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The ‘granite encapsulation’ route to the safe disposal of Pu and other actinides

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Abstract

Waste actinides, including plutonium, present a long-term management problem and a serious security issue. Immobilisation in mineral or ceramic waste forms for interim storage is a widely proposed first step. The safest, most secure geological disposal for Pu is in very deep boreholes and we propose that the key step to combination of these immobilisation and disposal concepts is encapsulation of the waste form in cylinders of recrystallized granite. We discuss the underpinning science, focusing on experimental work, and consider implementation. Finally, we present and discuss analyses of zircon, UO_2 and Ce-doped cubic zirconia from high pressure and temperature experiments in granitic melts that demonstrate the viability of this solution and that actinides can be isolated from the environment for millions, maybe hundreds of millions, of years.

1. Introduction

It is estimated [1] that 1800 tonnes of Pu have been produced worldwide from over 50 years of civil nuclear power generation and national weapons programmes. Much of this Pu exists in the form of spent fuel from which it has not yet been (and may never be) separated. Excess Pu not destined for burning as mixed oxide (MOX) fuel or in Generation IV nuclear reactors will constitute a major waste management problem and potential security issue for all the nuclear nations. The situation is exacerbated by substantial amounts of other equally problematic actinides, such as Np, Am and Cm, arising from spent nuclear fuel, particularly highly enriched (e.g. submarine reactor) fuel. Immobilisation in mineral and ceramic waste forms [1,2] for safe interim storage and eventual geological disposal is currently the preferred option for excess Pu but no scheme, route or exact form of geological disposal has been identified to date. Also, no method yet exists for the immobilisation and disposal of spent MOX.

2. Actinide waste forms

Pu and the other actinides do not lend themselves well to immobilisation in borosilicate glass (the currently preferred option for most of the fission products from spent nuclear fuel) and there is a consensus that they are better immobilised in mineral-based ceramics [1–8]. Considerable efforts are therefore being made worldwide to investigate mineral and ceramic structures that can accommodate meaningful amounts of Pu (and other actinides) in their crystal lattices. Prominent among these are zircon [7,8], monazite, perovskite, pyrochlore, zirconolite, cubic zirconia and uranium dioxide. Most of this, however, is being done with a view to safe interim storage and with very little focus on eventual disposal. An alternative currently being considered is to immobilise the Pu, possibly with depleted UO_2, in MOX using available fuel fabrication procedures and facilities. This unburned ‘low-specification MOX’ could then be

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placed, along with other long-lived high-level wastes, in a 'deep' (but, at 300–1000 m, geologically shallow) mined repository.

The main concern about any mined repository is that eventually groundwater will gain access to the waste, leach out radionuclides and transport them back to the biosphere before decay has rendered them radiologically harmless. Consequently, considerable attention is being focussed on the durability and leaching behaviour of these proposed actinide waste forms [1,2]. The situation is complicated further by concerns over the effects of radiation damage to the crystalline structure (metamictization) resulting in swelling and potentially enhanced leachability of the actinides [2,4,6,9,10]. A great deal of work has been undertaken to evaluate these effects using both external irradiation (heavy ion implantation) [9,10] and self-irradiation of waste forms doped with Pu and other actinides [4,9–11]. Results to date are inconclusive [4,12] but it is clear that some waste forms, e.g. zircon [2,4,13] and zirconolite [2] may be more susceptible to metamictization than others, e.g. cubic zirconia [11]. Nevertheless, the effects of radiation damage are often used to question the suitability of such waste forms for actinide containment in geological disposal [14].

What we propose here is that these uncertainties about the performance of the actinide waste forms can be rendered irrelevant by eliminating the possibility of aqueous leaching altogether by encapsulating the waste forms in recrystallized granite and resorting to an alternative form of geological disposal in very deep boreholes.

3. Deep borehole disposal

Deep borehole disposal (DBD) is emerging as a potentially superior form of geological disposal for several types of high-level radioactive waste (HLW) [15–17] and a particularly strong case can be made for DBD of Pu and other fissile materials [18]. Boreholes offer many advantages over mined and engineered repositories [15,16,18]. In particular, the greater depths (>4 km as against 300–1000 m) and less dynamic hydrogeological conditions increase confidence in the geological barrier against return to the biosphere of any radionuclides. DBD relies more on the geological barrier and less on engineered barriers, the performances of which are uncertain on the timescale necessary for the isolation of HLW (10^5–10^6 years). In addition to greater safety, other potential benefits of DBD include higher security (against terrorist or accidental intervention), wider availability of geologically suitable sites, less environmental disruption and potentially better cost-effectiveness.

In the USA a MIT study on the Future of Nuclear Power [17] recommended that for spent fuel DBD 'merited a significant R & D program'. In the UK the Committee on Radioactive Waste Management (CoRWM), in recommending [19] geological disposal for all HLW, stated that decision making about the exact form of such disposal 'should leave open the possibility that other long term management options' [*than mined repositories*] '(for example, borehole disposal) could emerge as practical alternatives'.

Two main arguments are sometimes advanced against DBD. Firstly, the large diameter (0.6–0.8 m) boreholes to a depth of over 4 km required by most versions of DBD for HLW are an 'unproven technology' or, more correctly, are at the limits of current drilling technology. Secondly, retrieval of the waste packages would be extremely difficult and costly. For the version of DBD proposed here for Pu the former is not relevant as the 5 or 6 km deep boreholes need be no wider than 0.27 m. Fully cased and cemented boreholes this size and larger are routinely sunk to these depths and beyond in the geothermal energy industry at a cost of around \$8 M [20] and commercial drilling rigs with this capability are currently in operation. For most HLW retrievability is a very debateable requirement [21] but for Pu, where security is paramount, it is highly undesireable and the difficulties of retrieval, which could certainly not be done easily or covertly, are a major advantage.

4. Encapsulation

The key to the proposed DBD of the Pu-bearing waste forms, including low-specification MOX, is their prior encapsulation in rock identical to the granitic host of the borehole deployment zone. This can be accomplished by mixing the waste form with the crushed granite which is then partially melted and completely recrystallized by controlled cooling. For many years it was widely believed that medium-coarse grained granite could only be formed by extremely slow cooling over hundreds, if not many thousands, of years. However, Attrill and Gibb have recently demonstrated that, under the conditions of DBD, a typical S-type [22,23] granite can be partially melted [22] and completely recrystallized [24] in a matter of months.

In a series of experiments designed to investigate high-temperature DBD of HLW, it was found [22] that at a pressure of 150 MPa (corresponding to a depth of ~4.5 km in the continental crust) the granite begins to melt at just under 700 °C in the presence of a small amount of H_2O. The amount of melting increases with temperature and H_2O content up to saturation (requiring between 4% and 5% H_2O depending on temperature). For example, 40% of melting occurs at 800 °C with 1.5% H_2O while 80% of melt can be generated 50 °C lower at 750 °C with 5% H_2O. The silicate liquids produced after more than 30 days at the higher temperatures and degrees of melting are believed to be close to equilibrium partial melts. Controlled linear cooling experiments [24] over the temperature range 800 °C to 560 °C demonstrated that these partial melts can be recrystallized to medium grained, holocrystalline granite when cooled more slowly than 0.1 °C per hour.

Based on these experimental studies there are various ways in which the encapsulation of the Pu-bearing wastes in granite could be implemented. Perhaps the simplest is by mixing millimetre to centimetre-sized pieces of the mineral- or ceramic-based waste form with the crushed granite and H_2O in a suitable cylindrical container of appropriate dimensions for the DBD. A refinement might involve forming a granite cylinder in which the Pu-bearing waste forms are absent from the outer margins. The mixture is then held at over 750 °C for ~30 days under the appropriate conditions ($P = 150$ MPa; H_2O content ~5%; $fO_2 =$ close to the Ni/NiO buffer) before cooling to under 550 °C at less than 0.1 °C per hour. From 550 °C the now solid granite could be cooled fairly quickly and the cylinder extracted for disposal. The entire process would take about 120 days.

5. Post-encapsulation disposal

Following manufacture, cooling and interim storage (if required) the granite cylinder is disposed of by inserting it into a fully cased borehole to a depth of ~6 km. After deployment of the cylinders is complete the casing could be withdrawn (although this is not essential) and the borehole sealed at intervals above the deployment zone. Sealing, which could use a variety of materials and methods including rock welding [16], is to deny the disposal zone fluids access to the surface. Eventually, the spaces around the granite cylinders will be invaded by the intra-rock fluids seeping slowly from the enclosing host rock. These fluids are expected to be dense saline brines which have equilibrated with their granitic host over many millions of years [25] and hence will also be in thermodynamic equilibrium with the cylinders of recrystallized granite. There will therefore be no tendency for reaction or mineralogical alteration of the cylinders that might allow the fluids access to the Pu-bearing waste forms. It is noteworthy in this context that natural zircons, monazites and uraninites in granites and similar rocks survive for thousands of millions of years under such conditions without any significant loss of their actinides (U and Th), even when completely metamict.

Interestingly, and perhaps slightly ironically, the ambient temperatures at depths of 4–6 km in the continental crust could be sufficiently elevated as to contribute to the annealing out of the structural damage to the actinide-bearing waste form caused by self-irradiation [26]. While this in no way negates the importance of encapsulation of the waste form in granite, it could be viewed as a possible additional benefit of the proposed DBD scheme.

The quantities of waste materials that may be disposed of in this way depend on the actinides, the exact waste form, the actinide loading of the waste form, the ratio of waste form to granite and the geometry of the borehole. Detailed discussion of the effects of different combinations of these factors is beyond the scope of this paper but a useful insight can be gained from a very conservative example. An yttria-stabilised cubic zirconia containing 5 wt% Hf and 14 wt% Pu encapsulated in a granite cylinder 0.25 m in diameter at a volume ratio of 10% zirconia to 90% granite would give a disposal of 4.18 kg Pu per m of borehole. Hence a 6 km deep borehole with waste cylinders deployed over the lowermost 2 km would dispose of ~8 tonnes of Pu.

6. Experimental results

Crucial to the viability of the proposed solution to the Pu problem is that during the encapsulation process there is no dissolution of the waste form, reaction with the

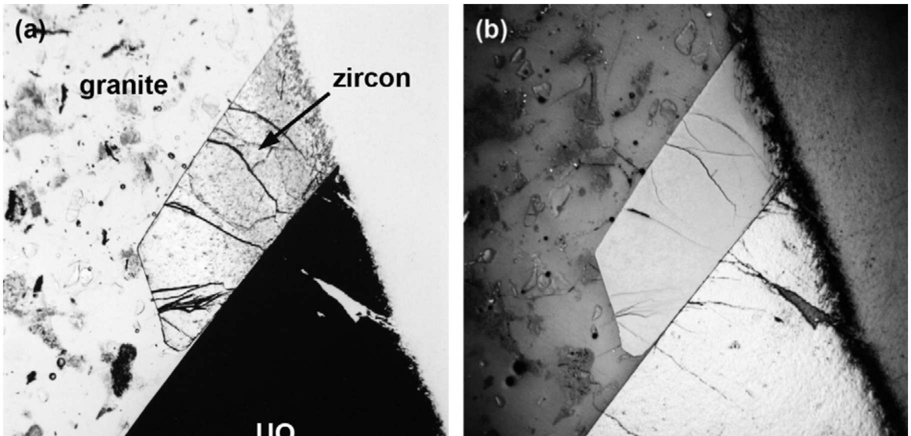

Fig. 1. Photomicrographs of zircon/UO_2/zircon 'sandwich' enclosed in partially melted granite: (**a**) in transmitted plane polarised light (PPL); (**b**) in reflected PPL.

silicate melt or diffusion of the actinides out of the waste form. Although the behaviour of the natural analogues crystallized from various parent magmas is encouraging in this respect, a series of experiments was carried out to investigate this. Using the same procedures as described by Attrill and Gibb [22], zircon, UO_2 and Ce-doped cubic zirconia were enclosed in crushed granite, which was then partially melted and held at high temperature and pressure for several months before quenching. Full details of these experiments will be presented elsewhere but we summarise below the most important of them and their significance for the disposal of Pu and other actinides.

A cylindrical pellet (0.187 g) of depleted UO_2 was sandwiched between two pieces of natural zircon (containing 1.3% Hf) with the ends of the pellet against flat faces of the zircon. The 'sandwich' was then placed in a gold capsule surrounded by 0.788 g of crushed granite E93/7 [22] to which 0.023 g of H_2O was added (total $H_2O = 3.44\%$). The sealed capsule was then held at 760 °C and 150 MPa for 6.6 months, generating ~60% melting [22], before quenching.

Polished thin sections cut from the sample (Fig. 1) show the zircon/UO_2/zircon 'sandwich' enclosed in partially melted granite and it appears that the contacts between the quenched silicate liquid and both the zircon and UO_2 are sharp with no obvious signs of reaction or corrosion (Figs. 1 and 2). All three types of contact (granite/zircon, granite/UO_2 and zircon/UO_2) were investigated by electron probe microanalysis (EPMA). A series of 4 μm spot analyses at less than 10 μm intervals across the granite/UO_2 interface showed no detectable U in the granitic melt adjacent to the contact and no detectable Si, Al, Na or K in the UO_2 close to the granite. Similarly, for the granite/zircon contact, EPMA detected no Si, Al, Na or K in the margins of the zircon crystal and no Zr or Hf in the granitic melt adjacent to the contact. [The original granite contains Zr = 49 ppm; Hf = 2 ppm and U = 4 ppm, which are below the detection limit of EPMA and, in any case, probably did not enter the melt phase.]

There is no evidence from the appearance of the contacts and the EPMA analyses that there has been any dissolution of either the zircon or UO_2 in the silicate liquid. Nor is there any indication of diffusive transfer of elements

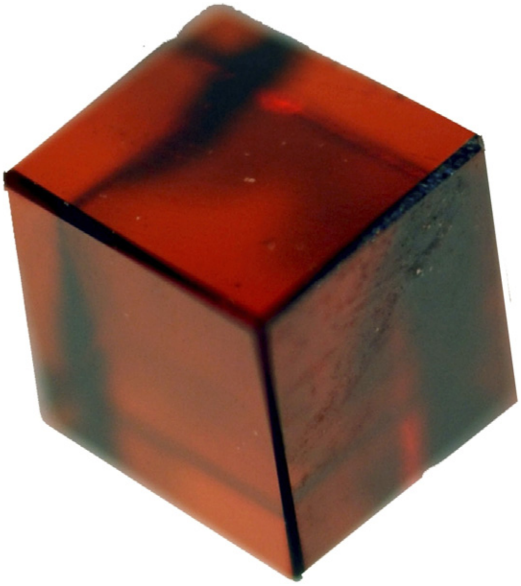

Fig. 3. Ce-doped, yttria-stabilised crystal of cubic zirconia as used in the experiments (Edge = 2.5 mm).

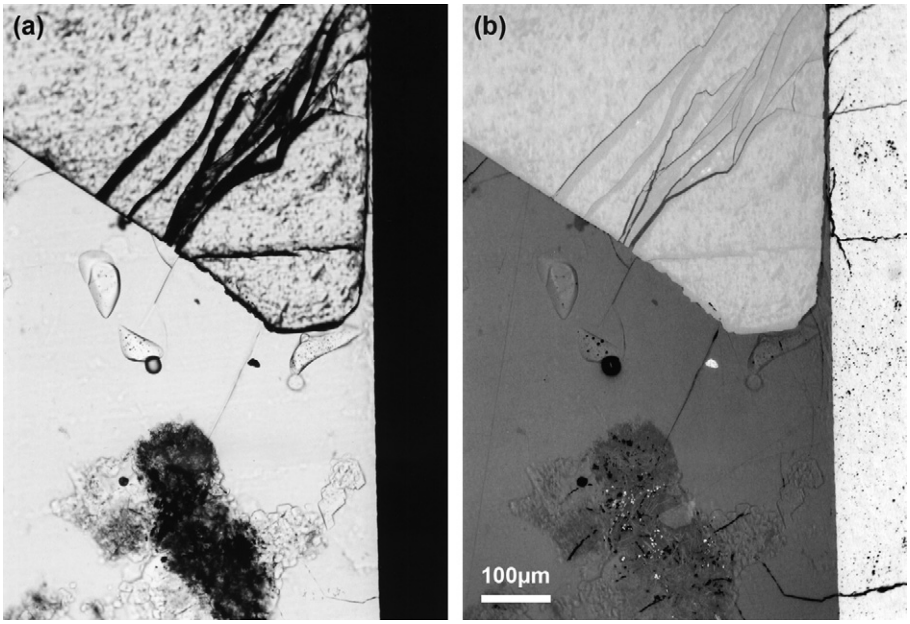

Fig. 2. Detail of Fig. 1: (a) transmitted PPL; (b) reflected PPL.

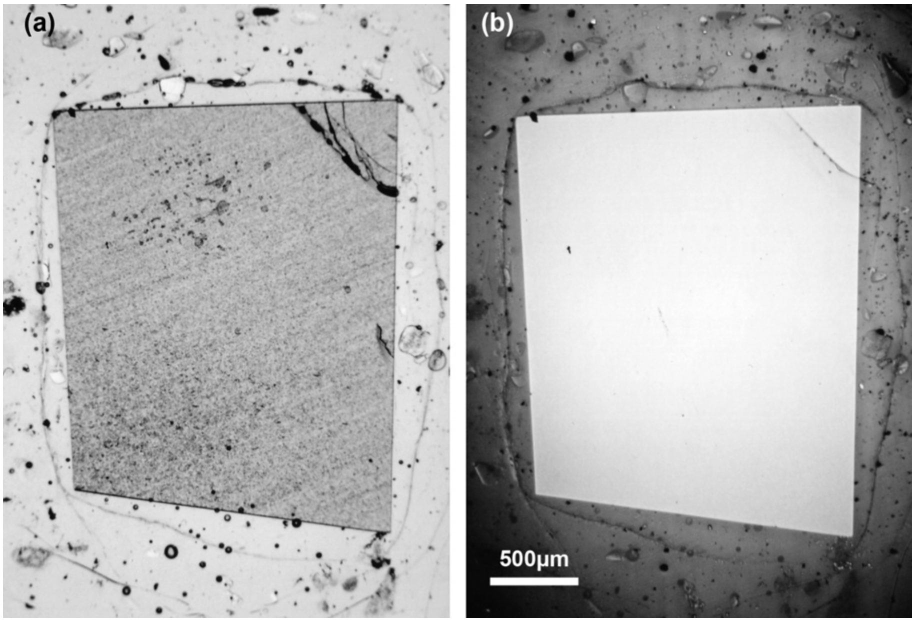

Fig. 4. Photomicrographs of Ce-doped cubic zirconia crystal enclosed in quenched granitic partial melt: (a) in transmitted PPL; (b) in reflected PPL.

across the interfaces despite the zircon and UO_2 having been in contact with granitic melt at 760 °C for over 6 months.

To investigate the behaviour of a ceramic-based waste form we used a gem quality single crystal of (20%) yttria-stabilised cubic zirconia doped with 0.3% CeO_2 to simulate tetravalent actinides such as Pu and Np. The 2.5 mm edge cube (Fig. 3), weighing 0.102 g, was placed in a sealed gold capsule with 0.735 g of powdered granite and 0.022 g of H_2O (total $H_2O = 3.43\%$). The capsule was held at 780 °C and 150 MPa for 4 months, generating ~70% melting [22], before quenching. Optical examination of sections through the sample (Fig. 4) and SEM imaging (Fig. 5) revealed a perfectly sharp junction between the zirconia crystal and the granitic melt with no evidence of corrosion or reaction between the zirconia and the silicate liquid.

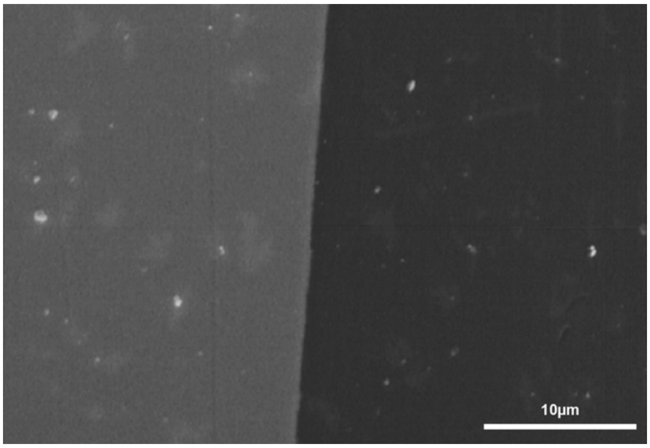

Fig. 5. Secondary electron image of the interface between Ce-doped cubic zirconia crystal (left) and quenched granitic liquid (right).

Electron microprobe analyses of the glass immediately adjacent to the interface (Fig. 6) found no Zr, Y or Ce above the detection limits indicating no material had diffused out of the crystal. Similarly analyses of the edges of the zirconia crystal revealed no Si, Al, Na or K had migrated in from the granitic melt. Laser-ablation ICP-MS analysis along traverses across the interface confirmed the absence of any reaction or diffusion of elements between the zirconia crystal and the silicate liquid during the experiment.

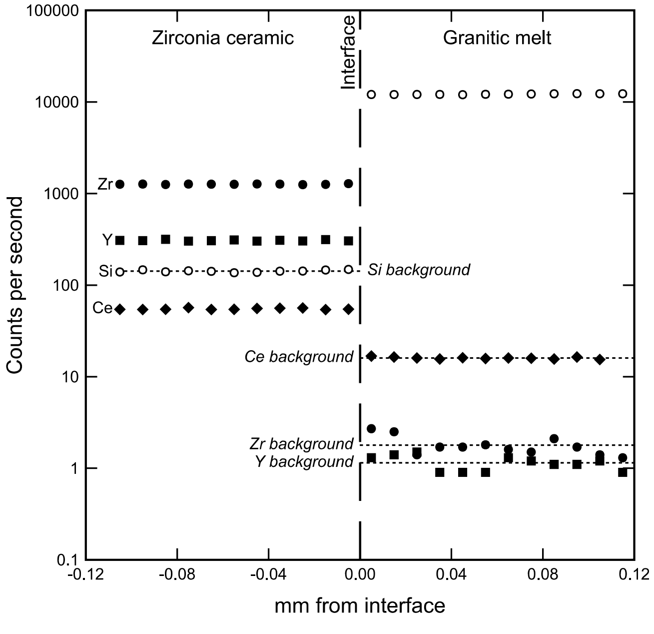

Fig. 6. EPMA count rates for Si, Zr, Ce and Y at points along a traverse across the cubic zirconia/granitic melt interface.

7. Conclusions

The results of these experiments demonstrate that mineral and ceramic waste forms proposed for the immobilisation of Pu and other actinides, such as zircon, zirconia and UO_2 (analogous to low-specification MOX) will not react with, or release their actinides to, granitic melts during the partial melting and recrystallization process required for their encapsulation in granite. Under the conditions of the proposed encapsulation they are either in thermodynamic equilibrium with the granite or they are so refractory that the kinetics of any reaction are too slow for any effects to be observed (i.e., they are in metastable equilibrium). It therefore follows that, under the much lower temperatures involved in the DBD, these phases, like their natural analogues, will survive and retain their actinides for as long as they are enclosed in the granitic rock and protected from aqueous leaching.

Hence, the Pu and/or other actinides would be contained in a stable (equilibrium) crystalline structure, which in turn, would be in stable or metastable equilibrium with the granite in which it is encapsulated. After disposal deep in the granitic continental crust, the granite cylinders would be in equilibrium with their host rock and its fluids. This 'triple equilibrium' should guarantee isolation of the radionuclides from their environment until the physical destruction of the enclosing crust by geological processes. By even the most conservative estimate this would take many millions, possibly billions, of years. On a human timescale the Pu would be effectively removed from the biosphere for ever.

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