indicating the contribution from individual grain-size fractions, towards the total activity of each radionuclide, in bulk sand are provided in Fig. 5e. Almost all (average of 94%) of the radionuclide activity was associated with material in the range 100–500 μm. The percentage of all three radionuclides associated with the finest material (<100 μm) was relatively minor (<8%). In contrast, the percentage of the magnetic signal associated with this fraction was significant (up to ~50%). The use of mass balance calculations to monitor activity levels during the grain-size separation of bulk sand indicated an average loss of 2% (range of recoveries was 88–106%).

4. Discussion

4.1. Assessment of magnetic property data

The variability in recovery of magnetic property values (Fig. 4b) illustrates some of the difficulties inherent in the use of small subsample sizes for magnetic measurements from inhomogeneous material. Most of the magnetic signal was associated with the ~0.1 T magnet extract (i.e. magnetite-dominated grains), which constituted <1% of the total sediment mass. Using an autoradiographic technique (CR 39 di electric detector) to determine the distribution of total α-emitting radionuclides on the surface of individual grains, it was observed that only ~30% of the 'magnetic' particles extracted from placer material were α-radioactive (Hamilton, 1996, 1998). The proportion of α-radioactive grains in the residue material was even lower (~14%). Despite the fact that only a minor proportion of the individual grains in Cumbrian shoreline sands is α-radioactive, the variability in radionuclide recovery during sample processing was somewhat better (Fig. 4c), most likely because their distribution between individual sediment grains was more homogeneous than the magnetic property values.

Aside from considerations of sample inhomogeneity, another potential problem is that the efficiency of magnetic extraction techniques has been shown to be

dependent upon sample magnetic mineralogy and whether magnetic species occur as discrete grains or as inclusions within host grains (Hounslow and Maher, 1996, 1999). Samples dominated by discrete magnetic particles have higher extraction efficiencies than those dominated by inclusion mineralogies. There are a multiplicity of sources of magnetic minerals in Cumbrian sediments including bacterial iron sulphide in anaerobic sediments (Watson et al., 2000), bacterial magnetite in fine-grained material (Oldfield and Yu, 1994), crystalline haematite in the red Permo-Triassic sandstone material which forms the bedrock on the beach at Seascale, and also the cliffs at St Bees (Ixer et al., 1979), and historic industrial wastes. For the samples examined here, the latter two sources are the most important, such that the magnetic mineral assemblages of sediments in exposed coastal areas along the Irish Sea are dominated by coarse multidomain magnetite, titanomagnetite and haematite (Oldfield and Yu, 1994).

The magnetic property data, in Fig. 5b, indicate that significantly greater amounts of coarse-grained magnetic materials were present in samples from the two northern sites (Whitehaven and Allonby). In addition, the lower HIRM values for materials from Allonby and Whitehaven compared with Seascale and St Bees indicate greater dominance of the magnetic signal by magnetite in the former. As a result of the spatial and temporal heterogeneity of mineral deposits in beach sands, the differences identified could be specific to these grab samples. It is, however, worth noting that our results are consistent with findings from surveys carried out in the 1970s indicating that quantities of wastes derived from the iron industry (ferruginous waste and slagcrete) were greatest at, and to the north of, Whitehaven (Perkins and Kendrick, 1978). The apparent variation in blast furnace residue in the samples analysed here is important. Its presence leads to some debris containing blebs of iron within other slag materials (Hamilton, 1998) and therefore some particles are composites of magnetic and non magnetic material (Hamilton, 1996). Consequently, the efficiency with which iron-rich particles can be extracted from Cumbrian sands could vary depending on the contribution from individual sources.

4.2. Association of radionuclides with magnetic minerals

Radionuclide data from the magnetic extraction experiments (Fig. 2b) indicated a significant enhancement (roughly 4–6-fold) of levels in both magnetic extracts relative to residue material. Similar levels of radionuclide enrichment within the magnetic fraction of a finer-grained, estuarine sediment were reported by Bulman et al. (1984) and Bulman and Johnson (1986). These authors used high gradient magnetic separation to characterise the distribution of $^{239+240}$Pu and ^{241}Am within the clay fraction (<2 μm). For clay particles with diameters in the range 0.2–2 μm, levels of $^{239+240}$Pu, ^{241}Am and stable Fe were enhanced in the magnetic extract fraction by a factor of ~7, 3 and 7, respectively, relative to the residue material. Even greater enrichment of α-emitting radionuclides (roughly two orders of magnitude) in the magnetic fraction has been reported by Watson and Ellwood (2001).

For the samples considered in the present study, although the magnetic signal was largely associated with the magnetic extracts, the extraction of stable Fe was incomplete. Given that there was no evidence of preferential association of radionuclides with ferrimagnetic minerals compared with antiferromagnetic minerals, it seems reasonable to conclude that paramagnetic (i.e. nonmagnetic) Fe minerals in the residue material might also contain enhanced concentrations. The combined magnetic extracts contained, on average, 10, 13 and 12% of the $^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb), respectively, and 29% of the total Fe. The average value for the three radionuclides is 12%. The incomplete Fe extraction means that 12% represents the lower limit for their association with Fe oxide phases. An upper limit was derived by normalising the percentage of extracted radionuclide to quantitative extraction of total Fe using Eq. 2. Normalised values for ^{210}Po(^{210}Pb), $^{239+240}$Pu and ^{241}Am were in the range 34–55, 28–55 and 35–54%, respectively (Fig. 6). The variability in the normalised values was slightly less than that in the original data (Fig. 4b).

In using normalised values to further interpret radionuclide behaviour, consideration needs to be given to confounding factors. In particular, iron is present in two main phases in oxic recent marine sediments: (i) an oxide phase, which is usually present as grain coatings and (ii) a silicate phase, as a component of the mineral grains (Malcolm et al., 1990). The majority of iron in the samples analysed here probably exists in the latter phase. In contrast, whereas a fraction of the ^{210}Po(^{210}Pb) could be a component of the mineral grains, $^{239+240}$Pu and ^{241}Am are most likely to be predominantly surface sorbed. In the absence of quantitative data for surficial Fe, it is impossible to assess the extent to which magnetic extraction
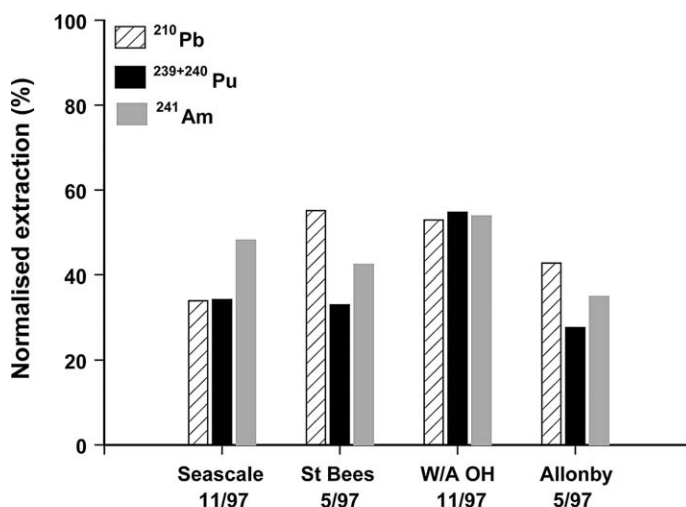

Fig. 6. Extrapolation of data to assess upper limit of radionuclide association with Fe minerals. Normalised values derived using Eq. (2) and information in Fig. 4c and Table 1.

selectively concentrates surficial Fe and associated radionuclides in relation to Fe within mineral grains.

4.3. Grain-size distribution

For all five samples, the magnetic mineral content was greatest in the finest fraction (<100 μm material). In other studies, magnetic measurements have been used as a tool to normalise for the effect of particle size upon radionuclide concentration (Clifton et al., 1999). Considerable care is, however, required in the application of magnetic property values as a grain-size proxy because: (i) the contribution of individual grain-size fractions towards the overall magnetic signal of a bulk sediment sample is variable between different magnetic properties (Oldfield, 1999) and (ii) even for a single magnetic property, the relationship between the magnetic signal and grain size may be variable between different environments (e.g. salt marsh and mud flat material).

In general terms, the highest concentrations of most radionuclides in bulk Irish Sea sediments are associated with fine-grained material. The lower levels observed in sands, compared with estuarine and saltmarsh deposits, have usually been interpreted as reflecting the lesser surface area available (per unit mass) for sorption (Hetherington and Jefferies, 1974; Aston and Stanners, 1982; Assinder, 1983; McDonald et al., 1990; McCartney et al., 1994). Such an interpretation is not substantiated by the limited data presented here. Instead, the results indicate a complicated distribution pattern that was variable between radionuclides and individual samples, although it is uncertain whether the differences reflect variations between sites/seasons or are specific to these particular grab samples. It is, however, worth noting that results from other studies (Hamilton, 1998; Jones et al., 1999) indicate that in order to understand the behaviour of radionuclides in marine and estuarine systems, site-specific characteristics must be recognised. Factors of relevance to the sites sampled here are (i) historic inputs of radionuclide reactive solid wastes derived from the iron industry appear to have been significantly greater at the two northern sites (Whitehaven and Allonby) and (ii) fractionation and separation of iron minerals within shoreline sediments (resulting in the concentration of placer deposits upon the surface of sand ripples) is enhanced by strong tidal currents and wave action. This would be expected to be greater at the two more exposed southern sites (Seascale and St Bees).

In more general terms, results from other investigations of the radionuclide grain-size distribution in the Irish Sea, indicate that the higher radionuclide concentrations sometimes occur on coarse-grained material compared with finer fractions (Livens and Baxter, 1988; Hamilton, 1989; MacKenzie et al., 1999). A variety of explanations have been provided to account for the observed distributions. These include binding by coarse organic debris (Livens and Baxter, 1988), organolith formation (Hamilton, 1989) or a localised direct influence of the Sellafield discharge (MacKenzie et al., 1999).

4.4. Mechanisms and implications of Fe mineral association

In the late 1970s, the period of peak Sellafield discharges, significant fractions of the Pu radionuclides and [241]Am were sorbed to iron floc material resulting from the neutralisation of acid liquors containing ferrous sulphamate (Pentreath et al., 1986; Leonard et al., 1995). Some were also associated with 'hot particles' (Hamilton, 1984). However, results from laboratory experiments involving a 1:10[4] dilution of sea tank effluent samples (containing the iron floc) into seawater revealed a progressive solubilisation of the particle-bound Pu, albeit over a period of almost a year (Pentreath et al., 1986). [241]Am solubilisation was also observed, with >30% being solubilised within the same period. Therefore, although reaction rates are slow, given the time elapsed between the large discharges of α-emitting radionuclides from Sellafield and the collection of samples for the present study, the association with Fe minerals observed in the present study is unlikely to be a legacy of source term composition.

As mentioned in the introduction, radionuclide association with Fe minerals may have implications for physical dispersion of contaminated sediment because of the higher density of iron-rich particles relative to quartz grains. For example, under appropriate tidal conditions and in certain locations, they can be concentrated into actinide enriched placer deposits, especially in sands (Hamilton, 1999). A worst case scenario would involve loss of fine-grained quartz material and selective retention of highly α-active iron minerals in the north-eastern Irish Sea. At present, evidence to support this hypothesis is meagre. Of greater import is the way association with Fe oxide coatings could affect the behaviour of a redox reactive element such as Pu. Results from experiments using well-characterised mono-mineralic phases (goethite, aragonite, calcite and δ-MnO_2) indicate that both the rate and extent of uptake of dissolved Pu species from seawater, the redox distribution of sorbed Pu, and Pu remobilisation differ significantly between individual minerals (Keeney-Kennicutt and Morse, 1985). Almost all of the particle-bound Pu in the Irish Sea (>98%) has been determined to be in the 'reduced' (Pu(IV)) form (Nelson and Lovett, 1981) whereas the majority of dissolved Pu (70–94%) is in an 'oxidised' (Pu(V)) form (Pentreath et al., 1986). It may not be coincidental that the only pure phase mineral on which the final redox distribution of sorbed Pu was similar to that bound to Irish Sea sediment was goethite (α-FeOOH).

The redox behaviour of Pu (as governed by distribution between sediment phases) may affect the rate and extent of remobilisation from contaminated sediment in the Irish Sea. Primarily, this is because the reduced form of Pu has a high affinity for particulate material whereas the oxidised form is more soluble. Haematite (α-Fe_2O_3) is a semiconductor with a band gap of ~2.3 eV; in energy this is equivalent to light with a wavelength of ~530 nm. Upon absorption of a photon of light with energy equal to, or greater than, the band-gap energy, an electron is promoted from the valence band into the conduction band. The photoelectron in the conduction band is strongly reducing and the photohole (h_{vb}^+) left behind in the valence band strongly oxidising. Therefore, the association of Pu to semiconducting Fe minerals may play a role in stimulating photoredox reactions by valence-

band holes/conduction-band electrons. It is also worth noting that the major component of beach sand (quartz) is an insulator. If Pu were predominantly associated with this component, then redox reactions would not be expected to be stimulated by light irradiation. Evidence that photochemical reactions may play a role in remobilisation of Pu from sediment particles has been obtained from laboratory studies (McCubbin et al., 2002). Oxidation of sorbed Pu(IV) species, the rate limiting step for redissolution of Pu from contaminated suspended particles into uncontaminated seawater, was increased by irradiation with visible light. In contrast to $^{239+240}$Pu, both dissolved ^{241}Am and particle bound ^{241}Am exist predominantly in the trivalent state (Pentreath et al., 1986) and consequently remobilisation is unaffected by oxidation reactions. The redox reactivity of Pu bound to iron oxide minerals could perhaps account for the predicted half-time for dissolution of $^{239+240}$Pu bound to surficial seabed sediment in the Irish Sea (in the order of 10^2 years) being significantly less than that for ^{241}Am (in the order of 10^3 years; Leonard et al., 1999).

5. Conclusions

Many workers have discussed the speciation of sediment bound Pu and Am based on geochemical extraction schemes, which have well-recognised problems. In this study, an assessment has been made of the association of selected α-emitting radionuclides with Fe minerals in beach sands using an alternative (magnetic extraction) technique. Significant uncertainties were also apparent in our dataset, arising from the use of small quantities of material and variable extraction efficiency dependent upon magnetic mineralogy. Nevertheless, the data have been used to derive lower and upper limits for the fraction of each radionuclide associated with Fe minerals. Average values for the lower and upper limit were 10–37, 13–45 and 12–46%, for $^{239+240}$Pu, ^{241}Am and ^{210}Po(^{210}Pb), respectively. The radionuclide and magnetic property grain-size distribution varied between individual samples, possibly as a result of site-specific factors. The association of Pu radionuclides and ^{241}Am with Fe oxide phases is unlikely to have a significant impact upon the physical dispersion of sediment contaminated by Sellafield discharges in the Irish Sea. However, it may be an important factor in governing Pu redox and redissolution behaviour.

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