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Investigation of water adsorption on metal oxide surfaces under conditions representative of PuO_2 storage containers.

Patrick Murphy[1], Colin Boxall[1] and Robin Taylor[2]
[1]Engineering Department, Lancaster University, Lancaster, LA1 4YR, UK
[2] Central Laboratory, B170, National Nuclear Laboratories, Sellafield, Seascale, Cumbria, CA20 1PG, UK

ABSTRACT

We have developed a QCM (Quartz Crystal Microbalance) based method for direct gravimetric determination of water adsorption on PuO_2 surrogate surfaces, especially CeO_2, under conditions representative of those in a typical PuO_2 storage can. In this application, the method of transduction of the QCM relies upon the linear relationship between the resonant frequency of piezoelectrically active quartz crystals and the mass adsorbed on the crystal surface. The spurious effect of high temperatures on the resonant frequency of coated QCM crystals has been compensated for by modeling the temperature dependence of the frequency response of the surrogate coated-QCM crystal in the absence of water. Preliminary results indicate that water is readily adsorbed from the vapor phase into porous metal oxide structures by capillary condensation, an observation that may have important ramifications for water uptake within the packed powder beds that may obtain in PuO_2 storage cans.

INTRODUCTION

Standardised packaging and storage of plutonium oxide powders involves sealing the materials in welded, stainless steel containers. Pressurization of these containers arises from decomposition of adsorbed water contained in and on the surface of hygroscopic PuO_2 [1]. In an attempt to remove water from the surfaces of these oxides, and thus minimize pressurization, PuO_2 samples are calcined at temperatures as high as 700°C but water often readsorbs onto the plutonia powders during packaging [2].

The potential of PuO_2 to generate a water vapor-derived pressure in a storage can headspace is directly related to its capacity for H_2O adsorption. This adsorption must be fully understood in order to reliably underpin the PuO_2 interim storage safety case. Water adsorption on PuO_2 has previously been investigated by measuring headspace pressure, as a function of temperature within a closed system containing a fixed quantity of PuO_2 in the presence of varying amounts deliberately added water [1]. This involves making a number of assumptions relating to the PVT behaviour of the headspace of the closed system, usually based on the behaviour of an ideal gas, in order to estimate the mass of water adsorbed at the PuO_2 surface. Assuming ideality at high temperatures and pressures is problematic and, at best, only gives an indirect measurement of water adsorption on PuO_2.

The Quartz Crystal Microbalance (QCM) measures mass per unit area by measuring the change in frequency of a quartz crystal resonator. In our system we have coated QCM crystals with a PuO_2 surrogate (CeO_2) so as to measure directly the mass of water adsorbing at the surrogate surface, thus avoiding many of the issues associated with indirect measurements inferred from PVT behavior. However, as well as responding to adsorbed mass, quartz crystal piezoelectrodes also respond to changes in temperature, exhibiting changes in their resonant frequency. For mass changes in a system with a dynamically changing temperature regime, this thermal effect can be compensated for by modelling the temperature dependence of the frequency response of a QCM crystal in the absence of water [3]. By extension, this approach can also be used for modelling the temperature response of PuO_2 surrogate-coated crystals in the absence of water adsorption, so allowing for the gravimetric measurement of water adsorption at the surrogate surface as a function of temperature. Thus, this paper presents preliminary results relating to QCM-measured water adsorption on CeO_2 coated crystals in a closed system representative of a PuO_2 storage container, where the spurious affect of temperature change on the crystal's resonant frequency has been compensated for by the above modeling technique.

EXPERIMENTAL DETAILS

The QCM crystals used in this study were 5MHz, AT-cut wafers with polished gold electrodes on both sides (Testbourne Ltd). The crystal mass sensitivity factor was 0.0566 Hz/ng/cm^2. Crystal dimensions were: 2.54 cm overall crystal diameter and 1.27 cm electrode diameter. The procedure for depositing thin films of CeO_2 (as a PuO_2 surrogate) onto these QCM crystals in the current work was adapted from the Lundberg [4] method. 1mmol of $CeCl_3.7H_2O$ and 0.5 g of p123 Pluronic (a non ionic surfactant) was dissolved in 10 g of methanol. 100 µl of the resulting solution was spin coated onto one face of the QCM crystal at 2900RPM for 10 seconds. The coated crystal was then calcinated in air at 400 °C for one hour, resulting in formation of an off-white layer which rigidly adhered to the QCM crystal. The diameter of the layer was roughly 2 cm (outermost edges of the quartz crystal remained uncoated).

A 100 ml volume pressure vessel, constructed of 316L stainless steel with a maximum operating temperature of 275 °C was used to simulate conditions of a PuO_2 storage container. The vessel was heated and its temperature controlled via an IKA® RET Basic safety control hotplate and IKA® ETS-DS Electronic Contact Thermometer which uses a PID control mechanism. The vessel was heated from its base by the hotplate. Addition of water into the vessel was achieved by removal of the vessel head for 1 second while water was injected. The crystals were mounted within the pressure vessel in a Pressure Equalized Crystal Holder (PECH), designed and constructed in-house, where both sides of the crystal were exposed to the pressurized environment of the vessel. The PECH was constructed of PTFE and was installed in the vessel using a wire gland purchased from Conax Technologies®. The PECH covered the edge of the QCM crystal and left an inner crystal diameter of 1.8 cm exposed to the environment within the vessel. This corresponds to an exposed area of 2.545 cm^2.

Measurement of water adsorption on CeO_2 coated crystals was achieved as follows: The CeO_2 coated QCM crystals were installed in the PECH holder and then placed in the vessel. The vessel temperature was controlled at 25 °C and the vessel was purged with N_2 (moisture content of 2 ppm). The temperature within the vessel was increased from 25 °C to 50 °C, 100 °C and finally 150 °C in a stepwise fashion. The temperature was held at the desired value until a steady value of frequency fluctuation (less than +/- 2 Hz at 50 °C and 100 °C and +/- 8Hz at 150 °C) was observed for 40 minutes. The vessel was then cooled back down to 25 °C. The CeO_2 coated crystals were thermocycled in this fashion until twice they exhibited the same frequency response to temperature change. This was recorded as the crystal's temperature response in dry conditions. After the last of these dry thermocycles, the vessel's temperature was held at 25°C for 24 hours, whilst recording the frequency behaviour of the CeO_2 coated crystal. 100 µl (100mg) of water was then introduced into the vessel and its temperature again held at 25°C for

24 hours whilst recording the crystal's frequency behaviour. These two frequency traces were compared as a means of measuring water adsorption on CeO_2 at 25°C. The vessel was then heated using the same stepwise temperature regime described earlier. The crystal's temperature response in dry conditions was used as a baseline against which water adsorption on CeO_2 at high temperatures was measured.

DISCUSSION

This work involves the deposition of a layer of CeO_2 onto the surface of a quartz crystal nanogravimetric transducer and the use of the resultant ceria-crystal composite to measure the mass of water adsorbed at the metal oxide surfaces as a function of temperature. However, in the first instance, the effect of the presence of CeO_2 on the QCM response needs to be determined. Deposition of a ceria layer onto QCM crystals typically resulted in a resonant frequency drop of 1240Hz. This corresponds to a mass change of 21.9 $\mu g/cm^2$. Thus 55.7 µg of CeO_2 was exposed to the pressurized environment within the cell by the PECH holder when installed in the pressure vessel. AFM imaging of the quartz-ceria interface on the edge of the QCM crystal (not shown) suggests the layer is approximately 100nm thick. From the mass deposited and the known density of CeO_2 (7.65 g/cm^3) [5], the volume of the ceria layer has been calculated to be 7.287×10^{-6} cm^3. The thickness of a perfect (non porous) cylinder with volume $7.287\ cm^3 \times 10^{-6}\ cm^3$ and radius 0.9 cm is equal to 28.6 nm. Comparing this value with the observed layer thickness suggests that the CeO_2 layer is highly porous, with over 70% of its volume comprised of voids.

Temperature response of CeO_2 –coated QCM crystal in dry conditions.

Due to the sensitivity of the resonance behavior of QCM crystals to temperature change, the temperature response of CeO_2 crystals needed to be quantified in the absence of adsorbing water. Thus, the response of a QCM crystal coated with CeO_2 to repeated thermocycling in a sealed, dry vessel was recorded and is shown in Figure 1. During the first cycle, when cooling from 150 °C to 25 °C, the CeO_2 coated crystal's frequency drops 110 Hz below its starting frequency at 25 °C. For the subsequent 2nd, 3rd and 4th cycles the crystal's frequency returns to its starting frequency upon cooling. Advantageously, the temperature response of the CeO_2 coated crystal is identical for cycles 3 and 4. Thus, this temperature response was used as a baseline against which to measure water adsorption on this particular CeO_2 coated QCM crystal.

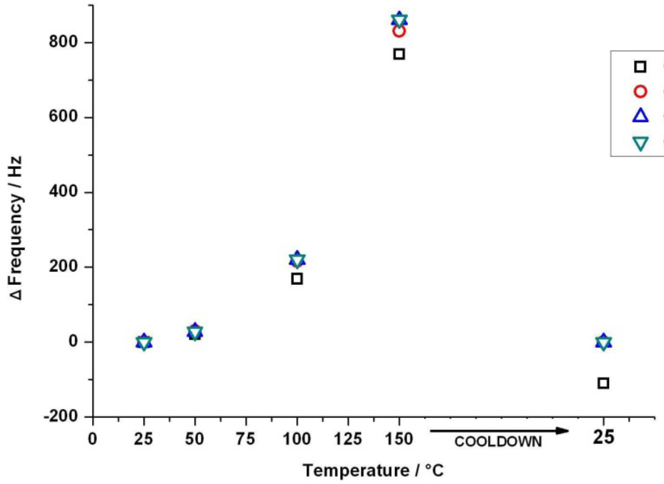

Figure 1: Repeated Thermocycling of a CeO_2 coated QCM crystal in dry conditions

Water adsorption on CeO_2 at 25°C.

Figures 2(a) and (b) show the results of water adsorption experiments on a CeO_2 coated crystal at 25 °C over a 26 hour period. As described in the experimental section, this experiment was conducted by mounting the crystal within a sealed pressure vessel, purging with dry N_2 and introduction of 100 mg of water to the vessel post-purging. Assuming the entire 100 mg of water introduced into vessel has completely evaporated and taking the saturation pressure of water at 25 ° C to be 3165 Pa [6], the relative humidity within the vessel was 100%

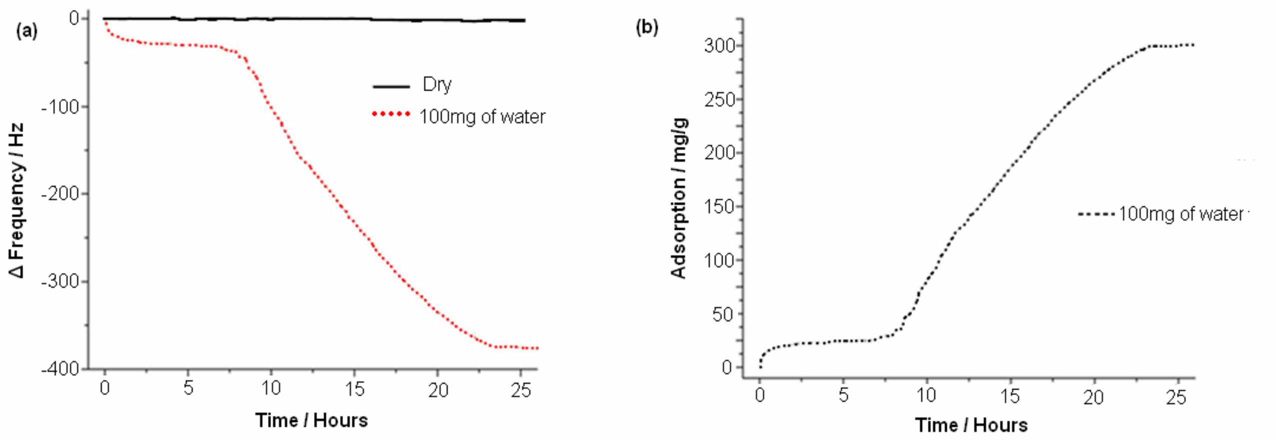

Figure 2: (a) Raw Frequency response of the CeO_2 coated crystal before and after addition of 100 mg grams water. (b) Mass adsorbed on the CeO_2 layer, expressed as milligram of adsorbate (water) per gram of adsorbent (CeO_2).

From Figure 2(a) three distinct of stages of adsorption can be observed: Addition of water into the vessel results in a frequency change of -20Hz after 1 hour. A more gradual frequency change of 10 Hz is observed over the next six hours. The rate of frequency decrease then increases dramatically resulting in a frequency change of -380 Hz after 23 hours. Figure 2(b) shows the same data, recast as mass of adsorbate adsorbed / unit mass of adsorbent with the recorded mass increasing as a result of water uptake on the coated crystal. The shape of Figure 3(b) strongly resembles a Type IV BET adsorption isotherm for adsorption in a mesoporous solid [7]. A plausible explanation for what is happening in Figure 2(b) is that, consistent with the Type IV isotherm, adsorption initially occurs over the interior surface of the CeO_2 pore structure prior to pore filling. This analysis is supported the adsorbed mass/time data at times longer than 7 hours. Considering that the voidage within the ceria layer before exposure to 100% RH was earlier calculated to be > 70%, the mass of water adsorbed after 7 hours in Figure 2(b) corresponds to a remaining voidage within the layer of 65%. This indicates that after 7 hours the pores within the CeO_2 layer are not full of adsorbed water and that adsorption had been occurring on the interior surface of CeO_2 pore structure. Conversely after 23 hours the remaining voidage within the layer is only 2%. Taking into account that the layer thickness of 100 nm is an approximate measurement and the shape of the adsorption curve from 7 to 23 hours shown in Figure 2(b) strongly resembles capillary condensation associated with a Type IV isotherm, it appears likely that the pore structure within the layer has been completely filled with adsorbed water after 23 hours.

The mass of water adsorbed at 25 °C and 100% RH of 300 mg /g is relatively high compared to literature values recorded for PuO_2 powder samples. Moseley [8] recorded a value of 50 mg /g for water adsorption PuO_2 powder at 25°C and 100% RH. A likely explanation for the relatively large amount of adsorption seen in Figure 2(b) is the highly porous nature of the CeO_2 sample. This porosity means the layer is likely to have a very high surface area. Thus, BET surface area-analysis needs to be conducted on the CeO_2 samples used in the current work and compared to typical surface areas of PuO_2 powders stored held interim storage containers. This work is currently underway.

Water adsorption on CeO_2 up to 150 °C.

In order to form a preliminary view of the temperature dependence of the water uptake seen in Figure 2, a CeO_2 coated crystal was heated to 150 °C in the same stepwise regime described earlier. Its frequency response was recorded in the presence and absence of 100 mg of added water within the vessel as a means of measuring water adsorption/desorption at high temperatures. This comparison is seen in Figure 3(a). Figure 3(b) shows the corresponding mass data for water adsorbed on the CeO_2 sample, calculated by the difference in delta frequency between the dry and wet cycles at each temperature stall (the dry experiments of Figure 1 having already demonstrated that after four dry cycles, the frequency response of the surrogate coated crystal as a function of temperature is highly reproducible).

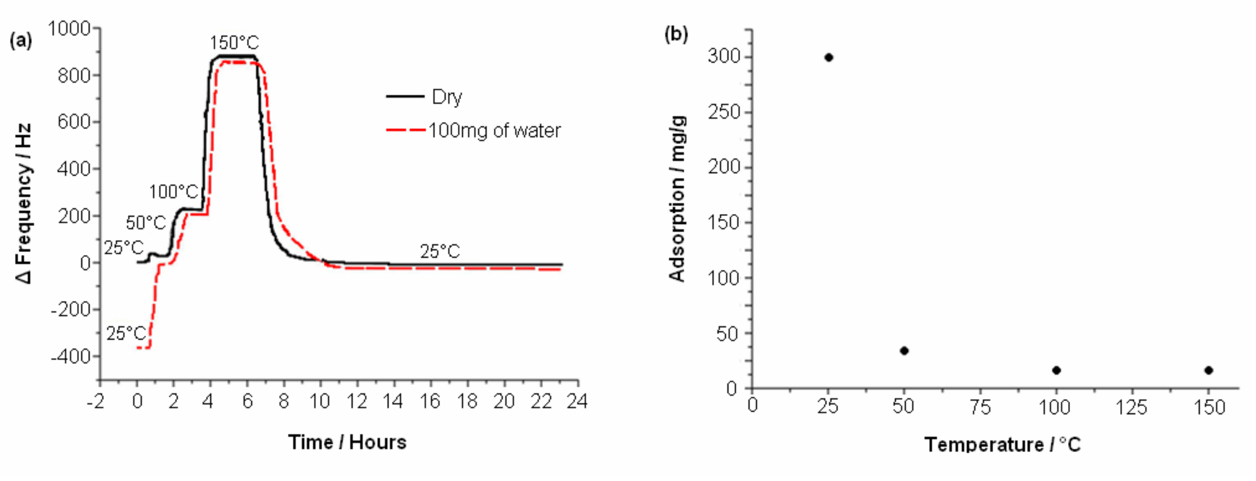

Figure 3: (a) Frequency response of the CeO_2 coated crystal after addition of 100 mg of H_2O into the vessel, compared to the crystal's dry temperature response. (b) Adsorption versus temperature graph up to 150 °C.

Figure 3(b) shows that a high percentage of 89 % of the water adsorbed at 25 °C was desorbed by heating the vessel to 50 °C. Further heating to 100 °C and 150 °C resulted in much smaller mass losses, with 95 % of the water being desorbed from the CeO_2 coated crystal at 150 °C. A control experiment where an uncoated gold QCM was crystal was exposed to the same temperature regime (not shown) and same % RH showed no adsorption taking place on the gold surface between 50 and 150 °C, so mass changes at these temperatures are as a result of water adsorption on CeO_2. The thermally induced desorption shown in Figure 3(b) is similar to that seen by Stakebake [9] for thermal desorption of water from PuO_2 powders under vacuum using a conventional microbalance. For comparison, Stakebake observed that a large percentage of the adsorbed water (70% approx.) is desorbed by heating to 50 °C. Through mass spectrometry and study of adsorption enthalpies both Stakebake and Hasckhe [10] have attributed this to desorption of physisorbed water molecules from PuO_2 by gentle heating. Chemisorbed hydroxyl groups, formed by the dissociation of water remain on the PuO_2 surface at temperatures as high as 900 °C [9]. It is likely the remaining adsorbed mass further recorded at 150 °C seen in Figure 2(b) is in the form chemisorbed hydroxyl groups. It is noticeable in Figure 3(a) that upon cooling the vessel from 150 °C back to 25 °C, very little readsorption of water onto the CeO_2 layer occurs. In an isothermal system, one would expect to see an adsorption curve similar to the one shown in Figure 2(a) upon cooling the vessel back to 25 °C. This discrepancy is likely to have been caused by water condensing in "cold spots" within the vessel's valves during the heating cycle, as these valves are far away from the hotplate heating source. We are in the process of addressing this experimental artifact by the application of band heaters to these parts of the reactor.

CONCLUSIONS

A Quartz Crystal Microbalance-based technique has been developed for measuring water adsorption on PuO_2 surrogate surfaces at temperatures as up to 150 °C. Studies on mesoporous CeO_2 layers as PuO_2 powder analogues indicate that significant water adsorption / condensation can occur within the capillary network/pore structure of the ceria layer. Temperature dependent studies indicate that as much as much as 5% this water remains adsorbed at 150 °C. As proof-of-concept has been achieved, the next step is to adopt an experimental rig which is more representative of a typical PuO_2 storage container, i.e. an isothermal vessel with a higher temperature limit.

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