

INVESTIGATION OF SPENT NUCLEAR FUEL RECOVERED FROM THE MARINE AND COASTAL FORESHORE ENVIRONMENTS

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ABSTRACT

We report the initial results of modelling studies performed on the Dounreay Database of Spent Nuclear fuel particles recovered from the marine environment and coastal foreshore adjacent to the UKAEA Dounreay Fast Reactor Complex located in the North East coast of Scotland. We demonstrate how interrogation of the fuel-particle frequency versus ^{137}Cs isotopic distribution allows us to generate particle behaviour models and residence lifetimes of various particle sub-groups. Similarly we find the recovered fuel particle's spatial distribution and shape characteristics are determined by environmental selection rules governed by properties of adjacent sediment and sediment transport mechanisms.

Analysis of the Spent Fuel particle database allows us to speculate on the original Site discharge pathways and fuel composition at the time of discharge. Further such studies correlate well with other sample morphology and compositional data and allow us to speculate upon the ultimate fate of different spent fuel types.

INTRODUCTION

Over 1100 sand-sized particles composed of Spent Nuclear fuel have been recovered from the Dounreay Foreshore, Sandside Beach and the marine environment adjacent to the Dounreay Fast Reactor Complex located in the North East Coast of Scotland [1]. These particles are mainly metallic in composition and have levels of radioactivity between $10^2 - 10^8$ Bq. Materials analysis by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDXA) of a number of these particles indicate that most of them are derived from two types of irradiated fuel: Materials Test Reactor (MTR) and Dounreay Fast Reactor (DFR) [2-5].

MTR fuel consists of small inclusions of enriched Uranium (U) within an Aluminium (Al) matrix and is similar to prototype fuel used in other reactors. It is likely that radioactive swarf

created during fuel milling activities associated with reprocessing is the initial source of these particles. DFR fuel consists of enriched U slugs in Niobium (Nb) cladding, the initial source in this case is considered to have occurred via dissolution procedures during reprocessing.

Gamma ray spectroscopy of the Caesium (Cs) isotopic content of some 20 particles suggests that the cooling time is (38 ± 3) years, indicating that they have been irradiated about 1966. Thus some of these particles have spent upwards of 35+ years in the marine environment. The current knowledge of the particle pathways to the environment indicates that the most likely route was through a low active drain which discharged effluent to the sea via a diffusion chamber which lies 23 m beneath the seabed, some 600 m offshore.

The anticipated fission products are predicted around mass numbers of 95 and 140 amu [6] and include Yttrium (Y), Nb, Molybdenum (Mo), Xenon (Xe), Cs, Barium (Ba), Lanthanum (La), Neodymium (Nd), etc. EDXA and Electron Probe Microanalysis (EPMA) measurements of these particles confirm the presence of U, Al, Nd, Xe, Cs along with various elements such as Potassium (K), Calcium (Ca), Iron (Fe), Silicon (Si), Phosphorus (P), Sulphur (S) and Chlorine (Cl), some of which constitute an adhering 'crud layer or phase' associated with the marine environment.

The Dounreay Spent Nuclear Fuel particles database catalogues a variety of data on each particle including: particle number, date recovered, geographical location, depth recovered, particle mechanical condition (fragmented or intact), particle dimensions and ^{137}Cs activity. The database serves as a useful instrument in investigating particle selection mechanisms, e.g., particle transport in the marine environment, particle dispersal, indication of physical and electro-chemical erosion/corrosion, and to better understand future trends in particle behaviour. A principal objective of this study is to gain an improved understanding of particle lifetime in the marine environment and to provide complementary data to use alongside other experimental studies of particle abrasion and the seabed environment. Interrogation of the database indicates the pathways by which particles appear in the littoral environment, including public beaches and the Dounreay foreshore, further these studies provide information on particle residence lifetimes.

This study is unique in several regards: first, it provides scientific evidence to assist the site cleanup and restoration plan. Potential restoration options currently range from passive monitoring through to particle recovery by remotely operated vehicles (ROV). Second, it acts as a useful reference work for long-term storage options of nuclear waste as we have gathered data concerning medium term environmental exposure. Lastly, it provides detailed information, including radio-isotope and materials analysis characterization, of the release into the marine environment of various fuel matrices including Al-U and Mo-U alloys, of which there is presently a scarcity of data.

EXPERIMENTAL

Approximately 74% of the 1100 sand-sized particles discovered to date have been recovered from the Offshore marine environment. The remainder have been recovered from the Foreshore directly adjacent to the Dounreay licensed nuclear site (21%) and Sandside Beach (5%) approximately 2 km SW of the diffusion chamber outlet, see fig. 1. Thus majority of the

collected particles have been found Offshore within approximately 600 m from the Dounreay Foreshore. The distribution of recovered seabed particles immediately lateral to the site is wholly consistent with initial seeding via the seabed diffuser, followed by dispersal by tidal currents running parallel to the shore [2]. The lack of particle finds >500 m from the foreshore is due to the difficulty of divers operating effectively in water depths >20 m. These data strongly suggest that it is the Offshore particle cohort that is seeding the Foreshore and Sandside populations

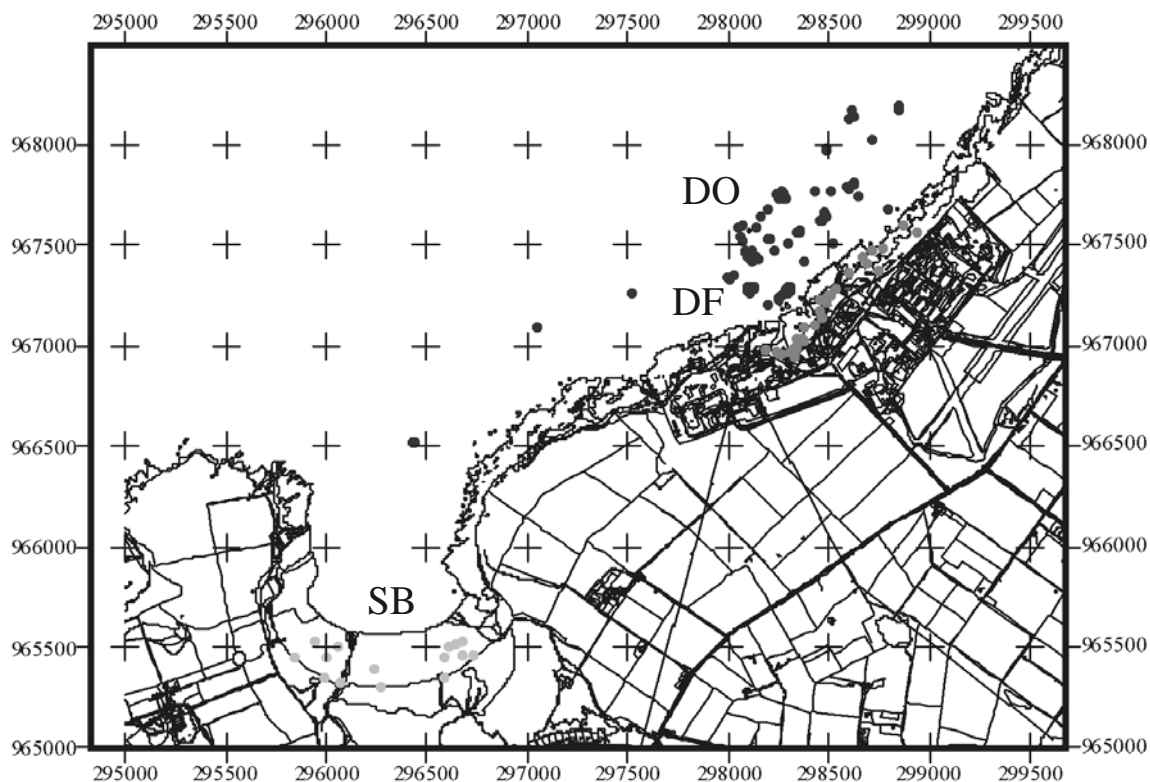


Fig. 1. Overview figure showing location of recovered particles: Dounreay Offshore (DO, black dots), Dounreay Foreshore (DF, gray dots) and Sandside Beach (SB, light gray dots).

The distribution of recovered seabed particles immediately lateral to the site is wholly consistent with initial seeding via the seabed diffuser, followed by dispersal by tides running parallel to the shore. At these relatively shallow depths we must consider sediment mixing and subsequent settling as the dominant process. Tides and storms periodically redistribute the sediments and incorporated particle pool, with the heavier particle masses being deposited nearer and the lighter masses further away from the initial location.

Examination of the relative lateral dimensions of MTR and DFR particles [7] shows that a size and shape differential is evident: DFR particles are in general smaller and more rounded than their MTR counterparts, which are more elongated. The shape differential may have arisen from a size selection mechanism within the local sediment but this could also be related to the initial

creation of the particles. Some DFR particles have travelled at least 2 km from their likely discharge point, suggesting they are more mobile, travelling further in tidal streams after sediments are disturbed. As particle activity typically decreases with particle size the activity of the Sandside particles is lower than that of the other cohorts.

As the marine residence time for some particles is considerable (≤ 38 years), coupled with the fact that they are located in a relative shallow depth (circa 20 m), we are obviously interested in the physical condition of the particles and gaining knowledge concerning their stability in the salt-water environment. Consequently a materials research program was initiated under contract with the Institute of Transuranium Elements, Karlsruhe, Germany to conduct Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Analysis (EDXA), Electron Probe Microanalysis (EPMA) and Gamma Ray Spectroscopy of both intact and sectioned particles recovered from the seabed. Although SEM/EDXA surveys of the outer layers of many particles have been conducted, data on the interior is restricted to a few.

Figure 2 (LHS) shows a SEM image of a $1.3 \times 0.3 \text{ mm}^2$ seabed particle derived from MTR fuel where debris from the marine environment, termed 'crud', has adhered to sections of the particle surface. The edges are well rounded suggesting some milling from the sediment, however the particle is obviously intact and we speculate that the native oxide layer (Al_2O_3) which is very corrosion resistant, together with the crud phase, has served to protect the particle from its environment.

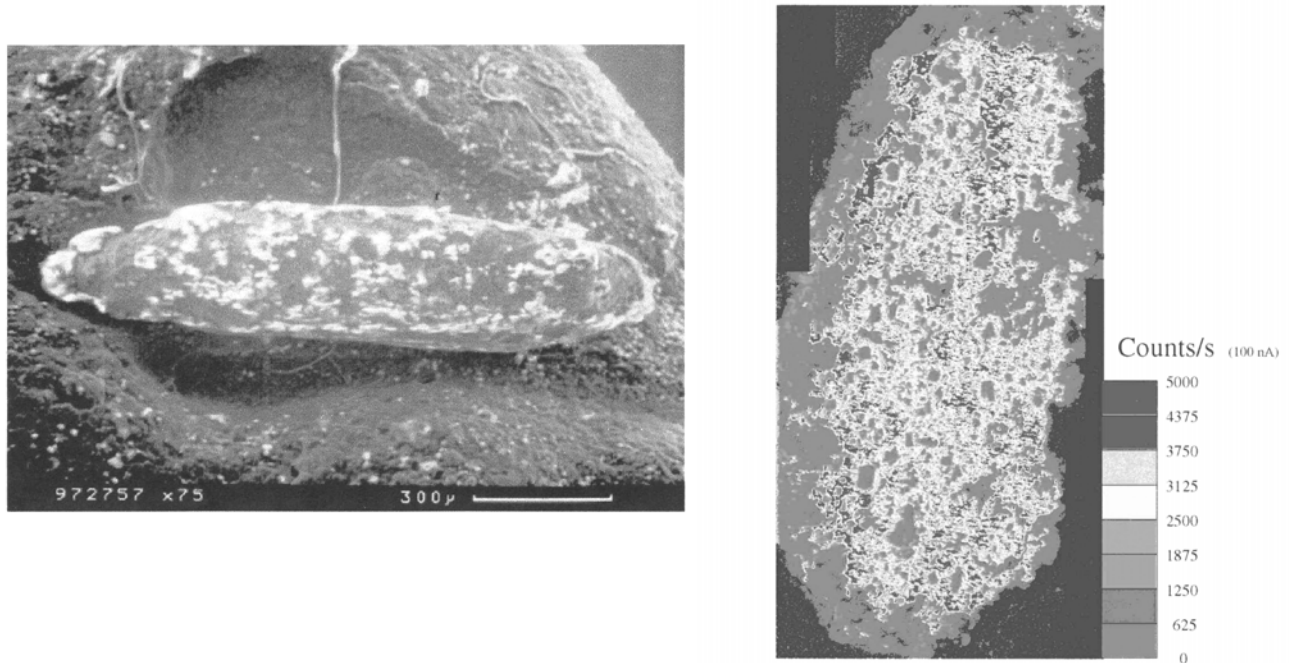


Fig. 2. LHS: SEM image of a seabed particle of approximate dimensions $(1.3 \times 0.3) \text{ mm}^2$ prior to polishing, RHS: EDXA dot map image for Al content across the whole polished section.

Figure 2 (RHS) shows an EDXA dot map analysis of the polished surface for Al, further studies indicate that the combined Al and U signals comprise 94-96% of the elemental composition with smaller amounts of, amongst others, Iron (Fe), Chlorine (Cl), Calcium (Ca), Neodymium (Nd), and Xenon (Xe). The latter two being fission products predicted from figure 1. EDX dot maps also indicate that Al and U components are present in the same areas indicating an alloying of the uranium. Similar elemental analysis of the crud phase show additional peaks of Potassium (K), Silicon (Si), Phosphorus (P) and Sulphur (S). A study of the backscattered electron (or atomic contrast) images (not shown) clearly indicate patches of U-Al rich inclusions or microcrystallites, some of which are visible right up to the polished edge. Such inclusions are continuous across the boundary of the particle and do not exhibit obvious signs of wear or corrosion. Further there appears to be no depletion of material at the periphery indicating that the radioisotopes are locked within the crystal matrix and are unlikely to diffuse away even if they are only a few microns from the edge.

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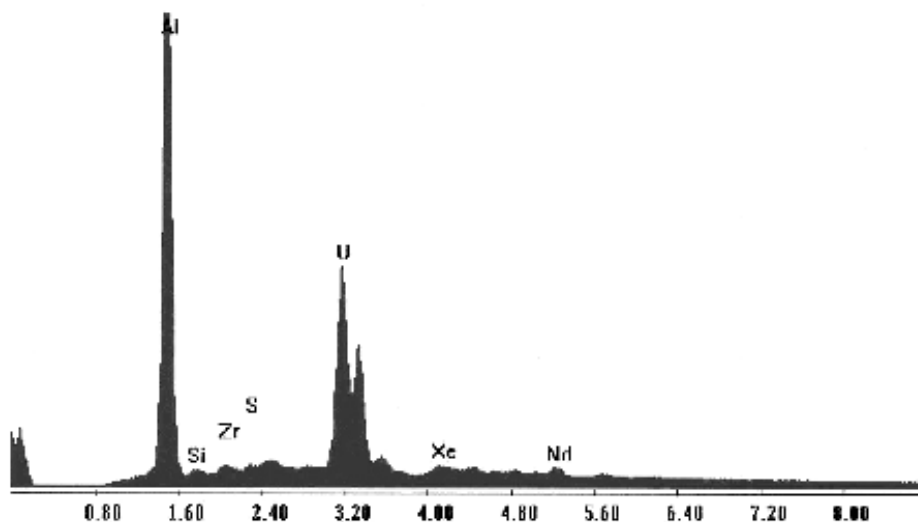
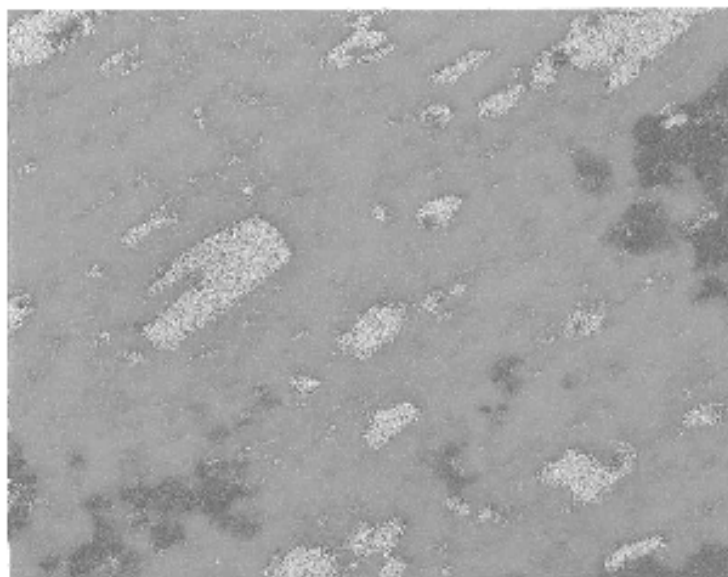


Fig. 3. Top: High resolution EDXA dot map showing U-Al inclusions in the Al matrix, Bottom: EDXA profile of the same region clearly demonstrating Al, U peaks together with fission products.

Figure 3 (Top) shows a high resolution Al/U EDXA dot map image of a region of the particle within the interior of the specimen. We can clearly observe the U-rich crystallites. Aluminium is depleted within the crystal grains and the uranium signal enhanced (although there is a distinct U background), pointing to a non-homogeneous fuel matrix. This region, see figure 3 (Bottom), displays a sharp EDX spectrum with background levels of the fission products zirconium (Zr), Nd and Xe. Other EDXA and EPMA mappings clearly show a range of fission products including Zr, Mo, ruthenium (Ru), rhodium (Rh), palladium (Pd), Xe, Cs, Barium (Ba) and Nd. High resolution EPMA maps (not shown) are broadly in agreement with the EDXA data and indicate that oxygen signals are present only at the particle/crud interface, which we associate with a Al_2O_3 (anti-corrosion) native oxide layer.

If we now consider the frequency of recovered particles versus their ^{137}Cs activity distribution, see figure 4, we observe that all the particle cohorts exhibit similar trends, i.e., they all display peaks at reasonably high count rates. The higher ^{137}Cs activity corresponds to larger mass so this data strongly suggests that even after ≤ 38 years marine residence time there is no evidence of a dominant particle erosion/corrosion mechanism serving to produce a large number of small (and therefore low activity) particles. This finding is reinforced by the fact that 92% of the particles are recovered intact (for the sub-set of fragmented particles the average fragmentation rate is 2.7). We must therefore conclude that fragmented particles, i.e. mechanically weaker, are not typical. One caveat in interpreting the activity data in figure 4 is that the probability of particle detection decreases towards the low activity end. However the presence of peaks and the clear negative gradient on the left-hand side of the peaks (at two different activity levels) suggest that these are *stable* particle populations. These populations would be very sensitive to particle disintegration, e.g., if a particle of 10^5 Bq activity became 10 particles of 10^4 activity, the particle frequency plot would very quickly shift to the left. We therefore suggest that such frequency 'snapshots' over time can be used as a sensitive indicator of particle stability and, via extrapolation, particle lifetime.

Figure 4 also indicates the presence of common peaks in different particle cohorts, supporting the thesis that the supply of particles to Dounreay Foreshore and Sandside beach is determined by the release from the offshore reservoir. As the Dounreay Foreshore is much closer than Sandside Beach this would also explain the relative activity of the corresponding peaks.

CONCLUSIONS

The majority of spent nuclear fuel particles have been recovered from the seabed close to the subsea diffuser supporting the thesis that this is a principal release point. It is this Offshore particle reservoir that is feeding the Dounreay Foreshore and Sandside Beach cohorts. Physically

smaller particles (containing smaller amounts of radioactivity) appear to travel furthest laterally from the probable release point suggesting they are more mobile and that sediment transport due to a combination of tides and storm events are the likely transport mechanisms.

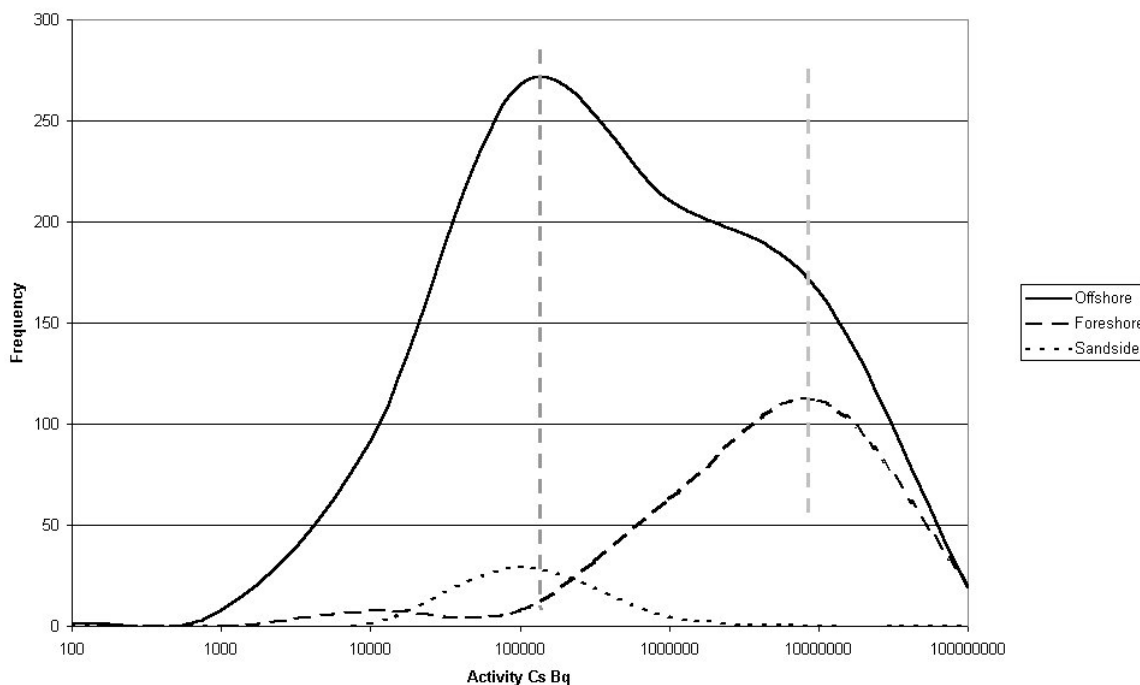


Fig. 4. Frequency of particles for the Offshore, Foreshore and Sandside Beach cohorts versus their ^{137}Cs activity.

Although many surface studies have been conducted on the crud-covered outer layers of various types of recovered irradiated fuel particles, sectional data is available only on a few. A program to expand our knowledge of the effects of the marine environment on these particles is currently in progress. Nevertheless the data presented here demonstrates that the interior polished section of this seabed particle is mechanically intact. A crud phase clearly exists on parts of the outer surface however the particle appears intact below the crud layer: any cracks observed appear stable and of limited length. Furthermore they would not appear to be present in sufficient numbers to render the particle unstable. Other EPMA studies at the sample periphery [5] indicate that any corrosion of aluminium surface is probably limited to < 20 microns. The uranium fuel is locked up in a U-Al matrix and where this material intersects an internal boundary (crack) or external periphery it appears continuous, i.e., there are no obvious signs of wear or corrosion.

If the marine environment produced a continuous surface removal, e.g., by etching or physical abrasion, the particle size would diminish, and at some point in the future the particle would fragment. This process would quickly consume the particle. However no macroscopic pitting artefacts were found on the particle surface. Furthermore 92% of the particles are recovered

intact and their ^{137}Cs activity distribution does not show signs of a large number of small, less active particles. This data suggests that these particles are relatively stable in the marine environment.

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