Interactions of HCl and H₂O with the surface of PuO₂

Sophie Sutherland-Harper^{a,*}, Francis Livens^a, Carolyn Pearce^{a,b}, Jeff Hobbs^c,
Robin Orr^d, Robin Taylor^{d,**}, Kevin Webb^d, Nikolas Kaltsoyannis^a

^a School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

^b Pacific Northwest National Laboratory, Richland, WA, 99354, USA

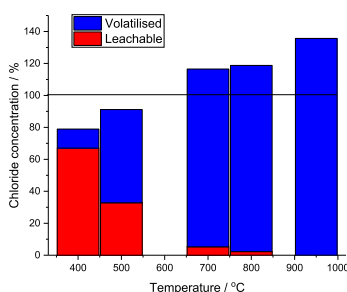
^c Sellafield Ltd., Sellafield, Seascale, Cumbria, CA20 1PG, UK

^d National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, UK

HIGHLIGHTS

- First study of UK chloride-contaminated PuO₂ retrieved from storage.
- >700 °C needed to volatilise chloride efficiently.
- Evidence of leachable and non-leachable species on PuO₂ surface.
- Unusual water adsorption behaviour on chloride-contaminated PuO₂.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 August 2018

Received in revised form

17 December 2018

Accepted 21 February 2019

Available online 22 February 2019

Keywords:

Chloride
Plutonium dioxide
Water
Adsorption
Desorption
Thermal treatment

ABSTRACT

In order to explore the potential of heat treatment to decontaminate chloride-contaminated legacy plutonium dioxide (PuO₂) powders from the UK stockpile, samples retrieved from storage have been heated in air from 400 to 950 °C. These samples also contain high levels of other adsorbed gases from the atmosphere, including water. The amounts of chloride remaining on the PuO₂ particles after heat treatment (measured by a caustic leaching process) decrease whilst the amounts of volatilised chloride increase with increasing heat treatment temperature. Clear evidence for a non-leachable (strongly bound) chloride species on the PuO₂ surface is found from the thermal treatments. The lattice parameter decreases with increasing heat treatment temperature, reflecting annealing of structural defects caused by over 35 years of radiation damage, with no change in the fcc Fm $\bar{3}$ m crystal structure. Heating chloride-contaminated PuO₂ powder to ~230 °C and cooling back to ambient temperature in a sealed vessel reveals the production of H₂, He, NO and CO gases. Water adsorption/desorption behaviour with the untreated PuO₂ powder is remarkably different than PuO₂ which had previously been heat treated at 700 °C. From thermal treatments in open and sealed systems it is concluded that water and chloride co-adsorb and interact on the PuO₂ surface and each affects the adsorption/desorption behaviour of the other. These data also support practical considerations for repackaging of chloride-contaminated PuO₂ for long term safe and secure storage at Sellafield.

© 2019 Elsevier B.V. All rights reserved.

1. Introduction

Plutonium dioxide (PuO₂), produced from the reprocessing of spent nuclear fuel, has been safely and securely stored in the UK for

* Corresponding author.

** Corresponding author.

E-mail addresses: sophie.sutherland-harper@postgrad.manchester.ac.uk (S. Sutherland-Harper), robin.j.taylor@nnl.co.uk (R. Taylor).

over fifty years, awaiting either reuse in mixed oxide (MOX) fuel or disposal in a geological disposal facility (GDF) [1–6]. Processing and storage of this material takes place at the Sellafield nuclear fuel reprocessing and decommissioning site in Cumbria. The majority of the inventory is high purity PuO_2 from reprocessing but a small fraction of the inventory has become contaminated with chloride. These legacy materials, dating mainly from the early 1970s, were stored in nested metal containers with a polyvinyl chloride (PVC) intermediate layer between the inner and outer cans. The chloride contamination is due to thermal and radiolytic degradation of the PVC bags, forming $\text{HCl}_{(\text{g})}$, which has been adsorbed onto the surface of the plutonium powder, together with water and other gases adsorbed from the air atmosphere by diffusion into these non-welded ('breathable') packages. This chloride and water-contaminated PuO_2 will require heat treatment in order to meet the conditions for acceptance (CFA) for repackaging and long term storage in modern facilities within welded cans. To underpin the design of the heat treatment process, it is necessary to characterise the chloride-contaminated powders and understand the process parameters which affect the partitioning of chloride between the product powder and off gas streams in a thermal treatment process. The properties of the product (heat treated) powder also need to be determined, in order to establish its suitability for long term storage and the ultimate disposition options. Based on previous simulant PuO_2 experiments, in which PuO_2 was artificially contaminated with chloride in the laboratory, increasing quantities of chloride were volatilised as the temperature of the heat treatment increased. Chloride adsorbed on the surface of the PuO_2 was determined by a caustic leaching method (this was termed 'leachable' chloride) and the experiments provided some evidence for a fraction of chloride that was strongly bound or 'non-leachable' when the powder was washed with NaOH solution [7].

CeO_2 is frequently used as a non-radiotoxic analogue to PuO_2 , as it has the same fcc $\text{Fm}\bar{3}\text{m}$ crystal structure, +4 oxidation state and similar metal ion radius ($\text{Ce}^{4+} = 0.97 \text{ \AA}$ and $\text{Pu}^{4+} = 0.96 \text{ \AA}$ for 8 coordinate structures) [8–10]. Initial studies of HCl and water adsorbed on CeO_2 have been carried out [11] and these experiments proved that:

- i. chloride is not incorporated into the CeO_2 crystal structure, as no crystalline phases other than the fcc $\text{Fm}\bar{3}\text{m}$ phase of CeO_2 are present,
- ii. the sorption mechanisms of water and chloride are linked and
- iii. heat treatment at 900°C removes chloride from the surfaces of high and low specific surface area CeO_2 particles (58 and $2 \text{ m}^2 \text{ g}^{-1}$, respectively).

As indicated above, the CeO_2 studies were then extended to cover the interactions of chloride and water with PuO_2 , using samples of high purity PuO_2 ('Magneox PuO_2 ') obtained from the reprocessing of spent Magnox fuel (a uranium metal fuel inside magnesium alloy cladding) which were artificially contaminated with chloride and humidified in the laboratory [7]. The aims were to establish the likely behaviour of chloride-contaminated PuO_2 in heat treatment, changes in properties before and after heat treatment, and to determine any similarities between the PuO_2 and CeO_2 analogues. This work showed that no crystal phase change is observed between chloride-contamination, humidification and heat treatment of the PuO_2 samples. Self-irradiation damage, caused by α -decay, is annealed at high heat treatment temperatures. The PuO_2 crystallites grow at temperatures higher than the original calcination temperature. A fraction of the chloride adsorbed onto the PuO_2 surface is stable with respect to heat treatment, but is leachable with caustic solution at ambient temperature. We

concluded that variations in PuO_2 specific surface area and production/storage history resulted in differences in behaviour, with respect to chloride desorption. These differences are likely to be accentuated when moving from studies of simulants produced in the laboratory to actual legacy chloride-contaminated materials retrieved from stores by, for instance, the differences in the chloride sources (dry HCl vapour versus *in situ* PVC degradation), radiation damage, storage temperature, the adsorption of atmospheric gases onto the surface and lengthened timescales of storage. Thus, the behaviour observed with simulants may not be fully representative of the stored high chloride materials. These experiments also suggested that the use of CeO_2 as a surrogate material for PuO_2 is of limited value in this case, as despite some similarities between the materials described above, substantial variations exist such as the differences in redox properties and self-irradiation effects [12].

This paper now reports the first studies on legacy chloride-contaminated PuO_2 powder retrieved from Sellafield stores, aiming to establish the likely inter-linked adsorption and desorption behaviours of chloride and water and their stabilities over a broad temperature range of relevance to the development of the heat treatment process. High temperature furnace experiments were carried out to study chloride-sorption, and lower temperature pressure vessel experiments were carried out to study water-sorption.

2. Experimental

Plutonium is an α -emitter, which presents both radioactivity and toxicity hazards. Manipulation and handling of these materials were performed only by qualified personnel in licensed radiological facilities.

2.1. Materials

A can of chloride-contaminated PuO_2 powder was retrieved from the Sellafield stores and opened. A series of sub-samples ($\sim 20\text{g}$) were taken from the can and stored in small aluminium screw-top containers. These samples were transferred to the laboratories and held in nitrogen or argon inerted glove boxes before being moved to an air atmosphere glove box for the experimental programme. No other pre-processing was applied to these samples prior to the experimental programme. The material had been produced on an old finishing line by calcination of the plutonium (IV) oxalate precipitate at $\sim 550^\circ\text{C}$ in 1980 and the plutonium isotopics are given in Table 1 following the original manufacture (measured) and at the start of the experimental programme (calculated). The specific surface area of the PuO_2 before heat treatment was determined by BET analysis using nitrogen as the adsorbate gas and measured to be $4.3 \pm 0.9 \text{ m}^2 \text{ g}^{-1}$. The loss on heating (LOH) at 950°C in argon was measured as $2.55 \pm 0.05 \text{ wt\%}$.

Table 1
Original plutonium isotopic analysis compared to calculated isotopics in 2016.

Isotope	13/01/1981	30/6/16
U-234	0	0.05
U-235	0	0.07
U-236	0	0.09
Np-237	0	0.13
Pu-238	0.19	0.14
Pu-239	70.69	70.62
Pu-240	23.58	23.49
Pu-241	4.51	0.81
Pu-242	1.03	1.03
Am-241	0	3.57

2.2. Thermal treatments

Five samples (0.5 or 1 g aliquots of PuO_2) to be heat treated were poured into a borosilicate glass tube and inserted into a vertical tube furnace (1,000 °C INSTRON, UK) in an air atmosphere radio-chemical (negative pressure) glove box. Based on preliminary experiments, the airflow was set to 250 mL min^{-1} to ensure adequate purging and capture of HCl and the furnace was heated to the specified temperature (400, 500, 600, 700, 800 or 950 °C) at $10^\circ\text{C min}^{-1}$, then held at temperature for 2 h. The furnace was then switched off and the powder was left to cool naturally to ambient temperature overnight, with the air flow maintained for the first hour of cooling. The effluent gas was passed through an NaOH trap (25 mL, 0.5 mol L^{-1}). Once the apparatus had cooled, the trap was emptied and washed out with ultra high quality water ($2 \times 10 \text{ mL}$). The thermal treatment experiments were essentially the same as those reported previously for the simulant studies [7].

2.3. Determination of chloride

A subsample of the NaOH solution from the trap solution (4 mL) was analysed for chloride by ion chromatography (IC) before and after heat treatment. Subsamples of PuO_2 powder were also taken before and after heat treatment, added to 4 mL of fresh NaOH solution, shaken, left for a few days to separate and the supernate filtered for IC, using an Anotop inorganic alumina membrane filter (pore size = $0.2 \mu\text{m}$ and diameter = 10 mm). IC was performed using a Dionex DX-500 with an AS18 column and a mobile phase of NaOH (0.023 mol L^{-1}) (current = 76 mA, flow rate = 1.30 mL min^{-1} and conductivity stabilised at $<5 \mu\text{S}$). Standards of 2, 5, 7 and 10 ppm Cl^- were used. The samples were diluted in ultra high purity water by a factor of 100 prior to analysis. Precision of the IC analysis was checked by triplicate analyses of selected samples (e.g. 3797, 3747, 3773 ppmCl) and also three replicate experiments at the same temperature using simulant samples gave good reproducibility ($4000 \pm 78, 2\sigma$) [7].

2.4. PuO_2 characterisation

Powder X-ray diffraction (XRD) analysis of the PuO_2 powders involved encapsulation of the oxide in epoxy resin. The methods have been described previously [7]. XRD patterns were recorded (Bruker D8) with step size = 0.02° and time per step = 9 s ($2\theta = 25\text{--}58^\circ$) and 18 s ($2\theta = 58\text{--}145^\circ$). Crystallite sizes, lattice parameters and uncertainties were obtained from the XRD patterns using Topas software [13].

2.5. PuO_2 – water interactions

The desorption/adsorption of surface species on the contaminated PuO_2 was investigated by heating a quantity of powder in a sealed vessel with and without small additions of water (typically 0.05 mL). The contaminated PuO_2 , ~10 g, was placed inside a custom-design pressure vessel (LBBC Baskerville, Leeds) with a volume of $41.0 \pm 1.2 \text{ cm}^3$. The sealed pressure vessel was heated inside a furnace (LBBC Baskerville, Leeds) with the whole experiment carried out in an argon atmosphere glove box. The target temperature of the furnace was maintained for 4 h before heating was turned off, allowing the furnace to cool naturally to room temperature. The vessel temperature and pressure were recorded throughout the heating and cooling cycle.

In the first series of experiments untreated PuO_2 powder was heated to successively higher temperatures of 100, 150, 200 and 230 °C. The 230 °C cycle was carried out twice. After the final heating the head space gas in the vessel was sampled for analysis

by gas chromatography (GC) using a Varian 490 micro GC with a 5 Å molecular sieve column operating with an argon carrier gas, column temperature of $\sim 90^\circ\text{C}$ and a thermal conductivity detector. Subsequently, 0.05 mL water was added to the vessel and the heating cycles were repeated with peak temperatures of 150 and 230 °C. Note that to maintain a safe operating envelope, ensuring strict compliance with the maximum permitted temperature in the 'Baskerville' vessel that is allowed under the safety case for its use in a plutonium glove box, the upper temperature was set between 220 and 240 °C for all experiments. This delivers a sufficient range of relative humidities within the vessel to study the physi-sorption of water on the PuO_2 surface.

In a second series of experiments, PuO_2 that had previously been heat treated at 700 °C in air in the tube furnace (following the procedure described in section 2.2) was heated in the sealed reactor to a temperature of 225 °C twice. After the second cycle, the vessel was opened and 0.05 mL water was added and the heating to 225 °C repeated.

3. Results

3.1. Thermal treatments

3.1.1. Ion chromatography

The leachable chloride content on the untreated PuO_2 solid is ~5,400 ppm, as measured by caustic leaching and IC. This equates to an average of 2.9 monolayers (ML) of leachable chloride present on samples of untreated, chloride-contaminated PuO_2 before heat treatment (calculated using Eq. (1)):

$$ML = \frac{\text{mol}_{\text{adsorbed}}}{n_m} \quad (1)$$

where $\text{mol}_{\text{adsorbed}}$ = number of moles of chloride adsorbed to the PuO_2 (determined from the chloride concentrations in the leached solutions) and n_m = number of moles of chloride per monolayer. The mass capacity for HCl on the PuO_2 surface is assumed to be 0.446 mg m^{-2} , compared to 0.22 mg m^{-2} for a water molecule [14]. That is, it is assumed that the surface area occupied by HCl on the PuO_2 surface is the same as for a water molecule. This is explained in more detail in Ref. [7]. The uncertainty ($\pm 9.3\%$) in the IC results shown are due to overall contributions from variations in the experiments as well as inherent heterogeneity in the powder, as chloride exposure varies through the powder within the can due to diffusion of HCl from outside the can into the powder during storage, despite mixing after sub-sampling.

The amount of volatilised chloride present in the caustic trap after heating compared with before heating is calculated using Eq. (2), and is shown in Fig. 1.

$$\text{Volatilised leachable chloride (\%)} = \frac{(FC - SC)}{SS} \times 100\% \quad (2)$$

The mass of chloride in the caustic trap after heat treatment is the final caustic (FC) and the mass of chloride in the caustic trap before heat treatment is the starting caustic (SC). The mass of leachable chloride on PuO_2 before heat treatment is the starting solid (SS). The amount of chloride volatilised increases with heat treatment temperature. There is no discernible difference in the percentage of chloride volatilised from either the 0.5 or 1 g samples of PuO_2 . In Fig. 1, 100% represents the chloride which is leachable on the untreated solid; that is, the measurement from the leached solid made before heat treatment. It is clear from the results that above 700 °C the volatilised chloride measured is more than 100% of the initial leachable chloride. This must infer that the total inventory of chloride in the solid is greater than that measured just by

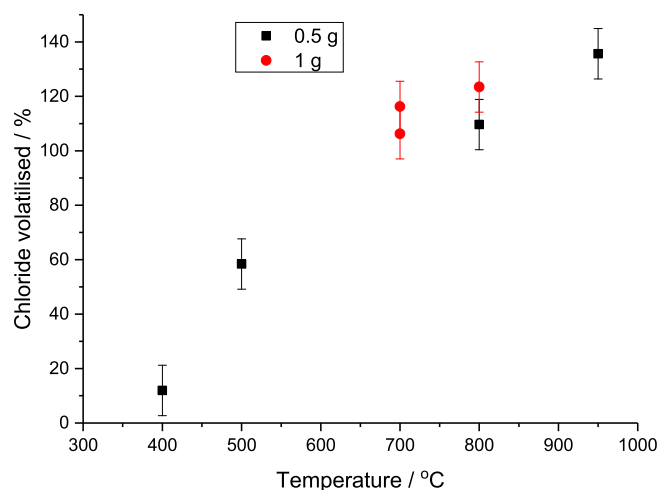


Fig. 1. The percentage of chloride volatilised and trapped in the NaOH solution post-heat treatment, c.f. the leachable chloride on the solid PuO_2 pre-heat treatment.

leaching with NaOH before heat treatment and that some of this 'non-leachable' chloride component is volatilised during the thermal treatments, at least above 700 °C.

Fig. 2 shows the volatilised and leachable chloride concentrations for the 0.5 g and 1 g samples measured after heat treatment relative to leachable chloride before heat treatment, which is taken as 100%. It is seen that the leachable fraction on the solid decreases and the volatilised fraction increases with increasing heat treatment temperature. >100% of the initial leachable chloride was recovered at higher heat treatment temperatures in these samples compared to lower heat treatment temperatures where <100% recoveries were obtained. The percentage of leachable chloride remaining decreases with increasing temperature, reaching almost zero at 950 °C. These data infer that heating up to 700 °C causes conversion of some of the leachable chloride initially present on the sample to a non-leachable form. However, this non-leachable form of chloride may still be volatilised, and at 700 °C and above, volatilisation is the dominant process. Also, as noted above, some non-

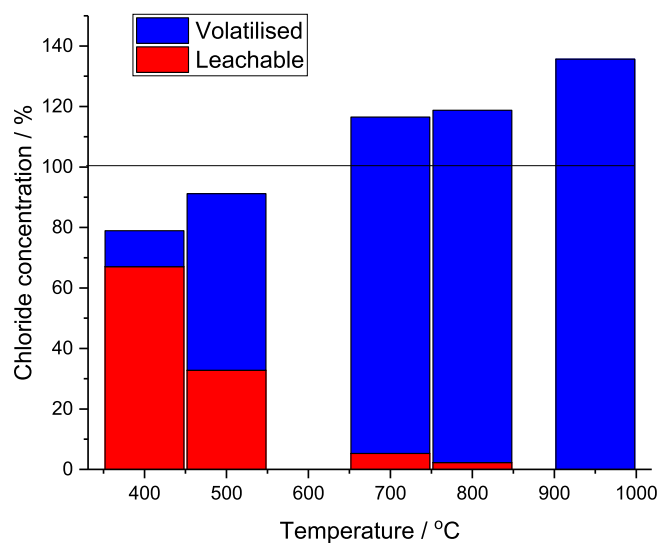


Fig. 2. The average percentage of chloride present in leachable and volatilised fractions, following heat treatment at a range of temperatures from the 0.5 and 1 g PuO_2 starting material samples, where 100% is leachable chloride measured from untreated PuO_2 samples.

leachable chloride species must be present initially in the powder as >100% recoveries are obtained at higher temperatures.

3.1.2. X-ray diffraction

Powder XRD patterns of chloride-contaminated PuO_2 before and after heat treatment at 400, 600, 800 and 950 °C are shown in Fig. 3; lines for a reference PuO_2 sample are also given. No additional phases are present in either the untreated or heat treated samples. The crystallite sizes (calculated from the peak widths, using the Scherrer equation) increase with increasing heat treatment temperature, almost doubling in size following treatment at 950 °C (Fig. 4). The Bragg peak positions shift for each heat treatment temperature as a consequence of the lattice parameters decreasing with increasing temperature.

3.2. PuO_2 – water interactions

3.2.1. Sequential heating of PuO_2 powder in the pressure/temperature 'Baskerville' vessel

An example of the recorded pressure variation with temperature for untreated, chloride-contaminated PuO_2 is shown (Fig. S11). The heating/cooling curves show a hysteresis due to non-isothermal conditions in the heating cycle. In practice, heating measurements were used only for monitoring the progress of the experiment. In the analyses of data, the heating cycles are thus disregarded and so are not included in the remaining figures.

Firstly, with heating it had been surprisingly observed in a preliminary test that non-condensable gas was produced; hydrogen and helium were quantitatively measured in this experiment (Table 2). This was investigated further by running successive cycles with increasing peak temperatures up to 230 °C (Fig. S11). The quantity of non-condensable gas increased as the furnace temperature was increased. The final pressure increases after each cycle compared to the starting pressure, even after heating the powder to 230 °C a second time; that is, there was no observed peak relating to a release at a specific intermediate temperature. The total pressure increase due to the non-condensable gas produced at ambient temperature over the five cycles is 0.056 MPa. The gas produced was qualitatively analysed by micro-gas

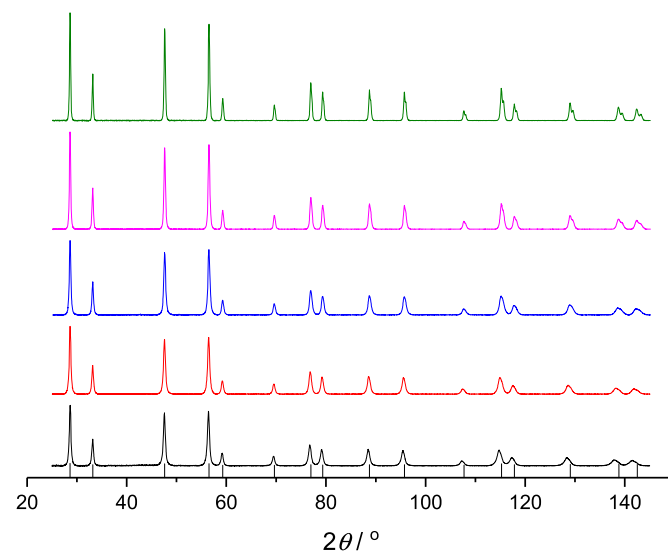


Fig. 3. Powder XRD patterns of the contaminated Magnox PuO_2 untreated (black) and heat treated at 400 (red), 600 (blue), 800 (pink) and 950 °C (green). Reference lines for PuO_2 are also shown (R. Roof, Los Alamos). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

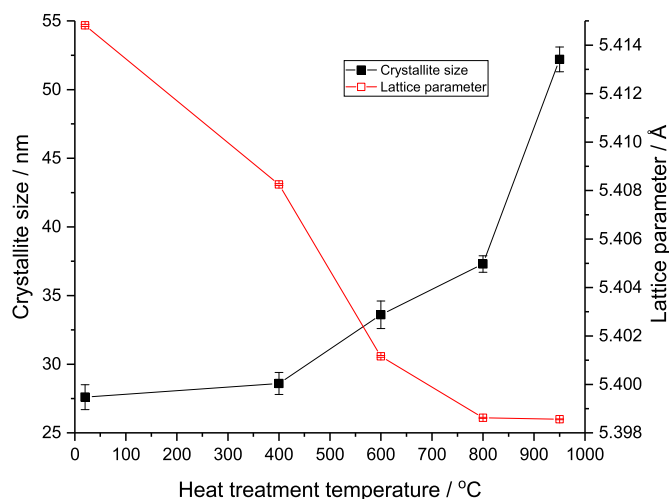


Fig. 4. Crystallite sizes and lattice parameters obtained from the XRD patterns in Fig. 3.

Table 2

Hydrogen and helium analyses from a Baskerville experiment with untreated chloride-contaminated PuO₂ (* = average of two samples).

Hydrogen		Helium	
ppm	μmol/gPuO ₂	ppm	μmol/gPuO ₂
4500*	1.4*	520	0.16

chromatography (μGC) and found to contain He, H₂, N₂, NO and CO (Fig. S12) although the sum of pressure calculated from the measured concentrations of these species cannot account for the majority of the gas produced. It must be assumed that gases which could not be separated and detected by μGC were also present. For example, CO₂ is likely to have adsorbed onto the surface during storage but would not be detected using the molecular sieve column if it desorbed.

Secondly, the monolayers of water (ML(H₂O)) adsorbed to the surface of the PuO₂, were calculated from the pressure measurements in Fig. S11. The measured pressure is then used to calculate the moles of water vapour in the vessel; the difference between the total estimated moles of water in the vessel (adsorbed water and water added to the vessel in the later wet experiments) and the moles of water vapour then gives the moles of adsorbed water. Using Eq. (1) (with water as the adsorbent), the adsorbed moles can be converted to adsorbed monolayers of water. The mass capacity of water on PuO₂ is taken as 0.22 mg m⁻² for a single monolayer [15]. Fig. 5 illustrates the variation of ML(H₂O) with the relative humidity (RH) in the vessel for the second cycle run to the maximum temperature (230 °C). RH is calculated from the ratio of the measured water vapour pressure and the saturated vapour pressure at the corresponding temperature.

This curve is compared with results obtained by Paffett et al. [14] who has previously reported the results of a similar study of water desorption from PuO₂ at Los Alamos National Laboratory and fitted data to the BET isotherm ([14,15] and references therein). The key point here is that the shapes of the curves are different. Much more water is adsorbed onto the chloride-contaminated PuO₂ than the pure PuO₂ used by Paffett et al. (for RH < 0.7). Whilst there may be differences in the materials used (e.g. surface area, porosity, morphology and isotopics) it is unlikely that these differences account for the significantly greater affinity for water adsorption seen here with the chloride-contaminated PuO₂.

The literature describes clear distinctions between strongly

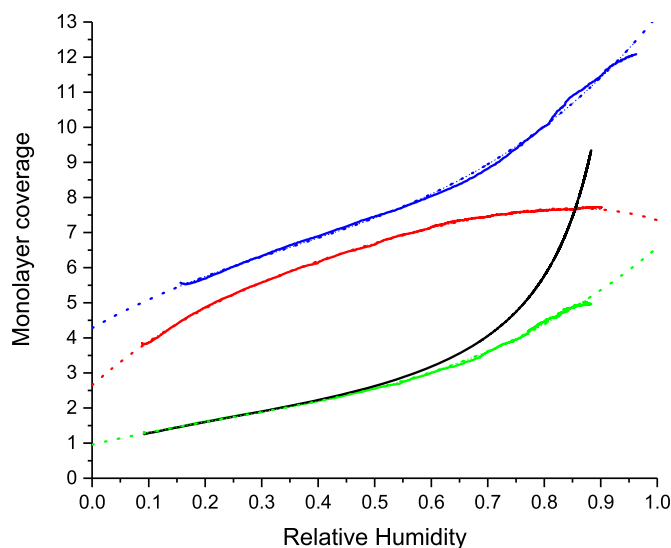


Fig. 5. The calculated monolayer coverages of water on the untreated PuO₂ (red), untreated PuO₂ with 0.05 mL water (blue) and PuO₂ heat treated at 700 °C with 0.05 mL water (green), with data extrapolated to 0% RH (dotted lines), compared with the results obtained by Paffett et al. [14] (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

adsorbed and weakly adsorbed water layers, although the exact nature of these layers is still a matter of debate – see section 4.1 [15].

The maximum number of monolayers able to adsorb to the PuO₂ surface, based on the sum of the initial measured water content of the PuO₂ (by LOH at 950 °C, see section 2.1) and available moles of water added to the vessel, are given in Table 3, as are the number of strongly adsorbed monolayers estimated as the intercept of the curves at 0% RH, using polynomial lines of best fit (see Fig. 5). With the untreated chloride-contaminated samples this gives an estimate of 2–3 ML(H₂O) for the strongly bound fraction; the monolayers above this number are more weakly bound and represent the water layers that adsorb and desorb during the Baskerville experiment.

In the experiments with an aliquot of water added to the untreated chloride-contaminated PuO₂ powder sample, a smaller amount of non-condensable gas was produced (pressure increase inside the vessel = 0.021 MPa). This indicates that desorption of adsorbed gases (other than water) from the PuO₂ surface was still incomplete and possibly influenced by addition of water. The cumulative increases in pressure for successive dry and then wet cycles are illustrated in Fig. 6, noting that the wet cycles were performed on the same material following on from the dry cycles.

As before, the pressure/temperature measurements were used to calculate the monolayers of water adsorbed to the PuO₂ surface during the cooling cycles (Fig. 5, 230 °C run only). The key observations in this experiment are that the curves do not overlap; the slopes are comparable in the region of low RH, and at higher RH the approach towards condensation is seen in the experiment with water added. The slope of the plot for the chloride-contaminated PuO₂ is consistently higher than reported in the results of Paffett et al. [14] at RH < 0.7.

As before, the monolayers of water which are strongly adsorbed to the PuO₂ can be calculated by a polynomial extrapolation back to 0% RH. The data for the full heating cycles are given in Table 3. This again highlights a change in behaviour when water is added to the system, with an apparent increase in the strongly bound fraction.

Table 3

The monolayers of water strongly adsorbed at 0% RH calculated from extrapolation of experimental data obtained from full heating cycles, using a polynomial gradient (see Fig. 5) and maximum number of ML(H₂O) available for adsorption in the system.

Experiment	Max. ML(H ₂ O)	Max. Temp./°C	ML(H ₂ O) at 0% RH
Untreated PuO ₂ no added water (dry, 1st cycle)	8.2	226	2.4
Untreated PuO ₂ no added water (dry, 2nd cycle)	8.2	225	2.6
Untreated PuO ₂ added water (wet)	14.3	225	4.3
Heat treated PuO ₂ added water (wet)	5.5	219	0.96

3.2.2. PuO₂ heat treated at 700 °C

Based on the above observation of the evolution of a non-condensable gas and in order to understand how water adsorption on the chloride-contaminated PuO₂ is affected by thermal treatment, a second study was initiated using a sample of PuO₂ which had previously been heat treated at 700 °C in air using the same methodology as described in section 2.2.

For the dry cycles it was apparent that (a) the pressure increase followed the ideal gas expansion as the material contains very little residual water following heat treatment at 700 °C and (b) a small amount of non-condensable gas was still released (0.009 MPa in the first heating cycle only). This may be due to either further release of helium from alpha decay or a small amount of gases (probably radiolysis products of air) that adsorbed onto the surface following heat treatment and before transfer into the inerted (argon atmosphere) glove box.

Repeating this experiment with the same PuO₂ in the presence of water produces a pressure rise, which is due to a non-ideal gas, condensable on cooling to ambient temperature in both cycles. Conversion of the experimental P/T data to the ML(H₂O) vs. RH in Fig. 5 shows a striking change in behaviour compared with the original untreated chloride-contaminated PuO₂ that was retrieved from stores. The water sorption behaviour now appears close to the results of Paffett et al. [14], at least below ~0.6 RH – there is some deviation at high RH but in this region the uncertainties in the method increase significantly and the influences of morphology, porosity etc. might increase.

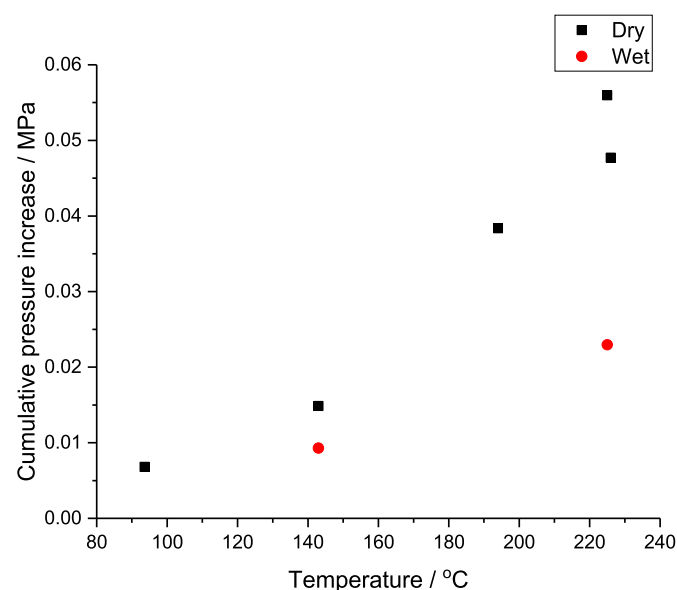


Fig. 6. Cumulative pressure increase within the sealed vessel for the dry and wet experiments on untreated chloride-contaminated PuO₂ vs. maximum temperature of the cycle.

3.2.3. Chloride analysis

Table 4 shows that the monolayers of chloride adsorbed to the untreated PuO₂ do not change significantly following dry and wet thermal cycling up to 225 °C. Given the data of Fig. 1 it is expected that chloride desorption at the temperatures reached in the Baskerville vessel will be very low; some changes in surface speciation with humidity, however, might be expected [7]. The chloride data obtained on the heat treated sample showed the expected reduction in leachable chloride due to the desorption that occurred during the heat treatment. There was a possible decrease following the experimental heating cycles with the untreated dry powder. This may reflect an inter-conversion between leachable and non-leachable species as, at these low temperatures, volatilisation is not expected. However, even if this has occurred, following the cycles with added water, the surface is obviously re-hydrated and the leachable chloride species returns to the value found before any Baskerville runs (0.6–0.7 ML(HCl)).

4. Discussion

4.1. Surface chemistry

The results show that when the PuO₂ powder is heat treated at <700 °C, less than 100% of the chloride leachable before heat treatment is recovered from the leachable and volatilised chloride after heat treatment. Even though some chloride is volatilised at these lower heat treatment temperatures, a significant proportion of leachable chloride remains bound to the PuO₂. However, more than 100% of the initial (leachable) chloride is detected in the caustic trap post-heat treatment at higher temperatures, with margins exceeding possible errors (c.f. pre-heat treatment, Fig. 1). This suggests that there is a non-leachable chloride component either strongly bound on the surface or contained within the bulk PuO₂. It appears that heat treatment temperatures >700 °C can volatilise the non-leachable chloride species. This is influenced by weakening the interactions between the adsorbed chloride and the surface, the additional energy input to overcome the barrier and loss of surface sites as SSA decreases. For example, in Fig. 2, IC of the leachable chloride remaining on the surface after heat treatment at 950 °C reduces to almost zero, yet the percentage of chloride recovered from the caustic trap for this heat treatment temperature is 135% (c.f. the starting solid PuO₂). So, from the heat treatment data, there is a clear indication that there are chloride species adsorbed on the PuO₂ surface that are not leachable in dilute NaOH as well as leachable species. At lower furnace temperatures, in an open system, it seems probable that leachable species are converted to non-leachable species. It is also possible that the humid atmosphere in the sealed system can re-hydrate the surface to regenerate leachable chloride species. The nature of these species requires the application of surface sensitive techniques such as infrared (IR) and Raman spectroscopies or X-ray photo-electron spectroscopy (XPS) and was not the object of this study. However, based on similar studies of chloride adsorption in the literature, dissociative adsorption of HCl, formation of a hydroxylated Pu^{IV}(H₂O)⁺Cl⁻ species and incorporation into the structure have

Table 4Leachable chloride monolayers on the untreated and heat treated PuO₂ solids, measured before and after the dry and wet heating cycles.

PuO ₂	Point of analysis	Chloride monolayers/ML
Untreated	Before dry cycles	3.1
Untreated	After dry cycles (before wet cycles)	3.2
Untreated	After wet cycles	3.3
Heat treated (700 °C)	Before dry cycles	0.64
Heat treated (700 °C)	After dry cycles (before wet cycles)	0.43
Heat treated (700 °C)	After wet cycles	0.70

been proposed as a hypothetical framework [7,16–23]. Other possibilities include an amorphisation of the surface to form PuO_{2+x} and radiation damage leading to defect formation. These sites could then be amenable to formation of PuO_xCl_y species. Since radiolytic degradation of plasticised PVC produces HCl_(g) as the only chloride-containing contaminant, the presence of at least two forms of chloride on the PuO₂ surface highlights the complex chemistry of the PuO₂ surface [24–26]. It is not impossible that there are adsorbed organic chlorides from exposure to air atmosphere under the conditions of storage [21–23] although we see no evidence for this possibility as yet.

Previous work on chloride-contaminated CeO₂ analogues revealed that the chloride homogeneously covered all available surface area, including within pores, but this was volatilised to the extent that the chloride remaining on the particles was below the limit of detection using energy dispersive X-ray analysis after heat treatment at 900 °C, showing that heat treatment removes chloride from all metal oxide surfaces, both exposed on the exterior of aggregates and within the aggregates [11]. The amounts of leachable chloride in the samples presented here are similar to those of simulant PuO₂, which was contaminated with dry HCl gas and humidified in the laboratory, before being heat treated at various temperatures [7]. However, the profiles for the simulant heat treated samples are significantly different. This is undoubtedly due to the age (>35 years storage) and storage history of the samples (self-heating, breathable containers), resulting in different amounts of radiation damage to the lattice, changing particle morphology and the evolution over time of the adsorbed gases on the surface. These are conditions that cannot be replicated in a laboratory and, overall, it appears that neither of our previous studies generated wholly realistic simulants for the actual legacy chloride-contaminated PuO₂.

The thermal treatments in the open system and the mechanism of Parfitt et al. imply a role for water in the surface chemistry of chloride-contaminated PuO₂. The adsorption of water on pure PuO₂ is a field of long-standing debate. Stakebake defines three types of water adsorption to the PuO₂ surface: (i) chemisorbed water, which forms strongly bound hydroxyls by dissociative adsorption onto Pu and O, (ii) quasi-chemisorbed molecular water, which either singly or doubly hydrogen bonds to the hydroxyls and (iii) physisorbed molecular water, which hydrogen bonds to adsorbed molecular water [27]. Haschke and Ricketts suggest that one monolayer of water tenaciously chemisorbs to the PuO₂ surface at low relative humidity and another monolayer physisorbs by RH of 0.50 [15]. Stakebake and Veirs et al. suggest that the chemisorbed hydroxyls cannot be desorbed below 1,000 °C and Farr et al. report the ubiquitous presence of surface hydroxyls when PuO₂ is exposed to water vapour, through both molecular and dissociative adsorption, which remain on the surface up to 590 °C [28,29]. Wellington et al. suggest that the first adsorbed water monolayer is either dissociatively or molecularly bound, depending on the Miller index of the surface [30]. Theoretical studies by Tegner et al. report the highest temperature of desorption of the hydroxylated PuO₂ (1 0 0) surface to be 377 °C under a pressure of 5 bar, higher than the

maximum temperature the powder was heated to in our P/T experiments of ~230 °C [31].

The co-adsorption of ~3 monolayers of chloride and other radiolysed gases adsorbed from the air on the untreated PuO₂, which has not been annealed, are the two main factors contributing to the differences between water sorption profiles in this experiment and previous theoretical and experimental data, such as the profile of Paffett et al. These differences lead to variations in the amount of adsorption sites available on the PuO₂ surface, such as increased oxygen vacancies within the crystal structure [32,33]. The P/T sealed vessel experiments show a significant evolution from a profile that is very different to the expected Paffett-type behaviour (untreated chloride-contaminated PuO₂, dry cycle) to profiles that are close to the expected behaviour after chloride-contaminated PuO₂ has been heat treated at 700 °C.

There is a clear implication that the presence of chloride (and possibly other adsorbates) on the surface changes the adsorption of water. The Baskerville experiments are consistent with literature that proposes multi-layer adsorption of water on PuO₂ [15].

We propose that the high chloride content present on the untreated PuO₂ surface (~3 ML) is closely associated with adsorbed water and, furthermore, can adsorb additional water under humid conditions leading to multiple layers of water adsorption in these powders. This is not observed in the 700 °C heat treated PuO₂ sample as much of the adsorbed chloride has been volatilised during heat treatment leaving only ~0.7 ML chloride on the surface. In this case, the water adsorption tends to behaviours expected for pure PuO₂ [14].

A final question relates to the nature of the strongly bound water layer. The P/T method with the Baskerville vessel used here was not designed to probe this layer but extrapolation of the experimental curves to 0% RH leads to estimates for the thickness of the strongly bound water layers. Paffett et al. have reported that they saw a slow change in their P/T cycles attributed to formation of a thickening hydroxide layer [14]. Other authors have also reported evidence for a transition from weakly bound to strongly bound water over time. The strongly bound layers calculated in these experiments are higher than expected from normal chemisorption models and appear to change depending on the conditions. However, unlike literature data, they are probably attributable to the formation of mixed chloride/water species that are more difficult to remove than simple physisorbed water layers, *i.e.* there is some chemical interaction between water and chloride when adsorbed on PuO₂. Finally, other adsorbed gases are present on the chloride-contaminated PuO₂, including NO_x from the radiolysis of nitrogen. These species will also most likely interact with chloride and water, complicating the surface chemistry. One conclusion is that the surface will be highly acidic.

4.2. Gas evolution

Non-condensable gas was evolved from the untreated sample when heated in the Baskerville vessel at varying temperatures. A small amount of helium was present in the gas sample; this is due

to α -decay of the plutonium isotopes during decades of storage and hold up of part of the helium formed in the PuO₂ matrix. It is interesting that heating even at these relatively low temperatures can cause helium diffusion out of the matrix. The production of H₂ measured by GC is attributed to the radiolysis of adsorbed water on the PuO₂ surface as it is in agreement with theoretical studies [30,31] and experimental studies by Veirs et al. [34], Sims et al. [35] and references therein. Some fraction of the NO and CO species adsorbed to the PuO₂ surface were volatilised in this experiment, but are not oxidised, as these experiments were carried out in an argon atmosphere glove box. NO_x is known to be formed from radiolysis of N₂ in the gas phase [36–38]. The maximum pressure reached at 230 °C was 0.505 MPa and more gas (particularly helium from within the pores) would have evolved, had the 230 °C cycle been repeated more times or the peak temperature been higher.

With thermal treatment at 700 °C under an air atmosphere, adsorbed volatile species, such as H₂O, CO₂ and NO₂, will have mostly been desorbed together with a substantial part of the chloride inventory [7]. However, after the PuO₂ sample was heat treated at 700 °C, it was stored in an air atmosphere glove box, potentially allowing oxidised gaseous species, such as H₂O, N₂ and CO₂, to re-adsorb to the PuO₂ surface (N₂ is subject to radiolysis and adsorption as NO_x) [7]. The non-condensable gas released during the first Baskerville run on the heat treated sample can likely be attributed to desorption of the species adsorbed during this short period of interim storage as no more gas is evolved on heating the powder a second time. This supports the assumption that thermal treatment followed by storage under dry argon is needed to stabilise the chloride-contaminated PuO₂.

None of the species detected by gas chromatography are of sufficient concentration to explain the total pressurisation observed in runs with untreated chloride-contaminated PuO₂. Therefore, dominant species produced by heating the PuO₂ must be a species such as CO₂, N₂O or Cl₂, which cannot be separated on the molecular sieve column.

4.3. X-ray diffraction

The XRD pattern of the chloride-contaminated PuO₂ (Fig. 3) shows only the fcc Fm $\bar{3}$ m crystal phase and no phase change as the sample is heated. The crystal sizes of the untreated PuO₂ are 27.6 (± 0.9) nm (Fig. 4). This is similar to previous work carried out on simulant PuO₂, which was contaminated with dry HCl vapour and humidified and yielded a crystal size of 29.1 (± 0.8) nm. The PuO₂ crystallite size increases as the heat treatment temperature increases, especially above 600 °C, since the powders were originally calcined at 550 °C. The maximum crystal size for PuO₂ powders heat treated at 950 °C is 52.2 (± 0.9) nm.

The lattice parameters, calculated from the XRD patterns (Fig. 4), show that the lattice contracts as the heat treatment temperature increases. The lattice parameter for the 950 °C heat-treated PuO₂ powder sample (5.3986 Å) is larger than that reported by Farr et al. (5.3975 Å) for stoichiometric PuO₂ and by Chikalla et al. (5.3954 Å) for ²³⁸PuO₂; however, the sample heat treatment (950 °C) was at a lower temperature than that used to anneal ²³⁸PuO₂ (>1,000 °C) [29, 39]. The lattice has expanded over time, due to radiation damage from alpha decay of the Pu isotopes; heat treatment of the powders at higher temperatures anneals these lattice defects and causes the lattice to contract [39–41]. The lattice parameter of the untreated, chloride-contaminated PuO₂ (5.4148 Å) is larger than that of simulant PuO₂, which had been contaminated with dry HCl vapour and humidified under laboratory conditions (5.4062 Å), as the PuO₂ simulant material was of recent production and the lattice parameter had not reached the steady state from radiation damage [7].

5. Conclusions

The effects of heat treatment on chloride and water-contaminated PuO₂ have been presented. As expected, high heat treatment temperatures of 700, 800 and 950 °C volatilise almost all of the leachable chloride present on the 0.5 g and 1 g PuO₂ starting material sample surfaces before heat treatment. More interesting is that chloride recoveries change from <100%, relative to initial leachable chloride, at lower heat treatment temperatures to >100% at high temperatures providing clear evidence for a ‘non-leachable’ fraction and probable inter-conversion between leachable and non-leachable fractions depending on the surface hydration. This is supported by lower temperature heating cycles in a sealed system (humid atmosphere). Further studies using spectroscopic techniques such as IR and XPS are needed to investigate the surface speciation and chemical interactions between water and chloride. XRD of the PuO₂ powders shows that heat treatment leads to an increase in crystallite size and a smaller lattice parameter due to annealing radiation damage but there is no evidence for bulk phases other than PuO₂. Untreated and heat treated chloride-contaminated PuO₂ powders behaved remarkably differently in thermal cycling experiments in a sealed vessel with regards to water adsorption and provided evidence that it is the presence of chloride on the untreated sample that contributes to these differences. Estimates of the number of layers of strongly bound water have also been made and are ~3 ML(H₂O) which compares with ~3 ML chloride present initially for the untreated sample. Overall, the data here present strong evidence that water and chloride co-adsorb on PuO₂ and that the sorption/desorption behaviours of each are affected by the other. These data also support practical considerations for repackaging of chloride-contaminated PuO₂ for long term safe and secure storage at Sellafield.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgements

We thank the EPSRC and Sellafield Ltd. for a studentship (to SSH). All experiments were carried out with the aid of Kevin Webb, Colin Gregson, Stacey Reilly, Catherine Campbell, Hannah Colledge, Josh Holt and Bliss McLuckie at the National Nuclear Laboratory Central Laboratory, Sellafield, Cumbria, UK; access (for SSH) was funded by the Nuclear Decommissioning Authority. We also thank John Waters (University of Manchester) for his guidance with powder X-ray diffraction.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jnucmat.2019.02.036>.

References

- [1] L. Cadman, A. Goater, Managing the UK Plutonium Stockpile, 2016. researchbriefings.files.parliament.uk/documents/POST-PN-0531/POST-PN-0531.pdf.
- [2] Nuclear Decommissioning Authority, Progress on Approaches to the Management of Separated Plutonium, 2014 doi:21100718.
- [3] Department of Energy and Climate Change, Management of the UK's Plutonium Stocks: A Consultation on the Long-Term Management of UK Owned Separated Civil Plutonium, 2011.
- [4] N.C. Hyatt, Plutonium management policy in the United Kingdom: the need for a dual track strategy, Energy Policy 101 (2017) 303–309, <https://doi.org/>

- 10.1016/j.enpol.2016.08.033.
- [5] P. Cook, H. Sims, D. Woodhead, Safe and secure storage of plutonium dioxide in the United Kingdom, *Actinide Res. Q.* August (2013) 20–25.
 - [6] R. Taylor, J. Hobbs, R. Orr, H. Steele, Characterisation of plutonium dioxide, *Nucl. Future* 14 (2018) 40–50.
 - [7] S. Sutherland-Harper, C. Pearce, C. Campbell, M. Carrott, H. Colledge, C. Gregson, J. Hobbs, F. Livens, N. Kaltsoyannis, R. Orr, M. Sarsfield, H. Sims, H. Steele, I. Vatter, L. Walton, K. Webb, R. Taylor, Characterisation and heat treatment of chloride contaminated and humidified PuO₂ samples, *J. Nucl. Mater.* 509 (2018) 654–666, <https://doi.org/10.1016/j.jnucmat.2018.07.031>.
 - [8] H.S. Kim, C.Y. Joung, B.H. Lee, J.Y. Oh, Y.H. Koo, P. Heimgartner, Applicability of CeO₂ as a surrogate for PuO₂ in a MOX fuel development, *J. Nucl. Mater.* 378 (2008) 98–104, <https://doi.org/10.1016/j.jnucmat.2008.05.003>.
 - [9] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. A* 32 (1976) 751–767.
 - [10] M.C. Stennett, C.L. Corkhill, L.A. Marshall, N.C. Hyatt, Preparation, characterisation and dissolution of a CeO₂ analogue for UO₂ nuclear fuel, *J. Nucl. Mater.* 432 (2013) 182–188, <https://doi.org/10.1016/j.jnucmat.2012.07.038>.
 - [11] S. Sutherland-Harper, R. Taylor, J. Hobbs, S. Pimblott, R. Patrick, M. Sarsfield, M. Denecke, F. Livens, N. Kaltsoyannis, B. Arey, L. Kovarik, M. Engelhard, J. Waters, C. Pearce, Surface speciation and interactions between adsorbed chloride and water on cerium dioxide, *J. Solid State Chem.* 262 (2018) 16–25, <https://doi.org/10.1016/j.jssc.2018.02.018>.
 - [12] J.C. Marra, Cerium as a Surrogate in the Plutonium Immobilization Waste Form, 2002.
 - [13] C.L. Corkhill, D.J. Bailey, F.Y. Tocino, M.C. Stennett, J.A. Miller, J.L. Provis, K.P. Travis, N.C. Hyatt, Role of microstructure and surface defects on the dissolution kinetics of CeO₂, a UO₂ fuel analogue, *ACS Appl. Mater. Interfaces* 8 (2016) 10562–10571, <https://doi.org/10.1021/acsami.5b11323>.
 - [14] M.T. Paffett, D. Kelly, S.A. Joyce, J. Morris, K. Veirs, A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces, *J. Nucl. Mater.* 322 (2003) 45–56, [https://doi.org/10.1016/S0022-3115\(03\)00315-5](https://doi.org/10.1016/S0022-3115(03)00315-5).
 - [15] J.M. Haschke, T.E. Ricketts, Adsorption of water on plutonium dioxide, *J. Alloy. Comp.* 252 (1997) 148–156, [https://doi.org/10.1016/S0925-8388\(96\)02627-8](https://doi.org/10.1016/S0925-8388(96)02627-8).
 - [16] G.D. Parfitt, J. Ramsbotham, C.H. Rochester, Infra-red study of hydrogen chloride adsorption on rutile surfaces, *Trans. Faraday Soc.* 67 (1971) 3100–3109, <https://doi.org/10.1039/tf9716703100>.
 - [17] P. Jackson, G.D. Parfitt, Infra-red study of the surface properties of rutile. Water and surface hydroxyl species, *Trans. Faraday Soc.* 67 (1971) 2469, <https://doi.org/10.1039/tf9716702469>.
 - [18] J.W. Elam, C.E. Nelson, M.A. Tolbert, S.M. George, Adsorption and desorption of HCl on a single-crystal α -Al₂O₃(0001) surface, *Surf. Sci.* 450 (2000) 64–77, [https://doi.org/10.1016/S0039-6028\(99\)01247-9](https://doi.org/10.1016/S0039-6028(99)01247-9).
 - [19] R.V. Siriwardane, J. Wightman, Interaction of hydrogen chloride and water with oxide surfaces, *J. Colloid Interface Sci.* 94 (1983) 502–513, [https://doi.org/10.1016/0021-9797\(83\)90290-4](https://doi.org/10.1016/0021-9797(83)90290-4).
 - [20] R.R. Bailey, J.P. Wightman, Interaction of gaseous hydrogen chloride and water with oxide surfaces, *J. Colloid Interface Sci.* 70 (1979) 112–123, [https://doi.org/10.1016/0021-9797\(79\)90014-6](https://doi.org/10.1016/0021-9797(79)90014-6).
 - [21] M. Heuberger, G. Dietler, L. Schlappbach, New aspects in Volmer-Weber 3D growth: an XPS intensity study applied to thin films of Au and Ce on polypropylene, *Surf. Sci.* 314 (1994) 13–22, [https://doi.org/10.1016/0039-6028\(94\)90209-7](https://doi.org/10.1016/0039-6028(94)90209-7).
 - [22] B.M. Weckhuysen, G. Mestl, M.P. Rosynek, T.R. Krawietz, J.F. Haw, J.H. Lunsford, Destructive adsorption of carbon tetrachloride on alkaline earth metal oxides, *J. Phys. Chem. B* 102 (1998) 3773–3778, <https://doi.org/10.1021/jip980185k>.
 - [23] K.H. Park, S.J. Oh, Electron-spectroscopy study of rare-earth trihalides, *Phys. Rev. B* 48 (1993) 14833–14842, <https://doi.org/10.1103/PhysRevB.48.14833>.
 - [24] J. Colombani, V. Laped, C. Jousot-Dubien, A. Périchaud, J. Raffi, J. Kister, C. Rossi, High doses gamma radiolysis of PVC: mechanisms of degradation, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 265 (2007) 238–244, <https://doi.org/10.1016/j.nimb.2007.08.053>.
 - [25] I. Boughattas, E. Pellizzi, M. Ferry, V. Dauvois, C. Lamouroux, A. Dannoux-Papin, E. Leoni, E. Balanzat, S. Esnouf, Thermal degradation of γ -irradiated PVC: II-Isothermal experiments, *Polym. Degrad. Stabil.* 126 (2016) 209–218, <https://doi.org/10.1016/j.polymdegradstab.2015.05.010>.
 - [26] A.H. Zahran, E.A. Hegazy, F.M. Ezz Eldin, Radiation effects on poly (vinyl chloride)-I. gas evolution and physical properties of rigid PVC films, *Radiat. Phys. Chem.* 26 (1985) 25–32, [https://doi.org/10.1016/0146-5724\(85\)90028-7](https://doi.org/10.1016/0146-5724(85)90028-7).
 - [27] J.L. Stakebake, A thermal desorption study of the surface interactions between water and plutonium dioxide, *J. Phys. Chem.* 77 (1973) 581–586, <https://doi.org/10.1021/j100624a003>.
 - [28] D.K. Veirs, M.A. Stroud, J.M. Berg, J.E. Narlesky, L.A. Worl, M.A. Martinez, A. Carillo, MIS High-Purity Plutonium Oxide Metal Oxidation Product TS707001 (SSR123): Final Report, 2017.
 - [29] J.D. Farr, R.K. Schulze, M.P. Neu, Surface chemistry of Pu oxides, *J. Nucl. Mater.* 328 (2004) 124–136, <https://doi.org/10.1016/j.jnucmat.2004.04.001>.
 - [30] J.P.W. Wellington, A. Kerridge, J. Austin, N. Kaltsoyannis, Electronic structure of bulk AnO₂ (An = U, Np, Pu) and water adsorption on the (111) and (110) surfaces of UO₂ and PuO₂ from hybrid density functional theory within the periodic electrostatic embedded cluster method, *J. Nucl. Mater.* 482 (2016) 124–134, <https://doi.org/10.1016/j.jnucmat.2016.10.005>.
 - [31] B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker, N. Kaltsoyannis, Water adsorption on AnO₂{111}, {110}, and {100} surfaces (An = U and Pu): a density functional theory + U study, *J. Phys. Chem. C* 121 (2017) 1675–1682, <https://doi.org/10.1021/acs.jpcc.6b10986>.
 - [32] D.R. Mullins, The surface chemistry of cerium oxide, *Surf. Sci. Rep.* 70 (2015) 42–85, <https://doi.org/10.1016/j.surfrep.2014.12.001>.
 - [33] M.A. Henderson, C.L. Perkins, M.H. Engelhard, S. Thevuthasan, C.H.F. Peden, Redox properties of water on the oxidized and reduced surfaces of CeO₂(1 1 1), *Surf. Sci.* 526 (2003) 1–18, [https://doi.org/10.1016/S0039-6028\(02\)02657-2](https://doi.org/10.1016/S0039-6028(02)02657-2).
 - [34] D.K. Veirs, J.M. Berg, D.D. Hill, D.M. Harradine, J.E. Narlesky, E.L. Romero, L. Trujillo, K.V.J. Wilson, Water Radiolysis on Plutonium Dioxide: Initial Results Identifying a Threshold Relative Humidity for Oxygen Gas Generation, 2012.
 - [35] H.E. Sims, K.J. Webb, J. Brown, D. Morris, R.J. Taylor, Hydrogen yields from water on the surface of plutonium dioxide, *J. Nucl. Mater.* 437 (2013) 359–364, <https://doi.org/10.1016/j.jnucmat.2013.02.040>.
 - [36] S.Y. Pshezhetskij, M.T. Dmitriev, Nitrogen fixation by the action of ionizing radiations, *Int. J. Appl. Radiat. Isot.* 5 (1959) 67–69.
 - [37] P. Harteck and S. Dondes, Radiation chemistry of gases, Proceedings of the second United Nations International Conference.
 - [38] C. Willis, A.W. Boyd, M.J. Young, Radiolysis of air and nitrogen-oxygen mixtures with intense electron pulses determination of a mechanism by comparison of measured and computed yields, *Can. J. Chem.* 48 (1970) 1515–1525.
 - [39] T.D. Chikalla, R.P. Turcotte, Self-radiation damage ingrowth in 238 PuO₂, *Radiat. Eff.* 19 (1973) 93–98, <https://doi.org/10.1080/00337577308232225>.
 - [40] N.P. Turcotts, T.D. Chikalla, Annealing of self-radiation damage in 238 PuO₂, *Radiat. Eff.* 19 (1973) 99–108, <https://doi.org/10.1080/00337577308232226>.
 - [41] W.J. Weber, Alpha-irradiation damage in CeO₂, UO₂ and PuO₂, *Radiat. Eff.* 83 (1984) 145–156, <https://doi.org/10.1080/00337578408215798>.