THERMODYNAMIC PROPERTIES OF THORIA-URANIA FUELS FOR THE ADVANCED HEAVY WATER REACTOR

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Introduction

Over the last thirty years there has been increased interest in utilizing thorium as nuclear fuel, primarily because, this potential actinide is three times more abundant in the earth’s crust. Many countries, particularly those rich in thorium resources, have focused on research and development on thorium-based fuels. In the last three decades the use of Th-based fuel cycles has been extensively studied in Germany, India, Japan, Russia, United Kingdom and the United States of America and significant experience has been gained on the performance of the fuel in power generation and breeding. India accounts for one-third of the world’s thorium reserves and is implementing thorium utilization through the three-stage fuel cycle concept: plutonium \(^{239}\text{Pu}\) generation from uranium in Pressurized Heavy Water Reactors (PHWR), \(^{233}\text{U}\) breeding from \(^{232}\text{Th}\) in Fast Breeder Reactors (FBR), and \(^{233}\text{U}\) burning for power production. India is also exploring the possibility of direct utilization of thorium in the Advanced Heavy Water Reactor (AHWR) configuration.

In the AHWR, thoria-based fuels will be used and the fuel will contain 2-4% of fissile isotopes of uranium \(^{233}\text{U}\) or plutonium \(^{239}\text{Pu}\) in mixed oxide forms: \(\text{Th}_{1-x}\text{U}_x\text{O}_2\) and \(\text{Th}_{1-x}\text{Pu}_x\text{O}_2\). In such a reactor, while the U/Pu isotopes undergo fission by thermal neutrons, there is simultaneous burning of the abundant isotope \(^{232}\text{Th}\) via in-situ generation of the daughter atom \(^{233}\text{U}\). About 60% of the AHWR power output is expected to be from the thorium burning process. AHWR being a new concept its technological implementation needs inputs of basic data of physics and chemistry of the fuel and its fission products (fps). The data would help in understanding whether the physical and chemical evolution of the fuel during long irradiation periods is conducive to the safe operation of the reactor.

A burnup of about 50 GWD ton\(^{-1}\) would be common in the thoria-based fuels considering reprocessing difficulty. To attain an average discharge burnup of 50 GWD ton\(^{-1}\) with a typical power rating of 180-200W/cm in AHWR, the fuel will be irradiated for over 60 months. During irradiation, the fuel pin (Fig.1) generally bears the thermal profile of 1300-1500 K as the central temperature (Fig. 2) and 800-900 K as peripheral temperature and occasionally above this range in power ramp situation. At high temperatures and under a steep thermal gradient, the fps undergo transport and redistribution within the cladded pin (Fig.1) and chemically react among themselves and with the thoria matrix and the clad. Under this situation, the integrity of the fuel pin and the clad is the main issue. The integrity is governed by the physico-chemical transformation of the fuel matrix and the clad with burnup.

For the analysis and evaluation of fuel-clad integrity during long irradiation periods, the knowledge of thermodynamic and transport properties of the fuel and...
fps is necessary. Using the thermodynamic and kinetic information, the integrity analysis would require the evaluation of (i) concentration built-up of gaseous and corrosive volatile species at the fuel-clad interface and inside the fuel matrix (ii) the possible extent and pathways of chemical damage of the clad by the corrosive volatiles and (iii) the extent of fuel swelling and disintegration by gas accumulation and by different solid phase formations. The chemical picture that would emerge out of the evaluation would help in the analysis of fuel performance in normal and also off normal situations of reactor operation.

The above mentioned aspects, though well-known for the conventional urania fuels, need to be re-established for new fuel like thoria. Thoria (ThO$_2$) has quite a number of advantages over urania (UO$_2$) such as better thermophysical properties, chemical stability and radiation resistance which ensure better in-pile performance and a more stable waste form. Like the case of the conventionally used oxide fuels, the thoria based fuels do not pose any difficulty in handling and fabrication, at least in the virgin state.

The fuel chemistry with thoria would not be the same as with urania in case of conventional reactors, though the same set of fps with similar yields (Table 1) are formed and settle down inside the respective fuel matrices made of MO$_2$ (M = Th$^{+4}, U^{+6}$) fluorite lattice, with similar crystal radii of the cations.

**Table 1: fps yields from reactor fuels**

<table>
<thead>
<tr>
<th>F.P.</th>
<th>a/O</th>
<th>239U</th>
<th>MOX 30%PuO$_2$</th>
<th>233U</th>
<th>239Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu + Kr</td>
<td>11</td>
<td>12</td>
<td>16</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Ru + Tc + Rh</td>
<td>11</td>
<td>24</td>
<td>7</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>16</td>
<td>11</td>
<td>17</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Y + RE</td>
<td>28</td>
<td>25</td>
<td>27</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Ba + Sr</td>
<td>10</td>
<td>5</td>
<td>9.5</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Cs + Rb</td>
<td>12</td>
<td>11</td>
<td>10.5</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Metalloids + Halogens</td>
<td>2</td>
<td>2</td>
<td>1.8</td>
<td>1.2</td>
<td>2</td>
</tr>
</tbody>
</table>

**Distinguishable features of thoria based fuels and the general scenario of the fission products inside the thoria matrix.**

The difference in chemistry of thoria originates from the rigid four valency of Th in its compounds as against the flexible valency of four to six in the case...
of U. In compounds like Cs-uranates, U acquires higher valencies. Urania can oxidize to hyperstoichiometric composition UO$_{2+x}$, and by this it can buffer oxygen pressure to a large extent. The chemical affinity for additional oxygen being absent in thoria, the buffering action will be evidently weak in thoria-based fuels. For the same reason oxygen transport in thoria-rich matrix is expected to be predominantly by self diffusion unlike in urania where oxygen makes faster transport through the chemical affinity-driven diffusion process. These subtle features as compared to urania, can lead to faster growth of oxygen pressure in the fuels and thereby alter the thermochemistry of fps.

Fission of the actinide M, in MO$_2$ generates the fps and releases oxygen. The released oxygen undergoes redistribution among reactive fps, fuel and clad for their

(i) How fast and to what extent oxygen pressure inside the thoria-based fuels grows with burnup

(ii) whether the O-pressure growth could be buffered by the oxidation of reactive fission products and clad or

(iii) whether there could be oxygen transport impediment in thoria-rich matrix resulting in much higher oxygen profile than in urania? If the last point is true then:

-what is the altered thermochemistry of the fps under the higher oxygen pressures inside thoria fuel?

-can it lead to increase in free iodine concentration and formation of oxygen-rich bulky phases and from there to the pin-clad incompatibility problem?

-can the fission product Mo buffer it by its ready oxidation?

Table 2: Chemical states of fps in oxide fuels

<table>
<thead>
<tr>
<th>Types of fps</th>
<th>Chemical states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-volatile</td>
<td>Dissolved state in fuel matrix (MoO$_3$).</td>
</tr>
<tr>
<td>Rare-earths (Nd, La, Ce etc), transition metals (Y, Zr, Nb)</td>
<td>Perovskite, MoO$_3$ (grey) phase.</td>
</tr>
<tr>
<td>Alkaline earths (Sr, Ba), K Zr, U, Pu, Mo, Ce</td>
<td>Alloy (white) phases.</td>
</tr>
<tr>
<td>Noble metals (Pd, Ru, Rh), and Mo</td>
<td>Dispersed microbubbles in fuel.</td>
</tr>
<tr>
<td>Gases at volatiles</td>
<td>Fractional release at fuel-clad gap sc. at plenum.</td>
</tr>
<tr>
<td>Inert gases (Xe, Kr)</td>
<td>Conversion of Mo to Mo$_2$Te at low-moderate burnup.</td>
</tr>
<tr>
<td>Alkali metals (Cs, Rb), Cd, Te, Sb</td>
<td>Conversion of Mo to Mo$_2$Te to uranate/molybdates at high burnup.</td>
</tr>
<tr>
<td>Te, I, Br</td>
<td>In alloy phases.</td>
</tr>
</tbody>
</table>

As alkali metal compounds.
oxidations. The states of oxidized fps inside the urania matrix are fairly well established and are summarized in Table 2 for typically high burnt fuel of pressurized water reactor [2]. For thoria fuels, the distribution of fps in metallic phases, oxides and gases is expected to be similar though there can be thoria-based compounds in the oxide phases. As in the case of urania, the fluorite lattice of thoria can accommodate many of the fps. The alkaline earth based thorates $\text{MThO}_3$ can be chemical components in the grey (perovskite) phase. Additionally, there can be tetragonal/cubic phases due to alkali thorates of composition $\text{M}_x\text{ThO}_3$. However, considering the stated subtle features of thoria, one needs to address to a couple of specific issues for the fuel. These issues are included in the text box given on the previous page.

In order to address the questions mentioned in the text box, one makes a detailed balance of fission generated oxygen, considering its consumption according to the hierarchies of oxidation of the fps. The thermochemistry that a fp assumes with evolution of the oxygen potential is to be considered, for understanding the oxygen consumption. The detailed balance of incessantly generated oxygen, takes note of the oxygen used in oxidizing the most reactive fps, and the distribution of the leftover part in alloy oxidation and as transported component to clad. The analysis of detailed balance requires not only thermodynamic data of the oxidized fps but also kinetic data of alloy oxidation, oxygen transport inside the matrix and across fuel-clad gap and oxygen incorporation in zircaloy clad.

**Detailed O-balance from thermodynamic and kinetic analyses**

As already mentioned, the actinide element undergoing fission from the oxide matrix, produces two fps and two oxygen atoms. The fission released oxygen is consumed by the fps, fuel and clad according to their oxidation hierarchies. The oxygen potentials of the two-phase mixtures of the fp elements and their oxides in the respective cases form the thermodynamic basis of oxidation -lower the oxygen potential or oxygen partial pressure ($p_{O_2}$) of the mixture, higher the hierarchy in oxidation. The potential is related to pressure as $\Delta G_{O_2} \equiv RT \ln p_{O_2}$. To understand oxygen redistribution among the fps and clad, the O potentials of the relevant metal/metal oxide systems are plotted as functions of temperature in Fig. 3a. The O-potential of the fuel, $\text{Th}_{0.97}\text{U}_{0.03}\text{O}_2$ at different temperatures is indicated in Fig. 3b. The intercomparison of the potentials when made, for example, at 1473 K, indicates, that at first, yttrium and rare earths (RE) will be oxidized to their respective trivalent oxides and this will be followed by the oxidation of alkaline earths (Sr, Ba) and zirconium to their divalent and tetravalent oxides respectively. The Zr in zircaloy clad will be oxidized approximately at the Zr/ZrO$_2$ potential. The result of the hierarchical oxidations is given in Fig. 3c. The extent of oxidation of the other fps (Cs, Mo, etc.) less oxidizing than Zr, cannot be deduced, without considering the oxidation of fuel and clad and the thermodynamic stabilities of their ternary compounds. Oxygen uptake by clad depends on both O-transport and oxidation kinetics, and these aspects will be discussed separately. Although Cs/Cs$_2$O potential (Fig. 3a and 3b) is way above that of the fuel, oxidation of Cs and fuel starts almost parallelly because of the formation of highly stable oxide-based compounds like alkali uranates, molybdates, zirconates and thorates. The Cs case suggests that the *prima-facie* knowledge of oxygen potential of the binary equilibria of metal/metal oxide systems of the fps is necessary but not sufficient for the oxygen consumption analysis. One needs to have complete information on the thermochemistry of the fps, which will be mentioned in the next subsection. The fuel $\text{Th}_{0.97}\text{U}_{0.03}\text{O}_2$ with typical O/M $= 2.0000$ will share an insignificant part of the fission-released oxygen to raise its O/M ratio. It is apparent from Fig. 3b that the O/M ratio will hardly rise when the O-potential of the fuel attains that of Mo/MoO$_2$ and Mo oxidation starts buffering the potential. In urania fuels, in
contrast, the O/M ratio at 1473 K should rise to the value of 2.001 (Fig. 3b) before Mo gets oxidized. The extent of Mo oxidation is however subjective to the detailed balance of fission generated oxygen considering the consumption. Using the fps yields in AHWR fuel (Table 1) and the oxidation hierarchies (Fig. 3a, 3c), the oxygen uptakes by the fps is given in Table 3. If all the fission generated oxygen is available for fps oxidation, the rare earths, alkaline earths, and zirconium use about 83.5 atom %O in forming their respective binary oxides RE₂O₃, Sr(Ba)O and ZrO₂. Another 3.7% is used for Ce₂O₅ oxidation to CeO₂ which gets stabilized as cerate.
components in the perovskite (grey) phase, \((\text{Ba},\text{Sr})(\text{Zr},\text{Th}, \text{U},\text{Ce})\text{O}_3\), constituted mainly of zirconates of the alkaline earth fps. From the balance of 12.8% oxygen (Table 4) a part would be transported to clad while the rest of the O will be used for the oxidation of Cs/Rb, fuel and Mo. To understand the redistribution behavior of the 12.8% oxygen, a brief mention is now made of the thermodynamic aspect of the fps states and kinetic aspects of the O-transport and oxidation.

Table 4: Oxygen uptake by fps and clad

Thermodynamic aspects

Fig. 4 shows the oxygen potentials of relevant chemical equilibria involving the alkali metal fps Cs. The metal oxide phases have O-potentials of roughly 200 kJ mol\(^{-1}\) above that of Zr/\(\text{ZrO}_2\) and almost the same amount below that of Mo/\(\text{MoO}_3\). In the figure, the potential values for different oxide systems are obtained from our experimental results and the reported information as summarized in Table 5. The thermodynamic stabilities of oxide compounds such as \(\text{BaThO}_3\), \(\text{SrThO}_3\), \(\text{Cs}_2\text{ThO}_4\), \(\text{Cs}_2\text{ZrO}_3\) and \(\text{Rb}_2\text{ThO}_3\) were measured using Knudsen effusion and transpiration techniques. The indigenously developed apparatus for these techniques are shown in Fig. 5 and Fig. 6. The remaining fission generated oxygen of 12.8 atom % which raises the potential above Zr/\(\text{ZrO}_2\), will cause the formation of O-rich ternary compounds of Cs. The extent of O-uptake by the alkali metals, depends on the amount of O-partitioning among their thorates/zirconates and uranates/molybdates.

Fig. 4: Relevant chemical states of Cs

Fig. 5: Knudsen effusion assembly
The alkali thorates formation would be favorable to zirconates, as Zr in the fps preferentially forms the more stable alkaline earth zirconates. The data of the thorates, zirconates, uranates and molybdates of alkali and alkaline earth fps are given in Table 5. As seen in Fig. 4 the oxygen potential rise will result in formation of cesium thorate and cesium uranate depending upon the temperature. Thermo-dynamically, $\text{Cs}_2\text{UO}_4$ conversion from the thorate is favored by the following reaction:

$$\text{Cs}_2\text{ThO}_3(s) + \left[\text{UO}_2\right]^+ + \frac{1}{2}\text{O}_2(g) = \text{ThO}_2(s) + \text{Cs}_2\text{UO}_4(s).$$

For similar reason, the interconversion of thorate to molybdate is also possible as

$$\text{Cs}_2\text{ThO}_3(s) + \left[\text{Mo}_{\text{alloy}}\right] + \frac{3}{2}\text{O}_2(g) = \text{ThO}_2(s) + \text{Cs}_2\text{MoO}_4(s).$$

Out of the two possibilities the former one is preferred. In the conventional urania-based fuels Cs is preferentially fixed in the uranate form. At 5 atom% burnup, alkali metals when consumed as their uranates, will take about half percent of the total uranium content of the fuel. Because of U-233 isotope production, the initial urania content of 3 mol% will hardly be lowered at a burnup of 50 GWD ton$^{-1}$. Cesium uranate formation will consume ten atoms of oxygen leaving thereby 2.8 % out of the 12.8%. It is to be noted here that one atom of oxygen is consumed per alkali atom in uranate formation. Thorate ($\text{M}_2\text{ThO}_3(s)$) and molybdate ($\text{M}_2\text{MoO}_4$) formations would have consumed 0.5 and 2.0 O atoms respectively. However, for evaluating oxygen consumption
by the alkali metals, one should consider the thermodynamic as well as kinetic aspects. The latter aspect comes into play due to the restricted accessibility of Cs by the competing reactants, thoria, urania and Mo-alloy. The restriction arises from very low diffusion of the alkali metal atom. The diffusion coefficient of Cs in the fuel is lower than even that of the oxygen in the fuel matrix. With low urania content in AHWR fuel and the presence of a small quantity of the evenly dispersed alloy phase, the Cs and oxygen uptake by thoria matrix, is expected to be predominant. All Cs and Rb preferentially converted to cesium and rubidium thorates, the oxygen balance will be set to 7.8 atom% instead of 2.8 obtained from purely thermodynamic considerations. The actual value of oxygen balance will lie somewhere in between. Any augmented consumption of oxygen by the alkaline earth molybdates/uranates formation is not possible, as their formation requires BaO/SrO components to be displaced from the more stable perovskite phase. In the absence of detailed information of cesium transport and alloy phase distribution in the matrix, kinetic considerations are difficult to quantify. Rest of the presentation is thus based on the redistribution of the residual oxygen of 2.8 % obtained from thermodynamic considerations. This will give a lower limit of oxygen potential rise in the fuel. The 2.8 a/o of the fission generated oxygen, constantly available from 12.5 mm dia. fuel pellet at 180 W cm\(^{-1}\) power rating, will have the O-flux of 4.5 \(\times 10^{-8}\) g.atom d\(^{-1}\) cm\(^{-1}\). Subsequent analysis considers these aspects.

**Kinetic aspects of residual flux of fission-released oxygen**

The residual flux of the fission released oxygen, will be consumed by molybdenum and parallely transported out to clad. The molybdenum oxidation kinetics is considered, taking the reported result studied on metal surface. The oxidation rate of Mo surface expressed as \(\frac{dN_{Mo}}{dt} = A \exp[-E/RT]\), \(A = 5.3 \times 10^{-3}\) g.atom cm\(^{-2}\) s\(^{-1}\), and \(E = 82.4\) kJ mol\(^{-1}\), suggests that the rate is as high as \(91 \times 10^{-4}\) g.atom cm\(^{-2}\) d\(^{-1}\) even at the lowest temperature of 800 K prevalent at the fuel surface. This value being several orders of magnitude higher than the residual O-flux of \(4.5 \times 10^{-8}\) g.atom d\(^{-1}\) cm\(^{-1}\), one may conclude that finely divided state of Mo can easily buffer the oxygen potential. Kinetically, freshly generated Mo is expected to oxidize faster, rather than forming alloy with the noble metals.

The parallel kinetic path of overall O-transport to clad will be governed by the slowest of the three processes: a) transport through matrix b) transport across fuel clad gap and c) oxidative incorporation in clad, which are briefly described below:

a) The reported data of the chemical diffusion of oxygen in thoria-urania matrix given in Fig.7 at 1000K shows that, the diffusion coefficient falls sharply to a low value when the urania content is less. Our study of AHWR SIMFUEL of 20 GWD
b) The O-flux flow from fuel to clad has to travel across a thin gap (typically 50 microns) filled with helium gas at high pressure (~25 bar). The transport coefficient \( D_g \) of oxygen according to the kinetic theory is of the order of \( \frac{u_{av}}{3\pi N \sigma^2} \), where \( u_{av} \) is the average speed of \( \text{O}_2 \) molecules at the gap temperature of ~800 K, \( N \) is the total gas density and \( \sigma \) is the mean collision diameter of \( \text{He} + \text{O}_2 \) gas mixture. \( D_g \) value works out to be 0.054 cm\(^2\) s\(^{-1}\). With this value, one thus addresses the question as to whether the residual O-flux load of \( 4.5 \times 10^{-8} \) g.atom d\(^{-1}\) cm\(^{-1}\) from the fuel can be transported radially outwards across the thin annular gap of 50 micron. This transport process through gas diffusion needs an \( \text{O}_2 \) concentration drop of \( 6 \times 10^{-15} \) g.mol cm\(^{-3}\), or, pressure drop of \( 3.5 \times 10^{-10} \) bar across the gap. It needs too high oxygen pressure gradient, than could be met by the low \( P_{O_2} \) (<10\(^{-23}\)bar), on the fuel surface decided by the O/M ratio. The oxygen transport across the gap, can however be enhanced, by the presence of augmented concentration of oxygen bearing gaseous species like \( \text{H}_2\text{O}(g) \), \( \text{Cs}_2\text{O}(g) \) and \( \text{CsOH}(g) \), formed via the involvement of various chemical equilibria between reactive species like \( \text{H}_2 \) or \( \text{Cs}(g) \) with the oxide fuel (for example, \( \text{MO}_{2+x} + \delta\text{H}_2(g) = \text{MO}_{2+x-d} + \delta\text{H}_2\text{O}(g) \)). The \( \text{H}_2/\text{H}_2\text{O} \) reductive equilibrium, effectively converts all hydrogen in contact with the fuel to moisture. Sources of hydrogen are in fact, the moisture impurity in the fuel and also that resulting out of nuclear reaction. \( \text{Cs}(g) \) is the product of volatilization process of Cs bearing condensed and vapor phases present in the fuel. Thus oxygen can undergo chemical vapor transport, to reach the clad and oxidize it as

\[
2\text{H}_2\text{O}(g) + [\text{Zr}] = \text{ZrO}_2(s) + 2\text{H}_2(g),
\]

\[
2\text{CsOH}(g) + [\text{Zr}] = \text{ZrO}_2(s) + 2\text{Cs}(g) + \text{H}_2(g).
\]

The products, hydrogen and cesium vapor return back to react with the oxide fuel forming the oxygenbearing species once again. Considering that the fuel reduction and zircaloy oxidation are nearly quantitative with least kinetic hindrances in them and noting that the transporting species (\( \text{H}_2\text{O}(g) \) or \( \text{CsOH}(g) \)) prevail at significantly higher partial pressures than the required values (\( \sim 3.5 \times 10^{-10} \) bar) for the diffusion flow of \( 4.5 \times 10^{-8} \) g.atom d\(^{-1}\) cm\(^{-1}\), one sees the effectiveness of chemical vapor transport mechanism for oxygen across the fuel-clad gap.

c) The clad oxidation takes place in steps. The oxide layer grows initially with cubic rate law and after a certain thickness is attained, it follows a comparatively slow growth linearly. The reported linear growth rate of \( 0.83 \times 10^{-6} \mu \text{m ZrO}_2/\text{d} \) (equivalently, \( 5.70 \times 10^{-7} \) g.atom d\(^{-1}\) cm\(^{-1}\)) is again an order of magnitude higher than the available O-flux.

The significance of oxidation of Mo as compared to that of clad, for the removal of the residual oxygen flux in thoria fuel, follows from the fact that the transport out process becomes competitive, only when the oxygen pressures inside the fuel develops much above the Mo/MoO\(_2\) potential. Fig. 8 shows the steady state oxygen profile (right axis), inside the thoria SIMFUEL, to be established for transporting out the residual O-flux of \( 4.5 \times 10^{-8} \) g.atom d\(^{-1}\) cm\(^{-1}\)) in the absence of Mo oxidation. The profile is calculated using the mentioned transport coefficient and under a given temperature distribution (left axis). The result
Fig. 8: Profiles of oxygen and O/M ratio under a given temperature distribution and O-flux (4.5 x10^4 g.atom d⁻¹).

Fig. 9: Mo activity in hexagonal phase of Mo-Ru-Pd ternary of such calculation suggests that the O-transport inside the fuel is the slowest of the kinetic steps and also proves the important role of Mo in buffering the oxygen potential in thoria-based fuel. Urania case shown in the figure is distinctly different.

Oxygen potential at high burnup situation

The Mo oxidation playing a decisive role of controlling oxygen pressure in the burning process of the fuel, the chemical states of oxygen-rich phases that can be formed in the neighborhood of [Mo]_{alloy}/MoO₂ potential will be considered in the subsequent analysis of high burnup situation. Depending on the oxygen potential the oxidized molybdenum may remain as pure MoO₂ or as molybdite component or get further oxidized to molybdate. The oxygen potential is governed by the following equilibria:

\[
[\text{Mo}]_{\text{alloy}} + O_2(g) = [\text{MoO}_2]_{\text{molybdate}}
\]

At 50 GWD ton⁻¹, the molybdenum content in the hexagonal phase of metallic inclusions (Mo-Ru-Rh-Pd quaternary) is about 34 atom%. Mo activity in the phase considering reported data of Mo-Ru-Pd ternary (Fig. 9) is assumed to be within 0.25-0.3 over the temperature range of 800 to 1500K. The molybdates will be formed out of alkaline earths, Sr and Ba, that are normally present as zirconates in the perovskite phase. Considering however, higher stability of BaZrO₃, the molybdate component will be mainly as SrMoO₄. Considering the residual part of oxygen as well as barium yield per fission and also the fact that practically all barium is present as
zirconate, the molybdate, to zirconate ratio is expected to be 0.44. In other words, the strontium molybdate mol fraction of the perovskite phase is 0.22. The oxygen potential is thus worked out considering the equilibrium

$$[\text{SrO}] + [\text{Mo}] + \text{O}_2(g) = [\text{SrMoO}_3]$$  \hspace{1cm} (1)

in which the SrO activity is governed by

$$[\text{ZrO}_2] + [\text{SrO}] = [\text{SrZrO}_3]$$  \hspace{1cm} (2).

The ZrO$_2$ activity in (2) can be expressed by noting the dissolved part of ZrO$_2$ in thoria and the solution behavior of ZrO$_2$-ThO$_2$ pseudo-binary. The dissolved part is essentially the total Zr yield minus Zr present as Ba(Sr)ZrO$_3$. The SrZrO$_3$ activity in the perovskite phase, is iteratively worked out from an initially assumed value of 0.5, using equilibrium reaction (2) and the observation that the neodymium oxide component of the fuel phase does not displace the ZrO$_2$ from SrZrO$_3$ to form Nd-pyrochlore. With the iterated value of SrZrO$_3$ activity as 0.25 together with the ZrO$_2$ activity, the equilibrium reaction (2) leads to the SrO activity as

$$\text{RTln}a_{\text{SrO}} = -115.7 + (0.047 - 0.0083\ln B)T.$$  

Use of this result in (1) and taking the Mo activity as 0.3 and SrMoO$_3$ activity as 0.22 yields the oxygen potential as

$$\Delta G_{O_2} = -559.4 + (0.117 + 0.0083\ln B)T \text{ kJ mol}^{-1}.$$  

At 5 atom% burnup, the oxygen potential obtained is shown in Fig.10.

The actual pressure under the constant flux of 2.8% oxygen will be higher because of the impediment of transport of the reactants participating in equation (1). The calculated oxygen potential under the kinetic impediment will be governed by local equilibrium.

Further, in view of the fact that we have used the lower limit of the residual oxygen flux for evaluating the oxygen potential, the actual extent of Mo oxidation and accordingly the O-potential will be somewhat higher, had we considered the local equilibrium with a residual O-flux of 7.8%. It may be recalled, that in actual situations, the residual flux will be somewhere between 2.8 to 7.8 %, depending on the extent of global equilibrium.
Chemical Scenario at high burnup

One can examine whether the phase equilibria involving oxygen-rich compounds other than molybdite have significance at the high burnup. The free energy considerations of the reaction, $2[\text{SrMoO}_3]+\text{O}_2(g) = 2\text{SrMoO}_4(s)$ shows that Sr-molybdite oxidation is not feasible at the high burnup. If the corresponding Ba compound had been present, similar reaction was possible at least in the peripheral region of the fuel pin (Fig 10). Since molydite oxidation to molybdate is not possible for the Sr case, the disproportionation forming the molybdate and Mo as $3[\text{SrMoO}_3]+[\text{ZrO}_2] = [\text{Mo}] + 2\text{SrMoO}_4(s) +[\text{SrZrO}_3]$ cannot occur. With the oxygen potential, one can examine whether there can be BaO partitioning from zirconate phase to result in the formations of the bulky phases like pyrochlore and molybdates, as $2[\text{BaZrO}_3]+ 2[\text{NdO}_{1.5}]+ 2[\text{Mo}]+3\text{O}_2(g) = \text{Nd}_2\text{Zr}_2\text{O}_7(s) + 2\text{BaMoO}_4(s)$. Considering the activities of the chemical components and the available thermodynamic data of the reactants and products it can be shown that even at high burnup like 10%, the pyrochlore and molybdate formations are feasible below 540 K. So for all practical purpose the forward reaction is absent within the fuel. If at all it occurs, it will be in the peripheral region (Fig. 10). Under the prevailing oxygen potential, one further shows that the UO$_2$ oxidation, such as $2[\text{UO}_2]+\text{O}_2(g) +2[\text{SrO}] = 2\text{SrUO}_4(s)$, leading to the formation of alkaline earth uranates is not feasible due to low activities of the alkaline earth oxides as well as urania in the fuel.

The uranate formation via reduction of SrO component in the fuel phase as $[\text{UO}_2]+2[\text{SrO}] = \text{Sr}(g)+ \text{SrUO}_4(s)$, depends on Sr atom transport from the reaction site. The reduction can also result in only gaseous products as $[\text{SrO}] +[\text{MO}_2] = \text{Sr}(g) + \text{MO}_2(g)$, ($M = \text{U, Mo}$). Considerations of standard free energy changes of the reactions and the activities of the chemical components, it can be shown that, the above reduction will cause SrMoO$_4$ volatilization from the central part of the fuel and this will lead to the transport of the vapor products and formation of SrMoO$_4(s)$ phase, in the peripheral part of the fuel pin.

The above mentioned findings about the oxygen potential and the resultant chemistry are based on the fact that residual flux of oxygen are easily consumed in molybdenum oxidations. However in high burn-up situations, the fuel matrix incorporating significant fractions of the fission gas in microdispersed states, oxygen accessibility to molybdenum alloy will be highly impeded. In this case, the oxygen potential can locally surpass the molybdenum/molybdite-control and lead to the formation of a number of oxygen-rich phases like: tellurites, tellurates and molybdates of the fps and clad materials. Thermodynamic data and volatilization characteristics of such O-rich phases have been generated in our laboratory. In the conventional oxide fuels, these phases are relevant only for the analysis of failed pin. Fuel pin failure occurs when the thin clad wall (~0.5 mm thickness) develops defects, providing permeation path of the coolant fluid with a higher oxygen potential to come in contact with hot fuel.

The thoria-based fuels will develop internal stress from the formation of the bulky oxygen-rich phase. As discussed before, the outer part of the fuel pin will be enriched with the molybdate precipitates as well as gas bubbles migrating out from the centre. Generally, all the nonvolatiles and the volatiles to a large extent (~99%), and a major fraction (90-95%) of the gaseous fps remain within the matrix (Fig 1), [2]. The dispersed bubbles as well as the undissolved solid phases formed by other fps impart internal stress to the matrix, under which the fuel pin swells, develops radial microcracks and voids and as the result, thermal conductivity of the fuel-matrix deteriorates. The gap conductivity also deteriorates progressively due to released gas that dilutes the helium column filling the gap at several tens of barspressures. As compared to the case reported for the conventional urania-based fuels, the extent of the fuel swelling from the dissolved and undissolved components of the fps will be more in thoria.
The volatile fps like I and Te, though produced in small amounts, can put stake on the fuel containment because of their corrosion and fatigue actions to the clad. Like the gases, these species undergo transport to reach the clad’s surface. Chemical interaction of I and Te with the clad, results in degradation of its mechanical property and in extreme situation, leads to its brittle fracturing and, stress corrosion cracking. The availability of free I and Te depends on two factors: their transport properties and relative stabilities of their cesium compounds as compared to the ternary oxide phases of cesium. The stability of Te-intermetallics is an additional factor in Te partitioning. The measured transport properties of I, Te, Cs, Xe etc. show that, these are significantly lower in thoria-based fuels than in urania. The transport data is presented in Fig.11.

Conclusions

Thoria-based fuel is shown to have poor transport property of oxygen. The present analysis suggests that the fuel will generally bear higher oxygen potential right from the early stage of burnup. Mo plays vital role in buffering the potential in thoria fuel. This is unlike the case in urania, where the oxygen potential is controlled by fuel oxidation and easy transport to clad for its oxidation. Mo oxidation starts at a much later stage when the urania matrix attains high O/M ratio and is morphologically degenerated with dispersed gas bubbles. The higher potential in the thoria fuel, results in formation of oxidized products like SrMoO$_3$. In the cooler part of the fuel pin, there is a likelihood of the formation of more oxidized products like SrMO$_4$ (M = Mo, U). The transport properties of the volatile reactive fps like I, Te, Cs are significantly low in thoria based fuels as compared to those in urania. The fuel containment problem from clad corrosion though less in the fuel, matrix swelling will be more due to the large retention of gaseous fps and formation of oxygen-rich phases.

References
