CORROSION OF BREACHED UF_6 STORAGE CYLINDERS

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ABSTRACT

This paper describes the corrosion processes that occurred following the mechanical failure of two steel 14-ton storage cylinders containing depleted UF_6. The failures both were traced to small mechanical tears that occurred during stacking of the cylinders. Although subsequent corrosion processes greatly extended the openings in the wall, the reaction products formed were quite protective and prevented any significant environmental insult or loss of uranium. The relative sizes of the two holes correlated with the relative exposure times that had elapsed from the time of stacking. From the sizes and geometries of the two holes, together with analyses of the reaction products, it was possible to determine the chemical reactions that controlled the corrosion process and to develop a scenario for predicting the rate of hydrolysis of UF_6, the loss rate of HF, and chemical attack of a breached UF_6 storage cylinder.

INTRODUCTION

Depleted UF_6 produced at the uranium enrichment gaseous diffusion plants has been stored in steel cylinders since the plants first went into production 40 years ago. As the number of cylinders became significant, each of the plants created outdoor storage yards as long-term depleted UF_6 repositories. These yards consist of concrete or compacted gravel storage pads, with lower cylinders positioned on wooden or concrete saddles, and a second level of cylinders supported by the lower level. In June 1990, during inspections at Portsmouth, Ohio, two steel cylinders, each containing 14 tons (12,730 kg) of depleted UF_6, were discovered with holes in the barrel section of the cylinders. The holes in both cylinders were very close to a stiffening ring welded to the circumference of the cylinder and were below the gas-solid interface of the UF_6 in the cylinder.

In each case the holes had formed directly opposite lifting lugs that extended outward from an adjacent cylinder. The larger of the holes was located in a top-row cylinder that had been in storage for 13 years, while the smaller hole was in a bottom-row cylinder stored for 4 years. An investigating team[1] concluded that the initial failures of both cylinders had been caused by mechanical impact from an opposing lifting lug on an adjacent cylinder. Because of the restraint of the stiffening rings, the impacts resulted in small tears in the cylinder wall, which then were greatly extended because of corrosion induced by UF_6 hydrolysis. A discussion of the mechanism and causes leading to the failures is presented elsewhere.[1,2] This report discusses the corrosion processes that led to growth of the holes and the model that was developed to predict the environmental consequences of a breach in a typical UF_6 storage cylinder.

RESULTS OF EXAMINATION

Visual and Chemical Observations

The holes formed in the two cylinders are shown in Figures 1 and 2 after the adjacent cylinders had been moved away and, in the case of the small hole, after the adhering reaction products were removed. The shape of the corrosion holes is particularly significant to scenario development as is the existence of the etched rivulets apparent in Figure 3. This is a photograph of the cylinder immediately below the one with the large hole after removal of the surface corrosion deposits. Corrosion of the lug of the adjacent cylinder intruding the small hole (not shown) similarly suggests attack by a strongly acidic solution containing some hexavalent uranium that oozed from the hole and oxidized the iron while being reduced to UF_4. The layered structure, identification, location, and color of the corrosion products provide additional information. The compounds identified are listed in Table 1 as they might be ordered from an iron surface to a solid UF_6 surface.

The backside of the deposit of reaction products in the cylinder with the small hole, viz., the surface that had been next to the UF_6, was examined using a color video fiberoptics boroscope. The deposit was noted as being orange on the surface and shaped like a hemisphere of a crude oblate spheroid about a golf ball in depth and a tennis ball in diameter. The reaction products within the cylinder with the large hole were obviously deep, and a partially successful core sampling was made. The depth of the UF_4 hydrate layer was about 10 cm, and the depth of the yellow hexavalent uranium oxyfluoride layer was in excess of 20 cm. Chemical analysis of the yellow layer showed the material contained three fluorides per uranium and closely fit the formula $U(OH)_4F_3$ or $UO_2F_2 \cdot 2H_2O \cdot HF$. A 50·50 mixture of UO_2F_2 and $[H_3O]_2[U(OH)_4F_4]$ also would give this same result. Both $U(OH)_4F_3$ (ref. 3) and $[H_3O]_2[U(OH)_4F_4]$ (ref. 4) have been identified in other studies; however, the yellow layer in the cylinder was amorphous.

Mass losses from the cylinders were small. The cylinder with the small hole lost about 0.45 kg, and the one with the large hole lost 13 kg. When the weight of the materials recovered outside the cylinders is accounted for, these mass losses become almost zero and 7.7 kg, respectively. The mass of iron oxidized in the two cylinders was estimated to be 0.16 and 3.6 kg, respectively. Based on the shape of the deposit within the cylinder with the small hole and the relative depths of the reduced and hydrolyzed layers in the cylinder with the large hole, the quantity of $UF_6(s)$ hydrolyzed exceeds the quantity reduced by a factor of about 25. When the chemistry is accounted for, the loss of uranium as UF_6 from within the cylinders would be about 1.8 and 50 kg, respectively.[5]

The fact that an open path for gas and vapor from the atmosphere to the ullage did not exist was indicated by the different pressures in the two cylinders. Pressure in the cylinder with the small hole was 74.7 kPa, and the pressure in the cylinder with the large hole was 156.4 kPa. Accumulation of HF was shown to have occurred in the ullage in both cylinders. The greater amount,

perhaps as much as 2 ℓ of liquid, was contained in the cylinder with the large hole.[6] Additionally, leakage of HF vapor to the atmosphere from the large hole was detectable both by odor and by instrumentation. HF vapor was not detectable in the vicinity of the small hole until after the cylinder and the adjacent cylinder were separated.

Corrosion Processes

Five features distinguish the chemical attack of the steel containment and UF_6 contents. First, the overall reaction is very slow, but the accumulation of reaction products does not stop the reaction. Second, hydrolysis reactions occurring at the surface of solid UF_6 result in the retention of most of the UF_6 in the cylinder as complex UO_2F_2 solvates (compounds containing both water and HF) that have limited solubility in the conductive solution of nearly anhydrous HF produced there. Third, this conducting solution permits the coating of the hydrolyzed hexavalent uranium complex by a thickening, less soluble layer of UF_4 hydrate. In this electrochemical process, iron is oxidized to an insoluble iron fluoride hydrate retained at the iron surface, while the U^{+6} material in the solution and at the UO_2F_2 solvate surface is reduced to produce UF_4 hydrates. This ties up much of the fluoride content of the solution and greatly reduces its acidity. Fourth, all solid products deposited as the outer coating layer are not very soluble in water and tend not to migrate far, limiting the environmental impact of these materials to the immediate vicinity of the cylinder. Fifth, when the hole becomes large, enough of the strongly acidic HF solution is produced that some seeps out of the plugging materials and can attack the cylinder wall below the hole and even the surface of the cylinder below, producing etched grooves. Corrosion deposits on the adjacent lifting lug and stiffening ring just below the small hole are believed to have been produced by this mechanism. The finding of a high concentration of uranium in a grab sample of the soil at the edge of the concrete pad, where the rain drained off the cylinder with the large hole, is additional supporting evidence.

SCENARIO FOR HOLE AND PLUG DEVELOPMENT

The interrelated actions of water, solid UF_6, and iron reported by R. L. Ritter[7] have been used to develop a scenario to explain the observations and deductions made during the investigaton. This scenario traces the development of holes through four phases, each illustrated by sketches of the affected areas. The hole development described here is for the presence of solid UF_6 at the bottom of the fracture. If wall penetration is in the top or along the bottom line of the cylinder, the scenario is not necessarily correct, once hole growth enters the fourth phase.

Phase 1 - Wall Fracture (Figure 4)

The duration of this phase is of the order of milliseconds. The sharp corner of a lifting lug of one cylinder strikes or is struck by another cylinder near a stiffening ring below the surface of the solid UF_6. On rare occasions, the result is an undetected fracture that extends completely through the wall of the cylinder. Immediate detection may or may not be possible as discussed under phase 2.

Phase 2 - Initial Plugging of the Fracture (Figures 5 and 6)

The next phase is development of a plug in the fracture produced in phase 1. The time frame for this phase is hours, and the plug will be developed fully in about 24 h. Figure 5 shows a very early stage in the plug development. Chemical attack begins in the fracture at or near the external surface of the cylinder wall. It must be here because the sublimation pressure of UF_6 is approximately four times the vapor pressure of water, and two moles of water are required for

each mole of UF_6 converted to UO_2F_2. This has been confirmed by crude computer simulation using reasonable values for the diffusion coefficients of water vapor and UF_6 vapor in air.[8] Only at the exterior surface is sufficient water vapor available to produce $HF-H_2O$ fog and some condensate on the steel surface. The UO_2F_2 hydrate formed in the fracture produces a plug which slows the diffusion of UF_6 to the surface. If the fracture is not detected before this plug is fully developed, it is unlikely to be detected until some time after completion of phase 3.

The initial fracture may or may not be immediately detectable because detection depends on seeing the $HF-H_2O$ fog formed upon the hydrolysis of UF_6 with water vapor.[9] Because of some combination of unfavorable conditions, fractures in the two cylinders went undetected during this phase.

The conditions illustrated in Figure 6 exist in the fracture just before final closure of the fracture by hydrolysis products makes another change in the time frame for reaction. The reactions at this point in the process are the same as in Figure 4, except for being slower.

Phase 3 - Corrosion of the Walls of the Fracture (Figures 7-10)

When the diffusion of the UF_6 to the surface is reduced sufficiently that water vapor is in excess at the fracture exit, aqueous HF is produced that dissolves some of the UO_2F_2. This conducting acidic solution attacks the iron producing green UF_4 hydrate and iron-fluoride hydrates. At the steel surface a very thin layer of FeF_2 is probable. (It is invisible.) Atop this, a layer of brick brown or gray Fe_2F_5 hydrate is found. (The color depends on the degree of hydration.) Next to this is a layer of greenish-white FeF_3 hydrate that becomes a yellowish tan on exposure to moist air. The UF_4 hydrate is at the center of the fracture and is somewhat porous. This UF_4 hydrate contains very little iron. UO_2F_2 solvate always exists between the UF_4 hydrate layer and the UF_6(s) as shown previously in Table 1. The time frame for the corrosion illustrated in the figures is on the order of months.

The initiation of chemical attack on the wall is illustrated in Figure 7. The reaction of UF_6(s) with H_2O within the fracture is given by:
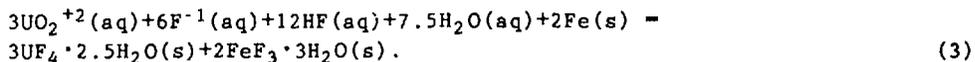
$$UF_6(s)+6H_2O(l) \rightarrow [H_3O]_2[U(OH)_4F_4](s)+2HF(l). \qquad (1)$$
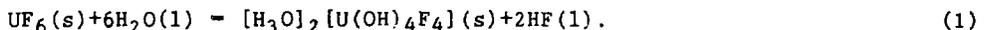
The principal reaction initiated at the exterior surface of this material and at the iron surface may be summarized by:

$$3[H_3O]_2[U(OH)_4F_4](s)+6HF(l)+2Fe(s) \rightarrow$$
$$3UF_4 \cdot 1.5H_2O(s)+2FeF_3 \cdot 3H_2O(s)+4.5H_2O(l). \qquad (2)$$
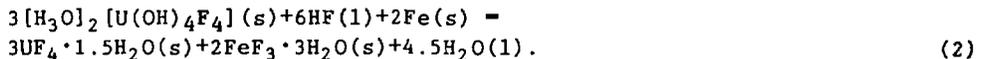
Note that all the fluorine in the starting UF_6 is consumed by the UF_4 and iron fluoride formed by reaction 2. Because HF accumulates within the cylinder ullage, more U (as UF_6) must be hydrolyzed by reaction 1 than is reduced by reaction 2, and the formation of the observed layer of UO_2F_2 solvate is explained.

Nearer the exit of the fracture, the reaction of HF(l) with H_2O vapor produces aqueous HF, which dissolves the previously produced UO_2F_2 hydrate, so the redox reaction given by the following equation may be considered representative. Similar equations may be written for the Fe to Fe^{+2} and Fe^{+2} to Fe^{+3} reactions:

$$3UO_2^{+2}(aq)+6F^{-1}(aq)+12HF(aq)+7.5H_2O(aq)+2Fe(s) \rightarrow$$
$$3UF_4 \cdot 2.5H_2O(s)+2FeF_3 \cdot 3H_2O(s). \tag{3}$$

These reactions require strongly acidic solutions, and if the acid content were to be reduced too much by dilution with rainwater, the escape of uranium as soluble uranyl ion in the form of UO_2F_2 becomes possible.

Figure 8 represents the condition existing in the fracture a few months later. The original plug of UO_2F_2 hydrate is entirely converted to UF_4 hydrate, and both the hydrolysis of the UF_6 and the conversion of the hydrolysis product to a UF_4 hydrate have proceeded deeper into the cylinder wall. The overall layering pattern of the products is established and perhaps includes, as shown, the development of the orange-colored layer. The rate of reaction is expected to be increasing as the fraction of the fracture surface attacked increases.

Figure 9, which represents the conditions in the fracture several months later, shows the hydrolytic attack of the $UF_6(s)$ has proceeded into the UF_6 inside the cylinder itself. The same redox reactions continue to deepen the UF_4 hydrate layer, and the area of the fracture surface attacked continues to enlarge. The degree of hydration of UF_4 is less in the locations where the concentration of H_2O is expected to be less, namely, toward the UF_4-uranium oxyfluoride complex interface. The overall rate of attack of the steel surface is increasing. Note that the ordered layering of the reaction products continues.

Phase 3 ends when attack on the iron is occurring over the full depth of the fracture, as illustrated in Figure 10. The attack on steel is proceeding from the outside in and is producing a hole with the bevel facing the outside. Once the bevel reaches through the wall thickness, the rate of attack will increase as the circumference of the crack increases, but the rate of attack per unit length of the circumference will remain practically constant. When this occurs, 10 to 14 months will have elapsed since the impact. As shown, $UF_4 \cdot 1.5H_2O$ and $UF_4 \cdot 0.75H_2O$ will have begun to be produced inside the cylinder, with a major yellow layer between it and the $UF_6(s)$.

Chemical analyses show that the average composition of the yellow layer corresponds closely to a 50:50% mixture of UO_2F_2 and $[H_3O]_2[U(OH)_4F_4](s)$ mole, so that some $HF(1)$ is formed and squeezed out. Production of UF_4 hydrate outside the hole can only begin when flow of the HF fluid from the yellow layer is more than is required to maintain saturation of UF_4 and iron fluoride hydrates, and to supply the acid requirements of the redox reactions producing additional UF_4 hydrate. This will not happen until the attack enters phase 4. Layering of the reaction products is maintained.

Phase 4 - Enlargement of the Hole and Production of External Products (Figures 11 and 12)

The last (or fourth) phase of hole development is entered when the fracture begins to grow. It begins about 1 year after the initiating impact and ends when all the UF_6 in the cylinder has been hydrolyzed, perhaps as much as 30 years later. Thus, the time frame for this process is years. In this scenario, enlargement of the effective hole diameter is assumed to occur at a relatively constant rate when viewed over a sufficiently long period. At some stage in growth, attack of the interior surface of the cylinder wall at the hole edge becomes significant, and wall thinning from the inside occurs by the same mechanism as it initially began from the outside. In fact, wall thinning extended on the inside beyond the hole by 13 or more centimeters in the case of the cylinder with the large hole (Figure 12).

Figure 11 is a schematic, cross-sectional drawing that illustrates distribution of reaction products in the small hole and on the lifting lug of the adjacent cylinder after a 4-year exposure. The layered isolation of products is seen, except that, directly over the hole where no iron remains, the different layers are mixed on a macroscopic basis with retention of identity. The pattern of attack on the cylinder wall below the hole, and on the top and sides of the lifting lug toward the cylinder and the stiffening ring, provides evidence of the acidic, hexavalent uranium-bearing solution that has oozed from the hydrolysis products being produced in the hole. At this stage of hole development, it appears that the hexavalent uranium being transported from the cylinder is reduced to the insoluble UF_4 hydrate by iron and retained at the reduction site.

As noted, the redox reaction occurring outside the cylinder hole between hexavalent uranium and iron to deposit insoluble UF_4 and iron fluoride hydrates also ties up large amounts of F^{-1}-ion from the oozing acid as suggested by Eq. (3). Additionally, dilute aqueous HF slowly attacks iron to form iron fluoride hydrates and hydrogen gas. For these reasons, the loss by evaporation of HF vapor from the hole, at this stage of development, would be expected to be quite limited. In fact, if any HF vapor is escaping, the quantity is so small that it does not produce a detectable concentration in the atmosphere in the immediate vicinity of the hole. The predicted maximum rate of escape of HF from the small hole at the time of discovery is 0.16 g HF/h. This includes both vapor and liquid.

An additional 9 years of exposure (13 years after impact) may produce the effects shown schematically in Figure 12. A portion of the green UF_4-hydrate layer sloughed off the center of the hole between the time of discovery (in June 1990) and October 1990. This revealed the presence of the deep yellow layer of hydrolysis products behind the UF_4-hydrate layer inside the cylinder. This yellow layer extended more than 30 cm into the cylinder, indicating the hydrolysis of a significant fraction of the UF_6 in the cylinder had occurred. Some slow drainage of the acidic solution from the hydrolysis zone occurred in the area where the UF_4 hydrate sloughed off. Vaporization of this oozing solution left the yellow deposit over the green UF_4-hydrate layer as shown.

All the reactions occurring earlier inside the cylinder are continuing at a rate that probably is increasing at least as fast as the area of the hole is increasing. Thus, the quantity of acidic solution produced gradually increases until the wettable iron surface on the cylinder with the hole will no longer reduce all the contained hexavalent uranium to UF_4. When this happens, the solution will slowly trickle down the cylinder wall and stiffening ring, etching them while producing the layered UF_4 and iron fluoride hydrates. When the solution reaches the cylinder below the hole, it spreads out and etches this cylinder, forming shallow rivulets in the steel surface. These coalesce into grooves and finally into a single deep groove as the pitch of the cylinder surface passes vertical. These are filled with layers of iron fluoride hydrates which, in turn, are covered with a layer of UF_4 hydrate. This condition, after removal of the deposits, is illustrated in Figure 3.

As suggested previously, when a hole becomes this large, loss of HF vapor by vaporization of the oozing liquid will occur. Estimation of the loss of HF from the cylinder with the large hole, using a simple model, indicates that the rate of loss of HF at the time of discovery might have been as large as 3.7g HF/h; however, not all of this quantity would have had to have been as vapor. Environmental samples taken in the vicinity of the cylinder with this large hole did not indicate concentrations of HF above 2.5 mg HF/m^3, which is the permissible exposure limit (PEL) for 8 h.

The etch pattern on the cylinder below the one with the hole suggests that not all the hexavalent uranium in the strongly acidic solution was reduced to UF_4 hydrate. The missing mass of 7.7 kg, which the chemistry indicates might be

equivalent to the loss of about 50 kg of UF_6 as uranyl fluoride solution, strongly supports this observation. Failure to find any general soil contamination at the edge of the pad, where rainwater drained from the cylinder with the large hole, is not counter indicative because uranyl ion is not retained well in soil.

MODEL FOR PREDICTING CONSEQUENCES OF CYLINDER FAILURE

The scenario may be employed to develop a simple model for semiquantitatively examining features of chemical attack initiated by an impact fracture, such as rate of hole radius enlargement (1×10^{-3} mm/h), loss rate of HF (8×10^{-3} g/cm^2-h), time to hydrolyze all the UF_6 in the cylinder (about 30 years), and size of the hole (about 0.6 m at 30 years). The bases for the model are given in Table 2. The fourth phase of the scenario is not expected to be applicable to cylinders with holes in the top or to cylinders with walls thinned by severe external corrosion.

SUMMARY AND CONCLUSIONS

The four-phase scenario presented allows for explanation of the observations made to date. It provides a simple model that can be used to estimate the seriousness of the effects of hole development in a cylinder with impact fractures below the level of the solid UF_6 for a longer time than 13 years. It also appears to apply for a period of one to possibly two years to an impact fracture above the solid UF_6 level. It does not apply to a large hole such as might be introduced above the solid UF_6 level by a projectile. It also does not apply to the rate of breach enlargement in cylinders with walls severely thinned by external corrosion before the breach occurs.

Investigation shows that an impact fracture of UF_6 storage cylinder walls does not cause an immediate insult to the environment. The data suggest that if the fracture is not noticed at the time of fracture, it will not be discovered until at least one year has passed. Even after four years, the environmental impact is not great, but a diligent effort should be made to find any breached cylinders as soon as possible after enlargement of the breach starts.

ACKNOWLEDGMENTS

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6. Appendix B2 of Ref. 1.

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9. W. Schotte, "Fog Formation of Hydrogen Fluoride in Air," *Ind. Eng. Chem. Res.* **26** (1987): p. 300.

DISCLAIMER

TABLE 1. REACTION PRODUCTS ARE LAYERED
IN THE FOLLOWING ORDER FROM IRON TO UF_6

Material	Color
Fe	metallic
FeF_2 (weak X-ray pattern)	white (not seen)
$Fe_2F_5 \cdot xH_2O$ (x = 7 or less)	gray to brown
$FeF_3 \cdot xH_2O$ (x = 3 or less)	whitish to light tan
$FeF_3 \cdot 3H_2O$ & $UF_4 \cdot 0.75H_2O$	light violet
$UF_4 \cdot 2.5H_2O$	green
$UF_4 \cdot 1.5H_2O$ & $UF_4 \cdot 0.75H_2$	lightly darker green
$UO_2F_2 \cdot nH_2O$	fluorescent yellow
$[H_3O]_2[U(OH)_4F_4]$ & UO_2F_2	yellow
$U_2O_3F_6$ (by color only)	orange
a-UOF4 (by color only)	bright orange
UF6	clear solid

TABLE 2. BASES OF A SIMPLE MODEL

· There is an induction period before hole enlargement begins which is dependent on the cylinder wall thickness (10 to 14 months for a 5/16-in. (0.794-cm) wall).

· Rate of enlargement of the hole diameter is practically constant once the wall is chemically attacked through the full thickness.

· Amount of UF_4 produced can be calculated from the mass of iron converted to iron fluorides. Use Eq. (2). These reactions effectively do not contribute to the formation of HF.

· Total amount of UF_6 hydrolyzed is about 26 times the amount reduced.

· Hydrolyzed UF_6 present in the cylinder has an average composition which corresponds to a 50:50 mixture of $[H_3O]_2[U(OH)_4F_4]$ and UO_2F_2. This weighs more than the UF_6 it replaces, as shown in reaction 4:

$$UF_6(s)+4H_2O(g) \rightarrow$$
$$UO_2F_2 \cdot 2H_2O \cdot HF(s)+3HF(l). \qquad (4)$$
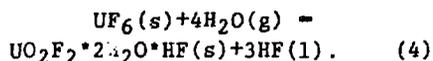
· HF not tied up with the hydrolysis product diffuses either through the solid UF_6 to the cylinder ullage for retention or to the exterior surface of the plug to be lost as solution or vapor.

· Loss rate of HF is proportional to the surface area of the hole.

Figure 1 - The width of the 4-year-old hole is about 10 cm. Note the UF_4 hydrate in the tail etched in the cylinder wall below the hole.
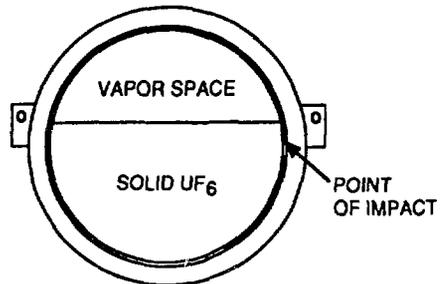

Figure 2 - The width of the 13-year-old hole is about 20 cm. A tail about 20 cm long is seen. The surface of the deposit in the tail region suggests a deposit from a viscous solution.

Figure 3 - When the deposits on the cylinder below the large hole are removed, a predictable etched rivulet-to-groove pattern is revealed.

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VAPOR SPACE

SOLID UF_6

POINT OF IMPACT

CYLINDER CROSS SECTION

Figure 4 - Initiating mechanism is impact fracture at the position shown.

$HF(g) + H_2O(g) = HF(aq)\ [log]$ $UF_6(g) + 2H_2O(g) = UO_2F_2(s) + 4HF(g)$

H₂O FILM

UO₂F₂·xH₂O(s)

CYLINDER WALL

FRACTURE

AIR + UF₆(g)

UO₂F₂·xH₂O(s)

UF₆ FILM

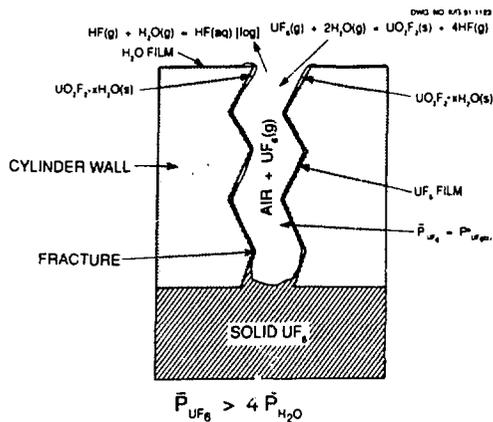$\bar{P}_{UF_6} = P_{UF_6}$

SOLID UF₆

$$\bar{P}_{UF_6} > 4\,\bar{P}_{H_2O}$$

Figure 5 - Schematic cross section of a fracture shortly after impact, showing results of chemical reaction initiation

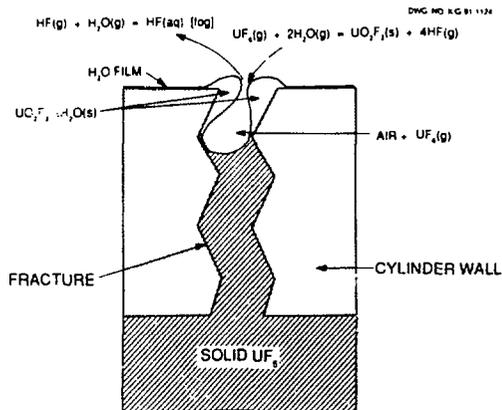$HF(g) + H_2O(g) = HF(aq)\ [log]$ $UF_6(g) + 2H_2O(g) = UO_2F_2(s) + 4HF(g)$

H₂O FILM

UO₂F₂·xH₂O(s)

AIR + UF₆(g)

FRACTURE

CYLINDER WALL

SOLID UF₆

Figure 6 - Schematic cross section of a fracture showing development of initial plug nearing completion

$3[H_3O]_2[U(OH)_4F_4](s) + 6HF(l) + 2Fe(s) = 3UF_4 \cdot 2.5H_2O(s) + 2FeF_3 \cdot 3H_2O(s) + 1.5H_2O(l)$

$HF(l) + H_2O(g) = HF(aq)$

UO₂F₂·xH₂O(s)

Fe₂F₅·7H₂O(s)

UF₄·2.5H₂O(s) [porous]

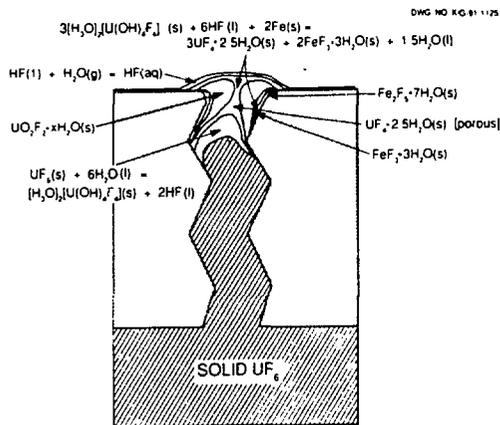FeF₃·3H₂O(s)

$UF_6(s) + 6H_2O(l) = [H_3O]_2[U(OH)_4F_4](s) + 2HF(l)$

SOLID UF₆

Figure 7 - Schematic cross section of a fracture showing initiation of reduction and interior hydrolysis reactions in phase 3

$3[H_3O]_2[U(OH)_4F_4](s) + 6HF(l) + 2Fe(s) = 3UF_4 \cdot 2.5H_2O(s) + 2FeF_3 \cdot 3H_2O(s) + 1.5H_2O(l)$

H₂O(g)   HF(aq) FILM   UF₄·2.5H₂O(s)

FeF₂ [invisible]

Fe₂F₅·7H₂O(s)

$HF(l) + H_2O(g) =$
HF(aq)

FeF₃·3H₂O(s)

HF(l)

[H₃O]₂[U(OH)₄F₄] (s)

HF(l)

$UF_6(s) + 6H_2O(l) = [H_3O]_2[U(OH)_4F_4](s) + 2HF(l)$
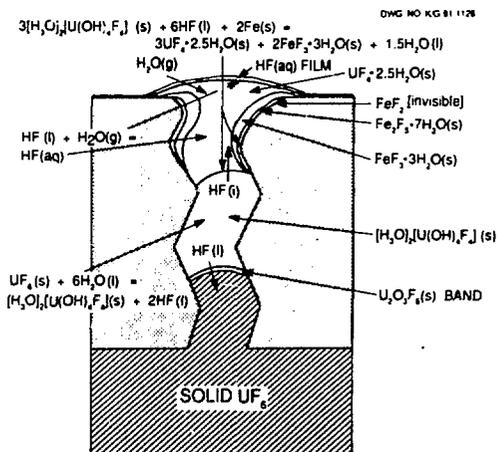
U₃O₅F₆(s) BAND

SOLID UF₆

Figure 8 - Wall attack at fracture continues. Outer layer of UO_2F_2 hydrate is replaced by UF_4 hydrate. Internal hydrolysis reaction continues down the fracture.
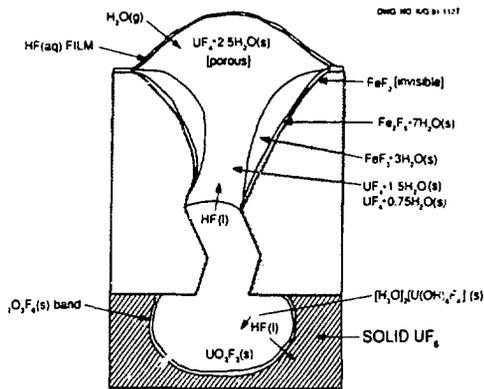
Figure 9 - Wall attack at fracture continues. Hydrolysis reaction enters the cylinder UF_6. Fracture is enlarging from the outside in.
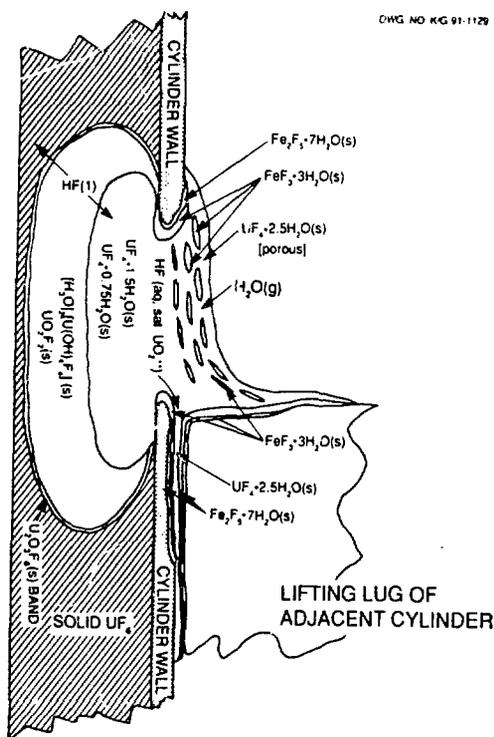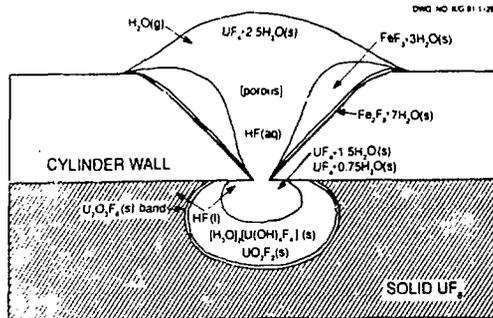
Figure 10 - Phase 3 is completed as fracture is enlarged along full depth. The UF_4 hydrate is now forming inside the cylinder. Hydrolysis of UF_6 reactions surrounds the UF_4 inside the cylinder.

LIFTING LUG OF ADJACENT CYLINDER

Figure 11 - Main reactions continue to be hydrolysis of UF_6 inside and reduction to UF_4 inside and outside the cylinder. The fracture has become a small hole after 4 years.
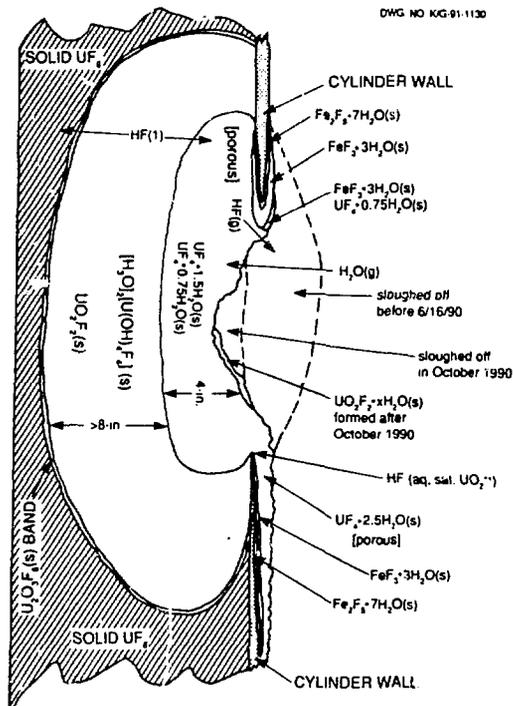
Figure 12 - Hydrolysis and reduction reactions continue. Deposits outside the cylinder slough off. HF escapes as both vapor and solution and builds up in the ullage. A small amount of hexavalent uranium in solution not reduced to UF_4 hydrate escapes as UO_2^{++} from the vicinity of the cylinder. Condition shown is for 13 years after impact. The hole is now more than 8 in. across.