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Radiation chemical processes in the water layer on the surface of PuO_2

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It is generally accepted that radiolysis of water on the surface of PuO_2 by alpha particles is the source of H_2 which can cause pressurisation in sealed storage containers if the material is not adequately conditioned before packing. The mechanisms for this have not been discussed in detail previously. Radiolysis mechanisms of bulk water are summarised and then applied to water at the surface of PuO_2. It is shown that the radiolysis processes occurring on timescales of less than 1 ps after energy deposition could have an impact on the storage behaviour of the PuO_2 and the potential gas volume generated. Some of the radiolysis products are highly reactive and would be expected to react with plutonium at the surface, affecting the usual water radiolysis processes. A corollary of this observation is that the surface should not be considered a completely crystalline PuO_2 solid. It is also highlighted that whilst there are significant uncertainties in the radiolysis process at the PuO_2 surface there are also significant uncertainties in H_2 formation mechanisms in bulk water. Finally, methods to model the radiolysis process at the surface and the prospects for predictive models are briefly discussed with suggestions for future areas of development.

KEYWORDS

plutonium oxide, radiation chemistry, hydrogen, water radiolysis, plutonium storage

1 Introduction

The potential for radiolytic production of H_2 from moist PuO_2 was recognised as soon there was a requirement to store plutonium powder outside of glovebox containment. As long ago as 1965 there was a report on pressurised sealed cans containing plutonium residues in the United Kingdom (UK) (Hodkin et al., 1965), and internationally there have been documented pressurisation events involving stored plutonium, with detailed reports most readily available in the public domain from the United States (US) (US DOE, 1979; Eller et al., 1999). These events led to pragmatic requirements for the conditioning of plutonium for storage in sealed cans based on a mixture of empirical studies and operational experience. Requirements for storage were initially developed for/by individual facilities, but with limited underpinning information published (Cuillerdier et al., 1984). It was in the early 1990s that the US Department of Energy issued the 3013 standard for storage of plutonium-bearing materials, which was first issued in 1994 to apply to US government facilities and has been updated several times based on new information from operational experience and research (US DOE, 2018).

It is only relatively recently that attempts have been made to systematically study the radiolytic gas generation from stored plutonium oxide; initially by Duffey and Livingston (2002) followed by several others (Vladimirova and Kulikov, 2002; Veirs et al., 2012; Sims et al., 2013; Narlesky, 2018; Veirs et al., 2019; Venault et al., 2019; Webb et al., 2023). Most of these papers reported measurements of H_2 production but little mention of mechanisms was provided although some general comments were made by Sims et al. (2013) From these studies it is seen that H_2 production increases with increasing water content, and in most studies radiation chemical yields of H_2 per unit dose $[G(H_2)]$[1] increased with water content, implying the H_2 production process is more efficient as the number of water layers increases. Key observations in the study by Duffey and Livingston (2002) were that, even with quite high levels of moisture on the PuO_2, adding an overpressure of H_2 to the apparatus initially resulted in a reduction in the net production rate of H_2, whilst increasing the pressure still further resulted in consumption of hydrogen. This indicates that there was a hydrogen removal mechanism. More recent studies of high purity PuO_2 in small, sealed vessels by Veirs et al. measured simultaneously the gas pressure, gas composition, and relative humidity providing further important insights. Specifically, that 1) molecular water on the surface reacts through a radiolytic process to form a phase that does not contribute to hydrogen generation, 2) the hydrogen and oxygen concentration reaches a peak in a closed system and then gradually decreases, and 3) radiolytic O_2 production is only formed at higher water contents (Veirs et al., 2012). Venault et al. (2019) studied the yield of hydrogen from PuO_2 exposed to constant relative humidity but observed some differences from other studies; the initial production rate of H_2 decreased until a steady state hydrogen concentration was reached that was much lower in concentrations for freshly produced PuO_2 than observed in US or UK studies. In contrast, the steady state was not observed for samples of PuO_2 that had aged. Repeated heating of the aged PuO_2 restored the original hydrogen generation behaviour suggesting a reaction that was dependent on the surface condition. Finally, experiments by Webb et al. (2023) have shown that subtle effects from the production route of the PuO_2 and ambient atmosphere influences the rate of radiolytic hydrogen production. Similar observations of varying radiolytic H_2 production rate with ambient atmosphere have also recently been made during irradiation of alumina (Parker-Quaife et al., 2020).

There have been a large number of measurements of H_2 formation during irradiation of water adsorbed on oxide surfaces other than PuO_2 as well as slurries of oxide powders (Nakashima and Masaki, 1996; Petrik et al., 2001; LaVerne and Tandon, 2003). This field was reviewed by LaVerne et al. (2011) and by Le Caër (2011) in 2011 and the topic remains an active area of research with significant further publications (Ali et al., 2012; Fourdrin et al., 2013; Lainé et al., 2017; Yin et al., 2019; McGrady et al., 2021; Conrad et al., 2022; McGrady et al., 2023). In the first major systematic study of oxides, Petrik et al. (Petrik et al., 2001) divided metal oxides into three groups: those that enhanced the yield of H_2 relative to their reference/control experiments with water/water vapour in sealed ampoules (Ga_2O_3, Y_2O_3, La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Yb_2O_3, Er_2O_3, HfO_2, and ZrO_2); those that had yields similar to reference experiments (MgO, CaO, SrO, BaO, ZnO, CdO, Cu_2O, NiO, Cr_2O_3, Al_2O_3, CeO_2, SiO_2, TiO_2, Nb_2O_5 and WO_3); and those that had lower hydrogen yields than the reference experiments (MnO_2, Co_3O_4, CuO, and Fe_2O_3). However, there is some uncertainty in these groupings because later studies measuring $G(H_2)$, evaluated with respect to the radiation energy directly absorbed by the adsorbed water layer, have found high yields for water adsorbed on CuO (Reiff and LaVerne, 2015a), Fe_2O_3 (Reiff and LaVerne, 2015b), ZnO (Southworth et al., 2018), and Al_2O_3 (Reiff and LaVerne, 2017) compared with the yield expected for bulk water (0.45 molec.100eV^{-1}, assuming scavenging of OH radicals) despite these oxides being grouped by Petrik et al. as oxides reducing or not affecting the yield. These differences may be a consequence of material properties and the basis of comparison between reference experiments by Petrik et al. that recorded $G(H_2)$ in the range 0.1–3 molec.100eV^{-1}, but it seems most oxides tend to increase the yield of hydrogen from radiolysis of adsorbed moisture relative to bulk water. The high yield of H_2 for water adsorbed on oxide surfaces implies an effective mechanism of energy transfer from the oxide to the water. The energy transfer mechanism has not been conclusively elucidated but the formation of excitons (electron-hole bound pairs) in the oxide from irradiation that migrate to the water interface and react causing dissociation of water has been proposed (Petrik et al., 2001).

For PuO_2, where self-irradiation of adsorbed water is from alpha radiation from the oxide, $G(H_2)$ has been consistently found to be very low for the first monolayer of adsorbed water and increases with increasing water content towards the yield for bulk water (Sims et al., 2013). This implies that energy transfer from the oxide, whatever the mechanism, does not occur effectively in this case. This could be because of the low band gap in PuO_2 (Pegg et al., 2018), the reactivity of the PuO_2 surface, or radiation damage within the PuO_2 results in effective trapping of excitons in competition with migration to the oxide/water interface. Consequently, energy transfer from the solid to adsorbed water is not discussed further in this review and we focus on the physicochemical effects at the surface of PuO_2 from radiation chemistry within the water. A further conclusion from this observation is that studies with what are often considered as surrogate oxides for PuO_2, such as CeO_2, are not relevant to PuO_2 in the context of radiation studies.

Haschke proposed that H_2 from PuO_2 may arise from a chemical reaction (Haschke et al., 2000; Haschke and Haire, 2002) (Eq. 1):

$$PuO_2 + H_2O \rightarrow H_2 + PuO_{2+x} \qquad (1)$$

This mechanism has been debated in the literature (Neck et al., 2007a; Neck et al., 2007b; Seibert et al., 2010a; Conradson et al., 2004; Gouder et al., 2007). However, in the context of the present discussion of radiolysis, it is clear that the observed H_2 yield in experiments is dose rate dependent, i.e., proportional to the specific activity of the PuO_2, and not dominated by a thermal chemical reaction. In this paper we concentrate on radiolysis in the adsorbed H_2O layer on PuO_2 and specifically H_2 and potential O_2 production.

The precise mechanism resulting in the small yield of radiolytic H_2 from water on PuO_2 may seem a little esoteric but the presence or absence of that H_2 can have significant ramifications for storage of PuO_2. Considerable effort has been put into establishing robust operational practice and controls for conditioning and packaging

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[1] $G(H_2)$ is defined as the number of molecules of H_2 produced per 100 eV absorbed. It should be noted that if the amount of water doubles and the amount of H_2 doubles $G(H_2)$ remains constant, because the energy absorbed increases with water content.

PuO_2 for storage (US DOE, 2018). However, by understanding the mechanisms involved and the factors that may affect the boundary between safe storage and potential pressurisation from gas generation, operational controls can be optimised to ensure robust safe storage while avoiding excessive conservatism in safety cases. This article supports this objective by discussing the differences in the fundamental radiolysis processes that occur in homogenous, bulk water and water adsorbed on the surface of PuO_2 powders and aims to discuss the remaining uncertainties and challenges in defining the mechanisms involved. Furthermore, the topic is of basic scientific interest because of the relevance of the fundamental radiolysis processes in water and the apparently unusual behaviour of PuO_2 compared with other metal oxides.

2 Radiolysis of bulk water

There has been a vast amount of work on radiolysis of homogenous water and aqueous solutions and this is reviewed in detail elsewhere (Allen, 1961; Buxton, 2008). However, to contrast with the conditions within water adsorbed on a PuO_2 surface the basic processes in water radiolysis are summarised here. As alpha particles pass through water they form tracks of discrete energy loss events. There is a spectrum of energy loss events from a few eV up to the kinematic limit, but for alpha particles in water the vast majority of events are less than 100 eV and the most probable and mean energy events around 20 eV and 60 eV, respectively (Pimblott and LaVerne, 2007).

The initial energy deposition processes are ionisation, to give an electron and water cation, and direct excitation to give an excited state H_2O^* (Eqs 2, 3):

$$H_2O \rightsquigarrow H_2O^+ + e\text{-} \tag{2}$$

$$H_2O \rightsquigarrow H_2O^* \tag{3}$$

The secondary electrons generated from the primary ionisation events also have a range of energies, with the most probable and mean electron energy approximately 10 eV and 50 eV, respectively (Pimblott and LaVerne, 2007). These secondary electrons may in turn cause further ionisations and excitations, but most have a range of around 10 nm such that most energy is deposited close to the primary ionisation event and form a spur that is a cluster of a small number of ions and excited molecules. A small number of higher energy electrons are generated that form tracks of their own, containing around half the total number of ionisations (Lea, 1962).

These spurs are widely separated with low Linear Energy Transfer (LET) radiation, typical of gamma and beta radiation, but they overlap for higher LET. For example, the range of 3 MeV $^4He^{2+}$ in water is 1.8×10^{-3} cm (Ziegler et al., 2010), so the average LET is 170 eV nm^{-1}. This implies that the primary energy loss events in water form almost a contiguous track of excited/ionised water molecules, with overlapping spurs forming a narrow cylindrical track. This overlap favours second order reactions of radicals in the track, which compete with diffusion away from the spur compared with the more isolated spurs of low LET radiation.

In times up to 1 ps the ionisation of water is followed by several fast reactions:

(i) The electrons from the ionisations lose their energy over a period of 100 fs, thermalise and then become hydrated as e^-_{aq} in the next 240 fs (Migus et al., 1987) (Eq. 4):

$$e^-_{pre} + H_2O \rightarrow e^-_{aq} \tag{4}$$

These electrons are referred to as pre-hydrated electrons, e^-_{pre}, to distinguish from the hydrated or aqueous electron.

(ii) Recombination of e^-_{pre} and H_2O^+ may occur to form H_2O^* (Eq. 5):

$$e^-_{pre} + H_2O^+ \rightarrow H_2O^* \tag{5}$$

(iii) H_2O^+ also reacts rapidly by proton transfer to an adjacent water molecule (Loh et al., 2020; Lin et al., 2021) (Eq. 6):

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH^\bullet \quad k_6 = 2.2 \times 10^{13} s^{-1} (t_{1/2} = 31.5 fs.) \tag{6}$$

(iv) excited states can form H_2, $H^\bullet$ and $OH^\bullet$ (Eqs 7, 8):

$$H_2O^* \rightarrow H_2 + O(^1D)/O(^3P) \tag{7}$$

$$H_2O^* \rightarrow H^\bullet + OH^\bullet \tag{8}$$

Where $O(^1D)$ and $O(^3P)$ are the singlet first excited state and triplet ground state of atomic oxygen. The branching ratios for reactions 7 and 8 are not known in liquid water but in the gas phase reactions 7 and 8 give (Rosen et al., 2000):

$OH^\bullet + H^\bullet$	0.2
$O + H_2$	0.09
$O + H^\bullet + H^\bullet$	0.71

However, cage effects in water could be important. The yield of $O(^3P)$ is reported to be very small at low and high LET (Brown and Hart, 1972; Brown et al., 1978), and $O(^1D)$ if formed would subsequently form H_2O_2 (Taube, 1957).

At 1 ps after energy deposition the radiolysis products are e^-_{aq}, $H^\bullet$, $OH^\bullet$, and part of the final H_2 and H_2O_2 yields. e^-_{aq} is a strong reductant, whilst $OH^\bullet$ is a strong oxidant and $H^\bullet$ is a slightly milder reductant but tends to react more slowly than e^-_{aq}.

Subsequent reactions are close to diffusion controlled in many cases. Although possibly formed by decay of excited states, H_2O_2 is probably largely formed by (Eq. 9):

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{9}$$

This leaves the question as to how H_2 is formed and where surprisingly there is some disagreement in the literature. It has long been known there are two components to the yield of H_2 (Taube, 1957), one easy to scavenge and another difficult to scavenge; the latter referred to here as "direct" H_2. The easy to scavenge H_2 is formed by inter-reactions of $H^\bullet$ and e^-_{aq} at times probably >1 ps and probably occurs outside the spur (Eqs 10–12):

$$H^\bullet + H^\bullet \rightarrow H_2 \tag{10}$$

$$H^\bullet + e^-_{aq} + H_2O \rightarrow H_2 + OH^- \tag{11}$$

$$e^-_{aq} + e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^- \tag{12}$$

The source of "direct" H_2 is still debated but generally it is thought to arise from either or both of two mechanisms occurring in timescales of <1 ps. That is, (i) decay of excited states formed either by recombination of the cation and electron or by direct excitation (Eq 13):

$$H_2O^* \rightarrow H_2 + O(^1D) \tag{13}$$

Or (ii), dissociative electron attachment whereby a high energy electron (>6 eV) reacts (Eqs 14, 15):

$$e^- + H_2O \rightarrow H^- + OH^\bullet \tag{14}$$

$$H^- + H_2O \rightarrow H_2 + OH^- \tag{15}$$

It is difficult to distinguish experimentally between the two mechanisms but some of the aspects were discussed by Sterniczuk and Bartels (2016). It is beyond the scope of this paper to discuss all the arguments, but the fact that reactants which are known to react efficiently with the pre-hydrated electron suppress H_2 in the order of their electron reactivity (Pastina et al., 1999) would tend to favour reaction (13) as the mechanism, and the strong dependence on LET indicates a second order process that suggests the excited state from recombination of the water cation and pre-hydrated electron (LaVerne and Pimblott, 2000). Whether H_2 is a direct product from the excited state or formed via an energetic hydrogen atom is also debatable. Finally, it is possible that H_2 is formed by reactions (10–12) in the spur. It is pertinent to observe that the primary yield for alpha radiolysis water is $G(H_2) = 1.4$ molec.100 eV^{-1} while the most probably energy loss event for an alpha particle is around 20 eV; consequently, only a fraction of these energy loss events result in the formation of a H_2 molecule.

Whatever the mechanism, it is thought that more than 50% of the H_2 yield from gamma radiolysis arises from this direct route, $G(H_2)_{direct}$ = 0.25–0.35 molec. 100 eV^{-1} where $G(H_2)_{total}$ = 0.45 molec.100 eV^{-1} (Pastina et al., 1999). The situation at higher LET is less clear. Bartels estimated $G(H_2)_{direct}$ = 1 molec.100eV^{-1} using the Stern-Volmer plots which seems high (Sterniczuk and Bartels, 2016), Pimblott used a value of $G(H_2)_{direct}$ = 0.6 molec. 100eV^{-1} for high LET whereas other modelers have used the same values as low LET (Sanguanmith et al., 2021). Only the e^-/H_2O^+ route might be expected to have an LET dependence along with reactions (10–12). In early deterministic modelling $G(H_2)_{direct}$ = 0.15 molec. 100 eV^{-1} was used (Schwarz, 1969), and $G(e^-_{aq})$ was taken to be 4.78 molec. 100 eV^{-1}; although this value may be too high and now considered to be closer to 4 molec.100 eV^{-1} (Bartels et al., 2000); in which case those models would require a higher yield of H_2 from direct processes, because of less e^- available for second order reactions. To a certain extent this debate is academic because H_2 is formed either via the pre-hydrated electron or the solvated electron, the precursor of which is the pre-hydrated electron which has been shown for a limited number of solutes to be a very reactive species with a radius of about 1 nm (Jonah et al., 1977).

Many, but not all, radiation chemical reactions between radiolysis products are fast and close to diffusion controlled (ca. 10^{10} dm^3 mol^{-1} s^{-1}) (Buxton et al., 1988). It is important to note though that there is only one aqueous phase radiation chemical reaction to remove H_2 which is the slow reaction (Buxton et al., 1988) (Eq. 16):

$$OH^\bullet + H_2 \rightarrow H^\bullet + H_2O \quad k_{16} = 4.2 \times 10^7 Lmol^{-1}s^{-1} \tag{16}$$

Furthermore, O_2 is not a direct radiolysis product and is formed by a set of reactions initiated by another relatively slow reaction (Eqs 17, 18):

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{17}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{18}$$

3 Radiolysis of water on the surface of PuO_2

The microstructure of PuO_2 creates a very different environment for the radiolysis of adsorbed water compared with bulk water. The microstructure has some dependence on the method and conditions used to prepare plutonium dioxide powder. Industrial scale production has typically used thermal decomposition of Pu(III) or Pu(IV) oxalate (Orr et al., 2015) or thermal denitration of plutonium nitrate (Koizumi et al., 1983) but decomposition of hydroxides or peroxides has also been used (Drummond and Welch, 1957). Waste or residue materials are also be generated from plutonium metal oxidation routes.

3.1 Microstructure of PuO_2

For PuO_2 produced from plutonium oxalate the particle size is largely determined by the oxalate precipitation conditions and is typically in the 5–30 μm range. Examples of scanning electron microscopy images of Magnox PuO_2 produced at Sellafield are shown in Figure 1A illustrating the typical size and morphology of particles. The Specific Surface Area (SSA), determined by the Brunauer Emmett Teller method using nitrogen as the adsorbate, is typically 5–20 m^2 g^{-1} and the crystallite size, determined by analysis of the powder X-ray diffraction line width, is typically 8–50 nm. The SSA decreases with increasing calcination temperature (Orr et al., 2015) and crystallite size increases with higher calcination temperature, Figure 1B. Consequently, particles are porous aggregates of much smaller crystallites. The small crystallite size in PuO_2 powders means that the pore dimensions are very small. For example, the pore size distribution of a typical Magnox PuO_2 sample produce by calcination at 600°C, analysed using the BJH method (Barrett et al., 1951), is shown in Figure 1C. This indicates a large fraction of the surface area is associated with pores that are a few nm in diameter. Therefore, migration of gas into and out of the porosity of particles occurs by Knudsen diffusion, where molecules are much more likely to collide with surfaces than other gases.

PuO_2 is generally considered hygroscopic, rapidly adsorbing moisture onto the surface from moist atmospheres. This is similar to other metal oxides and the capacity is largely a consequence of its generally high SSA and tendency of water to dissociate on the surface forming a hydroxyl layer (Seibert et al., 2010b). The structure of water on the surface of PuO_2 is an ongoing area of research but it is sufficient here to consider the main observations (Veirs et al., 2019). Water exposed to the surface both reacts and becomes strongly bound at the surface and also physisorbed. The nature of the strongly bound water is not well understood and is discussed further below. Paffett showed that the amount of physisorbed

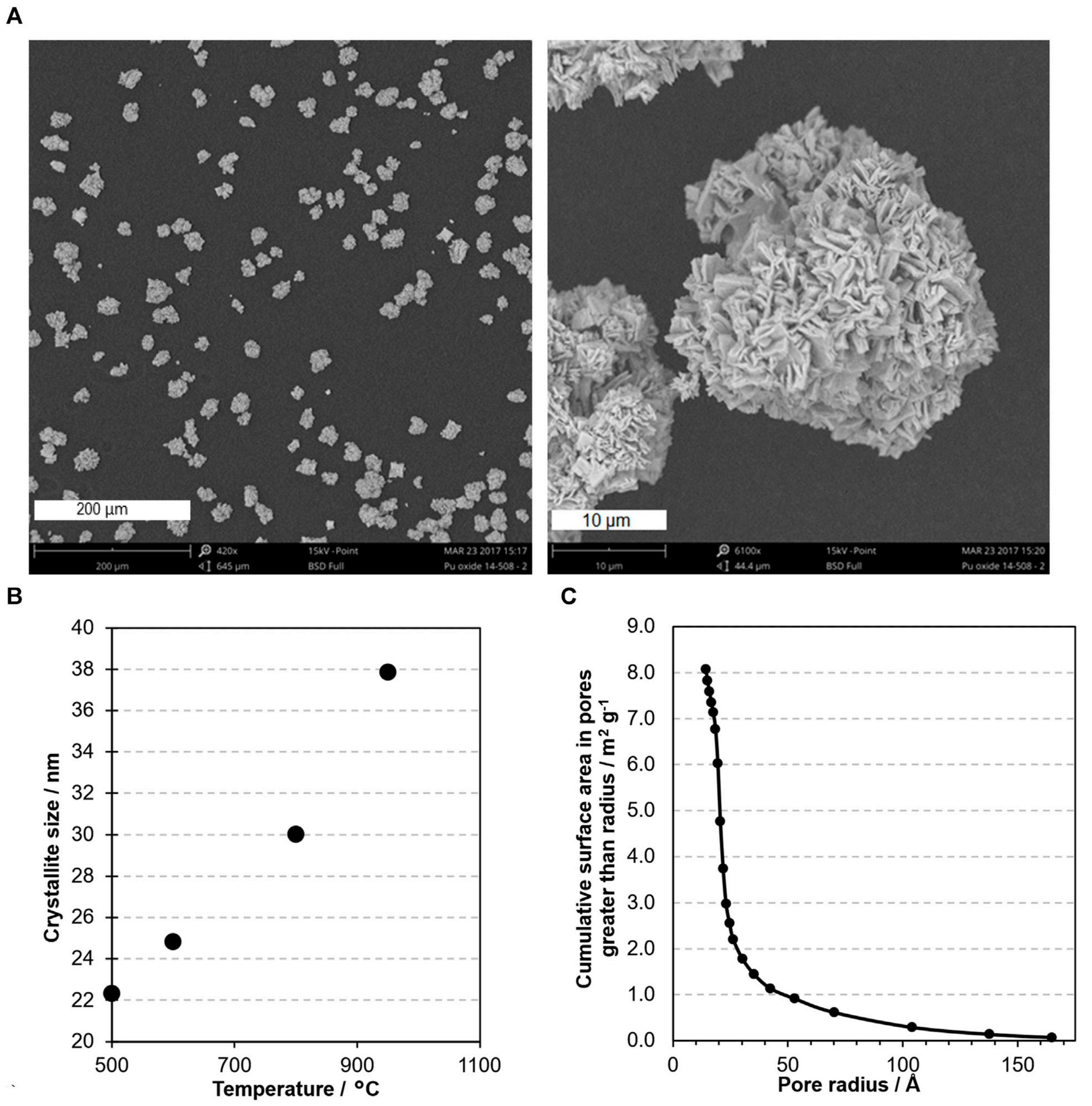

FIGURE 1
(A) SEM micrograph of Magnox PuO_2 illustrating the typical particle size and porous microstructure. **(B)** Example of crystallite size with calcination temperature of Magnox PuO_2. **(C)** Pore size distribution of typical Magnox PuO_2.

water on the surface depends mainly on the relative humidity of the gas at the surface of the powder (Paffett et al., 2003), and could be reasonably fitted using the BET model with an excess heat of adsorption between 4.3 and 6.8 kJ mol^{-1} (Brunauer et al., 1938). These extremes of adsorption curves calculated by Paffet et al. are plotted in Figure 2A. The amount of water adsorbed can be quantified in terms of average molecular layers of water and, between 20% and 70% relative humidity, 1 to 3 monolayers of water physisorb, with a water monolayer thickness of about 0.3 nm. In practice, water adsorbed does not build up in gradual layers, rather some areas have thicker layers and others thinner. For example, BET theory models the adsorption as stacks of molecules on the surface and can be used to predict the distribution of stack heights on the surface. This is illustrated schematically in Figure 2B.

The range of a 5 MeV alpha particle (typical of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu or ^{241}Pu decay) in crystalline PuO_2 is about 12 µm therefore an alpha particle will typically pass through one or two PuO_2 particles but will pass several hundred to a few thousand PuO_2 crystallites and their associated oxide-water interfaces.

The oxidation state of plutonium at the surface of PuO_2 has been investigated as part of studies into the potential for high binary oxides of PuO_2. There is evidence of higher oxidation states than Pu(IV) at the surface from X-ray photoelectron spectroscopy (Farr

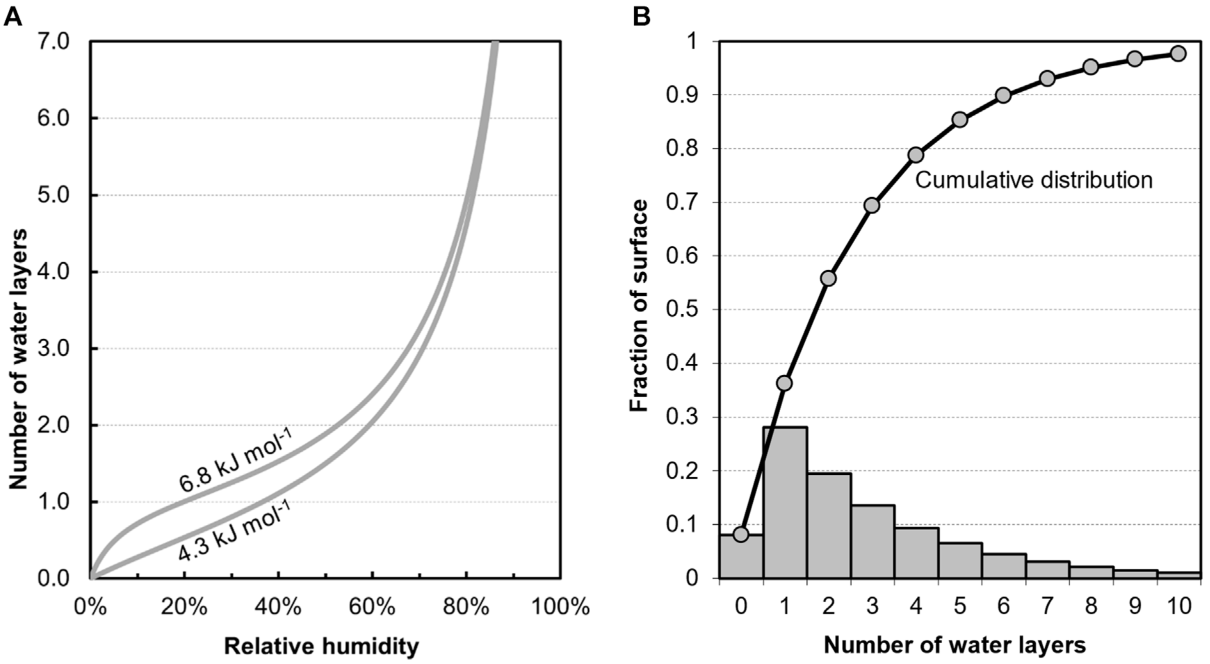

FIGURE 2
(A) Water physisorption on PuO_2 with relative humidity based on Paffett et al. (2003). **(B)** Site occupation for water adsorption based on BET model calculated for excess heat of adsorption of 5.4 kJ mol^{-1} and an average of 3 adsorbed water layers (approximately 70% relative humidity).

et al., 2004) and X-ray absorption fine structure spectra (Conradson et al., 2004) of PuO_2 samples exposed to water. Neck et al. investigated the solubility of plutonium hydrous oxide and concluded the hydrous oxide surface reacts with oxygen forming a mixed valence PuO_{2+x} surface of Pu(IV) and Pu(V) unless reducing or inert conditions are rigorously maintained (Neck et al., 2007c).

3.2 Effects of microstructure and surface on water radiolysis

The purpose of building up this schematic picture of the surface is to contrast the cylindrical track of an alpha particle in homogenous water with the truncated and confined water on the surface in which the spurs can evolve. The high LET of an alpha particle passing through three monolayers of physisorbed water on the surface could cause two or three primary ionisations. With a typical yield of $G(H_2)$ = 0.1 molec.100 eV^{-1} for 3 monolayers of water on PuO_2, in the order of only 1 in 10 of these short tracks through the water layer results in net production of a H_2 molecule. The track structure through the PuO_2 may be more similar to the isolated spurs of low LET radiation in bulk water, reducing second order reactions. Moreover, the small dimensions of the particles and pore cause further confinement of how the spur can evolve compared with the typical diameter of the core of a spur of around 10 nm. Even neglecting interactions of the radiolytically generated species at the surfaces of the water layer, constraining the dimension of the track alone could affect the hydrogen yield, but does not immediately explain the very low yields observed for PuO_2.

The surface of PuO_2 is not chemically inert. PuO_2 undergoes electron transfer reactions which occur, for example, during oxidative dissolution of PuO_2 by Ag^{2+} and reductive dissolution by Cr^{3+} (Bray and Ryan, 1982; Madic et al., 1992). By analogy it would be expected that $OH^\bullet$, e^-_{aq} and possibly $H^\bullet$ would also react with PuO_2 so the radiolysis of water should be seen in the context of the PuO_2 surface.

The first stage of radiolysis, ionisation, involves formation of H_2O^+ and e^-_{pre}. H_2O^+ is an extremely strong oxidant and has such a short lifetime (Ma et al., 2018) that reaction with adjacent water occurs before it has time to diffuse. However, if it were formed directly next to the oxide surface, in the first or possibly second layer of water, it may be able to react by oxidising Pu ions at the surface (Eq. 19):

$$Pu^{4+} + H_2O^+ \rightarrow Pu^{5+} + H_2O \tag{19}$$

This would probably be limited to the first monolayer, the majority of H_2O^+ species would still undergo proton transfer as in homogenous water.

The pre-hydrated electron, e^-_{pre}, was discussed above and may not solely hydrate but may react at the oxide surface by reaction with plutonium, in analogy with scavenging of pre-hydrated electrons by some metal ions at high concentration in aqueous solution (Eqs 20, 21):

$$Pu^{4+} + e^-_{pre} \rightarrow Pu^{3+} \tag{20}$$

$$Pu^{5+} + e^-_{pre} \rightarrow Pu^{4+} \tag{21}$$

As noted above, the reaction radius of the pre-hydrated electron in homogeneous water is typically 1 nm. This is important because that is 3–4 times the diameter of a water molecule, typical of the monolayers of physisorbed water on the surface of PuO_2 exposed to up to 60%–70% relative humidity. The importance of this reaction

TABLE 1 Rate constants for reactions of plutonium and americium ions with H, e– and OH Gogolev et al. (1991) and Pikaev et al. (1990).

Ion	Radical	Medium	k/L mol^{-1} s^{-1}
Pu(IV)	e^-_{aq}	0.04 mol L^{-1} H_2SO_4	4.2×10^{10}
Pu(VI)	e^-_{aq}	pH 6.1	5.8×10^{10}
Am(III)	e^-_{aq}	pH ~6	2.3×10^{8}
Pu(IV)	$H^\bullet$	0.6 mol L^{-1} H_2SO_4	4.5×10^{7}
Pu(VI)	$H^\bullet$	1.0 mol L^{-1} H_2SO_4	2.0×10^{8}
Pu(III)	$OH^\bullet$	1 mol L^{-1} $HClO_4$	4.2×10^{8}
Pu(IV)	$OH^\bullet$	3 mol L^{-1} $HClO_4$	2.4×10^{8}

depends on the reactivity of e^-_{pre} with Pu^{4+}/Pu^{5+} at the surface, which is unknown. A fraction of the initial products of water radiolysis could still be e^-_{aq} and $OH^\bullet$ but both are reactive and would be expected to react at the Pu surface. Gogolev et al. (1991) and Pikaev et al. (1990) reported rate constants for reactions of $H^\bullet$, $e^-_{aq}$and $OH^\bullet$ with plutonium and americium solutions, summarised in Table 1, which shows Pu(IV) in solution is a more effective scavenger of e^-_{aq} than the nitrate ion. Similarly, it might be expected that excited states of water could be quenched by interaction with the oxide the surface.

If $H^\bullet$ formed it would be relatively volatile. Sander (2015) gives a Henry's law constant of 2.6×10^{-4} mol bar^{-1} for $H^\bullet$ compared with H_2 7.8×10^{-4} mol bar^{-1}. Diffusion from the water-gas interface would be in competition with reaction in the water or at the oxide surface. However, given the tortuous, narrow porosity in the particles, $H^\bullet$ would diffuse via repeated collisions with the pore walls. Gouder et al. (2013) reported that plutonium oxide thin films did not reduce upon contact with atomic hydrogen, but that was for a thin oxide layer formed on plutonium metal. Moist PuO_2 may have a layer of Pu(V) at the surface if it has been exposed to trace oxygen or H_2 generated leading to oxidation of the surface that may react with $H^\bullet$ more readily than Pu(IV).

The above discussion suggests that a process of redox cycling of plutonium at the surface could be an important process in the radiolysis of water on PuO_2. (H_2) in bulk water is 0.45 molec. 100 eV^{-1} from gamma radiolysis and 1.4 molec. 100 eV^{-1} for alpha radiolysis and both these values are much higher than (H_2) observed for water on PuO_2, which is typically around 0.1 molec. 100 eV^{-1} for 2–3 monoloyers of water on the surface. This much lower yield on PuO_2 would tend to support a hydrogen production mechanism involving either rapid reaction of H_2 once formed or reaction of precursors to hydrogen (e^-_{pre}, e^-_{aq} or $H^\bullet$) are scavenged by the surface. Reaction of H_2 with $OH^\bullet$ in aqueous solutions (16) is slow, thermal reaction of H_2 with PuO_2 is also slow and only occurs at elevated temperatures (Gardner et al., 1965; Flotow and Tetenbaum, 1981), and Duffey and Livingston (2002) showed that a H_2 overpressure in the order of a few bar was required to suppress the net radiolytic production of hydrogen. These observations favour scavenging of the precursors to hydrogen as the most likely explanation. As the number of monolayers on the surface increase, the PuO_2 surface would have less influence and the radiolysis behaviour would tend towards that of bulk water.

The fate of H_2O_2 on the PuO_2 surface is not known but is presumably important in determining whether molecular oxygen is produced. Its formation would be suppressed if $OH^\bullet$ or e^- reacts with the surface and, consequently, may only be significant at high water loadings. It can react as an oxidant or itself be oxidised to O_2. Morgenstern and Choppin (1999) reported the reduction of Pu(V) by H_2O_2; O_2 was not measured but it is likely to be the product. Jonsson has shown H_2O_2 undergoes a complex set of catalytic decomposition reactions on UO_2 involving adsorbed $OH^\bullet$ radicals (Fidalgo et al., 2018; Kumagai et al., 2019). Analogous reactions may apply to PuO_2 but have not been investigated yet. In this scenario, an initial reaction step forming surface bound $OH^\bullet$ radicals (Eqs 22, 23) could be followed by a number of possible reactions involving an adsorbed $PuO_2 \cdots OH_{(ads)}$ species (Eqs 24–27).

$$PuO_2 + H_2O_2 \rightarrow PuO_2\cdots 2OH^\bullet_{(ads)} \tag{22}$$

$$PuO_2 + OH^\bullet \rightarrow PuO_2\cdots OH^\bullet_{(ads)} \tag{23}$$

$$PuO_2\cdots OH^\bullet_{(ads)} \rightarrow PuO_2\,(OH) \tag{24}$$

$$PuO_2\cdots OH^\bullet_{(ads)} + H^\bullet \rightarrow PuO_2 + H_2O \tag{25}$$

$$PuO_2\cdots OH^\bullet_{(ads)} + H_2 \rightarrow PuO_2 + H + H_2O \tag{26}$$

$$PuO_2\cdots OH^\bullet_{(ads)} + OH^\bullet \rightarrow PuO_2 + H_2O_2 \tag{27}$$

Once $OH^\bullet$ has built up on the surface it can react (Eqs 20, 28):

$$PuO_2\cdots OH^\bullet_{(ads)} + H_2O_2 \rightarrow PuO_2 + HO_2^\bullet + H_2O \tag{28}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{29}$$

The rate of reaction and further oxidation of the surface compared with O_2 formation reactions (reactions 17 or 23 followed by 18) may be key to understanding conditions resulting in O_2 production. The reaction of hydrogen peroxide on the PuO_2 surface would be a useful topic for further investigation to clarify the mechanism.

3.3 Effects of radiolysis on the surface

It is tempting to consider the surface of PuO_2 as a purely crystalline surface that is distorted by thermal dissociation of molecular water and interaction with overlying H_2O molecules to reach a surface at thermal equilibrium. For the purposes of atomistic modelling of the surface this has generally been a necessary simplifying assumption (Tegner et al., 2017). However, it follows from the above discussion that this cannot be the case. The reactions of oxidising and reducing radicals discussed above would suggest that the surface will be oxidised and reduced constantly with the disruption that would necessarily follow.

Since H_2 and $H^\bullet$ are volatile and experiments show there is little gaseous O_2 formed, unless high water loadings are present on the oxide, the surface must become oxidised as H_2 is released in order to retain redox balance. Overall, it would be expected that the surface would consist of Pu(V) in contact with PuO_2, i.e., $PuO_2OH(H_2O)$ or surface adsorbed $OH^\bullet$. The reactions of the surface with radicals from water radiolysis provide a possible route to form a kinetically stable, if not thermodynamically stable, phase incorporating water, perhaps as a hydrous oxide. There are two experimental studies that provide evidence for such a process. Firstly, we noted in the introduction that Veirs et al. (2012) have reported the important insight that the relative humidity in sealed reactors containing PuO_2 powder with adsorbed moisture decreases at a rate that increases with the specific power of the oxide. Furthermore, the rate of water loss could not be accounted for by the amount of hydrogen produced, implying that the physisorbed water had reacted to form a new surface phase. This reaction could proceed by radical reactions at the surface and/or via the production of H_2 and subsequent reaction with the oxidised surface. This difference is important because it determines whether reaction with water occurs in cases where hydrogen is not allowed to accumulate to a significant ambient pressure.

Secondly, Rai and Ryan (1982) reported the interconversion between crystalline, less crystalline and amorphous PuO_2 stored as a suspension in aerated water. Crystalline $^{238}PuO_2$, with its very high specific thermal power, transformed to an amorphous phase with properties similar to Pu(IV) hydrous oxide polymer after prolonged contact with water whereas $^{239}PuO_2$ and ^{239}Pu hydroxide precipitate aged to form a less crystalline $^{239}PuO_2$ phase. The radiolysis reactions competing effectively with the thermodynamic aging for the higher activity of $^{238}PuO_2$. The complete amorphisation of $^{238}PuO_2$ powder in water suggests the reaction is not limited to the powder surface and it should be able to react with multiple monolayers of physisorbed water present on humidified PuO_2 powders. The very low relative humidity that is eventually reached in the small-scale reactor vessel in the experiments by Veirs et al. (2012) suggests the reaction is strongly favoured for powders. Whatever the exact form, thermal analysis of aged PuO_2 samples shows that it is necessary to heat samples to over 800°C to fully desorb the water demonstrating that it is strongly chemically bound in the solid. The conditions of a slurry of PuO_2 used by Rae and Ryan where an overpressure of H_2 could not occur may also suggest that the reaction occurs directly with the radicals from water radiolysis rather than the via formation and reaction of H_2. If this picture of surface chemistry is correct, then the implications are that the process may influence aging of the microstructure of the powder as the surface of the oxide undergoes continuous reconstruction. The structure of the surface layer and effect of possible redox cycling of plutonium on local structure (Rotermund et al., 2023) in this context remains to be investigated further.

Further potential complexity in the radiation chemistry at the surface of PuO_2 could arise from co-adsorption of other chemical species. In addition to the adsorption of water, PuO_2 readily adsorbs CO_2 (Colmenares and Terada, 1975), HCl (Webb et al., 2019), and NO_x or HNO_3/HNO_2. The latter is formed from the alpha radiolysis of air in contact with the sample (Harteck and Dondes, 1958; Pshezhetskij and Dmitrieve, 1959; Harteck et al., 1965; Willis et al., 1970; Cuillerdier et al., 1984). These co-adsorbed species have two effects. First, they tend to increase the amount of molecular water adsorbed, for example, co-adsorption of HCl greatly changes the water adsorbed on PuO_2 (Sutherland-Harper et al., 2019). Secondly, these species can react with radiolysis products of water. For example, both nitrate and nitrite ions scavenge the pre-hydrated and hydrated electron (Spinks and Wood, 1990). According to Petrik (Aleksandrov et al., 1991), adsorbed NO_x can be decomposed radiolytically if, for example, the atmosphere is changed from air to an inert gas. The practical effects of co-adsorbed gases on the H_2 yield have not yet been investigated in systematic studies. However, it is often difficult to exclude other gases adsorbing when handling and storing the oxide, which might inadvertently influence the results of experimental studies and adds a complexity to the interpretation of results (Webb et al., 2023).

3.4 Modelling of the radiolysis of water on the PuO_2 surface

A few attempts at kinetic modelling of water radiolysis on PuO_2 have been reported. Vladimirova developed a kinetic model based on treating water as following the usual homogenous water chemistry of the primary radiolysis products but also allowing for surface reactions of H_2O_2 and H_2O with PuO_2 to form PuO_{2+x} (Vladimirova, 2002). The radiation chemical yields of H_2 and O_2 were derived from fitting experimental measurements while yields of $OH^\bullet$ and e^-_{aq}, and the rate constants for reaction of H_2O_2 and H_2O with PuO_2 were fitted. Lyman et al. developed a simple kinetic model that assumed a 2:1 yield of H_2:O_2 from the radiolysis of water that was followed by reaction of O_2 with the surface and gas phase heterogeneous catalytic or radiolytic recombination of H_2 and O_2 (Morales et al., 2000). These ambitious early attempts at modelling this complex system did not address the fundamental water radiation chemistry but did consider the surface might interact with the some of the products. More recently, Veirs et al. have fitted hydrogen production measurements in small scale studies with an empirical model of first order reactions that can be notionally interpreted as radiolysis of water to form H_2 that subsequently reacts to be in equilibrium with a solid phase which does not participate in radiolysis (Veirs et al., 2012). Very good fits to the data were achieved, but the uniqueness of this model fit and interpretation remains to be evaluated. For example, whether direct reaction of water radiolysis products to form a strongly bound water phase is dominant.

None of these models attempted to simulate the fundamental radiolytic processes. To investigate the physical and physico-chemical stages of water radiolysis on a surface, alternative modelling approaches are needed. Simulations of the radiolysis of bulk water break down into two approaches. A stochastic approach which simulates individual ionisation events (Clifford et al., 1986). The other is deterministic (Schwarz, 1969; Burns et al., 1984; Swiatla-Wojcik and Buxton, 1995) where initial product yields and distributions after the formation of e^-_{aq} and $OH^\bullet$ in a typical spur are defined and subsequent reaction and diffusion modelled with time.

In principle both methods could be used to model processes on the surface of PuO_2 but in practice can only be implemented in a general way. Deterministic models are generally limited to the physico-chemical stage, while stochastic models of water at an interface have yet to be developed. Even allowing for those developments, rate constants for reactions of radiolysis products with the surface are required but these are not currently available. However, qualitatively, the effect of including reaction of primary radiolysis species at the PuO_2 surface and volatilization at the water-gas interface is simple to infer. For example, if release of H_2 and $H^\bullet$ at the water-gas interface is included in a model then G(H_2) would be reduced because $H^•$ is released from the water rather than reacting within the track of the water layer to form H_2. Similarly, if reaction of e^-_{pre}, e^-_{aq}, $OH^•$ and $H^•$ at the PuO_2 surface is included in a model then the yield of H_2 and H_2O_2 would be reduced as the surface effectively scavenges precursors to H_2. When these reactions are included, their effect on the yield will clearly be greatest for a thin water layer because diffusion to the PuO_2 surface will compete more effectively with reactions in the track. These predictions have been verified by extending the deterministic 1D cylindrical track model in reference (Burns et al., 1984) to a 2D cylindrical track with axial boundaries of water with PuO_2 and gas and will be published separately.

4 Discussion

In the context of storing PuO_2 in sealed containers, it is the overall evolution of the gas phase within the container over time and not just the initial production rate of gases that matters. The initial gas within containers is usually argon, helium, air or nitrogen, dependent on the packaging atmosphere. Of principal concern is the release of hydrogen and oxygen from the radiolysis of adsorbed water, the latter being significant only when relatively large amounts of water are adsorbed (Veirs et al., 2012). The other main source of gas is helium released from alpha decay where the maximum potential release is easily quantified based on the isotopic composition of the plutonium. The release of other gases (mainly N_2, CO_2 and N_2O) from PuO_2 has also been observed in some experiments (Narlesky et al., 2022; Berg et al., 2012), presumably from radiolysis of surface adsorbed species, but these are generally observed to be minor components in full size packages where the PuO_2 powders have been heated before packaging (Veirs et al., 2018).

As well as gas-forming reactions there are thermal and radiolytic reactions of the gas phase species that decrease the pressure in packages. As already noted, radiolysis of N_2 and O_2 forms a mixture of ozone and NO_x that adsorbs on the oxide surface. Reaction of H_2 and O_2 may occur by radiolysis (Dautzenberg, 1989; Dautzenberg, 1990) or heterogeneous catalysis on the PuO_2 surface (Haschke et al., 2001; Lloyd et al., 1998; Morales, 1998). Homogeneous gas phase radiation chemistry is, in general, highly complex with a plethora of species that can form (Lind, 1961). Within the porosity of PuO_2 powder beds, the mean free path of gas species is greater than the pores sizes and the chemistry of the gas phase is presumably further modified by surface reactions. Some of the reactions may be between gas phase species and radiolysis products in the surface layer of the oxide or from radicals/ions generated radiolytically in the gas phase.

Focusing on H_2, firstly Veirs et al. (2012) have shown that in small-scale experiments with humidified PuO_2 in sealed vessels the partial pressure of hydrogen reaches a maximum before decreasing. Their measurements of a concomitant decrease in the relative humidity suggest the peak in hydrogen concentration is in part driven by the loss of molecular water. When the relative humidity falls to zero, and molecular water is no longer present on the surface, the reactions that normally produce H_2 in liquid water (Section 2) cannot now proceed, causing the H_2 production rate to decrease to zero. Secondly, Duffey and Livingston (2002) showed that increasing the H_2 partial pressure in contact with PuO_2 results a decreasing production rate of H_2 and at sufficient pressure a net loss of H_2 in experiments. Importantly, the conditions in these experiments differ from those of Veirs et al. because the duration of these measurements were (days) compared with those of Veirs et al. (months) and the initial physisorbed water content would have been changing by a relatively small amount in this time. H_2 only reacts thermally with PuO_2 to reduce the oxide at high temperatures, (Gardner et al., 1965) consequently reaction of H_2 with the surface must be radiolytic in nature and the net loss of H_2 presumably involves reaction with a previously oxidised surface to maintain redox balance (in addition reduction of PuO_2 would presumably be followed by oxidation of the surface by water to reform H_2). Reactions of H_2 with the aged dry surface may differ from those of the surface with physisorbed water. These two results point to at least two distinct mechanisms that prevent the hydrogen pressure in sealed packages reaching the levels that would result from complete radiolytic decomposition of the water. The former is likely to dominate in relatively dry powders and the latter for higher water levels.

Venault et al. (2019) also found a steady state hydrogen concentration occurred in experiments of freshly prepared PuO_2 exposed to a fixed relative humidity but in this case the steady state concentration was very low compared to measurements by Duffy and Livingston or Veirs et al. Aging of the surface affected the recombination process such that the steady state did not occur under their experimental conditions. These observations suggested an effective surface-catalysed recombination processes on the freshly prepared oxide at room temperature, but that the reaction is poisoned by aging of the surface. This discussion highlights the practical significance of the processes occurring and the interdependence of radiolytic gas generation and reactions of H_2 but it is beyond the scope of this present work to discuss the gas chemistry in further detail.

It is fortuitous that radiation chemistry of residual water on the surface of PuO_2 leads to reactions that result in low yields of H_2 and limit the potential for pressurisation by H_2. A compelling case has been made here for the effect of the surface on the water radiation chemistry. However, further experimental studies are needed to underpin the mechanistic details. Ideally the reactions of the initial products of water radiolysis at the PuO_2 surface would be studied but two challenges are present in taking this forward. Firstly, a consensus on the chemistry in homogeneous water is likely to be needed before progressing to investigate the additional complexity of surface reactions. Secondly, the usual tools of pulse radiolysis are not easily applied where plutonium poses specific challenges for experimental studies owing to its radiotoxicity, yet simulants are unlikely to adequately reproduce the chemical effects. Some further insight may be possible investigating the effect of co-adsorbed scavenging species such as N_2O, HNO_3 and Cl^- with water on PuO_2 and its effect on the hydrogen yield.

More amenable to study is the reaction of water with the surface of PuO_2, which is of direct practical application to assessments of storage scenarios where this process is likely to be key to limiting the production of hydrogen in sealed containers. It is clearly a radiolytic process but important questions remain to be addressed about the kinetics of the process and the capacity of the oxide to react with water as well as their dependence on SSA, alpha activity, and initial water content. Better understanding is needed of whether the reaction proceeds direct through the initial water radiolysis products reacting with the oxide surface or through production of hydrogen that in turn reacts with the surface as the partial pressure increases. Similarly, the reaction of H_2 with the hydrated PuO_2 surface investigated by Livingston and Duffey merits further quantification using PuO_2 prepared under different conditions: dry PuO_2, physisorbed water surface, aged surface with chemically bound water. The effects of hydrogen partial pressure, dose rate, SSA and water coverage are likely to be important. Such studies may be assisted by using thin films where the effects of radiation and thermal chemistry may be better distinguished, building on the studies by Gouder et al. (Seibert et al., 2010a) and preparation and characterisation methods of Wilkerson et al. (Wilkerson et al., 2020) A thin film of ~10 nm will expose adsorbed water to a very low dose rate, but samples could be irradiated before analysis using an external $(Pu,U)O_2$ pellet to investigate how alpha radiolysis of adsorbed water and reactions with hydrogen or other gases under radiation changes the surface structure. The reaction of H_2O_2 with the PuO_2 surface may also be important to the potential for O_2 production. Analogous studies to those undertaken for UO_2 by Kumagai et al. (2019) could be pursued and may also provide evidence for stability of surface adsorbed $OH^{\bullet}$ radicals.

Finally, the impact of surfaces on the fundamental water radiolysis processes are not unique to the PuO_2 surface, although other transition metal oxides appear to have H_2 yields that are generally enhanced by energy transfer from the solid during irradiation. There is a notable gap in the literature on the investigation of other alpha active actinide oxides. Am_2O_3, AmO_2 and NpO_2, $(Pu,Am)O_2$ and $(Pu,U)O_2$ powders are obvious candidates to provide comparisons that have different redox properties as well as practical application to their storage. Furthermore, measurements of H_2 generation from self-radiolysis of directly synthesised dry plutonium hydroxide would provide evidence that once water has reacted with the surface it does not significantly contribute to gas generation.

With regards to the ultimate goal of a mechanistic kinetic model for radiolysis of water at the surface of PuO_2, in the short-term this appears challenging. In the first instance, the outstanding questions around the fundamental processes in bulk homogeneous water need to be resolved and the reaction rates of e^-_{pre} and H_2O^+ and other species at a surface would also need to be included, which is a novel challenge for Monte-Carlo codes. Further extension to a multi-scale model as a predictive tool for gas generation in PuO_2 storage containers would also need to consider the complexities of the temperature distribution, water migration, and gas phase radiation chemistry. However, simpler phenomenological kinetic models, of the type applied by Veirs et al. (2012) and Venault et al. (2019) probably also have a role in interpreting experimental data. The process of formulating different types of models requires a detailed set of hypotheses about the processes and that itself has value in defining the outstanding questions, evaluating the potential significance of processes and developing the scope of experimental studies. Even where direct practical application is limited. The extent to which atomistic models of the surface of PuO_2, which have so far largely treated the interaction of water as purely a thermal process, can be extended to take into account the interaction with water radiolysis products remains to be explored. If these effects can be incorporated then atomistic models may be valuable for supporting mechanistic studies and investigation of the structure of water incorporated into PuO_2 via radiolytic processes.

5 Conclusion

Mechanistic theories from homogeneous, bulk water radiolysis mechanisms have been applied to water on the surface of PuO_2. It is proposed that the surface has a major impact on the radiation chemistry, which in turn changes the structure of the surface as a result of reactions with water radiolysis products. All processes leading to formation of H_2 in thin layers of surface water are expected to be affected by the plutonium surface resulting in lower yields than in bulk water, as observed, although effects of the surface should diminish with increasing water loadings. Further experiment and modelling studies are needed to fully underpin the mechanisms involved but significant progress has been made in recently reported work to define these areas of interest.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

Author contributions

HS: Conceptualization, Investigation, Writing–original draft, Writing–review and editing. RO: Conceptualization, Investigation, Writing–original draft, Writing–review and editing.

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Conflict of interest

Author RO was employed by the UK National Nuclear Laboratory.

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