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Investigation of Breached Depleted UF_6 Cylinders at the K-25 Site

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~~This report cont[illegible] prelim[illegible] information and wa[illegible]pared primarily for use by participants in [illegible] E[illegible]ironmental Restor[illegible] and Waste Management program. Because th[illegible] information is [illegible] to revision, it should not be disseminated beyond the [illegible]ient o[illegible] [illegible]uments prepared for public availability should no[illegible] this report.~~

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INVESTIGATION OF BREACHED DEPLETED UF_6 CYLINDERS AT THE K-25 SITE

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EDITOR'S NOTE

Although Oak Ridge National Laboratory has a policy of reporting its work in SI metric units, this report uses English units. The justification is that the uranium enrichment facilities at present operate completely with English units, and reporting otherwise would lose meaning to the intended readership. To assist the reader in obtaining the SI equivalents, these are listed below for the units occurring in this report.

Property	Unit used	SI equivalent
Dimension	in.	25.4 mm
Dimension	ft	0.3048 m
Density	lb/ft^3	$16.02\ kg/m^3$
Energy	calorie	4.184 J
Mass	lb	0.4536 kg
Mass	metric ton	1000 kg
Mass	ton	907.2 kg
Pressure	psi	6.896 MPa
Pressure	torr	133.3 Pa
Temperature	°F	°C = (5/9)(°F - 32)

1. INTRODUCTION

Depleted uranium hexafluoride (UF_6) produced at the U.S. gaseous diffusion plants has been stored in steel cylinders since the diffusion plants first went into production more than 40 years ago. The inventory exceeds 380,000 metric tons of depleted uranium in approximately 47,000 cylinders. Once a significant inventory was produced, the diffusion plants created outdoor storage facilities which evolved separately at each site and are now comprised of concrete and compacted gravel storage pads and wooden and concrete cylinder saddles. The handling equipment used to stack these cylinders in double-tiered rows has also evolved from mobile cranes hoisting the cylinders with removable bands to the Raygo Wagner loader, a specially designed tractor that grabs and lifts the cylinders with hydraulically actuated fingers. Storage cylinder designs have also changed over the years. These design modifications vary from lifting lug shapes and stiffening ring designs to a change in the reference grade of steel. The current storage cylinder model, the 48G, and its predecessors, models O and OM, were specifically created as economical containers for UF_6. Other thin-wall cylinders currently used for UF_6 storage include models T, H, and HX, which have skirted heads. Although these cylinders serve as long-term storage containers, they were designed primarily as pressure vessels to meet the conditions during liquid filling.

Under efforts to inspect these cylinders in long-term storage, two failed cylinders were discovered at the Portsmouth Gaseous Diffusion Plant (PORTS) in the summer of 1990. An investigation of these failures was conducted and documented in report ORNL/TM-11988, *Investigation of Breached Depleted UF_6 Cylinders,* September 1991.[1] Since these two failures, concerted efforts to improve the inspection rigor of these cylinders were developed at the Portsmouth, Paducah, and Oak Ridge K-25 Site facilities. During this development of improved inspections, additional failed cylinders have been discovered. Four cylinders were found breached at the Oak Ridge K-25 Site, one in December 1991, two in January 1992, and one in March 1992. In November 1992, a failure was discovered at the Paducah Gaseous Diffusion Plant (PGDP). In total, seven failed cylinders have been discovered in the three-site, long-term storage cylinder inventory.

The subject of this report, the four Oak Ridge K-25 Site failures, presents a unique challenge to the site in comparison to the operating gaseous diffusion plants. Previously, the K-25 Site operated as a gaseous diffusion plant, enriching uranium. It is because of this activity that the site established an inventory of UF_6 in long-term storage, approximately 10%

of the three-site inventory. In 1985, the plant ceased enrichment activities, and facilities to handle the UF_6 cylinders were shut down. Special equipment to transport the cylinders within the site has been reactivated to access and patch the failed cylinders. However, the current strategy for the site is not to reestablish the cylinder transfer facilities, but to ship the failed cylinders to an operating gaseous diffusion plant for transfer of their contents to new cylinders. The transportation logistics and Department of Transportation involvement are new and challenging avenues for UF_6 cylinder management.

The Martin Marietta Energy Systems, Inc., team initially formed to investigate the PORTS failures was called to investigate the K-25 Site failures. The team applied the PORTS charter to the K-25 Site failures and continued their investigation strategy described in the September 1991 report.[1] This report records the investigative findings and recommendations from the K-25 Site failures and is based on information available through September 1994. Additional findings relative to this investigation can be found in the PORTS investigation report.[1] Some operations and data collection requested by the team to yield supporting evidence for its conclusions are still in progress and may take considerable time to complete. Pending those findings, this report should be considered an interim report. When the team has assessed the latter findings, an updated report will be issued if such findings warrant a change in, or addition to, the conclusions presented herein.

The failure analysis of the PGDP cylinder was not part of the charter of this team; however, because of its relevancy to this investigation, this failure is referenced in the present report. Details of this failure can be found in the Occurrence Report MMES-92-011165 PAD-92-00454 (I0003657).

This report is organized first to give the location and histories of the K-25 Site failed cylinders. The probable failure causes are next discussed, followed by the perceived environmental impact from the four incidents. Implications of the failures on storage practices at the three sites are then addressed, together with recommended actions.

2. ANALYSIS OF FAILURE CAUSES

2.1 LOCATIONS AND HISTORIES OF FAILED CYLINDERS

Cylinder 101244

On December 16, 1991, a breach was discovered in Cylinder 101244 in K-1066-K yard, row 10, position 134 (upper tier). Figure 1 illustrates the K-1066-K yard and identifies breached cylinder locations. This model OM, thin-wall, 5/16-in. cylinder was discovered to have an approximately 5- to 6-in.-diam hole located at the 6 o'clock position on the plug side of the stiffening ring which was visible only from the plug end. The failed cylinder was detected by yellow and green reaction products which had fallen onto the support saddles below.

Cylinder 101244 was manufactured by Trinity Steel, Inc., as part of an order for 2,000 model OM cylinders. The PGDP records show this cylinder was shipped from the fabricator to the Paducah plant and filled with depleted uranium hexafluoride in May 1963. Paducah records also show that after approximately 3 years of storage in C-745-C yard, the cylinder was shipped to the Oak Ridge K-25 Site in July 1966. In the absence of historical records at the K-25 Site, it is probable that the cylinder contents were fed to the Oak Ridge diffusion cascade, filled with its existing contents (a lower assay from Paducah records), and then stored in K-1066-G yard shortly after arriving at the K-25 Site. During the 1960s, the three U.S. diffusion plants underwent a campaign to refeed partially depleted UF_6, which would explain this inter-plant shipment of depleted uranium. Internal correspondence at the K-25 Site indicates that K-1066-G yard provided inadequate storage (see failure analysis for further description) for approximately 3,000 cylinders, and K-1066-G yard cylinders were moved to K-1066-K yard between April 1983 and September 1984. From the comparable cylinder populations in the respective yards (~3000 cylinders), it can be assumed that all K-1066-K yard cylinders were subject to this move from K-1066-G yard and that during this location Cylinder 101244 was placed in row 10, position 134, where it was discovered breached. This location is an end row adjacent to the wet drainage field for the K-1066-K yard.

Cylinder 114951

On January 8, 1992, Cylinder 114951 in K-1066-E yard, row N19, position 15 (lower tier) was discovered breached. Figure 2 illustrates the K-1066-E yard and identifies breached cylinder locations. This model OM, thin-wall, 5/16-in. cylinder was discovered to have a hole approximately 8 to 12 in. wide by 15 to 17 in. long, extending beneath the valve-end stiffening ring at approximately the 4 o'clock position. Again, the failure was discovered by identifying the reaction products around the breach and those resting on the supporting saddle.

Cylinder 114951 was manufactured in 1974 to 1975 by Modern Welding Company as part of an order for 2,100 model OM cylinders. The PGDP and PORTS records show no receipt of this cylinder. Thus, it is probable that the cylinder was shipped to the Oak Ridge K-25 Site direct from the fabricator in 1975, filled with its existing contents, and placed in row N19, position 15, shortly after being received at the K-25 Site.

Cylinder 116797

On January 21, 1992, Cylinder 116797 in K-1066-E yard, row N29, position 25 (lower tier) was discovered breached. Figure 2 illustrates the K-1066-E yard and identifies breached cylinder locations. This model OM, thin-wall, 5/16-in. cylinder was discovered to have a hole of approximately 2 in. diam which could only be identified using an inspection mirror. No material had fallen off the cylinder to the ground at the time of the discovery of the evidence for the breach.

Cylinder 116797 was manufactured in 1976 to 1977 by Modern Welding Company as part of an order for 1,600 model OM cylinders. The PGDP and PORTS records show no receipt of this cylinder. Again, it is most likely that the cylinder was shipped to the Oak Ridge K-25 Site direct from the fabricator in 1976, filled with its existing contents, and placed in row N19, position 15, shortly after being received at the K-25 Site.

Cylinder 7953

On March 17, 1992, during a reinspection of K-1066-K yard that employed lessons learned since the earlier inspection in December 1991 and discovery of the above failed cylinders, Cylinder 7953, a 10-ton, 5/16-in. wall thickness model T, was found to have about a 9-in.-diam hole in the 6 o'clock position near the middle stiffening ring on the side toward the plug end of the cylinder. This cylinder, located in row 5, position 43 (lower tier) was in a drainage route for the yard where saddles inadvertently dammed rainwater runoff. Figure 1 illustrates the K-1066-K yard and identifies breached cylinder locations. The breach in the side wall was not visible; however, the failure was identified by the reaction products on the concrete yard inches below the cylinder. The identification of this material as reaction products required the use of a flashlight. To view the breach, a mirror and flashlight had to be utilized.

Cylinder 7953 was manufactured by J. B. Beaird Company as part of an order for 3,210 model T cylinders. The PGDP records show this cylinder was shipped from the fabricator to the Paducah plant and filled with depleted uranium hexafluoride in 1959. PGDP records also show that after approximately 3 years of inter-plant service the cylinder was shipped to the Oak Ridge K-25 Site twice, once in March 1967 and again in December 1967, as part of the partially depleted uranium refeed campaign. The location and conditions under which the cylinder was stored at the K-25 Site during these interim periods are unknown. On the final shipment to the K-25 Site, the cylinder contents were fed to the cascade, filled with its existing contents (a lower assay from Paducah records), and the cylinder apparently stored in K-1066-G yard shortly after arriving at the K-25 Site. As described above for Cylinder 101244, the cylinders in K-1066-G yard were moved to K-1066-K yard due to inadequate storage conditions. For purposes of this investigation, it is assumed that Cylinder 7953 was placed in row 5, position 43, during this relocation from K-1066-G yard, where it was discovered breached.

2.2 APPEARANCE OF FAILURES

Cylinder 101244 was the first of four breached cylinders to be identified at K-25. As shown in Figure 3, the breach in Cylinder 101244 appeared as a slightly elliptical, approximately 6-in.-diam hole located at the bottom (6 o'clock position) at the plug end of the cylinder on the plug side of the stiffening ring. The location of the failure was different from two previous failures investigated at PORTS, which were both induced by a lifting lug impinging into the side of the cylinders.[1] The discovery of the hole followed from the observation of greenish salt deposits that had fallen onto the saddles supporting the cylinders directly under the failed cylinder. Three relatively deep pits can be seen in Figure 3 between the hole and the girth weld joining the dished head to the cylinder body; however, there is no evidence of salt leakage at any of the pit sites. Although the cylinder was in an upper tier location at the time the failure was discovered, the bottom surface of the cylinder at the valve end showed rust markings which indicated that it had previously rested on support saddles. The cylinder had been moved from K-1066-G yard to K-1066-K between 1983 and 1984, and these apparent saddle markings indicate that the cylinder probably occupied a ground-level position in G-yard. Even though Cylinder 101244 was in an upper tier position, there were no salt deposits or unusual corrosion manifestations on the adjoining or underlying cylinders. This is a consequence of the 6 o'clock location of the hole and the separation distance between the underlying cylinders, which was wider than the hole.

Approximately 3 weeks after the discovery of the above-mentioned cylinder breach, a relatively large hole was found in Cylinder 114951 located in the K-1066-E storage yard. The cylinder was in the lower tier and supported by wooden saddles. The hole, pictured in Figure 4, was approximately 8 to 12 in. wide by 15 to 17 in. long and was located behind the stiffening ring at the valve end of the cylinder at approximately the 4 o'clock position. The lifting lug of an adjacent cylinder faced directly into the hole, and as shown in Figure 5, much of the lug was missing due to corrosive attack. This adjacent cylinder also showed significant scaling of the cylinder surfaces near the stiffening ring (see Figure 5). Likewise, the cylinder immediately above the hole (Cylinder 114921) showed extensive rusting and scaling, pictured in Figure 6, which by its proximity to the breach appears to have been associated with gaseous reaction products emanating from the hole. Although slightly larger, the hole was almost identical in shape and position to one examined in an earlier investigation[1] at PORTS (Cylinder 115688). The salt within the area of the hole was also similar in coloring to that of the PORTS cylinder, but the exterior surface of the salt was more recessed.

Further inspection of the K-1066-E yard uncovered one other breached cylinder, again with the hole directly under the lifting lug of an adjacent cylinder. This hole was relatively small, approximately 2-in. diam, and was located immediately behind the stiffening ring at the valve end of the cylinder near the 9 o'clock position (viewed from the valve end). The hole was almost completely obscured by the lifting lug of the adjacent cylinder and could only be seen with the aid of a mirror. Its appearance, shown in Figure 7, was very similar to that of the second cylinder failure examined at PORTS (Cylinder 127985).[1] Both cylinders were likewise located in lower tier positions. There was no evidence of salt deposits on the ground, and except for the opposing lifting lug, no evidence of corrosion of neighboring cylinders.

A fourth breached cylinder at K-25 (Cylinder 7953) was found in the K-1066-K yard approximately 4 months after discovery of the first breached cylinder in the same yard. Like the first cylinder, the hole was in the bottom (6 o'clock position) of the cylinder, but the hole was considerably larger, approximately 9 in. diam. The cylinder was in a bottom tier position, and despite its relatively large size, the hole could not be seen without the aid of mirrors because of the limited ground clearance and separation distance between cylinders. Direct photographing of the hole (see Figure 8) was not possible until the cylinder could be rotated 90° from its original position. The identification of the hole was aided by the observation of greenish salt deposits lying on the concrete surface directly beneath the hole, shown in Figure 9. The hole was located on the plug side of the cylinder approximately 6 in. from the middle stiffening ring. There was extensive external corrosion of the bottom surface of the cylinder, as evidenced by the heavy rust covering (see Figure 8), and by iron oxide scale that had sloughed off the cylinder onto the concrete pad below (see Figure 9). Adjacent cylinders at the lower level also showed a higher-than-normal extent of external corrosion of the lower surfaces; however, this appeared to be the result of the cylinders being located in a low spot in the yard, which retained water, rather than any effects from the failed cylinder.

2.3 PROBABLE FAILURE CAUSES

The failures of the two cylinders in E-yard were similar in appearance and general location to two earlier failures examined at PORTS.[1] Both of these failures, like the PORTS failures, were induced by mechanical damage at the time of cylinder stacking. The mechanisms that caused the two cylinder failures in K-yard have been more difficult to determine. Since the cylinders share a common bottom hole location, these two failures would appear to have resulted from the same root cause. Yet, there are important differences in the design of the two cylinders and in the locations of the holes along the length of the cylinders. Because of the many factors that entered into the K-yard failures, event-tree analyses were made of potential failure causes, and these are given in Tables 1 and 2. Reference to these tables will aid in following the discussions of the K-yard cylinder failures and will provide a summary of what are believed to be the root causes of the failures.

Cylinder 101244

When discovered, the breach in Cylinder 101244 represented a unique class of failure by virtue of its position at the very bottom of the cylinder. Until this failure, mechanical damage from a lifting lug had been the only established failure cause, and a 6 o'clock position of a hole is inconsistent with this mechanism. In assessing this failure, the following facts are pertinent. The initial usage of the cylinder was at PGDP, where it was filled with depleted

Table 1. Event-Tree Analysis for Breached Cylinder 101244

Event	Possible cause/contributing cause	Evidence
Cylinder manufactured (1963)	None plausible	None
Inter-plant service (1963-1966)	1. Mechanical damage during handling	1. Negative: training, procedures, lack of contamination evidence in the G- to K-yard relocation. Positive: other known failures and damage from handling.
G-yard storage (~1966-1983)	1. Accelerated corrosion from yard degradation 2. Chemical corrosion from contact with unidentified materials	1. Negative: no records of upper vs lower tier position. Positive: documented inadequate yard condition, documented corrosion on other cylinders in G-yard, evidence of saddle corrosion, neighboring pits surrounding hole, Paducah data on corrosion caused by in or near ground contact. 2. Negative: probability. Positive: no other breaches, asphalt construction of G-yard.
G- to K-yard relocation (~1983-1984)	1. Mechanical damage during handling	1. Negative: training, procedures. Positive: HF concentration in ullage, other known failures and damage from handling, hole size based on expected growth rate from mechanical breach.
K-yard storage (1984-present)	1. Accelerated corrosion from yard design	1. Negative: cylinder located on upper tier. Positive: proximity to yard runoff route and drainage area, neighboring pits, surrounding hole.

Summary Analysis: The evidence indicates the cylinder likely suffered accelerated corrosion while in G-yard, caused by in- or near-ground contact, which led to its susceptibility to physical damage in the relocation of G-yard cylinders and/or continued accelerated corrosion while in K-yard storage.

Table 2. Event Tree Analysis for Breached Cylinder 7953

Event	Possible cause/contributing cause	Evidence
Cylinder manufactured (1957-1958)	1. Weld defect	1. Negative: QA requirements. Positive: production statistics and location of failure with respect to weld.
Inter-plant service (1958-1968)	1. Final railcar transport damage to weld 2. Other mechanical damage to weld during handling	1. Negative: location of failure on cylinder with respect to railcar saddle design. Positive: known failures and sample of other shipped type T cylinders, documented rail shipments. 2. Negative: training, procedures, lack of identified contamination in the G- to K-yard relocation. Positive: dents on lower portion of cylinder, other known failures and damage from handling.
G-yard storage (~1968-1983)	1. Accelerated corrosion from yard degradation 2. Chemical corrosion from contact with unidentified materials	1. Negative: no records of upper vs lower tier position. Positive: documented inadequate yard condition, documented corrosion, asphalt/gravel in skirt, Paducah data on corrosion caused by in or near ground contact. 2. Negative: probability. Positive: no other breaches, asphalt construction of G-yard.
G- to K-yard relocation (~1983-1984)	1. Mechanical damage to weld during handling	1. Negative: training, procedures, HF concentration in ullage. Positive: physical dents on lower portion of cylinder, other known failures and damage from handling.
K-yard storage (1984-present)	1. Accelerated corrosion from yard design in combination with saddle design/position	1. Negative: none. Positive: proximity to yard runoff route and the positioning of the saddles to dam water underneath cylinder.

Table 2 (cont.)

Summary Analysis: The cylinder may have experienced accelerated corrosion while in G-yard. The cylinder also suffered accelerated corrosion damage in K-yard due to the wetness of the storage area. However, the plausible extent of corrosion for substandard storage in K-yard based on the duration of storage in this yard is not sufficient to be the single most cause. The cylinder could also have experienced other damage in the area of the breach previous to storage in K-yard. The presence of the weld may have contributed to the failure either by a manufacturing defect or its susceptibility to physical damage during handling targeting it for the initial penetration point.

UF_6 on May 13, 1963. The cylinder was stored at PGDP for 3 years in C-yard, location 130, and then was shipped to K-25 on July 29, 1966. The contents were fed into the K-25 cascade, and the cylinder was refilled with depleted UF_6 of a lower assay. (Records as to the filling date are no longer archived at K-25.) The cylinder was initially stored in the K-1066-G yard, most probably beginning in the 1966 to 1967 time frame, although its exact location in this storage yard cannot be determined. Sometime between 1983 and September 10, 1984, the cylinder was moved to row 10, position 134 (upper tier) in storage yard K-1066-K.

Three potential failure modes can be hypothesized: mechanical damage to the underside of the cylinder encountered during shipment of the cylinder from PGDP to K-25; mechanical damage to the underside during transport from G-yard to K-yard at K-25; and corrosion of the bottom surface initiated during the 16- to 18-year storage interval in G-yard. (See the event-tree analysis in Table 1.) None of these possible failure modes can be conclusively ruled out, since all evidence of the origin of the hole has been obscured by the corrosion that resulted once moisture from the atmosphere contacted the UF_6. With respect to circumstantial evidence, arguments supporting corrosion as the primary cause appear more convincing than arguments for mechanical damage. The first failure mechanism (damage during shipment) is predicated on a documented case[2] where through-wall cracks did occur at the bottom of a cylinder during transport between PGDP and K-25. Examinations of two other cylinders shipped from PGDP in the same time frame also showed cracks at the 6 o'clock position, but they did not penetrate the wall.[3] However, each of the affected cylinders had a longitudinal seam weld at the 6 o'clock position (model T), and the cracks occurred in the heat-affected zone of this weld where the weld bead had contacted a steel saddle support. Furthermore, the cracks were located inside the end stiffening ring where the steel support saddles had been placed. There has been no evidence of crack initiation during shipment of cylinder models such as 101244, in which the longitudinal weld was on the side rather than the bottom. In the absence of a seam weld, mechanical damage sufficient to compromise the cylinder wall would most likely be manifest as a dent or scrape and should have been detected during the visual inspection given the cylinder before filling at K-25. Also, the failure in Cylinder 101244 occurred on the outside of the stiffening ring, not on the inside where the cylinders were normally supported during shipment. Thus, damage during shipment from PGDP does not appear to have been a contributing cause to the failure.

In assessing the probability for damage during transport from G- to K-yard at K-25, drop tests of similar cylinders at PGDP[4] provide a useful reference. Although breaches have been induced in such drop tests, they have always occurred when the impact area was near a stiffening ring. This causes a tear in or near the weld joining the stiffening ring to the cylinder wall. The area of the hole in Cylinder 101244 was several inches away from the stiffening ring (see Figure 3). However, a condition could be postulated where, after corrosive attack and thinning from storage in K-1066-G yard, this cylinder may have been more susceptible to handling damage during the move.

The evidence supporting external corrosion as the original cause of the hole appears more substantial. The cylinder was in an upper tier position in K-yard when the failure was discovered; however, there was a pattern in the rust markings on the cylinder bottom near the valve end that was representative of a cylinder supported by a saddle. Although there is no record of the cylinder position during its 16- to 18-year span in G-yard, these rust markings indicate that the cylinder could have occupied a ground-level position during this period. One of the reasons for moving cylinders from G-yard was that saddles supporting some of the cylinders had broken through the asphalt pavement and sunk into the ground. For this reason, all of the cylinders were visually inspected during the move from G-yard, and 15 to 20 cylinders were ultrasonically inspected "to see if there had been any corrosion from the mud, gravel, or chock (support saddle) area."[5] The nondestructive tests detected some pitting in the vicinity of the support saddles, but the depths were less than 1/16 in.[6,7] There is no record of which specific cylinders were ultrasonically inspected, so the condition of Cylinder 101244 at the time of the move to K-yard is unknown. In more recent nondestructive (ultrasonic) examinations of randomly selected cylinders from K-yard, wall thickness losses have been shown to exceed 1/8-in. near the bottom of the cylinder.[8] However, the most significant losses have been in the area immediately inside the end stiffening rings rather than on the outside where the leak in Cylinder 101244 occurred. (The area inside the stiffening ring corresponds to the area of the support saddle blocks in G-yard.) Examinations of storage cylinders conducted at the PGDP have also shown evidence of thinning of the bottoms of cylinders where subsidence of the supports allowed the cylinders to touch the ground. Wall thickness losses in the case of a model O Cylinder (10150) were on the order of 0.100 in. but, again, were inside the end stiffening rings.[9]

If Cylinder 101244 had been in ground contact in G-yard, this could have initiated the process that led to its ultimate failure in K-yard. Ground contact can blanket the underside of the cylinder with wet soil or asphalt, a condition that will support an electrochemical process termed "differential oxygenation corrosion." Such a process is driven by an oxygen concentration gradient where the area with the more limited oxygen concentration (the area furthest removed from air access) corrodes much more rapidly than the areas where the oxygen concentration is higher. Several large pits seen around the hole area (see Figure 3) may be indications of such a corrosion process. Once this type of corrosion is started, it can be completely arrested only by cleaning off the rust from the cylinder or storage in a controlled, low-humidity (<40% RH) atmosphere, since the oxidation product (rust) forms as an adherent but porous coating that serves as an oxygen diffusion barrier even after the cylinder is no longer in ground contact. Whenever this coating is moist from high humidity, dew, or rain, corrosion can continue at a relatively accelerated rate. (For a discussion of corrosion by differential oxygenation and other accelerated external corrosion processes, see Appendix B.)

While differential oxygenation corrosion can account for relatively rapid wall penetration, any given event depends on so many variables that a reliable estimate of a penetration rate, or of the area over which it will occur, cannot be made. The boundary conditions needed to initiate this corrosion process are circumstantially linked to the 16- to 18-year storage period in G-yard. The minimum initiation time in G-yard would have been the time required for the cylinder saddle supports to settle sufficiently to establish an oxygenation cell at the bottom of the cylinder. There are no historical data from which to estimate this time, but based on observations of settling in other yards, it probably required a few years rather than a few months. Once initiated, corrosion by this mechanism would no longer be dependent on cylinder location, although the rate could have slowed during extended low-humidity conditions after the move to the upper-level position in K-yard.

The time of actual penetration is also indeterminable. Given that Cylinder 101244 was visually inspected during the move from G-yard, it can be inferred that the breach could not have occurred until after the move to K-yard. (Vapor associated with HF would certainly have been detected if a significant opening existed at the time of the move.) The finding that the contents of the ullage of Cylinder 101244 contained a solution of HF saturated with UF_6 (see Appendix C) indicates that a significant hole had developed much earlier than

December 1991. It is not surprising that it was not detected earlier because of the difficulty of visually examining the extreme bottom of a stacked cylinder, and as discussed in Appendix C, the breach could even have been disguised by a contiguous scale of iron oxide covering the hole. The hole, when discovered in December 1991, was approximately 6 in. diam. Based on examinations of hole growth associated with impact failures,[1] where prior external corrosion was not a factor, a 6-in. hole size in a 5/16-in.-thick cylinder takes about 8 years to develop from the time of the breach. Although this interval matches the storage time in K-yard, the assumption of a 5/16-in. wall thickness at the time of the breach is not valid, given that the failure area of this cylinder had undergone prior wall thinning by external corrosion. As discussed in Appendix C, hole growth in the case of an externally corroded cylinder should be faster than in the case of an instantaneous breach in the cylinder wall. Thus, it can be argued that the breach in Cylinder 101244 must have occurred some time after the 1983-84 move to K-yard, but at least a few years prior to December 1991, to account for the ullage chemistry. A very crude estimate of the time from the onset of external corrosion to the embryonic hole can be derived by adding the median time in G-yard to the median time in K-yard, an interval of approximately 12 years. Based on this time estimate, the average corrosion rate required to breach a 5/16-in. wall is roughly 26 mils/year (0.7 mm/y), a rate that is within the range of that associated with a differential oxygen electrochemical cell.

Assuming that the breach occurred sometime after the move to K-yard, the hole must have enlarged to its 6 in. diam in less time than the 8-year storage period in K-yard. This rate of hole enlargement is faster than that of cylinders where the breaches were induced by through-wall cracks. As discussed in Appendix C, this observation is consistent with external corrosion as the assumed failure mechanism, since general thinning of the wall would have preceded the breach, and growth of the hole would be accelerated due to the reduced volume of surrounding metal.

Cylinder 114951

The breach in Cylinder 114951 was caused by the lifting lug of an adjacent cylinder, which induced a small through-wall crack near a stiffening ring weld. The root causes of the failure were the same as those addressed in a previous investigation of two UF_6 storage cylinders at PORTS,[1] namely, inadequate spacing between cylinders and the deviation of the offending lifting lug from its intended horizontal position. Another key factor was that the offending lifting lug came in contact with Cylinder 114951 exactly at the point where the stiffening ring was welded to the cylinder shell. Because of the constraint of the stiffening ring, any deformation of the shell at this point would cause a tear in the shell, as opposed to a dent if deformation occurs a slight distance away. The hole size at the time of discovery in Cylinder 114951 was slightly larger than the largest hole found at PORTS (Cylinder 4G115688), but the position of the hole, its general shape, and the appearance of reaction products in and around the hole are almost identical. Using a model that was derived to account for the hole growth observed in the two PORTS cylinders, the hole size in Cylinder 114951 is predicted to require an elapsed time of 16 years following the initial breach (see Appendix C). This elapsed time matches very closely the period between the time that Cylinder 114951 was stacked (1976) and the time the hole was discovered (1992). Thus, it can be concluded that the breach in this cylinder was induced at the time of stacking.

Cylinder 116797

Like Cylinder 114951, the breach in Cylinder 116797 was located on the side and resulted from a crack induced by a neighboring lifting lug, which impinged on the area where the shell was joined to an end stiffening ring. The root causes were the same for Cylinder 116797 and for two storage cylinders which had been breached by the same mechanism at the PORTS.[1] The shape and size of the hole were much smaller than in the case of Cylinder 114951 and were almost identical to the smaller-hole PORTS Cylinder (4G127985). However, unlike the PORTS cylinder which had been stored for a period of only 4 years, Cylinder 116797 had been stored for an estimated 14 to 15 years. The correlation between hole size and storage time found for all the other cylinders that failed by the mechanical impingement of a lifting lug would predict the hole to have grown to at least 10 in. If the hole growth in Cylinder 116797 is to fit the model established for these other cylinders (see Appendix C), then the 2-in. hole in this cylinder must have started growing only 4 or 5 years before its discovery. Accordingly, even though it resulted from the impingement of a lifting lug at the time of stacking, the breach could not have fully opened until at least 10 years after this event. The credibility of this postulate can be argued from a recent observation at the PGDP, in which the breach in a mechanically damaged thin-wall storage Cylinder (120037) did not occur until a substantial time after the initial lug impingement. In this case, the cylinder was found to have a small crack near the stiffening ring, which had obviously occurred by impingement of a lifting lug when it was placed in the storage yard several years earlier. Although there was no indication that the crack was open to the UF_6 when it was first discovered, a small leak did develop a few days after the impinging lug was removed. Either the lifting lug causing the crack had occluded the crack from the atmosphere until the cylinder was moved, or the crack was only partially through the wall and was propagated during the move. Since the breach in Cylinder 116797 would have started as a similar-sized crack, a similar explanation can be applied to the delayed start of hole growth. In this case, however, crevice corrosion occurring from the outside could also have contributed to the ultimate propagation of the crack.

Cylinder 7953

A second breached cylinder in K-yard (Cylinder 7593) was discovered 3 months after the first failure, and like the first failure (101244), the breach was located at the extreme bottom (6 o'clock position) toward the plug end. However, the hole in Cylinder 7593 was closer to the center stiffening ring, rather than outside an end stiffening ring as in Cylinder 101244. Cylinder 7953 was a 10-ton model T design which had a longitudinal seam weld at the 6 o'clock position. It was received at PGDP in 1958, was filled twice at PGDP, and shipped both times to K-25. The first shipment was March 1967. It was emptied at K-25, sent back to PGDP, refilled, and shipped again to K-25 in December 1967. It was emptied, refilled, and stored in the K-1066-G yard, most probably in 1968, although the exact date and location in this storage yard cannot be determined. Sometime between 1983 and September 10, 1984, Cylinder 7953 was moved to storage yard K-1066-K to row 5, position 43 (bottom tier). The location was in a low-lying part of the yard where water tended to accumulate following a rain.

As in the case of Cylinder 101244, there are three potential failure modes that can be hypothesized for this cylinder. (See the event-tree analysis in Table 2.) The first mode, mechanical damage to the underside of the cylinder caused during shipment of the cylinder from PGDP to K-25, has a much higher level of probability than was true for Cylinder 101244. Cylinder 7953 was shipped two times from PGDP to K-25 laden with UF_6, and the cylinder was returned empty to PGDP between these shipments. Furthermore, the cylinder had a longitudinal seam weld along the extreme bottom of the cylinder. Failure of a cylinder of this same design (Cylinder 5078) occurred during shipment on a railroad flatcar from PGDP in 1965. The failure resulted from fretting and fatigue of the seam weld on the inside of the stiffening ring where the cylinder had been supported by a steel saddle.[2] The failure had developed as a crack along the fusion line of the seam weld, and similar cracks partially through the wall were seen at the saddle support site at the opposite end of the cylinder. In all cases, cracking was confined to the saddle support sites, and the weld bead in these areas showed deformation markings caused by hammering. In response to this occurrence, seam welds of six other cylinders shipped from PGDP were nondestructively examined, and two of these cylinders gave indications of weld cracks in the areas of the support saddles. The suspect weld areas of one of these Cylinders (8880) were metallographically examined,[3] and the findings were similar to the previously examined failed cylinder. Cracks partially through the wall had formed along the fusion line at both saddle support sites, and the exterior surface of the weld bead again showed deformation attributable to hammering by the support saddles. Notwithstanding the weld cracks, none of the welds examined showed any indications of substandard quality either in terms of penetration depth or micro-voids. Reports covering both examinations cited the deformation of the weld beads by "the steel saddles as the cause of cracking and recommended that the saddles be notched to accommodate the weld bead and allow uniform distribution of the load by placing the cylinder wall in contact with the (full) saddle surface."

Because of the bottom seam weld, Cylinder 7953 would have been susceptible to the same weld cracking mechanism during shipment as exemplified by Cylinders 5078 and 8880. However, the failure in the case of Cylinder 7953 does not fit the pattern shown by these latter cylinders. The hole in Cylinder 7953 appears to have originated at a point that is closer to the midpoint of the horizontal axis than where the support saddle would have been located during shipping. Also, if shipping damage had contributed to the failure, the weld bead at the end of the cylinder away from the failure could be expected to show some evidence of hammering and fretting where it rested on a saddle support, since this was a telltale sign in each of the cases where weld cracks were detected. However, visual examination in the case of Cylinder 7953 gave no indication of any deformation or distress of the longitudinal weld bead, even in the area inside the valve-end stiffening ring where a support saddle should have been located. Finally, the first shipment of Cylinder 7953 (March 1967) occurred several months after the weld cracking problem had been identified (July 1965) and remedial actions recommended (May 1966), and no further weld cracking problems associated with shipping are on record after the 1966 time frame. Accordingly, we could find no direct evidence to support the likelihood that weld cracking during shipping contributed to the failure, but the possibility cannot be absolutely ruled out given that the location of the seam weld corresponds with that of the failure.

The same conclusion can be drawn concerning the second failure mode, namely, handling damage in transporting the cylinder to G-yard and then to K-yard. The location of the failure is well away from a stiffening ring, the most likely area for a crack to occur if a cylinder is impacted. However, a defect in the bottom seam weld could possibly lead to a failure on dropping a cylinder, even under conditions where the cylinder would normally only have been dented. A small dent was, in fact, noted near the bottom (8 o'clock) position of the cylinder.

Recognizing that the bottom seam weld in this cylinder cannot be discounted as a contributor to the failure, the available evidence indicates that external corrosion was the most likely failure cause. In fact, the same arguments that support external corrosion by ground contact as a failure mode in the case of Cylinder 101244 can be applied in the case of Cylinder 7953. The histories of the two cylinders are similar in terms of the respective times of storage in G- and K-yards. Unlike Cylinder 101244, Cylinder 7953 was located in a lower tier in K-yard, and the saddle markings no longer give a clue as to which level the cylinder may have occupied in G-yard. The location in K-yard was in a relatively wet section of the concrete pad, with water standing under the cylinder during and after inclement weather. This may have accelerated the corrosion rate at the bottom of the cylinder during the storage period in K-yard. However, based on the appearance of neighboring cylinders, it is not likely that the exposure time (8 years) and environmental conditions in K-yard were in themselves solely responsible for the failure, and for external corrosion to be the cause of failure, the storage conditions in G-yard must have contributed in large measure to the breach. Because of the unstable condition of the G-yard surface, if Cylinder 7953 had been in a ground-level position in G-yard, the possibility existed for subsidence of the support saddles and eventual ground contact with the bottom of the cylinder.[7] As discussed above for Cylinder 101244 and described in Appendix B, such a condition can accelerate the rate of external corrosion through the process of differential oxygenation corrosion. Examinations at the time of the move from G-yard confirmed that pitting corrosion had occurred on the underside of some cylinders,[6,7] and PGDP has also seen evidence of accelerated corrosion of the undersides of storage cylinders which had been in ground contact.[9]

The 9-in. hole size in Cylinder 7953 is also indicative that external corrosion in G-yard must have preceded the failure. As discussed in Appendix C, this hole size is too large to have been caused by the growth of a breach in a 5/16-in. wall over the 8-year storage time in

K-yard. Accordingly, either the hole must have been present in the cylinder prior to the move from G-yard and not detected, or the wall must have been thinned prior to the move to K-yard, allowing faster growth of the embryonic hole. Either supposition leads to the conclusion that the cylinder was subjected to external corrosion in G-yard. In the case of the first supposition, there is some evidence that the hole may have grown underneath a relatively thick iron oxide scale, which obscured its detection. This evidence is based on the fact that the hole was missed during at least one extensive inspection within a year of its discovery, and the salt deposits under the cylinder appeared to have been exposed to the ambient atmosphere for only a very short period, yet were quite voluminous. Both observations could be explained if a rust covering had remained intact over the hole until shortly before it was discovered. An additional finding supporting the intact rust covering is given by the chemical analysis of the cylinder ullage. As explained in Appendix C, other cylinders with a hole size comparable to the 9 in. diam in Cylinder 7953 characteristically have attained HF concentrations in the ullage which are in equilibrium with a liquid solution of HF saturated with UF_6. Although this was the case for the 6-in. hole in the bottom of Cylinder 114951, the HF concentration in the ullage of Cylinder 7953 was much lower, typical of a cylinder hole which has not been open to the atmosphere.

Although the respective storage times of Cylinder 7953 in G- and K-yards are essentially the same as those of Cylinder 101244, the hole in Cylinder 7953 is larger (9 in. diam) than that in Cylinder 101244 (6 in. diam). As discussed above for Cylinder 101244, the rate of enlargement of a hole that results from extensive external corrosion is difficult to predict, since the rate depends on the volume of metal surrounding the embryonic hole. However, the greater hole size in the case of Cylinder 7953 compared to Cylinder 101244 could be due to (1) external corrosion causing more extensive thinning of the wall of Cylinder 7953 prior to hole formation, (2) hole formation starting earlier in Cylinder 7953, or (3) a faster rate of enlargement of the hole in K-yard for Cylinder 7953. The near-ground location of Cylinder 7953 in a relatively wet area in K-yard supports the latter supposition, particularly after the initial breach had formed and hole growth was driven by the generation of fluoride-containing acids.

As in the case of Cylinder 101244, there is no methodology for accurately determining the time required for the development of the initial breach in Cylinder 7953. Adding the median storage times in storage yards G and K, a period of 12 years, gives a crude estimate, as argued above for Cylinder 101244. However, the position of the hole in Cylinder 7953 is much closer to the center of the cylinder than in the case of Cylinder 101244, so the mechanisms which led to the accelerated external corrosion in G-yard must have been different for the two cylinders. The longitudinal seam weld in the bottom of Cylinder 7953 could also have played a role in the external corrosion mechanism, either as a consequence of a pre-existing weld defect or slight composition differences between the base metal and fusion zone.

3. ASSESSMENT OF ENVIRONMENTAL IMPACT

3.1 ENVIRONMENTAL SURVEYS

In the immediate vicinity of three of the four holes, the sharp biting odor of HF was detectable under the protective tarpaulins employed to prevent further release of solids to the environment; however, the odor was not noticeable a short distance away. HF is typically detectable by the human senses at very low concentrations, and Industrial Hygiene personnel were present to ensure that exposures conformed to acceptable limits. Soil and water samples were taken from the K-1066-K yard drainage route from the two breached cylinders. (See Figure 10 for the location of the sampling sites.) These samples were analyzed for radioactivity and none of the samples were sufficiently radioactive to require any remedial action. These data are reported in Table 3. Sample data from the K-1066-E yard are not available. However, given the similarity in failure mechanisms between the K-25 E-yard and PORTS cylinders, it can be argued that contamination resulting from the E-yard cylinder failures should have been similar to that occurring for the PORTS cylinder failures, which was below 12 picocuries/g.[1]

The amount of the material collected external to the breaches, including UF_6 reaction products and other debris (silt, rust, etc.), is reported in Table 4. The UF_6 reaction products are primarily in the form of UF_4 hydrates. UF_4 has a low solubility in water and is not readily dispersable. The uranium weights listed in Table 4 are not representative of the total amount of uranium released to the environment except possibly for Cylinder 116797, the smallest breach where no reaction products were found on the yard below the cylinder. In addition to the low-solubility UF_4 reaction products, hexavalent state reaction products are also produced, and they are highly soluble in water. These hexavalent state reaction products, including UO_2F_2, would not remain in the proximity of a breach under periodic rain showers.

3.2 URANIUM LOSSES

As was the case in the PORTS cylinder failures,[1] the conversion of UF_6 to UF_4 at the hole site acted as a barrier to prevent the loss of UF_6 to the environment. However, without measurements of the present cylinder weights, the extent of uranium loss from the four breached cylinders at the K-25 Site cannot be determined at this time. In the case of

Table 3. Analyses of Soil and Water Samples from K-1066-K yard

Sample Site	Type of Analysis	Result	Units
SOIL #1	Total Activity[*]	-40.8 ± 92.3	picocuries/g
SOIL #2	Total Activity[*]	-91.5 ±, 110	picocuries/g
SOIL #3	Total Activity[*]	-64.3 ±, 83	picocuries/g
WATER #1	Total Activity[*]	-938 ± 1800	pircocuries/L
WATER #2	Total Activity[*]	-847 ± 1800	picocuries/L
WATER #3	Total Activity[*]	-1440 ± 1800	picocuries/L
SOIL #1	Uranium Fluorometric[†]	25 ± 2 36 ± 2	µg U/g µg U/g
SOIL #2	Uranium Fluorometric[†]	3 ± 0.2 3 ± 0.2	µg U/g µg U/g
SOIL #3	Uranium Fluorometric[†]	8 ± 0.4 9 ± 0.4	µg U/g µg U/g
WATER #1	pH Fluoride[‡] Uranium Fluorometric[†]	7.8 ± 0.2 0.6 ± 0.03 0.36 ± 0.02 0.32 ± 0.02	 mg F^{-1} /L mg U/L mg U/L
WATER #2	pH Fluoride[‡] Uranium Fluorometric[†]	7.9 ± 0.2 0.6 ± 0.03 0.37 ± 0.02 0.36 ± 0.02	 mg F^{-1} /L mg U/L mg U/L
WATER #3	Uranium-235 Uranium Fluorometric[†]	0.29 ± 0.01 0.220 ± 0.011	weight % mg U/L

[*] Range around background mean.
[†] Accurate to ± 5% of value.
[‡] Precision/accuracy is ± 0.03 mg F^{-1}/L at determined value.

Table 4. Materials Collected External to the Breached Cylinders

Cylinder Number	Total weight of material collected, kg	Uranium contents of materials collected, kgU
101244	Not Available	0.160
114951	11.8	1.8
116797	0	0

cylinders 114951 and 116797, rough estimates of uranium lost to the environment can be derived from the calculated losses for the PORTS breached Cylinders 115688 and 127985, respectively. Breaches in Cylinders 114951 and 115688, are similar in size to those in the respective PORTS cylinders and appear to have been exposed to the environment for similar durations. The estimated uranium loss from the PORTS Cylinder 115688 was in the range of 17 to 109 lb UF_6.[1] The hole size of Cylinder 114951, by comparison, is a little larger than Cylinder 115688, and based on the correlation of uranium lost to hole size for mechanically induced breaches, Cylinder 114951 may have lost a larger quantity of uranium than the calculated estimates for PORTS Cylinder 115688 (see Appendix C). By comparison to calculations made for PORTS Cylinder 127985, where the hole size was approximately 2 × 4 in.,[1] Cylinder 116797 may have released on the order of 0 to 4 lb UF_6. Again, these values for the two K-25 breaches in K-1066-E yard are provided only as a comparison to the PORTS experience and not as calculated values for material loss estimates. Because of the dissimilar failure mechanisms for the two K-1066-K yard hole failures, the lack of weight data, and inexperience with cylinders that have bottom holes, no estimate of the amount of uranium released to the environment can be made at this time.

3.3 PRESENT AND FUTURE ENVIRONMENTAL IMPACT

It is likely the three larger hole Cylinders (101244, 114951, and 7953) have leaked several kilograms of uranium and fluoride to the environment, but based on the PORTS investigation and K-yard survey, not enough to be an apparent hazard in the yards at the time of discovery. There was some runoff across the K-1066-K yard concrete pad into an area of soil identified as the drainage point from the two breaches discovered in this yard. The amount of radioactivity detected from this area was below that requiring remedial actions. In the absence of K-1066-E yard environmental surveys, it cannot be determined if contamination did reach the soil. However, sampling data obtained in 1994 show no residual radioactive contamination in the surface soils or surface waters surrounding the K-1066-E yard.[10]

The absence of external uranium-containing deposits in the case of Cylinder 116797 confirms the conclusion reached in the PORTS investigation[1] that the environmental impact of a mechanically-induced cylinder breach can be greatly minimized if it is detected early. During early stages of hole growth (up to 2-4 inches), the exposed area of UF_6 is separated and protected from the environment by a relatively insoluble UF_4 layer. The hole in

Cylinder 116797 was approximately 2-in. in diam and is estimated to have grown over a 4-5 year period. Accordingly, visual inspections geared to detection of holes within this period, as recommended in the PORTS investigation report[1], were effective in limiting the potential uranium loss from this cylinder.

As discussed in the September 1991 report,[1] an incident involving a single cylinder might be postulated from present limited experience that would involve the generation of a large hole near the top of a cylinder and the accumulation of a large amount of water in the vessel. Another possibility is that cylinders in which external wall thinning has occurred could be breached in a relatively short time frame. Because of wall thinning prior to hole initiation, the growth of the hole caused by exposure of UF_6 to the environment would be faster than otherwise would occur. This and other possible events require safety analyses to evaluate their consequences.

4. IMPLICATIONS OF FAILURES ON PRESENT STORAGE PRACTICES

The investigating team provided a discussion on the implications of failures on present storage practices at the three storage sites in the September 1991 report.[1] An assessment of cylinder design faults, the potential existence of additional failed cylinders, the potential effects of failures on integrity of neighboring cylinders, and a general assessment of cylinder integrity for long-term storage was provided. The following section of this report provides an update of these topics based on the added findings from the present investigation.

4.1 POTENTIAL EXISTENCE OF ADDITIONAL FAILED CYLINDERS

Since the September 1991 report[1] was published, thorough visual inspections at the three sites have been completed providing greater assurance that large, visible breaches are not present in the storage yards today. These baseline inspections have provided extensive information detailing the physical conditions of all cylinders in long-term storage. The results of these inspections are documented, and a database is being established in order to utilize this information as a management tool to guide the direction of the Cylinder Management Program. However, these inspection data are limited as a result of storage conditions present at all three sites that prohibit the full visual inspection of all cylinder surfaces. These conditions include the lack of adequate aisles between cylinders required for inspection access and cylinders in ground contact, preventing visual inspection. The cylinders in ground contact appear to present the greatest potential for sizable breaches and significant quantities of uranium and fluoride releases. These cylinders should be removed from ground contact as soon as possible, thoroughly inspected for containment integrity, and either replaced or refurbished to arrest further corrosive damage.

Concerns were expressed in the September 1991[1] report from the investigation of failed Cylinder 127985 regarding a specific population of cylinders in long-term storage. These concerns expressed the need to provide increased surveillance of physically damaged cylinders from a population manufactured using a particular heat of A516 steel known to contain sulfide inclusions. This investigation has resulted in adding another specific population of cylinders where increased surveillance is necessary. The failure analysis of Cylinder 7953 and other previously failed model T cylinders that have been transported by railcar established the concern of weld damage promoting the likelihood of breaches. This particular thin wall cylinder model was manufactured with the longitudinal weld at the 6 o'clock position, making the weld susceptible to mechanical damage during transport and/or corrosive damage during storage. Approximately 4,200 model T cylinders were purchased in the 1950s and are presently distributed among the three sites. Special attention should be given to the weld integrity of the model T cylinders, if they are expected to continue serving as storage vessels for UF_6.

The failure at PGDP and the two K-25 Site cylinder failures resulting from mechanical impact increase the significance of the PORTS findings that cylinders suffering impingement by neighboring lifting lugs can lead to cylinder breaches. K-25 Cylinder 116797 and the PGDP failure, 120037, are evidence that a failure can occur from a combination of failure mechanisms: mechanical impact establishing partial wall thickness tearing and corrosion, or other mechanisms for crack growth completing through-thickness fracture. Consideration should be given to special surveillance of all cylinders mechanically damaged near non-yielding welds.

4.2 STORAGE DESIGN IMPLICATIONS

Three circumstances were apparent from the failed cylinders at the K-25 Site that can be attributed to or corrected by improving the saddle design. Cylinder 7953 in K-1066-K storage yard was positioned on wooden saddles that were butted against neighboring saddles. In the path of rainwater runoff, these saddles dammed water extending the time-of-wetness on the lower regions of the cylinder surface where the failure occurred. Circumstances where saddles are butted together preventing ready runoff of rainwater should be identified and corrected to reduce cylinder time-of-wetness. Other cylinder placement factors associated with K-25 Site failures include the cylinder-to-cylinder spacing within rows of cylinders. Failed Cylinders 114951 and 116797 in K-1066-E storage yard were impacted by adjacent cylinder lifting lugs which contributed to the onset of failure. A factor in permitting these cylinders to be adversely impacted was the closeness of their stacking, which is determined by the saddle length and placement. Administrative and physical controls should be thoroughly reviewed regarding use of saddles, and improvements should be developed to strictly control the proper spacing of cylinders and facilitate yard drainage.

The investigating team also noted that there may be adverse corrosion effects of wooden saddle contact with cylinders. Many cylinders in K-1066-K yard revealed evidence of previous contact with saddles in the form of accelerated corrosion at the points of contact. It is not known whether this is a generic concern of wooden saddle contact with cylinders, or if the saddles facilitated accelerated corrosion because the cyclinders were in or near ground contact, i.e., K-1066-G yard storage. Previous studies of various saddle materials show that the creosote wooden saddles do not, in themselves, provide a worse corrosive environment compared with other saddle materials.[11] However, it is possible that the wooden saddles may act as a wicking device, drawing water from the ground surface to the cylinder and locally extending the time-of-wetness around the contact point. Studies should be conducted to determine the effects on cylinder integrity from long-term saddle contact in order to better understand the conditions imposed on cylinders.

In addition, lessons learned can be established from the two failed cylinders in K-1066-K yard where cylinders should be kept clear of collective drainage routes that may retain water over extended periods and extend the time-of-wetness on cylinder surfaces. Yards should be designed and constructed to minimize time-of-wetness of cylinders. Consideration should be given to relocation of cylinders in existing yards where conditions do not permit adequate drainage.

5. ADDITIONAL ACTIONS REQUIRED TO COMPLETE INVESTIGATION

Additional actions are necessary to support the investigation team's conclusions. Table 5 lists the additional actions required by K-25 Site Operations staff to complete the subject investigation. The investigation team requests that it be kept informed of the schedule that the K-25 Site will follow in completing these actions. The team will address the findings from these actions and issue an addendum report if required.

Table 5. Additional Actions Required to Complete Investigation of K-25 Failures

Action
• Obtain cylinder weights of four failed cylinders.
• After emptying four breached cylinders of UF_6, visually inspect and weigh reaction products which plugged the hole, and examine cylinder to establish distribution of heels.
• Analyze above reaction products to determine U and F concentrations.
• After decontamination, retrieve representative sample from bottom longitudinal weld of Cylinder 7953.
• Map wall thicknesses of Cylinders 115017 and 114921 affected by the breach in Cylinder 114951.

6. CONCLUSIONS

Four failed cylinders were found breached at the Oak Ridge K-25 Site, one in December 1991, two in January 1992, and one in March 1992. An analysis was completed to assess the failure causes.

Two of the failures that occurred were similar to those which had previously occurred at PORTS and were induced by mechanical damage at the time of stacking. In both cases, the breaches were caused by a lifting lug of an adjacent cylinder which induced a small crack near a stiffening ring. The initial small crack in Cylinder 114951 is believed to have been through-wall, allowing the environment to begin hole growth immediately. However, the initial crack in Cylinder 116797 is believed to have been only partially through-wall, requiring external corrosion or mechanically-induced crack growth to complete the through-wall breach. The root causes for these failures were the same as those indicated in the previous investigation of the failures at PORTS,[1] i.e., inadequate spacing between cylinders and a deviation of the offending lifting lug from its intended horizontal position.

The causes of the failures of the other two cylinders in K-yard have been more difficult to determine. Both mechanical damage and corrosion mechanisms were considered, but the strength of evidence appears to point to external corrosion as the principal factor in causing the breach. Contact of these cylinders with the ground for long periods during storage is suspected to have resulted in accelerated corrosion due to an electrochemical process.

7. RECOMMENDATIONS

1. Cylinders currently in or near ground contact should be removed from these locations and thoroughly inspected. Measures should be taken to arrest corrosive attack before placing these cylinders back into long-term storage.

2. Criteria to evaluate the extent of corrosion damage and means to employ these criteria should be established to enable the identification of cylinders that no longer meet routine handling requirements and those that are no longer suitable for continued storage. Handling and storage procedures for substandard cylinders should be established. An evaluation of the safety concerns regarding continued storage (stacking and handling) of these cylinders should be an integral part of the development of these procedures.

3. Special surveillance and integrity evaluations of the longitudinal weld regions should be given to thin-walled cylinders with longitudinal welds at the 6 o'clock position that, in the past, have been shipped by railcar.

4. Special surveillance and integrity evaluations of visibly corroded areas (heavily scaled or pitted) should be given to the K-25 cylinders previously stored in K-1066-G yard. These cylinders should be identified and managed as if they had experienced significant wall thinning until they have been thoroughly evaluated.

5. As recommended in the PORTS failure report,[1] particular attention during cylinder inspections should be given to impact areas near non-yielding welds to ensure early detection of potential breaches.

6. Storage yards should be designed and constructed to minimize time-of-wetness on cylinder surfaces. Consideration should be given to relocation of cylinders in existing yards where conditions do not permit adequate drainage or where cylinders are exposed to excessive wetness.

7. Studies should be conducted to determine the effects on cylinder integrity of long-term saddle contact which may act as a wicking device to draw water from the ground surface.

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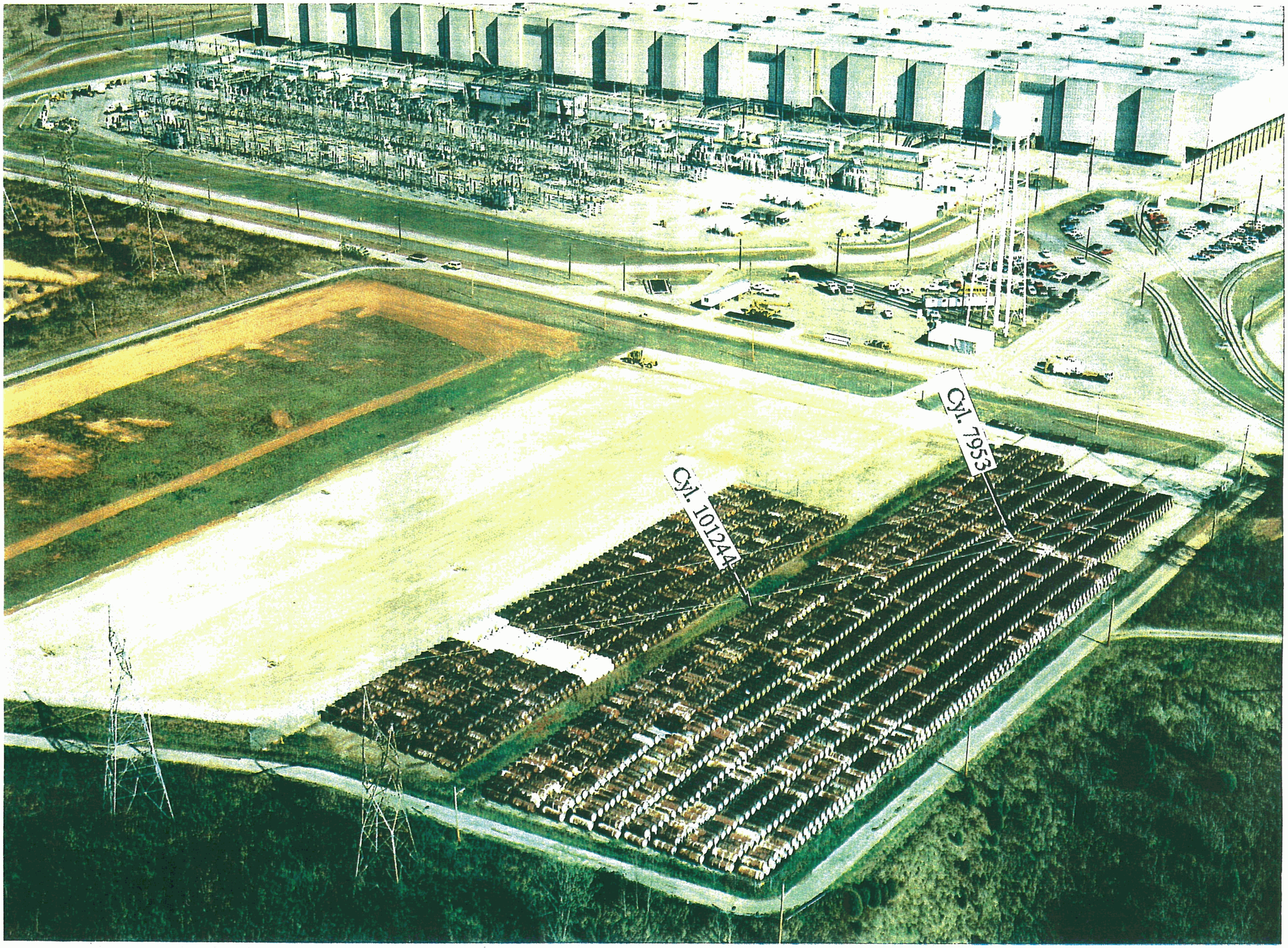

Fig. 1. K-1066-K yard. Photograph illustrates locations of failed Cylinders 101244 and 7953.

Fig. 2. K-1066-E yard. Photograph illustrates locations of failed Cylinders 114951 and 116797. Note the path of rust from breached Cylinder 114951.

Fig. 3. Breached Cylinder 101244 in stacked position as discovered. Note the three significant pits between the breach and the cylinder head weld.

Fig. 4. Breached Cylinder 114951 after neighboring cylinders have been relocated.

Fig. 5. Cylinder 115017 after being relocated. Note the extensive wastage of the lifting lug. This lug is believed to have mpacted and caused the breach in Cylinder 114951. Also note the cylinder wall wastage - an effect of corrosive materials released rom breached Cylinder 114951.

Fig. 6. Cylinder 114921 after being relocated. Note he corrosive attack from HF released from breached ylinder 114951. Cylinder 114921 was stacked on the econd tier directly above the breach in Cylinder 114951.

Fig. 7. Breached Cylinder 116797. Photograph taken after neighboring cylinders were relocated.

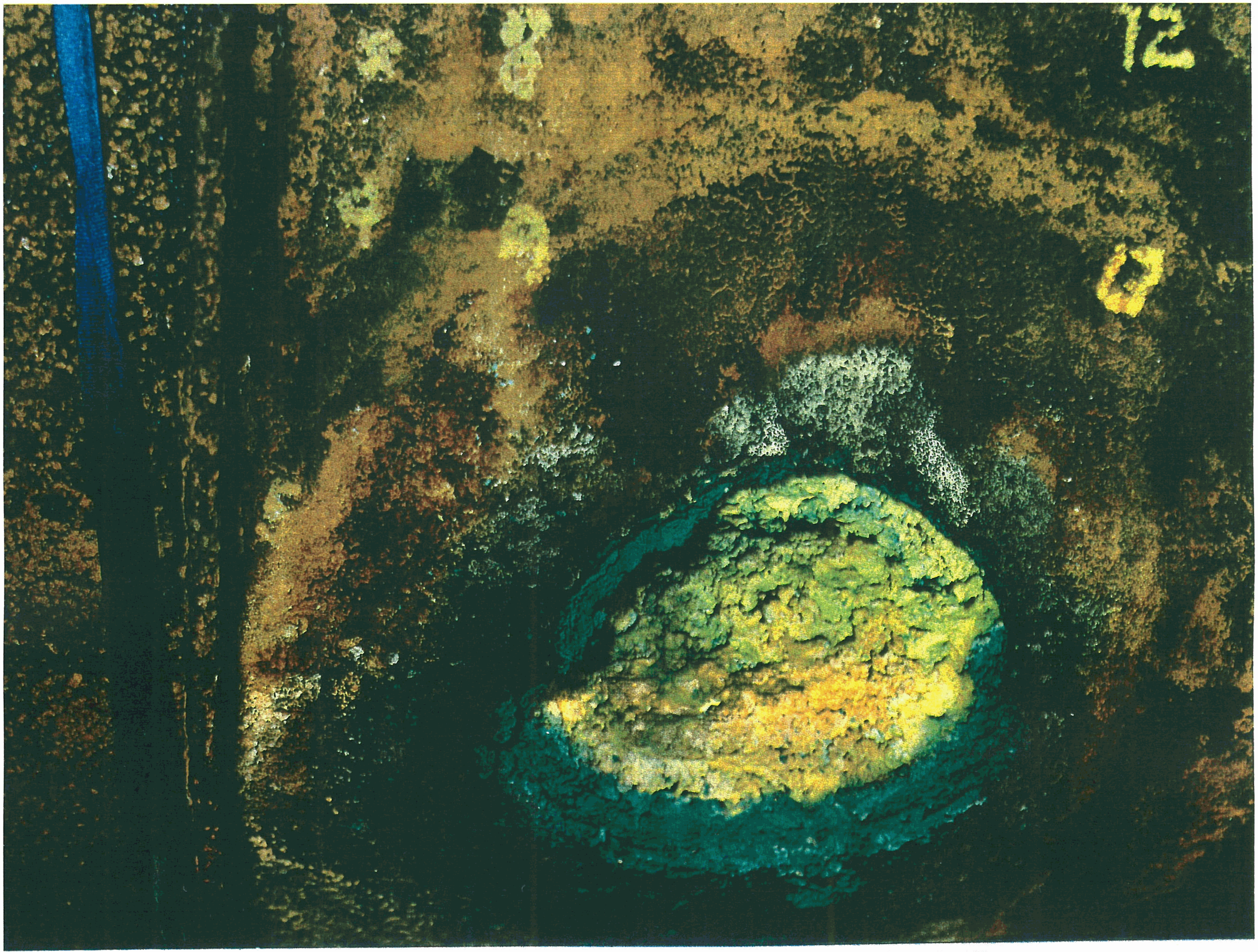

Fig. 8. Breached Cylinder 7953 after being relocated and turned approximately 45°.

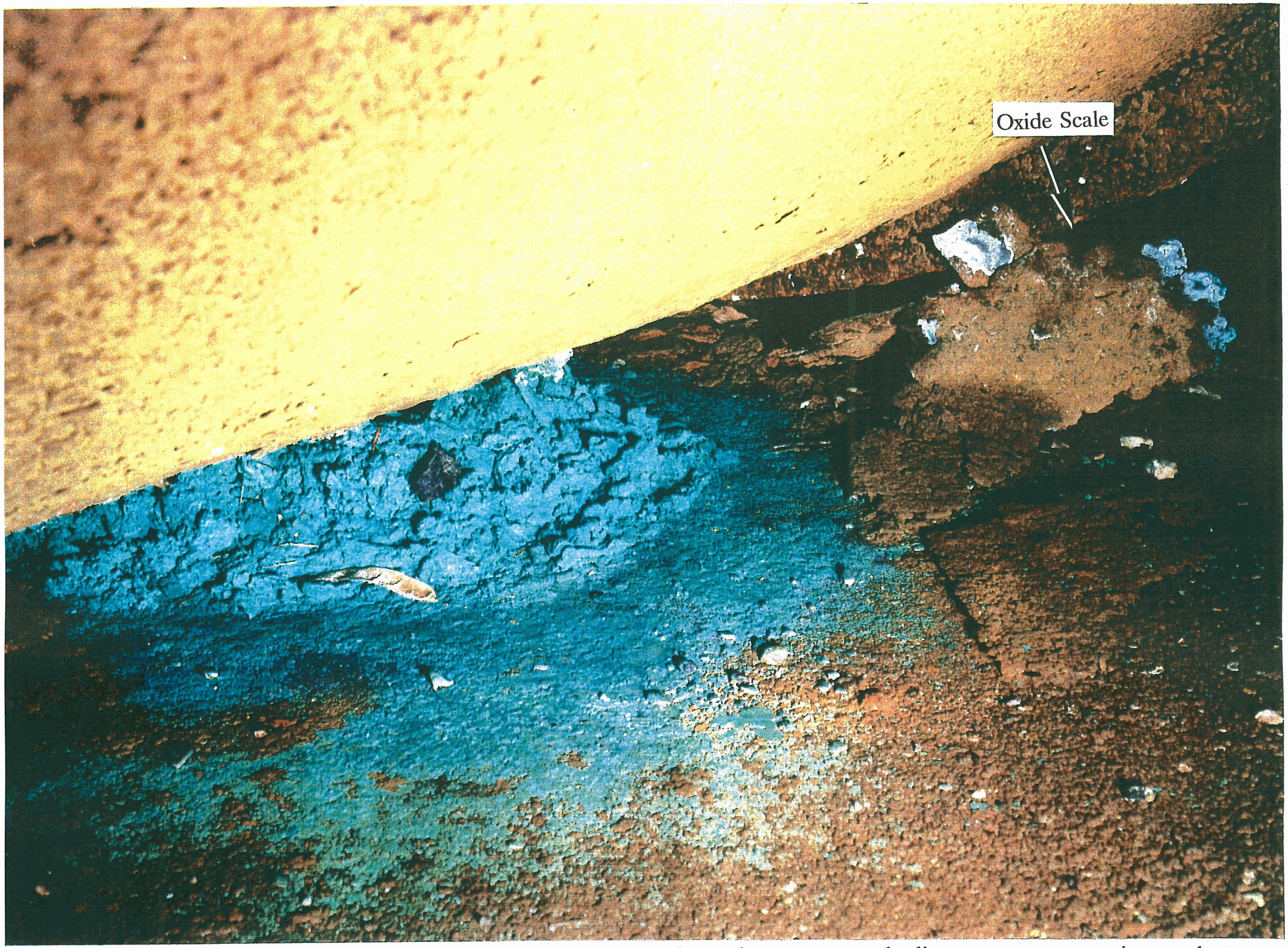

Fig. 9. Breached Cylinder 7953 as discovered. Note iron oxide scale on the concrete pad adjacent to green reaction products.

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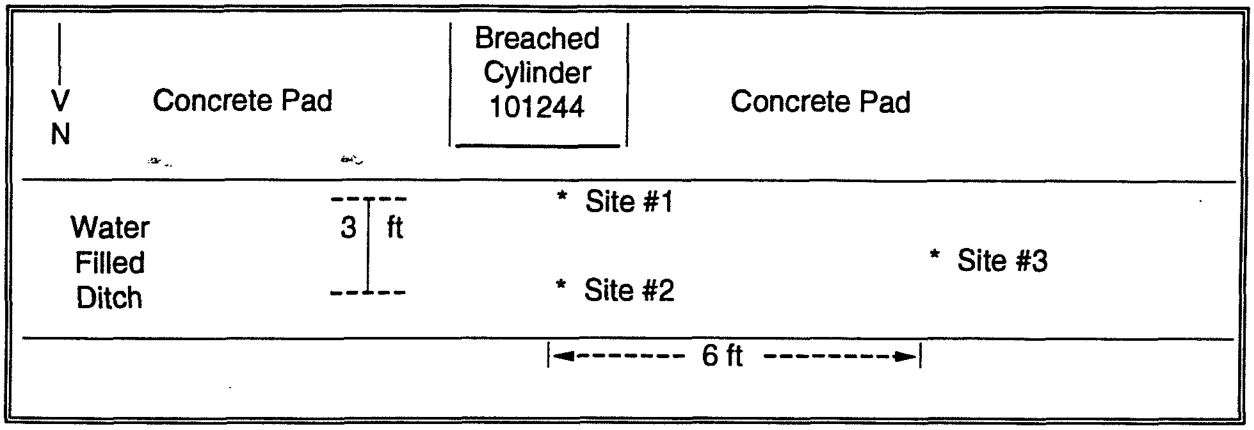

Fig. 10. Location in K-1006-K yard from which soil and water environmental samples were taken.

APPENDIX A

Breached Cylinders Design Specifications and Contents

Table A-1. Cylinder Design Specifications

Item	Cyl. #7953	Cyl. #101244
Cylinder Model	T	OM
Drawing No.	D-S-10137 REV 5	E-S-10313-F REV 2
Specification No./ Mfg. No.		2444
Manufacturer	J. B. Beaird	Trinity Steel
Fabrication Date	1958	1963
Steel Type	A285	A285
Design temp.° F.	235	235
Design pres. psig	100	100
Tare Wt.	2.468	2.580

Table A-1. Cylinder Design Specifications

Item	Cyl. #114951	Cyl. #116797
Cylinder Model	OM	OM
Drawing No.	E-S-12292-A REV 8	E-S-12292-A REV 9
Specification No./ Mfg. No.	3831	5677
Manufacturer	Modern Welding	Modern Welding
Fabrication Date	1975	1976
Steel Type	A285	A285
Design temp.° F.	235	235
Design pres. psig	100	100
Tare Wt.	2.610	2.538

Table A-2. Cylinder Contents

Item	Cyl. #7953	Cyl. #101244
Fill Date		
U^{235} assay, $\%U^{235}/U$	.002613	.001893
U content. %U		
Initial net wt., lbs.	27954	27752
Present gross wt., lbs.	30564	30290

Table A-2. Cylinder Contents

Item	Cyl. #114951	Cyl. #116797
Fill Date		
U^{235} assay, $\%U^{235}/U$	.002470	002613
U content. %U		
Initial net wt., lbs.	27954	27752
Present gross wt., lbs.	30564	30290

APPENDIX B

MECHANISMS OF ACCELERATED EXTERNAL CORROSION

Examination of Cylinders 101244 and 7953 suggests that when these cylinders were stored in G-yard, they had sunk a few inches into the ground. In a wet climate such as exists in East Tennessee, this permits setting up an electrochemical process called "differential oxygenation corrosion" in which the area with the more limited oxygen concentration corrodes much more rapidly than the areas where the concentration of oxygen is normal.[1,2] Once this type of corrosion is started, it can be successfully arrested only by cleaning off the rust from the cylinder surface or by storage in a controlled, low relative humidity (<40 % RH) atmosphere. This occurs because the oxidation product of steel forms an adherent, somewhat porous oxide coating (rust) which continues to serve as a diffusion barrier for oxygen even after the cylinder is removed from the mud. Whenever this coating is moist from high humidity, dew, or rain, the corrosion process continues at the relatively higher rate.

The differential oxygenation process proceeds by the reaction between iron and water to form hydrous iron oxide and hydrogen, as shown in Eq. (B-1).

$$2\ Fe + 4\ H_2O = 2\ Fe\ O(OH) + 3\ H_2\ . \qquad \text{(B-1)}$$

The discharge of hydrogen gas upon Fe is limited by a high overvoltage, so this reaction without a depolarizer would be extremely slow. Atmospheric oxygen, which reacts readily with atomic hydrogen to convert it back to water, serves as the depolarizer, but the generation of atomic hydrogen is itself normally a very slow process since the hydrogen ion concentration in water is only 10^{-7} M. However, if one limits the access of the oxygen to an area while leaving essentially unlimited access to the remainder, what may be viewed as an oxygen concentration cell is created as long as a film of liquid water is present to serve as a conductor. The area to which the oxygen is more readily available serves as the cathode at which the basic reaction is:

$$O_2 + 4\ H^+ + 4\ e = 2\ H_2O\ , \qquad \text{(B-2)}$$

and the area with the limited oxygen access is the anode where the basic reaction is:

$$\mathrm{Fe} = \mathrm{Fe}^{+3} + 3\ \mathrm{e}\ . \tag{B-3}$$

The total reactions at the cathode and anode needed to balance the chemical equation are:

$$\text{Cathode Reaction: } 3\ \mathrm{O}_2 + 12\ \mathrm{H}^+ + 12\ \mathrm{e} = 6\ \mathrm{H_2O}\ , \tag{B-4}$$

and

$$\text{Anode Reaction: } 4\ \mathrm{Fe} + 12\ \mathrm{H_2O} = 4\ \mathrm{Fe(OH)_3} + 12\ \mathrm{H}^+ + 12\ \mathrm{e}\ . \tag{B-5}$$

Summing Eqs. (B-4) and (B-5) gives the overall reaction which is occurring at the anode, since that is where the iron is being attacked, and is shown as Eq. (B-6). The $Fe(OH)_3$ readily loses water forming FeO(OH), the gamma modification of which is rust or lepidocrocite:

$$3\ \mathrm{O}_2 + 4\ \mathrm{Fe} + 6\ \mathrm{H_2O} = 4\ \mathrm{Fe(OH)_3}\ . \tag{B-6}$$

Setting up the differential oxygenation cell significantly increases the rate of attack in the anodic area. The requirement for a water film indicates that the bottom of the cylinder would be the favored position for this type of attack to occur, although the bottom of pits and crevices would also be preferred above any surrounding flat surface area.

Another mechanism for accelerated degradation of steel in contact with soil relates to microbiological corrosion, resulting from the activity of microorganisms or bacteria.[2] The class of bacteria most associated with underground corrosion is that which reduces sulfate ions to hydrogen sulfide. This class is active only under anaerobic conditions. Other types of bacteria are active under anaerobic conditions and usually oxidize organic material to organic acids or sulfur to sulfuric acid. Microbiological corrosion produces no new forms of corrosion; it is primarily metabolic products of the bacteria that cause corrosion. With both aerobic and anaerobic bacteria, carbonaceous material must be present to sustain the colony of microorganisms. Steel structures most likely to be affected by microorganisms are those in soils essentially devoid of oxygen that contain appreciable concentrations of sulfate ions.

Sulfate ions are reduced to hydrogen sulfide which, on reaction with steel, suppresses its potential low enough for the cathodic process to become the reduction of water molecules to hydrogen. The bacteria use the hydrogen to reduce sulfate ions, which in turn depolarizes the cathodic reaction and increases the corrosion rate. Generally, the soils in the Oak Ridge area are low in sulfate salts, and soil-induced microbiological corrosion has not been a recognized problem.

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[1] S. Glasstone, "The Deposition and Corrosion of Metals," Chapter XIV, *An Introduction to Electrochemistry*, D. Van Nostrand Company, Inc., New York, 1942; 498-502.

[2] Private communication from John Griess to J. H. DeVan, August 1993.

APPENDIX C

ANALYSIS OF CHEMICAL EFFECTS

The discovery of breaches in four cylinders at the K-25 Site and one developing in a cylinder at the Paducah Gaseous Diffusion Plant (PGDP) has provided an opportunity to observe the chemical behavior at breaches with orientations both different from and essentially identical to the orientations of the breaches in the two cylinders at the Portsmouth Gaseous Diffusion Plant (PORTS).[1] The observations and tests performed on these cylinders have been compared with the scenario developed from the PORTS data to determine what modifications, if any, might be necessary. To make this analysis requires both general observations about the cylinder history, what the breaches looked like, and what materials have been generated both externally and internally to the breach and, to the extent possible, their current locations. Recognition that one is dealing with quasi-steady state conditions and not equilibria is also necessary, since this may impose severe restraints on the possibility of obtaining the correct identification of products which tend to change quickly if they are removed from the particular environment in which they are formed. The major purpose of this section is to present the observations and findings of the investigating team relative to the similarities and differences in the failure mechanisms and subsequent enlargement of the breaches at the K-25 Site and at PORTS.

Appearance of the Uranium- and Iron-Containing Reaction Products Around the Failure Areas

Cylinder 101244

This model OM thin-wall (5/16-in.) cylinder had an approximately 6-in.-diam. hole located in the 6 o'clock on the plug side of the stiffening ring. Separable yellow and green lumps of material, which would be indicative of a mixture of $FeF_3 \bullet 3H_2O$ (yellow) and UF_4 hydrate (green), had fallen onto the support saddles leaving an internal dome-like void which was bright yellow at the top with a layer of green material forming the base of the hemisphere. The analysis showed that the fallen deposit contained 0.160 kg of uranium and that the assay was 0.2% U-235.

Cylinder 114951

This model OM thin-wall cylinder was determined to have a hole approximately 8 to 12 in. wide by 15 to 17 in. long extending beneath the valve-end stiffening ring in approximately the 4 o'clock position. A total of 26 lb (11.8 kg) of material, which was mostly dirt and gravel but contained about 1.8 kg of U, was scooped up from beneath the hole.

Based on the color, the uranium was present largely as UF_4 hydrates. The radioactivity of the material was estimated to be 0.0009 curies, well below the reportable value of 0.1 curies. The acid odor of escaping HF was detectable in the vicinity of the breach.

Cylinder 116797

This model OM thin-wall cylinder had a small 2-in. hole just beyond the stiffening ring closest to the valve end of the cylinder at the 9 o'clock position. No material had fallen off the cylinder to the ground at the time of the discovery of the breach.

Cylinder 7953

This 10-ton model T thin-wall (5/16-in.) cylinder had a large, 9-in.-diam. hole in the 6 o'clock position near the middle stiffening ring on the side toward the plug end of the cylinder. The appearance of this hole was that of a larger version of the hole in Cylinder 101244. The same layered structure visible in the corrosion deposits surrounding the large hole in the cylinder at PORTS is present around the holes in Cylinders 102144, 114951, and 7953. When the green UF_4 hydrate and the supporting rust and iron fluorides fell out of the hole in Cylinder 7953, a bright yellow hydrolysis product was left exposed. The material which had fallen out of the cylinder did not show evidence of dispersion (no grit or other debris on the UF_4) in spite of the fact that the cylinder was located in a drainage path for water on the pad. This may indicate that the material fell from the cylinder only shortly before the breach was discovered. The recovered material (mostly mud and gravel) weighed 21.6 lb (9.8 kg) and contained 2.2 kg U largely as UF_4 hydrates based on the color.

Chemical Analysis of the Ullage Vapors and Typical Solid Deposits

Samples were taken from the gas in the cylinder ullage and from the solid deposits in and around the breaches in Cylinders 101244 and 7953 in K-1066-K storage yard. Both breaches were in the 6 o'clock position. Samples of the solids were not taken from the other two cylinders because the deposits appeared to be identical to those in the breaches of the sampled cylinders at K-25 Site and at PORTS. The pressure within the ullage of Cylinder 101244, the ambient air temperature, and an approximation of the UF_6 cake temperature were taken over a period of time to examine possible relationships. The behavior of the cylinder ullage pressure before, during, and following the removal of the vapor from the ullage of Cylinder 101244 to an evacuated cylinder was also followed. The cylinder valve of Cylinder 101244 developed leakage problems. For this reason, the study was not repeated with Cylinder 7953.

Composition of the Ullage Vapor. Duplicate samples of the vapor in the ullage of the breached Cylinder 101244 were taken in June 5, 1992, and a similar pair of samples were taken from the ullage of breached Cylinder 7953 around September 9, 1992. The volume of the sample vessels was 750 mL. These were analyzed by D. A. Harkins using a Fourier transform infrared spectrometer (FTIR).[2] When the ullage of Cylinder 101244 was sampled, the ambient temperature was 77° F, the temperature of the outside bottom of the cylinder was 79° F, and the temperature of the top of the cylinder was 120° F. The total pressure of the cylinder ullage at the time of sampling was about 21.7 psia. Harkins estimated that the initial pressure of the samples from Cylinder 7953 was 16.7 ± 2 psia. The results of the analysis are given in Table C-1.

Harkins[2] indicates that the CO_2 and the SiF_4 may be artifacts of the analysis, although CO_2 is present in air at 0.033 mol %. The CO_2 and the SiF_4 were not seen in the ullage vapors from the two cylinders at PORTS as determined by mass spectrometric and gas chromatographic analyses. The weights of the samples indicate that a condensed phase in addition to vapor was collected in all samples, but much more condensed material was collected in the samples from Cylinder 101244. The anticipated weight of the samples for a vapor phase only is on the order of 3 g.

In spite of the difficulties with the analyses, the measured partial pressure of HF in the samples from Cylinder 7953 of about 210 torr shows that the association factor of HF at the FTIR measurement temperature of 25° C is 1.03 and that the vapor pressure of HF in the ullage of Cylinder 7953 cannot be the pressure of HF over a solution of HF saturated with UF_6 at the UF_6 solid (s) temperature of 65.5° F. On the other hand, the analytical results and the large amount of condensate in the samples from Cylinder 101244 indicate the presence of such a solution of HF saturated with UF_6 in the ullage of this cylinder. This conclusion is further supported by the extensive pressure and temperature measurements on Cylinder 101244 presented next.

Measured Pressures and Temperatures for Cylinder 101244. Measurements of the pressure of the vapor space of Cylinder 101244 and the ambient temperature were recorded beginning 1/22/92 through 7/21/92. Additionally, temperatures of the top and bottom of the cylinder were measured with both an insulated and an uninsulated thermocouple (TC) for the

Table C-1. Fourier transform infrared spectrometric analysis of the ullage contents of Cylinders 101244 and 7953

	Cylinder 101244		Cylinder 7953	
Species	Sample No. 1 composition mol %	Sample No. 2 composition mol %	Sample No. 1 composition mol %	Sample No. 2 composition mol %
UF_6	6.9*	4.7*	8.3†	8.3†
HF	53.2	43.2	23.6	24.8
CO_2	1.5	0.9	0.76	0.68
SiF_4	0.06	0.08	0.02	0.02
Air‡	38.34	51.12	67.32	66.20
Sample weights, g	37.0	35.9	8.5	8.7

*There is difficulty in transferring UF_6 from high to low pressure without condensation; thus, the higher value is taken as correct. The pressure of UF_6 is 1.50 psia which is the vapor pressure of UF_6(s) at 67.5°F. The mean temperature of the cylinder bottom for the period from 12 noon 6/04/92 to 12 noon 6/05/92 was 65.3°F.

†The pressure of UF_6 is 1.39 psia which is the vapor pressure of UF_6(s) at 65.5°F. This suggests that the two cylinders were sampled under quite comparable conditions.

‡The N_2 and O_2 in air, being homopolar molecules, do not have infrared spectra. The concentrations given are obtained by difference. This residual air was introduced into the storage cylinders to facilitate filling.

first time on 3/19/92 and then hourly from 4/15/92 through 7/21/92. The pressure of the ullage was read daily around 2 p.m. Between 06/12/92 and 06/16/92, the accumulated HF solution was removed from the ullage by intermittent evacuations to another initially empty cylinder of the same volume. Since vaporization of the HF solution removed heat, the surface would cool and the vapor removal rate would become very slow, requiring interruption of the process to allow temperature and pressure recovery. The pressure would recover in a period of hours after an evacuation until all the HF solution was finally removed on 06/16/92, after which the pressure built back only slowly over a period of weeks. The latter observation is suggestive that HF continues to be slowly generated, a condition entirely consistent with the scenario developed for the breaches in the PORTS cylinders.[1] Table C-2 lists dates and the ambient temperatures, the shielded top and bottom temperatures of the cylinders, and the ullage pressures observed on these dates. From 07/21/92 to 08/27/92, only the ullage pressures were

Table C-2. Measurement dates, bottom temperatures of cylinder, top temperatures of cylinder, ambient temperatures, and ullage pressures for Cylinder 101244

Date	Temperature of Bottom, °F	Temperature of Top, °F	Ambient Temp., °F	Pressure in Ullage, psia
03/19/92	63	105.0	60	16.2
04/20/92	71.5	102.2	77.4	21.7
04/21/92	65.8	74.7	67.4	18.7
04/22/92	71.6	108.5	73.8	19.2
05/13/92	75	109	72.8	20.7
05/14/92	82	127	80.0	22.7
05/15/92	84	122	80.0	22.7
05/18/92	81	91	71.5	19.7
05/19/92	81	90	71.5	19.2
05/20/92	72	73	66.7	17.2
05/26/92	75	99	67.9	17.7
06/01/92	66	81	64.5	17.7
06/05/92	79	120	77.0	21.7
06/12/92 to 06/16/92 --removed HF solution from ullage				
06/12/92				<u>before</u> <u>after</u>
13:35	72	79	68	18.2 <=== 1.5
14:40	73	84	70.3	17.7 <=== 1.7
15:35	73	83	70.3	17.2 <=== 2.5
06/15/92				
8:40	70	73	65.6	17.8 <=== 2.5
10:55	81	99	72.8	11.8 <=== 7.1
15:00	90	131	83.2	14.7 <=== 7.1
15:30	90	130	84.1	13.5 <=== 7.8
06/16/92				
9:00	73	75	67.9	11.3 <=== 7.4
14:45	91	126	84.6	14.7 <=== 7.8
15.15	91	123	85.5	12.5 <=== 8.8
06/25/92	81	109	77.0	12.7
07/07/92	73	72	67.9	19.7 <===
07/08/92	77	77	71.5	12.3
07/09/92	77	79	71.5	13.2
07/10/92	81	77	71.5	13.2
07/13/92	82	81	72.8	13.7
07/21/92	77	75	69.0	13.7
07/22/92				13.7
07/23/92				13.7
07/24/92				13.2
07/30/92				14.2
08/10/92				16.7 <===
08/19/92				14.2
08/24/92				14.2
08/27/92				15.7

Note: The <=== to the right of a pressure indicates that the cylinder ullage recorded. An arrow on the right-hand side of an ullage pressure indicates that gases were removed from the ullage to the collecting cylinder on that date. The pressure was bled down only twice between 06/16/92 and 08/27/92.

Based on the analytical data on the samples withdrawn from the ullage and the bottom temperature reading at 14:00 h when the samples were taken, the temperature of the $UF_6(s)$ is taken to be 11°F less than the measured bottom temperature at 2 p.m. The "cold pressure" or ullage pressure could be read to ±0.5 psia and the TCs to about ±1°F. Part of the 11°F discrepancy noted may be due to inadequacy of the thermal isolation and the method of attachment of the TCs. Plotting the "cold pressure" data given in Table C-2 between 03/19/92 and 06/05/92 as a function of the solid UF_6 temperature obtained by correcting the corresponding bottom temperatures by 11°F gives the datum rectangles shown in Fig. C-1. The solid curve in Fig. C-1 shows the pressure of a saturated solution of UF_6 in HF, and the dashed curve shows the same data with an added 6.2 psia of air. The pressures of the HF solutions saturated with UF_6 were computed from the vapor pressure equations given in K/ETO-37 (ref. 3). Table C-3 lists these equations and the computed pressures for HF solutions saturated with UF_6. The data in Fig. C-1 are further confirmation of the existence of an HF solution saturated with UF_6 in the ullage of Cylinder 101244. Based on the pressure built up in the collection cylinder and the assumption that the vapor samples collected are representative of the composition of the vapor removed from the cylinder ullage, the 139 std ft^3 collection cylinder is expected to contain about 5 lb UF_6, 2 lb HF, and 2.6 lb air for a total of 9.6 lb. Very similar results were obtained at PORTS for the cylinder with the large hole where about 8 lb of vapor and gas was removed from the ullage. This suggests the chemical processes occurring in a tails cylinder after a breach are similar at the two sites.

Description and Identification of Solid Products Produced. Colored photographs of the reaction product deposits were made at the time of discovery and again when the adjacent cylinders had been moved so that the breaches were clearly visible. The most striking thing about the deposits on the breached cylinders at the K-25 Site was the similarity to the deposits observed on the two breached cylinders at PORTS. In fact, the appearance of the small holes in Cylinder 4G127985 at PORTS and Cylinder 116797 at the K-25 Site are essentially identical. Similarly, the appearance of the large holes in Cylinder 4G115688 at PORTS and Cylinder 114951 at the K-25 Site differ only in that the hole in Cylinder 114951 is a little larger. All four of these breaches are in either the 3-to-4 or 8-to-9 o'clock positions on the

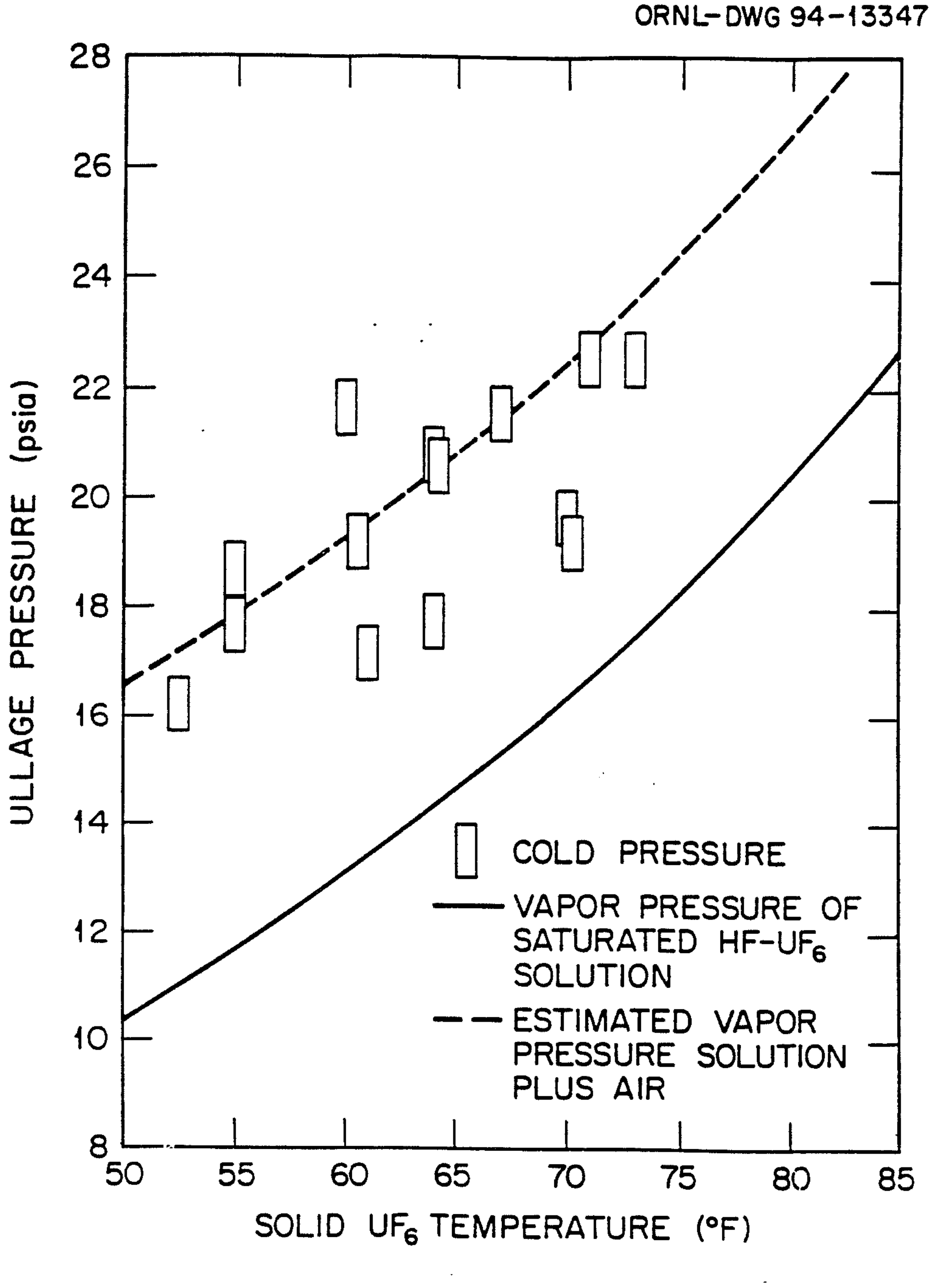

Fig. C-1. Cold pressure of Cylinder 101244 as a function of solid UF_6 temperature compared to vapor pressure of HF solution saturated with UF_6.

Table C-3. Pressure of saturated solutions of $UF_6(s)$ in HF(1)*

Temperature, °F	Temperature, °C	Reciprocal Temp $(1/T)*10^4$	Sat. Sol'n, mole frac UF_6	A_x-Constant,	B_x-Constant,	Sol'n Press, torr	Sol'n Press, psia
0.00	-17.78	39.16	0.0019	17.5792	-3207.52	151.3	2.93
5.00	-15.00	38.74	0.0023	17.5843	-3208.28	173.5	3.36
10.00	-12.22	38.32	0.0027	17.5893	-3209.03	198.5	3.84
15.00	-9.44	37.92	0.0031	17.5943	-3209.75	226.5	4.38
20.00	-6.67	37.53	0.0036	17.6003	-3210.63	257.8	4.99
25.00	-3.89	37.14	0.0041	17.6063	-3211.48	292.7	5.66
30.00	-1.11	36.76	0.0047	17.6133	-3212.45	331.8	6.42
35.00	1.67	36.39	0.0054	17.6212	-3213.55	375.3	7.26
40.00	4.44	36.02	0.0062	17.6300	-3214.73	423.8	8.20
45.00	7.22	35.67	0.0071	17.6395	-3215.97	477.8	9.24
50.00	10.00	35.32	0.0080	17.6487	-3217.14	537.4	10.39
55.00	12.78	34.97	0.0089	17.6575	-3218.23	603.1	11.67
60.00	15.56	34.64	0.0099	17.6670	-3219.35	675.9	13.07
65.00	18.33	34.31	0.0110	17.6769	-3220.49	756.2	14.63
70.00	21.11	33.98	0.0123	17.6881	-3221.71	845.3	16.35
75.00	23.89	33.67	0.0139	17.7011	-3223.04	944.4	18.27
80.00	26.67	33.35	0.0157	17.7147	-3224.34	1053.9	20.39
85.00	29.44	33.05	0.0175	17.7273	-3225.45	1173.8	22.70
90.00	32.22	32.75	0.0193	17.7390	-3226.40	1304.5	25.23
95.00	35.00	32.45	0.0215	17.7522	-3227.38	1449.3	28.03
100.00	37.78	32.16	0.0239	17.7654	-3228.26	1608.0	31.10
105.00	40.56	31.88	0.0260	17.7760	-3228.91	1777.9	34.39
110.00	43.33	31.60	0.0290	17.7898	-3229.70	1968.2	38.07
115.00	46.11	31.32	0.0329	17.8059	-3230.64	2179.4	42.15
120.00	48.89	31.05	0.0370	17.8211	-3231.65	2406.9	46.56
125.00	51.67	30.79	0.0424	17.8392	-3233.29	2657.2	51.40
130.00	54.44	30.53	0.0520	17.8692	-3237.78	2938.7	56.84
135.00	57.22	30.27	0.0640	17.9073	-3246.98	3226.1	62.40
140.00	60.00	30.02	0.0820	17.9675	-3266.00	3512.6	67.94
142.20	61.22	29.91	0.0980	18.0094	-3278.89	3652.9	70.66

* $\ln P(\text{torr}) = A_x + B_x/T$ where

$$A_x = 17.5538 + 13.8872x - 277.24x^2 + 3085.5x^3 - 12433x^4$$

$$B_x = -3203.59 - 2197.1x + 70964x^2 - 1043900x^3 - 4781000x^4$$

x is the mole fraction of UF_6 in the saturated solution and

T is the temperature in Kelvin

cylinder body side of an end stiffening ring. The two large holes extend underneath the stiffening ring. Corrosion products had sloughed out of the breaches to the pads below the two large holes. The stiffening ring on Cylinder 114951 and the lifting lug on the adjacent cylinder are more severely attacked than were the stiffening ring of Cylinder 4G115688 and the lifting lug of the adjacent cylinder. Both the relative size of the breaches and the extent of corrosion of the stiffening rings suggest that the hole in Cylinder 114951 is older.

The other two breaches at K-25 Site were both in the 6 o'clock position, one on the plug-end side of the plug-end stiffening ring (Cylinder 101244) and the other on the plug-end side of the middle stiffening ring (Cylinder 7953). These breaches show the same range of corrosion and reaction products as the other breaches. However, a main difference from the cylinders with breaches in the side is the inverse dome-like structure of the void which is created when the reaction products drop from these cylinders with 6 o'clock breaches. More of the uranium hydrolysis products appear to be exposed, and since they are no longer readily wetted by rain, the reduction of the hexavalent uranium to produce UF_4 becomes severely retarded. That some minor reduction of uranium might still be occurring is indicated by the fact that the only identifiable crystal pattern found in the bright yellow colored samples taken from the void, which were primarily solvates of uranyl fluoride, was UF_4 hydrates which are a distinctive green color.

As noted earlier, attempts were made to seal the breach in Cylinder 101244 against the loss of HF, but the HF attacked the silicone sealant and continued to escape. When that patch was removed, an attempt was made to prevent solid uranium compounds falling from the breach by tying a painted aluminum sheet against the breach. The sheet had been severely attacked, and aluminum fluoride now contaminated the corrosion products, particularly around the breach. The paint film is detached from the aluminum and is hanging from the edge of the hole. The corrosion had not been arrested. Comparison of the depth of the green UF_4 layer inside the cylinder with the width of the stiffening ring indicates that the UF_4 layer inside the cylinder was of the order of 1.5 in. in depth. The layer of UF_4 inside Cylinder 7953 appears to be of a similar depth. How far from the breach this layer of UF_4 extends is not known for either cylinder. The failure of the UO_2F_2 solvate layer to develop a coating of UF_4 indicates that a conducting solution which also contacts iron is not present.

The material which sloughed from Cylinder 7953 is shown in Fig. 9 in the main body of this report. Since none of the bright yellow material is seen in the material which fell from the cylinder, it appears to have separated at the UF_4 hydrate-uranium oxyfluoride solvate interface. Both yellow and green materials are seen in later materials that sloughed from the breach. Attention is called to the cleanliness of the deposit despite its lying in a runoff path for rain from the pad, which suggests that it was discovered shortly after sloughing off. This has implications with respect to the processes for hole development in the 6 o'clock position on cylinders. Features in the rusted areas in the form of pits and of a small hole were observed on the circumference of the breach. The thinning of the metal around the holes is discussed elsewhere in the report.

A comparison of the deposits and their physical arrangement indicates that the reaction products found at the breaches at PORTS are representative of the products formed in the K-25 cylinder breaches. Samples were taken from the two 6 o'clock breaches to confirm the identity of the materials and to attempt to improve the identification of the uranyl fluoride solvates which tend to be amorphous or to become so as they are exposed to the atmosphere outside their original environment. Using color as a basis for differentiation, D. P. Hoffmann carefully selected and immediately sealed in plastic bottles (for protection from further atmospheric exposure) four salt samples from the breach in Cylinder 101244 and three salt samples from the breach in Cylinder 7953. A fifth sample of a white material was taken from the aluminum sheet which was described earlier and used to catch the material from Cylinder 101244. (Not surprisingly, this latter material proved to be $AlF_3 \bullet 3H_2O$.) Hoffman[4] reports that he could see the materials change in appearance even while he was performing the XRD (x-ray diffraction spectra) and the EDS (energy dispersive x-ray spectra) analyses.[4] An XRD analysis requires about 6.5 h. He also determined weight changes while the samples were being analyzed and when heated to 90° C overnight. After cooling in a desiccator and reweighing, the XRD spectra of the heated samples were taken, and the samples were reweighed. All samples lost weight when subject to the drying treatment; otherwise, no overall consistent pattern of weight change was observed. Attack of the non-fluorinated plastic sample bottles and etching of the glass face plate of the XRD equipment prove that HF was evolved from the samples. The results of the XRD and EDS analyses are given for the samples from Cylinder 101244 in Table C-4 and for the samples from Cylinder 7953 in Table C-5.

The evolution of HF, the weight change studies on the yellow samples, and the accompanying spectral changes confirm the existence of crystalline, but unidentified, H_2O-HF

Table C-4. X-ray diffraction and energy dispersive x-ray analyses of samples from the breach in Cylinder 101244

Sample ID	Phase Color	Elemental Analysis (EDS)		X-ray Diffraction (XRD)	
		Major[@]	Minor[#]	Pattern[*]	Species[**]
Sample 1					
"As-Received"	Yellow	U,Fe	O,F	X	UID
"Heated"	Yellow			X/D	UID
Sample 2					
"As-Received"	Green	U	Fe,O	X	UF_4*H_2O $UF_4*0.75H_2O$
"Heated"	Green			X/S+	UF_4*H_2O
Sample 4					
"As-Received"	Green	U	Fe,O	X	UF_4*H_2O $UF_4*0.75H_2O$
"Heated"	Green			X/S+	UF_4*H_2O
Sample 5					
"As-Received"	Grey	Fe	Ca,O	X	$FeF_3\bullet 3H_2O$ UID
"Heated"	Grey			X/S-	FeF_3*3H_2O

[@] > 10 %

[#] < 10 %

[*] X = crystalline species present; D = diffraction patterns different; S+ = diffraction patterns are very similar; S- = diffraction patterns have some similarity.

[**] Identified species are given; UID = unidentifiable crystalline phases are present.

Table C-5. X-ray diffraction and energy dispersive x-ray analyses of samples from the breach in Cylinder 7953

Sample ID	Phase Color	Elemental Analysis (EDS)		X-ray Diffraction (XRD)	
		Major[@]	Minor[#]	Pattern[*]	Species[**]
Sample 1					
"As-Received"	Yellow	U	Fe,O	X	UID
"Heated"	Yellow			X/D	UID
Sample 2					
"As-Received"	Green	U	Fe,O	X	UID
"Heated"	Green			A/X/D	UID
Sample 3					
"As-Received"	Grey	Fe	O,U	X	FeF_3*3H_2O UID
"Heated"	Grey			X/S+	FeF_3*3H_2O UID

[@] > 10 %

[#] < 10 %

[*] X = crystalline species present; D = diffraction patterns different; S+ = diffraction patterns are very similar; A = amorphous patterns.

[**] Identified species are given; UID = unidentifiable crystalline phases are present.

solvates of hexavalent uranium oxyfluoride which are stable under the conditions existing within the breach but unstable under desiccating conditions in the atmosphere. Only the hydrates of two materials, ß-FeF3$\bullet 3H_2O$, UF4$\bullet H_2O$, and $UF_4 \bullet 0.75H_2O$, were definitely identified. A poorly defined pattern for $UF_4 \bullet 2.5H_2O$ was also obtained. The X-ray spectra of the first three phases are the only XRD patterns which survived the drying treatment. The material giving the pattern identified as $UF_4 \bullet H_2O$ may well be the same as that identified at PORTS as $UF_4 \bullet 1.5H_2O$. Other spectral lines were obtained, but they do not match any of the patterns for previously defined uranium oxyfluorides or fluorouranylic acids.

This experience is similar to that of D. L. Scott and coworkers at PORTS[5] who also had some difficulty in identifying which solvates of uranyl fluoride they had sampled. It is quite likely that the materials identified in the Russian studies[6,7] as $[H_3O]_2[U(OH)_4F_4]$ and $[H][U(OH)_4F_3]$ will lose HF if left exposed to the atmosphere. The yellow core sample material at PORTS very slowly gave off HF vapor if removed from the core sample tube. The materials identified in the PORTS investigation are discussed in detail in Appendix B, Part 1, of ref. 1. The materials believed to be present in the layered deposits in the breaches at PORTS and the K-25 Site are listed for convenient reference in Table C-6.

Table C-6. The reaction products from breached cylinders are layered in the following order from iron to UF_6

Material	Color
Fe	metallic
$FeFe_2$ (weak x-ray pattern)	white (not seen)
$Fe_2F_5 \bullet xH_2O$ (x = 7 or less)	gray to brown
$Fe_3F_2 \bullet xH_2O$ (x = 3 or less)	whitish to light tan
$Fe_3F_2 \bullet 3H_2O$ & $UF_4 \bullet 0.75H_20$	light violet
$UF_4 \bullet 2.5H_2O$	green
$UF_4 \bullet 1.5H_2O$* & $UF_2 \bullet 0.75H_2O$	slightly darker green
$UO_2F_2 \bullet nH_2O$	fluorescent yellow
$[H_30]_2[U(OH)_4F_4]$ & UO_2F_2†	yellow
$U_2O_3F_6$ (by color only)	orange
α-UOF4 (by color only)	bright orange
UF6	clear solid

*Hoffman suggests this material is more likely $UF_4 \bullet H_2O$.

†The equivalent $[H_3O][U(OH)_4F_3]$ or $UO_2F_2 \bullet 2H_2O \bullet HF$ has been identified by Pickrell[8] and by Seleznev et al.[6]

Environmental and Health Safety Sampling

In the immediate vicinity of three of the four holes, the sharp biting odor of HF was detectable under the protective tarpaulins but was not noticeable a short distance away. This resulted in the requirement that masks be worn when working at the breaches but not if one were just nearby in the cylinder yard. Of course, protective clothing suitable for radiation areas was worn in the yard at all times. Soil and water samples were taken and analyzed for radioactivity where the rainwater ran from the storage pad; however, none of the samples was sufficiently radioactive to require any action.

The absence of radionuclides in soil samples is not surprising in light of the high solubility of uranyl fluoride in water; one PORTS soil sample, taken at the edge of the pad immediately after deposits which sloughed off the cylinder hole had been washed with rainwater, showed a uranium concentration above background. When resampled later, no uranium concentration above 12 picocuries/g was found, and most of the samples were below 8 picocuries/g.[1]

The odor of HF in the vicinity of the breach in Cylinder 101244 raised the issue of environmental protection, and remediation was attempted by placing a temporary patch over the hole. Since the cylinder surface was rough and heavily rusted, a sealant was needed in applying the patch if the vaporization of HF was to be stopped. Silpruf™ patch sealant, a silicone base material, was used. Both HF and UF_6 attack silicones readily, and the patch failed. The attack of the silicone and other sealant materials by UF_6 was studied by Harkins[9,10] who confirmed that silicones failed quickly but that the epoxy materials marketed under the tradename FixStix™ would serve as a temporary seal. Harkins concluded that only a metal seal (braze or weld) would be permanent.

DISCUSSION

The Growth of Breaches and the Accompanying Loss of Hydrogen Fluoride Based on the Impact Fracture Model[1]

The chemistry involved in the enlargement of cracks or microscopic holes to the sizes found is quite involved but results in the formation of a stable, multilayered plug which exposes insoluble UF_4 hydrates to the atmosphere and a complex hexavalent uranium oxyfluoride acid to the UF_6. The HF produced by the hydrolysis of UF_6 is consumed in part during the redox reaction which produces the iron fluorides and the UF_4. The complex hexavalent uranium solvate also retains HF in the plug of uranium oxyfluoride compounds within the cylinder, and some of the HF diffuses to the ullage where it is retained and ultimately condenses to yield an HF solution saturated with UF_6. Despite these complex retention mechanisms, some of the HF does escape to the environment at a slow enough rate that its escape goes unnoticed a few feet from the breach.

Loss of HF from a breached cylinder cannot begin until the cylinder wall is totally penetrated. The two breaches investigated at PORTS were attributed to impact fractures completely through the cylinder wall that were produced during the stacking operation. Data were accumulated which suggested that the enlargement of the crack through its entire cross section did not start until 10 to 14 months later. Once this enlargement of the crack began, the diameter of the hole apparently increased by a relatively constant amount each year. Since the enlargement is a result of chemical reactions, it is obvious that the hole diameter would increase more rapidly in summer than in winter, but year to year the increase appears to be relatively constant. In Appendix B, Part 2, of ref. 1, page 92, an equation for estimating the total quantity of HF lost from the cylinder at any time after initiation of hole growth is given as shown below:

$$Q = \int_{t_o}^{t} \pi(1.08x10^{-4}t)^2\, k\, dt = (\pi/3)(1.08x10^{-4})^2\, k\, (t-t_o)^3\ , \qquad \text{(C-1)}$$

where:

Q is the total quantity of HF lost from the cylinder in grams,
t_o is the time in hours when the hole actually began to enlarge,
t is the total exposure time in hours,
k is a constant at a given temperature with the dimensions g/cm^2-h,
1.08×10^{-4} is the rate of increase of the hole radius in cm/h.

The average value of k at the mean annual temperature at PORTS is 0.00791 g/cm^2-h.

The effect of temperature on the reaction rate constant, k, is expressed by the Arrhenius equation:

$$2.303 \log_{10} k_T = - \Delta E/RT + C\ . \qquad \text{(C-2)}$$

For the change in the reaction rate constant from the mean temperature at PORTS, T_p, to the mean temperature at the K-25 Site, T_k, one obtains:

$$2.303 \log_{10} [k_{Tk}/k_{Tp}] = (\Delta E/R)[1/T_p - 1/T_k] . \qquad \text{(C-3)}$$

The ratio of the reaction rate constants is thus a function of the activation energy of the reaction. For a given difference in T_p and T_k, the larger the activation energy, the greater is the dependence of the rate of reaction on temperature. For many reactions, the typical activation energy at room temperature is about 10 kcal/mole. Employing Eq. (C-3) with this activation energy and noting that the mean temperature at PORTS is about 55°F and the mean temperature at the K-25 Site is about 59°F, one has a 4°F (2.2°C) increase in temperature. The ratio of the reaction rate constant at the K-25 Site to the reaction rate constant at PORTS is thus 1.145 for a value, of k_{Tk}, of 0.00906 g/cm^2-h of HF. The error band for k_{Tp} very likely includes this value, and one is justified in ignoring the small effect of a slightly higher mean temperature in East Tennessee.

On this basis, Eq. (C-1) above can be used to calculate the total amount of HF released at any time after the actual enlargement of the hole begins. The minimum value of t_o can be taken as 1 year. This value of t_o is relevant only for breach growth resulting from through-the-wall impact fractures. For fractures partially penetrating the wall or for penetration by wall corrosion from the outside, t_o may be many years. Figure C-2 shows the cumulative loss of HF in kilograms HF as a function of $(t-t_o)$. The actual value of t_o must be subtracted from the total exposure time to give the time shown in the plots.

The minimum value of t_o is the time required for the reactions of UF_6, water, and iron to begin to increase the hole cross section through the entire depth of the wall. For impact fractures extending part way through the wall, the time for mechanical crack extension and external atmospheric oxidation to complete the penetration must be added to the minimum t_o. Thereafter, one would expect behavior similar to that in which the impact fracture went totally through the wall. If the wall penetration is due to general corrosion over a wide area, the actual enlargement of the hole, once the wall is penetrated, may proceed much faster than is predicted from the PORTS experience, or the hole may already be several inches in diameter when its existence first becomes obvious. As noted for Cylinder 7953, there is evidence that the reaction products on the ground underneath the cylinder had only recently fallen, and the amount of HF in the ullage of Cylinder 7953 at the K-25 Site was significantly less than in the case of the large hole at PORTS. Thus, while the quantity of HF accumulated in the ullage

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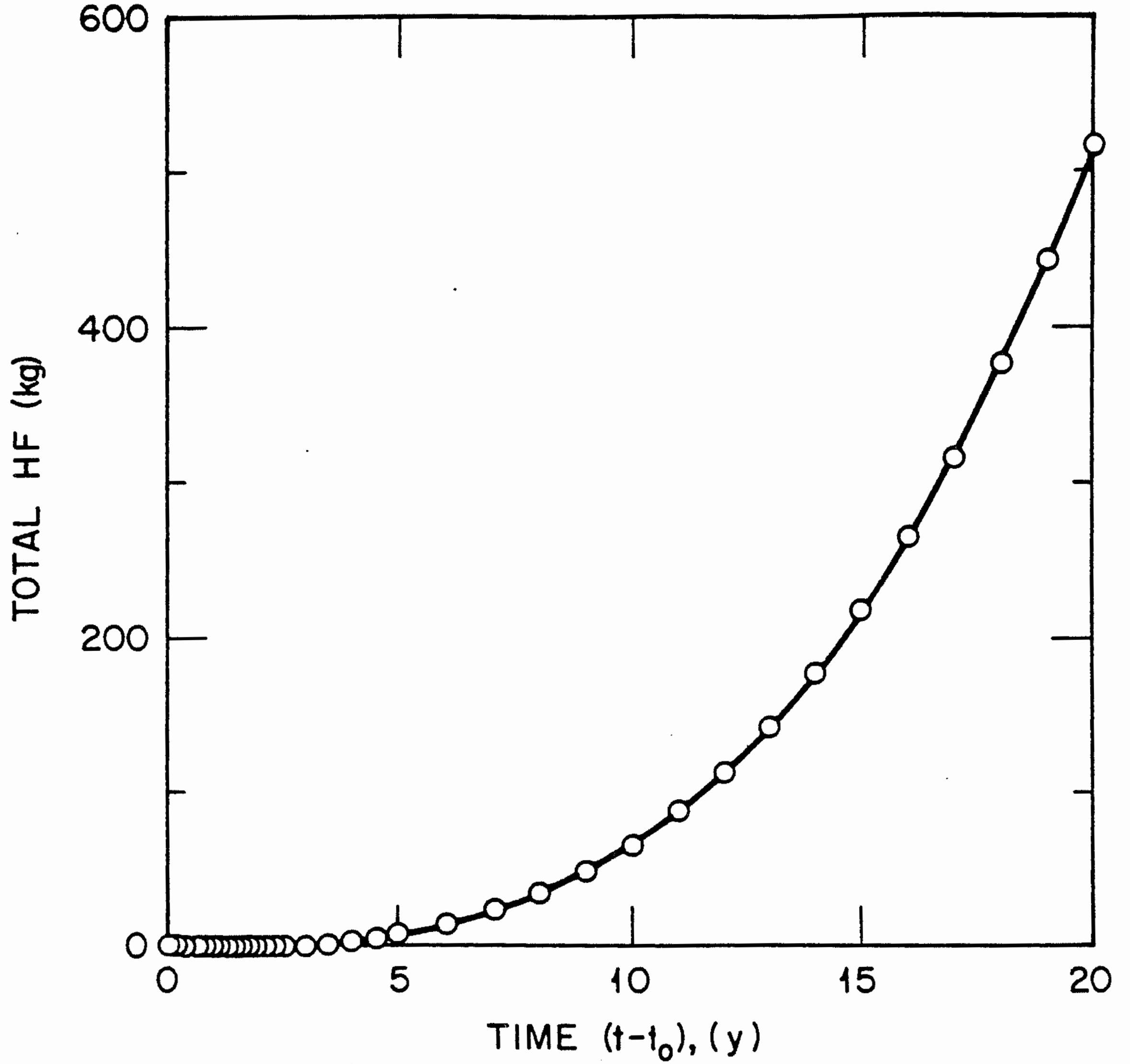

Fig. C-2. Expected cumulative loss of HF vs. time for impact breaches.

affords a useful index for detecting a cylinder breach, the sensitivity of this inspection method will depend on the initial cause and location of the breach.

At least for impact fracture cases, the relationships shown in Figs. C-2 through C-4 can be employed for estimating the loss of the HF from the cylinders by assuming that the relationship between hole size and time shown in Fig. C-3 holds for all cylinders so that the value of $(t-t_o)$ can be determined by the measured (or estimated) hole diameter. Figure C-3 shows the relationship between hole diameter and time, which correlates the data obtained from the two breaches at PORTS. The rate of loss of HF as a function of time for impact fracture breaches is given in Fig. C-4. To the extent that breaches may be similar to the two breaches in the UF_6 cylinders stored at PORTS, crude estimates based on the size of the existing holes may be made using the model developed to correlate the information obtained from the data on the PORTS cylinders. These values, which may be valid to ±50 %, are in order of increasing breach size in Table C-7.

If the assumption is made that the rate of loss of HF from a breached cylinder depends only on the size of the breach and not on how the breach developed, then the results shown in Figs. C-3 and C-4 can be used to estimate the rate of loss of HF from the four breached cylinders at the K-25 Site. These are shown in Table C-8. The cumulative loss is also given for the two cylinders to which the estimate is believed to be applicable.

Since the concentration of uranium in the HF solution oozing from the large breach at PORTS could not be determined because the quantity was too small to be collected and since a significant amount of the hexavalent uranium in solution was reduced to essentially insoluble UF_4 hydrates by contact with iron and retained, no correlation between HF loss and uranium loss could be established. Actually, only the loss in cylinder weight was directly measurable, and this, because of the complex hydrolysis chemistry of solid UF_6 and the reduction by iron, is not the weight of UF_6 lost. Because of the many uncertainties, it would appear fruitless to attempt to correlate the uncertain overall uranium losses from a cylinder with time.

Impact breaching upon stacking may be viewed from the chemical viewpoint as a short circuiting event which eliminates the need for penetration of the wall by external corrosion, and the failure mechanism is that described for the two cylinders at PORTS.[1] By use of the estimates of exposure time after filling with depleted UF_6 made in the main text for the two cylinders with the holes in the bottom (101244 and 7953) and the time since stacking of the other two Cylinders (114951 and 116797), a comparison can be made with the hole size

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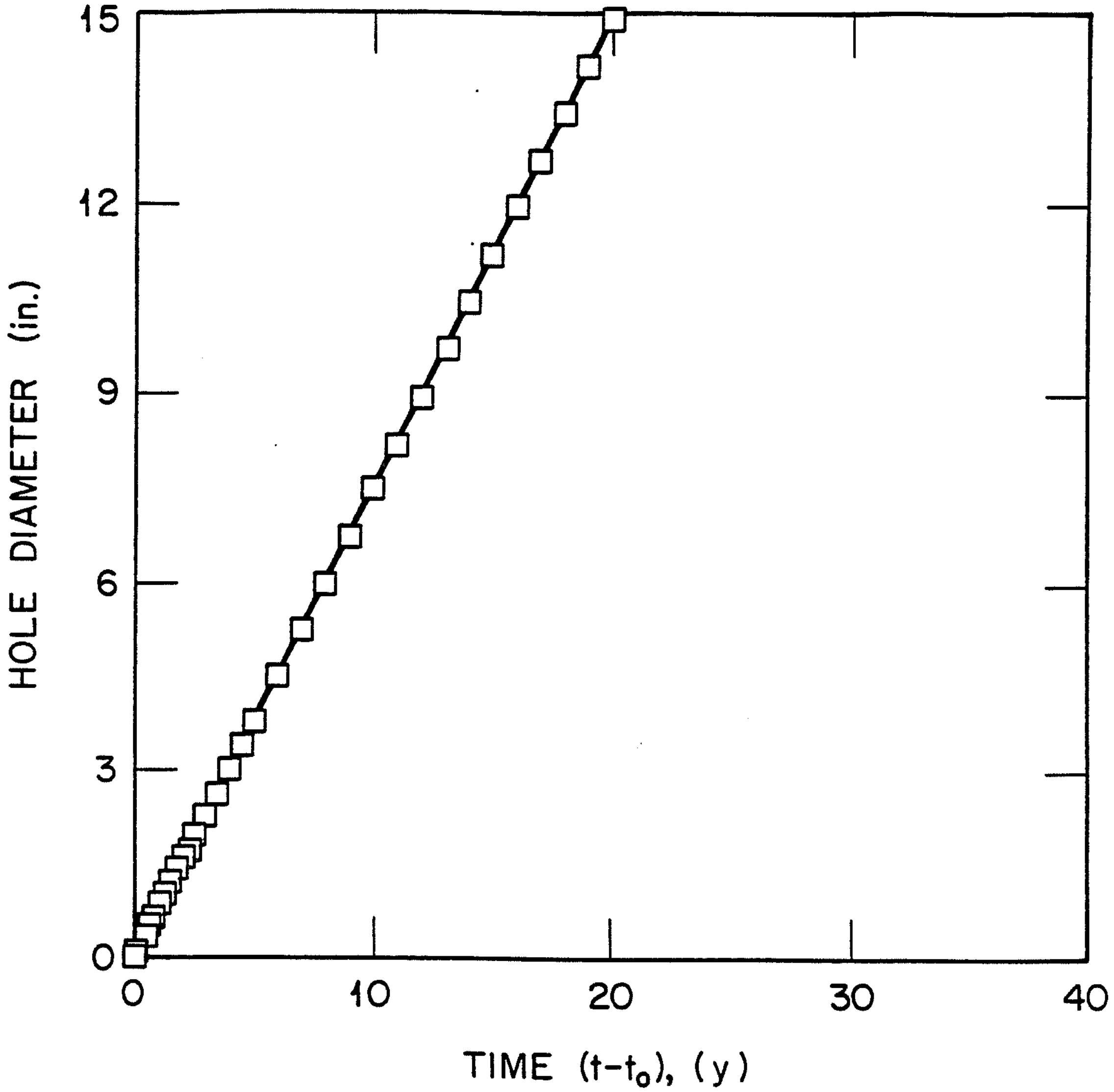

Fig. C-3. Hole size as a function of time for impact breaches.

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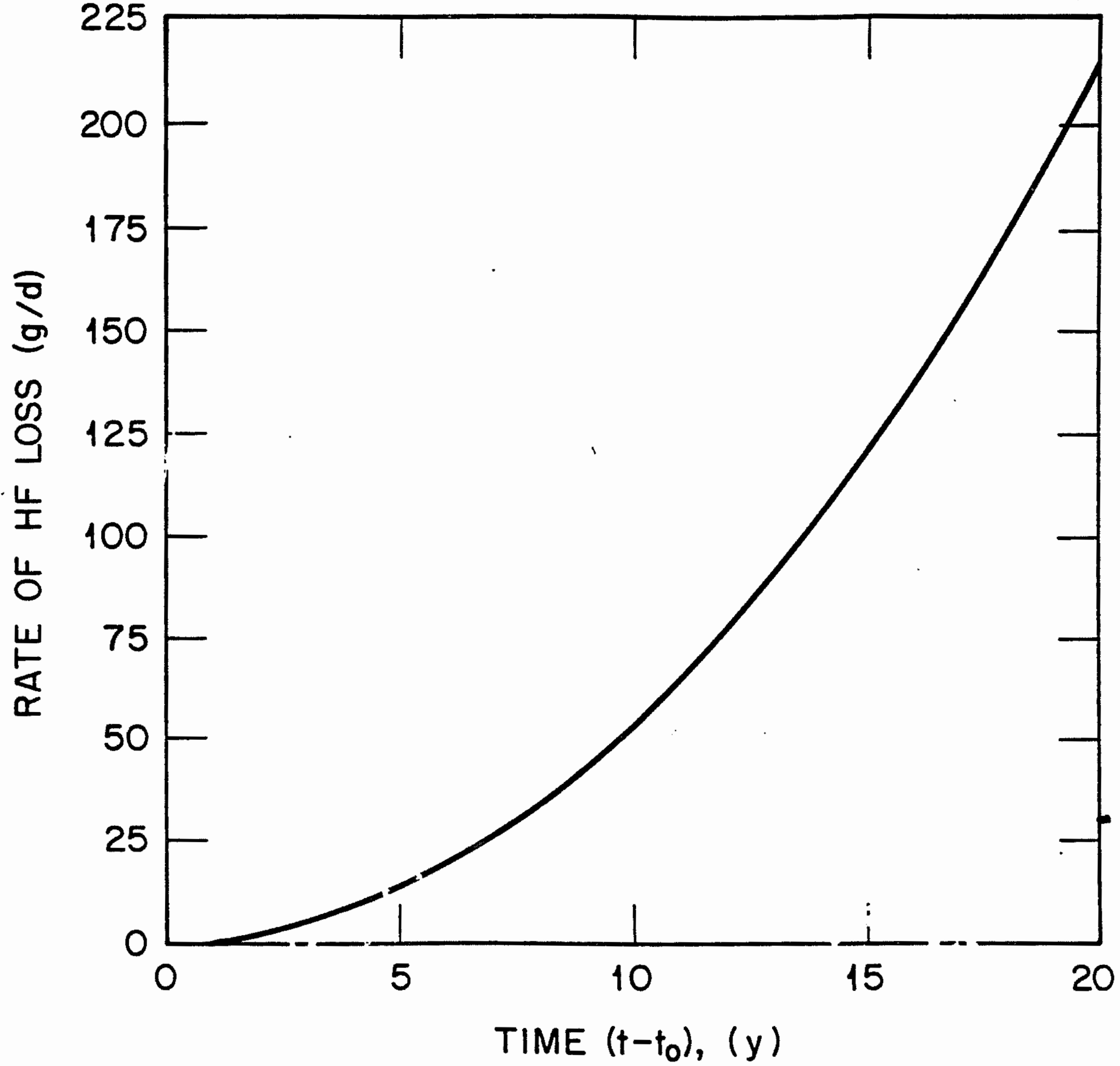

Fig. C-4. Rate of HF loss vs. time for impact breaches.

Table C-7. The hole size, the rate of loss, and cumulative loss of HF from cylinders as a function of the hole enlargement time for through-the-wall impact fractures

years	months	Time, hours	Hole Size, in. diameter	HF Lost, grams	HF Lost, pounds	HF Lost, kg	Time, years	Rate of Loss of HF, g/d
0	0	0	0	0	0	0	0.00	0.000
0	3	2160	0.18	0.97	0.0021	0.0010	0.25	0.032
0	6	4320	0.37	7.79	0.0172	0.0078	0.50	0.130
0	9	6480	0.55	26.29	0.0580	0.0263	0.75	0.292
1	0	8640	0.73	62.32	0.137	0.0623	1.00	0.519
1	3	10920	0.93	125.8	0.277	0.126	1.25	0.830
1	6	13080	1.11	216.2	0.477	0.216	1.50	1.19
1	9	15240	1.30	342.0	0.754	0.342	1.75	1.62
2	0	17520	1.49	519.6	1.146	0.520	2.00	2.14
2	3	19680	1.67	736.4	1.624	0.736	2.25	2.69
2	6	21840	1.86	1006.	2.219	1.006	2.50	3.32
3	0	26280	2.23	1754.	3.866	1.754	3.00	4.80
3	6	30600	2.60	2768.	6.103	2.768	3.50	6.51
4	0	35040	2.98	4157.	9.164	4.157	4.00	8.54
4	6	39360	3.35	5891.	12.99	5.891	4.50	10.7
5	0	43800	3.72	8118.	17.90	8.118	5.00	13.3
6	0	52560	4.47	14030	30.93	14.03	6.00	19.2
7	0	61320	5.21	22280	49.11	22.28	7.00	26.2
8	0	70080	5.96	33250	73.31	33.25	8.00	34.2
9	0	78840	6.70	47350	104.4	47.35	9.00	43.2
10	0	87600	7.45	64950	143.2	64.95	10.00	53.4
11	0	96360	8.19	86440	190.6	86.45	11.00	64.6
12	0	105120	8.94	112200	247.4	112.2	12.00	76.9
13	0	113880	9.68	142700	314.6	142.7	13.00	90.2
14	0	122640	10.43	178200	392.9	178.2	14.00	105.
15	0	131400	11.17	219200	483.2	219.2	15.00	120.
16	0	140160	11.92	266000	586.5	266.0	16.00	137.
17	0	148920	12.66	319100	703.5	319.1	17.00	154.
18	0	157680	13.41	378800	835.0	378.8	18.00	173.
19	0	166440	14.15	445500	982.1	445.5	19.00	193.
20	0	175200	14.90	519600	1145.	519.6	20.00	214.
25	0	219000	18.62	1015000	2237.	1015.	25.00	334.
30	0	262800	22.35	1754000	3866.	1754.	30.00	480

Table C-8. Estimated rate of loss of HF and cumulative loss of HF from the breached cylinders at the K-25 Site

Cylinder	Hole size, in.	Rate of HF loss, g/d	Cumulative HF loss kg	 lb
116797	2	2.1	0.5	1.1
114951	12	137	270	590
101244	6	34	NA	NA
7953	9	77	NA	NA

NOTE-NA means not applicable.

development experience for the two PORTS cylinders. In Fig. C-5, this correlation of the hole size with cylinder storage time, less 1 year to allow the time needed to begin to enlarge impact breaches, is shown for all the breached cylinders including the two at PORTS. The hole sizes of Cylinders 101244 and 7953 are also plotted versus the approximate time since these cylinders were moved from K-1066-G yard to K-1066-K yard. The curve for prediction of hole size as a function of enlargement time after impact breaching, which was developed from the PORTS data, is included for reference. The breach in Cylinder 114951, as noted previously, conforms to the expectations for a through-the-wall impact fracture. The breach in Cylinder 101244 also conforms if the breach resulted from a through-the-wall impact fracture at the time of restacking in K-yard, but other observations indicate that this is not the most probable failure mechanism. The breach in the wall of Cylinder 116797 is smaller than would be predicted for an impact breach at the time of stacking. It is concluded that the fracture either did not initially extend through the wall and additional time was required for crevice corrosion to complete the wall penetration, or that the presence of the lifting lug in the fracture somehow slowed the process. The breach in Cylinder 7953 does not fit the model developed for impact breaching at the time of stacking.

If the assumption is made that enlargement of all breaches after discovery goes at least as fast as with impact breaches, the dashed curves in Fig. C-5, which pass through the hole sizes for the three non-conforming K-25 cylinders with the same slope as the PORTS model,

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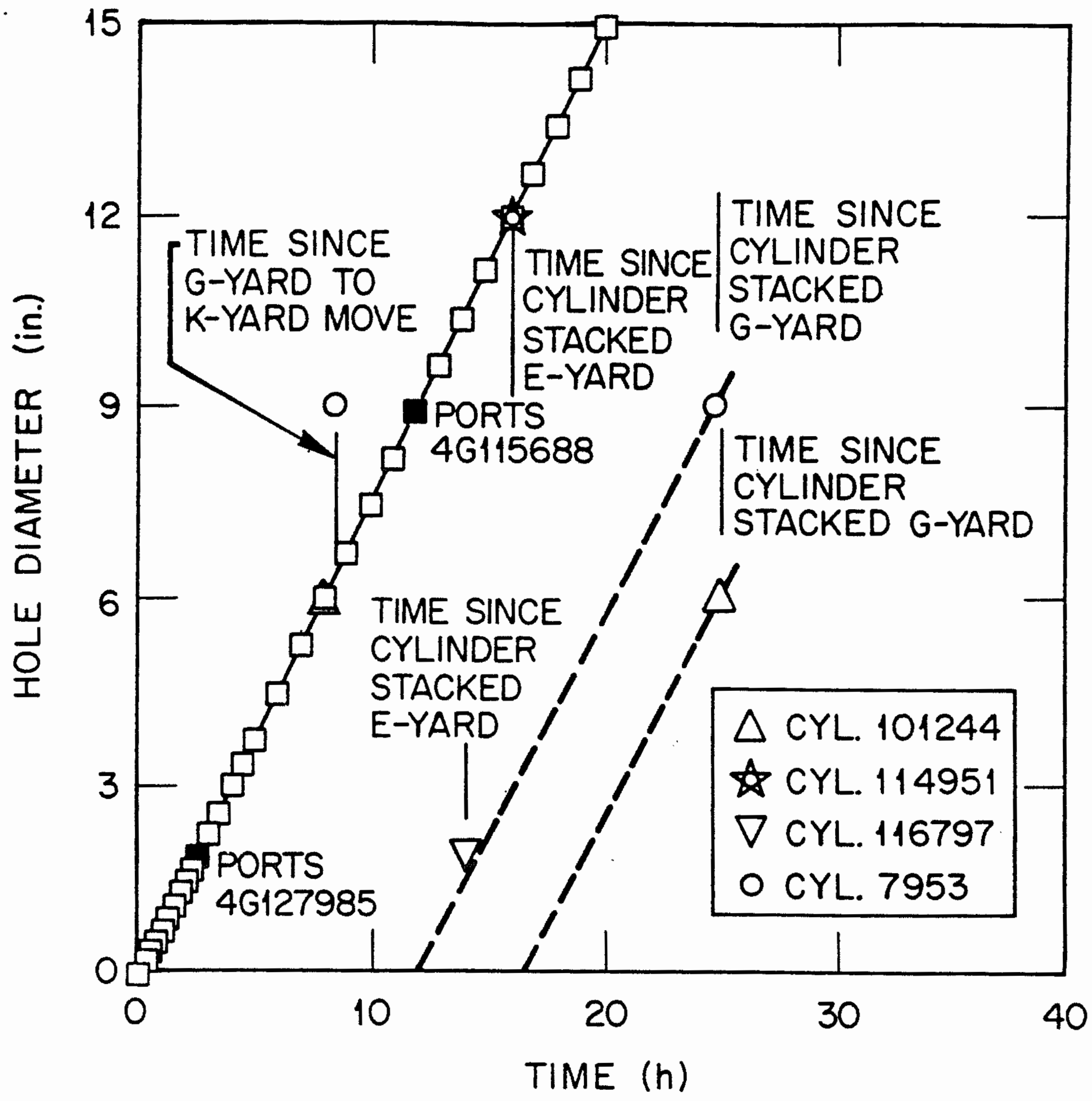

Fig. C-5. Correlation of hole sizes of K-25 breached cylinders with sizes resulting from mechanically-induced breaches.

intercept zero hole size at about 12, 12, and 16 years for Cylinders 116797, 101244, and 7953, respectively. If these times are interpreted as the minimum time required for penetration of the wall, the respective maximum attack rates of the steel by a differential oxidation corrosion process (see Appendix B) are of the order of >26, 26, and 20 mils/year. The "greater-than" designation is used for Cylinder 116797 because the wall is partially penetrated by the impact fracture.

Chemical Processes During Hole Growth

Although qualitatively the same reaction products were generated by the breaches in the cylinders at K-25 and PORTS, there could be quantitative differences in the amounts of the UF_4 hydrates generated which are dependent on the mechanism of wall penetration. In this regard, it is instructive to compare the chemical effects of breaches which are mechanically induced with those of breaches which result from more prolonged external corrosion. While the chemical reactions taking place with $UF_6(s)$ are the same whether the wall penetration results from an impact fracture or from some form of differential oxygenation corrosion, the 5/16-in. thickness of the steel comprising the cylinder wall makes for possible differences in the development of breaches initiated by these processes. The result of impact fracturing has already been described in detail in the report of the investigation of the breached cylinders at Portsmouth.[1] A peculiarity of this breaching process is the very small amount of iron which is consumed in making iron oxide. Most of the iron which reacts is oxidized to iron fluoride, and an equivalent amount of hexavalent uranium is reduced to form UF_4 hydrates. Both the iron fluorides and the UF_4 hydrates are relatively insoluble in water. These conditions set up a relatively stable and predictable condition for hole enlargement. Even in the case of probable partial penetration by impact fracture, the completion of the penetration is likely by crevice corrosion, a highly localized differential oxygenation process, or some other localized electrochemical cell attack. These processes also require the oxidation of very little iron to obtain completion of the penetration of the wall. (See Appendix B for a more detailed description of accelerated corrosion mechanisms.)

By contrast, the process of external accelerated corrosion involves the oxidation of the iron surface over an appreciable area. That this process occurs has been demonstrated by ultrasonic measurement of the cylinder wall thickness over areas which have been in ground contact.[11] Since differential oxygenation corrosion is not uniform over such an area, the rate of penetration of the wall over the affected area is not uniform nor can the actual penetration rate be predicted from basic principles. Nevertheless, the requirement of differential oxygenation corrosion for a conducting film of water is such as to permit prediction that breaches from this process will be found at or near the 6 o'clock position as found to be the case in K-yard. As suggested in the preceding section, an empirical estimate of the minimum time for the penetration of a 5/16-in. steel cylinder wall by differential oxygenation corrosion is 12 to 16 years. Peculiar storage conditions, such as storage with the bottom of the cylinder in contact with soil or gravel and in areas where water tends to stand on the storage pads, are needed to initiate and promote this external corrosion mechanism. However, once initiated, removal from the initiating conditions in areas where the relative humidity is high will not interrupt the process unless the rust film is also removed.

Once external corrosion has completely penetrated the steel wall, the access of water to the UF_6 is by diffusion through a thick, adherent, somewhat porous rust layer. It is this rust layer which, for an indefinite period, can stabilize the existence of a UF_4 hydrate by acting as a source of water but preventing air access. The most likely hydrate is a mixture of $UF_4 \bullet 0.75H_2O$ and $UF_4 \bullet 1.5H_2O$, produced shortly after water contacts the UF_6. The stress induced by the formation of these reaction products will be less than if more highly hydrated ones are formed, since they will occupy less volume than the UF_6 which they replace. Furthermore, solid UF_6 readily creeps under stress, so a slow enlargement of the volume of the hydrolysis and reduction products would not be expected to overstress the thick rust layer. The apparent integrity of the rust covering on Cylinder 7953 for perhaps as long as 13 years is evidence that the layer is not forced to undergo much strain. The reactions at this point involve the reaction of $UF_6(s)$ with water to form fluorouranylic acid and HF,

$$UF_6(s) + 4\,H_2O(l) = H[U(OH)_4F_3](s) + 3\,HF(l)\,, \tag{C-4}$$

followed almost immediately by reaction with iron as shown below:

$$\begin{aligned}3H[U(OH)_4F_3](s)+9HF(l)+2Fe(s) &= 2UF_4\bullet 0.75H_2O+UF_4\bullet 1.5H_2O\\ &\quad +2FeF_3\bullet 3H_2O+3H_2O\,.\end{aligned} \tag{C-5}$$

This pair of reactions cannot continue without the continual diffusion of water to the reaction zone and the presence of elemental iron to reduce the hexavalent uranium to the tetravalent state and to tie up the fluoride as iron fluoride. Observations of the layering of products in Cylinders 101244 and 7953 indicate that the UF_4 hydrate layer was about 1.5 in. thick, whereas the estimate of the depth of this layer in the cylinder with the large hole at PORTS was about

Since water is ubiquitous, reaction C-4 will continue even if reaction C-5 ceases, and the HF produced can attack the rust layer, converting it to iron fluoride as suggested by Eq. C-6:

$$3\ HF(l) + H_2O(l) + FeO(OH)(s) = FeF3 \bullet 3H_2O(s)\ . \qquad (C\text{-}6)$$

Reaction C-6 produces an abrupt change in the crystal structure as the hydrous iron oxide converts to the hydrated iron fluoride, which is not adherent to the rust layer. Accordingly, the layer is gradually thinned and thereby weakened. Eventually, the rust crust becomes so thin it can no longer support the weight of the $FeF \bullet 3H_2O$ and the UF_4 hydrates, which do not adhere to the fluorouranylic acids above them in the cylinder. Then some event, such as a severe blow to the cylinder, an abrupt change in the temperature, or a freezing and thawing of the water in the rust crust, causes the crust to suddenly break away, dropping the iron and uranium fluorides it has supported and leaving a well-developed hole several inches in diameter, most probably in the 6 o'clock position.

In dropping away, the material in the cylinder separates at the fluorouranylic acid-UF_4 hydrate interface leaving it directly exposed to atmospheric moisture. This would be expected to speed the hydrolysis of the UF_6 in the cylinder and possibly increase the diffusion rate of HF to the ullage. The finding of liquid HF in the ullage of Cylinder 101244 supports this prediction, in that the 6-in. hole in this cylinder might have been no more than a year old when the ullage was sampled, whereas no liquid HF was found in the ullage of the 4-year-old impact-fracture hole at PORTS. As suggested by reactions C-4, C-5, and C-6, the absence of liquid HF in the ullage of Cylinder 7953, which had a 9-in. hole, could indicate that a larger fraction of the entering water was indirectly used in the production of UF_4 and FeF_3 hydrates in this cylinder than in the cylinder with the large hole at PORTS and Cylinder 101244, both of which did contain liquid HF in the ullage.

Because the fluorouranylic acid layer forms a domed surface above the bottom of the cylinder when the iron fluoride and UF_4 hydrates fall from holes in the 6 o'clock position, rain cannot wash the fluorouranylic acid surfaces to aid in regeneration of the insoluble, less hygroscopic UF_4 and iron fluoride hydrates. Thus, no significant coating of the fluorouranylic acid surface with these materials was observed to develop over a period of months. The best current assumption would be that, once the hydrous iron oxide and its supported materials fall from the hole, it will enlarge at least as fast as the same-sized hole caused by an impact fracture, and the rate of loss of HF and additional accumulation of HF will follow the same pattern. Because an intact crust of rust apparently is impermeable to HF, HF cannot escape from the cylinder, but there is nevertheless little accumulation in the ullage until the crust breaks away, since prior to this, most of the HF is consumed in producing UF_4 and ferric fluoride hydrates. Using this proposition, one would predict the hydrolysis of the UF_6 to be completed about 44 years after the initiation of the external corrosion by the differential oxygenation corrosion process. Again, the final hole would be about 24 in. in diameter.

Since iron which already has been oxidized by oxygen to form rust is not available for the redox reactions that form the insoluble iron fluorides and UF_4 hydrates, the thickness of these materials, which serve as diffusion barriers to slow the reaction of water with UF_6, is less than in the case of impact failures. Note the estimated 1.5-in.-thick layer of UF_4 hydrates for the two cylinders with 6 o'clock breaches compared with an estimated 4 in. for the large hole at PORTS. With a lesser iron wall thickness to react and a more rapid diffusion of water to the UF_6, the rate of hole enlargement is likely to be greater than for a comparable sized hole resulting from an impact fracture. It follows that the predictability of both the time when hole enlargement will begin and the rate of enlargement are poor when the wall penetration is by differential oxygenation corrosion or another external corrosion process. Perhaps it should be noted that the two largest breaches found (one at the K-25 Site and one at PORTS) were initiated by impact breaches, which led to the holes developing much earlier in time.

Another feature noted in the case of holes positioned at 6 o'clock was that, when the rust, the iron fluorides, and the UF_4 hydrates break away, the UO_2F_2 solvates (fluorouranylic acids) are left exposed, giving direct access of water vapor to the soluble hexavalent uranium fluorides. When this occurred in the case of the larger holes resulting from impact fracture and rain ran over this exposed material, contact of the resultant solution with iron metal renewed the coating of insoluble materials over the soluble materials. The only evidence that this might be occurring to a very limited extent with holes resulting from external corrosion after scale breakaway was the dulling of the bright yellow color and the presence of a trace of a crystalline UF_4 hydrate in the yellow UO_2F_2 solvates (fluorouranylic acids). Since rainwater is not able to contact directly the UO_2F_2 solvate if the hole is at the 6 o'clock position, one of the plug stabilizing reactions operating with impact fractures in the 3 or 4 o'clock position is lost.

One similarity in the behavior of the materials which form in the holes during breach enlargement is shown by the temperature and the cold pressure measurements which were made on Cylinder 102144. As with the two breached cylinders at PORTS, there was no connection from the atmosphere to the ullage of the cylinder and HF accumulated there. The data which are plotted in Fig. C-1 show that Cylinder 102144 contained liquid HF saturated with UF_6 in the ullage. This solution was successfully removed by vapor transfer to an empty cylinder. These results prove that there is no exchange of the contents of the ullage space of a breached cylinder and the atmosphere whether the breach results from impact fracture or external corrosion. The experimental evidence available shows that there have been abnormal amounts of HF in the ullage of every cylinder that has been breached. The quantity depends on the size of the breach and the time that the breach has been open to the atmosphere.

In the case of the two cylinders with 6 o'clock holes, there is a question as to whether the breaches were simply overlooked in the June 1991 inspection, which is reasonable considering their location, or if the material was contained within an unnoticed rust-covered bulge at the time of the June 1991 inspection and the brittle rust coating had cracked sufficiently by December to permit the otherwise unsupported UF_4 hydrates and other materials to fall off the bottom of the cylinders. An argument could even be made that the material fell from Cylinder 7953 between December 1991 and March 1992 based on the cleanliness of the UF_4 hydrate deposit. The deposit was in a location where with time it would be expected to admix with mud washed in from other parts of the concrete pad. The finding that the contents of the ullage of Cylinder 101244 included a solution of HF saturated with UF_6 suggests, however, that the open breach in the cylinder wall had occurred much earlier than December 1991.

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