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Hydration of uranium residues contained in enriched UF₆ cylinders

Mathieu Milin*	Julien Rannou*		
Lucile Viaulle*	Grégory Caplin*	Stéphane Evo*	

* IRSN (Institut de Radioprotection et de Sûreté Nucléaire), Fontenay-aux-Roses, France

Abstract

The transport of uranium hexafluoride (UF₆) is carried out in large steel cylinders. During filling and extraction operations, some air in-leakage in cylinders is possible and its moisture content results in the hydrolysis of UF₆ and the creation of non-volatile uranium residues, in particular UO_2F_2 complexes with H₂O and HF. This paper presents justifications for considering, in criticality safety assessments of enriched UF₆ transport cylinders, a bounding hydration ratio H/U of 6 for uranium residues, based on the operating conditions of UF₆ cylinders in fuel facilities.

Introduction

The packaging and transport of UF₆ are performed in accordance with the standards ISO 7195 [1] and ANSI N14.1 [2] which provide safety requirements. UF₆ is shipped in solid phase and is transformed in gas or liquid phase to be processed in nuclear facilities. The minimum purity of UF₆ has to be equal to 99.5 wt% according to the standards. All the remaining compounds (0.5 wt%) which are allowed in the content (for "product quality" concerns) are volatile compounds, such as the hydrofluoric acid gas (HF). However, during the use of UF₆ cylinders, non-volatile products may be created (the so-called residues), in particular uranyl fluoride compounds (UO₂F₂) which are one of the products of UF₆ hydrolysis.

Papers [3] to [5] show that taking into account uranium residues in UF₆ cylinders leads to an increase of reactivity and so to a diminution of the safety margin. The figure 1 of paper [5] shows the impact on reactivity of the presence of uranium residues for an infinite array in the 3 directions of 30" cylinder filled with UF₆ enriched at 5 wt% in ²³⁵U (with a total steel thickness - cylinder plus overpack - of 10 mm and optimum interstitial moderation between the cylinders). It can be observed that the consideration of a lower value of the moderation ratio H/U from 11⁽¹⁾ to 6 leads to a decrease of the impact of uranium residues on reactivity, from ~ 2 % to ~ 1 % for a residues mass of 11.4 kg (maximal mass of heels indicated in the standard ISO 7195 [1]) which provides margin from administrative criteria for transport or storage of full cylinders. The purpose of this paper is to justify,

¹ This value, considered in papers [3] to [5], corresponds to a very pessimistic hydration ratio of uranium residues (hydration of UO_2F_2 with 4 molecules of water and adsorption of 3 molecules of HF).

for criticality safety assessments of enriched UF_6 transport cylinders, this bounding hydration ratio H/U of 6 for uranium residues, based on the operating conditions of UF_6 cylinders in fuel facilities.

1. General information

1.1. Lifecycle and states of UF₆ cylinders

The different operations on UF_6 cylinder during its lifecycle are the following:

- 0. Manufacturing of the cylinder. After manufacturing and before its first use, the cylinder undergoes various tests and controls. At this state, the cylinder is referred as <u>"new"</u>.
- 1. First filling of UF₆. After the filling, the cylinder contains UF₆ in solid form (the cylinder is partially filled of UF₆) and non-volatile residues. At this state, the cylinder is referred as <u>"full"</u>.
- 2. First extraction of UF₆. This operation leads to extract the main amount of UF₆, but a heel, composed by the non-volatile residues and a residual amount of UF₆, remains in the cylinder. At this state, the cylinder is referred as <u>"empty"</u>.
- 3. First pumping of UF₆. The pumping (by vacuum emptying) leads to remove the residual amount of UF₆ in the cylinder. After this operation, only the non-volatile residues stay in the cylinder. At this state, the cylinder is referred as <u>"pumped"</u>.
- 4. Second filling of UF_6 . The cylinder is again <u>"full"</u>. This filling may occur on an "empty" cylinder.
- 5. Repetition of the lifecycle (extraction / pumping / filling) until the cleaning of the cylinder. The purpose of cleaning is, among other things, to remove all the residues. After these operations, the cylinder is referred as <u>"cleaned"</u> (or washed out).

Between each operation, the cylinder is transported and stored.

1.2. Nuclear criticality safety evaluation of enriched UF₆ cylinders

The nuclear criticality safety evaluation depends on the cylinder states:

- <u>New or cleaned cylinder:</u> there is no criticality risk, due to the absence of fissile material.
- <u>Empty or pumped cylinder</u>: the criticality risk comes from the presence of uranium residues (pumped cylinder) or uranium residues and residual amount of UF_6 (<u>"empty"</u> cylinder). The nuclear criticality safety is based on geometrical dimensions (diameter and length of cylinder, steel thickness) and on the heel or residues mass (assuming optimum moderation).
- <u>Full cylinder:</u> the criticality risk is mainly due to enriched UF₆. But, as demonstrated in papers [3] to [5], the presence of uranium residues leads to an increase of reactivity. The nuclear criticality safety is usually based on geometrical dimensions (diameter and length of cylinder, steel thickness), on a limited moderation of the content (both UF₆ and uranium residues) and a limitation of the uranium residues mass. For the moderation of the content, the practice in France is to model the HF (conservatively used for modelling the impurities in UF₆) homogeneously distributed in UF₆ (an heterogeneous distribution of HF in cylinder is considered unrealistic due to processes used) and, in recent studies, to consider a limited hydration of uranium residues.

It could be noted that these hypothesis for moderation of the content in function of the cylinder state are consistent with the IAEA regulation for the safe transport of radioactive material [6] for uranium enriched up to 5 wt% in ²³⁵U (paragraph 680(b)).

1.3. Characteristics of non-volatile residues

The residues, created during the whole lifecycle of the cylinder, are grease, slag, oxides, dirt and other foreign matters. Many of them are insoluble and non-volatile reaction products of uranium, like UF₅ (formed by the reaction between iron and UF₆), UF₄ (formed by the reaction $2 \text{ UF}_5 \rightarrow \text{ UF}_4 + \text{ UF}_6$) and uranyl fluoride solids (UO₂F₂) formed by hydrolysis reaction between UF₆ and moisture introduced by air in-leakage in the cylinder (UF₆ + 2H₂O \rightarrow UO₂F₂ + 4HF). Others of these residues are reaction products of iron, like FeF₂, FeF₃ and Fe₂O₃. However, the proportion of iron products in non-volatile residues and their impact on reactivity are not quantified. Thus, the presence of these products is not credited in criticality safety evaluations which is penalizing because of the neutron absorbing property of iron. Besides, from a nuclear criticality safety point of view, it is assumed that UO₂F₂ residues bound all others non-volatile reaction products of uranium (UF₅, UF₄), because of the existence of hydrated complexes (also called compounds) of UO₂F₂. Indeed, during and after its formation, UO₂F₂ may incorporate HF and may be hydrated. So, the main hydrolysis reaction of UF₆ in the conditions prevailing in a cylinder can be written as below:

 $UF_6 + (2+x) H_2O \rightarrow UO_2F_2 - xH_2O - yHF + (4-y) HF$ (1)

where x and y values depend on the cylinder state (full, <u>"empty"</u> or pumped) and on the operation (filling/extraction/pumping). The justification of bounding values for x and y is presented below.

2. Hydration ratio of uranium residues

2.1. Hydration during the lifecycle of a cylinder

First filling

During the first filling of a cylinder, UO_2F_2 complex could be created by hydrolysis of UF_6 due to the moisture content of the air already present in the cylinder before the filling, to air in-leakage during the operation process (the engagement (or accosting), the filling and the disengagement of the cylinder) and to the storage/transport of the full cylinder. This UO_2F_2 complex being created in excess of UF_6 , the following conclusions may be drawn from the review of past experiments:

- Regarding the formation of UO_2F_2 -xH₂O-yHF by the UF₆ hydrolysis:
 - Eduljee ([9]) studied the hydrolysis reaction of UF₆ in 4 situations. The complexes obtained are:
 UO₂F₂-2.4H₂O-0.4HF by hydrolysis of UF₆ with liquid water (but, this case is not representative of the filling process due to the presence of liquid water).
 - \circ UO₂F₂-1.5H₂O-0.4HF by hydrolysis of UF₆ with liquid/gaseous water (ratio UF₆/H₂O~1.4).
 - \circ UO₂F₂-0.6H₂O-0.3HF and UO₂F₂-0.66H₂O-0.2HF by hydrolysis of UF₆ with gaseous water (ratio UF₆/H₂O~3.75 at room temperature).

- \circ UO₂F₂-1.7H₂O-0.43HF by hydrolysis of UF₆ with gaseous water (ratio UF₆/H₂O~18; temperature = 0°C).
- From Brooks works ([8]), the mean composition of the complexes formed in excess of UF₆ and in presence of gaseous water is UO₂F₂-1H₂O (equimolar mixture of anhydrous UO₂F₂ and UO₂F₂-2H₂O). But, no information is given about the presence or absence of HF in this complex.
- Regarding the hydration of anhydrous UO_2F_2 : different experiments ([7], [8], [10] and [11]) show that anhydrous UO_2F_2 absorbs quickly and easily, even for low vapor pressure, a slight amount of water and can accept in his structure (without modifying it) up to ~ 0.6H₂O.
- Regarding the adsorption or the substitution of water by HF in hydrated UO₂F₂: from Neveu and Brooks works (respectively [10] and [8]), the action of HF in excess on UO₂F₂-2H₂O leads to the association of HF in the complex (respectively of 2 HF and 1.8 HF).

Due to the lack of detailed information about these experiments and due to the non-representativeness of these experiments with all the conditions encountered in the cylinder, it is not evident to conclude on the exact complex created during UF_6 hydrolysis. However, based on these experiments, the complex UO_2F_2 -1.5H₂O-2HF (H/U ratio of 5) may be retained as a bounding hydrated complex for the criticality safety evaluation of a full cylinder during and after its first filling.

First extraction

During the extraction process, the cylinder is heated (in order to transform UF_6 from the solid to the gaseous phase, possibly with a liquid phase). Such operation may "dehydrate" uranium residues created before this operation. In this situation, the following conclusions may be drawn:

- Regarding the loss of water from hydrated UO_2F_2 complexes:
 - The UKAEA report [11] shows that loss of water in complex UO₂F₂-1.5H₂O depends both on the temperature and the relative vapor pressure. But, even at high temperature, this reaction could be very slow, due to low dissociation vapor pressure of UO₂F₂-1.5H₂O to anhydrous UO₂F₂ (reported to be, for example, 21 mbar at 60°C).
 - From Morato works [7], made in air at atmospheric pressure, an UO₂F₂ hydrated complex around UO₂F₂-1.5H₂O is stable up to 70°C and begins to dehydrate at approximatively 90°C.
 - From Neveu works [10], UO₂F₂ is anhydrous for temperature higher than 100°C. Moreover, the exact temperature of dehydration of low hydrated UO₂F₂ complex (~2H₂O) depends strongly of the ambient hygrometry (for example, at 50 °C and 75°C, UO₂F₂ is anhydrous for relative humidity lower than respectively 18 % and 40 %).
- Regarding the loss of HF, no theoretical or experimental works on this subject are known.

Based on these experimental results, it is not possible to quantify the loss of water or HF in uranium residues due to the heating of the cylinder during the extraction. Consequently, without further data, the complex UO_2F_2 -1.5H₂O-2HF (H/U ratio of 5) should be kept for the criticality safety evaluation of a cylinder during and after the first extraction.

First pumping (vacuum emptying)

The moisture content in the air which penetrates in the <u>"empty"</u> cylinder before the pumping (storage/transport of <u>"empty"</u> cylinder and accosting of the cylinder) leads to hydrolyze the residual amount of UF_6 in the heel in the same conditions as during the extraction. So, it could be considered that others complexes in the penalizing form UO_2F_2 -1.5H₂O-2HF are created and are added to the non-volatile residues already present in the cylinder.

At the end of the pumping and after this operation (during storage/transport of pumped cylinder), UF_6 is no more in excess in the cylinder. In this case, the moisture content in the air in-leakage may directly hydrate UO_2F_2 complexes rather than hydrolyze UF_6 . In this case, based mainly on the UKAEA, Neveu and Morato works ([11], [10] and [7]), the following conclusions may be drawn:

- Regarding the hydration of UO₂F₂ complex:
 - All those studies show the presence of several UO₂F₂ hydrates which could be present at the same time: anhydrous UO₂F₂ which can accept up to 0.6H₂O, UO₂F₂-1.5H₂O, UO₂F₂-2H₂O, UO₂F₂-2.5H₂O, UO₂F₂-3H₂O, UO₂F₂-3.5H₂O, UO₂F₂-4H₂O...
 - At constant low partial water pressure, it seems that the complex has an amount of water around 1.5 to 2 H₂O. Moreover, when the studies conclude to a stable compound UO₂F₂-1.5H₂O, they mention the presence at the beginning of the hydration of the intermediate complex UO₂F₂-2H₂O and show a very slow reaction of dehydration.
 - At high partial water pressure (corresponding to a relative humidity higher than 80 % at atmospheric pressure), higher hydrates might be formed. From UKAEA works [11], the hydration of samples of 1 g and 0.1 g of anhydrous UO₂F₂ leads to the formation of intermediate trihydrate or tetrahydrate which tend, as final composition, to a stable compound (UO₂F₂-1.5H₂O) for the relative humidity prevailing in the cylinder (less than 90 %). Moreover, it could be noted that for thicker samples, a hydration bed is observed through the sample. Although during the initial period of hydration the surface of the bed may lead to high hydrate, the hydration would diffuse into the sample and the mean composition of the whole sample tends directly to the stable form UO₂F₂-1.5H₂O.
- Regarding the HF which may be associated with the hydrated UO₂F₂ (by adsorption or substitution with water):
 - From Eduljee works [9], after UF_6 hydrolysis, the complex UO_2F_2 -1.3H₂O is associated with 0.35HF.
 - From Neveu and Brooks works (respectively [10] and [8]), the action of HF in excess (at room temperature) on UO₂F₂-2H₂O leads to an adsorption respectively of 2HF and 1.8HF.
 - From Neveu works [10], the action of HF on UO₂F₂-2.5H₂O, UO₂F₂-3H₂O and UO₂F₂-4H₂O leads to the association in the complex respectively of 1.6 HF, 2.44HF and 2.8HF (but these last two complexes are unstable and dissociate quickly).

Based on very pessimistic considerations, the most hydrogenated uranium residues is formed by the hydration of 4 molecules of water and the adsorption of 3 molecules of HF. The chemical

composition of this complex is UO_2F_2 -4H₂O-3HF, corresponding to a hydration ratio H/U of 11 (this is the complex considered in papers [3] to [5]). But, the formation of such a complex in quantities having an impact on reactivity requires temperature, pressure and air moisture conditions that are not realistic compared to the conditions within pumped cylinders. So, in realistic conditions, complex with a hydration higher than 2 molecules of water is formed only superficially and during a transitory period and can't be present in quantities which have an impact on reactivity.

In conclusion, the stable hydrate of UO_2F_2 in usual conditions of pressure, temperature and air moisture (1 bar, 25°C and a relative humidity between 40 and 80 %) is UO_2F_2 -1.5H₂O, but the dihydrate UO_2F_2 -2H₂O could also be present. Considering the adsorption of HF, the bounding uranium complex is assumed to be UO_2F_2 -2H₂O-2HF, corresponding to a ratio H/U of 6.

Besides, it could be noted that this previous analysis does not consider the impact of the vacuum state of the cylinder during the pumping, in particular, an eventual "dehydration" of uranium residues under very low pressures. Indeed, a part of H_2O and HF from the complex UO_2F_2 -x H_2O -yHF might be freed due to equilibrium between these molecules in the complex and their partial pressure in the cylinder. In this situation, the following conclusions may be drawn:

- Regarding the loss of water from hydrated UO₂F₂ complexes:
 - From Neveu works [10], a dissociation of the complex UO₂F₂-2H₂O to anhydrous UO₂F₂ is observed at low partial water pressure (below 5 mbar of water at 25°C).
 - As said previously from Morato works [7], in air at atmospheric pressure, UO₂F₂-1.5H₂O begins to dehydrate at approximatively 90°C. But, the temperature of dehydration is lower (~ 60°C) for lower residual vapor pressure (observed for 2 experiments at 4 mbar and 0.01 mbar).
 - As said previously, from UKAEA report [11], the dissociation vapor pressure of UO₂F₂-1.5H₂O to anhydrous UO₂F₂ is small.
 - Brooks works [8] showed a dehydration of UO₂F₂-2H₂O at 19°C for a very low partial water pressure (~ 0.5 mbar).
- Regarding the loss of HF: from Neveu works [10], a dissociation of UO₂F₂-2H₂O-2HF to UO₂F₂-2H₂O-0.5HF is observed at low HF partial pressure (below 8.5 mbar of HF at 25°C).

However, these partial pressures of dissociation are relatively low and, except Neveu works, there is no other experimental study of "dehydration" of UO_2F_2 -xH₂O-yHF complex due to low pressure. So, it is not possible to conclude with certainty on the "dehydration" of uranium residues during the vacuum emptying.

In conclusion, without dedicated experimental studies, the bounding hydrated complex for the criticality safety evaluation of pumped cylinders is $UO_2F_2-2H_2O-2HF$ (H/U ratio of 6).

Second filling

The moisture content in the air in-leakage during the second filling and during the storage/transport of the full cylinder leads to the UF_6 hydrolysis in the same conditions as during the first filling. So, it

could be considered that complexes in the penalizing form UO_2F_2 -1.5H₂O-2HF are created. These new uranium residues are added to the non-volatile residues already present in the cylinder (with a different composition because these old complexes might be more hydrated, according to the previous paragraph). In this case, on penalizing consideration, the composition of uranium residues in criticality safety assessment should be UO_2F_2 -2H₂O-2HF (H/U=6), because:

- It is difficult to establish a distinction between new uranium residues and old residues.
- During the filling, the cylinder is put at low temperatures (around 5° C when UF₆ is in liquid form and -25° C when UF₆ is in gaseous form), which does not privilege the release of hydrogen (H₂O or HF) from uranium residues.
- Although the action of UF_6 on hydrated UO_2F_2 complexes probably leads to dehydrate those complexes, there is no experimental study dealing with this question. It could be noted that old uranium residues are in equilibrium with a partial water pressure (in the millibar order according to different works) in pumped cylinders. Thus, the filling of UF_6 in the cylinder leads to consume the vapor water (moisture form air) present in the cylinder (decrease of the residual vapor pressure) which might lead to dehydrate UO_2F_2 . But, the kinetic of the dehydration reaction and the absence of equilibrium between UF_6 , HF, H₂O and hydrated UO_2F_2 are not established. This question is probably the best way to challenge the proposed bounding complex composition.

Repetition of the cylinder lifecycle

During the following lifecycle extraction/pumping/filling, the creation of uranium residues follows the same principles:

- UO₂F₂-1.5H₂O-2HF are created during air in-leakage in presence of UF₆ and are added to non-volatile residues already presents and potentially more hydrated (UO₂F₂-2H₂O-2HF).
- Uranium residues in pumped cylinder might be hydrated due to air in-leakage (moisture in air). In this case, the envelop composition of uranium residues is UO₂F₂-2H₂O-2HF.

Consequently, a bounding composition of uranium residues in criticality safety assessment could be $UO_2F_2-2H_2O-2HF$ (H/U=6).

2.2. Hydration during Accidental Immersion of a Cylinder

The immersion of a cylinder is required by international IAEA regulation [6] for accidental condition. Only the criticality safety evaluation of a full cylinder is impacted by water in-leakage during immersion of cylinders (since <u>"empty"</u> or pumped cylinders are evaluated at the optimal moderation conditions). As seen on Eduljee works (cf. paragraph 2.1), the compound created after UF₆ hydrolysis with liquid water could be more hydrated than those considered created during the filling. But, for 30" cylinder surrounded by an overpack, the ingress of water in the cylinder during the immersion test is limited (around hundreds of grams considering the leakage rate of the cylinder and one week of immersion) and is in vapor phase due to the conditions in the cylinder. Moreover, Mallet and Barber works (respectively [12] and [13]) show that an ingress of liquid water by small entries (for example an untightness of the valve) lead, after hydrolysis reaction, to the formation of a plug

which slow (or stop) the ingress of water inside the cylinder. UF₆ hydrolysis and hydration reactions could be considered identical (UF₆ is still in excess compared to water) to those occurring during the filling of the cylinder (creation of a UO_2F_2 -1.5H₂O-2HF complex). So, the proposed bounding composition of uranium residues (UO₂F₂-2H₂O-2HF) is not challenged in case of the accidental immersion of a full cylinder.

Besides, gaseous HF is released from UF_6 hydrolysis. But, this amount of HF is very limited and so has limited impact on reactivity of the full cylinder.

IRSN requires for the transport of full 30" cylinders to consider the mass of heel indicated in the ISO 7195 [1] standard (i.e. 11.4 kg of heel) and additional uranium residues created due to water ingress during immersion. Indeed, before the transport, the mass of non-volatile residues should respect the standards ISO 7195 [1]. So, water ingress during the immersion leads to increase this mass of uranium residues to be considered in criticality safety assessment. The mass of uranium residues ($UO_2F_2-2H_2O-2HF$) created, estimated from the equation (1) with x = 2 and y = 2, is presented in the Table 1.

	Ingress water mass (g)				
	100	300	500	700	1000
Additional uranium residues (g)	533	1598	2664	3730	5328

Table 1 mass of uranium residues created due to water ingress

From figure 1 of paper [5], considering the bounding composition of uranium residues $(UO_2F_2-2H_2O-2HF)$, it could be noted that for mass of uranium residues higher than 15 kg, the impact on reactivity of uranium residues is important (> 2 %). During an immersion of a cylinder consecutive to an accident of transport, such a mass of residues could be obtained with an ingress of 700 g of water (considering that the initial mass of uranium residues is 11.4 kg).

Conclusions

During the whole lifecycle of an UF₆ cylinder (filling, extraction and pumping operations and during storage/transport periods), some air in-leakage are possible and its moisture content results in the hydrolysis of UF₆ and the creation of non-volatile uranium residues, in particular UO₂F₂ complexes including H₂O and HF. Based on literature results concerning hydration of UO₂F₂ after UF₆ hydrolysis and adsorption of HF within these residues and according to operating conditions during the whole lifecycle of a cylinder, a bounding hydration of uranium residues H/U ratio of 6 could be accepted for criticality safety assessment, corresponding to the composition (UO₂F₂-2H₂O-2HF). But, it could be noted that several considerations to justify this bounding hydration ratio were driven by the lack of experimental results (for example, no experimental evidence of the action of UF₆ on hydrated UO₂F₂ during the fillings of a cylinder).

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