Mineralogical Magazine, December 2012, Vol. 76(8), pp. 2911–2918

Durability of potential plutonium wasteforms under repository conditions

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[*Received 27 November 2011; Accepted 14 April 2012; Associate Editor: Nicholas Evans*]

ABSTRACT

Separated stocks of UK civil plutonium are currently held as a zero value asset in storage, as there is no final decision about whether they should be treated as a resource for future use as nuclear fuel or as waste. Irrespective of future UK government strategies regarding plutonium, at least a portion of the UK civil plutonium inventory will be designated for geological disposal. In this context, we performed a high-level review of the performance of potential wasteforms for the disposal of separated civil plutonium. The key issues considered were the durability and chemical reactivity of the wasteforms in aqueous environments and the long-term radionuclide release under conditions relevant to geological disposal. The major findings of the review, relevant not only to the situation in the UK but to plutonium disposal in general, are summarized in this paper. The review showed that, in the event of a decision being taken to declare plutonium as a waste for disposal, more systematic studies would be required to constrain the wasteform performance under repository conditions in order to derive realistic source terms for a safety case.

Keywords: plutonium, wasteforms, repository.

Introduction

Plutonium is generated in nuclear reactors from the uranium present in nuclear fuel through the capture of neutrons. It is contained within spent nuclear fuels when they are removed from the reactor, and can be extracted and recovered by reprocessing the fuels. The amount of plutonium produced during reactor operations and its isotopic composition depend on a number of factors including the type of reactor and its neutron spectrum, the mode of reactor operation, the initial level of uranium enrichment in the fuel, and the burn-up of the fuel at the time of discharge. The majority of the plutonium consists of ^{239}Pu and ^{240}Pu, with the proportion of the heavier isotopes (^{241}Pu and ^{242}Pu) increasing with increasing fuel burn-up (e.g. International Atomic Energy Agency, 1998). Separated plutonium has to be managed safely and it is currently stored in purpose-built facilities within high integrity containers at reprocessing sites, mainly as plutonium oxide powder.

Separated stocks of UK civil plutonium are currently held as a zero value asset in storage, as there is no final decision about whether they should be treated as a resource for future use as nuclear fuel (e.g. as mixed-oxide fuel (MOX) in light water reactors (LWRs), or potentially in a future generation of fast reactors) or as waste. The major part of the UK civil plutonium stocks (about 85%) originates from the reprocessing of spent fuel from Magnox reactors and the remaining part results primarily from the reprocessing of spent fuel from UK Advanced Gas-cooled Reactors (AGR) and from foreign LWR fuels (British Pugwash Group, 2009). According to the UK Office of Nuclear Regulation, the current UK holdings of civil unirradiated

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DOI: 10.1180/minmag.2012.076.8.06

plutonium (as of 31 December 2010) are 114.8 t, including 28 t of plutonium belonging to overseas organizations (Health and Safety Executive, 2011). Recently, the UK government issued a policy paper stating that its preliminary preferred policy on the long-term management of plutonium is the reuse as MOX fuel, but consideration of disposal options will continue (DECC, 2011). However, irrespective of future UK government strategies regarding plutonium, at least a portion of the UK plutonium inventory (i.e. some tonnes) will probably be designated for geological disposal (DECC, 2011).

The Nuclear Decommissioning Authority (NDA) is responsible for planning and implementing geological disposal in the UK. The NDA has set up the Radioactive Waste Management Directorate (RWMD) to develop an effective delivery organization to implement a safe, sustainable and publicly acceptable geological disposal programme. The RWMD is developing a detailed programme for research activities required to provide information on the disposal of plutonium to inform the national strategy for this material. In this context, we have performed a high-level review of the performance of potential wasteforms for the disposal of the UK stocks of separated civil plutonium under contract to the NDA RWMD (Deissmann *et al.*, 2011). Key issues considered were the durability and chemical reactivity of the wasteforms in aqueous environments and the long-term radionuclide release under conditions relevant to geological disposal in the UK. The overall aim was to improve the knowledge base about wasteform performance and to assist in the development of strategies for future experimental and modelling studies that will enhance the understanding of disposability and the expected post-closure performance of different plutonium wasteforms. Due to the generic nature of the UK programme, a number of environmental conditions that encompass possible conditions in a geological disposal facility (GDF) and various disposal scenarios were considered. In this paper we summarize the major findings from our detailed review, focussing on issues relevant not only to the situation in the UK but to plutonium and minor actinide disposal in general.

Important issues for plutonium wasteforms

A variety of potential wasteforms for plutonium and other actinides have been proposed and discussed throughout the last decades, focusing mainly on various types of glasses and a large variety of crystalline ceramic matrices. Regarding the selection of a suitable wasteform, several material properties of plutonium have to be taken into account, besides the achievable waste loading. Plutonium isotopes (and several of their longer-lived daughter nuclides, e.g. ^{237}Np and ^{235}U) pose a significant radiotoxicity hazard, requiring long-term isolation of the radionuclides from the geo−/biosphere after geological disposal. Most plutonium isotopes exhibit half-lives ranging from several thousands to hundreds of thousands of years, thus placing constraints and requirements on the long-term durability and leaching resistance of the wasteforms. The decay of plutonium isotopes produces alpha particles (energies 4 to 8 MeV) and recoiling nuclei (energies 70 to 160 keV), which can disrupt the parent matrix of the wasteform, leading to a potential deterioration of the wasteform matrix in the long-term. Helium gas formation due to alpha decay can lead to pressure build up and mechanical disruption of the matrix. The generation of heat due to radioactive decay and self-heating by release of stored energy (resulting from alpha radiation and loss of structure) requires an appropriate thermal stability of the wasteform. Furthermore, the decay of plutonium isotopes immobilized in a wasteform results in the ingrowth of (long-lived) daughter nuclides with different chemical properties to their parents, requiring a certain chemical flexibility of the wasteform to retain the daughter nuclides in the long-term. Another issue is the potential for criticality, due to the presence of fissile material (i.e. either plutonium or ^{235}U formed by the decay of ^{239}Pu). Criticality can be controlled, for example, either by the addition of neutron poisons such as gadolinium or hafnium to the wasteform, and/or by suitable design of the wasteform (e.g. regarding waste loading, size and geometry) and the geometrical arrangements in the disposal facility.

From the point of view of post-closure safety, which mostly determines disposability, the main issue is the leaching resistance of the wasteform under the conditions encountered in a GDF and the rate at which radionuclides are released and can subsequently migrate into the near- and far-field of the repository. Important factors in this context are the instability of the wasteform resulting from radiation damage, for example amorphization of a (crystalline) waste matrix, which may enhance the wasteform leachability,

https://doi.org/10.1180/minmag.2012.076.8.06 Published online by Cambridge University Press

and adverse effects induced for example by the build up of helium and the associated mechanical stress. The potential for post-closure criticality events due to the accumulation of fissile material leached from the waste matrix or due to preferential leaching of neutron poisons is similarly related to the aqueous durability of the wasteforms under repository conditions.

Potential wasteforms for plutonium and their durability under repository conditions

For more than a decade, various studies have addressed the issue of the disposition of the UK stocks of separated plutonium, by considering different options such as long-term storage, reuse as MOX fuel, or immobilization and disposal in a GDF (e.g. The Royal Society, 1998; CoRWM, 2005; British Pugwash Group, 2009; Nuclear Decommissioning Authority, 2009). The potential wasteform groups for geological disposal currently discussed by the NDA (Nuclear Decommissioning Authority, 2009) and considered in our study included nuclear waste glasses, ceramic wasteforms, low specification (storage) MOX and cementitious wasteforms (Deissmann *et al.*, 2011). Each of these alternatives is considered in more detail below.

Glasses

Vitrification of high level waste (HLW) streams from spent fuel reprocessing has been established as a suitable immobilization route for these wastes during the last decades. At present, glasses, in particular borosilicate glasses, are used on an industrial scale for the immobilization of high level wastes in the UK, France, the USA, Russia, Belgium, Germany, and Japan (e.g. Stefanovsky *et al.*, 2004; Donald, 2007; Weber *et al.*, 2009). Due to the maturity of the vitrification technology and the ability of glasses to accommodate ions with a wide range of radii and charges, a variety of nuclear waste glasses have also been investigated for the immobilization of actinides and plutonium. Glass formulations explored in this context alongside borosilicates include lanthanide borosilicate (LaBS) glasses, phosphate glasses and alkali-tin-silicate glasses (e.g. Donald *et al.*, 1997; Stefanovsky *et al.*, 2004; Harrison and Scales, 2008*a*,*b*; Harrison *et al.*, 2007, 2008). However, investigations of plutonium-bearing glasses with respect to their long-term performance in the repository environment and the associated radionuclide release are relatively rare compared to those of glasses used for the vitrification of HLW streams from fuel reprocessing, with most work being performed on borosilicate and LaBS glasses in recent years.

Investigations of the durability of glasses for plutonium immobilization have, to a large extent, been performed using short-term static test methods (e.g. Materials Characterization Center (MCC) tests, vapour hydration tests, and/or product consistency tests (PCT); see Strachan, 2001 for a description of these tests) using deionized water and more rarely explored under dynamic conditions in flow-through or column experiments (e.g. Wellmann *et al.*, 2005; Pierce *et al.*, 2007). In the majority of the experiments, inactive surrogates such as cerium, hafnium or gadolinium were used instead of plutonium. The observed leaching rates for plutonium or its surrogates are commonly between 10^{-6} and 10^{-4} g m^{-2} d^{-1} and are significantly lower than the release rates of glass matrix elements such as boron. Although these experimental results are valuable in increasing the knowledge base for these nuclear wasteforms, the information and data obtained is not directly applicable, in all cases, to the assessment of their long-term behaviour and the radionuclide release under repository-relevant conditions, because of the experimental methods applied (e.g. short-term static leach tests with deionized water).

Many of the experiments with glasses indicate that plutonium and/or its surrogates are retained in secondary phases such as plutonium oxides and/or plutonium silicates (e.g. Fortner *et al.*, 2000; Wellmann *et al.*, 2005). However, the stability of secondary plutonium-bearing phases under repository conditions (e.g. the effects of complexation of plutonium by carbonate ions) is difficult to extrapolate from short-term experiments with deionized water as the leaching agent. In addition, the influence of pH and groundwater composition under repository conditions on the glass dissolution rate (and the formation of secondary phases) is usually beyond the scope of these standardized test methods. In particular the enhanced glass dissolution rates that may occur in highly alkaline conditions due to interactions with cementitious buffer/backfill materials or cemented ILW would have to be considered.

The effects of internal alpha decay on glass wasteforms used for actinides have been investigated, for example by Weber *et al.* (1997) and Deschanels *et al.* (2007). Due to the relatively

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small effects of internal irradiation regarding changes in stored energy, glass structure and volume, it is generally thought that the chemical durability of glass wasteforms is not impaired due to alpha decay of incorporated actinides. Based on recent investigations, the effect of radiation damage due to alpha decay on the durability and leaching rates seems to be less significant in glasses compared to some ceramic wasteforms (e.g. Stefanovsky *et al.*, 2004; Wellmann *et al.*, 2005; Weber *et al.*, 2009).

Ceramic wasteforms

Various single-phase and polyphase crystalline (ceramic) wasteforms have been considered for the immobilization of plutonium and other minor actinides as an alternative to vitrification over the last few decades (e.g. Ewing, 1999, 2007; Lumpkin, 2006; Weber *et al.*, 2009; Burakov *et al.*, 2011). These matrices consist of ceramics based on a variety of single-phase formulations such as zircon, zirconia, monazite, zirconolite, pyrochlore and others as well as polyphase 'Synroc' ceramics, consisting primarily of mixtures of zirconolite, perovskite, rutile and/or pyrochlore. Crystalline ceramic matrices can incorporate plutonium and other actinides at specific lattice positions in their structures, allowing for higher loadings of specific radionuclides. In general, regarding the long-term durability and the leaching resistance, ceramic wasteforms can be seen as the most promising immobilization matrices for plutonium and actinides, as they exhibit low radionuclide release rates (e.g. Weber *et al.*, 2009). Actinide-bearing natural analogues for several of these ceramics provide further evidence of their long-term durability (e.g. Lumpkin, 2006). However, internal radiation effects due to alpha decaying nuclides can lead to lattice defects in some crystalline ceramic matrices. Therefore, the potential decrease of the durability is a matter of concern and debate for various ceramic wasteforms.

Although a wealth of information on plutonium disposal in polyphase systems, such as Synroc, or single-phase systems, such as pyrochlores and zirconia, exists in the literature (see Deissmann *et al.*, 2011 and references therein), these data are not always directly comparable, and this hinders comparison between different ceramic hosts. In particular, the assessment of the durability of different ceramic wasteforms in aqueous environments, and insight into the radionuclide release under conditions relevant to a GDF, are rather difficult to obtain by direct comparison of literature data, due to the different processing/fabrication routes employed, and different experimental conditions, as well as the widespread use of various plutonium surrogates in the experiments. In addition, rather different chemical formulations in the same ceramic systems (e.g. pyrochlore or zirconolite) have been investigated. Even when addressing compositionally similar phases that were prepared by different synthesis routes (e.g. hot isostatic pressing, cold crucible melting or sol-gel routes), the final wasteforms may exhibit some differences in their durability and leaching characteristics, due to different grain sizes, microstructure, lattice defects and/or amounts of impurities.

Many of the reported leaching data have been obtained by rather short duration tests at elevated temperatures, using deionized water as a leachant, without taking into account the influence of the pH and groundwater composition on the waste-form durability and the solubility of plutonium and/or other actinides. Thus a more systematic approach is required to derive a realistic source term for the radionuclide release under potential repository conditions. However, in general, the dissolution and leaching rates of ceramic wasteforms such as pyrochlore, zirconolite, or monazite are significantly lower compared to glasses (e.g. Weber *et al.*, 2009).

The methods that are generally used to investigate radiation effects in crystalline actinide wasteforms are heavy-ion-beam irradiation, self-irradiation by short-lived actinides (e.g. ^{238}Pu or ^{244}Cm) contained in the wasteform, or the investigation of actinide-bearing natural analogues (minerals). The response of the various ceramic wasteforms to self-irradiation is rather diverse (e.g. Lumpkin, 2006; Weber *et al.*, 2009; Ewing, 2011). For example, matrices based on zircon or zirconolite can become completely amorphous ('metamict') due to internal alpha radiation, whereas zirconia-based ceramics have a rather high radiation tolerance, and wasteforms based on monazite and zirconate-pyrochlore do not undergo a radiation-induced transformation to the amorphous state, but rather remain crystalline even up to very high doses (e.g. Lumpkin, 2006; Ewing, 2007, 2011). However, data on the leaching resistance of zirconate-pyrochlores are comparatively rare to date. Despite the crystalline-to-amorphous transitions, even completely

https://doi.org/10.1180/minmag.2012.076.8.06 Published online by Cambridge University Press

metamict zirconolites have been found to exhibit a high corrosion and leaching resistance.

Storage MOX

The storage MOX concept is based on the utilization of unirradiated MOX pellets produced in (existing) MOX fabrication facilities as a wasteform for plutonium, which would subsequently be disposed of in a GDF (e.g. Kang *et al.*, 2002; Macfarlane, 2007). The storage MOX wasteform, also referred to as 'low spec(ification) MOX' is capable of achieving high plutonium loadings of up to 20 wt.% PuO_2. In general, for storage MOX concepts it is assumed that the low spec MOX fuel pins would be mixed directly with spent fuel in disposal casks, either as assembled storage MOX elements combined with spent fuel elements, or by exchanging individual rods in the spent fuel elements, to provide a radiation barrier against illicit reuse.

Compared to the immobilization of plutonium in glasses or ceramic wasteforms, this disposal concept has received considerably less attention. Thus explicit investigations aimed at the long-term performance of low specification MOX in a GDF are rather limited. Short-term static leaching tests in deionized water, granitic water, and carbonated water indicate plutonium leaching rates around 10^{-5} g m^{-2} d^{-1}, about an order of magnitude lower than those for uranium in these tests (Harrison *et al.* 2008). Analogue evidence from the behaviour of spent MOX/UOX fuels under repository conditions suggest a high durability of this wasteform under reducing (long-term) conditions in a GDF, with plutonium release rates similar to those from ceramic wasteforms (Deissmann *et al.*, 2011). Although the long-term structural integrity of pure PuO_2 pellets is suspect due to helium accumulation and embrittlement (e.g. Ronchi and Hiernaut, 2004), this is generally not deemed to be a relevant concern for (storage) MOX.

Cementitious wasteforms

Cement and cement-based materials are widely used in radioactive and nuclear waste disposal either as immobilization grout (especially for intermediate level waste (ILW) and low level waste (LLW)) and/or cementitious backfill to maintain a high pH in the near-field, or as construction materials for disposal vaults and tunnels. Due to the low radiation stability of cement wasteforms, immobilization by cementation is mainly used for ILW/LLW rather than for HLW (e.g. Stefanovsky *et al.*, 2004).

In an analysis of credible options, the disposal of separated plutonium in a cement matrix as an option was considered, using the current ILW disposal facility concept (Nuclear Decommissioning Authority, 2009). The concept was based on mixing dry cementitious powder, water and plutonium waste leading to a homogeneous monolith in a 500 litre drum. For the reference case, a plutonium-loading of 250 g per 500 litre drum was adopted (i.e. immobilization of 100 t plutonium would produce a wasteform volume of about 200,000 m^3). In contrast to the immobilization matrices discussed before, such a wasteform would rely only on physical containment of the PuO_2 powder rather than incorporating or converting the plutonium into the structure of the matrix.

We are not aware that any investigations with respect to the long-term performance of a cemented wasteform for PuO_2-powders and/or the radionuclide release from such wasteforms under repository conditions have been conducted to date. However, the plutonium release from a cemented wasteform will be essentially governed by the dissolution kinetics of PuO_2 and its solubility under highly alkaline conditions, as well as the evolution of the cement pore water with time. The evolution of the pore water chemistry and the pH–Eh-conditions in cementitious systems have been the focus of a variety of studies during the last decades, and are reasonably well understood; various models exist to describe cement degradation and pore water evolution depending on groundwater flow rates and chemistry (e.g. Berner, 1988; Harris *et al.*, 2002). Solubility and sorption of plutonium in cementitious environments have been addressed in various experimental and modelling studies suggesting a strong sorption of plutonium to the cement matrix and a rather low solubility of about 5×10^{-11} mol l^{-1} at pH 12.5 (e.g. Baston *et al.*, 1995; Berner, 2002). We are not aware that any systematic investigations on the dissolution kinetics of calcined PuO_2 in a cementitious repository are available, although it might be inferred to be lower than for UO_2 under comparable conditions.

Discussion and conclusions

In the context of a potential future disposal of separated civil plutonium in the UK, a variety of

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potential immobilization matrices have been considered, such as different glasses and ceramic wasteforms as well as low-specification MOX and cementitious wasteforms. The amount of available information regarding their durability and leaching resistance is rather diverse for the different matrices. Regarding the development of wasteforms for plutonium disposition and their durability, work performed during the last decade has mainly focused on single-phase ceramic wasteforms and (lanthanide) borosilicate glasses. In contrast, information regarding performance and durability of 'unconventional' plutonium wasteforms such as storage MOX or cementitious wasteforms is generally sparse. In general, each of the immobilization matrices offers distinctive strengths and weaknesses. Regarding the long-term durability and the leaching resistance, in general, ceramic wasteforms can be seen as the most promising immobilization matrices exhibiting low radionuclide release rates. However, a detailed understanding of the relevant processes that govern the long-term radionuclide release and the systems behaviour under repository conditions on a molecular level is still missing. Compared to the efforts made especially during the last decade regarding the assessment of realistic source terms for the disposal of HLW from reprocessing and/or spent fuel under repository conditions, information with respect to the performance of plutonium wasteforms is rather limited.

Investigations into plutonium wasteform durability and radionuclide leaching have, to a large extent, been performed using (short-term) static test methods. These tests are closed-system tests and the experimental conditions employed (e.g. regarding solution chemistry and atmosphere) are rather different from the conditions that the wasteforms will be exposed to in a geological disposal facility in the long-term. In particular, these test methods cannot address the open-system behaviour in a repository and especially processes involving mass transport. Furthermore, most investigations used surrogates such as cerium, hafnium and gadolinium instead of plutonium. Thus the results can only be applied with some limitations, because none of the surrogate elements/compounds is capable of simulating all facets of the behaviour of plutonium (e.g. with respect to its solution chemistry, Bingham *et al.*, 2008; Curti *et al.*, 2012).

Overall, for the disposal of separated plutonium as a waste, more systematic studies are required to assess the long-term performance of a wasteform in the disposal environment. These studies should aim to determine the impact of the range of conditions that might be encountered in a GDF on the long-term behaviour and the radionuclide release rates from different plutonium wasteforms to derive realistic source terms for a safety case and to explore the safety margins of the various potential wasteforms.

In order to derive more realistic source terms, future experimental programmes on the performance of wasteforms for plutonium disposal should focus on (1) wasteform dissolution and radionuclide release rates under realistic repository conditions; (2) characterization of secondary phases formed during plutonium wasteform dissolution; and (3) effects of radiation damage on wasteform performance and aqueous durability. For this purpose, in addition to simple short-term leaching tests, more fundamental and mechanistic studies are required to pair experiments and theory at the molecular level with modelling at larger spatial and time scales, to predict the long-term performance of the potential wasteforms, taking also into account factors affecting plutonium solubility in the repository environment (e.g. colloids, organics, redox processes and microbial effects).

Acknowledgements

The work summarized here was funded by, and undertaken for NDA RWMD. The manuscript benefited from the comments of three anonymous referees.

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