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Heat treatments of Cl⁻ and water-contaminated PuO₂ and its analogues

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Magnox PuO₂ packaged before 1975 has become contaminated with Cl⁻, from thermally degraded PVC bags it was stored in, and water, from exposure to the atmosphere. Heat treatment is the preferred method for decontaminating the PuO₂ for storage before either subsequent reuse as Mixed Oxide (MOX) fuel or safe disposal in a Geological Disposal Facility (GDF). Ion chromatography experiments carried out on the contaminated PuO₂ show that leachable chloride on the solid decreases and volatilised chloride increases with increasing heat treatment temperature. Powder XRD shows no change in fcc Fm $\bar{3}$ m crystal phase with heat treatment, although high heat treatment temperatures (> 600°C) sinter the crystals, increasing the crystal size, and anneal the lattice damage caused by self-irradiation, decreasing the lattice parameter. When PuO₂ is heated to 225°C and cooled in a sealed (Baskerville) vessel, a non-condensable mixture of gases (including hydrogen, helium, NO and CO), ideal above ~113°C, is produced, and the monolayers of water on the surface of the PuO₂ decrease. Repeating this experiment with 0.05 mL water in a side chamber increases the number of water monolayers on the PuO₂ surface.

PuO₂ artificially chloride-contaminated, by exposure to dry HCl vapour, and humidified in a sealed pot with H₂SO₄ (conc.) shows similar results to the Magnox PuO₂ when heat treated at various temperatures. CeO₂ analogue nanocrystals have also shown an increase in size when exposed to HCl vapour and following heat treatment at temperatures higher than the original calcination temperature. Studies on CeO₂ analogues also showed that the sorption mechanisms of chloride and water are linked. Upon heat treatment of the contaminated CeO₂ at 900 °C, the nanocrystal morphology resembles that of PuO₂ in TEM images, and the chloride, which was homogeneously spread on and within the CeO₂ particles, is no longer detectable by EDX.

XPS and UPS studies on CeO₂, CexO_{2-x}, ThO₂, UO₂ and U metal thin films, involving in situ sputter deposition synthesis, HCl/Cl₂ contamination and Thermal Programmed Desorption-Mass Spectrometry (TPD-MS), showed that adsorbed Cl⁻ is not volatilised up to 800°C, but diffuses beneath the surfaces of the films. No change in oxidation state is observed for the metals in the metal oxides, but U metal oxidises upon contamination and TPD, with Cl⁻ the only Cl species detected. XPS studies on spin coated CeO₂ thin films contaminated with HCl vapour ex situ show a change in Ce oxidation state at high heat treatment temperatures from +4 to +3 for the thin films originally calcined at low temperatures, but Cl⁻ remains the only Cl species present and also decreases on the CeO₂ surface, following heat treatment at high temperatures.

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