Behaviour of Alpha Emitters in Cement – 16139

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ABSTRACT

Alpha emitting radioelements can interact with cements in a number of ways. Alpha-radiolysis of water produces hydrogen that may pressurise and damage the structure, and it is postulated that the intense alpha radiation field around waste particles containing high alpha activity can cause mineralogical changes in the hydration products. In addition, their solubility in cement pore fluid can be increased by complexation with organic materials such as the degradation products of cellulose, which itself may be promoted by alpha irradiation. Analysis of pore fluid expressed from cements containing plutonium and a range of organic materials has demonstrated their effect on plutonium solubility. Calculations of hydrogen pressurisation as a result of alpha radiolysis suggest that radiolytic hydrogen will not exceed tensile strength of the cement. Further work is described in which cements containing high loadings of plutonium will be examined in the NNL Central Laboratory to investigate mineralogical changes during and after hydration.

INTRODUCTION

In the UK, Portland cements blended with fly ash (pulverised fuel ash, PFA) or blast-furnace slag (BFS) are typically used to encapsulate wastes containing actinides. The resulting immobilised waste products comprise the waste, cement hydrate phases and a network of pores containing free water, with the latter typically making up 20% or more of the mass of the waste product [1].

The waste products are to be stored for several decades before transporting to a geological disposal facility (GDF) where further storage will take place over an extended period prior to backfilling and closure. During the stages prior to backfilling and closure, the waste products are designed to remain essentially monolithic.

Following closure, chemical conditioning by a combination of solubility control and sorption is a key component of a multi-barrier disposal concept [2]. Factors which may affect the solubility and sorption of long-lived radioelements are therefore an important consideration, since dissolution in the pore solution and subsequent diffusion/leaching may provide a route to mobilisation. Prior to GDF closure, factors affecting the physical properties of the waste products are also important.

This paper considers a range of processes involving the interaction between actinides and cements which are relevant to waste product storage and disposal, including;

- The effect of some organic materials on the solubility of plutonium within cement pore fluid, part of a programme carried out for UK Nirex and the European Commission [1]
- The radiolytic generation of hydrogen gas and its potential to cause changes to the cement structure, potentially detrimental to intermediate and long term storage.
- Modifications to cement chemistry and microstructure resulting from highly localised damage around actinide-rich particles present within products containing spent fuel and plutonium contaminated materials and which may affect mechanical properties relevant to storage and transport, or the sorption properties relevant to geological disposal.

The latter process is a project within the DISTINCTIVE programme [3], and early progress with this work is described here.

DESCRIPTION

Pore Fluid Extraction

The experimental approach most often used to investigate behaviour of radionuclides under disposal conditions involves measurement of their solubility and their sorption onto cements [4,5]. In a project supported by UK Nirex and the European Commission an alternative approach was adopted. The method of pore-fluid extraction (PFE) was used to study radionuclide behaviour in cementitious materials and simulated immobilised wastes. A selection of the results from this project that are relevant to the behaviour of alpha emitters are included here. The organic constituents of some ILWs have the potential to degrade and increase the solubility of many significant radionuclides**.** The most significant organic waste constituent appears to be cellulose. Cellulose powder, its alkaline degradation products, including isosaccharinic acid (ISA)(2-C-(hydroxymethyl)-3-deoxy-D-pentonic acid) and a simulated Plutonium Contaminated Material (PCM) were incorporated into cement specimens. Cellulose leachate was prepared by contacting tissue with water at 80°C for 28 days under anaerobic conditions, and the leachate was added to cement at 1% by mass of cement powder. ISA was added to the mix water at concentration 0.01 mol.dm^{-3}. The PCM simulant was a mixture of cellulose (6 wt % paper and cotton) with a range of other polymers (PVC, polyethylene "Hypalon", "Neoprene" and "Latex"), added at 45% by mass of cement powder. The test specimens used in all experiments were cylinders of 45 mm diameter and 90 mm height. Cements were prepared using either demineralised water or a simulated groundwater with salinity equivalent to 0.5 mol.dm^{-3} sodium chloride. A mixed isotope process liquor, containing plutonium as nitrate was included in the mix water at time of mixing. Organic materials were also incorporated at time of mixing. Samples prepared using demineralised water represent, for example, in-drum mixing, where the cement is hydrated in contact with radionuclides. This is

relevant to the encapsulation grouts 3:1 BFS/OPC and 3:1 PFA/OPC currently used in these processes. However, even with the incorporation of saline ground water simulant, this mixing method is less relevant to backfill materials, represented in these experiments by the Nirex Reference Vault Backfill (NRVB) [6], as this material will not come into contact with radionuclides or groundwater during hydration. After curing for 28 days at ambient temperature and at 80°C, the free pore-water was extracted under high tri-axial pressure using the extraction technique initially developed by Longuet et al [7]. The pore-water expressed (typically 2-10 cm^3) was passed through a 0.45µm filter. For specimens cured at 80°C, the die body was pre-heated to minimise any temperature decrease during pore fluid extraction. Heating was maintained during pore-fluid extraction. The pore solutions were analysed by electrodeposition followed by α-spectrometry using a plutonium-236 internal standard.

Effect of Radiolytic Hydrogen

The implications of gas generation from a range of sources in GDF conditions has been extensively studied and modelled, for example in [8]. The approaches used generally consider macro-scale effects. This is also the case for previous investigations of the effects of alpha radiolysis, which have involved the measurement of the volume of gas evolved from cemented samples to obtain G-values which are then used to calculate the rate of gas volume production and consequently, pressurisation of waste product.

Alpha radiolysis is a source of hydrogen generation in cemented wasteforms. The rate of hydrogen generation in a variety of materials has been determined experimentally, and an effective radiolytic gas generation rate, or G, value of 0.5 molecules/100eV has been recommended by US Nuclear Regulatory Commission for solidified aqueous concreted waste [9]. Using the bounding $G(H_2)$ value approximately 0.09 litres hydrogen per day would be generated in a 500 litre wasteform containing 1 TBq of alpha emitters (with average alpha energy 5.35 MeV), for example.

To calculate the maximum resulting pressure within such a wasteform, the method described by Farmer [10] has been used, simplified to provide a steady state solution for a one-dimensional system, with no radial dependence. If it is pessimistically assumed that all hydrogen escapes at the top surface of the cylindrical wasteform, with no leakage pathways around the base or edge of the drum the steady state pressure at height X above the base of the wasteform drum is estimated by:

$$\rho^2 = \frac{\rho_A^2 + Q\,(H^2 - X^2)}{\lambda} \qquad \text{(Eq 1)}$$

where
ρ = gas density (kg m^{-3})
ρ_A= atmospheric density (hydrogen) 0.083 kgm^{-3} at 293K
H = the height of the drum (1.125 m for a 500 ℓ drum)
X = the height above the base of the drum
T = temperature (K)
Q = gas generation rate (kg m^{-3} s^{-1})

$$\lambda = \frac{k\ R\ T}{\mu M}$$

where
k = gas permeability (m^2)
T = temperature = 293K
R = gas constant = 8.314 J mol^{-1} K^{-1}
M = molecular weight = 2.00×10^{-3} kg mol^{-1}

Using the ideal gas law, the gas density may then be converted to pressure in $N.mm^{-2}$, to allow comparison with tensile strength. If the equilibrium gas pressure is less than the tensile strength of the cement, then it is assumed that the product will not crack.

Mineralogy of Irradiated Cements

Recent investigations of the gamma irradiation resistance of blast furnace slag-containing cements indicated that, even up to an unrealistically high dose rate of 18.6 kGy/hr and total dose of 4.77 MGy over a 256 hour period, the crystalline phases present in the system were not modified [11]. However, a reduction of water within the cement binder resulted in micro-cracking and increased porosity. No work has yet been carried out to investigate the effects of alpha irradiation on either mineralogy or microstructure.

As part of the DISTINCTIVE programme, University of Sheffield and NNL are collaborating to extend the understanding of the interaction between alpha emitters and cements. Investigations by NNL involve the preparation of specimens of cement with plutonium dioxide loading up to ~0.5% by mass. This is considerably higher than in any wastes that are currently immobilised in cement, but are intended to understand the nature of any interactions. A range of cement blends will be prepared, including PFA/OPC, BFS/OPC and a Magnesium Phosphate cement.

Following curing over a period of approximately one year, these will be characterised using a range of methods available in the NNL Central Laboratory, including electron microscopy (scanning and transmission), X-ray microtomography, X-ray diffractometry and thermogravimetric analysis. These methods are intended to examine the cement mineralogy, particularly in the region of the interface between cement hydrates and plutonium oxide particles. By measuring the volume of gas evolved during curing, the project will also add to the

body of information on alpha radiolytic gas production.

There is continuing interest in the interaction between organic materials and cement. In particular, it is expected that organic cement additives such as superplasticisers will be used in the construction of a GDF and may also be present in some wasteforms. Therefore, samples containing a polycarboxylate superplasticiser will also be produced. Leach testing of the cured samples will be used to provide additional information on the interaction between organic materials and cement under conditions of alpha radiolysis.

Several phases present in cement blends used for radioactive waste immobilisation have been shown to sorb plutonium, with the dominant phase being CSH [12]. The DISTINCTIVE project at University of Sheffield will therefore investigate the effect of alpha radiation on these phases, which due to high energy and short penetration distance, may result in localised effects in the immediate vicinity of waste particles.

DISCUSSION

Pore Fluid Extraction

The solubility of plutonium in reducing conditions and at alkaline pH has generally been found to be in the region of 10^{-10} mol.dm-3, with Thomason and Williams [3] reporting $7x10^{-11}$ mol.dm^{-3} and Greenfield et al [4] reporting $4x10^{-10}$ mol.dm^{-3} for example. The latter also investigated the effects of anaerobically degraded cellulose degradation products on solubility and found that the solubility increased to $7.5x10^{-10}$ mol.dm^{-3} in solutions of 10% cellulose loaded leachate.

Table I reports the measured plutonium concentrations in the pore-fluid extracted after curing grout samples at ambient temperature and 80°C and in the absence of organic additives. In most cases, the plutonium concentration in the pore-fluid was reasonably comparable to the expected solubility. In some cases, significantly higher values were observed. This may reflect the presence of colloidal material that passed the filter but, alternatively may be due to experimental scatter. It was concluded that the plutonium concentrations are controlled by solubility at high pH.

The results of experiments containing quantities of organics cured under anaerobic conditions, are summarised in Table II and Figure 1, which also includes Total Organic Carbon (TOC) measurements for parallel experiments on non-radioactive samples for comparison.

TABLE I. Plutonium Pore Fluid Concentrations at Ambient Temperature and 80°C, Aerobic Conditions for 28 Days

Cement	Mix Water	Initial Plutonium Concentration in Mix Water ($mol.dm^{-3}$)	Plutonium Pore Fluid Concentration ($mol.dm^{-3}$)	
			Ambient	80°C
3:1 PFA/OPC	Demineralised	$5.8x10^{-6}$	$(1.8\pm0.5)x10^{-10}$	$9.0x10^{-10}$
3:1 PFA/OPC	Demineralised	$5.8x10^{-7}$	$3.2x10^{-10}$	$\leq 1.3x10^{-10}$
3:1 PFA/OPC	Saline	$5.8x10^{-6}$	$1.0x10^{-9}$	$5.7x10^{-10}$
3:1 PFA/OPC	Saline	$5.8x10^{-7}$	$2.7x10^{-10}$	$3.2x10^{-10}$
3:1 BFS/OPC	Demineralised	$5.8x10^{-6}$	$9.1x10^{-10}$	$3.0x10^{-10}$
3:1 BFS/OPC	Demineralised	$5.8x10^{-7}$	$8.0x10^{-9}$	$4.8x10^{-10}$
3:1 BFS/OPC	Saline	$5.8x10^{-6}$	$2.7x10^{-10}$	$3.5x10^{-9}$
3:1 BFS/OPC	Saline	$5.8x10^{-7}$	$5.5x10^{-9}$	$3.4x10^{-9}$
NRVB	Demineralised	$5.8x10^{-7}$	$3.2x10^{-10}$	$\leq 1.1x10^{-10}$
NRVB	Saline	$5.8x10^{-6}$	$2.1x10^{-9}$	$5.3x10^{-10}$
NRVB	Saline	$5.8x10^{-7}$	$5.6x10^{-10}$	$\leq 1.0x10^{-10}$

TABLE II. Effect of Organics on Plutonium Concentrations in Pore Fluid Expressed From Specimens Prepared with Saline Groundwater. Anaerobic Curing for 28 Days at 80°C. Initial Pu concentration 10^{-5} $mol.dm^{-3}$

Cement	Organic	Plutonium Final Concentration ($mol.dm^{-3}$)	pH	Total Organic Carbon (ppm)
3:1 PFA/OPC	None	$2.7x10^{-10}$	12.8	510
3:1 PFA/OPC	Cellulose Leachate (1%)	$9.4x10^{-10}$	12.5	900
3:1 PFA/OPC	Cellulose (12%)	$1.9x10^{-9}$	7.8	-
3:1 PFA/OPC	PCM simulant	$6.8x10^{-9}$	12.3	-
NRVB	None	$3.6x10^{-10}$	12.2	390
NRVB	ISA (0.001 $mol.dm^{-3}$)	$3.5x10^{-10}$	12.1	-
NRVB	ISA (0.01 $mol.dm^{-3}$)	$5.1x10^{-10}$	12.5	1120
NRVB	Cellulose Leachate (1%)	$5.9x10^{-10}$	12.4	560
NRVB	PCM simulant	$5.9x10^{-9}$	11.8	-

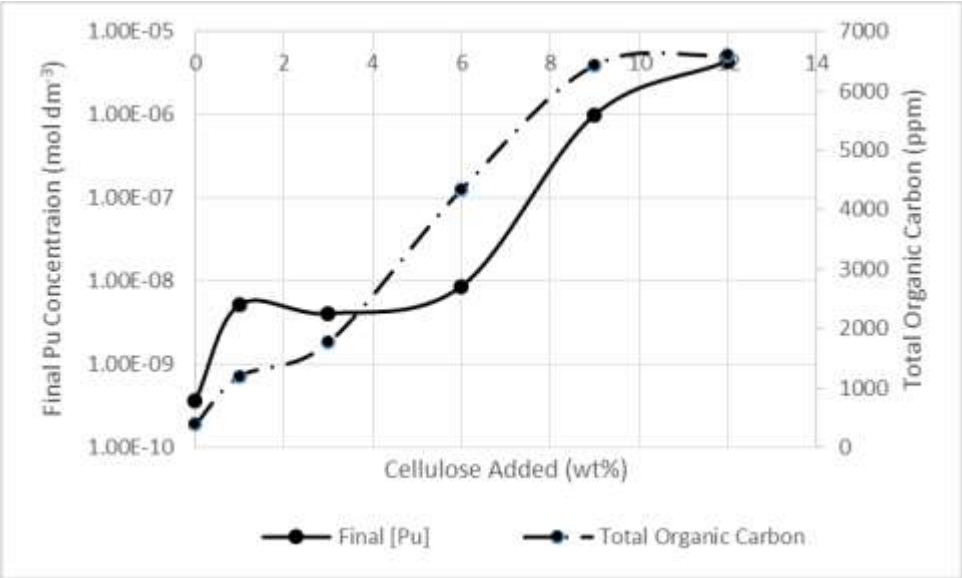

Fig 1. Influence of Cellulose Powder Loading on Plutonium Concentration and Total Organic Carbon Levels for NRVB Prepared From Saline Groundwater, Anaerobic Curing at 80°C for 28 Days. Initial Pu concentration 10^{-5} mol.dm^{-3}

The addition of ISA and cellulose leachate appeared to have little effect on the plutonium concentration. There was an apparent increase in the plutonium concentration by up to an order of magnitude using a realistic loading of PCM simulant. Only moderate enhancements in concentration were found for higher organics loadings, including up to 3% cellulose powder and PCM simulant. With exaggerated additions of greater than 6% cellulose powder, it was possible to increase plutonium pore fluid concentrations by four orders of magnitude.
The absence of an effect of ISA may be due to degradation during curing at elevated temperatures. It is possible that dissolved species in the mix water could be incorporated in the cements as they set and cure. If this applied to the cellulose degradation products and ISA it could reduce their concentrations in the pore fluids and decrease their impact on plutonium solubility. For samples that incorporate cellulose powder, the extent of degradation of the cellulose during curing is uncertain and it is also possible that degradation products might be incorporated into the cement during curing. These uncertainties may explain the differences between the plutonium concentrations found in the extracted pore fluids and those measured by other researchers in leachates from the degradation of cellulose.

Effect of Radiolytic Hydrogen

The peak pressure in a cylindrical wasteform pressure occurs at the base of the drum, assuming no leakage pathways around the base or edge of the drum. Figure 2 shows the predicted pressure at the drum base as a function of grout gas permeability for a wasteform containing a high alpha inventory of 1 TBq with average alpha energy 5.35 MeV and assuming $G(H_2)$=0.5 molecules/100eV.
For most wasteforms, the gas permeability is likely to be in the region of 10^{-18} m^2, although this is dependent on saturation of the material. If the tensile strength of

the cemented waste is similar to concrete at ~2-4 N/mm^2 depending on class [13], there would be insufficient gas pressure from alpha radiolysis alone to exceed the tensile strength and alpha-radiolytic gas generation would not result in wasteform cracking.
However, the modelling approach is somewhat simplified and would benefit from refinement to take account of factors such as;

- the effect of high local concentration of alpha activity, for example due to inhomogeneity of the waste itself or segregation prior to initial set due to differential density of the waste and grout;
- the effect of hydrogen generation within closed porosity that does not contribute to measured gas permeability;
- chemical reactions between the cement and waste which may result in changes to material properties. For example, reaction products may form at the interface between waste particles and the cement matrix, thereby reducing the local porosity/permeability, and;
- alpha radiolysis of the cement hydration products may result in changes to the physical properties. For example, changes to the structure of the calcium silicate hydrates which provide most of an aged cement's strength may decrease the tensile strength.

The experiments described above to investigate the microstructure and mineralogy of cement incorporating plutonium dioxide aim to better understand these possible effects.

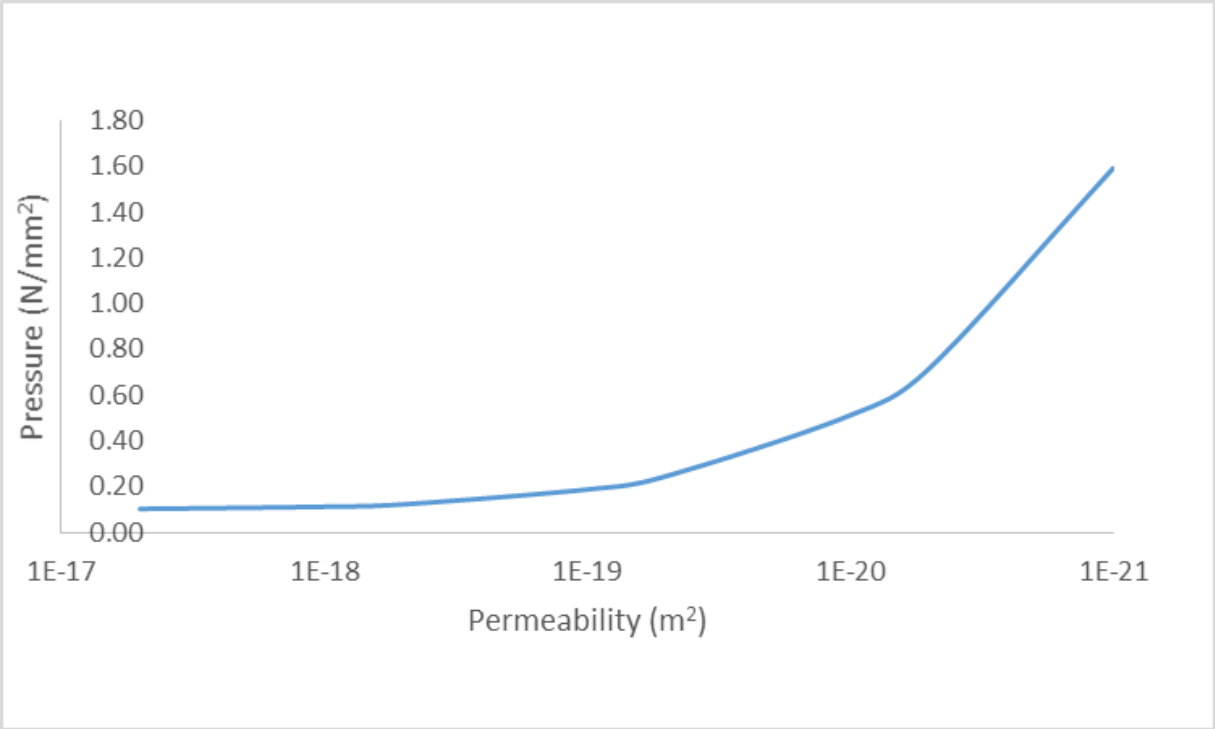

Fig 2. The Effect of Permeability on Maximum Hydrogen Pressure in a 500 litre Cemented Wasteform Containing 1 TBq Alpha Activity

CONCLUSIONS

The pore fluid expression method has confirmed that organic materials, in particular cellulose, are capable of enhancing the concentration of plutonium in the pore fluid of cements used in waste immobilisation and as potential backfill in a geological disposal facility. This is consistent with previous studies using solubility and sorption measurements. However, previous work has not examined the effect of high levels of alpha irradiation on organic materials either within the cement pore fluid, sorbed onto, or incorporated within cement hydrates. The current DISTINCTIVE project provides the opportunity to investigate these conditions.

Based on bulk cement properties and using conservative assumptions, the rate of hydrogen production due to alpha radiolysis is unlikely to generate gas pressures that would exceed the tensile strength of cement blends used for waste immobilisation. However, the modelling approach is somewhat simplified and would benefit from refinement to take account of a range of factors, particularly the highly localised deposition of alpha energy.

The facilities available within the NNL's Central Laboratory are capable of handling high inventories of alpha materials. In conjunction with the DISTINCTIVE project, the NNL and University of Sheffield are collaborating to prepare and analysis plutonium dioxide containing cement samples. These experiments will investigate the mineralogical and microstructure changes as a result of alpha radiation to better understand degradation mechanisms and retention of radionuclides in wasteforms, including the influence of organic materials.

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