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Hydrogen yields from water on the surface of plutonium dioxide

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HIGHLIGHTS

- Hydrogen evolution due to water radiolysis on samples of Sellafield PuO_2.
- Sharp increase in hydrogen evolution above 75% relative humidity.
- Hydrogen evolution due to radiolytic rather than thermal reaction.
- Analysis of trends from literature data.

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ABSTRACT

The long term storage of separated plutonium dioxide (PuO_2) in sealed canisters requires an understanding of the processes occurring within the cans. This includes potential mechanisms that lead to can pressurisation, including the radiolysis of adsorbed water forming hydrogen. New measurements of H_2 production rates from three sources of PuO_2 show low rates at low water monolayer coverage but a sharp increase between 75% and 95% relative humidity. This behaviour being quite different to that reported for CeO_2 and UO_2, which, therefore, cannot be considered as suitable analogues for PuO_2/H_2O radiation chemistry. It is concluded that surface recombination reactions are likely to be important in the radiation chemistry and that the H_2 production arises from a radiolytic process and not a thermal reaction, at least in these experiments.

1. Introduction

There is a large amount of plutonium dioxide (PuO_2) in storage around the world, including a large stockpile at the Sellafield site (United Kingdom). The vast majority of UK PuO_2 is derived from reprocessing of spent uranium metal fuels from UK Magnox reactors ("Magnox" PuO_2) or reprocessing of spent oxide fuels from UK Advanced Gas Cooled reactors or foreign light water reactors in the Thorp reprocessing plant ("Thorp" PuO_2). The UK stockpile has accumulated over the last ~50 years. The UK Government is now considering eventual re-use of this Pu as mixed oxide fuel for thermal reactors [1,2]. Current "Magnox" PuO_2 product is contained in an aluminium screw top container, inside a polyethylene (PE) bag and contained in a welded outer steel container. Similarly, "Thorp" PuO_2 is contained in a stainless steel screw top inner can held within a vented intermediate can placed inside a welded outer container. Conditions are carefully controlled during production and packaging to limit water adsorption into the PuO_2 powder and to meet acceptance criteria for storage (e.g. specific surface area). Very similar arrangements have been adopted by the United States Department of Energy (DOE) for storing US PuO_2, as described in the DOE 3013 standard [3].

Of thousands of cans in stores only a few "out-of-specification" cans containing very wet material are known to have pressurised. This empirically vindicates the acceptance criteria specified for storage. Even so, this is perhaps surprising because PuO_2 adsorbs water up to many monolayers and it might be expected that this water would be radiolysed to hydrogen and oxygen, thus pressurisation should be observed even for cans that meet specifications for water content (*via* LOH: Loss on Heating measurements). It is highly unlikely that at these high dose rates, typically 8 W kg^{-1}, radiolysis does not occur so it must be assumed that a reverse reaction, such as recombination of radiolysis products on the surface of PuO_2, also occurs. Little is known about either process, although there are other reports of hydrogen production from PuO_2 [4–6] and can pressurisation was reported at Harwell nearly 50 years ago [7].

Abbreviations: DOE, (US) Department of Energy; GC, gas chromatography; LOH, Loss on Heating analysis; PE, polyethylene; RH, Relative Humidity; SSA, specific surface area.

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Table 1
SSA of PuO_2 samples.

Sample	SSA ($m^2\ g^{-1}$)	Specific activity (Bq-α g^{-1} Pu)	MeV (total) ($s^{-1}\ g^{-1}$ Pu)
Magnox	8.9 ± 1.1	5.5×10^9	2.9×10^{10}
Thorp	6.1 ± 1.0	1.8×10^{10}	9.6×10^{10}
Ex-LOH	2.1 ± 0.8	6.1×10^9	3.1×10^{10}
Slurry samples	8.9 ± 1.1	5.2×10^9	2.8×10^{10}

Although the vast majority of cans do not pressurise, it is clear that there is a considerable amount of chemistry occurring within them [8]. In "Magnox" PuO_2 cans N_2 and O_2 are radiolysed initially to oxides of nitrogen and PE undergoes thermal and radiolytic reactions which adsorb oxygen. The result is that some cans actually depressurise initially. "Thorp" PuO_2 is stored under argon with a metal intermediate can rather than a PE bag so neither of these mechanisms applies. Due to its higher specific activity, "Thorp" PuO_2 self heats to higher temperatures and develops higher pressures from He production. Furthermore, there is still controversy as to whether PuO_2 can thermally react with H_2O to form PuO_{2+x} and H_2 [9]. Note also that during prolonged storage the morphology of the PuO_2 is expected to change as ^{241}Pu decays to ^{241}Am, He from alpha decay builds up and is gradually evolved into the gas phase and radioactive decay products damage the PuO_2 lattice [10].

So whilst there is plenty of operational experience in the safe and secure storage of PuO_2 in sealed canisters on nuclear licensed sites, there remains a clear need to underpin storage through better understanding of the fundamental chemical and physical processes occurring within the storage cans. Improved scientific understanding can also reduce some of the pessimisms built into stores' safety cases giving operational benefits such as allowing wider package specifications or extended package lifetimes.

In work described in this report, production line samples of "Thorp" and "Magnox" PuO_2 were used to provide material with different specific activities and specific surface areas (Table 1). Both plants use the oxalate conversion route with calcination at ~600 °C leading to variations in SSA [11]. Also a "Magnox" PuO_2 sample that had been used for measurement of weight changes from heating (LOH analysis) was used. As this material had been heated to >950 °C the specific surface area was substantially reduced due to partial sintering causing closure of pores with consequent loss in porosity and morphological changes [11]. These three samples thus provide variations in the number of monolayers of water that will be adsorbed onto the PuO_2 and the energy (dose) transferred to the adsorbed water molecules, the key factors that should determine radiolytic yields of H_2. Also a range of relative humidities (RHs) were studied from 0% to 95%. All experimental work was carried out at room temperature.

2. Experimental methods

2.1. Overview

Four different sources of PuO_2 samples were obtained for study:

- "Magnox" PuO_2 (denoted M).
- "Thorp" PuO_2 (T).
- Ex-Loss on Heating PuO_2 (L) – a sample of "Magnox" PuO_2 production material heated to ~950 °C during routine LOH analysis (to check product quality) thus altering morphology and reducing specific surface area (SSA), and
- Second sample of "Magnox" PuO_2 used for slurry experiments (S).

Samples were dried and then equilibrated in atmospheres with a range of relative humidity from 0% to 95% with intermittent weighing to confirm hydration levels. Samples were labelled M*X*, T*Y* or L*Z* to represent the material type and the degree of humidity to which they were exposed. For example, M95 denotes "Magnox" PuO_2 exposed to 95% humidity and *LD* for Loss on Heating "Magnox" PuO_2 that has been kept dry, i.e. exposed to 0% humidity. Two experiments using slurries of PuO_2 were labelled S and SN, the N denoting nitrite doping. Finally, gas samples were taken at intervals and analysed for H_2. Three series of measurements were taken to enable an average H_2 evolution rate to be calculated. The atmosphere in the irradiation vessels was completely refreshed to remove evolved hydrogen between each series. Further experimental details are given below.

2.2. Plutonium oxide samples

The specific surface area (SSA) and specific activity (alpha) for each of the samples are given in Table 1 and the isotopic composition in Table 2.

Approximately 0.4–1.0 g of PuO_2 powder was used in these experiments. All of the samples were 'dried' for 30 days prior to the experiment by storing in desiccators. Initially calcium sulphate anhydrite, $CaSO_4{\cdot}nH_2O$ (where n = 0–0.05), was used as a desiccant. Half-way through the drying period the desiccant was changed to phosphorus pentoxide (P_2O_5) to further improve the drying process. The mass of each sample was recorded at intervals through the drying period to check progress. It is assumed that two monolayers of water were not removed during the drying process, one being chemisorbed to the PuO_2 surface and a second being physisorbed to the first. Similarly, Stakebake and Steward [12] reported three monolayers of water on PuO_2 which had been repeatedly equilibrated with water vapour and dried.

At the end of the drying process the samples were transferred to a vessel with a controlled atmosphere to equilibrate with a humid atmosphere. For the samples which required equilibrating at 25%, 50%, 75% and 95% Relative Humidity (RH), the appropriate molarity of sulphuric acid based on literature information was used to generate the RH required [13].

The slurry samples (~0.05 g PuO_2) were treated differently in that they were mixed with deionised water (~1 mL), sample SN also being doped with 2 mM sodium nitrite solution.

The sample vessel for the radiolysis experiments consisted of two parts: a small glass "inner vessel" which held the plutonium dioxide, and an "outer vessel" of a quickfit test tube which held the drying agent or sulphuric acid. The quickfit test tubes were fitted with a vacuum rated valve to enable gas samples to be removed for analysis.

The quickfit test tube was first loaded with the drying agent or sulphuric acid then with the tube containing PuO_2. The valves were placed on the tubes but were initially left open so that hydrogen associated with the samples could escape. Once all the vessels were filled with drying agent/sulphuric acid and PuO_2, the vessels were carefully agitated and evacuated to 0.1 bar using a hand pump to further remove hydrogen before back filling with air. A further evacuation to 0.1 bar was undertaken to leak test the equipment plus ensure complete removal of hydrogen gas associated with the PuO_2. The vessel was then back filled with air before shutting the valve.

Table 2
Isotopic composition of the PuO_2 samples used.

Isotope fraction	Magnox	Thorp	Ex-LOH	Slurry (Magnox)
Pu-238	0.0025	0.0217	0.0028	0.0025
Pu-239	0.7119	0.5379	0.6935	0.7119
Pu-240	0.2341	0.2862	0.2505	0.2341
Pu-241	0.0373	0.0745	0.0377	0.0390
Pu-242	0.0119	0.077	0.0131	0.0119
Am-241	0.0023	0.0026	0.0023	0.0006