Global Nuclear Fuel

K-Infinite Comparison of Uranium Compounds at 5 wt. % U235

NCSD Technical Session
Data, Analysis and Operations in Nuclear Criticality Safety - II

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Marriott Wardman Park
Agenda

- Intro
- Uranium
- Uranium Speciation
- SCALE6.1 Model
- Results
- Conclusions
**Introduction**

Recent efforts to expand authorized contents of existing NPC Type A, Fissile nuclear package resulted in further study of select uranium compounds

- GEH/GNF owned design
- Licensed in the U.S. by NRC to 10CFR71 & IAEA requirements [USNRC CofC 9294]
- Type A container used to transport unirradiated fissile uranic material
- A cubic stainless steel and foam outer packaging with nine (9) ~ 8 inch ID inner containment canister assemblies (ICCAs)
- Currently used for transport of Type A quantities of low-enriched uranium oxide powder, pellets, and compounds of uranium
- Unique encased cadmium sheet used for reactivity control
- Planned future expansion of authorized content to include Type B material quantities (>5%, HALEU material forms)
Uranium

- The element uranium was discovered in 1789 in the pitchblende ores of Saxony by M. H. Klaproth (1743-1817), a notable analytic chemist and professor and the university of Berlin. Klaproth name the new element “Uranit”, after planet Uranus, discovered earlier in 1781. A year later he changed the name to uranium.

- Uranium is a soft, silvery white metal. Its atomic number is 92 and its atomic weight is 238.03; thus it is the heaviest element found in nature.

- Certain chemical characteristics of uranium govern its behavior in chemical / geochemical processes. The element uranium has six valence electrons in the configuration [Rn]5f^36d^17s^2. The most common oxidation state of +6 involve the loss of all outer electrons; but the element may also exist in lower oxidation states including +3 (5f^3), +4(5f^2), +5(5f^1) and +6(5f^0).

- Uranium is recognized as a ubiquitous element. Its concentration is sea water (3.34 μg/l) appears remarkably constant. The earth’s crust contains 0.0004% uranium., which is more than gold, silver, mercury contents.

- Uranium has an ion size of about 1.05 A and is never found in its elemental state, but always in chemical combinations with other elements.
Uranium Speciation - I

- Aqueous solutions of uranium salts have an acid reaction as a result of hydrolysis; for instance $\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{U(OH)}^{3+} + \text{H}^+$. The order of increasing hydrolysis depend on the charge and the size of the ion and is indicated by $\text{U}^{4+} > \text{UO}_2^{2+} > \text{U}^{3+} > \text{UO}^{2+}$. Thus the $\text{U}^{4+}$ ion has a strong tendency for hydrolysis, and when present in solution, form much stronger complexes with a given ligand than does the uranyl ion.

- Fuel fabrication facility take advantage of these chemical characteristics; precipitation recipes are vast and the resulting speciated uranium compounds involve complicated chemical reactions that continue to be studied to the present day.

- Depending on the byproduct waste streams, liquid lime slurry ($\text{Ca(OH)}_2$), nitric acid ($\text{HNO}_3$), ammonia ($\text{NH}_4$), ammonium bicarbonate ($\text{(NH}_4\text{)HCO}_3$), and sodium hydroxide ($\text{NaOH}$) may be used to precipitate uranium and ultimately dried into solid form.

- $\text{U}_3\text{O}_8$ is considered to be the more attractive form for disposal purposes because, under normal environmental conditions, $\text{U}_3\text{O}_8$ is one of the most kinetically and thermodynamically stable forms of uranium.
Uranium Speciation - II

- $\text{UO}_2$
- $\text{U}_3\text{O}_8$
- $\text{UF}_4$
- $\text{UF}_6$
Uranium Speciation - III

\[ \text{UO}_2 (\text{NO}_3)_2 \]

\[ \text{UO}_2 (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \]
Uranium Speciation - IV

\[ \text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O} \]
Uranium Speciation - V

Table A.1 Composition of ADU(I), (II), (III) and (IV)

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemical formula</th>
<th>Theoretical density(^{1)}) g/cm(^3)</th>
<th>N / U atomic ratio</th>
<th>H / U atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>(\text{UO}_3 \cdot 2\text{H}_2\text{O})</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(II)</td>
<td>(3\text{UO}_3 \cdot \text{NH}_3 \cdot 5\text{H}_2\text{O})</td>
<td>4.831</td>
<td>0.333</td>
<td>4.333</td>
</tr>
<tr>
<td>(III)</td>
<td>(2\text{UO}_3 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O})</td>
<td>5.144</td>
<td>0.5</td>
<td>4.5</td>
</tr>
<tr>
<td>(IV)</td>
<td>(3\text{UO}_3 \cdot 2\text{NH}_3 \cdot 4\text{H}_2\text{O})</td>
<td>5.201</td>
<td>0.667</td>
<td>4.667</td>
</tr>
</tbody>
</table>

\(^{1)}\) Natural uranium (\(^{235}\text{U}\) enrichment 0.711 wt %)
Uranium Speciation - VI

\[(\text{NH}_4)_4\text{UO}_2\text{(CO}_3\text{)}_3\]
## Uranium Compounds

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Uranium Compound</th>
<th>Density (g/cc)</th>
<th>UFACT</th>
<th>Molecular Weight (g/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium oxides/ oxide bearing ash / sludges</td>
<td>UO$_2$</td>
<td>10.96</td>
<td>0.88144</td>
<td>269.8974</td>
<td>[1]</td>
</tr>
<tr>
<td>Uranium oxides/ oxide bearing ash / sludges</td>
<td>UO$_2$</td>
<td>4.5</td>
<td>0.88144</td>
<td>269.8974</td>
<td>[2]</td>
</tr>
<tr>
<td>Uranium oxides/ oxide bearing ash / sludges</td>
<td>U$_2$O$_8$</td>
<td>8.3</td>
<td>0.84793</td>
<td>841.691</td>
<td>[1]</td>
</tr>
<tr>
<td>Uranyl nitrate [UN]</td>
<td>UO$_2$(NO$_3$)$_2$</td>
<td>2.203</td>
<td>0.60395</td>
<td>393.9072</td>
<td>[1]</td>
</tr>
<tr>
<td>Uranyl nitrate hexahydrate [UNH]</td>
<td>UO$_2$(NO$_3$)$_2$·6H$_2$O</td>
<td>2.807</td>
<td>0.47390</td>
<td>501.9989</td>
<td>[3]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>CaUO$_3$</td>
<td>6.97</td>
<td>0.72981</td>
<td>325.9752</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_2$UO$_4$</td>
<td>7.45</td>
<td>0.69566</td>
<td>341.9746</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_2$UO$_4$</td>
<td>5.67</td>
<td>0.59766</td>
<td>398.0524</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_2$UO$_4$</td>
<td>7.806</td>
<td>0.62268</td>
<td>382.053</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_3$UO$_6$</td>
<td>5.337</td>
<td>0.52386</td>
<td>454.1302</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_3$UO$_6$·4H$_2$O</td>
<td>5.25</td>
<td>0.72395</td>
<td>985.8294</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_3$UO$_6$·11H$_2$O</td>
<td>5.16</td>
<td>0.72470</td>
<td>1969.6268</td>
<td>[4]</td>
</tr>
<tr>
<td>Calcium uranium oxides</td>
<td>Ca$_3$UO$_6$·10H$_2$O</td>
<td>5.1</td>
<td>0.73152</td>
<td>1952.5245</td>
<td>[4]</td>
</tr>
<tr>
<td>Sodium diuranate</td>
<td>Na$_2$U$_2$O$_7$</td>
<td>6.57</td>
<td>0.75074</td>
<td>633.7726</td>
<td>[5]</td>
</tr>
<tr>
<td>Sodium uranate</td>
<td>Na$_2$UO$_4$</td>
<td>5.74</td>
<td>0.68386</td>
<td>347.8758</td>
<td>[6]</td>
</tr>
<tr>
<td>Uranium tetrafluoride (insoluble)</td>
<td>UF$_4$</td>
<td>6.7</td>
<td>0.75790</td>
<td>313.8922</td>
<td>[1]</td>
</tr>
<tr>
<td>Sodium diuranate – uranium tetrafluoride</td>
<td>4Na$_2$U$_2$O$_7$·UF$_4$</td>
<td>6.5862</td>
<td>0.75153</td>
<td>2848.9825</td>
<td>[5,7]</td>
</tr>
<tr>
<td>Ammonium diuranate [ADU]</td>
<td>3UO$_3$·2NH$_4$·4H$_2$O</td>
<td>5.201</td>
<td>0.74049</td>
<td>963.8126</td>
<td>[8]</td>
</tr>
<tr>
<td>Sodium diuranate hexahydrate</td>
<td>Na$_2$U$_2$O$_7$·6H$_2$O</td>
<td>6.57</td>
<td>0.64135</td>
<td>741.8642</td>
<td>[5]</td>
</tr>
<tr>
<td>Ammonium uranyl carbonate [AUC]</td>
<td>(NH$_4$)$_2$UO$_2$·(CO$_3$)$_3$</td>
<td>2.77</td>
<td>0.45568</td>
<td>522.0780</td>
<td>[9]</td>
</tr>
</tbody>
</table>
Ex. SCALE6.1 Model Constructs

=csas6
infinite medium of theoretical $\text{uo}_2 + \text{h}_2\text{o}$, 5% enr, var. wtfr_h2o
ce_v7_endf
read composition
$\text{uo}_2$ 1 den=9.9655 0.99 300
92235 5
92238 95 end
$h\text{o}_2$ 1 den=9.9655 0.01 300 end
end composition
read parameter
gen=600
npg=5000
nsk=100
htm=yes
end parameter
read geometry
global unit 1
com="global unit"
cuboid 10 10 -10 10 -10 10 -10
media 1 1 10
boundary 10
end geometry
read bnds
body=10
all=mirror
end bnds
end data
end

theoretical $\text{uo}_2(\text{no}_3)2 + \text{h}_2\text{o}$, 5% enr, var. wtfr_h2o
read composition
$\text{uo}_2(\text{no}_3)2$ 1 den=2.1767 0.99 300
92235 5
92238 95 end
$h\text{o}_2$ 1 den=2.1767 0.01 300 end
end composition

theoretical $\text{uo}_2(\text{no}_3)2*6\text{h}_2\text{o} + \text{h}_2\text{o}$, 5% enr, var. wtfr_h2o
read composition
atomunh 1 2.7570 4
92000 1
8016 14
7014 2
1001 12
0.99 300
92235 5
92238 95 end
$h\text{o}_2$ 1 den=2.7570 0.01 300 end
end

theoretical $\text{cau}_6\text{o}_19*10\text{h}_2\text{o} + \text{h}_2\text{o}$, 5% enr, var. wtfr_h2o
read composition
atomcauxoy_f8 1 4.8987 4
92000 6
8016 30
1001 22
20000 1
0.99 300
92235 5
92238 95 end
$h\text{o}_2$ 1 den=4.8987 0.01 300 end
Results – I (Calcium uranium oxides)
Results – II (Uranium compounds)
## Results – III (Tabulated Parato)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Keff</th>
<th>$\sigma$</th>
<th>$K_{\infty}$ [Keff + 2$\sigma$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
<td>1.46513</td>
<td>0.00040</td>
<td>1.46593</td>
</tr>
<tr>
<td>U$_3$O$_8$</td>
<td>1.46499</td>
<td>0.00048</td>
<td>1.46595</td>
</tr>
<tr>
<td>CaU$<em>6$O$</em>{19}$*11H$_2$O</td>
<td>1.45901</td>
<td>0.00040</td>
<td>1.45981</td>
</tr>
<tr>
<td>UF$_4$</td>
<td>1.45875</td>
<td>0.00045</td>
<td>1.45965</td>
</tr>
<tr>
<td>4Na$_2$U$_2$O$_7$*UF$_4$</td>
<td>1.44496</td>
<td>0.00040</td>
<td>1.44576</td>
</tr>
<tr>
<td>Na$_2$U$_2$O$_7$</td>
<td>1.44306</td>
<td>0.00042</td>
<td>1.44390</td>
</tr>
<tr>
<td>Na$_2$U$_2$O$_7$*6H$_2$O</td>
<td>1.44295</td>
<td>0.00041</td>
<td>1.44377</td>
</tr>
<tr>
<td>Na$_2$UO$_4$</td>
<td>1.42173</td>
<td>0.00041</td>
<td>1.42255</td>
</tr>
<tr>
<td>3UO$_3$*2NH$_3$*4H$_2$O</td>
<td>1.41478</td>
<td>0.00041</td>
<td>1.41560</td>
</tr>
<tr>
<td>UO$_2$(NO$_3$)$_2$</td>
<td>1.31546</td>
<td>0.00037</td>
<td>1.31620</td>
</tr>
<tr>
<td>UO$_2$(NO$_3$)$_2$*6H$_2$O</td>
<td>1.31270</td>
<td>0.00047</td>
<td>1.31364</td>
</tr>
<tr>
<td>(NH$_4$)$_4$<em>UO$_2$</em>(CO$_3$)$_3$</td>
<td>1.20346</td>
<td>0.00040</td>
<td>1.20426</td>
</tr>
</tbody>
</table>
Conclusions - I

- Theoretical UO₂ is bounding when compared to other solid uranium compounds containing a uranium content less than a weight fraction of 0.88144.

- There is no statistically significant difference between UO₂ and U₃O₈ (as they are within 1σ)

- Uranium tetrafluoride compound is more reactive than the sodium diuranate compound. The representative 4:1 ratio evaluated for the complex compound of both substances (sodium diuranate – uranium tetrafluoride) is less reactive than UF₄. Thus, no molar ratio would be any more reactive than the bounding theoretical compound.

- The hexahydrate of sodium diuranate is less dense than the anhydrous form. It is therefore conservative to use the higher anhydrous density for this hexahydrate.

- Other modeled uranium compounds are demonstrated to be less reactive than UO₂ due to the presence of other neutron absorbing compounds (e.g., Ca, Na, N, F, etc.) or other diluents.
Conclusions - II

• These results support the overall conclusion that theoretical uranium dioxide compound may be considered bounding insofar as authorized solid uranium scrap, sludge, ash, and residue byproduct compounds resulting from uranium recovery processes.

• Additional dry solid uranium byproducts not specifically evaluated herein that contain a uranium weight fraction less the theoretical UO2 would also be conservatively bounded.