ON HYDROLYSIS BEHAVIOUR OF URANIUM FLUORIDE AND FORMATION OF HYDRATED OXYFLURIDE OF U(VI)


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ABSTRACT

The all fluoride molten salt reactor is aimed to use enriched UF₄ along with ThF₄ and LiF. Thus the study on thermophysical and chemical stabilities of ThF₄ and UF₄ is one of the area of basics research of nuclear technology. The production of enriched UF₄ is likely to have UF₆ due to its production strategy. The complexity of U-F system compared to Th-F system arises from the formation of various stable oxyfluorides with uranium compared thorium. In the aspect of stability actinide tetrafluorides under hydation condition, a case study with UF₄ has been carried out and they are presented.

Subsequent to enrichment of UF₆, either depleted or enriched, should be converted either to UF₄ or UO₂ which are practically usable form of nuclear fuels based on uranium. UF₄ is the preferred product en route to production of U metal as well as enriched oxide fuel. In the conversion process of UF₄ to UF₆, the products inter alia may contain impurities such as intermediate uranium fluorides, hydrated compounds of UF₄, UO₂F₂ etc. as well as occluded or trapped UF₆ in UF₄ matrix. Likewise exposure of UF₄ to ambient environmental condition may also form hydrated phases of UF₄. Identification and subsequent removal of these impurities is necessary to smoothly conduct the onward reduction of UF₄ to U metal. The possibility of trapped UF₆ can form adducts or Physis or chemisorbed and they are likely to undergo hydrolyses to give UO₂F₂. In the reported work, hydration and crystallization process of uranium fluoride or oxy fluoride is presented. In the course of hydration of impurity containing UF₄, highly soluble UO₂F₂ crystallizes as hydrated product on drying, which in turn transforms to the fine powder of UO₂F₂. The hydrated complex of tetravalent UF₄ is also observed in minor quantity in this process. Also it has been revealed that UF₄ is not hydrolyzed to oxides or oxyfluorides under the present experimental conditions. It can be mentioned that under similar condition ThF₄ can completely transform to oxides (ThO₂).

INTRODUCTION

The fabrication of enriched nuclear fuel is often relied on the UF₆ precursor [1], which is unstable under normal moisture containing environment. Hence for safe storage and then for further use, UF₄ is considered to be a desired phase due to its amenability for metallic fuel production and easier usability to be converted back to UF₆ for future up gradation. In UF₆ to UF₄ conversion process, there may be several intermediate fluorides of uranium, uranium oxyfluorides and hydrated UF₄ phases present in the product which are essentially formed either due to incomplete conversion or due to interaction of uranium fluorides with moisture vapor. In particular, the all fluoride molten salt reactor is aimed to use enriched UF₄ along with ThF₄ and LiF. The production of enriched UF₄ is likely to have UF₆ due to its production strategy. Additionally, UF₄, during its formation can also trap UF₆ which mostly remains as occluded phase and thereby poses a concern for long term storage due to its reactivity with moisture and container material. Furthermore, UF₆ is known to be severely reacting with water forming UO₂F₂, which is highly soluble in water (65.6 g/100 g of water at 25 °C) [2]. Often UF₆ is hydrolyzed to solid powder of UO₂F₂ in a fluidized bed process where the solid particles of the desired phase can accumulate on the bed of UO₂F₂, which can be transformed to oxide like U₃O₈ and UO₃. Presence of UO₂F₂ in larger quantities can
be deleterious to reduction of UF₄ to metal as it causes formation of uranium oxides which behave like ceramics having a high melting point. Though tetrafluoride of uranium (UF₄) is relatively inert with moisture containing atmosphere, it may form hydrated complexes like UF₄ₓH₂O and also complexes such as UF₄ₓ(OH)ₓ(n = 0 to 3). UF₄ can also oxidize to UO₂F₂ in strongly oxidizing atmosphere. In order to see the hydration behaviour of UF₆ in the UF₄ sample produced by the reduction of UF₆, it was reacted with water and, the soluble and insoluble parts of the reactions were separated and analyzed. The solution phase on drying crystallizes to a hydrated oxyfluoride phase as (UO₂F₂(H₂O))(H₂O)₀.₅₇. This hydrated oxyfluoride is relatively stable and is a non-hygroscopic intermediate product. The details of the experiments and results are presented herein.

**EXPERIMENTAL**

A simple experimental procedure as described below was followed in the reported study. A weighed quantity of UF₄ powder was taken in a Borosil flask, Flask-1 and, 100 ml of demineralised water (DM) was added into it. The solution was left idle for around 2 hours. Solid layer at the bottom surrounded by yellowish fluid in the flask was seen after 2 hours. Later, the supernatant fluid was decanted and transferred to another Borosil flask, Flask-2. This fluid was crystallized by heating at 100°C to leave behind yellowish solid particles labelled UOUF-1. Subsequently, another 100 ml of DM water was added to the residue in the Flask-1, kept for two hours and the above procedure was repeated to get UOUF-2 in Flask-3, which was found to be yellow with light shades of green in colour. Another round of addition of water followed by crystallization of the supernatant fluid in Flask-4 produced UOUF-3, which has light greenish yellow in colour. However, in the fourth step, when water was added into the residue and the supernatant fluid was heated in Flask-5, no crystals could be obtained and the flask was found to be free of any solid after the boil-off. Consequently, the residue in the Flask-1 at step-4 was dried out by heating to yield a dark green with a light yellowish shade solid labelled UOUF-4. The observed cumulative weight percentage of UOUF-1 to 3 with respect to UF₄ taken was less than 6%. The block diagram depicting the sequence of operation is shown in Figure 1.

![Figure-1: Block diagram of the experimental set-up](image)

The products UOUF-1 through UOUF-4 were characterized by powder XRD recorded at ambient temperature. The powder XRD studies were carried out by using CuKα x-ray source. The results are presented as follows:

**RESULTS AND DISCUSSIONS**
The products obtained after each hydrolysis steps were analyzed by powder XRD patterns for characterization of solid phase. The powder XRD patterns of some representative composition are shown in Figure 2. Formation of crystallize phase of hydrated UO$_2$F$_2$ is observed in all the samples. The reaction can be explained as UF$_6$ + H$_2$O $\rightarrow$ UO$_2$F$_2$, which dissolves in water in large excess ((64.4 g/100 g of water at 20 °C). The solution on drying leaves yellow products instead of UO$_2$F$_2$, but crystallizes as hydrated phase. The analyses of the XRD pattern of the product matches to the reported as (UO$_2$F$_2$ (H$_2$O)) (H$_2$O)$_{0.57}$ earlier reported by Mikhailov et al. [3]. The phase analyses details of the solid phases obtained after several experiential conditions are given in Table 1. The hydrated phase was earlier reported by reacting gaseous UF$_6$ to make a saturated solution and then by crystallization in ambient temperature. The complete powder XRD patterns of UOUF-1 and UOUF-2 could be assigned to this hydrated phase while the relative proportion of this phase decreases in the sample UOUF-3 and 4. Also the XRD patterns indicate that the oxyfluoride phase is similar in all the samples. The complete powder XRD pattern of UOUF-1 could be assigned to the crystal structure reported for the composition. The hydrated phase is decreased to a minor phase in the last round, suggesting that all the UF$_6$ phases are separated quite fast. Typical unit cell parameters observed for the phase observed in UOUF-1 sample are obtained by fitting the profile of the XRD pattern with reported structural parameters reported by Mikhailov et al. [3]. The refined unit cell parameters of the hydrated oxyfluoride phases in UOUF-1 sample are: a = 13.843(1), b = 9.793(1), c = 24.958(2) Å, $\beta$ = 104.277(2)$^\circ$, V= 3279.0(5) Å$^3$ and the calculated density from the unit cell volume and unit cell contents (number of formula units in unit cell, Z = 28) is 4.72 gm/cc. It is further observed that the crystallized hydrated oxyfluorides is non-hygroscopic and stable at ambient conditions. The experimental results also revealed no formation oxides and oxyfluorides of tetravalent uranium. In contrast, under similar experimental conditions can completely hydrolyze ThF$_4$ to thorium oxides through oxyfluorides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases</th>
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<tbody>
<tr>
<td>UOUF-1</td>
<td>(UO$_2$)$_2$F$_2$ (H$_2$O) (H$<em>2$O)$</em>{0.57}$, UO2F2 (major phase)</td>
</tr>
<tr>
<td>UOUF-2</td>
<td>(UO$_2$)$_2$F$_2$ (H$_2$O) (H$<em>2$O)$</em>{0.57}$, UF4. 2.5H2O (minor)</td>
</tr>
<tr>
<td>UOUF-3</td>
<td>(UO$_2$)$_2$F$_2$ (H$_2$O) (H$<em>2$O)$</em>{0.57}$, UF4. 2.5H2O (minor)</td>
</tr>
<tr>
<td>UOUF-4</td>
<td>(UO$_2$)$_2$F$_2$ (H$_2$O) (H$<em>2$O)$</em>{0.57}$ (minor), UF4.2.5H$_2$O (minor)</td>
</tr>
</tbody>
</table>

Table -1. Phases observed in the XRD patterns of the solid UOUF products.

![Figure -2. Powder XRD pattern of UOUF-1 sample fitted with structure of UO$_2$F$_2$(H$_2$O))(H$_2$O)$_{0.57}$ reported in ref 3.](image-url)
It can be mentioned here the structure of the $\text{UO}_2\text{F}_2(\text{H}_2\text{O}))((\text{H}_2\text{O})_{0.57}$ as reported in literature has two types of water molecules, namely about 0.5 $\text{H}_2\text{O}$ as coordinated water and 1 $\text{H}_2\text{O}$ as isolated water molecules occupying the empty spaces present in the structure. There are four crystallographically distinct $\text{U}^{6+}$ in the unit cell and all of them have typical pentagonal bipyramidal structure with a coordinated water molecule as a corner in pentagonal basal plane. The typical coordination around $\text{U}^{6+}$ can be mentioned as $\text{U}(\text{O})_2\text{F}_4(\text{H}_2\text{O})$ and they are connected by sharing the F atoms. This arrangement produces empty cavities which are occupied by the isolated water molecules. Typical crystal structure depicting the different water molecules and $\text{U}(\text{O})_2\text{F}_4(\text{H}_2\text{O})$ coordinated polyhedra is shown in Figure 3.

Figure 3. Typical crystal structure of $\text{UO}_2\text{F}_2(\text{H}_2\text{O}))((\text{H}_2\text{O})_{0.57}$. The $\text{U}(\text{O})_2\text{F}_4(\text{H}_2\text{O})$ units are shown as polyhedral unit and darkest spheres are for oxygen of water molecules.

CONCLUSIONS

This study suggests a simple technique to separate the trapped $\text{UF}_6$ from $\text{UF}_4$. The $\text{UO}_2\text{F}_2$ solution can be dehydrated to solid $\text{UO}_2\text{F}_2$ which can subsequently be converted to oxides of uranium on heating. Besides $\text{UO}_2\text{F}_2$, hydrated $\text{UF}_4$ phase is also seen in the hydrolyzed $\text{UF}_4$. Such methods may be used to determine the amounts and type of impurity present in solid $\text{UF}_4$. It can also be an alternate method for production of oxides of uranium other than ADU or ADC precipitation methods. This study also indicated an easier method to separate $\text{UF}_6$ from depleted or enriched $\text{UF}_4$ for further usage or storage.

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REFERENCES