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Drying characteristics of thorium fuel corrosion products

R.-E. (Lords) Smith *

Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-3404, USA

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Abstract

The open literature and accessible US Department of Energy-sponsored reports were reviewed for the dehydration and rehydration characteristics of potential corrosion products from thorium metal and thorium oxide nuclear fuels. Mixed oxides were not specifically examined unless data were given for performance of mixed thorium–uranium fuels. Thorium metal generally corrodes to thorium oxide. Physisorbed water is readily removed by heating to approximately 200 °C. Complete removal of chemisorbed water requires heating above 1000 °C. Thorium oxide adsorbs water well in excess of the amount needed to cover the oxide surface by chemisorption. The adsorption of water appears to be a surface phenomenon; it does not lead to bulk conversion of the solid oxide to the hydroxide. Adsorptive capacity depends on both the specific surface area and the porosity of the thorium oxide. Heat treatment by calcination or sintering reduces the adsorption capacity substantially from the thorium oxide produced by metal corrosion.
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1. Introduction

Some experimental spent nuclear fuel, such as thorium metal fuel, has been exposed to wet or damp storage with the potential for localized conditions of aggressive corrosion. Thorium corrosion products are assumed to be simple thorium oxides similar to those found in US Department of Energy (DOE) spent fuel rather than complex mixed compounds analogous to natural minerals. The drying of such spent nuclear fuel will require aggressive drying conditions to remove water associated with corrosion products [1]. Actual drying conditions depend on the nature of the corrosion products. Available literature was reviewed for information pertinent to drying and stabilization of thorium fuel materials for transfer to dry storage. Characteristics indicative of drying performance in the anticipated drying range of 150–350 °C and of potential for rehydration at or near ambient conditions are identified to support choice of process parameters. Rehydration is considered to assess the need for environmental constraints on lag storage after drying.

This review focused on thorium oxide and thorium hydroxide [1] (ThO_2 and $Th(OH)_4$, respectively). A wide range of potential environmental conditions for corrosion were considered, including high and low pH and unknown concentrations of carbonate species, the entire potentially hydrated family of carbonates, oxycarbonates, and hydroxycarbonates.

The accessible literature was searched for the following data for thorium corrosion products:

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* Tel.: +1-208 526 3874.
E-mail address: rzl@inel.gov (R.-E. (Lords) Smith).

[1] Although the literature did not indicate a clear distinction in morphology between thorium hydroxide and hydrated thorium oxide, the following convention was adopted for this review. The term 'thorium hydroxide' and the stoichiometric '$Th(OH)_4$' formula have been used to describe the amorphous precipitate, regardless of the presence of excess water. Alternately, where one or more monolayers of water are associated with the surface of thorium oxide, the term 'hydrated thorium oxide' and the formula '$ThO_2 \cdot nH_2O$' are used, with the implication that $n < 2$ for the bulk solid even though the layer at the interface may be identical to thorium hydroxide.

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- The measured values or thermodynamic predictions of the equilibrium water vapor pressure of the hydrated corrosion products as a function of temperature.
- Experimental transformation data, including transformation sequence and the characteristic temperatures, for the dehydration (e.g., thermogravimetric analysis [TGA], differential scanning calorimetry [DSC], mass spectroscopy [MS] data).
- Drying kinetics.
- Observations on the significance of the material form and microstructural changes (e.g., agglomeration, sintering, exfoliation, and comminution) during drying.
- Observations on the rehydration of the dried material.

The review covered the available open literature, unclassified and declassified DOE reports and personal communications from technical personnel at the Idaho National Engineering and Environmental Laboratory (INEEL) and other DOE sites. Four areas of thorium research were evident from the literature reviewed: (1) nuclear breeder fuel production and its irradiation performance, (2) fuel dissolution for recovery of bred uranium, (3) waste package performance for repository disposal and (4) catalysis. Many of the early thorium corrosion studies focused on gross physical changes (i.e., weight, metal thickness) to the exclusion of suitable chemical analysis of corrosion products. Much of the reported data is ancillary to the drying and rehydration interests that prompted this review. However, where available, such sources were considered.

The literature review of thorium corrosion products identified only anecdotal rate data and an empirically derived rate equation for the dehydration and rehydration reactions, respectively. Isothermal vapor pressure curves, thermogravimetric test runs, and supporting discussions offer some quantitative data for specific samples and test conditions. However, by themselves, these data are not likely to be very useful for interpolating or extrapolating to process conditions.

2. Thorium corrosion products

The thorium fuels considered were thorium metal rods or mixed oxide bundles of ThO_2 with minor amounts of UO_2. DOE has several thorium fuels, primarily Light Water Breeder Reactor (LWBR) mixed oxide fuel as well as some High Temperature Gas-cooled Reactor (HTGR) carbide fuels, such as Fort Saint Vrain and Peach Bottom. Thorium carbide fuels are not addressed in this review.

Like most metals, thorium metal is highly reactive. Thorium has only one stable oxidation state, Th(IV), simplifying the thorium chemistry by comparison to that of uranium [2–4]. Thorium corrodes in air or water with the primary product being ThO_2, the only naturally occurring thorium oxide. Thorium hydroxide forms at the interface as one or more monolayers. Corrosion resistance of the metal in water decreases with increasing temperature, exhibiting a linear weight loss rate of nearly 1.5 mg/cm^2 per h during 1 week in distilled water at 200 °C [5]. However, thorium oxide exhibits no change in weight after a 400 h exposure to 315C water [6].

Thorium oxide from corrosion of the thorium metal fuels is expected to take up much greater amounts of water than the thorium oxide of the oxide fuels. Firing and sintering of the thoria at high temperatures and under controlled atmosphere during fuel fabrication significantly reduces the specific surface area and the available adsorption sites [7–9]. Thoria samples that were fired at 600 °C picked up almost an order of magnitude more water ($\sim$1.8% by weight) than similar samples fired at 1000 °C [8]. Thorium oxide fuel meat approaches theoretical density, while thorium oxide corrosion product may be flocculent powder. Most of the adsorption–desorption studies have been done with thorium oxide powder for catalyst development; these studies reflect the behavior of the loose crystalline oxide not the oxide fuel element.

Thorium metal and oxide corrosion were studied to assess fuel form viability, and corrosion studies were generally limited to well-defined distilled water or laboratory air conditions. For these conditions, ThO_2 and interfacial $Th(OH)_4$ have been reported to be the primary corrosion products. However, other products may be possible in environmental conditions. An extended family of carbonate, oxycarbonate, and hydroxycarbonate species have been reported for thorium, with postulated forms including $Th(CO_3)_2 \cdot nH\ _2O$ (for the precipitate), $ThOCO_3 \cdot 8H_2O$ and $Th(OH)_2CO_3 \cdot 6H_2O$, [10–13] $Th(OH)_2CO_3 \cdot 2H_2O$, [14,15] $ThOCO_3 \cdot ThO\ _2 \cdot 1.5H_2O$, [16] $ThOCO_3 \cdot nH_2O$ ($n = 1, 2, 3, 7$), and $ThO_2 \cdot ThOCO_3 \cdot 0.5H_2O$ [17]. While the literature does not identify these species as thorium corrosion products, metal corrosion is dependent on water quality and environmental conditions, and such products can be formed.

Under the locally extreme and variable conditions possible in some fuel storage locations, thorium dissolution and precipitation may result. Thorium oxide may adsorb water and carbon dioxide, and several mobile thorium complexes may be possible. Thorium hydrolysis yields complex polycations with multiple hydroxyl groups, and these hydrolyzed species can form mixed salts. However, the oxide/hydroxide system is stable under most groundwater conditions and is unlikely to form large quantities of thorium phosphate, sulfate, or silicate compounds or lead to significant migration of thorium [18–23].

Thorium oxide, often referred to as thoria, is unreactive in most gases at temperatures up to its melting point, 3390 °C [7]. As a pure solid, ThO_2 demonstrates only one crystalline phase [8]. Thorium oxide and thorium hydroxide hydrolyze readily even in moderately acidic conditions to form soluble species [24,25]. Thorium oxide is soluble in acid solutions [7,8,10,26] (particularly sulfuric, [3] but also nitric in combination with HF [4,27,28]). In alkali waters thorium primarily forms $Th(OH)_4$ [29]. It tends to precipitate as thorium hydroxide and hydrated thorium oxide in soils [24,25]. Thorium hydroxide forms a gelatinous precipitate, which is soluble in dilute acids and alkali carbonate solutions.

Thorium oxide is relatively insoluble in neutral to basic aqueous systems. Thorium solubility in seawater, with ThO_2 as the solubility-limiting solid, has been found to be approximately 4.3×10^{-13} mol per l. For pure water with pH above 4, the solubility of thorium is typically on the order of 10^{-9} mole per liter. However, much higher solubility has been found in some lakes with fairly high pH waters, a detail attributed to high carbonate concentrations and the formation of mixed thorium-hydroxo-carbonate complexes [29,30].

Thorium oxide does have the capacity to adsorb both water and carbon dioxide quickly, and detectable quantities are taken up within minutes to within a few days [7,9,31–35]. Infrared analysis indicates the presence of hydroxyl groups from hydrolysis of adsorbed water at the thorium oxide surface [32,36–38]. But adsorption of carbon dioxide did not demonstrate any detectable change in the oxide bond structure. There was no indication of chemical bonding with adsorbed carbon dioxide. Evidence from one source suggests preferential adsorption of water to carbon dioxide. So, carbon dioxide adsorption on thorium oxide from corroded fuel seems unlikely to have a significant impact on the composition of the corrosion products, even though various hydrated carbonate and oxycarbonate species have been identified [10–14,17,32,36,39–43]. Brookins [21] discounts the existence of any significant thorium carbonate complexes based on thermodynamic arguments.

The dominant thorium fuel corrosion product from exposure to air and water is expected to be thorium oxide with some unknown quantity of surface adsorbed water. The primary thorium metal corrosion reaction proceeds by $Th + 2H_2O \rightarrow ThO_2 + 2H_2$. Thorium hydride may be formed as a consequence of a side reaction, but it has not been detected in quantity [44–48].

From the hydrolysis reaction, complex ions of the form $Th_x(OH)_y^{+4x-y}$ are expected in aqueous solution, [19,25] so $Th(OH)_4$ is a credible aqueous corrosion product. Brookins [21] suggests that $Th(OH)_4$ ages to ThO_2 and H_2O, so thorium hydroxide may be a transitory phase that ages to the oxide. Alternately, the thorium oxide may form hydroxide moieties at the surface.

3. Drying characteristics

Drying thorium oxide corrosion products requires the removal of physisorbed water. If chemisorbed water is a significant water source, its removal may also be necessary.

The adsorption and desorption of water on thorium oxide are limited to the surface and do not result in bulk hydration even in immersion in liquid water at 25 °C [49,50]. The chemisorbed water at the oxide surface forms a hydroxyl bond structure, so data for the decomposition of small samples of $Th(OH)_4$ may indicate the drying behavior of chemisorbed water, decomposition of hydroxyl groups on the oxide surface.

Thorium hydroxide decomposes smoothly to the oxide with the most significant drop occurring between room temperature and about 160 °C. This is probably because of loss of physically adsorbed water. X-ray diffraction (XRD) analysis of $Th(OH)_4$ decomposition indicates direct conversion to ThO_2 above 300 °C with no intermediate substructure formed. A representative TGA plot for thorium hydroxide precipitate heated at 400 °C/h is shown in Fig. 1, which indicates that most water loss is complete by 200 °C [51].

Fig. 1 indicates a 31% weight loss at the end of the run. However, the theoretical dehydration of $Th(OH)_4$ to ThO_2 with the removal of $2H_2O$ only accounts for a 12% weight loss from the change in formula weight. The rest is attributed to physisorbed water, although the sample preparation process is not described.

The general shape for TGA and differential thermal analysis (DTA) curves for the decomposition of thorium hydroxide is confirmed by several sources with similar

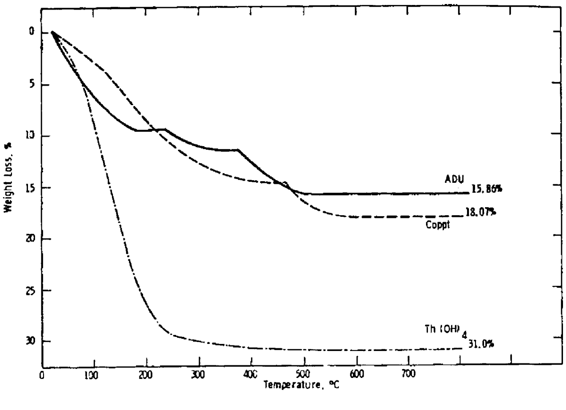

Fig. 1. Thermogravimetric analysis of $Th(OH)_4$, uranium/thorium mixed oxide (34% ThO_2 by volume) coprecipitate (Coppt), and ammonium diuranate (ADU).

rapid temperature ramp rates ranging from 7–8 °C/min up to 10 °C/min [52–55]. Different heating rates show no qualitative differences in the smooth, featureless TGA curves. Broad endotherms and exotherms indicate the gradual dehydration of an amorphous colloid at temperatures below 200 °C. Variations in these curves may be due to release of nitrate from impurities in the original hydroxide sample. Weight loss may also be highly sensitive to uncontrolled parameters like surface area or purity. While the literature shows some differences in the detail of the TGA curves, they are consistent in their representation of a comparatively featureless weight loss profile for the decomposition of thorium hydroxide at low temperatures. These curves are much simpler than those of the uranium and aluminum oxides [1].

In Fig. 2, a slower constant temperature ramp (linear rate of 2.5 °C/min) curve and a 'quasi-static' curve plotted from stepwise temperature increase upon weight stabilization (a series of constant temperature holds at 35, 150, 210, 300, 350, 400, 500, and 1000 °C) provide further data for the smooth, featureless decomposition as a function of temperature for thorium hydroxide [56]. The hydroxide decomposition curves reproduced in Fig. 2 give the most definitive data, confirming the smooth shape of the TGA curves discussed above and demonstrating the effect of rapid temperature ramp common to the previous references. Fig. 2 shows the majority of the weight loss to be complete by 400 °C by comparison to 200 °C in Fig. 1. Because the sample in Fig. 2 was dessicated over phosphorous pentoxide for 2 weeks prior to the decomposition, the TGA data in Fig. 2 likely reflect loss of chemisorbed water whereas the data in Fig. 1 are dominated by the loss of physisorbed water.

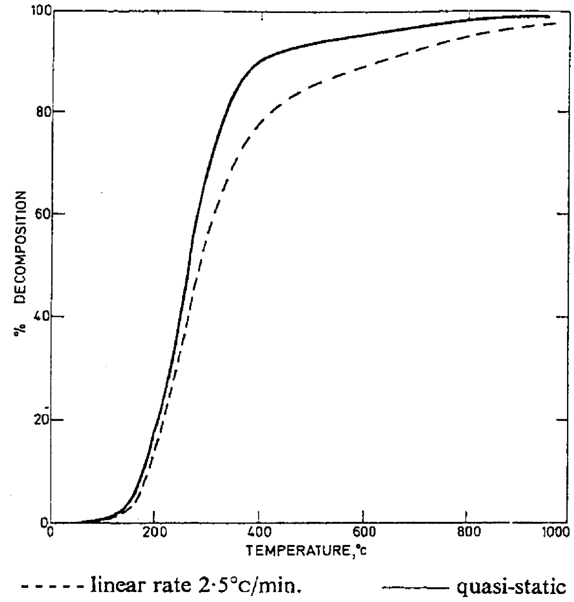

Fig. 2. Percent decomposition of thorium hydroxide as a function of temperature.

The changes in surface area with temperature indicate thermally induced changes in microstructure. Specific surface areas were given as 100.5 m^2/g at 35 °C, 90.70 m^2/g at 150 °C, 23.10 m^2/g at 210 °C, 4.20 m^2/g at 300 °C, 30.30 m^2/g at 350 °C, 17.20 m^2/g at 400 °C, 2.10 m^2/g at 500 °C, and 1.0 m^2/g at 1000 °C. Mikhail and Fahim used XRD analysis to confirm that amorphous thorium hydroxide gel crystallizes to the cubic ThO_2 at 300 °C and that a perfect crystalline ThO_2 structure was obtained after 5 h at 1000 °C [56]. Above 900 °C, necking between particles indicated occurrence of sintering [51].

The published data from powder samples generally indicate progressive removal of chemisorbed water with increasing temperature, rather than a discrete threshold temperature for rapid decomposition of $Th(OH)_4$ to ThO_2. (Some infrared analysis results indicate significant amounts of hydrogen bonding at temperatures as high as 500 °C [32].) Surface hydroxyl groups are probably not removed at outgassing temperatures below 250 °C, even under vacuum conditions of 10^{-7} kPa [38,56]. Anecdotal evidence indicates temperatures of at least 800–1000 °C are necessary to remove all chemisorbed water from the ThO_2 surface [57–59]. Outgassing at temperatures as high as 1300 °C may be necessary to reduce the surface hydroxyl content of thorium oxide below levels detectable by infrared spectroscopy [36,38]. This is consistent with the dehydration theory developed at Oak Ridge National Laboratory (ORNL), as indicated by Fig. 3 [49].

Of course outgassing under vacuum will help, but water affiliated with thorium oxide may be tenacious at any fuel drying temperature. The drying (and rehydration) behavior may be dependent on the material's history as well as powder characteristics [8,35]. Weight loss data demonstrate that a temperature of 500 °C is 'far from adequate' [60] to remove all of the tenaciously bound water at a vacuum of 10^{-6} kPa [36,38,60,61]. 'Dry' weight at this pressure (indicated by absence of further weight loss upon prolonged exposure) is not achieved until 1000 °C [60].

Clayton [62] reports on moisture adsorption and desorption on LWBR ThO_2 reflector pellets as determined by mass spectrometry with vacuum extraction. Much of the adsorbed moisture was initially evolved at 75 °C with the major fraction of the adsorbed water released by 400 °C. Some moisture was retained up to 950 °C [62]. While sintered fuel materials may have less surface area and fewer adsorbtion sites, the desorption temperature dependence appears to be comparable to that of powders.

Apart from the anecdotal observations that lengthy time periods are required to establish equilibrium, dehydration kinetics has not been determined. Thoria

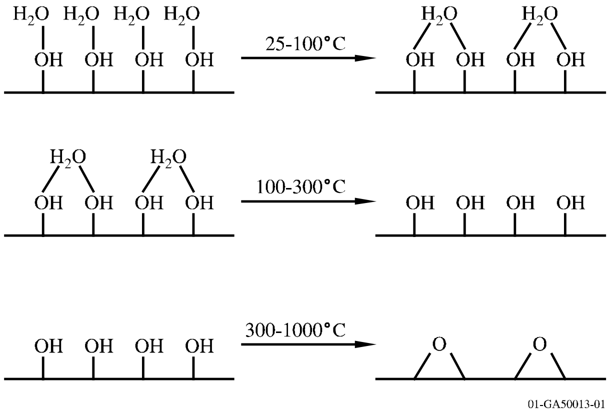

Fig. 3. Schematic representation of the theory for dehydration and dehydroxylation of surface adsorbed water from thorium oxide with temperature.

gel (prepared from thoria calcined from the oxalate), dried at 90 °C for 16 h before the study, was shown to have first order dehydration kinetics between room temperature and about 130 °C [63].

Only limited information is available for decomposition of thorium oxycarbonate species. The decomposition of $ThOCO_3 \cdot 8H_2O$ is reported to be complete at 430 °C, and decomposition of the anhydrous oxycarbonate is said to occur between 400–600 °C [13]. Decomposition of $ThO(CO_3) \cdot 0.5H_2O$ to ThO_2 is claimed to occur at 300 °C with decomposition progressing at 160 °C via the unstable intermediate $ThO_{1.5}(CO_3)_{0.5}$ [43]. Hussein and Ismail [43] recorded the TGA and DTA curves shown in Fig. 4. The DTA curve shows three inflections, suggesting three stages in the decomposition. The first decomposition stage occurs at 100 °C and is consistent with the loss of 0.5 moles of water. The subsequent two inflections are the stagewise decarboxylation of the oxycarbonate to thorium oxide. The very rapid 20 °C per minute temperature ramp makes accurate interpretation of the temperature axis difficult. Temperatures of interest are likely to be inflated even more than in Fig. 1 for the thorium hydroxide where the temperature ramp was indicated as 400 °C per hour. The thermal analysis of the thorium carbonate in Fig. 4 is uncorroborated and unrefuted by the available literature sources. The thorium carbonate sample was stated to be 99.9% pure, but powder characteristics were not assessed for the TGA sample. Specific surface area was estimated as 56 m^2/g for a sample after treatment for 1 h at 500 °C [43].

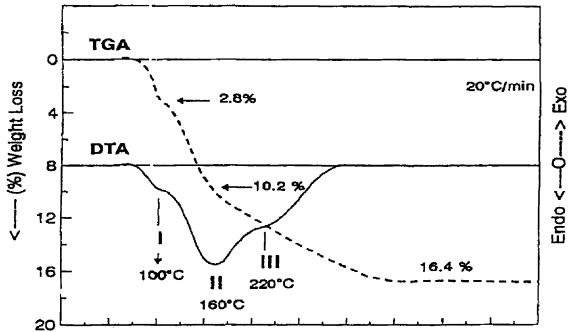

Fig. 4. TGA and DTA curves for the decomposition of $ThO(CO_3) \cdot 0.5H_2O$ to ThO_2 in a dynamic (20 ml/min) air atmosphere.

4. Rehydration

Upon exposure to moisture, the thorium oxide surface rapidly hydrolyzes to form an initial surface hydroxyl layer. Additional water can be slowly adsorbed by diffusion-limited formation of further hydroxyl layers or by irreversible physisorption of molecular water. This second stage of adsorption is not so easily accomplished with exposure to water vapor, because prolonged cycled (adsorption/desorption) exposure is necessary to obtain an equilibrium isotherm [50,60,61]. The final stage is reversible physisorption of additional layers of molecular water.

Large heats of immersion, 29–92 kJ mol^{-1} at 25 °C, and their apparent dependence on outgassing temperature are attributed to chemisorbed water [36,38, 57]. Theoretically, chemisorbed water is dissociatively adsorbed to form hydroxyls at the oxide surface. Irreversible adsorbed water, whether chemisorbed or physisorbed, cannot be removed by evacuation at the temperature of adsorption. Reversibly physisorbed water is less tenacious, because it is hydrogen bonded and can be removed by isothermal evacuation. Multiple adsorption/desorption cycles are required to achieve an equilibrium isotherm. The cycling may facilitate progressive development of a multilayer structure with stronger (more optimal) hydrogen bonding [49,50,57,60,61]. Analysis of the heat of immersion of thorium oxide in water indicates three hydration reactions with immediate, slow, and very slow kinetics, respectively. Immediate hydration is assumed to correspond to the formation of chemisorbed species [57].

Thoria powder adsorbed varying quantities of water depending on calcination temperature, powder origin, surface area, crystal morphology, and extent of exposure to moisture. Thoria samples fired at 600 °C picked up ~1.8% water by weight while samples fired at 1000 °C showed only an ~0.2% weight gain. This is almost an order of magnitude difference over the same 24 h exposure to atmospheric conditions. Data ranged from 0.2% to 6.4% weight gain for thoria powder exposed to ambient air with ~70% relative humidity (RH) for 24 h. These weight gain data do not indicate equilibrium after a 24 h exposure [8].

At room temperature (25 °C), water adsorption equilibrium took periods of over 50 h to achieve. This 50 h period required to reach equilibrium was experimentally validated by monitoring the decline in vapor pressure and increased in sample weight until stable (equilibrium) values were attained [64]. The gravimetric study of water adsorption on thoria required at least 16 h at each temperature (25–500 °C) to attain a steady sample weight [36,60].

Rehydration may be a complex process, typified by slow kinetics. Meaningful reversible adsorption isotherms are difficult to produce experimentally. For water adsorption on thoria and thorium hydroxide, equilibration is slow at or below 300 °C, typified by hysteresis unless equilibrated by multiple adsorption/desorption cycling. In order to reproduce the isotherms, outgassing for not less than 72 h at room temperature was necessary [56]. Therefore, the extent of rehydration of thorium corrosion products will be difficult to project.

Reversible adsorption was not observed at temperatures above 350 °C, but irreversible adsorption was identified over the entire temperature range from 25 to 500 °C. The change in character of the irreversible binding of water above and below 300 °C seems to indicate that above 300 °C only chemisorbed water remains. This hypothesis is further supported by the rapid irreversible adsorption observed and the apparent absence of slow adsorption above 300 °C and by the long time and number of adsorption/desorption cycles required to obtain reversible isotherms below 300 °C [50].

Generally, the literature sources give nonequilibrium isotherms [59,64] indicative of the problems associated with rehydrating this material. The only data for reversible equilibrium water vapor pressure isotherms at moderate temperatures are given for 25, 100, 200, 300, 400, and 500 °C and were composed over a period of two years [50]. These are shown in Figs. 5 and 6. Davis generated equilibrium isotherms for his thorium oxide adsorption work, but only at 400 °C [63].

In Fig. 5, an oxalate-derived porous thorium oxide sample, Sample B, calcined at 800 °C, was outgassed at 500 °C under a vacuum of 10^{-7} kPa until overnight evacuation produced a weight change of less than 2 μg (nominal sample size being 200 mg). The specific surface area was estimated to be 11.20 m^2/g. At the selected temperatures the sample was exposed to water vapor pressure up to 3.2 kPa, evacuated, and reexposed until a stable, reproducible isotherm was achieved. Adsorption and desorption were tracked by weight at each pressure. Temperature was then reduced, the sample evacuated to achieve stable weight, and the exposure cycled again to produce the next isotherm. At 200 °C, laboriously slow kinetics required twenty adsorption/desorption cycles over a 3 month period to establish the equilibrium isotherm. Equilibrium isotherms at lower temperatures were established more quickly by the cycling than by exposure to water vapor at constant pressure [50]. Fig. 6 shows the adsorbed water per unit mass of oxide as a function of the RH at 25 °C.

Evidence from ORNL work and from Smid indicate dependence of water adsorption/desorption on porosity as well as specific surface area [31,50,61,65]. A porous sample exhibits a classic capillary condensation hysteresis loop, which is absent from a comparatively nonporous sample of similar specific surface area. Mikhail and Fahim also comment on the hysteresis loops in their adsorption isotherm development [56]. Likewise, Davis [63] and Gammage and co-workers [35,66] observe stepped isotherms in some of their ThO_2 samples. Theoretically, the diffusive resistance to liquid water entering these small pores explains the slow heat of immersion for the porous sample. In either case, chemisorption of water appears to reduce the free surface area [31,36,60,61,67]. These factors should be considered carefully for the application and interpretation of thorium oxide–water vapor pressure isotherms.

The amounts of H_2O and CO_2 adsorbed on thoria increase with decreasing particle size and appear to be directly dependent on the surface area. Unlike powders, sintered materials appear to be less susceptible to the adsorption of water. Exposure to 50% RH did not result in detectable moisture adsorption on sintered thorium oxide fuel pellets with specific surface area on the order of 0.1 m^2/g. However, exposure to 75% RH resulted in the adsorption of 10^{-3} cc H_2O/g ThO_2 standard temperature and pressure (STP). Exposure to 100% RH resulted in comparable data to 75% RH, possibly due to limitations in the instrumentation used for detection [65].

A classical algebraic adsorption model appears to fit the empirical data from moisture adsorption on high density pellets [62]. While heat treatment of thorium oxide fuels may leave them less susceptible to water adsorption, ThO_2 pellet fabrication experience indicates

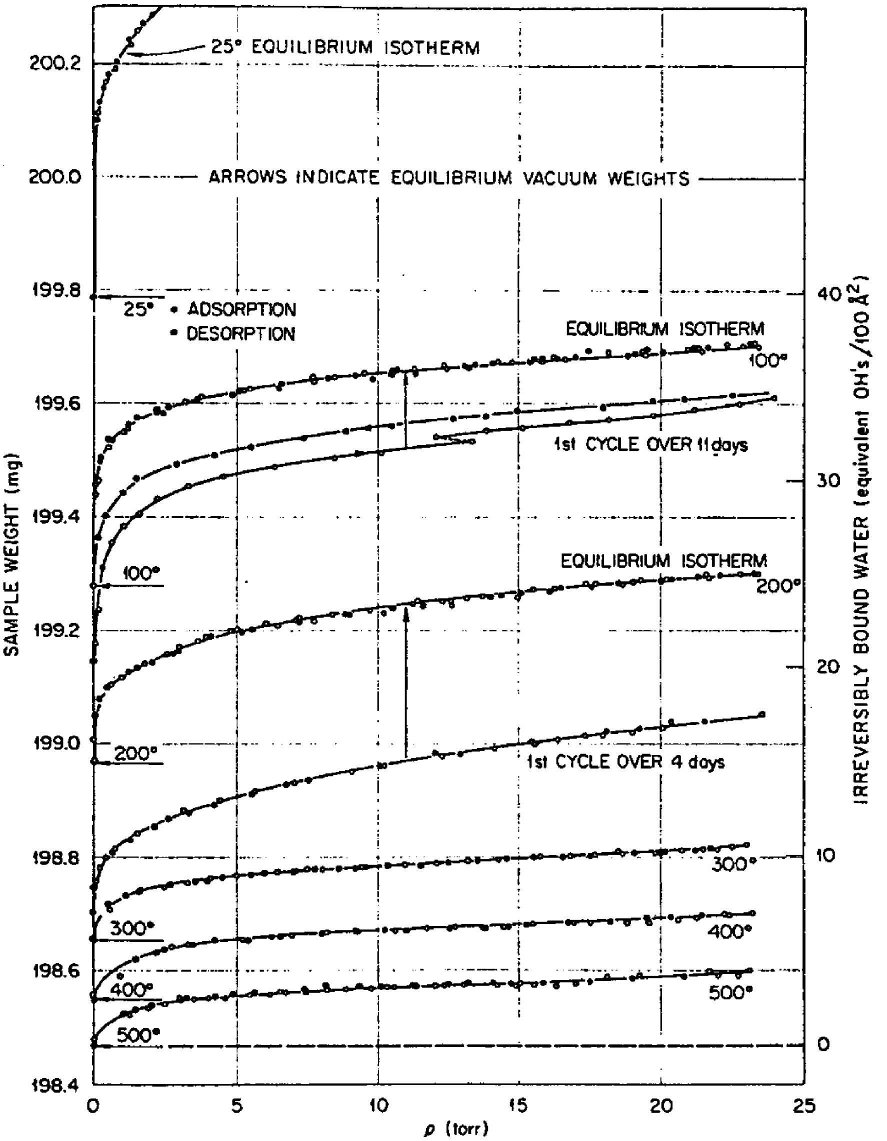

Fig. 5. Adsorption of water vapor on a porous sample of thorium oxide with repeated isothermal desorption under vacuum and readsorption to achieve reversible equilibrium. The published data were given in Torr, so the scale on the abscissa can be divided by 7.5006 Torr/kPa to give the SI unit, kPa. Also, the ordinate at the right refers to 'equivalent OH's/100 Å', this converts to equivalent hydroxyls per 10 nm.

that even the high density pellet materials adsorb increasing amounts of moisture with increasing humidity and time of exposure. At relative humidities up to about 70%, empirical data for the water adsorption on the pellets were computer fit to the 'classical' Freundlich-type equation

$$y = (4.409 \times 10^{-6}D)\{(7.5006P)^{[1/(1+0.1245D)]}\}, \qquad (1)$$

where y is the volume of moisture absorbed on thoria, expressed in cc/g at STP; D the time, in days; and P is the partial pressure of water, in kPa [62].

Test data were for durations of 24 and 96 h of exposure [62]. For relative humidities greater than 70%, pellet moisture adsorption data diverge from this model, but the equation offers an independent estimate from the adsorption theory developed at ORNL [31,50,57,62].

5. Conclusions

$Th(OH)_4$ and ThO_2 are the anticipated products from corrosion of thorium metal and thorium oxide. If

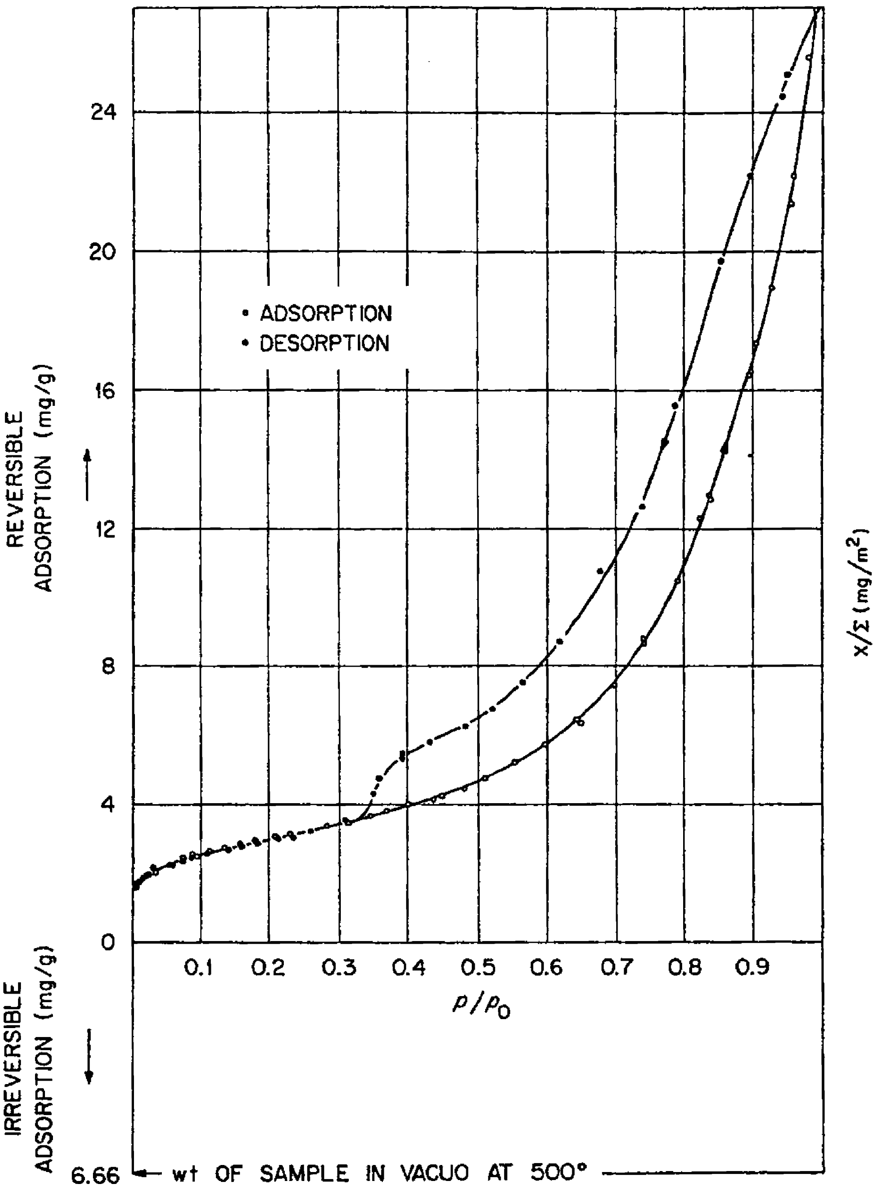

Fig. 6. Equilibrium isotherm for the adsorption and desorption of reversibly adsorbed water vapor on a porous sample of thorium oxide at 25 °C.

the reactive water source is carbonate rich, $ThOCO_3 \cdot nH_2O$ and $Th(OH)_2CO_3 \cdot nH_2O$ may form as well.

ThO_2 takes up a significant amount of physisorbed water as well as one or more monolayers of chemisorbed water. In general, one to three monolayers of surface adsorbed water can be expected on thoria, [68] with the first monolayer being chemisorbed [64] and additional layers exhibiting at least some tenacious hydrogen bonding.

Physisorbed water is removed relatively easily at temperatures less than 200 °C; removal of chemisorbed water requires temperatures over 300 °C. The comparatively featureless TGA data for thorium hydroxide samples indicate no clear characteristic threshold temperatures for dehydration as in the uranium and aluminum oxide systems. While some chemisorbed water can be removed at 300 °C, complete dehydration requires temperature above 1000 °C. Dehydration kinetics is not known.

Rehydration may occur by a three-stage process. The first stage, resulting in the formation of a monolayer of hydroxyl, is immediate. The second stage, forming either subsequent monolayers of hydroxyls by diffusion of water or an irreversible physisorbed layer, is complex and extremely slow. The third stage forms additional layers of reversibly physisorbed water that are easily desorbed. But rehydration to an equilibrium state is extremely slow and difficult to achieve.

Rehydration kinetics is not available for powder, but a single reference gives a mathematical fit for sintered fuel pellets.

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