Investigation of the interaction of water with plutonium oxide analogues

D. M. Laventine*[1], C. Boxall[1], R. Taylor[2] and R. Orr[2]

[1] *Department of Engineering, University of Lancaster, Lancaster, LA1 4YR, UK.   (* d.laventine@lancaster.ac.uk)*
[2] *Central laboratory, B170, National Nuclear Laboratory, Sellafield, CA20 1PG, UK*

Introduction

Approximately 250 tonnes of separated Pu are currently stockpiled worldwide. ~50% is in interim storage in the UK whilst further processing or long-term storage options are considered.

Interim storage of PuO_2 involves sealing in inert steel containers under an inert atmosphere. Under certain circumstances, these gas canisters have been observed to spontaneously heat up and pressurise.

5 routes to gas production have been suggested:

(i)   Helium accumulation from α decay;
(ii) Decomposition of polymeric packing material;
(iii) H_2O desorption (steam) from hygroscopic PuO_2;
(iv) Radiolysis of adsorbed water;
(v)   Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

The last 3 processes all involve PuO_2/H_2O interactions and are complex, inter-connected and poorly understood.

The aim of this project is to investigate the interaction of plutonium oxide (and less radioactive analogues) with water electrochemical and crystal microbalance methodologies.

Crystal Microbalance Methodology

Crystal microbalances utilise the piezoelectric effect to accurately measure very small changes in mass of a crystal, via changes in the frequency of the crystal vibration in response to an applied current. Through coating the crystal with a thin layer of the metal oxide of interest, any changes in frequency due to absorption or desorption of gases at the oxide surface can be measured, and the change in mass determined using the Sauerbrey equation.

$$\Delta f = -\left(\frac{nf_0^2}{A\sqrt{\rho_q\mu_q}}\right)\Delta m$$

The calculated mass can then be used to determine, for example, the amount of hydrogen lost, or the number of water layers de-/absorbed onto the oxide surface.
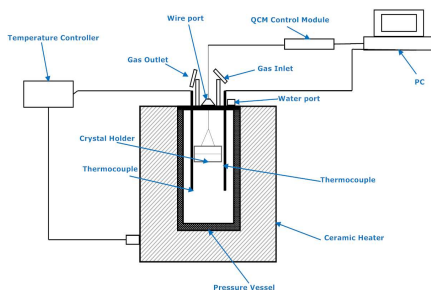
Fig. 1. Diagram of crystal microbalance experimental setup.

Initial microbalance studies have been performed using quartz crystals coated with ceria. The temperature response of the crystal was first measured (fig. 2). For quartz, a logarithmic change in frequency with increasing temperature was observed. An alternative crystal, $GaPO_4$ was also assessed, showing a much smaller effect of temperature.
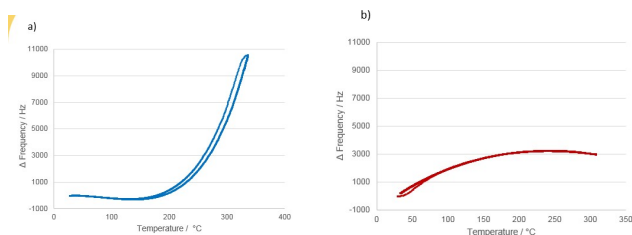
Fig. 2. Temperature dependence of uncoated a) Quartz and b) Galium phosphate crystals, between 30 and 300°C, using high temperature QCM probe.

Results

The two crystal types were then coated with cerium, uranium or thorium oxides via spin coating with a metal nitrate solution containing a polymeric surfactant or aqueous metal oxalate suspension. Changing the concentration of this precursor solution allowed layers of different thicknesses to be manufactured. Scanning electron microscopy was used to determine the thickness and surface area of the coatings (fig. 3).
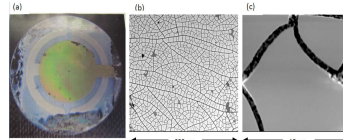
Fig. 3. Scanning electron micrographs of 400 nm thick ceria-coated quartz crystals. The ceria layers were found to be well adhered. Cyclic voltametric studies indicate the surface cracks do not penetrate to the underlying electrode material.

The resonant frequency of the coated crystals was then measured in a sealed reaction vessel in the presence of water, which showed that an increase in mass occurred as water was absorbed onto the metal oxide layers in a manner consistent with type II/IV absorption isotherms (fig. 4). Application of the BET equation afforded straight line plots (fig. 5), allowing the calculation of the enthalpy of absorption of water and the surface area of the samples.

	C (BET const.)	Volume H_2O monolayer, m^3	Surface area MO_x, cm^2g^{-1}	ΔH_{ads}	$\Delta H_{binding}$
CeO_2	2.4	1.50×10^{-12}	4.46	44.3	2.5
U_3O_8	71.6	3.00×10^{-12}	8.92	54.1	12.3
ThO_2	9.7	$3.1 \; 10^{-12}$	4.85	48.3	6.5

$$1/\left[Va\left(\frac{P_0}{P}-1\right)\right] = \left(\frac{C-1}{V_MC}\right)\left(\frac{P}{P_0}\right) + \frac{1}{V_mC}$$

CeO2   y = 392.83x + 27.315
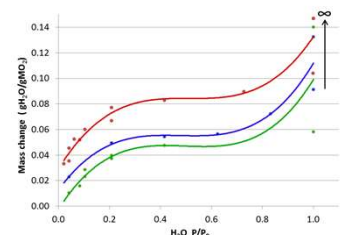U3O8   y = 338.17x + 3.4925
ThO2   y = 356.5x + 6.6474

Fig. 4. Mass change due to water adsorption on 40-60 nm thick MO_x coated $GaPO_4$ crystals at 75°C.
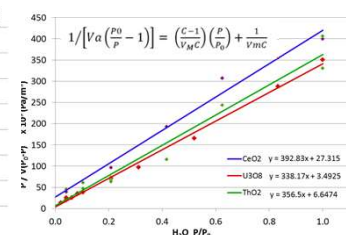
Fig. 5. BET plot of water adsorbed on 40-60 nm thick MO_x coated $GaPO_4$ crystals at 75 °C.

The temperature of systems at initial saturated vapour pressure (at 75ºC) was then varied up to ~375ºC, showing that the absorbed water is desorbed as the sample is heated and the partial pressure of water in the atmosphere is reduced (fig. 6).
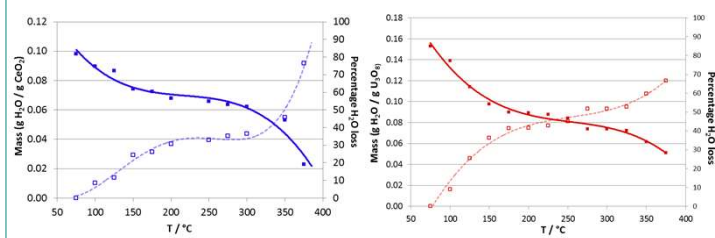
Fig. 6. Mass change due to water adsorption on 40 nm thick a) CeO_2 and b) U_3O_8 -coated $GaPO_4$ crystals from 75 °C (at sat. VP) to ~350°C.

Conclusion and Further work

Initial studies have shown that absorption and desorption of water onto and from metal oxide layers can be measured using crystal microbalance methodology. $GaPO_4$ crystals that evince a quasi-linear temperature dependence were used to allow higher temperature measurements.
Ceria, thoria, and uranium oxide nanoscale layers have been produced and the absorption of water across a range of partial pressures of water has been investigated, leading to estimated for the enthalpy of binding of water to the surface of the oxides. Increasing the temperature of the system to mimic real-world storage conditions has show that significant amounts of water are still present on the oxide surface even up to 400ºC, indicating that nuclear waste-forms will contain appreciable amounts of water even after heat treatment.

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