CHARACTERIZATION OF SPENT NUCLEAR FUEL WASTE FOUND IN THE MARINE AND FORESHORE ENVIRONMENTS

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ABSTRACT

Over 1100 sand-sized particles of Spent Nuclear Fuel have been recovered from the littoral and marine environments adjacent to UKAEA Dounreay nuclear licensed site, located on the north coast of Scotland. As part of the Dounreay Site Restoration Plan (DSRP) a significant program of work is currently being undertaken to characterize these particles together with non-radioactive analogues using several material analysis techniques. The objectives of this program is to identify the particle lifetime in the marine environment and propose likely corrosion-erosion models for the wide ranging nuclear fuel types using during the operational lifetime of the site.

The diverse environments where the particles were located, coupled to relatively long fuel-particle residence times (up to 35 years) allow insight to be gained into the behavior of the particles in the natural environment. This includes the effect of physical, chemical and mechanical processes, such as particle erosion, corrosion, abrasion and particle saltwater interaction. Individual particles have been characterized with respect to activity concentration using gamma-ray spectroscopy, microstructure by Scanning Electron Microscope (SEM) and back scattered electron image (BS), distribution of the elemental composition by Energy Disperse X-ray (EDX) analysis. From these data we demonstrate that a marine base crud exists on regions of the surface however the particles appear both chemically and mechanically intact below this layer: any cracks observed appear stable and have limited length.

This study is unique in that involves the effects of long–term saltwater and abrasion interaction with fuel waste containing U-Al and U-Mo of which there is little literature reported.

INTRODUCTION

Over 1100 particles containing spent nuclear fuel have been recovered by UKAEA from littoral and marine environment adjacent to the Dounreay nuclear licensed site [1]. The offshore cohort constitutes the majority (75%) of the particles finds; the littoral cohort comprises 25% of the particles. These particles are metallic and their levels of radioactivity range between 10^3 – 10^8 Bq of Cs-137. Gamma-ray spectroscopy of a limited number of

particles shows that they contain caesium (Cs-134/Cs-137) isotopic ratios which suggest particle irradiation during the mid 1960s [2].

Analyses 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). MTR fuel consists mainly of aluminium (Al) with small inclusions of enriched uranium (U-235) in the fuel plates. The amount of U in MTR fuel plate was typically 2.8% (atomic composition). These types of particles originated during the preparation for reprocessing of various MTR fuels types, from a number of reactors. DFR particles consist of uranium-molybdenum (Mo) alloy with 15% atomic concentration Mo, in a niobium (Nb) cladding. DFR fuel rods consisted of enriched uranium fuel slugs, which were encased in a niobium metal cladding.

The different sea water environments where the particles were located, together with relatively long fuel-particle residence times (up to 35 years) allow insight to be gained into the behavior of the particles in the natural environment. This includes the effect of physical, chemical and mechanical processes, such as particle erosion, corrosion, abrasion and particle salt-water interaction. A materials research program was initiated under contract with the Institute of Transuranium Elements, Karlsruhe, Germany [3], [4] to conduct the characterization of the particles with respect to activity concentration using Cs-137 measurement, microstructure by scanning electron microscope (SEM) and back scattered scanning electron image (BS), distribution of the elemental composition by energy dispersive X-ray (EDX) analysis. These data should reveal the spent fuel particle mechanical and chemical stability.

Experimental Results

Figure 1 shows a back-scattered scanning electron image of a littoral particle. The presence of aluminium on this particle indicates it is derived from MTR fuel. Two different regions are clearly visible in this particle, the left part of the particle is derived from the MTR fuel and the right part is essentially aluminium with little uranium present. This latter part was probably from the fuel element cladding and has a very smooth appearance. The white spots observed in Figure I represent the distribution of uranium of both parts of the particle. The left side shows the distribution across the fuel rich region; while the right side presents a predominantly aluminium region with just two significant spots of uranium.

Figure 1 reveals that this particle is rounded at each end and is distinctly elongated. This morphology is likely to have been produced by the wave action and milling of the particle by the sediment.

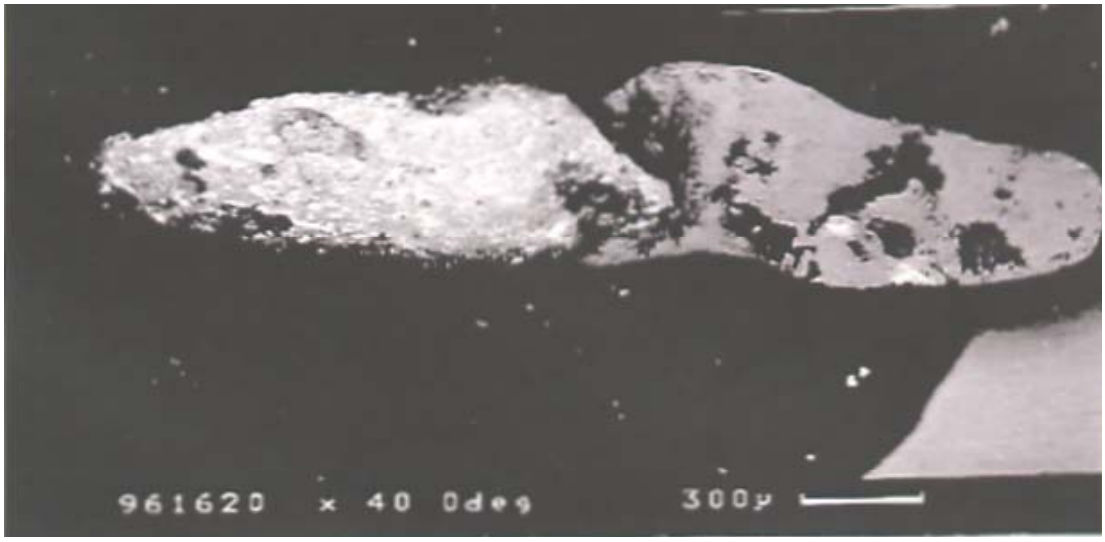

Fig. 1. Back-scattered electron image of a foreshore particle, whose weight is 1.25 mg, length is 2.5mm and maximum width is 0.5 mm, ^{137}Cs radioactivity is 1.6 10^6 Becquerel per sample. The white spots show the distribution of uranium on the particle.

Figure 2a and 2b shows a more detail back-scattered electron image of both sections of the particle, the MTR fuel and the aluminium cladding respectively. The MTR fuel part of the particle (figure 2a) indicates that the crud coverage is patchy and incompleate. This particle will have been subject to a vigorous mechanical regime, given that it has been recovered from a wave dominated, high energy, littoral environment. McManus [5] indicates that aluminium particles placed into a wave tank containing 2kg of Dounreay beach sand and 1.5 litres of sea water for a period of two weeks, achieved an equilibrium in which the crud layer is formed and removed in different regions of the particle over this period of time.

Figure 2 also display that the number of cracks in the crud phase are few in number and relatively small.

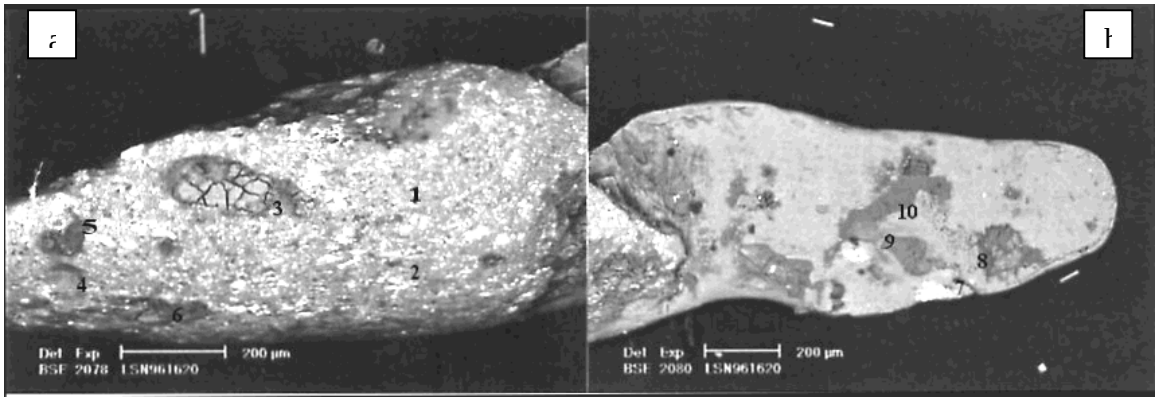

Fig. 2.(a) Back-scattered electron image of the fuel section of the particle, indicating areas subject to chemical analysis. Fig. 2.(b) Back-scattered electron image of the cladding section of the particle indicating areas subject to analysis.

Six areas of the MTR fuel part of the particle were subject to analysis (Figure 2a). From Table I we observe that Al and U have been found on areas 1, 3, 4, and 5 when analyses of the surface of the particle have taken place. This indicates that the crud layer must be sufficiently thin to observe the metallic U and Al behind the insulating crud. The mass distribution of fission products arising from the thermal neutron irradiation of U-235 is well

known [6].At position 1 a U fission product, neodymium (Nd) is observed, EDX mapping shows that the distribution of U and N coincide. Iron (Fe) is present in all the positions that were subject to analysis. From Table I indicate that the elements present on the crud phase of the MTR fuel part of the particle are potassium (K), calcium (Ca), Fe, magnesium (Mg), silica (Si), phosphorus (P), sulphur (S) and chlorine (Cl). Fe and Si are the predominant components. K, Ca, and Fe are most probably present as cations while the anions would be silicate, phosphate sulphate and chloride. There also likely to be oxide, hydroxide and carbonate anions present. EDX system used was not capable of detecting elements of low atomic mass.

Table I. Summary of the Analysed Areas of the MTR Fuel Section of the Particle

Position in Figure 2a	Description, grain size (μm)	EDX
1	less than 10μm. diameter	Al, U, K, Ca, Fe, and Si are the main components. There are significant amounts of P, S, Cl, and Nd. Al, U, and Nd are from the fuel matrix.
2	Small agglomerate of crystallites on the surface of the particle 20μm.	Fe is the main component, traces of Ca
3	Aglomerate of grain size 30 -40 μm.	Fe, Ca and P are the main components, small quantities detected of Na, Mg, Al, U, Si and Cl
4	grain size 10μm.	Al main component, significant quantities of Ca, Fe, and P, traces of Mg, U, Si and S.
5	grain size 50μm.	Al and Si main components, Small quantities of Mg, Ca, Cl, U and Fe.
6	grain size up to 50μm.	Fe

Four positions on the aluminium cladding section of the particle were analysed (Figure 2b). Table II reveals that aluminium is the predominant element in this section of the particle. There is also evidence in Table II that there are phases in the particle containing some magnesium (Mg), calcium (Ca), iron (Fe), silica (Si), phosphorus (P), sulphur (S) and chlorine (Cl). Again this may be an indication that the crud is thin enough to allow primary electron penetration and X-ray generation and detection from the aluminium in the particle.

Table II. Analyses from Areas of the Aluminium Section of the Particle

Position in Figure 2b	Description	EDX
7	Amorphous grains	Al main component
8	Grains size of 20 μ.	Al main component, with small quantities of Mg, Ca, Fe, Si, P, and Cl
3	'Paved' structure. Grain size 5 – 10 μ	Al main component, Small amounts of Si, P, Cl., Ca and Fe.
4	Crud with pores	Al main component traces of Ca, Fe , Si and P

The region of the particle containing fuel was sectioned, then polished flat with silicon carbide paper, prior to cleaning in an ultra-sonic bath.

Figure 3 is a back-scattered SEM micrograph of the polished section of the fuel containing region of the particle.

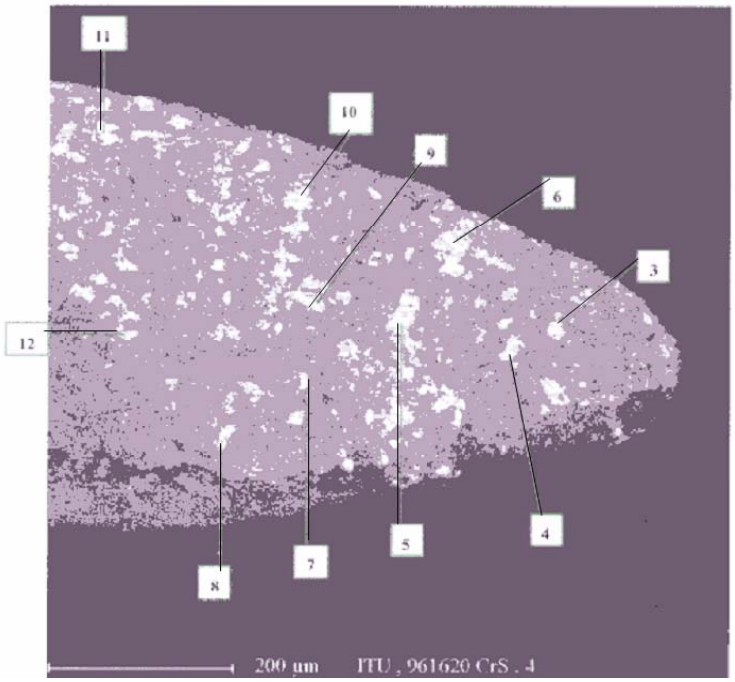

Fig. 3. Polished section of the uranium rich region of the particle, showing the inclusions analysed by EDX.

The inclusions marked in Figure 3 were examined by EDX. The measurements are shown in Table 3; measurements give a semi-quantitative indication of the composition of the alloy.

Table III. EDX Measurements of the Inclusions Mark in Fig. 2.

Inclusion number	Al at%	U at%	Nd at%	Cs at%	Fe at%	Cr at%	Ni at%	Ca at%
	Fuel		Fission Products		Impurities, Contaminations, Crud			
3	83.02	12.13	0.54	1.12	1.51	0.62	0.16	0.89
4	84.54	11.99	0.73	1.33	0.08	0.21	0.06	1.06
5	83.18	11.91	0.83	2.02	0.11	0.63	0.06	1.26
6	83.34	12.50	0.91	1.48	0.14	0.42	0.07	1.13
7	84.34	12.29	0.39	1.14	0.10	0.29	0.06	1.40
8	84.86	11.83	0.38	1.02	0.35	0.45	0.07	1.03
9	84.06	13.34	0.32	0.64	0.23	0.25	0.07	1.08
10	83.51	12.37	0.92	1.70	0.13	0.36	0.09	0.92
11	83.87	12.80	0.49	1.42	0.14	0.28	0.05	0.95
12	83.77	10.70	0.78	1.44	1.55	0.70	0.16	0.90

Although the average amount of U in MTR fuel was typically 2.8 atomic % [2], Table III indicates that the local U concentration is approximately 12 atomic %. This discrepancy can

be explained because the U% in Table III is local measured from uranium rich inclusion, the global level for a complete fuel element is likely to be nearer 2.8 atomic %.

Inclusions 3, 4, 7, 8, and 12 have areas visible on the metallographic section with an average diameter of approximately 20 μm, inclusions 9,10 and 11 have an average diameter of 30μm, while inclusions 5 and 6 are comparatively large with an average diameter of approximately 80μm.

Table III indicates that Al and U signals comprise 94 -97 % of the elemental composition while the significant levels of Cs and Nd are uranium fission products. Ca, chromium (Cr), Fe, nickel (Ni), present in the sample may be a contaminant from the surface of the particle, which may have its origin in smearing from the edge of the original particle during sample preparation.

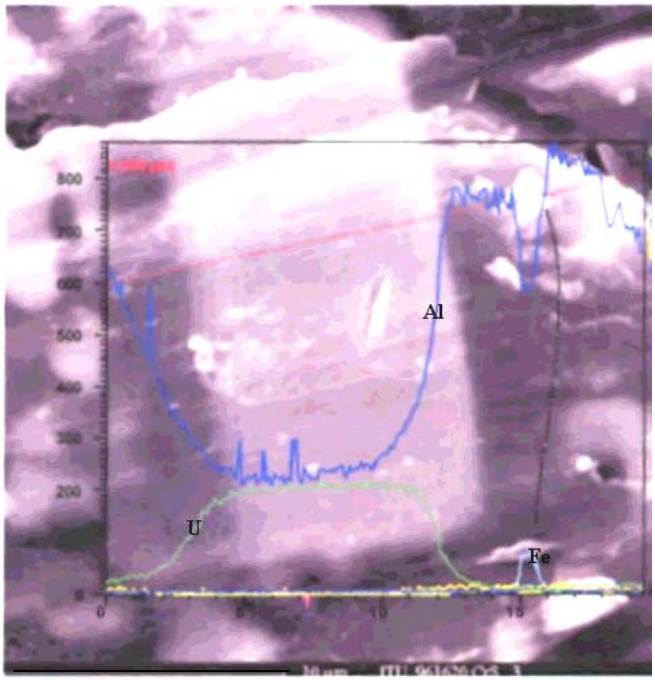

Fig. 4. A line scan across inclusion 7 (Fig. 3.) and neighbouring aluminium matrix, showing the variation of concentration of Al, U and Fe in the U rich inclusion.

Figure 4 shows increased uranium and decreased aluminium concentrations at the interfaces between the inclusion and the aluminium matrix. The Al used in the cladding has Fe as an impurity, which explains the increased Fe concentration with decreased Al concentration in the aluminium matrix. The typical amount of Fe used in the cladding was 0.27 % the amount of Fe reported in Table 2 is higher than this. Therefore it is possible that Fe also arises from the crud layer, which may have its origin in smearing from the edge of the original particle on SEM sample preparation.

CONCLUSIONS

A crud phase (or phases) clearly exist at some locations of the outer surface of this MTR particle foreshore particle; however the particle is shown to be mechanically intact. The crud is essentially based on Ca and Fe with Si, P, S and Cl. The chemical composition and the morphology of the deposits depend on the chemical and physical environment to which these materials have been exposed over a long period. Al and U were detected on analysis of the particle. This is an indication of a crud phase thin enough in some points of the particle to

allow the detection of these elements. The U fuel is locked in a U-Al matrix. An increase of uranium and a decrease of aluminium concentrations are apparent at the uranium- aluminium matrix.

If the marine environment produced a continuous surface removal by etching, physical abrasion or other processes, the particle size would diminish and at some point in time the particle would fragment ending in the destruction of the particle. However no macroscopic evidence of pitting artefacts was found on the particle surface. Furthermore 92% of the particles recovered until now are intact and their Cs-137 activity distribution does not reveal signals from a large number of small, less active particles [7].

Although some surface studies have been conducted on the crud phase 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.

ACKNOWLEDGEMENTS

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