Chemical Reactions of UF$_6$ With Water on Ingress to Damaged Model 48X 10-Ton Cylinder*

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INTRODUCTION

Chemistry studies of the effects of water flooding in Model 48X 10-ton UF$_6$ storage cylinders, as a result of impact fractures, were conducted to support the Safety Analysis Report for Packaging (SARP) review of the Paducah Tiger Overpack for transportation of those cylinders. The objectives of the study were to determine the maximum amount of water that could be admitted to the interior of such a damaged cylinder, the resulting geometries and chemical compositions from reactions of water with the UF$_6$ contents of the cylinder, and the end-state water moderated and reflected configurations for input to nuclear criticality safety analyses.

The case identified for analysis was the flooding of the inside of a cylinder, submerged horizontally in 3 ft of water. The flooding was driven by an initial pressure drop of 13 psig, through an assumed fracture (1/32 in wide x 1/2 in deep x 18 in long) in the barrel of the cylinder. During the initial addition of water, transient back pressures occur from the effects of the heats of reaction and solution at the water/UF$_6$ interface, with some chugging as more water is added to alternately cool the reaction surface and then heat it again as the added water reacts with more UF$_6$.

As the system cools, the process is terminated by compression of the noncondensable gases when the ullage volume (initially 1.21 x 10^3 L at an assumed pressure of 3 psia) is reduced by a factor of 5. It was determined that the final configuration in the flooded cylinder was a 1.07 x 10^3 L aqueous-phase blanket over a 1.77 x 10^3 L bed of undissolved UF$_6$. The rest of the space in the cylinder consisted of a 2.4 x 10^2 L ullage volume, which was originally 1.21 x 10^3 L before the hypothetical flooding event.

The conservative upper limit to the (room-temperature) uranium concentration in the aqueous phase was determined to be 330 g/L, at HF and H$_2$O mole fractions of 0.18 and 0.79, respectively. Density of that aqueous phase was determined to be 1.237 kg/L. These results have not yet been analyzed for their impact on the k-effective of the configuration.

POSSIBLE MODES OF WATER ENTRY INTO UF$_6$ STORAGE CYLINDER

Three entry modes of water vapor or liquid to the UF$_6$ storage cylinder of the overpack have been identified:

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(1) Entry of moist air from the ambient atmosphere outside the overpack, through an impact fracture of the cylinder wall, into the (lower-pressure) solid UF_6 below the gas/solid interface in the cylinder;

(2) Entry of moist ambient air, through an impact fracture at a higher elevation, to the (partial vacuum in the) ullage above the UF_6, and

(3) Flooding of the inside of the submerged cylinder with liquid water through an impact fracture to the ullage above the UF_6.

Entry Mode 1

The scenario for further corrosion and entry of moist air at the breach of a UF_6 storage cylinder by Entry Mode 1 was investigated by Barber [1992]. Post-mortem inspections of two depleted-UF_6 storage cylinders that were damaged at the Portsmouth Gaseous Diffusion Plant showed that both holes were in the barrel section of the cylinders, very close to a stiffening ring welded to the circumference of the cylinder and below the gas/solid interface of the UF_6 in the cylinder. The hole size increased because of corrosion of the steel by reduction of the reaction products, which consisted of solid products containing various proportions of the basic constituents (UO_3, HF and H_2O). However, those products formed a plug that reduced the effective opening for entry of the ambient atmosphere. As the hole became plugged, the various acidic oxides that were formed limited the rate of further attack by limiting the rates of diffusion of HF and H_2O vapors across the diminished hole size and/or the oxide barrier. The process is slow, requiring $\approx$10-15 years, and because the reaction products contained limited hydrogen, it is assumed that there is little concern about criticality inside the cylinder.

Entry Mode 2

The potential for criticality from Entry Mode 2 is comparable to or lower than that for Entry Mode 1. It is anticipated that even though an oxide plug might not be formed at the damage site, a protective acidic oxide coating would be formed over the UF_6 surfaces within the cylinder. The reaction rate would then be limited by the rates of (a) diffusion of water vapor, at its nominal ambient saturation pressure ($\approx$25 torr), through the protective oxide coating; (b) diffusion of water vapor inside the cylinder to the reaction surface where it is depleted by reaction with the UF_6 solid; and (c) diffusion of the HF reaction product through the coating and away from the reaction surface. Only a very small quantity of moist air would be necessary to bring the partial vacuum within the cylinder to atmospheric pressure. Consequently, this process should produce noncritical configurations.

Entry Mode 3

A more serious concern is the accidental flooding of the storage cylinder, as in an hypothetical shipping accident. The purpose of this paper was to investigate that type of accident. The case identified for analysis was the flooding (driven by an initial pressure drop of 13 psig) of the inside of a cylinder, submerged horizontally in 3 ft of water, through an assumed fracture (1/32 in wide x 1/2 in deep x 18 in long) in the barrel of the cylinder. To analyze for the worst flooding conditions, it was assumed first that the barrel fracture was located at the top of the circumference of the submerged cylinder. Second, it was assumed that there is a simple gas/solid interface, with no adsorbed UF_6 in the ullage inside the top barrel of the cylinder, that could form plugs from reactions of UF_6 and the water. Others [Mallett 1967; Wangler 1994] have reported observations of such a simple gas/solid interface for water immersion tests of UF_6 cylinders. That condition provides for the most rapid flooding of the interior of the cylinder, as well as the most rapid reaction of its UF_6 contents with the entering water. Third, chemical reaction of UF_6 with the entering water was assumed to be instantaneous.

MODEL FOR WATER ENTRY AND CHEMICAL REACTION IN UF_6 CYLINDER

From its system specifications [ORO-65.1 1987], the main characteristics of the storage cylinder and its contents are:

Maximum UF_6 shipping limit: 21030 lb
Room-temperature UF_6 density: 317.8 lb/ft^3
Maximum U-235 enrichment: 4.5 wt. %

Inside diameter: 47 in, or 3.917 ft
UF$_6$ volume: 66.17 ft^3
Ullage volume: 42.73 ft^3
L(eff): 9.04 ft

L(eff) is the equivalent length of a right circular cylinder representation of the storage vessel. This is an approximation for the geometric model discussed in the next section, even though it is recognized that the cylinder is rounded at the top and bottom. With this length-to-diameter ratio, it is assumed that the cylinder will fall on its side if dropped in standing water.

Physical Chemistry Model for Water Flooding of UF$_6$ Cylinder

The scaled cross-section view of the base of the up-ended cylinder is given in Figure 1, with display of those base areas in the ullage and solid volumes. In the figure, a fracture at the top barrel of the upended cylinder, for unimpeded entry of water, and a small reaction zone, or pool depth, h, resulting from early water flooding of the UF$_6$, are also shown. The radius, r, of the cylinder is 23.5 in, or 1.96 ft. Prior to water entry, the chord length, C, for the upper surface of the UF$_6$ is 46.3 in, or 3.86 ft; and is at a distance, d, 4.0 in. above the midplane of the upended cylinder. This distance decreases slightly during the flooding due to the loss of UF$_6$ by dissolution in the reaction zone. For the early flooding, it follows that the (bulk) UF$_6$ surface area, A(solid), exposed to water entering the reaction zone would be given by

$$A(\text{solid}) = L(\text{eff}) \times C = 9.04 \times 3.86 \text{ ft}^2 = 34.89 \text{ ft}^2.$$

Of course, the actual surface area of that porous solid could be much greater during its reaction with the incoming water. Assuming no back-pressure effects from chemical reactions, Oras [1993] determined an initial water delivery rate of 0.139 ft^3/s to a cylinder submerged in 3 ft of water through an assumed fracture (1/32 in wide x 1/2 in deep x 18 in long) of the barrel of the cylinder. The initial driving force for the flooding was a pressure drop of 13 psig through the fracture to an assumed initial pressure of 3 psia inside the cylinder. Figure 1 displays a pool depth when about 25% of the initial 42.7 ft^3 ullage volume of the cylinder is occupied by the reaction zone. Neglecting the small 1-2% loss in UF$_6$ from the dissolution, the depth, h, of the pool or reaction zone (drawn to scale in Figure 2) would be 3.7 in at the end of that time period.

Under those conditions, water flow into the cylinder would be turbulent. The agitation of the solid UF$_6$ would prevent the early formation of protective surface coatings and would be vigorous. Fine breakup of the solid is anticipated with very good mixing and an instantaneous reaction with dissolution of the reaction products. The heat of reaction, i.e., the heat released as UF$_6$ reacts to form ionized UO$_2$F$_2$ in aqueous solution, is highly exothermic (50.5 kcal per gram-mole of UF$_6$). Therefore, the temperature of the UF$_6$ and water reactants could be heated locally to build up the sublimation pressure of UF$_6$ and vapor pressure of water, provide further agitation by the surface flashing of vapors, and slow the incoming flow of water as the heat is dissipated and the system is cooled to repeat the cycle of water reentry and expulsion again, i.e., a chugging flow. The chugging would be dampened by the buildup of a water-solution layer between the incoming liquid and the unreacted solid UF$_6$. As a result, the reaction zone should become very hot until the heat is lost to the (more thermally conducting) UF$_6$ solid as the pool height increases with entry of more water. Because the aqueous volume (of dissolved UF$_6$ in water) formed in the system is greater than the loss in volume of the dissolved UF$_6$, there is a progressive decrease in ullage volume as the cylinder is flooded. When the steady-state ullage volume (i.e., with the system cooled to room temperature) is reduced by 80%, the compression ratio of the noncondensable gases present in the cylinder would be 5. At an assumed initial pressure of ≈3 psia for the noncondensable gases, that effect alone would yield a final pressure of 15 psia. Therefore it is assumed that, at that point, the flow of liquid would be stopped (this assumption takes no credit for such factors as the back pressure from vaporization of the incoming water by its reaction with UF$_6$, or the thermal expansion of the reacting liquid).

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No credit could be taken for the release of HF from the reaction zone, particularly when the system has cooled to room temperature, to yield additional back pressure to shut off the flow of the incoming water any sooner. Pure HF is a liquid with a boiling point of $\approx 19°C$. Therefore, in aqueous solution at room temperature, and at the calculated upper limit mole-fraction of 0.12, HF would have a partial pressure of only 0.12 atm if it formed an ideal solution. Information on its dissociation and Henry's law constants in water suggests that it would not, and that its partial pressure would be much lower. Furthermore, due to this affinity between HF and water, with minimal losses of HF to the ullage, discussions in the remainder of this paper will show that the large excess of HF in solution from the hydrolytic dissolution of UF_6 would greatly limit the solubility of uranium in the resulting solution.

ANALYTICAL APPROACH

The analytical approach was to, first determine from the UO_3-HF-H_2O phase diagram the physical phases present and their compositions (in mole fractions of UO_3, HF, and H_2O) as water is added stepwise to the contents of the cylinder to yield progressively higher H_2O/UF_6 ratios; and second, determine the maximum concentration of uranium in the aqueous phase from known solubility data. The analytical approach was applied to the steady-state condition, with the system cooled to a nominal room temperature comparable to that for the reported phase equilibria and uranium solubility data used in the analysis. Also, the analysis determined the density of the aqueous phase and the configuration of solid, aqueous, and gas phases in the cylinder for consideration in nuclear criticality analyses.

Chemistry of UO_3-HF-H_2O System

The map, or phase diagram, of physical and chemical states for the UO_3-HF-H_2O system at 20°C was determined by Buslaev [1963]. The solubility of uranium in aqueous solution, as a function of HF concentration, is given by Martin Marietta [1992]. The UO_3-HF-H_2O phase diagram is displayed in Figure 2. Those three constituents represent the minimum number required to specify the chemical system completely at a given temperature and pressure and may be mixed freely to give any composition (and the corresponding physical and chemical phases) indicated in the diagram. Two subsets of this system that determine the range of compositions are those arrived at by mixing either UO_2F_2, H_2O, and HF, or UF_6 and H_2O. For the first subset, in mixing just UO_2F_2 and H_2O, the uranium solubility according to Figure 3 is very high (1,240 g/L). If excess HF is added, Figure 3 indicates a progressive dropoff in solubility. The compositions of those solutions saturated in UO_2F_2 are indicated in Figure 2.

For the highest solubility of UO_2F_2 (see Point A in Figure 2), the phase diagram indicates that the solid in equilibrium with the solution has the composition of $2HF \cdot 2UO_3 \cdot H_2O$, with the chemical structure $UO_2F_2 \cdot UO_2(OH)_2 \cdot H_2O$. This information suggests that pure UO_2F_2 hydrolyzes as it dissolves according to the equilibrium

$$UO_2F_2(solid) + H_2O(liquid) \rightleftharpoons UO_2^{++}(aq) + F^-(aq) + OH^-(aq) + HF(aq). \tag{1}$$
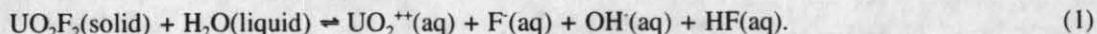
Also, the solutions formed from this hydrolysis are saturated with respect to solids (or solid solutions) composed of $UO_2(OH)_2 \cdot H_2O$ and the basic salt $UO_2F_2 \cdot UO_2(OH)_2 \cdot H_2O$. Figure 2 gives the composition, at Point A, of the solution in equilibrium with the basic salt, which agrees with the composition of a solution saturated in UO_2F_2 given by Katz [1961]. In addition, HF is weakly ionized in aqueous solution according to the equilibrium

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq). \tag{2}$$

In aqueous solutions with more acidic pH, the predominant mode of dissociation is

$$2\,HF(aq) \rightleftharpoons H^+ + HF_2^-. \tag{3}$$

According to Eqs. 1, 2, and 3, the complex equilibria with UO_2F_2 and its basic salt are pH sensitive; any addition of water would cause more dissolution of uranium, and the addition of OH^- or F^- ions would precipitate it. Therefore, due to production of 6 moles of HF from hydrolysis of each mole of UF_6 in water, the solubility of UF_6 is much lower than that of pure UO_2F_2.

Addition of Limited Amounts of Water to UF_6

Initially, with very limited sources of water, such as water vapor at a low partial pressure, the stepwise addition of water to UF_6 proceeds first according to the key-initiation equation

$$UF_6(solid) + 3 H_2O(vapor) \rightleftharpoons UO_3(solid) + 6 HF, \tag{4}$$
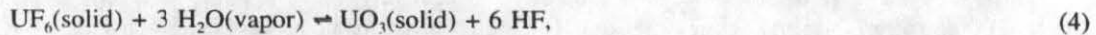
where, depending on the temperature and total pressure of the system, the highly volatile HF could be vapor, liquid, or both. For this addition, the phases present are solid UO_3 and pure HF as indicated at Point B on the right (UO_3-HF) side of the phase diagram of Figure 2. The right-hand side of Eq. 4 gives an HF-to-UO_3 molar ratio of 6 for that point, which corresponds to its composition shown in Figure 2, namely:

Mole Fraction of UO_3 = $N(UO_3)$ = $1/(1 + 6)$ = 0.14,
Mole Fraction of HF = $N(HF)$ = $6/(1 + 6)$ = 0.86.

With successive water vapor additions, the composition will follow the broken line in the phase diagram that represents compositions with an HF-to-UO_3 ratio of 6. As more water is added, the following reaction occurs:

$$6 HF + UO_3(solid) + 3 H_2O(vapor) \rightleftharpoons 4HF \cdot UO_3 \cdot 3H_2O(solid) + 2 HF. \tag{5}$$
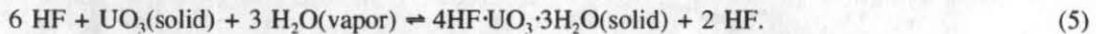
The composition is then calculated to be

$N(UO_3)$ = $1/(6 + 1 + 3)$ = 0.1,
$N(HF)$ = $6/10$ = 0.6, and
$N(H_2O)$ = $3/10$ = 0.3.

This corresponds to that composition at the intersection of the 6:1 ratio broken line with the phase-boundary line of the complex solid ($4HF \cdot UO_3 \cdot 3H_2O$) on the HF-rich side of the diagram. At that point, the phase diagram indicates HF in equilibrium with or dissolved in $4HF \cdot UO_3 \cdot 3H_2O$ (see Point C in Figure 2). The solid is one of the main constituents reported by Barber [1992], who indicated that a significant part of the reaction products from the reaction of UF_6 with moist air was a yellow deposit consisting of a 50:50 mixture of UO_2F_2 and $4HF \cdot UO_3 \cdot 3H_2O$. These were not the only products; but a clear assessment of all the reaction products could not be obtained from his report.

## Aqueous Uranium Solutions with Water Flooding of UF_6 Cylinders

Mallett [1967] identified a solid UO_2F_2 reaction product, but no $4HF \cdot UO_3 \cdot 3H_2O$ product, in water immersion tests of cylinders containing UF_6. Therefore, very rapid additions of liquid water to the UF_6 under the hydraulic pressure head assumed for this analysis eventually could lead to the composition UO_3, 6HF, $27H_2O$, at Point D in Fig. 2, for which

$N(UO_3)$ = $1/(1 + 6 + 27)$ = 0.03,
$N(HF)$ = $6/34$ = 0.18, and
$N(H_2O)$ = $27/34$ = 0.79.

That composition yields a point on the UO_2F_2 saturation line of the phase diagram of Figure 2, which would be in equilibrium with (solid) $UO_2F_2 \cdot 2H_2O$ at room temperature, after cooling of the hot reaction

zone. The basic (UO_3, H_2O, HF) coordinates of the liquid could be expressed as the actual solution components through the chemical identity relation

$$UO_3 + 6 \, HF + 27 \, H_2O = (UO_2)^{++} + 2 \, F^- + 4 \, HF(aq) + 28 \, H_2O(liq). \tag{6}$$
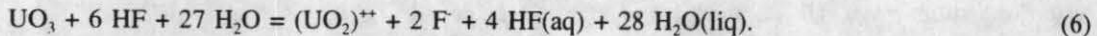
From Figure 3, the uranium concentration corresponding to an HF mole-fraction of 0.18 is 330 g/L (as uranium). The corresponding uranium molarity would be 330/238.07, or 1.386 M, which would also be the molarity of the UO_2F_2 on the right side of Eq. 6. The corresponding respective HF and H_2O molarities would be 4 x 1.386 (or 5.54 M) and 28 x 1.386 (or 38.8 M). With gram-molecular weights of 308.07, 20.01, and 18.02 for UO_2F_2, HF, and H_2O, respectively, this yields the following saturated solution composition in terms of mass per unit volume required for neutron physics analysis:

<u>U</u>: 330 g/L, present as 427 g/L of UO_2F_2,
<u>HF</u>: 111 g/L, and
<u>H_2O</u>: 699 g/L.

While the mole-fraction of HF expressed in UO_3-HF-H_2O coordinates is 0.18, it is 0.12 of the actual solution components. The density of this saturated solution, ρ, is then given by

$$\rho = (0.427 + 0.111 + 0.699) \text{ kg/L} = 1.237 \text{ kg/L}. \tag{7}$$

The slightly higher uranium solubility (330 g/L from UO_2F_2) at the reference composition given above for very rapid flooding of UF_6 with water, rather than the 270 g/L solubility given for the addition of UF_6 to water [Martin Marietta 1992], or the 267 g/L limit observed by Mallett [1967], indicates a complex equilibrium condition. The basic chemical reaction, or the hydrolysis, from the addition of UF_6 to water would be

$$UF_6(solid) + 3 \, H_2O(liq) \rightleftharpoons UO_2^{++}(aq) + 2 \, F^-(aq) + 4 \, HF(aq) \tag{8}$$

and the heat of hydrolysis would be 50.5 kcal per mole of UF_6. The concentration of uranium in solution would be limited to 270 g/L, present as 349 g/L of UO_2F_2, if there were excess UF_6 present in the reaction zone, since the 270 g/L solubility depends upon equilibrium (or intimate contact) between the undissolved UF_6 and the aqueous phase in the reaction zone. But there is also some conversion of the solid UF_6 to UO_2F_2 through the equilibrium

$$UF_6(solid) + 2 \, H_2O(liq) \rightleftharpoons UO_2F_2(solid) + 4 \, HF(aq). \tag{9}$$
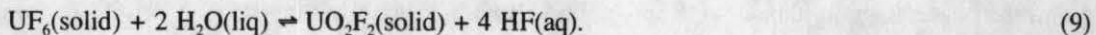
The slightly higher 330 g/L uranium solubility from UO_2F_2 at the reference composition given above for the addition of water to UF_6, rather than the 270 g/L value for the addition of UF_6 to water, suggests that the free-energy change for the above conversion is small. Assuming conservatively that as the flooded system is cooled, the aqueous solution is in equilibrium with excess UO_2F_2 that is precipitated in the cooling process and that coats the underlying bed of undissolved UF_6, then the mixing would yield the slightly higher 330 g/L uranium solubility given above. Such insoluble UO_2F_2 coatings of UF_6 were observed experimentally by Mallett [1967].

FINAL RESULTS FOR H_2O-FLOODED UF_6 STORAGE CYLINDER

Table 1 gives the initial and final volumes of the material phases for neutron physics criticality analysis in the water flooding case given above. The detailed composition for the aqueous phase is that given in the previous section of this paper for the uranium concentration of 330 g/L.

As indicated in the table, addition of water is terminated when the volume of rather low density (1.237 kg/L) aqueous UF_6 solution (formed by the flooding and chemical reactions) exceeds the volume of the higher density UF_6 (5.091 kg/L) lost in its dissolution sufficiently to reduce the (gas) ullage

volume by a factor of 5. At that point, the volume of aqueous-phase blanket over the bottom UF_6 bed was calculated to be 1.07×10^3 L, or 37.8 ft³. Referring to Figure 1, due to the dissolution of UF_6 into the aqueous phase, there would be shrinkage in the volume of the UF_6 phase, with the result that the chord length, C, for the top surface of the UF_6, and its distance, d, from the midplane of the upended cylinder, would be 46.7 and 2.8 in., respectively. The length of the chord for the top surface of the aqueous pool and depth of that pool would be 31.8 and 14.5 in, respectively.

**Table 1. Volumes of Initial and Final Material Phases in Flooding of UF_6 Storage Cylinder**

Time	Bottom UF_6 Bed Volume (L)	Aqueous Blanket Volume (L)	Ullage Volume (L)
Start of flooding	1.87×10^3	0.0	1.21×10^3
End of flooding	1.77×10^3	1.07×10^3	2.4×10^2

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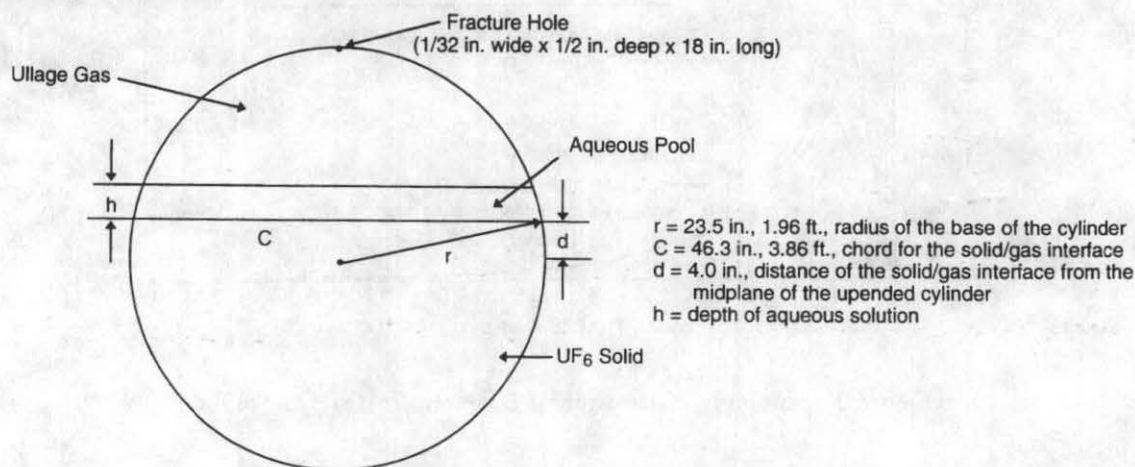
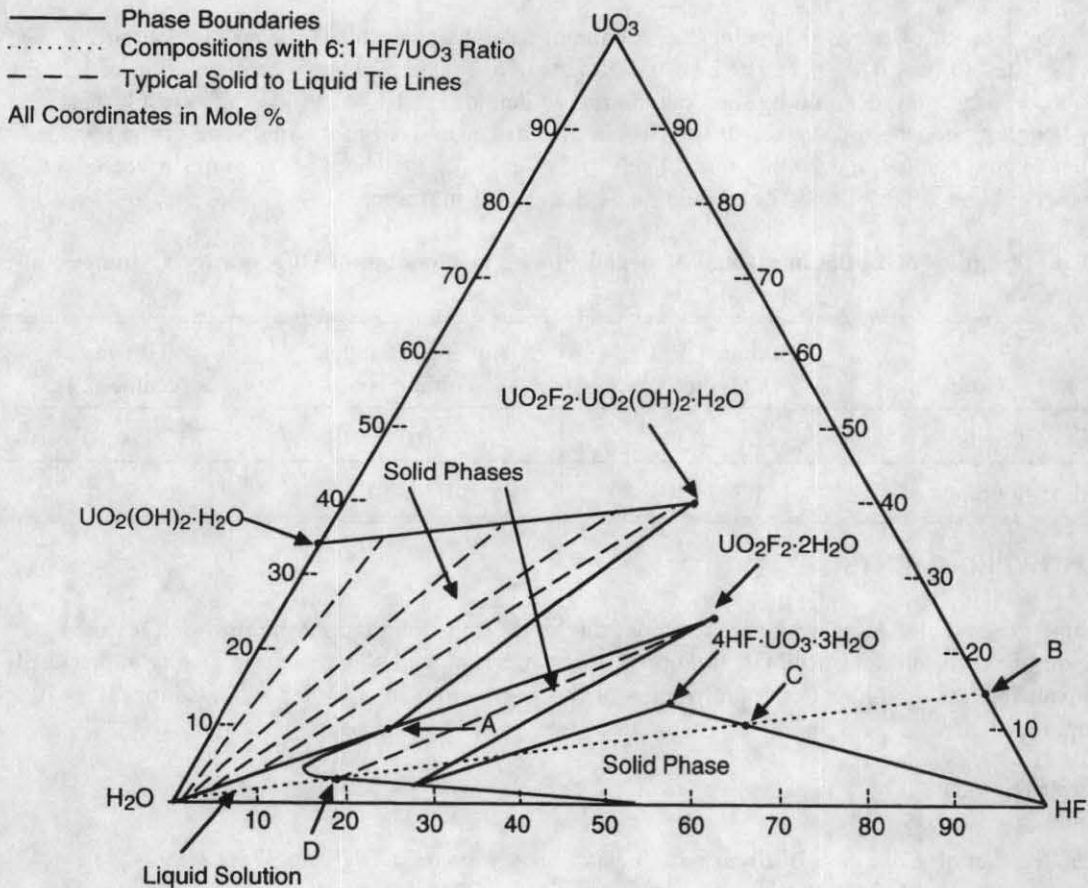Figure 1. Scaled Cross-Sectional View of Upended Cylinder

Figure 2. Phase Diagram of UO₃-HF-H₂O System

Legend shown on figure:
— Phase Boundaries
········· Compositions with 6:1 HF/UO₃ Ratio
– – – Typical Solid to Liquid Tie Lines
All Coordinates in Mole %

Labels on figure: UO₃, UO₂F₂·UO₂(OH)₂·H₂O, Solid Phases, UO₂(OH)₂·H₂O, UO₂F₂·2H₂O, 4HF·UO₃·3H₂O, A, B, C, D, Solid Phase, Liquid Solution, H₂O, HF
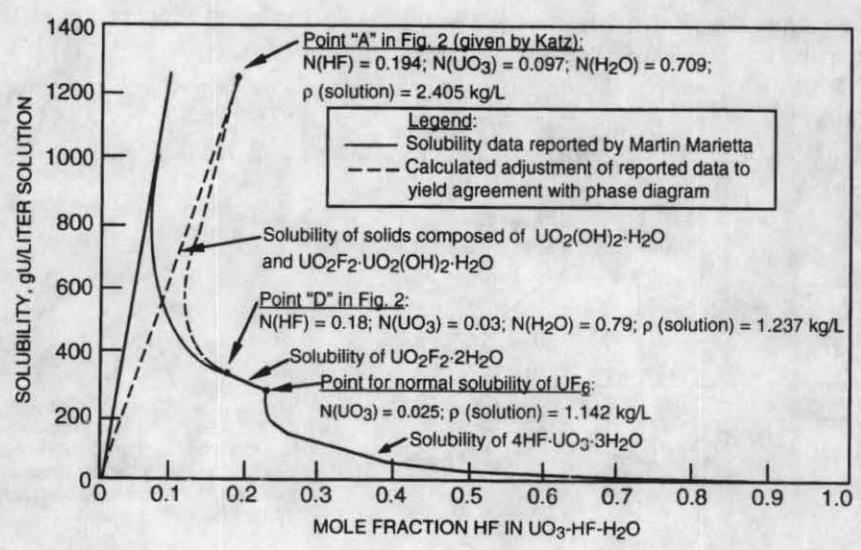

Figure 3. Solubility of Hexavalent Uranium in HF-H₂O Solutions

Labels on figure:
Point "A" in Fig. 2 (given by Katz):
N(HF) = 0.194; N(UO₃) = 0.097; N(H₂O) = 0.709;
ρ (solution) = 2.405 kg/L

Legend:
—— Solubility data reported by Martin Marietta
– – – Calculated adjustment of reported data to yield agreement with phase diagram

Solubility of solids composed of UO₂(OH)₂·H₂O and UO₂F₂·UO₂(OH)₂·H₂O

Point "D" in Fig. 2:
N(HF) = 0.18; N(UO₃) = 0.03; N(H₂O) = 0.79; ρ (solution) = 1.237 kg/L

Solubility of UO₂F₂·2H₂O

Point for normal solubility of UF₆:
N(UO₃) = 0.025; ρ (solution) = 1.142 kg/L

Solubility of 4HF·UO₃·3H₂O

Y-axis: SOLUBILITY, gU/LITER SOLUTION
X-axis: MOLE FRACTION HF IN UO₃-HF-H₂O