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

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).

The potential of PuO_2 to generate a water vapour derived pressure in a storage can headspace is directly related to its capacity for H_2O adsorption. 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.

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 our system, we have coated QCM crystals with a PuO_2 surrogate so as to measure directly the mass of water adsorbing at the surrogate surface. However, as well as responding to adsorbed mass, quartz crystals also respond to changes in temperature, exhibiting changes in both resonant frequency and mass sensitivity. 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 (2), so allowing for the gravimetric measurement of water adsorption at the surrogate surface as a function of temperature.

Water adsorption isotherms for CeO_2 have been generated to high temperatures, allowing for the extraction of key adsorption isotherm parameters. Gravimetric data will be used to compliment PVT data for water adsorption on PuO_2 generated at the UK National Nuclear Laboratory.