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Uranium Hexafluoride Handling

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FOREWORD

The United States Department of Energy, Oak Ridge Field Office, and Martin Marietta Energy Systems, Inc., are co-sponsoring this Second International Conference on Uranium Hexafluoride Handling. The conference is offered as a forum for the exchange of information and concepts regarding the technical and regulatory issues and the safety aspects which relate to the handling of uranium hexafluoride. Through the papers presented here, we attempt not only to share technological advances and lessons learned, but also to demonstrate that we are concerned about the health and safety of our workers and the public, and are good stewards of the environment in which we all work and live.

Increasing levels of environmental awareness and concern on the part of the general public, as well as increasingly stringent governmental controls and regulations, place every greater emphasis on the need for safety in handling and processing of uranium hexafluoride in all phases of the nuclear fuel cycle. The increasingly restrictive public climate in which the industry operates requires that we maintain a continuing scrutiny of our operations, procedures, and attitudes, and that we demonstrate continuing improvement in all aspects of safe handling of uranium hexafluoride. The present conference is a step in that direction.

These proceedings are a compilation of the work of many experts in that phase of world-wide industry which comprises the nuclear fuel cycle. Their experience spans the entire range over which uranium hexafluoride is involved in the fuel cycle, from the production of UF_6 from the naturally-occurring oxide to its re-conversion to oxide for reactor fuels. The papers furnish insights into the chemical, physical, and nuclear properties of uranium hexafluoride as they influence its transport, storage, and the design and operation of plant-scale facilities for production, processing, and conversion to oxide. The papers demonstrate, in an industry often cited for its excellent safety record, continuing efforts to further improve safety in all areas of handling uranium hexafluoride.

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Laying the Foundation: Properties of UF_6

ASPECTS OF URANIUM CHEMISTRY PERTAINING TO UF_6 CYLINDER HANDLING

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ABSTRACT

Under normal conditions, the bulk of UF_6 in storage cylinders will be in the solid state with an overpressure of gaseous UF_6 well below one atmosphere. Corrosion of the interior of the cylinder will be very slow, with formation of a small amount of reduced fluoride, probably U_2F_9. The UO_3-HF-H_2O phase diagram indicates that reaction of any inleaking water vapor with the solid UF_6 will generate the solid material $[H_3O]_2(U(OH)_4F_4)$ in equilibrium with an aqueous HF solution containing only small amounts of uranium. The corrosion of the steel cylinder by these materials may be enhanced over that observed with gaseous anhydrous UF_6.

NOMENCLATURE

R	Rate of penetration of steel by UF_6 corrosion, mil/day
T	Temperature, K

INTRODUCTION

Uranium hexafluoride (UF_6) is employed in many phases of the nuclear industry. Therefore, we should be familiar with any physical or chemical properties which affect safe use and storage of this material. The basic physical and chemical properties of UF_6 were summarized by Barber(1) in a paper presented at this conference three years ago, so these will not be considered in detail in this paper. However, a few of the most important of these basic properties will be briefly discussed to serve as an introduction for the remaining material to be presented.

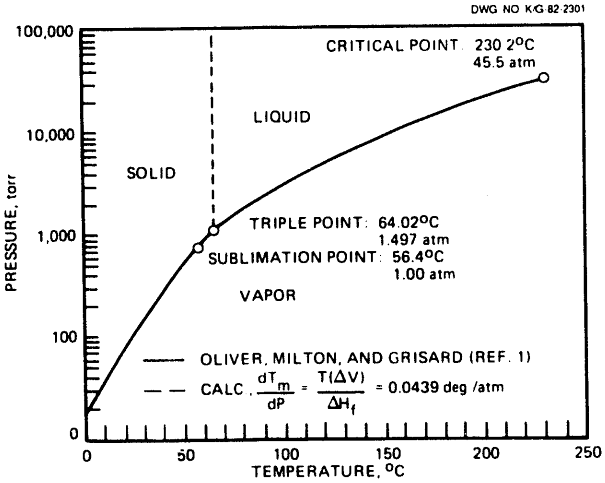

Fig. 1. UF_6 phase diagram.

The phase diagram for pure UF_6, in which the logarithm of the pressure is shown as a function of temperature, is presented in Fig. 1; the data shown are those of Oliver et al.(2) Several important points can be made from this diagram. At room temperature, UF_6 is a solid which exhibits a small but significant vapor pressure, about 80 torr. The sublimation temperature (the temperature at which the vapor pressure of the solid is one atmosphere) is 56.4°C. The relatively high vapor pressure of UF_6 makes it by far the most volatile uranium-containing compound known, which is, of course, the principle reason that UF_6 is employed in most of the world's uranium isotopic enrichment plants. At temperature and pressure conditions above those of the triple point, (the point at which solid, liquid, and vapor can all coexist and which occurs for UF_6 at 64.02°C and 1.497 atmospheres), a liquid phase can exist up to the critical temperature of 230.2°C, above which point the liquid and vapor phases cannot be distinguished. Thus, for UF_6 to exist in the liquid state, the pressure, of necessity, must be in excess of 1.5 atmospheres, so that if a defect, such as a crack or a hole, is produced in the container wall the result will be primarily outleakage of the UF_6. On the other hand, when the material is handled at temperatures below the sublimation temperature, the bulk of the UF_6 will be in the solid state and the cylinder pressure will be below atmospheric. Under these conditions, inleakage of the ambient air will be the primary flow path through any defects which might develop in the container wall.

UF_6 is a very stable material in the vapor state, with an extremely low fluorine dissociation pressure of about 10^{-30} atm at 400 K in equilibrium with solid uranium pentafluoride(3), as given by the reaction

$$2UF_6(g) \rightleftharpoons 2UF_5(s) + F_2(g). \qquad (1)$$

As a result, UF_6 is a relatively mild fluorinating agent, but, because of its strong chemisorption on most surfaces, its reaction rate with these materials is greater than might otherwise be expected. Thus, UF_6 is an oxidizing agent toward metals such as nickel as given by the reaction

$$2UF_6(g) + Ni(s) \rightarrow 2UF_5(s) + NiF_2(s). \qquad (2)$$

While this reaction indicates the reduced uranium fluoride to be UF_5, in actuality the reduced fluoride formed depends on the UF_6 pressure, the temperature, and the specific metal involved, and may be any of a series of reduced fluorides, including UF_5, U_2F_9, U_4F_{17}, or UF_4.

REDUCED URANIUM FLUORIDES

Solid uranium pentafluoride, UF_5, exists in two allotropic forms, commonly designated α-UF_5 and β-UF_5, with the transition temperature being about 125°C; α-UF_5 is the higher temperature form of the material. Both allotropic forms have a tetragonal crystal structure with different unit cell dimensions. In the anhydrous state, the material is light blue to almost white, and is rapidly hydrolyzed in air to form a mixture of uranyl fluoride and UF_4 as shown by the reaction

$$2UF_5 + 2H_2O \rightleftharpoons UO_2F_2 + UF_4 + 4HF. \qquad (3)$$

Under anhydrous conditions, the material eventually comes to equilibrium with UF_6 and UF_4 as shown by the disproportionation reaction

$$2UF_5(s) \rightleftharpoons UF_4(s) + UF_6(g). \qquad (4)$$

Solid uranium enneafluoride, U_2F_9, is a black solid material, mistakenly thought when first prepared to be a crystal modification of UF_4 and hence termed "black UF_4." It is formed under appropriate pressure and temperature conditions by the reaction of UF_6 with UF_4 and also in the corrosion of certain metals by UF_6. It possesses a cubic crystal structure and, like UF_5, is hydrolyzed in air, but at a significantly slower rate. Under anhydrous conditions, U_2F_9 will, like UF_5, come to equilibrium with the eventual end products UF_6 and UF_4.

Solid U_4F_{17} is also black; the material is not well characterized, although it is known to possess a unique diffraction pattern and apparently has a distorted UF_4 crystal geometry. It also will disproportionate, under anhydrous conditions, into UF_6 and UF_4.

Any of the three reduced fluorides can be produced by the reaction of UF_6 with UF_4 under the proper pressure-temperature conditions. Similarly, the disproportionation of the materials occurs in a step-wise fashion shown by the following series of reactions:

$$3UF_5(s) \rightleftharpoons U_2F_9(s) + UF_6(g) \qquad (5)$$
$$7U_2F_9(s) \rightleftharpoons 3U_4F_{17}(s) + 2UF_6(g) \qquad (6)$$
$$2U_4F_{17}(s) \rightleftharpoons 7UF_4(s) + UF_6(g). \qquad (7)$$

The equilibrium pressures of UF_6 in this series of dissociation reactions have been determined by Agron(4), from whose data Fig. 2 has been developed. In this diagram, the logarithm of the UF_6 pressure is shown as a function of the temperature in °C. Formation of UF_5 is favored at higher pressures and lower temperatures, with β-UF_5 formed at temperatures below 125°C and α-UF_5 formed at temperatures above this point. Formation of the various other reduced fluorides is favored by lower pressures and higher temperatures. Under any reasonable conditions of storage of UF_6-containing cylinders, this diagram indicates that the reduced fluoride expected to be formed by reaction of UF_6 with the cylinder walls would be UF_5.

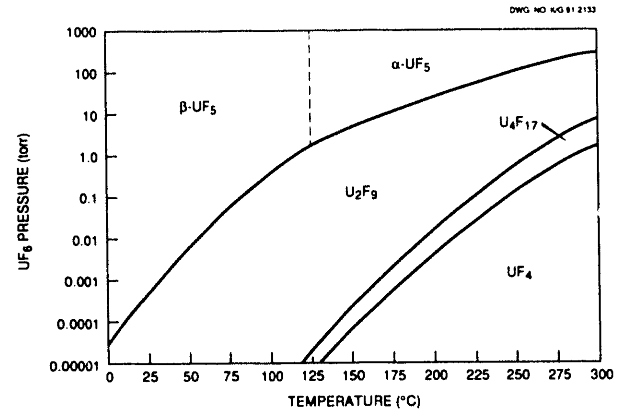

Fig. 2. Reduced uranium fluoride equilibrium.

However, the UF_6 pressure and temperature are not the only factors determining the reduced fluoride formed, but, as mentioned above, the specific metal involved also must be considered. For example, in gaseous diffusion cascade equipment, U_2F_9 has consistently been identified as the reduced fluoride formed on steel surfaces under conditions in which the equilibriam diagram would predict formation of UF_5.

CORROSION OF STEEL BY GASEOUS UF_6

The corrosion rate of steel surfaces by gaseous UF_6 is difficult to quantify, since the corrosion rate is influenced not only by the composition of the specific alloy under consideration, but also by other factors which are often difficult to characterize. The corrosion rate can vary widely for different melts of supposedly the same composition, and it is also strongly influenced by the mechanical working of the surfaces, for example, in rolling operations. In fact, widely different corrosion rates have been measured on opposite sides of the same test coupon. Nevertheless, an equation has been developed which seems to give at least a good approximation of the corrosion rate of 1020 or A-516 steel; this relationship is given by equation (8)

$$\ln R = 22.2712 - 12380/T \qquad (8)$$

where T is the temperature in K and R is the steel penetration or corrosion rate in mil/day. Using this equation, the time required to penetrate the 5/16-in wall of a UF_6 storage cylinder at 70°C (assumed to be the maximum temperature experienced by such a cylinder when exposed to direct rays of the sun) is on the order of a million years. Thus, there is little reason to be concerned about the internal corrosion of steel storage cylinders by anhydrous UF_6.

REACTION OF UF_6 WITH WATER VAPOR

The reaction representing the hydrolysis of UF_6 is usually written in the form

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF. \qquad (9)$$

This equation is probably valid, as far as the end products are concerned, for the reaction of gaseous UF_6 at high temperatures. Actually, to avoid the necessity of the three body collision required by equation (9), the mechanism probably involves the formation of an intermediate species, for example, as described by the reaction

$$UF_6 + H_2O \rightarrow UF_5OH + HF. \qquad (10)$$

However, equation (9) certainly does not adequately describe the reaction of water vapor with solid UF_6. The phase relationships in the UO_3-HF-H_2O system have been reported by

Buslaev et al(5) at 20°C, and in the UO_2F_2-HF-H_2O system by Kunin(6) at 25°C. The resulting phase diagrams in each of these studies were reported on a weight % basis, and on this basis the results were difficult to relate to each other. However, if both sets of data are first converted to a mole % basis, and the data of Kunin further converted to a UO_3-HF-H_2O basis, the data are in excellent agreement with each other and a meaningful interpretation of the results becomes possible. The results of such an exercise are shown in Fig. 3.

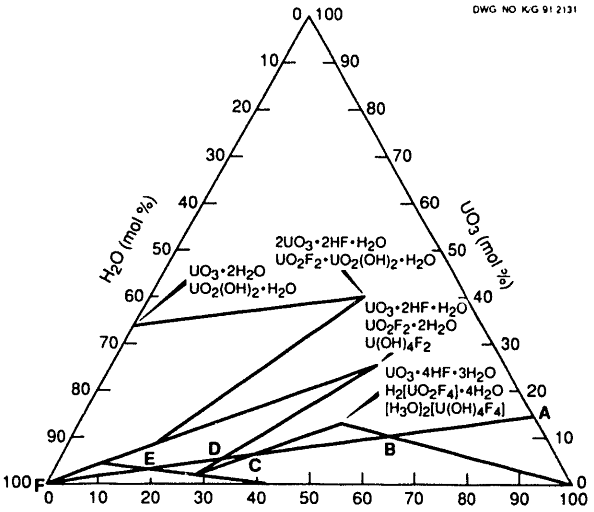

Fig. 3. Phase diagram of the UO_3-HF-H_2O system.

Four distinct solid phases, as identified by Buslaev et al, are shown in the diagram, with compositions as follows:

(1) $UO_3 \cdot 2H_2O$, or $UO_2(OH)_2 \cdot H_2O$;

(2) $2UO_3 \cdot 2HF \cdot H_2O$, which can also be written as $UO_2F_2 \cdot UO_2(OH)_2 \cdot H_2O$;

(3) $UO_3 \cdot 2HF \cdot H_2O$, which is simply the dihydrate of uranyl fluoride, $UO_2F_2 \cdot 2H_2O$, which can be written as $U(OH)_4F_2$; and

(4) $UO_3 \cdot 4HF \cdot 3H_2O$ (or $UO_2F_2 \cdot 2HF \cdot 4H_2O$), which is probably better written in the form $H_2(UO_2F_4) \cdot 4H_2O$ or $[H_3O]_2[U(OH)_4F_4]$.

The line AF in Fig. 3 represents the products resulting from complete hydrolysis of UF_6, i.e., the line representing a constant ratio of HF:U of 6:1. The first meaningful event on this line occurs at point B, where the solid phase of composition (4) is formed in equilibrium with essentially anhydrous liquid HF. As the water content increases further, varying amounts of this solid material remain in equilibrium with increasingly dilute aqueous HF solutions, until point C is reached. Upon further water addition, the concentration of the HF solution remains constant while the solid of composition (4) is converted to composition (3), $U(OH)_4F_2$; the conversion is complete at point D. Addition of further water produces more dilute HF solutions and higher uranium solubilities, with all of the uranium in solution at point E.

These results will change the steel corrosion rates significantly from the very low rates discussed above for corrosion by gaseous UF_6. Manuta(7) has shown that acidic hexavalent uranium solutions are reduced to UF_4 by iron, with the iron being oxidized to either the ferrous or ferric state. Thus, a possible corrosive reaction might be

$$3[H_3O]_2[U(OH)_4F_4] + 6HF + 2Fe \rightarrow UF_4 \cdot 2.5H_2O + 2FeF_3 \cdot 3H_2O + 4.5H_2O. \quad (11)$$

SOLUBILITY OF URANIUM IN AQUEOUS HF

From the data shown in Fig. 3, the solubility of uranium in aqueous HF solutions can be determined. The results are shown in Fig. 4,

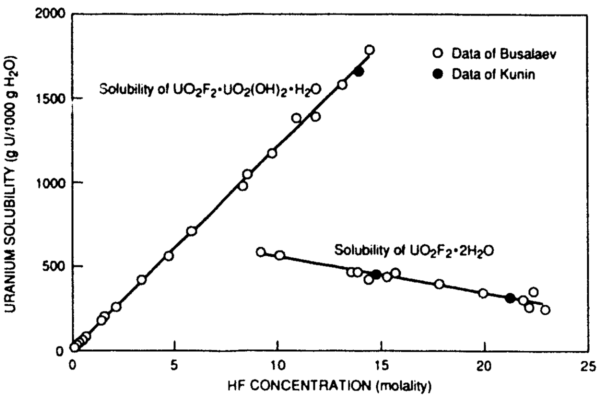

Fig. 4. Solubility of uranium in aqueous HF.

where the uranium solubility in g U/1000 g water is plotted as a function of HF molality (moles HF/1000 g water). The solubility of solid (2), $UO_2F_2 \cdot UO_2(OH)_2 \cdot H_2O$, is much greater than that of solid (3), $UO_2F_2 \cdot 2H_2O$, and increases linearly with increasing molality HF. The solubility of $UO_2F_2 \cdot 2H_2O$ decreases slightly with increasing HF concentration. This decreasing solubility trend continues for solid (4), as can be seen from the phase diagram in Fig. 3, until the uranium compound becomes only slightly soluble in anhydrous HF.

SUMMARY

Under normal storage conditions, the bulk of the UF_6 in a cylinder will be in the solid state with overpressures of gaseous UF_6 well below one atmosphere. Reaction of this gaseous UF_6 with the cylinder walls will be negligible, with the small amount of reduced fluoride formed likely to be U_2F_9. This corrosion picture is likely to be altered when solid UF_6 reacts with inleaking water vapor. It is apparent that the reaction usually cited for the hydrolysis of UF_6 [reaction (9) above] is an oversimplification of reality for conditions likely to be experienced in UF_6 storage cylinders, and especially in the case of the reactions involving solid UF_6. In this latter case, aqueous HF solutions may be produced in equilibrium with a solid material of the composition $[H_3O]_2[U(OH)_4F_4]$, with the net result being an enhanced corrosion rate of the steel container above that observed with gaseous UF_6.

REFERENCES

1. Barber, E. J., *The Physical and Chemical Properties of Uranium Hexafluoride*, Uranium Hexafluoride - Safe Handling, Processing, and Transporting - Conference Proceedings, CONF-880558, Martin Marietta Energy Systems, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, May 1988.

2. Oliver, G. D., Milton, H. T., and Grisard, J. W., *The Vapor Pressure and Critical Constants of UF_6*, J. Am. Chem. Soc. **76**, 2827-9, 1953.

3. Leitnaker, J. M., *Thermodynamic Data for Uranium Fluorides*, K/PS-352, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, March 1983.

4. Agron, P. A., *Thermodynamics of Intermediate Uranium Fluorides from Measurement of the Disproportionation Pressures*, Chemistry of Uranium, Collected Papers, Book 2, edited by Katz, J. J., and Rabinowitch, E., United States Atomic Energy Commission, Technical Information Service Extension, Oak Ridge, Tennessee, 610-26, 1958.

5. Buslaev, Yu. A., Nikolaev, N. S., and Tananaev, I. V., *On the Solubility and Composition of the Solid Phases in the System HF-UO_3-H_2O*, Academy of Sciences **148**, USSR, 1963.

6. Kunin, R., as cited by Katz, J. J., and Rabinowitch, E., *The Chemistry of Uranium*, National Nuclear Energy Series Division VIII - Volume 5, McGraw-Hill Book Co., Inc., 570, 1951.

7. Manuta, D. M., *Electrochemical and Thermodynamic Analyses of Breached Tails Cylinder Reaction Products*, POEF-522-90-541, Martin Marietta Energy Systems, Inc., Portsmouth Gaseous Diffusion Plant, Piketon, Ohio, August 2, 1990.

CHEMICAL ASPECTS OF CYLINDER CORROSION AND A SCENARIO FOR HOLE DEVELOPMENT

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ABSTRACT

In June 1990, two cylinders in the depleted UF_6 cylinder storage yards at Portsmouth were discovered to have holes in their walls at the valve-end stiffening ring at a point below the level of the gas-solid interface of the UF_6. The cylinder with the larger hole, which extended under the stiffening ring, was stacked in a top row 13 years ago. The cylinder with the smaller hole had been stacked in a bottom row 4 years ago. The lifting lugs of the adjacent cylinders pointed directly at the holes. A Cylinder Investigating Committee was appointed to determine the cause or causes of the holes and to assess the implications of these findings. This report contains a listing of the chemically related facts established by the Investigating Committee with the cooperation of the Operations and Technical Support Divisions at the Portsmouth Gaseous Diffusion Plant, the scenario developed to explain these findings and some implications of this scenario.

In summary, the interrelated reactions of water, solid UF_6 and iron presented by R. L. Ritter[1] are used to develop a scenario which explains the observations and deductions made during the investigation. The chemical processes are intimately related to the course of the last three of the four stages of hole development. A simple model is proposed which permits semiquantitative prediction of such information as the HF loss rates as a function of time, the rate of hole enlargement, the time to hydrolyze a cylinder of UF_6 and the approximate size of the hole. The scenario suggests that the environmental consequences associated with a developing hole in a depleted UF_6 cylinder are minimal for the first several years but will become significant if too many years pass before detection. The overall environmental picture is presented in more detail elsewhere.[2]

NOMENCLATURE

The symbols (g), (l) or (s) following a chemical formula indicate that the material is in the gas, liquid or solid phase; e.g., $H_2O(s)$ is ice.

BACKGROUND

In June 1990, as a result of an inspection of the depleted UF_6 cylinder storage yards at the three sites for a valve-stem corrosion problem, two cylinders in the yards at Portsmouth were discovered to have holes in the walls at the valve-end stiffening ring. Both holes were below the level of the gas-solid interface of the UF_6 in the cylinder. The cylinder with the large hole which extended under the stiffening ring was located in a top row and had been stacked for 13 years. The cylinder with the small hole was in a bottom row and had been stacked for 4 years. The lifting lugs of the adjacent cylinders pointed directly at the holes and apparently had struck and cracked the cylinder walls near the stiffening ring at the time of stacking. This observation is discussed more fully by J. H. Devan in a later presentation.[3]

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

Fig. 1. The width of the 4-yr old hole is about 2 in. Note the UF_4 hydrate in the tail etched in the cylinder wall below the hole.

The backside of the deposit of reaction products in the cylinder with the small hole, viz, the surface which had been next to the UF_6, was examined using a color video fiberoptics boroscope. The deposit was noted as being orange in color on the surface and shaped like a hemisphere of a crude oblate spheroid about a golf ball in depth and a tennis ball in diameter. The reaction products within the cylinder with the large hole were obviously deep and a partially successful core sampling was made. The depth of the UF_4 hydrate layer was about 4 in. and the depth of the yellow hexavalent uranium oxy-fluoride layer was in excess of 8 in. Chemical analysis of the yellow layer showed the material, which was essentially amorphous to x-rays, contained three fluorides per uranium and closely fit the formula $U(OH)_4F_3$ or $UO_2F_2*2H_2O*HF$. A 50:50 mixture of UO_2F_2 and $[H_3O]_2[U(OH)_4F_4]$ also would give this result. Both $U(OH)_4F_3$[4] and $[H_3O]_2[U(OH)_4F_4]$[5] have been identified but the yellow layer in the cylinder was amorphous.

Fig. 2. The width of the 13-yr old hole is about 8-in. A tail about 8-in long is seen below. The surface of the deposit in the tail region is suggestive of a deposit from a viscous solution.

Other Observations. The mass losses from the cylinders were small. The cylinder with the small hole lost about a pound and the one with the large hole lost 29 pounds. When the weight of the

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

Table 1. The reaction products are layered in the following order from iron to UF_6.

Material	Color
Fe	metallic
FeF_2 (weak x-ray pattern)	white (not seen)
$Fe_2F_5*xH_2O$ (x=7 or less)	gray to brown
Fe_3*xH_2O (x=3 or less)	whitish to light tan
FeF_3*3H_2O & $UF_4*0.75H_2O$	light violet
$UF_4*2.5H_2O$	green
$UF_4*1.5H_2O$ & $UF_4*0.75H_2O$	slightly darker green
$UO_2F_2*nH_2O$	fluorescent yellow
$[H_3O]_2[U(OH)_4F_4]$ & UO_2F_2	yellow
$U_2O_3F_6$ (by color only)	orange
-UOF4 (" " ")	bright orange
UF_6	clear solid

materials recovered outside the cylinders is accounted for, these mass losses become almost zero and 17 pounds, respectively. The mass of iron oxidized in the two cylinders was estimated to be 0.16 and 3.6 kg, respectively. Based on the shape of the deposit within the cylinder with the small hole and the relative depths of the reduced and hydrolyzed layers in the cylinder with the large hole, the quantity of $UF_6(s)$ hydrolyzed exceeds the quantity reduced by a factor of about 25. When the chemistry is accounted for, the loss of uranium as UF_6 from within the cylinders would be about 4 and 110 pounds, respectively.[6]

The fact that an open path for gas and vapor from the atmosphere to the ullage did not exist was indicated by the presence of a -4 psig vacuum in the cylinder with the small hole and 8 psig pressure in the cylinder with the large hole. Accumulation of HF was shown to have occurred in the ullage in both cylinders with the greater amount, perhaps as much as 2 liters of liquid, having collected in the cylinder with the large hole.[7] In addition to this HF retained in the ullage within the cylinders, HF vapor in the atmosphere was detectable both by odor and by instrumentation in the vicinity of the large hole. The HF vapor was not detectable in the vicinity of the small hole until after the breached cylinder and the adjacent cylinder were separated.

Features of the Chemical Attack. Five features of the chemical attack on the cylinder need to be explained. First, the overall reaction is very slow but the accumulation of reaction products does not stop the reaction.

Second, the hydrolysis reactions occurring at the surface of solid UF_6 result in the retention of most of the UF_6 in the cylinder as complex UO_2F_2 solvates (compounds containing both water and HF) which have limited solubility in the conductive solution of nearly anhydrous HF produced there.

Third, this conducting solution permits the coating of the hydrolyzed hexavalent uranium complex by a thickening, less soluble layer of UF_4 hydrate. In this electrochemical process, the iron is oxidized to an insoluble iron fluoride hydrate retained at the iron surface while the U^{+6} material in the solution and at the UO_2F_2 solvate surface is reduced to produce UF_4 hydrates. This ties up much of the fluoride content of the solution and greatly reduces its acidity.

Fourth, all the solid products deposited as the outer coating layer are not very soluble in water and tend not to migrate far, limiting the environmental impact of these materials to the immediate vicinity of the cylinder.

Fifth, when the hole becomes large, there will be enough of the strongly acidic HF solution produced that some will ooze out of the plugging materials and attack the cylinder wall below the hole and even the surface of the cylinder below, producing etched grooves. The corrosion deposits on the adjacent lifting lug and stiffening ring just below the small hole are believed to have been produced by this mechanism. This condition may be aggravated by rain since more hexavalent uranium is dissolved in more dilute HF solutions. The finding of a high concentration of uranium in a grab sample of the soil at the edge of the concrete pad where the rain drained off the cylinder with the large hole is additional supporting evidence.

SCENARIO FOR HOLE AND PLUG DEVELOPMENT

The observations, measurements, analyses and deductions can be accounted for by the following scenario which traces the development of holes through four phases using illustrative sketches. The hole development being described here is for the presence of solid UF_6 at the bottom of the fracture. If the fracture is in the top of the cylinder, the scenario being presented is not necessarily correct once hole growth enters the fourth phase.

Phase 1 Wall Fracture (Fig. 4). The duration of this phase is of the order of milliseconds. The sharp corner of a lifting lug of one cylinder strikes or is struck by another cylinder near a stiffening ring below the surface of the solid UF_6 in the cylinder as shown. On rare occasions (2 in more than 40,000), the result is an undetected fracture which extends completely through the wall of the cylinder. Almost immediate detection may or may not be possible as discussed under phase 2.

Phase 2 Initial Plugging of the Fracture (Figs. 5 and 6). The next phase is the development of a plug in the fracture produced in phase 1. The time frame for this phase is hours and the plug will be developed fully in about 24 hours. Figure 5 shows a very early stage in the plug development. The chemical attack begins in the fracture at or near the external surface of the cylinder wall. It must be here because the sublimation pressure of UF_6 is approximately four times the vapor pressure of water and two moles of water are required for each mole of UF_6 converted to UO_2F_2. This has been confirmed by crude computer simulation using reasonable values for the diffusion coefficients of water vapor and UF_6 vapor in air[8]. Only at the exterior surface is sufficient water vapor available to produce HF—H_2O fog and some condensate on the steel surface. The UO_2F_2 hydrate formed in the fracture produces a plug which slows the diffusion of UF_6 to the surface. If the fracture is not detected before this plug is fully developed, it is not likely to be detected until some time after the completion of phase 3.

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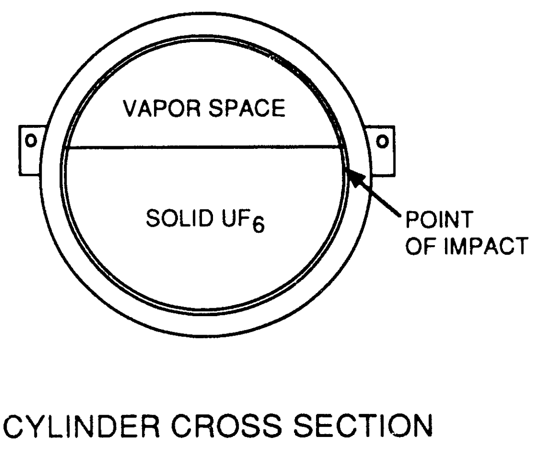

Fig. 4. Initiating mechanism is impact fracture at position shown.

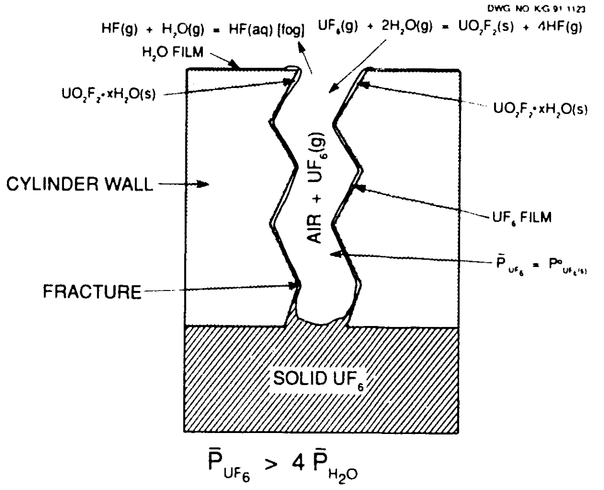

Fig. 5. Schematic cross section of fracture shortly after impact showing results of chemical reaction initiation.

The initial fracture may or may not be immediately detectable since detection depends upon seeing the HF—H_2O fog formed upon the hydrolysis of UF_6 with water vapor.[9] Conditions in winter are less favorable to fog formation because the stored UF_6 is colder, the rates of reaction slower, and the concentrations of the reactants lower. Storing cylinders longer before stacking also lowers the probability of detection. By some combination of factors, the fractures in the two cylinders went undetected during this phase.

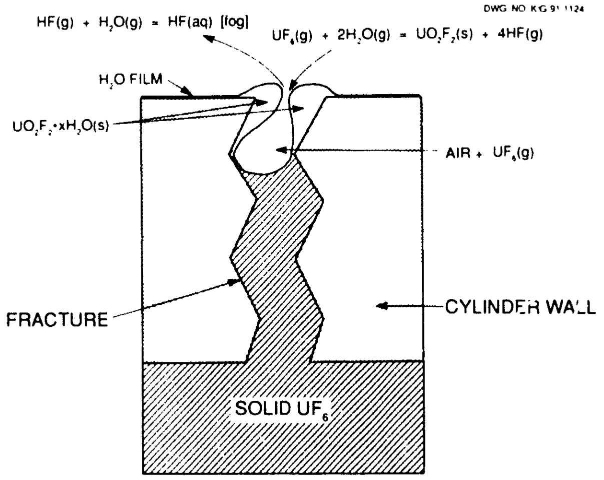

Fig. 6. Schematic cross section of fracture showing development of initial plug nearing completion.

The conditions illustrated in Fig. 6 exist in the fracture just before final closure of the fracture by hydrolysis products makes another change in the time frame for reaction. The reactions at this point in the process are the same as in Fig. 5 except for being slower.

<u>Phase 3 Corrosion of the Walls of the Fracture</u> (Figs. 7 through 10). When the diffusion of the UF_6 to the surface is reduced sufficiently that water vapor is in excess at the fracture exit, aqueous HF is produced which dissolves some of the UO_2F_2. This conducting acidic solution attacks the iron, producing green UF_4 hydrate and iron fluoride hydrates. At the steel surface a very thin layer of FeF_2 is probable. (It's not visible.) On top of this a layer of brick brown or gray Fe_2F_5 hydrate is found. (The color depends on the degree of hydration.) Next to this is a layer of greenish white FeF_3 hydrate which becomes a yellowish tan on exposure to moist air. The UF_4 hydrate is at the center of the fracture and is somewhat porous. This UF_4 hydrate contains very little iron. There is always UO_2F_2 solvate between the UF_4 hydrate layer and the $UF_6(s)$ as shown previously in Table 1. The time frame for the corrosion illustrated in the figures is on the order of months.

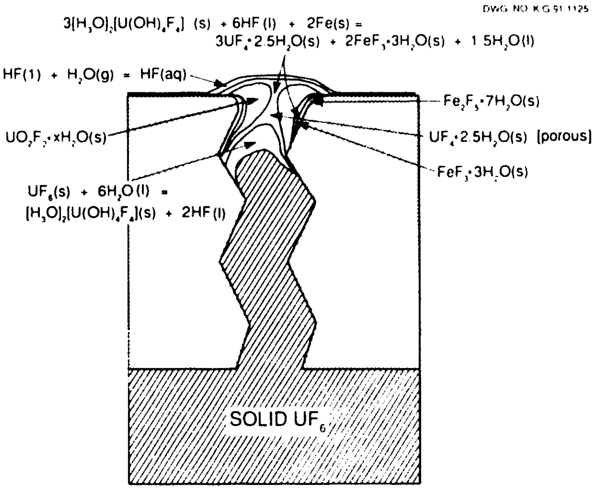

Fig. 7. Schematic cross section of fracture showing initiation of reduction and interior hydrolysis reactions in phase 3.

In Fig. 7 the initiation of the chemical attack on the wall is illustrated. The reaction of the $UF_6(s)$ with H_2O within the fracture is given by the equation:

$$UF_6(s)+6H_2O(l) = [H_3O]_2[U(OH)_4F_4](s)+2HF(l). \quad (1)$$

The principal reaction which is initiated at the exterior surface of this material and at the iron surface may be summarized by:

$$3[H_3O]_2[U(OH)_4F_4](s)+6HF(l)+2Fe(s) = 3UF_4{*}1.5H_2O(s)+2FeF_3{*}3H_2O(s)+4.5H_2O(l). \quad (2)$$

Note that all the fluorine in the starting UF_6 is consumed by the UF_4 and the iron fluoride formed by reaction 2. Since HF accumulates within the cylinder ullage, more U as UF_6 must be hydrolyzed by reaction 1 than is reduced by reaction 2 and the formation of the observed layer of UO_2F_2 solvate is explained.

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

$$3UO_2^{+2}(aq)+6F^{1}(aq)+12HF(aq)+7.5H_2O(aq)+2Fe(s) = 3UF_4{*}2.5H_2O(s)+2FeF_3{*}3H_2O(s). \quad (3)$$

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

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

Figure 9, which represents the conditions in the fracture several months after Fig. 8, shows the hydrolytic attack of the $UF_6(s)$ has proceeded into the UF_6 inside the cylinder itself. The same redox reactions continue to deepen the UF_4 hydrate layer and the area of the fracture surface attacked continues to enlarge. The degree of hydration of the UF_4 is less in the locations where the concentration of H_2O is expected to be less, namely, toward the UF_4-uranium oxyfluoride complex interface. The overall rate of attack on the steel surface is increasing. Note that the ordered layering of the reaction products continues.

Phase 3 comes to completion when the attack on the iron is occurring over the full depth of the fracture as illustrated in Fig. 10. The attack on the steel is proceeding from the outside in and is producing a hole with the bevel facing the outside.

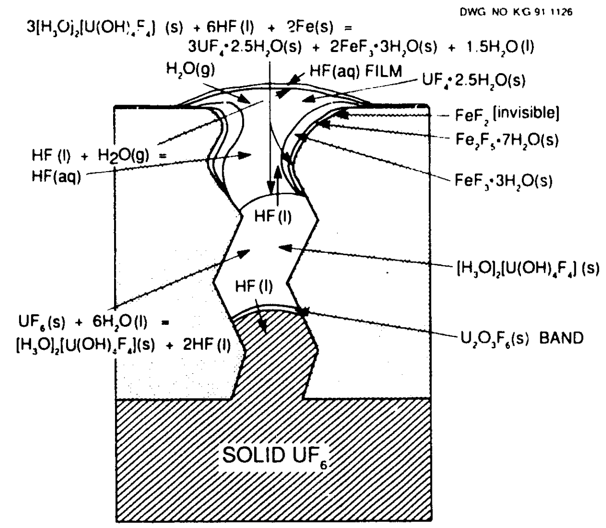

Fig. 8. Wall attack at fracture continues. Outer layer of UO_2F_2 hydrate replaced by UF_4 hydrate. Internal hydrolysis reaction continues down fracture.

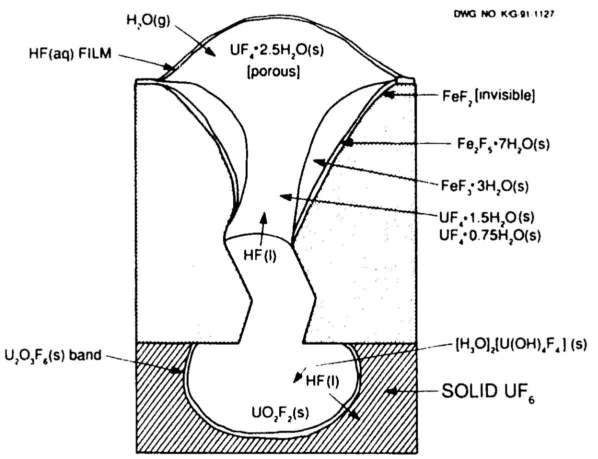

Fig. 9. Wall attack at fracture continues. Hydrolysis reaction enters into cylinder UF_6. Fracture is enlarging from outside in.

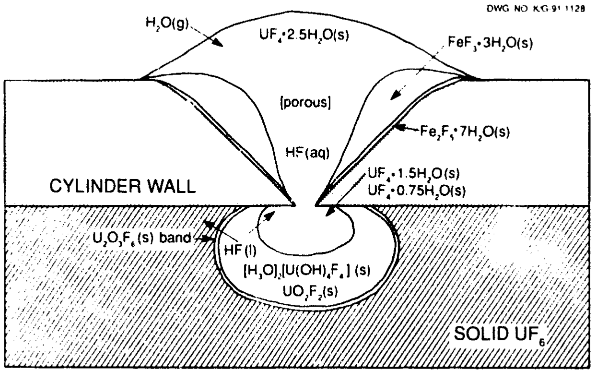

Fig. 10. Phase 3 is completed as fracture is enlarged along full depth. The UF_4 hydrate is now forming inside the cylinder. Hydrolysis of UF_6 reactions surround the UF_4 inside the cylinder.

Once the bevel reaches through the wall thickness, the rate of attack will increase as the circumference of the crack increases, but the rate of attack per unit length of the circumference will remain practically constant. Ten to fourteen months will have elapsed since the impact when this occurs. As shown, UF_4*$1.5H_2O$ and UF_4*$0.75H_2O$ will have begun to be produced inside the cylinder with a major yellow layer between it and the UF_6(s).

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

Phase 4 Enlargement of the Hole and Production of External Products (Figs. 11 and 12). The last or fourth phase of hole development is entered when the fracture size begins to increase. It begins about one year after the initiating impact and ends when all the UF_6 in the cylinder has been hydrolyzed perhaps as much as 30 years later. Thus, the time frame for this process is years. In this scenario the enlargement of the effective hole diameter is assumed to occur at a relatively constant rate when viewed over a sufficiently long period of time. At some stage in the growth of the hole, attack of the interior surface of the cylinder wall at the hole edge becomes significant and wall thinning from the inside occurs by the same mechanism as it initially began from the outside. In fact, the wall thinning extended on the inside beyond the hole by 5 or more inches in the case of the cylinder with the large hole. (See Fig. 12.)

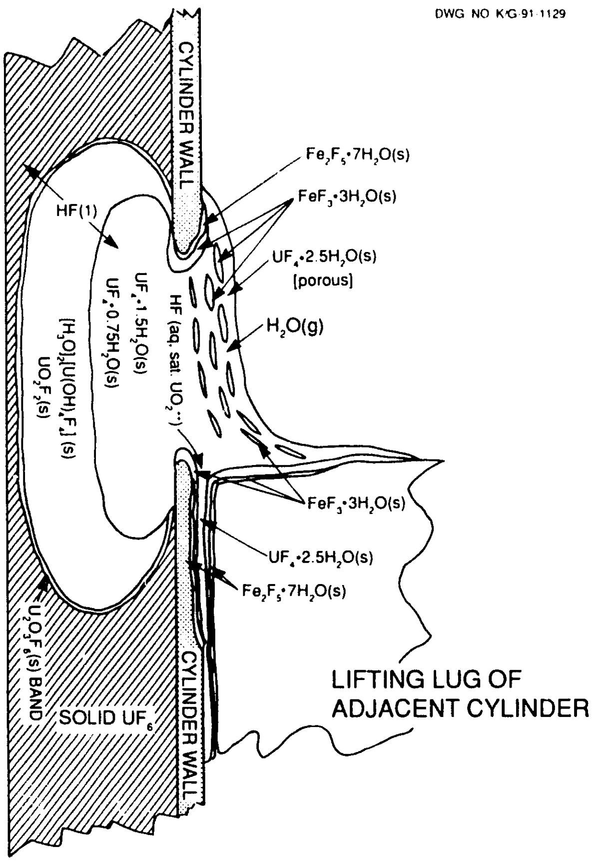

Fig. 11. The main reactions continue to be hydrolysis of UF_6 inside and reduction to UF_4 inside and outside the cylinder. The fracture has become a small hole after 4 years.

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

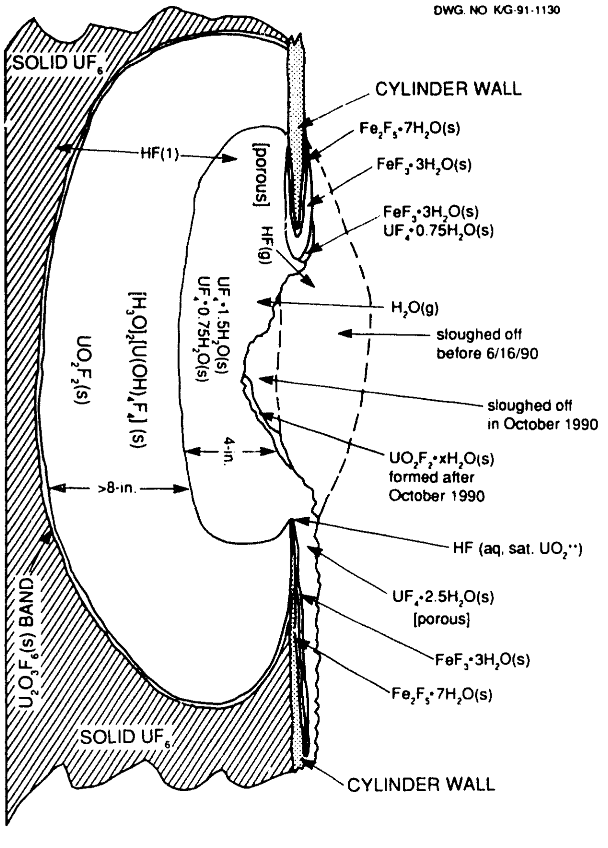

Fig. 12. The hydrolysis and reduction reactions continue. Deposits outside the cylinder slough off. The HF escapes as both vapor and solution and also builds up in the ullage. A small amount of hexavalent uranium in solution not reduced to UF_4 hydrate escapes from the vicinity of the cylinder as UO_2^{++}. Condition shown is for 13 years after impact. The hole is now more than 8 in. across.

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

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

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

As is suggested above, when a hole becomes this large there will be loss of HF vapor by vaporization of the oozing liquid. Estimation of the loss of HF from the cylinder with the large hole using a simple model indicates that the rate of loss of HF at the time of discovery might have been as large as 3.7 g HF per hour; however, not necessarily all of this material would have been lost as vapor. Environmental samples taken in the vicinity of the cylinder with this large hole did not indicate concentrations of HF above the permissible exposure limit (PEL) of 2.5 mg HF/M^3 or 8 hours.

The etch pattern on the cylinder below the one with the small hole suggests that not all the hexavalent uranium in the strongly acidic solution was reduced to UF_4 hydrate. The missing mass of 17 pounds, which the chemistry indicates might be equivalent to the loss of about 110 pounds of UF_6 as uranyl fluoride solution, is strongly supportive of this observation. Failure to find any general soil contamination at the edge of the pad where the rainwater drained from the cylinder with the large hole is not counterindicative because uranyl ion is not retained well in soil.

A SIMPLE MODEL

The scenario provided may be employed to develop a simple model for examining semiquantitatively features of the chemical attack, such as the rate of hole enlargement, the loss rate of HF, the time to hydrolyze all the UF_6 in the cylinder and the size of the hole. The bases for the model are given in Table 2. Some of the results are shown in Table 3.

Table 2. The bases of a simple model.

- There is an induction period before hole enlargement begins which is dependent on the cylinder wall thickness (10 to 14 months for 5/16-in. wall.)
- The rate of enlargement of the hole diameter is practically constant once the wall is chemically attacked through the full thickness.
- The amount of UF_4 produced can be calculated from the mass of iron converted to iron fluorides. Use Equation 2. These reactions effectively do not contribute to the formation of HF.
- The total amount of UF_6 hydrolyzed is about 26 times the amount reduced.
- The hydrolyzed UF_6 present in the cylinder has an average composition which corresponds to a 50:50 mixture of $[H_3O]_2[U(OH)_4F_4]$ and UO_2F_2. This means the retained hydroysis product weighs more than the UF_6 it replaces as shown in Reaction 4

$$UF_6(s)+4H_2O(g) = UO_2F_2{*}2H_2O{*}HF(s)+3HF(l) \quad (4)$$

- The HF not tied up with the hydrolysis product either diffuses through the solid UF_6 to the cylinder ullage for retention or to the exterior surface of the plug to be lost as solution or vapor.
- The loss rate of HF is proportional to the surface area of the hole.

Table 3. Estimated quantities of UF_6 hydrolyzed and HF released, hole groth rates and other model parameters.

Quantity Estimated	Cyl. 4G127985	Cyl. 4G115688
Mass of iron oxidized (fluorinated), kg	0.16	3.6
Mass of UF_6 reduced, kg	1.5	34.0
Mass of UF_6 to produce recovered deposits, kg	0.32	4.9
Mass of UF_6 hydrolyzed and reduced in cyl., kg	1.2	29.1
Total mass of UF_6 hydrolyzed, kg	13.7	916.
Mass of UF_6 producing HF retained in cyl., kg	4.8	42.
Mass of UF_6 producing escaping HF, kg	7.4	840.
Total mass of HF which escaped hole, kg	1.26	143.
Predicted HF escaping in 5th & 14th yr, resp., kg	1.99	35.6
Predicted mass UF_6 hydrolyzed next year, kg	11.7	209.
Est. rate of HF escape at discovery, g/hr	0.16	3.73
Steady state rate of escape of HF, g/sq cm-hr	7.91×10^{-3}	7.91×10^{-3}
Rate of hole radius enlargement, cm/hr	1.08×10^{-4}	1.08×10^{-4}
Est. time to steady state rate, year	1	1
Est. time to hydrolyze all UF_6 in cyl., yr		32
Est. diameter of hole for above, in.		24

SUMMARY

The four phase scenario presented explains the observations made to date. It provides a simple model which can be used to estimate the seriousness of the effects of hole development in a cylinder fractured below the level of the solid UF_6 over a longer time than 13 years. It also appears to be applicable for a period of one to possibly two years for an impact fracture above the solid UF_6 level. It is not applicable to a large hole such as might be introduced above the solid UF_6 level by a projectile.

ACKNOWLEDGMENTS

This study would not have been possible were it not for the cooperation and assistance of many persons at the Portsmouth Gaseous Diffusion Plant. The author wishes to recognize the work of the persons who assisted in gathering and interpreting the chemical information reported here:

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REFERENCES

1. Ritter, R. L. and Barber, E. J., *Aspects of Uranium Chemistry Pertaining to UF_6 Cylinder Handling*, Proceedings of this Conference.
2. Boelens, R. A., *Breached Cylinder Incident at the Portsmouth Gaseous Diffusion Plant*, Proceedings of This Conference.

3. Devan, J. H., *Investigation of Breached Depleted UF_6 Cylinders*, Proceedings of This Conference.
4. Pickrell, P. W., *Characterization of the Solid, Airborne Materials Created by the Interaction of UF_6 with Atmospheric Moisture in a Contained Volume*,(K/PS-144) p-13, Union Carbide Corporation, Nuclear Division, Oak Ridge, Tennessee, April 30, 1982.
5. Buslaev, Yu. A., Nikolaev, N. S. and Tananaev, I. V. *On the Solubility and Composition of the Solid Phases in the System HF-UO_3-H_2O*, Akademy of Sciences, USSR, 148, 832-834 (1963) [8].
6. Taylor, M. S. Ed., *Investigation of Breached Depleted UF_6 Cylinders*, Martin Marietta Energy Systems, Inc. and U. S. Department of Energy, Oak Ridge Operations, Oak Ridge, Tennessee, In Preparation, August 1991.
7. *Appendix B2* of Reference 6.
8. L. D. Trowbridge, Enrichment Technical Operations, Martin Marietta Energy Systems, Inc. made the computer estimates.
9. Schotte, W., *Fog Formation of Hydrogen Fluoride in Air*, Ind. Eng. Chem. Res., 26, pp. 300-306, 1987.

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HEALTH PHYSICS CONSIDERATIONS IN UF_6 HANDLING

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INTRODUCTION

Uranium is a radioactive substance that emits alpha particles and very small amounts of gamma radiation. Its daughter products emit beta and gamma radiation. In uranium handling operations these are the radiations we must consider. In this presentation we will look at the characteristics of the radiations, the isotopes from which they originate, the growth and decay of the uranium daughter products, and some specific health physics practices dictated by these factors.

NOMENCLATURE

dpm	Disintegrations per minute.
ALI	Annual Limit on Intake. The radioactivity of a radionuclide which taken alone would irradiate a person, represented by Reference Man, to the limit set by the ICRP for each year of occupational exposure.
DAC	Derived Air Concentration. The ALI (of a radionuclide) divided by the volume of air inhaled by Reference Man in a working year (i.e. 2.4×10^3 m^3) The unit of DAC is Bq m^{-3}.
Bq	becquerel, the unit of activity equal to 1 disintegration per second.
A	Activity of a radionuclide after a given time period of radioactive decay.
A_0	Activity of a radionuclide at the beginning of a period of radioactive decay.
e	Base of natural logarithms.
λ	Decay constant. The fraction of the number of atoms of a radioactive nuclide which decay in unit time.
t	Time elapsed for radioactive decay or buildup.
A_{eq}	Activity of a radionuclide when it is in radioactive equilibrium with its parent isotope.

CHARACTERISTICS OF RADIATIONS

This is a brief reminder of the penetration characteristics of alpha, beta, and gamma radiations.

Alpha radiation— very little penetration. Stopped by a sheet of paper or the dead outer layer of the skin.

Beta radiation— Range in tissue of the body about 1 cm. Stopped by 1/4 inch of aluminum.

Gamma radiation— reduced by heavy shielding, 1/2 inch of lead for example.

These degrees of penetration are illustrated in Figure 1.

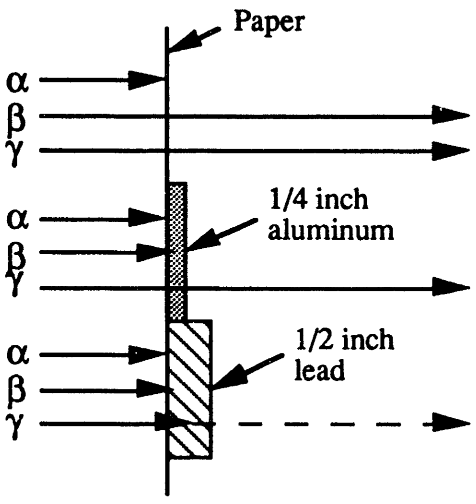

Figure 1. Relative penetration of radiations

EXPOSURE POTENTIALS FROM URANIUM

Since alpha particles cannot penetrate the dead outer layer of the skin, uranium does not present a radiation exposure potential as long as it is kept outside of the body. Skin and clothing contamination produce no direct exposure, but may serve as sources of uranium materials that can enter the body by becoming airborne and entering the body by inhalation. Possible routes of exposure include smoking cigarettes with contaminated hands, with uranium being transferred to the cigarettes, becoming vaporized as the cigarette burns, and thereby being inhaled with the smoke. Eating with contaminated hands may result in the ingestion of radioactive materials. With contamination on the clothing body movements can dust off some of the materials and cause airborne activity that is subject to inhalation. Surface contamination in the work place can also become airborne through air movements to produce a potential for inhalation exposure.

Estimates of the amounts of exposure from these sources at the radiation protection guide values were developed on the basis of tests made at the K-25 Site many years ago, and a few comparisons are made with calculations based on data from other sources. With respect to the K-25 data the calculations are based on extreme conditions for exposure and ignore all good health physics controls such as requirements for washing hands and the prohibition of eating and smoking in contaminated areas.

Smoking with contaminated hands — 0.3 % average.of the DAC.

Basis: (1) The radioactivity guide for hands is 1000 dpm/ hand surface (100 cm^2) as interpreted from meter calibrated with a plated source; 1% of contamination on the palmar surface of one hand is transferred to each cigarette; 0.2 % of the transferred material is inhaled; 20 cigarettes smoked per work day; no hand washing; continually handling the source of contamination so the hands are always freshly contaminated; assuming the uranium inhaled to be oxides which have a long biological half-life in the body (Class Y), and including a correction for the fact that the counting geometry for hand contamination is 30% of that for a plated source..

Oral intake of uranium from contaminated hands — 7.1% of the ALI.

Basis: (2) The annual limit on oral intake of soluble uranium compounds is 4×10^5 Bq. For every working day an individual consumes all of the uranium on both of his/her hands; hands are contaminated to the radioactivity guide of 1000 dpm/100 cm^2 with a soluble uranium compound; the same correction noted above for difference between hand-counting geometry and plated source geometry applies.

Airborne contamination from contaminated clothing — 0.87% of the DAC for compounds of intermediate solubility (Class W compounds) or 13% if the compounds are class Y.

Basis: (3) Airborne contamination in dpm/m^3 = 0.0967 x maximum point contamination on clothing in dpm/100 cm^2; average contamination on front surfaces of clothing is one third the highest value; radioactivity guide = 1000 dpm/100 cm^2 as defined above, actual counting geometry for clothing contamination = 12% of that for a plated source, DAC for a uranium of intermediate solubility (Class W) = 3×10^{-10} µCi/mL = 666 dpm/m^3. If we use the ratios derived from the data of Butterworth and Donoghue (4) as obtained with personal air samplers worn on the chest, the calculated airborne levels would be approximately 15 times greater.

Resuspension of contamination into the air — 0.38 % of DAC

Basis: Resuspension factor of 5×10^{-6} (µCi/m^3)/(µCi/m^2) relating airborne activity to surface activity, suggested by the International Atomic Energy Agency (IAEA) (5).used to calculate airborne activity from a surface contaminated to the radioactivity guide of 5000 dpm/100 cm^2.

A number of papers dealing with the relationship between surface contamination and airborne contamination were presented at a symposium on surface contamination held in Gatlinburg, Tennessee in 1964 (6). Results reported by various investigators varied widely. The value suggested by the IAEA supports our present guide values very well.

Obviously a major objective in handling radioactive materials should be to keep them properly confined. In a UF_6 handling operation a primary concern is to keep the UF_6 from being released to the atmosphere. This includes the routine control of small releases which can occur when the connections of transfer lines to cylinders are uncoupled. Several papers in this session deal with experiences and handling methods in UF_6 operations, and I am confident that these aspects of UF_6 operations will be adequately addressed.

ENRICHMENT AND SPECIFIC ACTIVITY

In natural uranium the activity of ^{234}U is approximately equal to that of ^{238}U, and the activity of the ^{235}U constitutes only a small fraction of the total. In the uranium enrichment process the separation of the isotopes depends on the differences of the atomic weights of the isotopes, so the ^{234}U is enriched along with the ^{235}U. Since its specific activity is about 2,900 times that of ^{235}U, most of the radioactivity of enriched uranium is due to the ^{234}U isotope, and the specific activity of 93% enriched uranium is approximately 100 times that of natural uranium. The relationship between enrichment and specific activity is shown in Figure 2 which was taken from the Nuclear Regulatory Commission's Regulatory Guide 8.11.

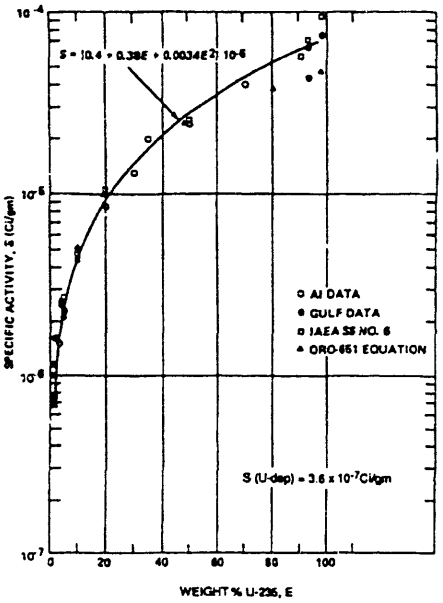

Figure 2. Specific activity for mixtures of ^{234}U, ^{235}U, and ^{238}U

I will point out that the higher specific activity of enriched uranium does not affect the applicable radiation protection guide values, which are expressed in terms of activity. On an activity basis there are no appreciable differences among the natural uranium isotopes as far as radiation exposure potentials are concerned. The higher activity does mean that it takes a smaller mass of enriched uranium to produce a given level of airborne or surface contamination. Also the levels of contamination that can be experienced with enriched uranium are higher than those possible with normal or depleted uranium.

GROWTH AND DECAY OF DAUGHTER PRODUCTS

When a radioactive daughter product that is initially at equilibrium with its parent isotope is removed from the parent isotope the daughter product will decay with a characteristic half-life, decreasing to one-half its initial activity in one half-life, to one fourth its initial activity in two half-lives, to one eighth in three half-lives, etc. The daughter product will also "grow back" into the parent isotope to achieve one-half its equilibrium activity in one half-life, three-fourths its equilibrium activity in two half-lives, etc. The equations governing this decay and growth are:

For decay: $A = A_0 e^{-\lambda t}$. (Eq. 1)

For growth $A = A_{eq}(1 - e^{-\lambda t})$. (Eq. 2)

The growth and decay of daughter products are illustrated in Figure 3, and the initial daughter products of the natural uranium isotopes are shown in Table 1.

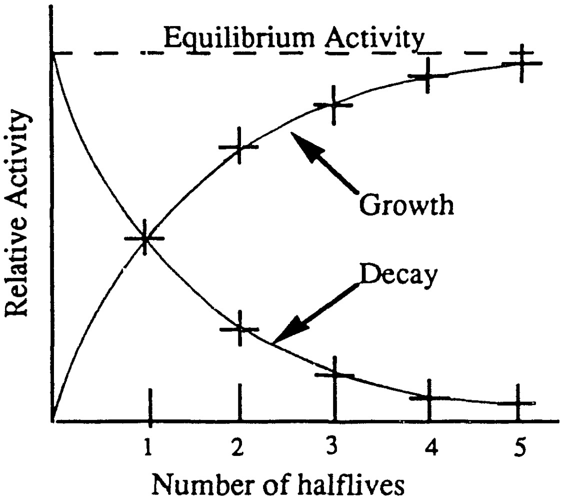

Figure 3. Growth and Decay of a daughter product

None of the uranium daughter products form volatile fluorides, so the daughter products do not remain with the parent isotopes if they are formed in UF_6 that is in the gaseous phase. The daughter products formed within a gaseous diffusion plant deposit on the surfaces inside the equipment and remain there. Therefore, UF_6 withdrawn from the diffusion plant into a clean cylinder is initially free of its daughter products. The first daughter product of ^{238}U, ^{234}Th, then grows in at a rate characteristic of its 24.1-day half-life. It will reach one-half its equilibrium value in 24.1 days and will continue to approach its

Table 1. Initial daughter products of ^{234}U, ^{235}U, and ^{238}U (7)

Nuclide	Half-life	Major radiation energies (MeV) and intensities*		
		α	β	γ
^{238}U	$4.51x10^9y$	4.15 (25%)	---	---
^{234}Th	24.1d	---	0.103 (21%) 0.193 (79%)	0.063 (3.5%) 0.093 (4%)
$^{234}Pa^m$ 99.87% 0.13%	1.17m	---	2.29 (98%)	0.765 (0.30%) 1.001 (0.60%)
^{234}Pa	6.75h	---	0.53 (66%) 1.13 (13%)	0.100 (50%) 0.70 (24%) 0.90 (70%)
^{234}U	$2.47x10^5y$	4.72 (28%) 4.77 (72%)	---	0.053 (0.2%)
^{230}Th	$8.0x10^4y$	4.62 (24%) 4.68 (76%)	--- ---	0.068 (0.6%) 0.142 (0.07%)
^{235}U	$7.1x10^8y$	4.37 (18%) 4.40 (57%) 4.58 (8%)	---	0.143 (11%) 0.185 (54%) 0.204 (5%)
^{231}Th	25.5h	---	0.140 (45%) 0.220 (15%) 0.305 (40%)	0.026 (2%) 0.084 (10%)
^{231}Pa	$3.25x10^4y$	4.95 (22%) 5.01 (24%) 5.02 (23%)	---	0.027 (6%) 0.29 (6%)

*Intensities refer to percentage of disintegrations of the nuclide itself, not to original parent of series.

equilibrium value as we have just discussed. Since UF_6 is solid at room temperature, the daughter products will remain dispersed throughout the UF_6 where they are formed. When the UF_6 is transferred from the cylinder by gas-phase transfer, the daughter products tend to remain in the cylinder, although some fraction of them may be carried out by entrainment in the exiting gas stream. Papers to be given later is this program deal with radiation levels from UF_6 cylinders.

When UF_6 is transferred from cylinders by liquid transfer, the daughter products tend to deposit in the transfer line, which is called a "pig tail" at the diffusion plants. Resulting radiation levels can amount to a few tens of mrem/hr gamma radiation at the surface of the pig tail and to a few tens of rem beta radiation at the open end of the pigtail. Any loose uranium materials dropping off the pig tails when they are removed from the connections can result in elevated beta-gamma contamination in the area. Also, any solutions used to clean the pig tails can contain high concentrations of the daughter products, and must be handled with due care. Plugging the ends of the pig tails with screw-in metal plugs when they are removed from the connections and holding them for, say, three months before cleaning them can reduce beta-radiation exposure potentials for personnel doing the work.

All uranium isotopes are parents of long chains of radioactive isotopes. In general, however, only the first one or two decay products have significant impact on UF_6 handling operations. The reason is that after one or two decays, the isotopes decay to very long-lived daughters. The long lived isotopes and their daughter products which are present in uranium ores are removed from natural uranium in the uranium milling and UF_6 feed production steps. As we have seen, it takes time for the long-lived daughter products to build up in the purified uranium. The degree of buildup of these daughter products is limited by relatively short time periods through which they could have built up their activities. For example, suppose we look at the amount of ^{230}Th that could have developed in surface contamination that occurred at the beginning of diffusion operations at the K-25 Site approximately 50 years ago. The first daughter of ^{234}U, ^{230}Th, with a half-life of 8.0×10^4 years, will have reached only 0.043% of the activity of the parent uranium. In terms of contamination control for surfaces outside the diffusion equipment itself, this isotope and isotopes below it in the chain can generally be ignored.

Inside the cascade, however, this isotope was being formed during all the plant's operating years in proportion to the total amount of ^{234}U in the equipment, and was deposited on interior surfaces of the equipment. The principal impact of this isotope may be on future decontamination and decommissioning activities since its presence may affect options for disposal of wastes generated during plant dismantling operations.

Uranium recovered from spent reactor fuels requires some special considerations with respect to diffusion plant operations and the final utilization of the uranium product. The consumption of the uranium fuel in reactors results in the formation of fission products, the transuranic elements neptunium and plutonium, and the artificial isotopes of uranium, ^{232}U, ^{233}U, and ^{236}U. Although most of the fission products and transuranic isotopes are removed from the uranium in the uranium recovery process, traces of these materials do carry through and can be introduced into the diffusion plants. The artificial uranium isotopes require various considerations in the final utilization of diffusion plant product, but to my knowledge they have not impacted the actual UF_6 handling operations significantly. The daughter products of ^{232}U might impact diffusion plant operations if they accumulate in the plant equipment to a level where their gamma radiations interfere with nondestructive measurements designed to locate possible deposits of uranium materials in the equipment.

The presence of the fission product technetium-99 in reactor return uranium requires special considerations with respect to diffusion plant operations and maintenance activities. It may also require special consideration in some aspects of the utilization of diffusion plant product, but again I am not aware of any impact of ^{99}Tc of UF_6 handling outside of the diffusion plants. The transuranic elements plutonium and neptunium form volatile fluorides and can carry through to the UF_6 product of the uranium recovery process. These elements tend to deposit on the insides of the cylinders in which UF_6 is shipped and to remain behind when the UF_6 is transferred from the cylinder by vaporization. These isotopes will be removed when the cylinders are cleaned, and appropriate handling methods will be required for any cleaning solutions. Their presence in the diffusion plants requires special evaluations to ensure that all required controls for these elements are observed. Like ^{230}Th, their greatest impact may be felt in the decommissioning of the plants, in that their presence may affect to a marked degree what disposition can be made of the wastes generated in the decommissioning process.

REFERENCES

1. Bailey, J. C. and Rohr R. C. "The Inhalation of Radioactive Materials as Related to Hand Contamination," Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, 1953 (K-1071).

2. "Limits for Intakes of Radionuclides by Workers," A Report of Committee 2 of the International Commission on Radiological Protection, Pergamon Press, Oxford: New York: Frankfurt.

3. Bailey, J. C., Becher, A. F., and Henry, H. F., "Inhalation from Uranium Contaminated Clothing,".*Proceedings of the Health Physics Society,* Pergamon Press,June, 1956.

4. Butterworth, R. and Donoghue, J. K., "Contribution of Activity Released from Protective Clothing to Air Contamination Measured by Personal Air Samplers," *Health Physics* 18, No.4, pp 319-323, April 1970.

5. International Atomic Energy Agency (IAEA) Technical Report Series No. 120, "Monitoring of Radioactive Contamination on Surfaces," 1970.

6. "Surface Contamination," Proceedings of a Symposium held in Gatlinburg Tennessee, June 1964, Pergamon Press, Oxford, 1967.

7. Radiological Health Handbook, Revised Edition, p 112, U. S. Department of Health, Education, and Welfare, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, 1970.

Uranium Facilities:
An International Overview

URENCO'S EXPERIENCE OF UF_6 HANDLING

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Abstract

Urenco operates enrichment plants at three sites (Figures 1, 2 & 3):- Almelo (Netherlands), Capenhurst (United Kingdom) and Gronau (Germany). Current installed separative work capacity is 2,500 tSWpa. Since 1971, when the first pilot plants were built, enrichment production has totalled 18,000 tSW. During this last 20 years over 3,500 48" containers of UF_6 have been fed to the plants, over 3,700 30" containers have been filled with product and delivered successfully to Urenco's customers worldwide and over 3,000 48" containers of depleted tails have been filled and have either been returned to customers or retained for long term storage on site.

The paper gives a brief outline of Urenco's experience in handling UF_6: the equipment and methods used in receiving, feeding, filling, blending, liquid sampling, storing, moving on site and despatching of UF_6 containers. Some of the difficulties experienced with UF_6 containers are appended.

Introduction

The Urenco Standards Procedures document describes, in general, what the minimum container acceptance criteria are and how Urenco handles UF6.

General principles for handling UF_6 are described in the ORO 651 series of reports. These are basic to the Urenco Standards Procedures but national statutory regulations have necessitated changes in some areas.

Fig.1. Urenco (NL) Almelo

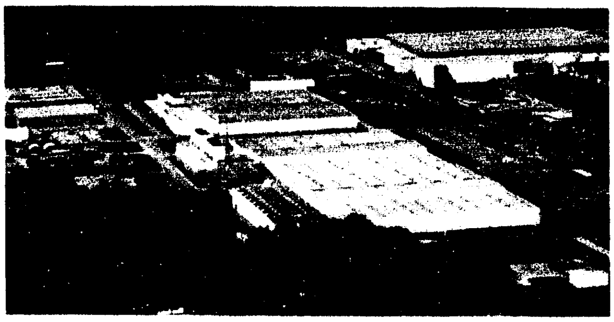

Fig.2. Urenco (UK) Capenhurst

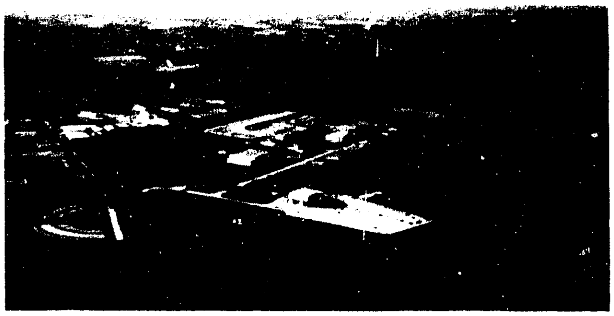

Fig.3. Urenco (D) Gronau

Receipt

Urenco has received feed containers from all the major conversion plants in the world (USA; Canada; France; UK and USSR).
Containers are inspected on receipt. Inspection criteria cover container identification and surface condition, valve and valve protector, plug, shell and heads, skirt and stiffener rings. Normally everything is in order but, when problems occasionally are found, the supplier is notified promptly. Examples of such problems are: faulty tie-downs, missing or incorrect paperwork, wrong labelling and name-plate data, inadequacies in the actual transport vehicles and the spares carried. Although rare there have been instances of surface contamination, missing or loose valve covers, bent lifting lug and shell head gouge.

After receipt and unloading containers are weighed prior to their move to temporary storage.

The control of nuclear material entering and leaving a Urenco plant is effected by a system of inventory weighings. The net weight of UF_6 feed accepted by Urenco is determined on the basis of weights of the container before and after emptying. The weighscales are periodically calibrated and regular check weighings are carried out to ensure the scale variation does not exceed prescribed limits. Calibration and certification of scales is by the applicable statutory authority.

Feeding

Containers, installed in the feed stations (Figure 5), are sampled and cold vented prior to being heated to produce gaseous UF_6 for supply to the centrifuge cascades. This may be either by steam heating in feed chests, feeding from solid UF_6, or by electrical (hot air) heating in autoclaves, feeding from liquid UF_6.

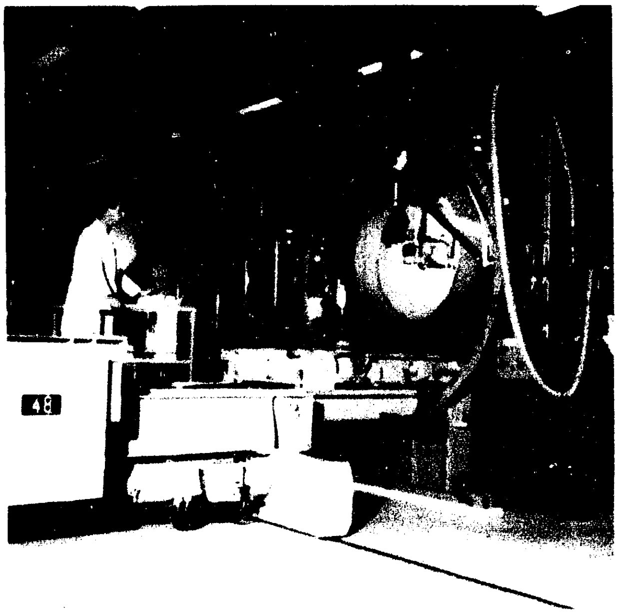

Fig.4. Feed Autoclaves

Emergency protection systems are provided to detect and protect against release of UF_6 either from within the feed station or from the primary, superatmospheric, feed distribution pipework. Although tested on a regular and frequent basis these systems have never yet been required to operate in a real emergency. Over the 20 year period there have been a limited number of minor UF_6 leaks from valves or pipework connections but they have been insignificant both in frequency and consequence.

Enrichment

From the feed containers UF_6 flows through pressure reduction and control equipment such that the centrifuge cascades (Figure 5) are fed at a very low pressure of 100's of Pa (a few mbar). Within the cascades centrifuges rotate at high speed to achieve an increase in the proportion of the active isotope U_{235} in the product stream.

The UF_6 is passed through the cascade by the pumping action of the centrifuges themselves. Urenco has around 100 cascades in operation consisting of hundreds of thousands of centrifuges in total.

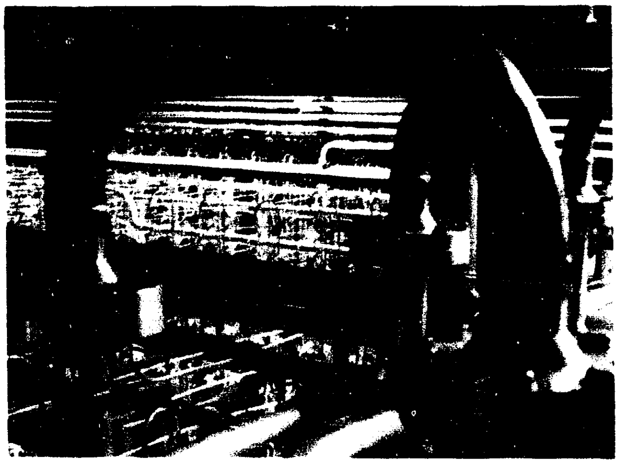

Fig.5. Centrifuge Cascade Pipework

Product and Tails Take-Off

After separation the two streams of UF_6 gas, one enriched in U_{235} and one depleted, are increased in pressure directly using pumps or indirectly using cold/heated desublimers. The UF_6 condenses as a solid in transit containers (Figure 6) which are cooled by water or air (5-10°C) either in the open or in enclosed chests.

Blending and Liquid Sampling

Part of Urenco's product is blended, or transferred from plant containers to customer containers. This involves gaseous transfer from 48" or 30" into 30" containers.

The quality of UF_6 despatched is controlled by analysis of samples withdrawn from the customers' containers. The sample withdrawal procedure has to ensure that the sample is representative of the container contents. Therefore all product is liquefied, homogenised and a liquid sample taken prior to delivery to the customer.

The entire liquid sampling operation is carried out in an autoclave at 85°C (Figure 7).

The container contents are maintained liquid for at least 20 hours which experience has shown to be adequate to ensure complete homogenisation. The autoclave is then tilted to pour out the samples. Subsequently containers are allowed to cool down to ensure the contents are solid prior to disconnection and moving.

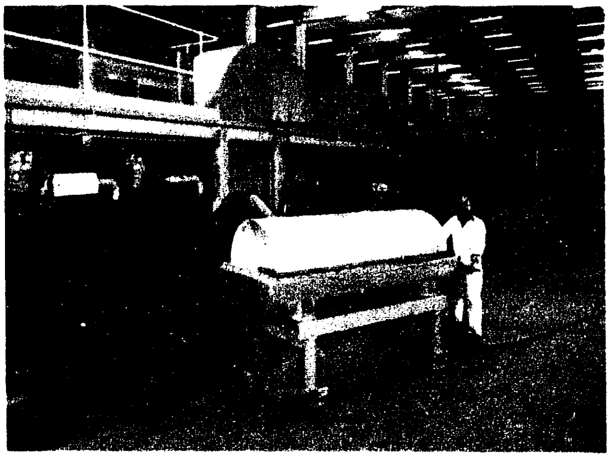

Fig.6. Product Take-Off Chest

There have been no major problems associated with liquid sampling operations although difficulties were experienced in obtaining samples, in the early days, due to vapour locks in the sampling manifold.

Fig.7. Blending & Sampling Stations

On-Site Movements and Storage

A range of diesel and electric vehicles are used for moving UF_6 containers around the Sites: eg. straddle carriers, forklift trucks, towed trailers, hydraulic lift and hover-trucks.

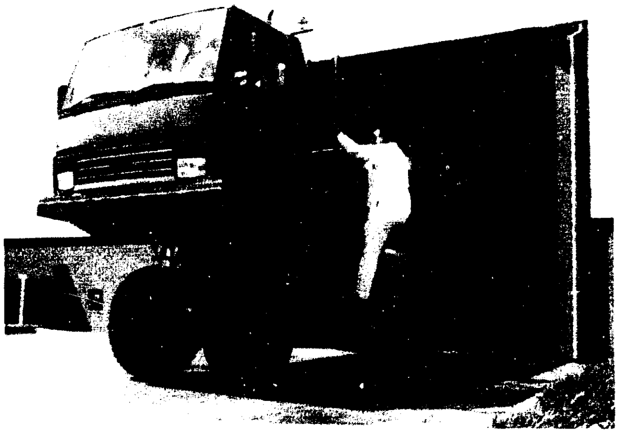

Fig.8. Straddle Carrier

Despite this variety, and the large number of container movements per annum, incidents resulting in injury to persons or damage to containers have been very few with none resulting in any serious consequence. Nevertheless appropriate emergency equipment is provided, both locally and centrally on the Sites, and emergency arrangements are established and regularly practised.

Strategies for the safe long term storage of UF_6 containers at Urenco Sites have been developed identifying minimum standards to be adopted in relation to storage raft construction, security and housekeeping and criteria and scheduling for routine container and container support damage inspection.

Despatching

Normally the transport of containers is organised by the customer, although for some customers Urenco provides the transport service. Detailed arrangements are made in accordance with the Urenco Transport Pack. Whoever organises the transport, Urenco loads the 30" containers into the overpacks on the vehicles using a fork-lift truck, mobile crane or fixed overhead crane. Containers and vehicles are monitored for radiation dose rates and surface contamination and appropriate transport labels affixed. A full set of transport documentation is provided. Urenco ensures that all outgoing shipments fully comply with national or IAEA transport guidelines and regulations.

Conclusion

Urenco has 20 years experience of operating centrifuge enrichment plants and handling UF_6. In this there is a high premium placed on training, supervision and control of all operational activities. Systems and procedures aim to ensure that operations are performed in a considered and consistent manner taking due regard to the probability and consequences of any inherent associated hazards, potential system faults or maloperation. The fact that there have been no major incidents, ever, at any Urenco Site reflects the high safety standards to which all facilities are designed and operated.

Fig.9. Plant Control Room

APPENDIX

Some of the Difficulties Experienced

As might be expected when handling UF_6 containers, and in dealing with such a wide range of customers and suppliers, Urenco has experienced a variety of operational problems (opportunities for improvement). The following is a selection:-

1. Faulty tie-downs on incoming containers

In particular there was one consignment of 12 full feed containers where the cradles were oversized and metal bands had been used to tie-down the containers. On receipt it was evident that 2 containers had broken free during transport and were sitting loose in their cradles.

2. Water in overpacks

Many instances of small amounts of water but also occasions where the amounts were significant, i.e. up to several inches of water.

3. Uranic contamination on incoming feed containers

Although feed suppliers have comprehensive procedures for inspection of containers prior to delivery the following two examples are instances where such procedures were clearly not fully effective (Figures 10 & 11).

4. Surface corrosion on incoming containers

This is a continuing and frustrating problem, not the least because of its adverse effect on public relations and the difficulties it poses in attempting to perform satisfactory container inspections and any surface decontamination that may be necessary. In addition material from the container surface, ie flaking, can cause problems within closed-loop heating and cooling systems.

Depending on circumstances where a container surface condition is deemed unacceptable, it may be either rejected or cleaned and re-painted at the suppliers expense (Figure 12).

5. Cracking of container valve gland nuts

Not only is there the potential for increased hazard arising from cracking of container valve gland nuts, a problem which has been observed both on incoming containers and during their use on plant over the past 12 years, the phenomenon has required additional inspections and checks to be introduced.

Fig.10. Contaminated Feed Container Valve

Fig.11. Blockage Beyond Feed Container Valve Cap

Fig.12. Corrosion on Incoming Feed Containers

18 YEARS EXPERIENCE ON UF_6 HANDLING AT JAPANESE NUCLEAR FUEL MANUFACTURER

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ABSTRACT

In 1991 spring,our company,a leading nuclear fuel manufacturing company in Japan,celebrated its 18th anniversary.Since 1973, company has produced over 5000 metric ton of ceramic grade UO_2 powder to supply to Japanese fabricators,without major accident /incident and especially with successful safety record on UF_6 handling.Company's 18 years experience on nuclear fuel manufacturing tells that key factors for the safe handling of UF_6 are 1)installing adequate facility equipped with safey device,2)providing UF_6 handling manuals and executing them strictly,and 3)repeating on and off the job training for operators. In this paper,equipment and operation mode on UF_6 processing at our facility are discussed.

INTRODUCTION

Since 1973,Japan Nuclear Fuel Conversion Co.,Ltd.(formerly Sumitomo Metal Mining Nuclear Fuel Division),has produced more than 5000 metric ton of ceramic grade uranium dioxide powder and supplied to domestic BWR and PWR fuel fabricators.Company's nuclear fuel reconversion capacity is 715 T-U per year for less than 5% enriched uranium LWR fuel and 3 T-U per yearfor less than 20% enriched uranium FBR fuel.All that adds up to a manufacturing capacity of 718 T-U per year.Main sources for starting materials of reconversion at our facility are either uranium hexafluoride,mostly delivered from DOE and EURODIF,or uranium oxide pellet/powder, delivered from our customers.
So far,at our company's Tokai plant about 5900 metric ton of uranium hexafluoride have been converted to uranium dioxide using SMM ADU process,developed by Sumitomo Metal Mining, with an outstanding safety record.

PROCESS

In the SMM ADU process shown in Fig.1,vaporized UF_6 is fed into hydrolysis column filled with aluminum nitrate solution to give uranium nitrate and fluorine complex.Purification of uranium nitrate from fluorine complex is carried out at TBP solvent extraction column and diluted nitric acid strip column.Purified uranium nitrate is then precipitated as ADU by ammonia. The ADU is filtered and then

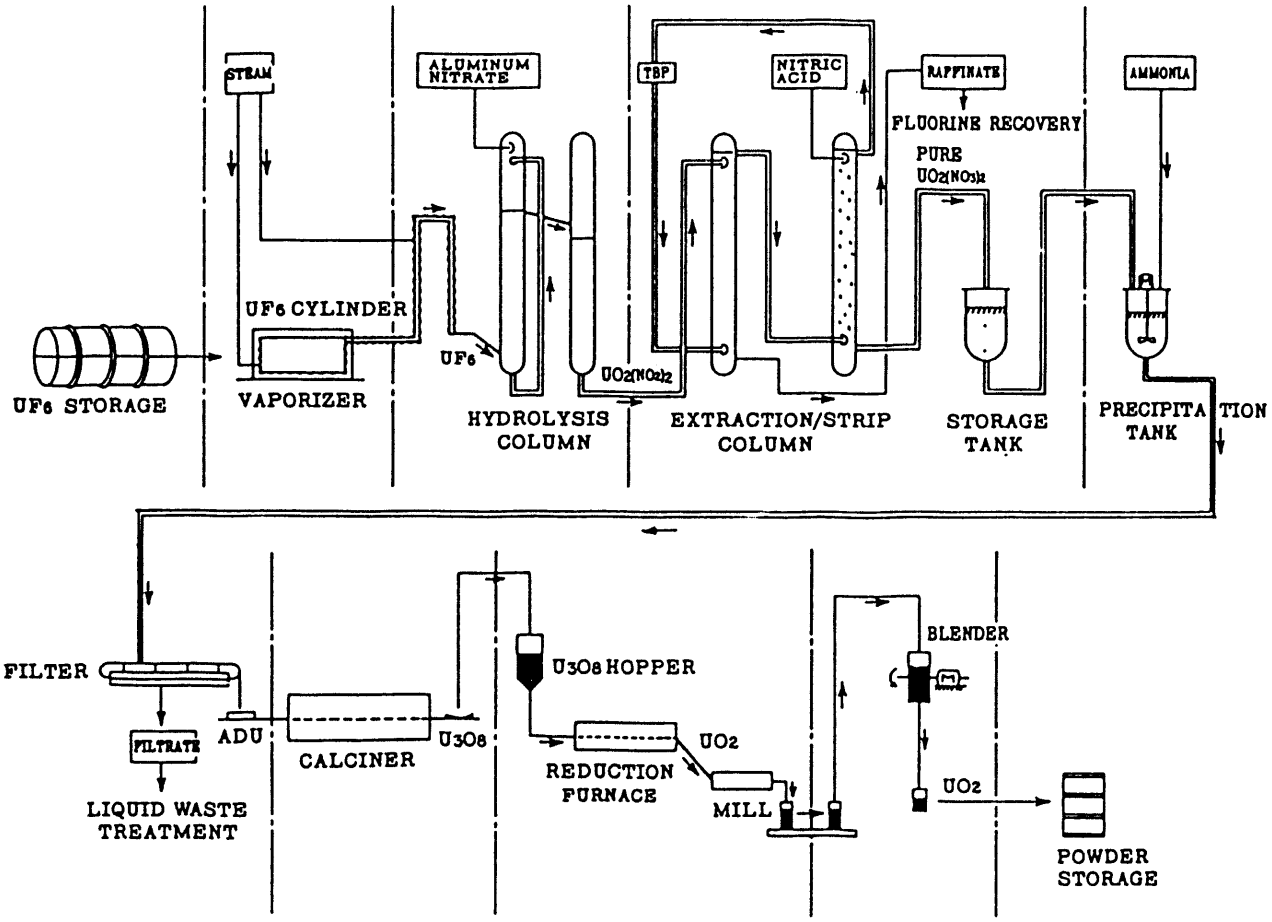

Fig. 1.

SMM ADU PROCESS

calcined to U_3O_8 and finally converted to UO_2 using cracked ammonia. Fluorine transferred into raffinate at the solvent extraction is recovered as aluminum fluoride for industrial reuse. The overall reaction of the SMM ADU process may be shown as follows:

$$UF_6+2Al(NO_3)_3+2H_2O \rightarrow UO_2(NO_3)_2+2AlF_3+4HNO_3$$

$$UO_2(NO_3)_2+2TBP \rightleftharpoons UO_2(NO_3)_2\cdot 2TBP$$

$$2UO_2(NO_3)_2+6NH_3+3H_2O \rightarrow (NH_4)_2U_2O_7+4NH_4NO_3$$

$$(NH_4)_2U_2O_7 \rightarrow 2/3U_3O_8+2NH_3+H_2O+1/3O_2$$

$$U_3O_8+2H_2 \rightarrow 3UO_2+2H_2O$$

UF_6 PROCESSING EQUIPMENT

UF_6 vaporizer, hydrolysis column, heel collecting equipment and their accessories are major concern for UF_6 processing equipment.

UF_6 Vaporizer

Two steam autoclaves, available to

30′ and 12′ cylinder, are provided for process line to supply continuous operation. These autoclaves are set inside of draft room, which provides third containment. Vaporization of UF_6 is carried out by indirect steam heating through jacket.

Hydrolysis column

Hydrolysis column is associated with cooling column, holding column and their accessories such as back-flowing prevention column and scrubling column. These columns are cylindrical and made from stainless steel AISI 304 equivalent which is allowed to use extensively at UF_6 hydrolysis using aluminum nitrate solution. In hydrolysis reaction, aluminum reacts instantly with fluorine to give stable aluminum-fluorine complex and the potential of HF_6 corrosion is minimized.

Heel collecting equipment

Small amount of UF_6, normally less than 10kgs, is still left in cylinder at the end of UF_6 vaporization cycle. So called UF_6 heel in cylinder is evacuated by means of ejector using aluminum nitrate solution, instead of vacuum pump, mainly from safety standpoint and is led into either heel collecting cylinder or hydrolysis holding column. Heel collecting system is consisted of heel collecting cylinder, ejector and mist separater.

The schematic flow diagram of abovementioned equipments are shown in Fig 2.

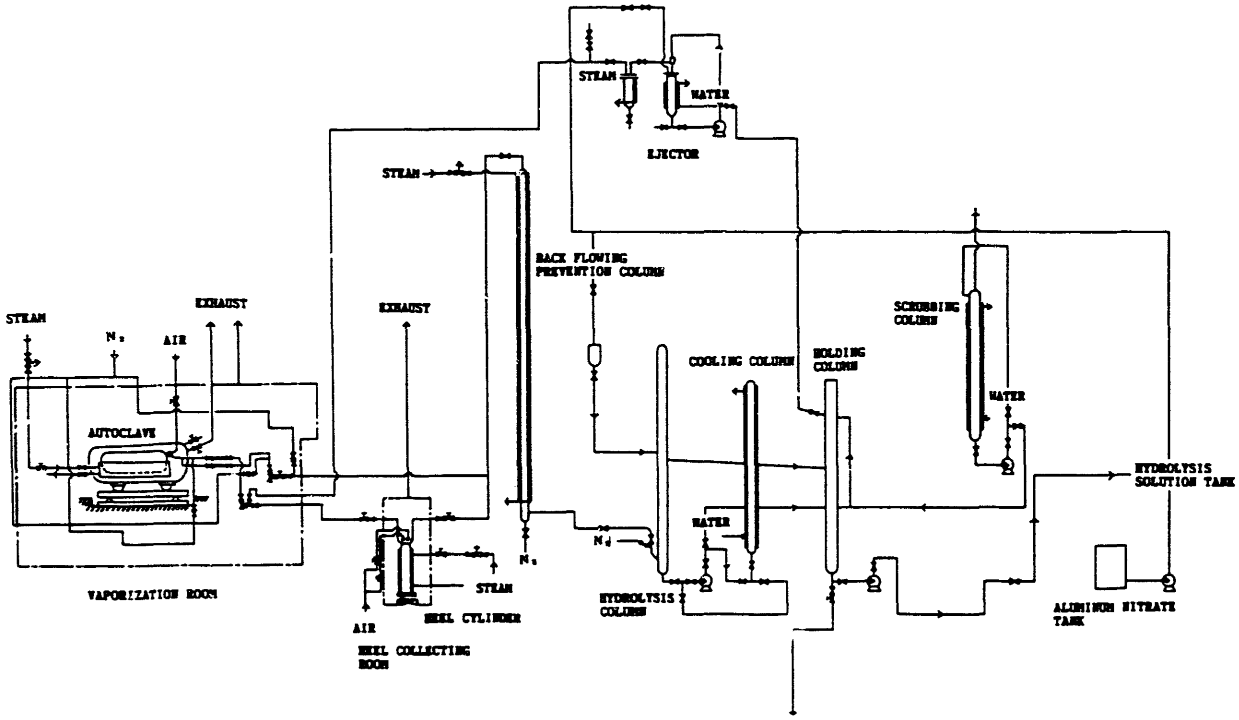

Fig. 2.

EQUIPMENT FLOW DIAGRAM

SAFETY FEATURES

Autoclave operation

1)Temperature control

To avoid tremendous reaction of steam and UF_6 ,in the case of UF_6 leakage from cylinder valve, indirect steam heating method is applied at autoclave operation. It is essential to eliminate risk of cylinder overtemperature and overpressure for autoclave operation.Surface temperature of UF_6 cylinder is controlled to maximum 100℃ and when it exceeds 100℃,the supply of steam is automatically stopped by means of closing steam valve.The first pressure regulating valve is set at 5㎏/㎠·G with the downstream pressure relief valve at10㎏/㎠·G. The second pressure regulating valve is set at 0.8㎏/㎠·G with the downstream pressure relief valve at 1㎏/㎠·G.Pressure of 1㎏/㎠·G at the second regulating valve is correspond to 116℃.It means that at our autoclave operation cylinder temperature of higher than 116℃ will be never attained.

2)Radiological control

In order to minimize the effect to enviroment and reduce personnel exposure in the case of UF_6 leak during operation, autoclave and vaparization room are provided for second and third containment.Also these containments are associated with plant's integrated exhaust system.When UF_6 leak is detected by the continuous and redundant detection system,the cylinder valve is automatically closed and the system is shut down with an alarm.Leaked UF_6 is vent to the scrubber followed by pre and HEPA filter banks.UF_6 leak detection is carried out by continuous monitoring HF which is formed by the reaction of released UF_6 and available moisture in the atmosphere. Total six electrochemical HF_6 detectors with detection range of 0~9ppm are furnished at UF_6 cylinder handling area. Continuous and independent sampling of autoclave and vaporization room exhaust is performed to monitor possible emission of HF.Recording and alarm function of detector are located in control room to allow for superintendent to manage emergency situation.

To avoid pressure rise due to solidification of vaporized UF_6 , UF_6 line from the autoclave to the next equipment is either electrically heated or heated by steam to 80~100℃.
Line temperature is monitored continuously and deviation from target temperature results in an alarm.

3)Criticality control

Criticality control of the autoclave system is achieved by maintaining such limiting condition that single 30′or12′ cylinder is set for one autoclave.Also,control of H/U limiting condition is performed by providing back-flowing prevention column between autoclave and hydrolysis column.

Hydrolysis operation

1)Radiological control

To avoid over-flow of hydrolysis solution from holding column, a level guage is provided at holding column.If hydrolysis

solution level shoud exceed at set point, UF_6 cylinder valve is automatically closed. In order to avoid the back-fflowing of hydrolysis solution into 30″ cylinder, a blank column equipped with level guage is furnished. The level guage of blank column has a quite same function as that of holding column level guage.
Eevry hydrolysis line is either electrically heated or heated by steam. The line temperature is sensored by thermometer with alarm.

Special attention is paid for prevention of UF_6 injection nozzle plugging by UO_2F_2 at inlet of hydrolysis column. UF_6 injection nozzle is fabricated minutely so as to obtain continuous flow of UF_6 and nitrogen carrier gas without interruption due to UF_6 solidification or UO_2F_2 formation.

2)Criticality control

Each column is desined to be geometrically safe configuration with 260mm diameter.

Heel collecting operation

1)Radiological control

Heel collecting is carried out by the following two steps

1st step	collected till approximately 10Kgs heel
2nd step	collected till approximately 300grs heel.

Operation is performed by means of ejector using aluminum nitrate solution. At 1st step, UF_6 heel is evacuated into heel collecting cylinder under vaccum provided by ejector and then is led into hydrolysis column.
At 2nd step, rest of heel is collected into holding column via ejector circulation tank. Circulation tank is equipped with level guage and alarm.
UF_6 heel collecting cylinder is set inside of small draft room attached with HF detector and its gross weight is controlled to maximum 250Kgs. Once HF formation due to UF_6 leakage at draft room or overweight of heel cylinder is monitored, UF_6 cylinder valve is automatically closed with an alarm.
Heel cylinder temperature is also controlled to maximum 100℃. When cylinder temperature exceeds 100℃, steam supply to cylinder is stopped.

2)Criticality control

Heel collecting system is also designed to be geometrical safe configuration with equipment's diameter of 260mm.

Summary of operational control

Major interlock and control system adopted at our autoclave, hydrolysis and heel collecting operation are shown in Table 1 and Table 2.

SAFETY RECORD

Incident/Accident

Since 1973's reconversion operation commencement, neither incident nor accident on UF_6 processing has been experienced, though we have met with several troubles as usual. These troubles

Table 1. Interlock System

Detection/Monitoring Device	Interlocked Equipment
HF detector at autoclave and UF₆ vaparization room	Cylinder valve Control valves
HF detector at exhaust system of vaparization room	Cylinder valve Control valves Exhaust system damper
Level guage at back-flowing prevention column and holding column	Cylinder valve Control valves Aluminum nitrate solution supply pump
HF detector at exhaust system of heel cylinder room	Cylinder valve Control valves

Table 2. Control System

	Monitoring/Detection/ Control Item	Function at control room			Function on the field		
		A	B	C	A	B	C
UF Vaporization equipment	Cylinder Temperature		○	○	○	○	
	HF at autoclave	○	○		○	○	
	HF at vaporization room	○	○		○	○	
	UF₆ line temperature		○	○	○	○	
Hydrolysis/ Heel Collecting/ Equipment	Solution level at holding column	○	○		○	○	
	U conc.in hydrolysis soln.		○	○	○	○	
	Heel cylinder temperature		○	○	○	○	
	Heel line temperature		○	○	○	○	
	HF at heel cylinder room	○	○		○	○	
	HF at hydrolysis room	○	○		○	○	

Remarks A:Indication
B:Alarm
C:Record

are minor but are accompanied by the possibility of developing to serious one with UF_6 release.

Troubles

Typical troubles on UF_6 processing experienced so far and corrective action taken for them are summarized in Table 3.

Evaluation on radiological control

To evaluate our radiological control at UF_6 processing area, past 5 years average data on radiation, indicating quite satisfactory, were compiled and shown in Table 4.

CONCLUSION

Over 18 years, UF_6 reconversion of about 5900 metric ton has been performed at our facility without any incident or accident accompanied by UF_6 release. Provision of multiple better containment and reliable interlock and control system and the use of aluminum nitrate solution for hydrolysis and heel collecting operation may be the highlight of safety features on UF_6 processing at our facility.

Table 3. Summary of Troubles

Trouble	Cause	Corrective Action
Poor indication on pressure guage	UF_6 plugging due to use of improper guage with poor diaphragm	Inspected all UF_6 line guages Replaced with good one Re-examined specification of guage
Poor UF_6 flow	UF_6 solidification at valves and flanges due to lack of heating	Heated valves and flanges with infrared lumps
Discontinuing of hydrolysis operation	UO_2F_2 plugging at UF_6 injection nozzle	Modified nozzle (under patent application)
HF detector misalarm	Poor maintenance and calibration	Prepared detailed maintenance manual

Table 4.

Weekly doze equivalent (μSv/W)	National Regulation	1000
	UF_6 vaporization room	160
	Hydrolysis room	<50
Airborne concentration (Bq/cm^3)	National Regulation	5×10^{-7}
	UF_6 vaporization room	1.3×10^{-8}
	Hydrolysis room	9.6×10^{-9}
Surface contamination (Bq/cm^2)	National Regulation	4
	UF_6 vaporization room	2.4×10^{-2}
	Hydrolysis room	6.5×10^{-2}

SAFETY PROVISIONS FOR UF_6 HANDLING IN THE DESIGN OF A NEW UF_6 CONVERSION PLANT

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ABSTRACT

BNFL Fuel Division is currently undertaking the final design and construction of a new UF_6 conversion plant at its production site at Springfields near Preston in the north of England. The Company has gained much experience in the handling of UF_6 during operation of plants on site since 1961.

The major hazard occurs during the liquification cycle and the basis of the maximum credible incident scenario adopted for safety assessment and design purposes is discussed.

This paper considers the design features which have been incorporated in the new plant to counter the hazards presented by the presence of UF_6 in gaseous and liquid form and explains current thinking on operational procedures in areas of potential risk such as cylinder filling.

The plant emergency response philosophy and systems are described and specific design provisions which have been included to satisfy the UK regulatory bodies are outlined in some detail.

BNFL'S HEX PROCESS

Initial studies into the fluidised bed hex production process were carried out at Springfields in the 1950s and a series of pilot plants were operated successfully. There was a delay in development until the early 1960s when a prototype plant was built. This was followed in May 1968 by the commissioning of the Line 1 UF_6 production plant with a capacity of 3,000 te U per year. The Line 2 UF_6 production plant, having a capacity of 6,000 te U per year, was commissioned in 1974. The Line 1 plant was shut down in 1982.

A diagram of the overall process is shown in Figure 1. The system comprises a recirculating gas loop driven by a reciprocating compressor which maintains the pressure in the loop essentially below atmospheric. The reactor is a vertical cylindrical monel vessel. The fluidising gas flow of fresh fluorine and recycle gas (which includes nitrogen and unused fluorine) enters via a distribution plate at the base. Uranium tetrafluoride is screw fed at a controlled rate into the fluidised reactor bed. The bed consists of classified Calcium Fluoride which acts as a thermal moderator to facilitate temperature control and prevent overheating. During normal operations the reactor is externally air cooled to remove the heat

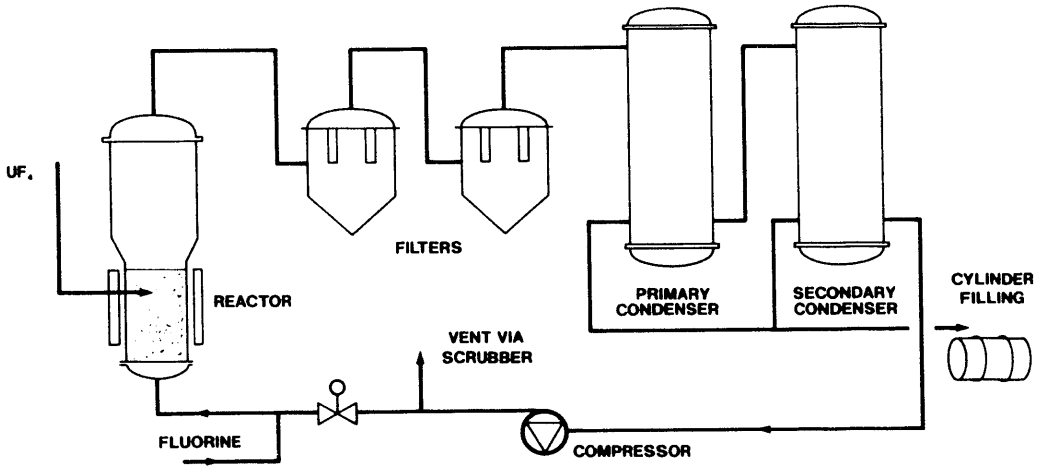

FIGURE 1 OUTLINE FLOW DIAGRAM

generated in the reaction. After filtration to remove entrained CaF_2 fines the product gas stream is routed through a primary and a secondary condenser, cooled to -30°C, where the UF_6 product is condensed as a solid. The residual gas stream is recycled to the compressor where the system pressure is regulated by a bleed via scrubber to vent.

The primary condenser is taken off-line when it contains approximately 20 tes of UF_6. The secondary condenser is brought onto primary duty and a fresh unit switched to secondary duty. The full condenser is then heated to approximately 90°C until the UF_6 has liquified at a pressure of around 2 bar. The product hex is run off into cylinders and removed from the plant. This part of the cycle presents the maximum potential risk for a release of UF_6.

HAZARDS

The main hazards identified for the process are as follows:

- Minor UF_6 Leakage
- Major UF_6 Release
- Radiological Hazards

Minor UF_6 Leakage

BNFL has experienced a number of minor plant problems over the years, which have resulted in localised UF_6 releases. With a few exceptions, these have all occurred during the liquefaction and cylinder filling cycle and have been associated with
a) flexible cylinder connectors,
b) cylinder valves, or
c) hex sampling equipment.

Major UF_6 Release

During operation of its UF_6 conversion plants BNFL has maintained adequate control to restrict releases outside the plant to minor quantities, and plant improvements have been introduced to mitigate the effects further. Other UF_6 converters have experienced significant problems which serve as a sobering reminder of the potential effect of a major loss of UF_6 to the environment. The greatest potential risk occurs during the condenser heating stage of the cycle, when up to 20 tonnes U may be present as UF_6 in liquid form.

Radiological Hazards

The main radiological dose uptake in the plant results from the accumulation of the out of equilibrium uranium daughters Th_{234}, $Pa_{234}m$ in the CaF_2 reactor bed material which may typically have an activity of 1.25 M Bq/gm and leads to restricted working times for the operators during the weekly discharge of the post reactor filters and the three times a year reactor bed change. These operations contribute a significant percentage of the annual operator dose uptake.

Maximum Credible Incident

For safety assessment purposes the worst credible event has been taken as rupture of the condensers, failure of filled cylinders and total building collapse allowing escape of all UF_6 released to the environment. A mean condenser UF_6 inventory based on the process cycle has been calculated as 9 tonnes (only one condenser is liquified at a time). It has been assumed that half of the filled cylinders remaining on the plant during solidification each containing 50% liquid hex will fail. Applying calculated vapour fractions of 0.6 and 0.5 respectively gives a worst credible release of 14.8 tonnes UF_6. Such a release has been calculated to give a dose of 3.8 mSv to a member of the public at the site boundary.

The worst credible major leak has been taken to occur as a result of valve damage on a recently filled 48Y cylinder containing 12.5 tonnes UF_6. A calculated vapour fraction of 0.6 gives a release of 7.5 tonnes of UF_6 vapour. This figure is greater than that calculated for an equivalent leak in the condenser area contained by the building and has been used when designing emergency response equipment.

DESIGN CRITERIA

BNFL's general approach to the design of UF_6 facilities follows the following general principles:

1. Provision of high integrity vessels and equipment to achieve reliable primary containment.
2. Where potential for release of UF_6 exists, to provide additional secondary containment incorporating interlocks and alarms where necessary.
3. In areas of identified risk, to provide automatic leak detection and response equipment.

In the event of a leak in one of the plant areas the main objectives are:

1. To protect operating personnel.
2. To limit the scale of the release.
3. To contain the UF_6 and products within the plant.
4. To remove the UF_6 and decontaminate the area.

The design target for routine occupational exposure is that the whole body dose to an individual employed on the plant shall not exceed 15 mSv pa, and average exposure for all persons employed in the plant shall not exceed 5 mSv.

In addition, BNFL has developed a suite of Accident Risk Criteria which are incorporated in the Company's Health and Safety Manual. The relevant criteria for the design of the UF_6 Plant are:

- Frequency of Member of Public dose of 100 mSv shall be less than 10^{-4} per year.
- Frequency of Member of Public dose of 10 mSv shall be less than 10^{-3} per year.
- Frequency of Site Emergencies shall be less than 10^{-2} per year.
- Frequency of other minor events of lesser off-site significance shall be less than 10 per year.

These criteria apply to the sum of risks from all plants on site.

REGULATORY REQUIREMENTS

The regulatory body in the UK for nuclear sites is the Nuclear Installations Inspectorate (NII). Proposals for new plants are subject to a series of safety submissions and require approval by them. There have been two major areas of impact on the plant design where the NII have insisted on design provisions. These were:

- Design to seismic standards.
- High integrity emergency shut down system

BNFL had not expected to design the plant to meet seismic criteria. The NII applied their own safety principles, however, which required that the maximum credible event (see above) did not occur more frequently than 1 in 1000 years. Consequently, it became necessary to design the building for a 1 in 1000 year earthquake equivalent to a horizontal ground acceleration of 0.1 g.

The emergency shutdown system was installed to prevent a large escape of UF_6 in the event of accidental damage or pipe failure.

It was then necessary to demonstrate the integrity of the vessels and structure under all conditions up to 0.1 g. To avoid designing the UF_6 pipework to stringent seismic criteria a seismic switch set at 0.05g (1 in 50 years) has been incorporated into the emergency shutdown system to guarantee that liquid UF_6 in the condensers is isolated before the pipelines fail.

Much greater design consideration than envisaged was needed for the plant steelwork and many problems with vessel support and location had to be solved. The emergency shutdown system is designed to shutdown the plant and isolate UF_6 in the condensers using a hard wired trip system. Key components, including the condenser liquid UF_6 outlet valves, have had to be doubled up to meet a NII requirement that no single failure can render the system ineffective.

It is worth noting that the new UF_6 Plant safety submission to NII were based on average conditions (eg average weather conditions, average UF_6 inventory). Recent trends indicate that future safety submissions will have to be based on co-incident worst case situations which will impose even more restrictive requirements on plant designs.

DESIGN FEATURES

Hex Containment Principles

Liquid UF_6 will only be present in the following area:

The Condenser Room
The UF_6 Cylinder Filling Station
The UF_6 Cylinder Storage Area

The main reactor circuit contains gaseous UF_6 and fluorine, but the operating parameters are such that the pressure is sub-atmospheric in the majority of the system. Hence, there will only be in-leakage to the process. The quantity of material in the circuit, except for the condensers, is comparatively small and the potential for a major release is considered to be low.

The building housing these areas is designed to a high integrity level to achieve a satisfactory standard of leak tightness and incorporate features such as self sealing doors, door alarms etc. The plant ventilation system ensures that these rooms are maintained slightly below atmospheric pressure to guarantee a net in-flow of air. Where pipework carrying UF_6 between the areas passes outside it is enclosed in sealed ductwork to isolate it from external areas.

The importance of the UF_6 filling station has been recognised and particular attention has been paid to achieving a high containment standard. The station itself has been made as small as possible, consistent with satisfactory access for operations. Interlocks, alarms and warning signs will be used to ensure containment is maintained during filling operations.

The following features, building on experience gained within BNFL and by other UF_6 converters, are incorporated into the filling station to protect against overfilling, leakage and damage during the filling cycle:

- Completely Sealed Filling Station
- Remote external operator Control Panel
- Removal of Cylinder Transporter Motive Power
- Automatic Cylinder Overweight Trip
- Automatic/Remote Valve Closure Device
- Hex Release Detection Alarm and Trip System
- Semi-Automatic Hex Sampling Rig
- Emergency Extraction
- Closed Circuit TV Surveillance
- Temperature Monitoring and Trip on Hex Line Trace Heating

The condenser area has been designed according to similar principles where applicable, specifically a fully sealed containment area is provided and a UF_6 leakage alarm system is installed which activates the emergency extraction.

UF_6 Release Alarm System

The UF_6 release alarm system is installed in the condenser room, the cylinder filling station, and the cylinder storage area. Detectors (particle ionisation type) are placed at strategic points and an alarm is raised if any two detectors alarm simultaneously. This is done for reliability reasons. In event of an alarm the following actions take place automatically.

1. An alarm sounds locally and at all entry points
2. An alarm sounds in the control room
3. An alarm is raised in the Site Emergency Control Room
4. A controlled plant shutdown is initiated
5. A vacuum is applied to the cylinder filling system through a stand-by condenser
6. The emergency scrubber is activated providing a vent path
7. The area is automatically isolated form the normal ventilation system
8. All key valves on the liquid UF$_6$ lines, including condenser drain valves and cylinder valves, are closed automatically

Emergency Scrubber

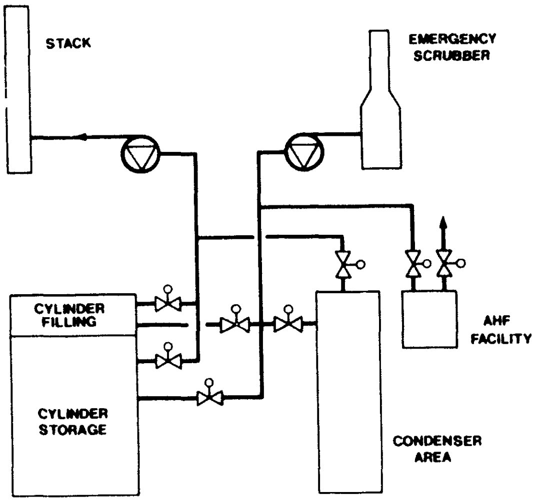

FIGURE 2 EMERGENCY EXTRACTION SYSTEM

The emergency scrubber is a shared facility serving the existing site UF$_6$ plant and AHF facilities as well as the new UF$_6$ plant and operates on a 1st up basis. Figure 2 shows the overall system. The scrubber has been designed to cope with a worst credible major leak of 7.5 tes UF$_6$ at an initial rate of 56 kg/min. A spray tower scrubber operating with water has been selected to avoid problems with blockages. It has been calculated that the vapour exiting the scrubber will contain up to 49,000 ppm UF$_6$ or 11,670 ppm of AHF which will be diluted further in the main plant discharge stack to 410 ppm UF$_6$ or 98 ppm AHF. The normal discharge limit for HF is 10 mg/m^3 (9 ppm), however, this facility is designed to mitigate environmental impact in an emergency and calculations indicate that there would be insignificant effect on a member of the public at the site boundary.

OPERATIONAL CONTROL

The plant control philosophy has been designed with the intention of reducing the potential for operator error on important control operations to an absolute minimum. This has been backed up with a system of alarm and automatic trips to prevent unsafe situations occurring. The operator interface is via a computerised Distributed Control System within which important sequences are initiated by the operators, carried out automatically by the system and require operator confirmation of crucial steps before proceeding. Condenser sequencing and cylinder filling operations are examples. In the latter case a satellite panel is provided at the filling station to permit direct supervision.

In the important cylinder filling station the design has ensured as far as possible that it is difficult for operators to carry out the process incorrectly. For example, the cylinder is positioned in the filling station on an air powered bogie; the air supply must be disconnected to allow the door to close, and the control system will not allow the filling sequence to proceed unless the door is shut.

PROJECT STATUS

The main building contractor completed work on site in July 1991. Mechanical, Electrical and Instrument installation is in progress and all major plant items have been positioned. Installation is scheduled to be completed in phases during 1992. Installation checking and system performance demonstration for each plant section will then follow. Commissioning on uranic feeds will commence in January 1993 and full scale production is scheduled for April 1993.

IMPLEMENTATION OF CONDUCT OF OPERATIONS AT PADUCAH URANIUM HEXAFLUORIDE (UF_6) SAMPLING AND TRANSFER FACILITY

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ABSTRACT

This paper describes the initial planning and actual field activities associated with the implementation of "Conduct of Operations." Conduct of Operations is an operating philosophy that was developed through the Institute of Nuclear Power Operations (INPO). Conduct of Operations covers many operating practices and is intended to provide formality and discipline to all aspects of plant operation. The implementation of these operating principles at the UF_6 Sampling and Transfer Facility resulted in significant improvements in facility operations.

INTRODUCTION

This paper is intended to provide an overview of the activities associated with the implementation of Conduct of Operations' principles at the UF_6 Sampling and Transfer Facility. The UF_6 Sampling and Transfer Facility receives UF_6 shipments from domestic and foreign customers and feed suppliers for enrichment. The facility was constructed in 1981 and ships and receives approximately 4,000 UF_6 cylinders annually. A statistical number of these cylinders are heated in steam autoclaves to obtain a homogenous liquid sample for laboratory analysis. Samples are also obtained from a statistical number of process product and by-product cylinders. The analysis is performed as part of the Nuclear Materials Quality Control program. The facility also has transfer capabilities that allow the transfer of UF_6 from Department of Energy (DOE) cylinders to customer cylinders. The development of the implementation plan and the methods used in the field will be described.

BACKGROUND INFORMATION

Following the initial development of the guidelines for Conduct of Operations by INPO, Martin Marietta Energy Systems' Operations Division, Paducah, initiated actions in August of 1989 to develop a similar document for non-reactor nuclear facilities. As a result of these efforts, "Guidelines for the Conduct of Operations at Gaseous Diffusion Plants" was issued in March 1990. In July 1990, DOE issued Order 5480.19, "Conduct of Operations Requirements for DOE Facilities," which superseded the gaseous diffusion document.

Prior to issuance of the above documents, a need had been identified by Martin Marietta senior management to improve the formality of operations and facility appearance throughout all Energy Systems' facilities. In order to accomplish this upgrade, a pilot facility was selected at each site to achieve the desired standard of operations. The UF_6 Sampling and Transfer Facility was selected to serve as the pilot for the program at the Paducah Plant.

PROJECT PLANNING

In order to establish an overall scope for the project, a steering team was appointed. The team developed an action plan that served as the initial focal point. The action plan contained numerous steps. These action items can be categorized into seven areas:

1. Facility Appearance or Material Condition
2. Design Basis Documentation Review
3. Training Program Enhancement
4. As-Built Drawings
5. Procedure Upgrades
6. Maintenance Planning
7. Operations Control System Upgrades

To provide an understanding of the desired bench mark, steering team members visited several nuclear reactor power generating stations within the United States that had received top ratings by INPO.

IMPLEMENTATION OVERVIEW

Meetings were held with other plant support groups to provide an explanation of the project objectives and to obtain input from these groups. Support organizations, such as Quality Assurance, were solicited to afford each an opportunity to implement a program improvement from their area of expertise. This activity was successful in not only informing the plant of the implementation plan, but also in obtaining their commitment to provide needed support. In addition to these meetings with the support groups, meetings were held with the facility operators. When the initial meetings with the operators were held, we did not realize the vital importance of obtaining the input and support of these individuals.

DOE 5480.19 is divided into 18 chapters, listed as follows, to show the comprehensive nature of the program.

1. Operations Organization and Administration
2. Shift Routines and Operating Practices
3. Control Area Activities
4. Communications
5. Control of On-Shift Training
6. Investigation of Abnormal Events
7. Notifications
8. Control of Equipment and System Status
9. Lockouts and Tagouts
10. Independent Verification
11. Logkeeping
12. Operations Turnover
13. Operational Aspects of Facility Chemistry and Unique Processes
14. Required Reading
15. Timely Orders to Operators
16. Operational Procedures
17. Operator Aid Postings
18. Equipment and Piping Labeling

To provide direction concerning the facility specific requirements for each of these chapters, a total of 22 administrative procedures were identified for development. As these procedures were developed, trial field implementation was conducted at the Transfer and Sampling Facility. This provided invaluable insight into the barriers associated with the change prior to site-wide implementation.

SUMMARY

Conduct of Operations is a disciplined and formal way of operating a facility. The benefits are improved operational safety, improved efficiency, and an ability to instill a sense of pride and ownership in facility personnel. Implementation of the Conduct of Operations philosophy at the Transfer and Sampling Facility has provided an example of "how things are to be done" for other plant facilities and has provided near-term evidence of what would be required in achieving excellence in all aspects of facility operations. Implementation of Conduct of Operations is an ongoing process. As the principles are implemented, other areas of improvement are identified. The principles have proven themselves in reducing reactor trips and improving safety in nuclear power generation. Similar benefits are achievable through applying Conduct of Operations in non-reactor facilities, as has been recognized by Martin Marietta Energy Systems, Inc. and the United States Department of Energy.

ACKNOWLEDGEMENTS

I would like to thank the operating personnel at the Transfer and Sampling Facility for their input and support throughout the program implementation.

Uranium Facilities: Improvements in Safety and Operations

URANIUM HEXAFLUORIDE: A MANUAL OF GOOD PRACTICE
ORO 651 REVISION 6

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ABSTRACT

The United States Department of Energy publishes a document containing UF_6 handling procedures and descriptions of the approved UF_6 cylinders. Since its initial publication in 1966, it has been frequently revised to provide more and better information. The principle additions to the sixth revision which will be discussed are:

- more detail on the physical and chemical properties of UF_6
- cold trap description and operation
- cylinder emptying and filling concepts
- basis for cylinder fill limits
- short- and long-term cylinder storage
- cylinder photographs and drawings showing major dimensions

INTRODUCTION

ORO 651 is a document that DOE and its predecessors publish to provide guidelines for packaging, handling, and measuring uraniumhexafluoride. Since the first issue in 1966, it has undergone five revisions, each time to expand on the previous version and include additional information. For the past year we have solicited suggestions for improvement from domestic and foreign uranium processors. A team of knowledgeable people from the Oak Ridge, Paducah, and Portsmouth Gaseous Diffusion Plants have taken these thoughts, along with many of their own, and have produced the sixth revision that is being first issued at this conference. Our goal is to provide a compendium of data and fundamental concepts on which to base safe operations with, and transportation of UF_6.

The document is not intended to be a source of engineering detail cylinder or specifications but rather to present information about what UF_6 is and how to safely handle it. The purpose of this paper is to make point out the changes that have been made between the fifth and this, the sixth revision.

First of all, in recognition of the new emphasis that the document is taking, its title has been changed from *Uranium Hexafluoride: Handling Procedures and Container Descriptions* to *Uranium Hexafluoride: A Manual of Good Handling Practices.*

CYLINDER HEEL RECYCLE

One of the major concerns in filling a cylinder is the possibility of a vigorous reaction if the liquid UF_6 were to come in intimate contact with liquid hydrocarbon oil. There is no way to sample an empty cylinder to determine the presence of oil. Therefore an agreement between customer and supplier as to the type of equipment to be used for cylinder evacuation must provide the safety assurance for a cylinder heel recycle program.

By cylinder heel recycle we mean that if a UF_6 cylinder has been emptied until only a heel quantity of UF_6 remains, and there is assurance that there has been no chance that any hydrocarbon oil could have been accidently introduced into the cylinder, it can be returned to the diffusion plant for refilling without having to be cleaned. The assurance of no oil is provided by inspection of cylinder processing equipment at the customers facility. Things that are looked for are the kind of vacuum pump--some utilize hydrocarbon oil, while others do not. If it is an oil sealed pump, is there an oil trap?

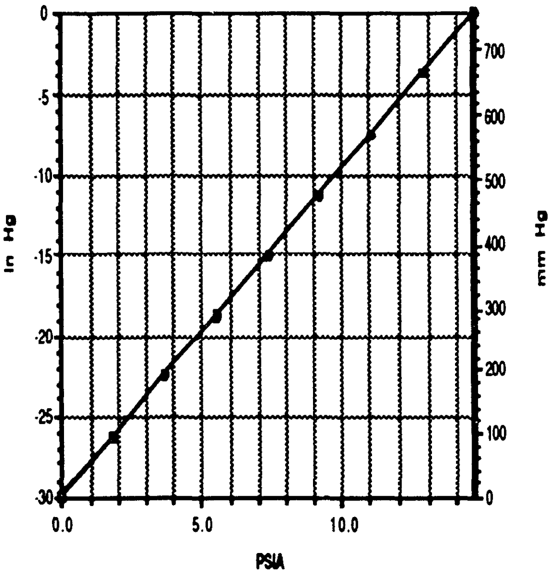
The section concerned with customers returning empty 30A and 30B cylinders with heels in them for refilling has been expanded to recognize the

5A and 5B cylinder flow, and that DOE returns empty cylinders with heels in them to the feed manufacturers, all of which transactions should be considered a part of the cylinder heel recycle program.

PHYSICAL PROPERTIES

In order to work with UF_6 it is important to thoroughly understand its physical properties. Drawing heavily on the document *Uranium Hexafluoride: A Survey of the Physico-Chemical Properties,* R. DeWitt, January 29, 1960, Goodyear Atomic Corporation, the phase diagram has been redrawn and applicable portions of it included in the operating sections. Also new density curves are presented for the solid and liquid phases to emphasize this aspect which is so important to understand in calculating cylinder fill limits.

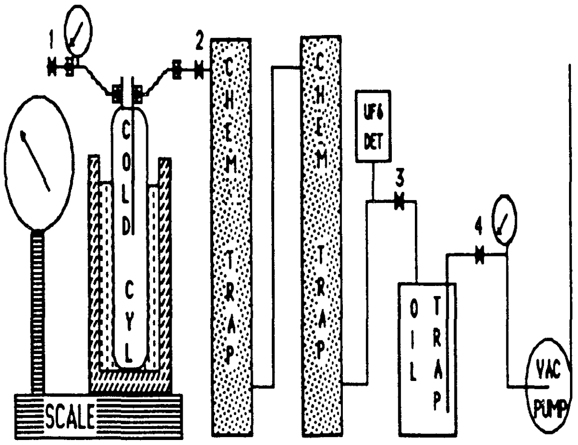
To those of us who grew up with the gaseous diffusion process, vacuum or negative pressure conditions are second nature; however, we frequently find that others who are used to working only with positive pressures do not understand vacuum the way we do. To help overcome the difficulties encountered in discussing sub-atmospheric pressures, or vacuum, we have included a description of the common scales used to measure vacuum and a scale conversion curve.



VACUUM UNIT CONVERSION

COLD TRAP DESCRIPTION AND OPERATION

A chapter has been included to give a general overview of a cold trap system that can be used for purging UF_6 from cylinder connections. This schematic drawing illustrates the concept.

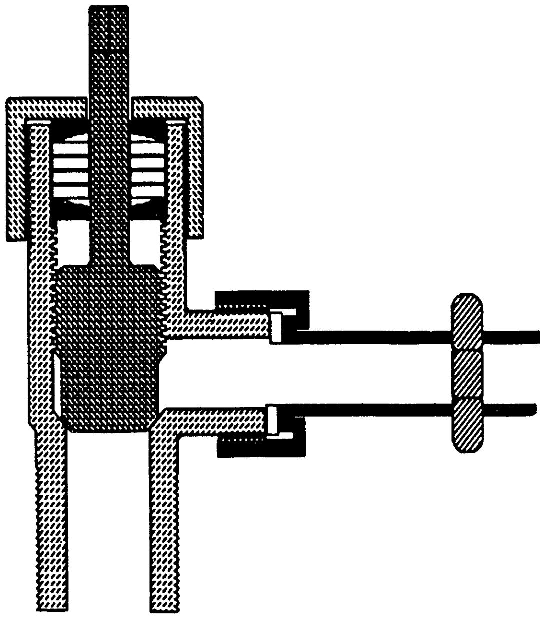


A 5B, 8A or 12A cylinder is mounted in a mechanically refrigerated cold bath on a scale. The ANSI N14.1 design temperature for these cylinders is -40°F which establishes the minimum temperature for the bath. The dip tube valve is connected to two chemical traps in series followed by a UF_6 detector, an oil trap, and a vacuum pump. The purging technique of alternately pressuring and evacuating the pigtail is explained.

UF_6 CYLINDER EMPTYING

A section has been included concerned with general concepts of emptying the UF_6 from a cylinder. The importance of thoroughly inspecting the cylinder and checking its cold pressure before heating so that any abnormalities can be detected and corrected while the UF_6 is cold and at subatmospheric pressure is stressed.

A general description of a pigtail to connect the cylinder to the process is given. The following cross section of a cylinder valve with connected pigtail is included to illustrate that the valve packing gland is also leakrated when the pigtail is leakrated because of the loose fit of the ACME threaded valve stem and body. If no leak is evidenced, there is no necessity to tighten the nut.



Any non-condensible gas, like air, in the ullage of a full UF_6 cylinder will be compressed to a higher pressure due to the 30% expansion of the UF_6 as heat changes it from solid to liquid. If a full cylinder is heated with the valve closed, it is possible to exceed the cylinder design pressure. The significance of the value obtained by measuring the cold cylinder pressure is discussed. A safe cold pressure of less than 10 psia is advocated.

When a cylinder is emptied to a process whose operating pressure is greater than atmospheric, the heel of UF_6 remaining in the cylinder will be greater than the maximum heel weight for shipping. A technique for utilizing the sub-atmospheric pressure in a cold empty UF_6 cylinder is suggested as a heel reduction system.

FILLING A CYLINDER WITH LIQUID UF_6

A section has been added to describe the concepts to be considered when filling an empty cylinder with liquid UF_6. Again it is stressed that a thorough cylinder inspection be made so if anything is out of specification it can be corrected before the UF_6 is admitted.

The internal pressure should be measured to assure that it is less than 5 psia. If the cylinder is part of the heels recycle program, 5 psia is the vapor pressure of UF_6 at 100°F and, because the gas is condensible UF_6, it will not contribute significantly to the final total pressure of the cylinder. However, if the cylinder is a new or recently cleaned cylinder, the 5 psia or less pressure will be air. When the liquid is admitted to the cylinder, this contained air will be compressed by the incoming fluid and the total cylinder pressure will be the vapor pressure of the liquid UF_6 plus the ever increasing air pressure as it is compressed into the diminishing volume of the ullage.

When the liquid is first admitted to the evacuated cylinder, it will flash to gas and solid, and this will continue until the cylinder pressure exceeds the 22 psia triple point condition. The pigtail and cylinder valve must have external heat applied to them to avoid plugging while this initial phase change is taking place.

UF_6 CYLINDER FILL LIMITS

A detailed explanation is given of the logic for establishing safe UF_6 cylinder fill limits. At the completion of fabrication, a cylinder is filled with water, weighed, and this weight is stamped on the cylinder nameplate. The American National Standard, *Uranium Hexafluoride - Packaging for Transport,* ANSI N14.1 specifies minimum water weights for each type of cylinder. As long as the nameplate weight exceeds the ANSI N14.1 value, the internal volume of the cylinder is guaranteed to be greater than a minimum acceptable value.

The published fill limit weight is derived by using the density of liquid UF_6 at 250°F and calculating the quantity required to fill 95% of the minimum cylinder volume. By this method of calculation, because all cylinders are larger than the minimum, at least 5% ullage to avoid hydraulic rupture is assured when a full cylinder is heated to 250°F. In ANSI N14.1 these weights are designated as "Maximum Fill Limits" and are the values recognized by the Department of Transportation for shipments. In ORO 651 Rev 6, they are designated as "Shipping Limits" to connote that these are the maximum values that can be shipped out of a plant on the highway. This distinction is made to recognize that internal plant conditions may require safe handling of cylinders containing greater than "Fill Limit" weights. For example, some cylinder liquid filling applications require exceeding the fill limit by several hundred pounds, which is then removed as vapor to purify the liquid UF_6 by removing volatile impurities. In this operation, the liquid is at a lower temperature than 250°F. The density of the liquid UF_6 at this lower temperature can be used with the certified minimum volume to calculate a safe 5% ullage for this operation.

SHIPPING

The section concerned with shipping UF_6 cylinders has been expanded to recognize present day conditions. A compilation of the principal DOE orders, regulations, certificates, standards, and resource material pertaining to UF_6 transportation has been included.

SHORT- AND LONG-TERM STORAGE

Operation of the uranium enrichment enterprise necessitates the storage of large numbers of UF_6 cylinders. The practices and criteria for this activity at the United States operations are included.

CYLINDER DESCRIPTIVE SECTION

In response to popular demand, the outline drawings with major dimensions have been returned to the cylinder descriptive section. These drawings were removed from Revision 5 to emphasize that ORO 651 data was not to be used for cylinder criteria. Cylinder specifications and criteria are only found in ANSI N14.1

REFERENCES

Uranium Hexafluoride - Packaging for Transport, ANSI N14.1-1990, American National Standards Institute, New York

UF6 OVERFILLING PREVENTION AT EURODIF PRODUCTION GEORGES BESSE PLANT

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ABSTRACT

Risk of overfilling exists on different equipments of Georges BESSE Plant : cylinders, desublimers and intermediate tanks.

The preventive measures are composed of technical devices : desublimers weighing, load monitoring alarms, automatic controls...and procedures, training, safety organisation.

In thirteen years of operation, some incidents have occured but none of them has caused any personal injuries. They are related and discussed.

The main factors involved in the Sequoyah fuel facility accident on 1/4/1986 have been analyzed and taken into account.

NOMENCLATURE

I.P.S.N. : Nuclear Protection and Safety Institute (Atomic Energy Commision)
P.C.E. : Ethylene, Tetrachloro $Cl_2 - C = C - Cl_2$
REC : Reception, Control and Shipping Unit
S.C.C. : Central Control Room
SCSIN (DSIN) : Nuclear Facilities Safety National Department.

TCE : Ethylene, Trichloro $HCl - C = C - Cl_2$

INTRODUCTION

Eurodif's Georges Besse gaseous diffusion enrichment plant, located in the Rhone Valley in France, can provide each year the enriched uranium requirements for one hundred 900 MWe light water nuclear plants.
Today, its customers consist of 45 utility operators from all over the world, Electricité de France (EdF) being the most important (1). Eurodif's European shareholders are the Italian companies AGIPand ENEA, the Spanish company ENUSA, the Belgian company SYNATOM, the main shareholder is COGEMA.

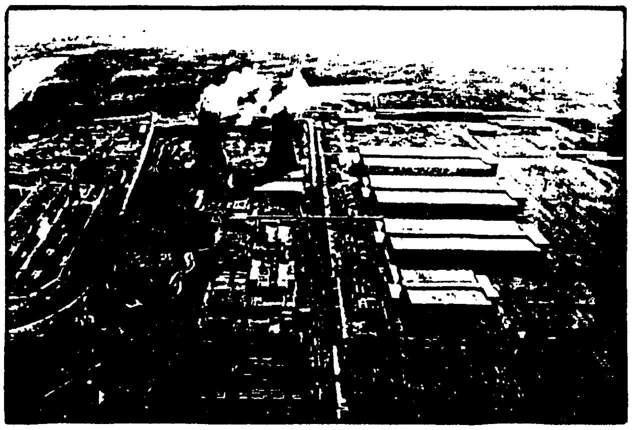


Figure 1. Eurodif Georges Besse Plant

The plant went into operation in December 1978, and reached its full capacity of 10,8 MSWU in June 1982. Since its start-up, the plant has been operated as planned.
The groups are located inside four buildings, the process pipes run between the six sub-cascades and the connection lines to the "Annexe U" (the installations for introduction and extraction of UF6 to and from the cascade). The cascade feed and withdrawal can reach 35000 metric tons of UF6 per year. The units concerned by overfilling risks are those where UF6 is liquified : U Annex and Control and Shipping Unit. Inside these units, equipment exposed to UF6 overfilling risks are mainly cylinders, cold traps and intermediate tanks.

OVERFILLING RISKS

An overfilled UF6 cylinder is one that contains a quantity of UF6 which, when heated to working temperature, would expand sufficiently to reduce the gas volume above the liquid (ullage) to less than 5% of the cylinder volume. If the quantity of UF6 is sufficiently large, the ullage can be completely filled at which point hydraulic deformation and possible rupture of the cylinder can occur (**2**).

. An overfilled desublimer can be damaged for the same reasons.

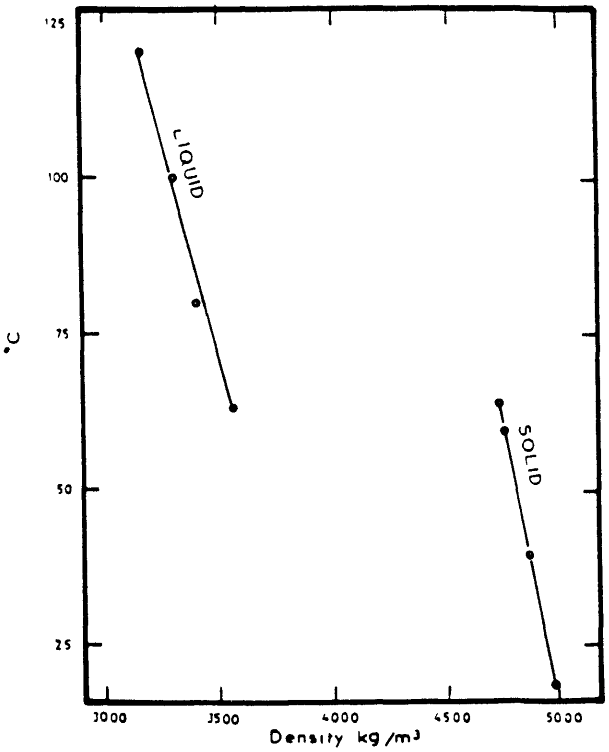


Figure 2. Densities of Solid and Liquid UF6

UF6

One physical characteristic which must be considered when UF6 is handled in cylinders is the density change when the material changes from solid to liquid and the continuing liquid density change as a function of temperature. **see Figure 2**.

The volume of the liquid produced on melting is about four-thirds of the volume of the solid (**5**). So, if some solidification of the UF6 occurs during several hours of filling, it is possible to fill a cylinder with more UF6 than it can physically hold at elevated temperatures (**3**)

The important physical characteristic that must be considered too when liquid UF6 is placed in cylinders is the change of liquid density as a function of temperature. Figure 2 shows this relationship and it is this factor which can create an overfilling if not properly taken into account. (**4**)

So, for handling liquid UF6 sufficient freeboard called ullage must be maintened for liquid expansion for the temperature range at which the liquid is to be heated.

FILLING LIMITS FOR EQUIPMENTS
SHIPPING LIMITS OF CYLINDERS

The shipping fill limits of cylinders shown in the next table are calculated from the known liquid UF6 density-temperature relationship and the temperature for each kind of cylinder (**2**). Shipping limits are based on 121°C maximum UF6 temperature which provides a 5% ullage for safety. The operating limits apply to UF6 with a minimum purity of 99,6 %.

UF6 CYLINDER DATA SUMMARY

cylinder model n°	minimum volume (liters	Approximative tare weight (kg	Shipping limit max	
			kg	pounds
30B	736	635	2 277	5 020
48G	3 936	1 179	12 174	28 001
48Y	4 041	2 359	12 501	27 560
48F	3 964	2 359	12 261	27 031
48Z	4 445		13 750	30 314

COLD TRAPS

Because of their crystallisation - melt down cycle, cold traps are exposed to major hydraulic rupture risk. The UF6 cold traps used at Eurodif are described in the following chart.

Number : 61
contents : 29 to 3 100 liters
Routine UF6 loads 20 kg to 4 500 kg
Full limits 100 kg to 10 450 kg
Operating temperatures
+ 15° + 100°C ethylene, tetrachloro
- 35° + 100°C ethylene, trichloro
- 76° + 80°C FREON 11 $C\ Cl_3F$

The test pressure of the desublimers is 11 bars (11.10^5 NEWTONS/m^2) and a burst test showed that a pressure of 160 bars is required to cause the first signs of cracking, the weak points being the sensor lines.

OVERFILLING RISKS

More or less serious incidents can occur on facilities in France or elsewhere that carry out activities equivalent or similar to those of Eurodif, namely in UF6 operations.

SEQUOYAH FUELS ACCIDENT

On January 4 th, 1986, a 48 Ymodel cylinder of uranium hexafluoride opened up while it was being heated in an oven, at the uranium fluorination plant located near Gore, Oklahoma (USA) and operated by Sequoyah Fuels Corporation.

This accident caused the death of a plant employee and intoxication of several other people subsequent to exposure to the vapors produced by the released uranium hexafluoride (UF6), especially the hydrogen fluoride. Emission of toxic vapors lasted roughly 40 minutes. Carried by winds blowing at 40 km/h, the cloud was visible more than 1.5 km away from the site of the accident.

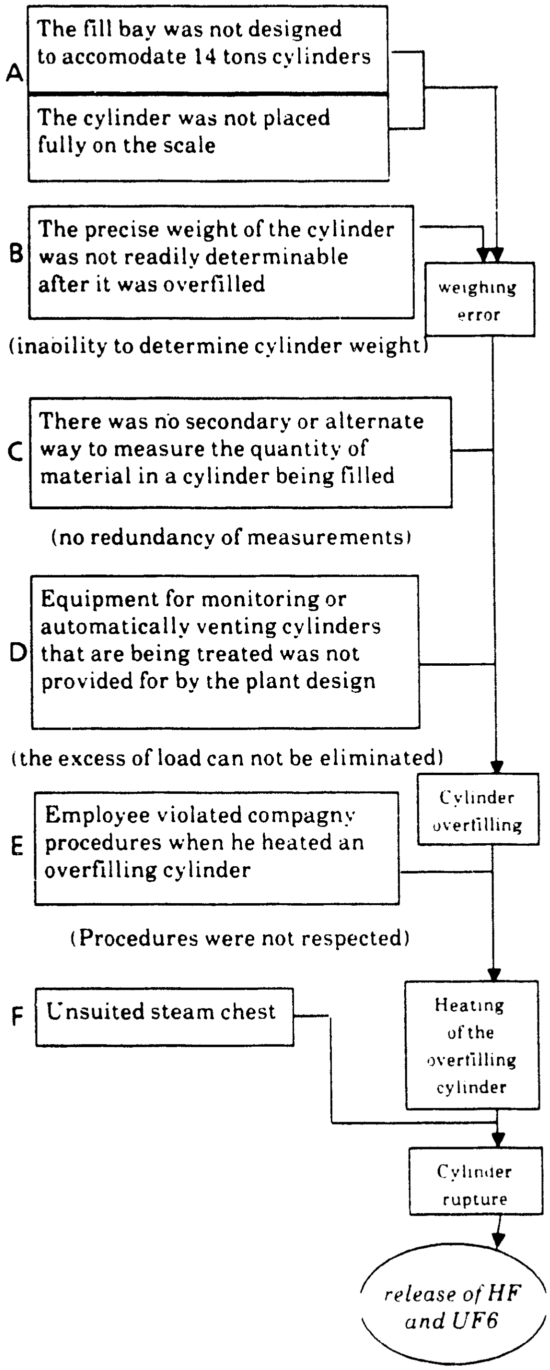
The report by the investigation committee, entitled "Rupture of 48 Ymodel UF6 Cylinder and Release of Uranium Hexafluoride", was published in February 1986 under the reference "NUREG - 1179, Vol.1.".

The accident is one of the most serious accidents known yet involving uranium hexafluoride (UF6), given both the human consequences as well as the amount of UF6 released : approximately 13 tons of natural UF6.

The cylinder was filled with an amount exceeding 12 501 kg (27 560 pounds).

The "Fault Tree" is shown here (7).

Analysis of Sequoyah Fuels accident
Fault Tree



In the french plants handling UF6, incidents or accidents for overfilling reasons have never occured..Nevertheless, a working group was constitued in 1986 for studying the causes of the accident of "Sequoyah fuels" and an inquiry was made by the S.C.S.I.N. *

Each plant analysed every cause of the accident and a report was published by I.P.S.N.

EURODIF EXPERIENCE

No incident occured on cylinders.

A few incidents have caused the deformation or rupture of equipment items such as sensors and valves on the desublimers due to overpressure during defreezing, subsequent to excessive accumulation of UF6. This was caused by one of the situations described in the next paragraph.

3 incidents occured on desublimers during the period of startup. Then, an extra weighing device was installed.

OVERFILLING PREVENTION AT EURODIF

At Eurodif, operations equivalent to those involved in the accident at Sequoyah Fuels, namely cylinder filling and emptying, are carried out in specific units of U Annex and REC.

These operations correspond to very precisely defined functions :

- withdrawal of enriched product,
- withdrawal of depleted product (or waste product),
- feeding cascade with UF6,
-extraction and filling,
- skimming and emptying damaged cylinders.

Although each of these functions is specific, with numerous configuration alternatives due to the complexity of connecting circuits, a cylinder filling operation, in theory, is based on the following procedure :

1. After liquification of the UF6 at 80°C or 100°C, it is transferred in the liquid state from a desublimer to intermediate vessels referred to as the UF6 Intermediate Tanks.

2. UF6 flows from the intermediate tanks into a cylinder.

This principle is illustrated by the process diagram of the enriched product withdrawal function.**see Figure 3**.

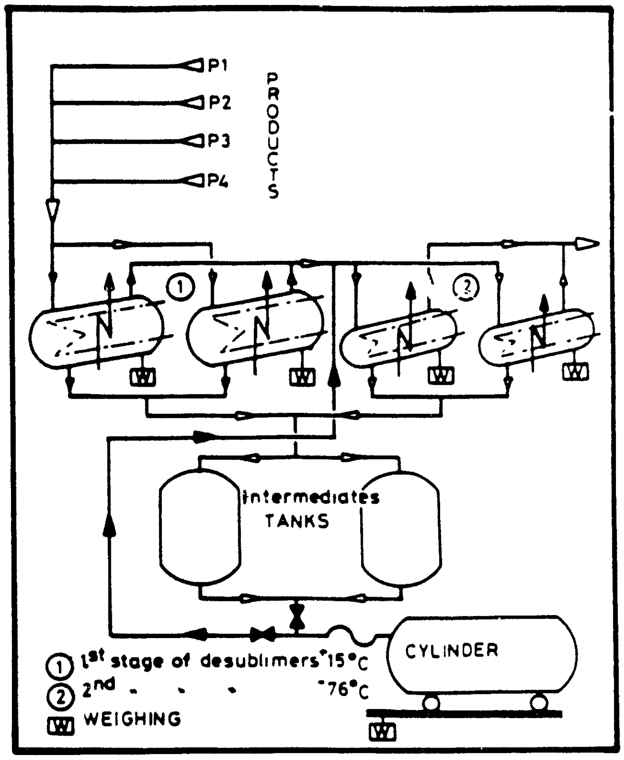


Figure 3. Enriched P withdrawal unit

Overfilling at Eurodif potentially involves intermediate tanks, desublimers and cylinders. The following discussion covers "overfilling" conditions, the measures to be taken to avoid them, and procedures to be followed in the event that overfilling should occur.

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* See NOMENCLATURE

CYLINDERS

No handling or filling operations involving cylinders require heating with valves closed. Each filling cell is designed for only one model of cylinder, the cylinders normally used in the plant are models 30 B, 48Y and 48Z (cylinder specific to Eurodif, having the same diameter as model 48Y, but with a greater nominal capacity : 13.7 tonnes of UF6). Only these cylinders are used at the filling stations. Thin-wall models 48G can be used to feed UF6 into the cascade by means of low-pressure feed procedure (UF6 sublimated at 85°C at a pressure of 0.5 bar). (6).

UF6 FEED STATIONS

Cylinder accosting is carried out according to the normal procedure, and at the end of a defined time period, if pressure has not reached a predetermined threshold, an "alarm" is indicated on a screen in the SCC.

Through pressure monitoring and the accosting procedure it is possible to avoid heating a feed cylinder while the needle valve is closed.

When a cylinder is heated, its valve is always open. It can be closed from outside the oven.

A temperature controller maintains the electrical heating at 110°C and switches off at 120°C.

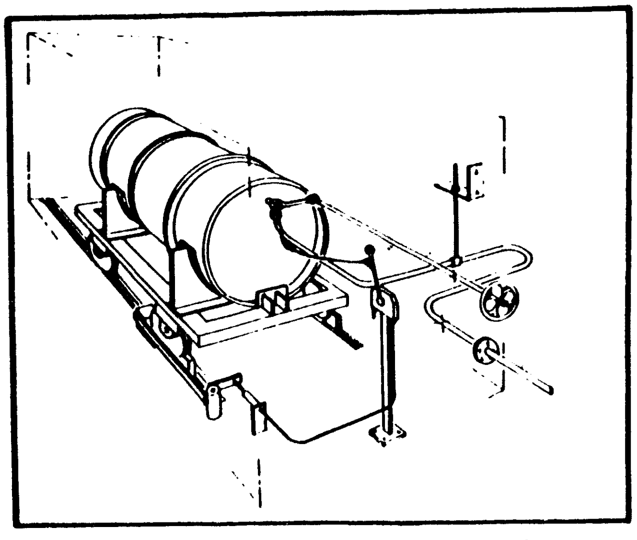

Figure 4. Brake shoe locking device

CYLINDERS FOR WITHDRAWAL OF ENRICHED OR DEPLETED PRODUCT (P and W)

The only possible place where heating could occur is at the liquid flow pigtail heated by infrared tubes.

Weighing devices are installed on the cylinder filling stations, designed for the cylinder models in use, i.e. 48Y and 48Z at all stations, and 30 B at the transfer unit.

This equipment provides accurate measurements of the cylinder filling rate. In addition, the measurements are checked to ensure coherency and are verified by a computer by comparing the quantity extracted from the upstream vessel and the quantity received, making sure that this quantity is less than the maximum admissible limit.

- Preventive routine maintenance is conducted by qualified personnel. Any occurence of derailing due to a wheel malfunction would be detected by the fact that, in this case, the carriage wheel brake would not lock.

- The filling station has been designed so that the only possible contact between the carriage-cylinder assembly and the filling equipment is provided by the carriage wheels and the flexible tube used upon accosting.

- Accosting the cylinder in the facility by means of a rigid or semi-rigid coupling guarantees that the cylinder and the carriage are in correct operating condition. The carriage is locked in place by a brake shoe locking device connected to the flexible tube for accosting in such a way that accosting cannot be completed unless the cylinder is positioned correctly. **see Figure 4.**

The cylinder and its cart are totally free from the equipment, thus handily operated and controlled.

The limits of filling are given by ORO 651 for cylinder temperatures respecting a 5% ullage. **see Figure 5.**

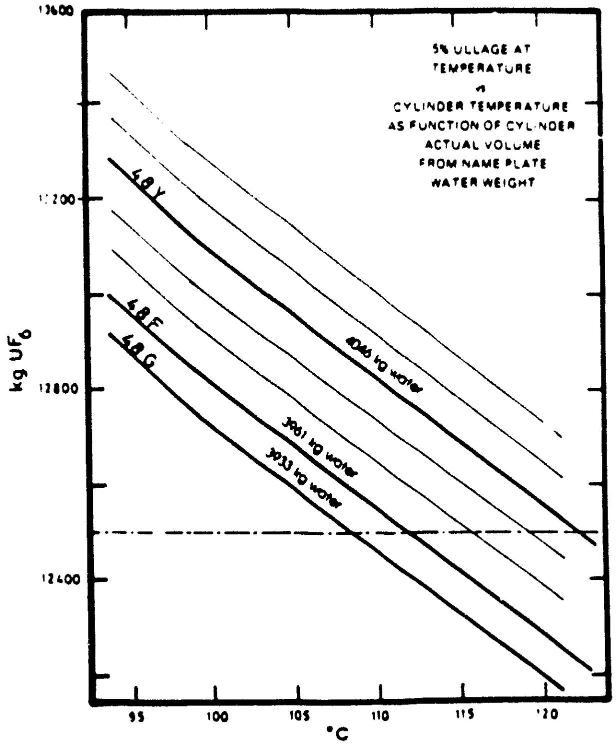

Figure 5. Model 48 (F,G,Y) cylinder safe fill limits

Weighing System of cylinders

- Cylinder filling is stopped by automatically closing the liquid flow valve when one of the following conditions occurs :

. The predetermined mass of product to be transferred is reached, which is the normal operating situation.

. The high threshold representing maximum admissible mass is reached.

. The variation of the level measurement from the UF6 intermediate tanks (source vessel) corresponds to the quantity to be transferred.

The mass of the flow is monitored by the central control room, and checked by the operator.

See Figure 6.

The cylinders presented at the filling station are first checked by weight. The residual mass of the product is generally less than 10 kg. The operator takes into account the residual mass, indicated on the accosting sheet, by modifying the predetermined mass of UF6 to be transferred.

If the weight of an empty cylinder (tare weight) or a full cylinder (gross weight) shows an excess greater than 500 kg, an alarm is signalled in control room.

A model 30 B cylinder that is supposedly empty cannot be accosted if the difference between the measured weight and the tare weight is greater than 2 kg.

- Depending on the unit, cylinders are filled from the intermediate tanks in one or two phases (maximum 4 hours).

The extraction and filling functions

The UF6 extract and fill functions are carried out at the same station. The corresponding operations are performed in three ovens equiped with weighing devices.

At Eurodif this is the only cylinder filling station equiped with a heating system.

In the extraction-filling operation the ambient temperature is kept above 80°C, making crystallization of UF6 impossible.

INTERMEDIATE TANKS

- The level sensor of the intermediate tank ensures normal filling. A threshold equal to 95% of the maximum value stops all flow from the desublimer. The level is checked systematically each time the unit is drained.

- Pressure in the intermediate tanks is monitored by threshold when it is exceeded, an audible alarm is triggered in Central Control Room (SCC). The intermediate tanks are heated at 80°C. UF6 flows from the desublimers at a temperature of approximately 95°C-100°C (no overheating of a liquid in a closed vessel).

- A computer program is used to compare the difference between the amounts of UF6 trapped in the desublimer and that which has flowed into intermediate tanks.

If the difference is greater than a given quantity (around 200 kg) a alarm state is indicated on the screen in the SCC.

COLD TRAP OVERFILLING PREVENTION

All desublimers are equipped with a weighing system that checks the mass trapped and verifies that this mass does not exceed a high threshold. **See Figure 6.**
The mass accumulated in the desublimers is double-checked :
. by "overfilling detectors" mounted on the desublimers, based on the use of load cells or strain gauges. The filling rate is controlled too by computer on the basis of integrated mass (flow rate x time),
. by level detectors mounted on the UF6 intermediate tanks to avoid overfilling (and also used to determine the amount of UF6 transferred to the cylinders).
An excessive accumulation of UF6 in a desublimer may be caused by any of the . following :

- Flowmeter malfunction.
- interruption and re-start of automatic cycling,
- leakage of UF6 through insufficiently sealed cutoff valves in the case of prolonged freezing,
- feeding of unexpected quantities of UF6 in the case of residual UF6 recovered from a device or circuit.

The principle of overfilling detectors consists in monitoring the development of micro-deformations engendered in the support structure.This system detects a high threshold which is signalled :
- in local operator's room, on a panel common to all desublimers, with data on each desublimer,
- in central control room, on the process panel, with an alarm that centralizes all alarms.

For the first freezing stages (high capacity desublimers) four strain gauges were placed on the two beam that support the upstream and downstream ends of the desublimer. For smaller desublimers, with low trapping capacity, two or four load cells were installed, depending on the configuration.

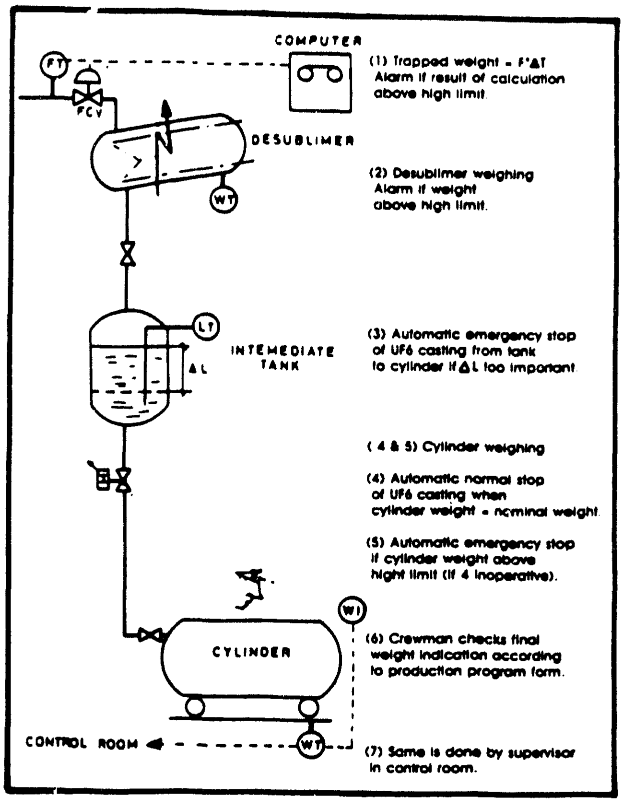

Figure 6. UF6 load monitoring

IN CASE OF OVERFILLING

At Eurodif plant, in case of overfilling, cylinders are always connectable to a trapping unit which operates in continuous running duty.
Treating an overfilled cylinder is always performed without heating by trapping in a cold state desublimer under continuous control of the UF6 removal.
There is a factor of almost 2 between the high threshold and the maximum accidental weight which would correspond to a desublimer full of liquid UF6.
The procedure to be followed upon detection of overfilling is given in an instruction. Most of the high thresholds detected since the system has been put into operation correspond to threshold overruns on desublimers in the second freezing stages, always well below the safety threshold.
These overruns appear only when the units are stopped, during draining and cleaning

operations of the corresponding unit.
Overfilling is therefore handled according to a pre-established operating procedure.

Summary of the General Instruction Applied at Eurodif

For cylinders

1. The cylinder filling rate is determined by at least two independent means : continuous weighing of cylinder, measurement of the variations level or calculation of the mass contained in the vessel located upstream.
2. After filling, the cylinder is systematically weighed a second time in a different facility.
3. Before any heating operations, the cylinder is weighed a second time to ensure that the cylinder mass does not exceed the admissible mass.
4. Instructions explicitly prohibit heating of an overfilled cylinder. Excess product is removed from the cylinder without application of heat by trapping at low temperature in a desublimer.
5. When a cylinder is heated, the valve of the cylinder must be left open. The cylinder heating operation is monitored by measuring pressure and temperature, regulated to 115°C with cutoff of power supply at 120°C. A cold trap is kept "cold" at a standby state to continuously absorb any eventual overpressure.

Ovens are located in a confinement area forming a third barrier, and the air inside the ovens is monitored by leak detectors.

Operating procedures

- The person in charge (shift or unit supervisor) can be replaced by his assistant or a person with the same status from another shift.
- The operating procedures and instructions are made available to personnel. Modified or new procedures are submitted to the person in charge who must sign them to attest that they have been received.

Members of personnel are tested to ensure that understanding of the procedures is up to level.

- Training in safety measures is ensured by a mandatory training class. All new operators must participate in a three-month practical training session, accompanied by an experienced operator.
- The engineer on standby duty at home is kept informed of any incident.
- Operations are recorded in a station register or log.

CONCLUSION

Appliance of all these UF6 load survey devices and regulations avoided overfilling incidents and accidents, for an amount of 2200 cylinder and 20 000 desublimers fillings in Eurodif during 1990.

It has been very important for EURODIF to know the circumstances and consequences of the accidents which occured in other UF6 enrichment or processing plants.

A large exchange of data, reports and experiences is essential for limiting the risk of handling nuclear materials ; we hope this exchange will be maintained.

REFERENCES

(1) J.F. PETIT, J.Y. BARRE - An enrichment plant for the present and beyond the year 2000. April 1990 TOKYO - JAPAN
(2) ORO 651 rev.5. Sept 1987 - page 15.
(3) NCR SURVEY - NUREG 1179 - Vol 1.
Rupture of model 48 Y - UF6 cylinder.
(4) Safety - related events at U.S. gaseous diffusions plants - J.E. SHOEMAKER Conf. 880 558.
(5) E.J. BARBER - The physical and chemical properties of UF6 - MMES.
(6) J.L. SALANAVE and J.M. RENEAUD-Conf. 880 558.
(7) Study of protection and Nuclear Safety Institute on Sequoyah Fuels accident.

SUMMARY

UF6 overfilling risks are known by all operators of enrichment and processing plants. Some incidents or accidents occured, the latest in Sequoyah fuels facilities.
The overfilling prevention at EURODIF Plant is described, it consists of three fields : equipments, controls and procedures.
Cold traps present a special problem, the mass of UF6 is difficult to appreciate by flow control, so, an extra equipment of weighing has been implemented in addition to the current monitoring.
The experience of all operators handling UF6 is very important to improve Safety.

REUSE OF ACTIVATED ALUMINA

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ABSTRACT

Activated alumina is used as a trapping media to remove trace quantities of UF_6 from process vent streams. The current uranium recovery method employs concentrated nitric acid which destroys the alumina pellets and forms a sludge which is a storage and disposal problem. A recently developed technique using a distilled water rinse followed by three dilute acid rinses removes on average 97% of the uranium, and leaves the pellets intact with crush strength and surface area values comparable with new material. Trapping tests confirm the effectiveness of the recycled alumina as UF_6 trapping media.

INTRODUCTION

The uranium hexafluoride (UF_6) process gas in the Portsmouth Gaseous Diffusion cascade contains low molecular weight gases or "lights", chiefly nitrogen or air which must be removed to maintain cascade operations. Several processes and/or operations are involved in separating the light gas impurities which are eventually drawn by an air-jet ejector through banks of activated alumina or sodium fluoride traps to reduce the residual uranium content prior to discharge to the atmosphere.

The chemical traps are used at several process vents to assure radioactive discharges are maintained as low as reasonably achievable. Several monitoring systems determine the need for trap changeout, and include space recorders, continuous vent samplers, trap breakthrough gamma monitors and grab samples.

The sodium fluoride traps are capable of in-place regeneration through multiple cycles of use, while activated alumina is a one-time use trapping agent. Exposure of the activated alumina to process vent streams eventually renders the alumina ineffective as a trapping agent because of uranium loading- and/or irreversible conversion to a less effective trapping form due to the presence of corrosive gases. The alumina in this state is considered "spent" and, unlike the sodium fluoride, there is no in-place process available for facile regeneration and reuse. Currently the spent alumina is either stored or processed for uranium recovery. Mounting costs of storage associated with accumulation of spent alumina and the uncertainty of ultimate disposal prompted feasibility studies for reuse of the alumina. These two handling methods are not appropriate for either waste minimization goals or cost effective handling of the alumina waste. In reprocessing, the alumina is currently treated with 3N HNO_3 which effectively removes the uranium, but also destroys the physical integrity of the alumina pellets. Disposal costs of the resultant sludge are about one dollar/pound a year for storage and \$60/ft^3 for burial. New material costs are about \$0.80/lb with current usage ranging from 12,000 to 15,000 lbs/year. The reuse of 50% of the annually consumed alumina would result in direct annual savings of about \$70,000. Reclamation of used material currently stored, but untreated, could eliminate new material purchases for several years.

EXPERIMENTAL

The tests consisted of; (1) evaluating simple aqueous based leaching procedures to remove the bulk of the uranium from the spent alumina, (2) evaluating the physical properties of recovered alumina, and (3) performing UF_6 trapping tests with the recovered alumina from several trap sources.

Leaching Tests -- The uranium concentration on the spent alumina varies widely depending on the trap location. The alumina also varies with respect to the (AlF_3) aluminum fluoride content which can range from 0 to a high percent AlF_3. Samples of spent alumina utilized in this study contained .2544 grams U/grams and .0003 grams U/grams, and were selected as being representative of high and low values typically encountered. For initial tests, fifty (50) gram quantities of spent alumina containing little or no AlF_3 (this source represents more than half of the alumina waste) were subjected to various reagents and concentrations with an attempt to minimize waste solution generation and retain compatibility with current recovery methods. Each 50 gram sample of material was placed in a 500ml beaker and covered with 200ml of reagent. It was found that 80% to 85% of the uranium could be removed using distilled water. Uranium concentration in the solution reaches a maximum in about one hour. Subsequent uranium removal is enhanced by the use of dilute (0.3N) HNO_3. Three (3) tests using the initial distilled water wash followed by three consecutive HNO_3 treatments gave a total U removal of 95.3%, 98.8% and 96.9%. Following the leaching tests, the material was air-dried at 200°F to remove excess moisture.

Leaching tests were also conducted on spent alumina which was partially converted to aluminum fluoride (AlF_3) as a result of exposure to reactive fluorinating gases and contained considerably lower uranium loading. Material with two different levels of AlF_3 were evaluated, namely, 2.4% and 80% AlF_3. For this type of spent alumina, the initial distilled water treatment was found to be ineffective, however, two (2) 0.3 N HNO_3 treatments reduced U content to background or non-detectable levels.

In all tests pellet integrity of the spent alumina was essentially preserved in the leaching process.

Physical Properties and Trapping Efficiency of Recovered Alumina - The crush strength and surface area of the recycled alumina pellets and new alumina pellets, are compared in Table 1. To test the trapping effectiveness of the recycled alumina, 530 grams were prepared using the distilled water/nitric acid rinse procedure described above. The recycled material was introduced into 3" OD x 18" traps, and UF_6 was passed through the trap at 8.1g per hour at 2 psia. Tests were also performed comparing the performance of the regenerated alumina as a function of the AlF_3 content as shown in Table 2.

Table 1 Physical Properties

	New Alumina	Recycled Alumina
Crush Strength	300 lbs/in^2	750 lbs/in^2
Surface Area	274 m^2/gm	200 m^2/gm

*AlF_3 component is absent as determined by x-ray diffraction.

Table 2 Comparative Uranium Loading After Regeneration

Spent Material % AlF_3*	U-Content (%) after Trap Test
0	13.1
2.4	5.6
80	2.9

*Determined by x-ray diffraction.

CONCLUSIONS

With a large percentage of the alumina used on plantsite being potentially recyclable, the dilute nitric acid leaching method has the possibility of reducing the inventory of stored contaminated waste, reducing new material purchases, and allowing uranium recovery using available material and technology.

Operations:
Safety in Cylinder Handling

ALTERNATIVE METHOD OF RETESTING UF_6 CYLINDERS

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ABSTRACT

The paper describes an alternative method to perform the periodic inspection of UF6 cylinders. The hydraulic test is replaced by ultrasonic checking of wall thickness and by magnetic particle testing of all the weld seams. Information about the legal background, the air leak test and the qualification of inspectors is also given.

INTRODUCTION

The standard method of periodical inspection and test of UF6 cylinders is layed down in ORO-651 (Rev. 5) chapter 7.4.2 and consists of internal/external examination, a hydrostatic test and an air leak test.

The disatvantage of the hydrostatic test on packagings having contained radioactive materials is that the water used for the test becomes contaminated. This is not a problem when the hydraulic test is performed following a emptying and cleaning procedure as in this case waste water has to be processed anyway. Outside of plants receiving UF6 however it would be preferable to have a "dry" test.

Therefore a non-hydraulic alternative test procedure has been developped and been approved. Also the air leak test has been modified to avoid high pressing testing. There is no change in respect to internal inspection.

LEGAL BACKGROUND

The possibility to apply alternative non destrucctive test procedurcs for retesting pressure vessels in general and specifically UF6 cylinders is layed down in the follow regulations and guidelines:

a) German pressure vessel regulations (1)

b) German and European regulations for transport of dangerous goods (2)

c) IAEA TECDOC 423 (3)
"For retesting any other equivalent non destructive examination acceptable to the competent authority may be applied"

d) Draft ISO-Standard 7195 (4)
"... or an equivalent procedure acceptable to the national competent authority"

In compliance with b) the proposed procedure has been reviewed and approved by the Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, as the competent authority for mechanical/thermal evaluation of packagings for the transport of radioactive material.

PROCEDURES TO CHECK MECHANICAL INTEGRITY

The hydraulic test is replaced by checking wall thickness and the integrity of weld seams.

For checking wall thickness a portable ultrasonic wall thickness gauge is used. It employs the pulse-echo method with transit time evaluation. The nominal accuracy can be optimized continously in the measuring range to ± 0.1 mm.

Before testing begins, the operator calibrates the instrument with a test piece of known thickness.

Readings are taken on the surface of the cylinder at about 100 - 150 mm intervalls. This is assumed to be sufficient to evaluate general corrosion effects.

Weld seams of the cylinder and seams attaching the stiffening rings are 100 % inspected for cracks by the magnetic particle test. This test procedure has been selected because under the given conditions the preparation is easier and crack indication is more reliable than using the dye penetration method. Moreover, existing paint need not to be removed.

AIR LEAK TEST

The test is performed by checking the valves and fittings with the soup bubble method. In a transparent bell attached to the area of the valve and of the plug a vacuum of about 0.5 bar is produced and maintained for at least 1 min. Soap bubbles indicate non acceptable leaks.

INSPECTORS

The periodic inspections and tests are performed by a qualified inspector of a state-operated inspection agency entitled to approve and retest pressure vessels. Such inspectors must have a degree in mechanical engineering and be trained in non destructive testing.

REFERENCES

(1) Druckbehälterverordnung
(German Pressure Vessel Ordinance), 27.2.1980
Bundesgesetzblatt I, S. 184

(2) GGVS, GGVE, ADR, RID:
Provisions for packaging and transport of Uranium hexafluoride,
marginals 3771. 4(e) respectively 1771, 4(e)

(3) IATA-TECDOC-423
Recommendations for providing protection during the transport of uranium hexafluoride
IAEA Vienna, 1987

(4) Draft ISO/DIS Standard 7195, proposed changes agreed on the London Meeting of TC85/SC5 WG4 in January 1989

TEMPORARY PATCHING OF DAMAGED UF_6 CYLINDERS

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ABSTRACT

Patching techniques based on application of epoxy resins have been developed for temporarily repairing UF_6 cylinders which have sustained relatively minor damage and must be safely emptied. The method is considerably faster and simpler than metallurgical weld repairs. Laboratory tests, detailed operational procedures, and case histories of experience at the Portsmouth Gaseous Diffusion Plant are described.

INTRODUCTION

UF_6 cylinders are susceptible to several types of damage during handling, transportation and storage. The valve area, bosses, and walls of cylinders are particularly vulnerable to impact-induced leaks, and create problems in rapidly implementing corrective action to prevent or minimize UF_6 outgassing during disposition of the cylinder. Standard metallurgical repair methods are time consuming and relatively different with UF_6 filled cylinders. Since normal UF_6 transfer procedures are impossible under such circumstances, a simple, rapidly-applied and temporary leak-repair procedure is essential to stop the active leak and allow the safe emptying of the cylinder. Temporary patching techniques based on application of epoxy resins therefore have been developed to handle relatively minor or small cylinder breaches. This method has been employed with 2½, 10 and 14 ton UF_6 cylinders for sealing cracked valve couplings, breached walls, and a pinhole in a weld area. Laboratory tests, detailed operational procedures and case histories of experience at the Portsmouth Gaseous Diffusion Plant are described.

MATERIAL EVALUATION

Laboratory screening tests were initially performed on a series of epoxy patching materials to evaluate their resistance to thermal cycling, and resistance to corrosive gas atmospheres. Lap joints of corroded steel and aluminum prepared with the candidate epoxies were exposed to thermal cycles of between 250°F and 75°F, and to thermal cycles between -103°F and 131°F. These tests were followed by exposure to UF_6 gas at 400 mm pressure and 200°F for extended periods.

In more severe tests the candidate epoxy patching materials were also evaluated for resistance to fluorinating gases. Monel plates (1" x 1") were joined with the adhesive and exposed to F_2/ClF_3 atmospheres at 300°F and 400mm pressure for test periods ranging from one to three weeks. The corrosives gas atmospheres were changed daily during the test periods.

Following exposure to the corrosive gas atmospheres, pressure leak testing was also conducted on samples containing a pin hole which had been covered with epoxy.

The best results of the laboratory evaluation were obtained with the Epoxi-Patch 6C Aluminum compound. It demonstrated excellent adhesive properties after the thermal cycle testing, and showed no evidence of exothermic reaction or burn-up during the corrosive gas exposure. The results of the pressure leak testing showed that no degradation had occurred after a one-week exposure to any of the corrosive gases. However, three minute leaks were detected after a two-week exposure, and extensive mechanical degradation of the patch occurred after the three-week exposure to the F_2/ClF_3 atmospheres.

Finally, a field test was conducted on a simulated defective weld on a ten-ton thick-wall cylinder exposed to the steam environment of an autoclave.

Cold rolled steel plates, measuring 1" x 4" x 0.0195" were curved to fit the contour of the weld. The surfaces of both the plates and cylinder were prepared for bonding and then mated with the epoxy. The patch was allowed to cure for sixteen hours before the cylinder was placed in the autoclave. An inspection after exposure to the autoclave atmosphere showed that the patching material had excellent resistance to the steam.

MATERIALS AND EQUIPMENT FOR PATCHING DAMAGED CYLINDERS

1) Wire brush
2) File (metal)
3) Portable electric drill with a rotary wire brush
4) Emery cloth
5) Acetone and/or Freon 113 Degreasers
6) Kim Wipes
7) Aluminum plates 1/16" thick (fabricated to cover the damaged area)
8) Split aluminum collars 1/16" thick with a 1 3/8" hole or with hole (fabricated)
9) Nickel wire mesh screen
10) Pig Putty (brand name) - 2 component epoxy stick
11) Epoxi-Patch 6C Aluminum (brand name) - 2 component epoxy system - diethylene triamine curing agent
12) Masking tape

PATCHING PROCEDURE

The damaged areas on the cylinders to be patched should be of free of iron oxide, oil/grease, and uranium deposits.

The surface to be patched is cleaned with a wire brush, rotary wire brush, metal file, and emery cloth followed by degreasing with either acetone or Freon 113. Aluminum cover plates and/or split cover plates or collars are custom fabricated to cover the damaged areas. These plates or collars are sanded on the bonding side to provide more surface area for better adhesion. The plates or collars are then epoxied to the cylinder over the damaged area. Cylinders with ruptured walls are patched by first attaching a nickel wire mesh screen cut to the size of the hole. The back side of the screen is covered with a thick coat of "Pig Putty" and forced into the hole. The top side is then coated with the "Pig Putty", feather edged with water, and allowed to cure. The cylinder wall is coated with epoxy and the contoured cover plate applied. Slight pressure on the plate is maintained by taping the patched area with masking tape. Normally, 24 hours are necessary for the epoxy to cure during warm or summer seasons. If ambient temperatures are lower, between 48 and 72 hours are required.

CYLINDER PATCHING HISTORY

1) A ten-ton thin-walled cylinder started leaking in the process of being loaded into an autoclave.

   A pin hole on a weld was successfully sealed with epoxy without the use of a cover plate. The cylinder was then emptied by cold feeding to the cascade.

2) Four 10-ton cylinders with small leaks in the valve thread region due to a cracked boss or improper seating of the valve have been successfully patched.

   In these instances patching was accomplished using a three square inch collar fabricated from 1/16" aluminum plate. A 1 3/8" hole was cut in the center of the plate which was then sectioned in half. The two halves of the collar were contoured to fit around the boss area.

   The surfaces were prepared for bonding and mated with the epoxy. The collar was pressed against the boss area and held in place with masking tape.

   The patches on the cylinders were inspected after the successful completion of the cold feeding and they were found to be in very good condition, with no leaking experienced during the feeding.

3) A 2½-ton cylinder was accidentally hit in the valve area which resulted in a bent valve boss. The damaged area was kept cold with bags of dry ice to prevent outleakage. The damaged area was inspected and deposits around the valve stem area indicated the presence of a small leak.

   The leaking area was cleaned and a split aluminum collar was contoured around the boss/valve area. The surfaces were prepared for bonding and then mated with the epoxy (Figure 1).

Because of the decreased temperatures, the cure time for the resin was increased from 24 hours to 48 hours. The patched area was inspected four days later and showed no evidence of leakage. The dry ice packs were removed, and no leaks were detected when the cylinder reached ambient temperature. The cylinder was successfully emptied by cold feeding.

Figure 1 Valve Boss Patch On 2½-Ton Cylinder Employing Split Collar

4) A 14-ton tails cylinder was found to be leaking during an inspection of tails cylinders in storage yards. Apparently the lifting lug from an adjacent cylinder had impacted the cylinder during stacking and resulted in a depression approximately 4" long, and 3/4" to 1" wide (the width of the lifting lug) located near a stiffening ring. The actual size of the hole was 1" x 1½". The damaged area of the cylinder was cleaned and the 1" x 1½" hole was first plugged by forcing a section of nickel screen, coated with "Pig Putty" into the hole. This initial patch was applied to prevent HF from reacting with the cover epoxy during curing. The epoxy putty was then applied to the top side. Water was used to smooth and feather the epoxy.

   An aluminum cover plate (6" x 7" x 1/16" thick) was fabricated with a 1½" right angle bend so that the plate conformed to the curvature of the cylinder and the stiffening ring. The cylinder and cover plate surfaces were prepared for bonding and then mated with epoxy in such a manner that the right angle of the plate seated against the stiffening ring and also covered the plugged hole (Figures 2A and 2B). Masking tape was used to hold the cover plate and apply pressure to the patch area. After curing, the cylinder was successfully emptied by cold feeding.

5) An inspection of a 2½ ton cylinder showed that half of the plug boss external to the cylinder was missing. It was also observed that the boss had probably not been recently damaged because the area had a new coat of paint. The damaged area did not appear to be detrimental for the normal transfer of UF_6 because the plug had five threads engaged and there was no indication of leakage. However, to ensure the integrity of the cylinder, the damaged area was patched. Only half of a split aluminum collar was contoured to cover the damaged area. The surfaces were prepared for bonding and then mated with the epoxy. The patched area was inspected and the cylinder released for cold feeding according to approved methods.

SUMMARY

Using the epoxy patching technology, eight damaged UF_6 cylinders have been successfully patched and safely emptied. The patching technique effectively sealed leaking areas of a defective weld, damaged bosses, and in one case a breached cylinder wall. Operations was able to successfully transfer the UF_6 from the patched cylinders by cold feeding at ambient temperatures of approximately 100°F.

The removal of UF_6 from a damaged cylinder has extremely high priority because any release is a major environment concern. The advantage of applying an epoxy patch is that it can be rapidly applied. In contrast, a metallurgical weld patch involves considerably greater time and cost because of the required permits, fabrication of a specific cover plate, and the services of the weld shop, as well as the required monitoring of the welding.

The disadvantage of the epoxy patch is that it is only temporary and the removal of the UF_6 from the patched cylinder should be performed as soon as possible. These patching methods are effective for leaks resulting from relatively minor damage and are not intended for situations involving major cylinder damage.

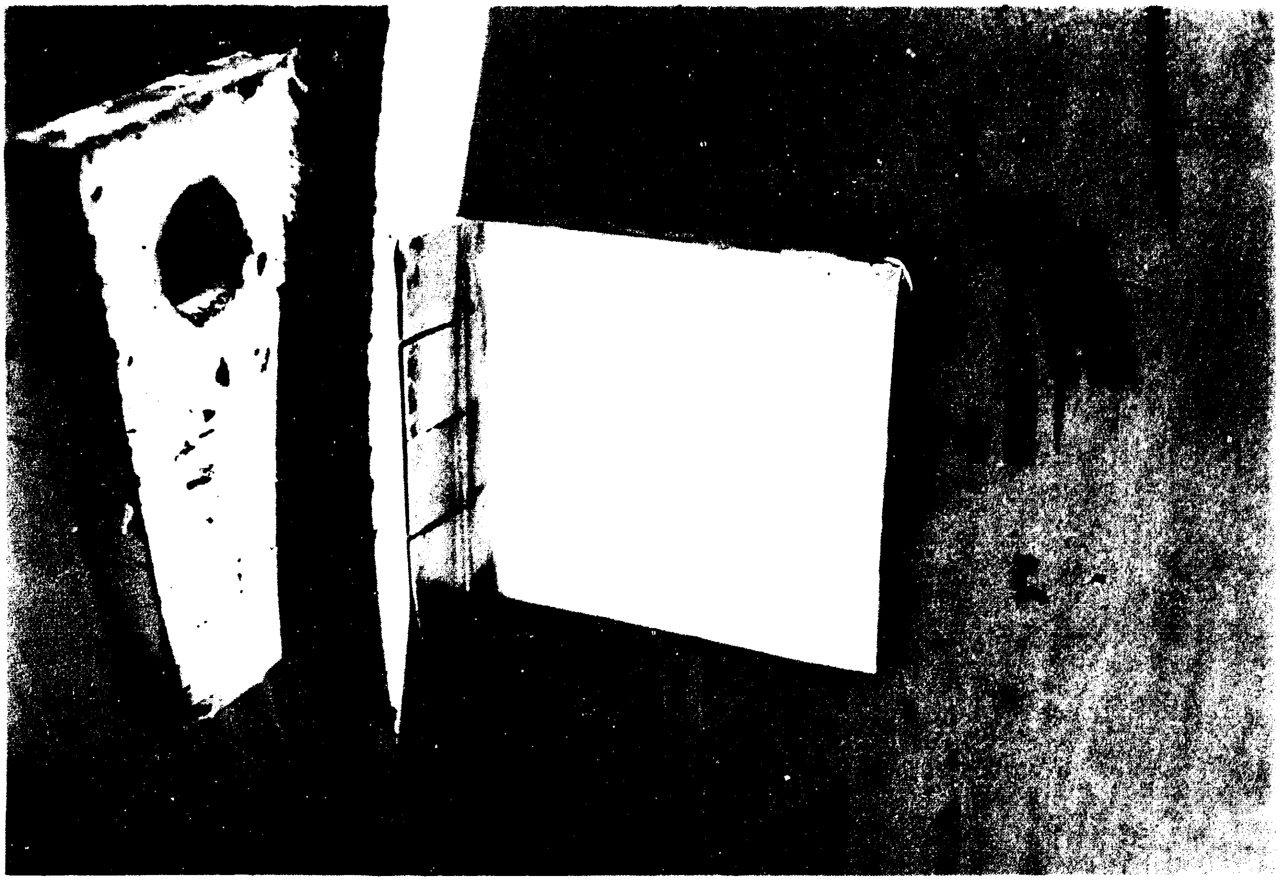

Figure 2A Aluminum Plate Contoured To Fit Over Damaged Area of 14-Ton Cylinder

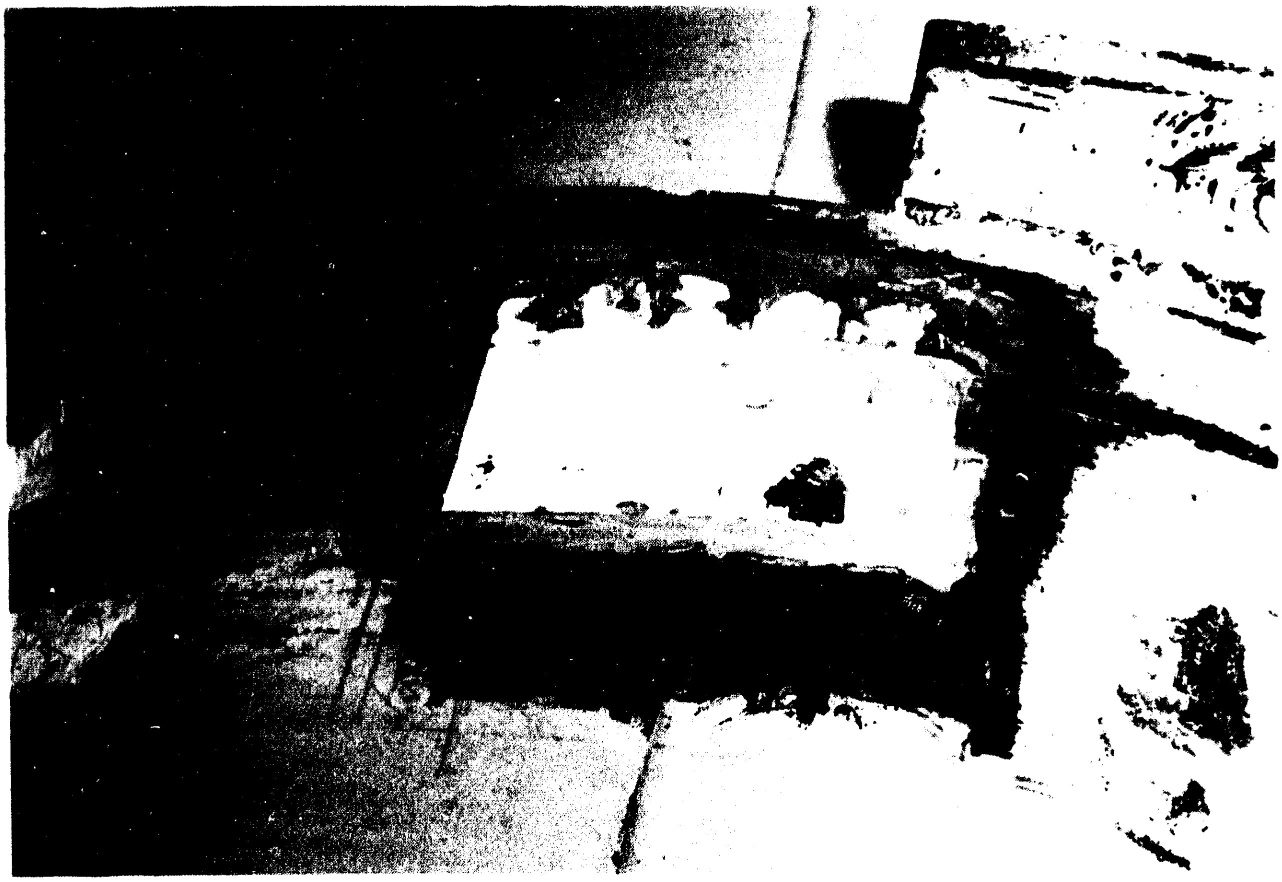

Figure 2B Completed Patch Over Damaged Area of 14-Ton Cylinder

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URANIUM HEXAFLUORIDE...

Liquid Thermal Expansion, Elusive Eutectic with Hydrogen Fluoride, and Very First Production using Chlorine Trifluoride.

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ABSTRACT

Three unusual incidents and case histories involving uranium hexafluoride in the enrichment facilities of the USA in the late 1940's and early 1950's are presented.

The history of the measurements of the thermal expansion of liquids containing fluorine atoms within the molecule is reviewed with special emphasis upon uranium hexafluoride. A comparison is made between fluorinated esters, fluorocarbons and uranium hexafluoride. The quantitative relationship between the thermal expansion coefficient, α, of liquids and the critical temperature, T_c is presented. Uranium hexafluoride has a α that is very high in a temperature range that is used by laboratory and production workers - much higher than any other liquid measured. This physical property of UF_6 has resulted in accidents involving filling the UF_6 containers too full and then heating with a resulting rupture of the container. Such an incident at a uranium gaseous diffusion plant is presented.

Production workers seldom "see" uranium hexafluoride. The movement of UF_6 from one container to another is usually trailed by weight, not sight. Even laboratory scientists seldom "see" solid or liquid UF_6 and this can be a problem at times. This inability to "see" the UF_6-HF mixtures in the 61.2° C to 101° C temperature range caused a delay in the understanding of the phase diagram of UF_6-HF which has a liquid - liquid immiscible region that made the eutectic composition somewhat elusive. Transparent fluorothene tubes solved the problem both for the UF_6-HF phase diagram as well as the UF_6-HF-ClF_3 phase diagram with a miscibility gap starting at 53°C.

The historical background leading to the first use of ClF_3 to produce UF_6 in both the laboratory and plant at K-25 is presented.

NOMENCLATURE

T temperature

T_c critical temperature

α the expansion coefficient, α, is defined as $(d_1-d_2)/d_2(T_2-T_1)$ where d_1 is the density at the lower temperature, T_1, and d_2 and the density at T_2.

Tav $(T_1+T_2)/2$; average temperature

LIQUID THERMAL EXPANSION

As a research fellow at the University of Tennessee in the 1946-1948 time period, one goal was to make density measurements of liquids and identify some with very high coefficients of thermal expansion (α). As reported in the thesis (1) and later in a scientific journal (2) the fluorination of an organic compound increases the coefficient.

Ethyl acetate has a high expansion coefficient typical of esters. Ethyl difluoroacetate has an even higher coefficient and ethyl trifluoroacetate has a coefficient 30% higher than that of the difluoroacetate, 1.83×10^{-3} per degree centigrade, compared with 1.41×10^{-3} at the same temperature.

Ethyl trifluoroacetate had the highest coefficient measured during the University of Tennessee research that ended in early 1948. Another goal of the U-T research was to develop an equation that would correlate the α with the critical temperature (T_C) of the liquid (3).

Upon joining the uranium gaseous diffusion laboratory at K-25 in June of 1948, there was an obvious curiosity in knowing the thermal expansion and critical temperature of more fluorocarbons since additional data were now available. However, the liquid that really excited me at K-25 was not organic but inorganic uranium hexafluoride. Of the seven atoms in this compound six are fluorine.

The fluorocarbons examined in report K-419 (4) did indeed have high thermal expansion coefficients and one of the compounds, hexadecafluoroheptane, had a higher thermal expansion, 1.9 x 10^{-3}, than ethyl trifluoroacetate.

Now for that unique and important compound, UF_6. The α is very high. In fact, it is higher than any liquid measured and reported in the literature. Using density measurements available in 1948, the expansions coefficient reached 1.84 to 2.86 x 10^{-3} in the 81° to 146°C temperature range (5) (6). This 2.86 x 10^{-3} value is much greater (over 50%) than anything reported in the U-T project or in K419. Note the UF_6 measurement is made at a pressure greater than one atmosphere. Liquid UF_6 does not exist at a pressure less than 1.5 atmospheres and temperatures below 64° C. Nevertheless the comparisons with other fluorinated compounds are of great interest.

With respect to the safe handling of UF_6, it is important to be aware that the liquid thermal expansion of UF_6 is huge even in the temperature range of normal production operations. For example, at 235° F(113°C), an operating temperature (7) for liquid UF_6 transfers, the liquid thermal expansion coefficient is 2.2 x 10^{-3}.

For a more complete view of the thermal expansion of UF_6, Table 1 shows the thermal expansion of both solid and liquid UF_6 using density measurements documented in K-445 (5) (6) and density as a function of temperature equations for solid UF_6 and liquid UF_6 at the critical temperature (8).

Table 1. Volume Percent Increase $(d_1/d_2-1)(100)$ of UF_6 as a function of temperature

Temp. °C Density g/ml	Volume Increase	Comments
0 to 64.02 5.194 to 4.863	6.8%	Solid, UF_6 to the triple point
64.02 to 64.02 4.863 to 3.630	34.0%	Solid to Liquid, change of state, triple point
64.02 to 113 3.630 to 3.316	9.5%	Liquid, handling temp. range:triple point to 235°F
113 to 230.2 3.316 to 1.302	155%	Liquid, temp. approaches T_C
79 to 121 3.539 to 3.259	8.6%	Liquid, 175° to 250° F. ORO-651

Note that the volume percent increase column numbers cannot merely be added for a wider temperature range. The volume percent increase in going from solid UF_6 at 0°C to liquid UF_6 at 113°C is 56.6% not 50.3%. Per UF_6 handling procedures, ORO-651, Rev. 5, p. 9, "to fill or empty UF_6 cylinders, all lines are heated to maintain a temperature in the range of 170° to 250° F (79° to 121° C)." If an operator somehow does heat UF_6 from a solid at 0° C to the triple point at 64.02° C and on through the change of state from solid to liquid at 64.02° C and then the liquid to 121° C (250° F), the volume percent increase is 59.4%. Table 1 clearly shows that care is very necessary in the handling of both solid and liquid UF_6.

If a worker does load a container with too much UF_6, the container may rupture upon heating. A rupture did occur at a gaseous diffusion plant in the 1955 time frame. The container was a small cylinder with a diameter of about 3-1/2 inches and length of about 11-1/2 inches. As a member of the safety committee investigating the incident, calculations clearly showed that the accident was caused by overfilling and then heating. At this time most of the production workers at this facility had only a few months operating experience.

As for the liquid thermal expansion of a liquid and the critical temperature, two correlations were developed. The relationship between the liquid thermal expansion coefficient of a liquid and the critical temperature of that liquid was first derived from a mathematical combination of the Ramsey-Shields-Eotvos and the McLeod and Sugden equations. Another simplified equation has been obtained empirically with the aid of experimentally determined critical temperatures and densities (3). Using measurements on 29 organic compounds including anhydrides, hydrocarbons, alcohols, fluorocarbons, esters, ketones, nitriles, ethers and others, the best curve by the method of least squares is represented by the equations:

$$T_C=(\alpha/0.04314)^{-1.56}+Tav$$
$$\alpha = 0.04314\ (T_C - Tav)^{-0.6410}$$

Using the above equation the critical temperature of uranium hexafluoride was calculated to be 218.5° C (5) which is not too far off from the measured value of 230.2° C (9) considering UF_6 is not an organic compound.

In a private communication to Farrar and Smith, who did the absorption of ClF_3 on porous nickel fluoride, the critical temperature of ClF_3 was predicted to be 174 C (10). Hands on experiments with mixtures of ClF_3, UF_6 and HF at temperatures as high as 101°C are discussed next.

THE ELUSIVE UF_6-HF EUTECTIC

It is well known that those who handle UF_6 seldom actually see the UF_6. The UF_6 is usually in a metal container that in not transparent. When assigned the task of determining the UF_6-HF phase diagram, the decision was made to "see" the mixture using a fluorothene tube (11).

Starting with pure UF_6 at a triple point of 64.02°C, small increments of HF were added and the phase change measured from 64.02°C to 61.2°C with results somewhat as expected. The melting point of the UF_6-HF mixture was declining toward an expected eutectic temperature somewhat below that of pure HF i.e. - 83.6°C (12).

More HF was added to the mixture and the temperature was 61.2°C. Even more HF was added and the melting point was still 61.2°C. Now with "eyes" it was possible to see what was going on. The HF_6-HF mixture formed a liquid-liquid immiscible (like water and oil) gap as shown in Figure 1.

Earlier researchers had made similar measurements in metal containers and were apparently baffled at the sudden lack of drop in the freezing point with the addition of more HF to the system at the 80 formula % UF_6 composition . These data, recorded in a notebook, were not reported. For the UF_6-HF system a miscibility gap starts at 61.2° and extends over the composition range 10 to 80 formula % UF_6 to a consulate temperature of 101°at about 50% formula % UF_6. The eutectic temperature was -85°C.

For the UF_6-ClF_3 -HF system the lowest temperature at which the miscibility gap exists for two liquids saturated with solid UF_6 is 53° at a composition of 49 formula % UF_6, 13 formula % ClF_3 and 38 formula % HF. Below -91°C all three compounds are solid at all compositions (13).

With respect to using fluorothene tubes in either the laboratory or plant operations, the above laboratory experiments pushed the fluorothene tubes to, and even beyond, their temperature and pressure limits in the 100°C range. On two measurements the tubes ruptured. Also, impurities in ClF_3 caused a minor explosion in a hood on one occasion in the course of doing the ternary experiment.

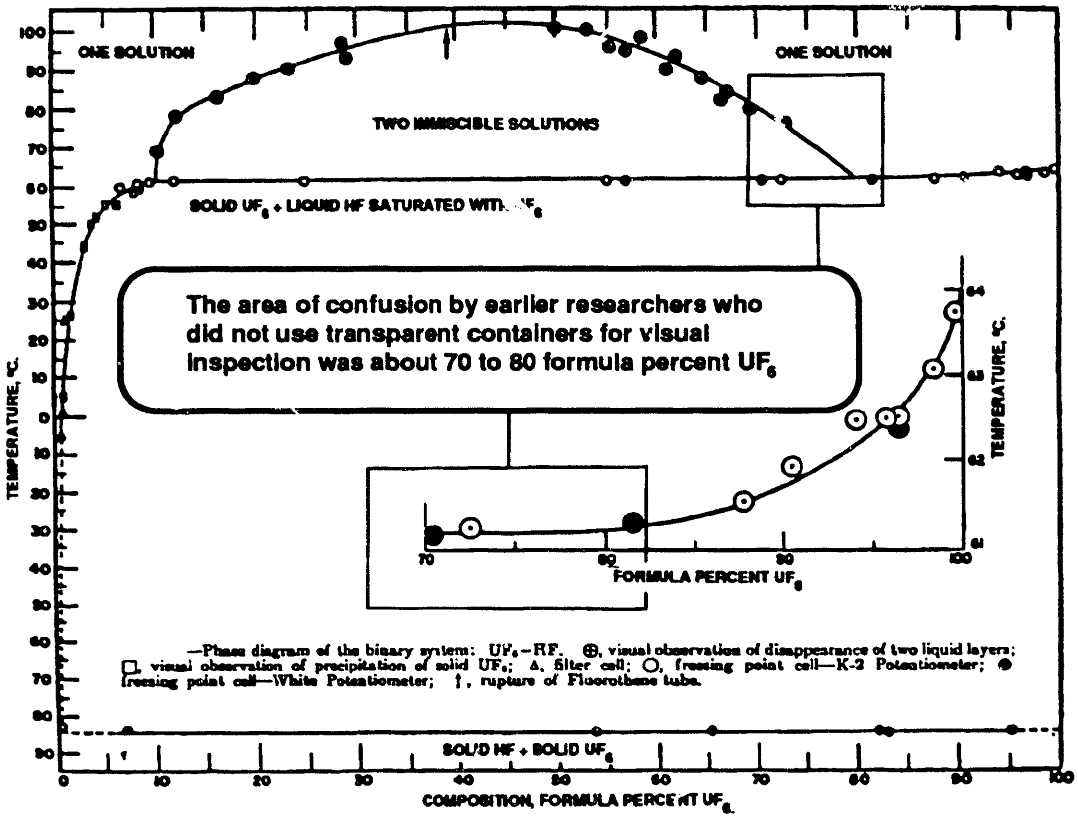

Figure 1. UF_6-HF phase diagram.

The scope of this report does not cover the safety and care needed in handling UF_6, HF and ClF_3 except to alert those who handle UF_6, and impurities found in UF_6 that special training is mandatory. A mixture of these compounds is corrosive, radioactive and subject to violent reactions with hydrocarbons.

THE VERY FIRST PRODUCTION OF UF_6 USING ClF_3

In late 1948 to early 1949 time frame some uranium pentafluoride, UF_5, was needed for an experiment underway in Lab D at K-25. A small amount had been obtained earlier from the cascade engineers in the K-25 plant. Uranium pentafluoride is a white crystal with a definite x-ray diffraction patterns when it is pure. Time after time my reactions of UF_4 with F_2 gave a grey mixture of U_4F_{17} and U_2F_9 according to the x-ray diffraction patterns, not UF_5.

A colleague working next to me using the same equipment support rack had his high vacuum manifold hooked up to chlorine trifluoride for other experiments. As a long shot, the suggestion was made to react UF_4 with ClF_3 in an effort to make UF_5. This reaction experiment was strongly encouraged; however, a mild fluorination that would not really produce the needed UF_5 was expected.

My colleague put UF_4 in a nickel boat (so he claimed) and placed the boat into his small reactor tube. He opened the ClF_3 valve, let the mixture react and then pumped out all the volatile gases. Next he pulled out the boat and, somewhat puzzled, showed it to me. It was empty. Solid green UF_4, a mixture of grey solid uranium fluorides or perhaps solid white UF_5 crystals was expected in the boat depending upon the amount of fluorination that took place.

My colleague was accused by me of forgetting to load the boat with UF_4. He insisted he did load the UF_4 into the boat. Nevertheless, a forgot-to-load incident of this type, but with different reaction compounds, did occur with operators at Y-12 in 1945 so the belief was strong that a mere loading oversight had occurred.

The immediate decision was to repeat this experiment; however, this time he was watched carefully to confirm that UF_4 was loaded into the boat. Following the reaction the volatile gases were pumped out and the reactor tube was opened and the boat was removed. It was indeed completely empty!!!

To my shock, it was now obvious to me beyond any doubt that ClF_3 was a more (much more) powerful fluorinating compound than fluorine with respect to uranium. It had reacted with solid UF_4 to go all the way to produce gaseous UF_6 very swiftly.

The first thought was one of failure - no UF_5 was made in this experiment. The next step a day or so later was to go again from Lab D to the K-25 plant engineers and try to get some UF_5. Discussion with the engineers revealed that they would not be able to supply any UF_5 from the cascade. During this visit the engineers expressed deep concern with respect to their problem of the cascade being plugged with nonvolatile uranium compounds. (Apparently on one occasion an opossum got into a transformer which resulted in a power loss to the plant. This permitted air with some moisture (H_20) to enter which in turn reacted with the UF_6 to form unwanted solid products such as UO_2F_2 which plugged the barrier).

In this discussion with the plant engineers, they were told rather boldly that they really had no problem. Merely pump ClF_3 into the cascade and all the solid uranium compounds would become gaseous UF_6. It was suggested that they confirm my statement by coming to Lab D and talking with my colleague who conducted the UF_4 plus ClF_3 experiment in his equipment for me. (From the office of engineers to Lab D was about a quarter mile.) The engineers did come to our room in Lab D, inspect the equipment where the experiment was conducted and had more technical discussions. Soon thereafter the engineers conducted an experiment(s) with ClF_3 into plugged barrier equipment that had been removed from the plant to test stands. A trip was made from the laboratory to the plant to witness one experiment. Uranium solid deposits (hidden inventory) that had been "lost" since start-up years ago were recovered. The cascade barrier was successfully unplugged. A significant advancement in uranium gaseous diffusion technology was confirmed as a result of the outstanding fluorinating properties of ClF_3. A literature search revealed that ClF_3 had never before been reacted with uranium or a uranium compound.

The Atomic Energy Committee's General Advisory Committee met on October 29 and 30, 1949 and recommended, in response to the Soviet A-bomb on September 23, 1949, increasing the production of fissionable materials in the USA (14). And so not only was the ClF_3 discovery significant but the timing of the discovery had a major impact on the mix of our nation's production facilities with expenditures of many billions of dollars allocated for uranium enrichment using gaseous diffusion.

A K-25 manager noted that without the discovery of the ability of ClF_3 to produce UF_6 from solid uranium fluorides, the K-25 plant would not have been expanded, and the Paducah enrichment facility would not have been built. The same holds true for the Portsmouth plant. Without the ClF_3 discovery more dollars would have been spent on other production facilities

The reaction of chlorine trifluoride with uranyl fluoride has now been investigated and reported in scientific journals by a number of scientists (15) who confirm the production of UF_6. Also a quantitative study by Labton shows "the fluorination (of uranium tetrafluoride) by chlorine trifluoride is 160 times faster than by fluorine (at 265°C)"(16). At lower temperatures the ratio is even higher.

Patent disclosures have been made utilizing the outstanding fluorination properties of ClF_3. For example, Robert A. Gustison, Harvey A. Bernhardt, Eugene J. Barber, and Samuel T. Benton were awarded U.S. Patent 3825650, July 23, 1974 (application 6/18/54), for decontaminating uranium by reaction with chlorine trifluoride and hydrogen fluoride and volatizing the uranium hexafluoride product.

As for the experiment requiring UF_5 that accidentally triggered the ClF_3 to UF_6 discovery, the K-790 report was published July 13, 1951 (17).

SUMMARY

After seeking for two years liquids, especially organofluoro compounds, with high liquid thermal expansion coefficients at the University of Tennessee as a Knoxville student research fellow, the author joined the laboratory at K-25 in Oak Ridge in June 1948. Within weeks, using available K-25 data, two liquids were calculated to have higher liquid thermal expansion coefficients than anything measured in the UT project. One liquid was a fluorocarbon, hexadecafluoroheptane. The other was an inorganic liquid, uranium hexafluoride. The UF_6 has an exceptionally high liquid thermal expansion coefficient in a temperature range of routine production operations which means handling is a significant safety concern. The expansion coefficients of liquids are related to the liquid's critical temperature according to two mathematical equations presented.

In the late 1940's research workers at K-25 were reluctant to report data being collected on the freezing point of mixtures of UF_6 and HF in the temperature range of 61.2°C and composition a little less then 80 formula % UF_6. Once the experiment was done in a fluorothene tube, it was possible to "see" the formation of two immiscible solutions that was confusing those who used non-transparent (nickel) containers. The complete freezing point diagram for the system uranium hexafluoride - hydrogen fluoride is presented including temperature measurements near 100°C where the fluorothene tube holding the immiscible solutions ruptured during two experiments.

In the quest to make UF_5 for an isotopic exchange experiment in 1949, the author and his colleagues stumbled upon a significant scientific discovery - the powerful fluorinating properties of ClF_3 on uranium compounds. The ability of ClF_3 to react swiftly and completely with uranium fluorides and UO_2F_2 to form UF_6 provided a method for the unplugging and clean up of uranium gaseous diffusion production facilities.

The USAEC chose to expand the production of uranium and plutonium in 1949 following the unexpected Soviet atomic bomb explosion on September 23, 1949: therefore, the timing of the ClF_3 discovery had a major impact on the direction of the expenditure of these USAEC funds. The decision was to expand the uranium gaseous diffusion facilities at Oak Ridge, TN, build a new plant at Paducah, KY, and build still another plant near Portsmouth, OH. Many billions of dollars were spent in the early 1950's on this major expansion program.

ACKNOWLEDGEMENTS

Assistance provided by Joseph Russell in obtaining needed documents from K-25 that were classified at one time is appreciated. The technical review of the manuscript by W. Davis, Jr., former supervisor of the author and world authority in the field of uranium and fluorine chemistry, permitted an improved paper. The use of the time and laboratory manifold of my colleague, Roger Jarry, to react ClF_3 with UF_4 deserves a special thank you. William Bishop suggested the author try the use of chlorine trifluoride rather than fluorine to add another fluorine atom to UF_4 to make UF_5; however, the resulting compound was UF_6 which opened the door to significant improvement in uranium gaseous diffusion technology. Larry Hayden and Sue Bybee assisted with the art work on Figure 1. The credit for the typing of many drafts of this paper goes to Karen Kilgore and Betsy Cottle.

REFERENCES

1. G. P. Rutledge, *"Thermal Expansion Coefficients of Organic Liquids,"M.S.* Thesis, University of Tennessee, Knoxville, 1948.

2. G. P. Rutledge and W. T. Smith, Jr., "Densities and Thermal Expansion Coefficients of Several Organofluoro Compounds," J. *Am. Chem. Soc., 75,* p. 5762, 1953.

3. Wm. T. Smith, Jr., S. Greenbaum, and G. P. Rutledge, "Correlation of Critical Temperatures with Thermal Expansion Coefficients of Organic Liquids," *J. Phys. Chem., 58,* p. 443,1954.

4. G. P. Rutledge, *"Correlation of Critical Temperature with Thermal Expansion Coefficients of Liquid Fluorocarbons,"* Carbide and Carbon Chemicals Company, K-25 Plant, K-419, June 13, 1949; Nuclear Science Abstracts, AECU-295, Volume 3, ABS. 7055.

5. G. P. Rutledge, *"Correlation of Critical Temperatures with Thermal Expansion Coefficients of Liquid Uranium Hexafluoride,"* Carbide and Carbon Chemicals Co., K-25 Plant, K-445, July 15, 1949; Nuclear Science Abstracts, AECD3264, Vol. 5, ABS.7055.

6. Hoge, H.J. and M.T. Wechsler, *"Density of Liquid UF_6 from Triple Point to 162°C and Density of the Solid Near the Triple Point",* National Bureau of Standards, A 1591, Dec. 18, 1943.

7. R.H. Dyer, *"Safe Heating of 48G Cylinders Containing UF_6",* Conference Proceedings: Uranium Hexafluoride-Safe Handling, Processing and Transporting, p. 56, Oak Ridge, TN, May 24 - 26,1988.

8. E.J. Barber, *"The Physical and Chemical Properties of Uranium Hexafluoride'",* Ibid, p. 2.

9. Oliver, G.D., Milton, H.T. and Grisard, J.W., "The Vapor Pressure and Critical Constants of UF_6", *J. Am. Chem. Soc., 75,* pp. 2827 - 9, 1953.

10. G. P. Rutledge, "Critical Temperature of Chlorine Trifluoride," priv. communication, *J. Am. Chem. Soc., 77,* p.4503, 1955.

11. W. Davis, Jr., L. L. Conley, and G. P. Rutledge, *"Apparatus for Rapid Determination of Liquid-Liquid and Liquid-Solid Equilibria Involving Corrosive Materials",* Rev. Sci . Inst., 24, No. 6, pp. 431 - 2, 1953.

12. G. P. Rutledge, R. L. Jarry and W. Davis, Jr., "Freezing Point Diagram and Liquid Liquid Solubilities of the System Uranium Hexafluoride-Hydrogen Fluoride," *J. Phys. Chem., 57,* pp. 541-4,1953.

13. G. P. Rutledge and W. Davis, Jr., "Solid Liquid and Liquid-Liquid Equilibria of the Ternary System Uranium Hexafluoride Chlorine Trifluoride-Hydrogen Fluoride," *J. Phys. Chem., 63,* pp. 166-8,1959.

14. R. Rhodes, *"The Making of the Atomic Bomb",* Simon and Schuster, Inc., p. 767, 1986.

15. R. C. Shrewsberry and E. L. Williamson, "Chemistry of the Chlorine Trifluoride Uranyl Fluoride Reaction," *J. Inorg. Nucl. Chem.,* Vol. 28, pp. 2535-9, 1966.

16. V. Y. Labton "Kinetic Studies of the Fluorination of Uranium Tetrafluoride by Chlorine Trifluoride," *J. Inorg. Nucl. Chem.,* Vol. 10 pp. 86-93, 1959.

17. W. Davis, Jr. and G. P. Rutledge, *"Exchange of Uranium Between Beta Uranium Pentafluoride and Gaseous Uranium Hexafluoride",* Carbide and Carbon Chemicals Company, K-25 Plant K-790, July 13, 1951 declassified with deletions, Feb. 27, 1957.

UF_6 CYLINDER LIFTING EQUIPMENT ENHANCEMENTS

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ABSTRACT

This paper presents numerous enhancements that have been made to the Portsmouth lifting equipment to ensure the safe handling of cylinders containing liquid uranium hexafluoride (UF_6). The basic approach has been to provide redundancy to all components of the lift path so that any one component failure would not cause the load to drop or cause any undesirable movement.

ACRONYMS

AISI - American Iron and Steel Institute
ASTM - American Society of Testing Materials

INTRODUCTION

Liquid UF_6 is handled at the Portsmouth site in partially filled or full 2½, 10 and 14 ton cylinders. Autoclaves are used to heat the 14 or 10 ton cylinders for UF_6 transfer into the 2½ ton customer cylinder. Because of the 5-day cool down time for a cylinder containing liquid UF_6, it is necessary to move the cylinder to a storage position so that the autoclave can be reused. An overhead crane in conjunction with a lifting fixture which interfaces with the cylinder is used for moving the cylinder.

In the X-344 Toll Enrichment Facility there are four autoclaves and two overhead cranes which service the autoclaves. One crane is a 20-ton P&H with a single-point pick-up which dates back to the late 1950's. The other is a 20-ton Orley-Meyer crane installed in 1985, which originally had a two-point pick-up. Because of the potential sloshing of the liquid UF_6, only the two-point pick-up crane was used for moving cylinders with liquid UF_6.

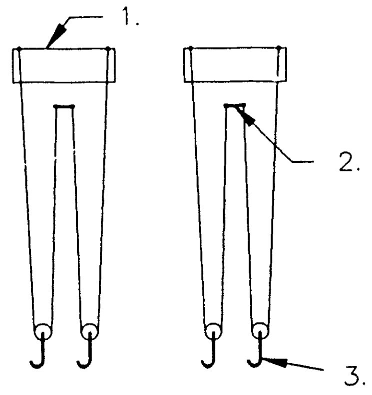
In 1988, lift height safety was re-evaluated, and a new emphasis was placed on single-point failures for equipment that handled liquid UF_6. A single-point failure on the two-point lift would cause a pendulum type movement which could cause the other pick-up point to potentially fail or cause considerable damage, injury, and/or cylinder rupture.

Hence, the criteria of a redundant lift path was established. The approach at Portsmouth was to replace both cranes with ones having redundant features. The two-point crane would now be a four-point crane with four independent hooks. New lift fixtures would be designed to accommodate the four hooks and also to have redundant lift paths.

INTERIM MEASURE

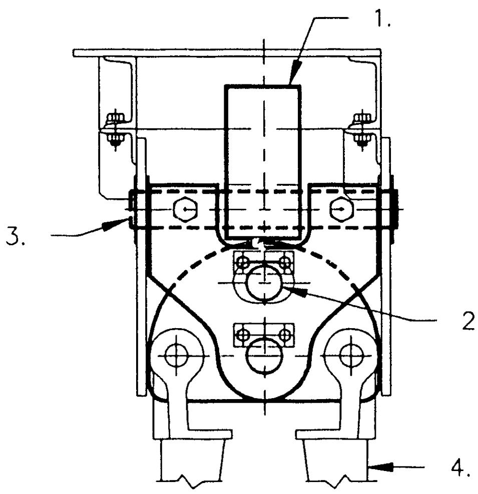
Due to the long lead time to fund and procure a new crane with redundancy features, the existing two-point Orley-Meyer crane was evaluated to determine the interim measures that could be taken to enhance the safety of the crane. Historically, the cabling on a crane has been the most susceptible component for failure on the lift path. Therefore, a redundant set of cabling was added to each of the two hoist drums enabling the modification of the crane from a two-point pick-up to a four-point pick-up. A schematic of the four-point pick-up is shown in Figure 1.

High strength cable was specified to minimize the effect of cable diameter on the hoist drum grooving. The existing equalizer shieve was replaced with an equalizer bar which incorporated redundancy features. An elevation of the equalizer bar is shown in Figure 2.



1. Lift Drum
2. Equalizer Bar
3. Hook

Figure 1. Four Hook Schematic



1. Safety Strap
2. Redundant Pin
3. Shear Pin
4. Cable Connection

Figure 2. Equalizer Bar

LIFT FIXTURE

A new four-point lifting fixture was designed by Martin Marietta Energy Systems, and fabricated in-house. An elevation of the fixture is shown in Figure 3. The fixture interfaces with the four hooks on the crane and the different types of cylinders. The primary lift path is through chain shackles which attach to lifting lugs on the cylinder. A redundant lift path is accomplished with belly bands which drape below the cylinder and are supported by separate arms on the fixture.

The main lift frame and shackles are made from ASTM A36 or AISI C1018 steel. The chain and connecting link on the lift arms are made from grade 8 alloy steel. The upper connecting pins are fabricated from AISI 41L40 steel. The pick-up point at the cylinder lug utilizes a stainless steel quick disconnect pin which has a "ball-lock" locking feature. The belly band is made from a stainless steel flexible cable utilizing a "cable-laid" design.

A separate attachment below the main fixture is used for moving 2½ ton cylinders. Redundancy is accomplished by the use of four cable arms with hooks. See Figure 4.

NEW CRANES

The replacement cranes for the two existing cranes will have built-in redundancy up to the gearbox. This includes dual cable systems, redundant hooks, redundant hoist drums, and redundant brakes on the lift path. Redundancy will also be included in the crane anticollision system. The crane is to be fabricated in accordance to the Crane Manufacturer's of America Specification No. 70. The hoist gear box will have a factor of safety against load failure of 10:1.

SUMMARY

Redundancy on the lift path has successfully been accomplished in a UF_6 cylinder lifting system. The system modifications include dual cabling, and incorporation of a four-point lifting fixture. These system upgrades significantly increase the safety of equipment operation and the handling of cylinders containing liquid UF_6.

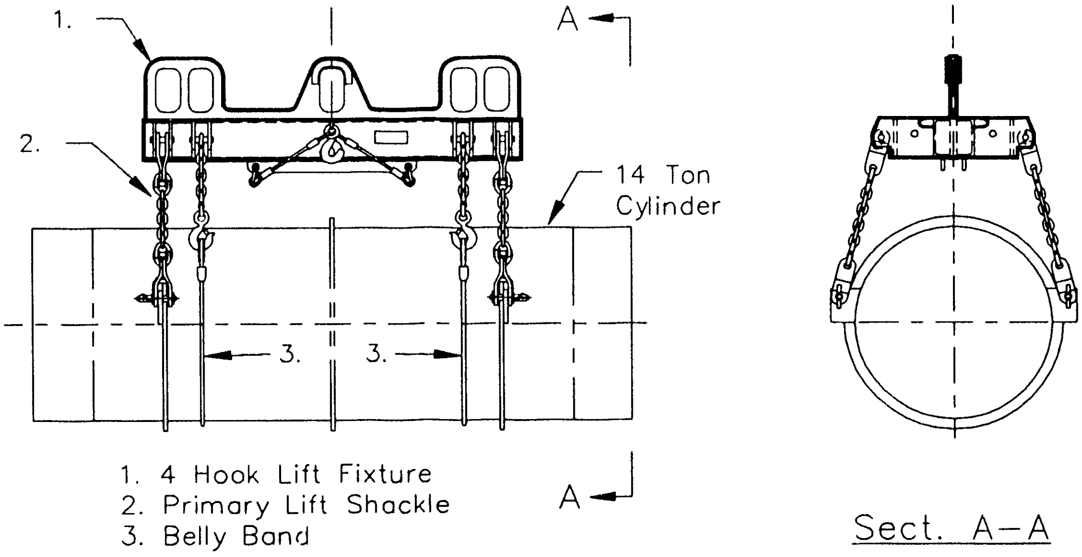


Figure 3. New Lift Fixture

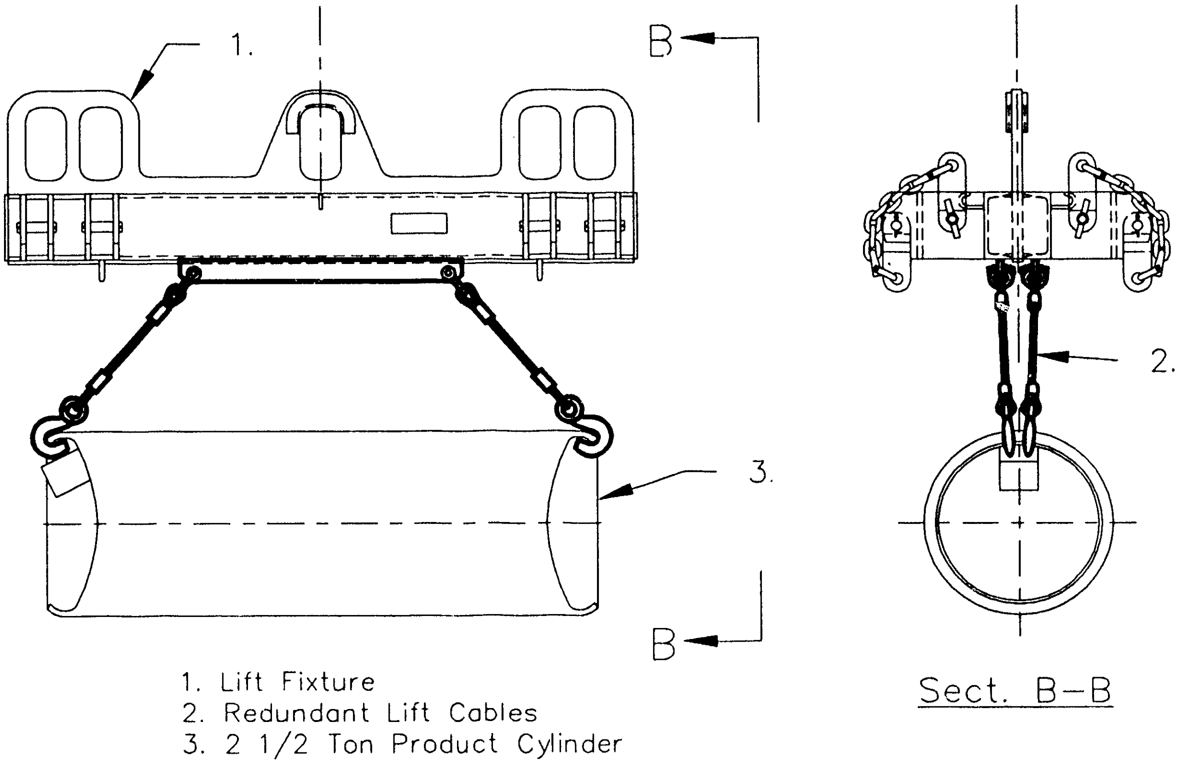


Figure 4. 2½ Ton Lift Attachment

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Operations:
Analyzing for Safety

AUTOCLAVE NUCLEAR CRITICALITY SAFETY ANALYSIS

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ABSTRACT

Steam-heated autoclaves are used in gaseous diffusion uranium enrichment plants to heat large cylinders of UF_6. Nuclear criticality safety for these autoclaves is evaluated.

To enhance criticality safety, systems are incorporated into the design of autoclaves to limit the amount of water present. These safety systems also increase the likelihood that any UF_6 inadvertently released from a cylinder into an autoclave is not released to the environment.

Up to 140 pounds of water can be held up in large autoclaves. This mass of water is sufficient to support a nuclear criticality when optimally combined with 125 pounds of UF_6 enriched to 5 percent U^{235}. However, water in autoclaves is widely dispersed as condensed droplets and vapor, and is extremely unlikely to form a critical configuration with released UF_6.

INTRODUCTION

For nearly twenty years steam-heated autoclaves have been used in gaseous diffusion uranium enrichment plants in the United States to heat large UF_6 cylinders. At the Portsmouth Gaseous Diffusion Plant in Piketon, Ohio steam-heated autoclaves are used in three facilities for feeding the cascade, sampling, and transfer. Four of the thirteen autoclaves are 96 inches in diameter and are used for sampling and transfer operations. Five autoclaves are 84 inches in diameter and are used for feed and sampling operations. There are four 72-inch diameter feed autoclaves. These steam-heated autoclaves generally heat 2 1/2-, 10-, and 14-ton UF_6 cylinders. Occasionally 10- or 12-inch diameter cylinders are heated in autoclaves for transfer to larger cylinders. The steam pressures in the autoclaves normally range from 8 to 12 psig. In addition to being an efficient means for heating UF_6 cylinders, the autoclaves provide containment in the event of a UF_6 release.

When UF_6 reacts with water or water vapor, HF and UO_2F_2 are formed. The reaction is exothermic, and the HF gas can cause pressure in the autoclave to increase by a factor of 10 or more. If the pressure in an autoclave exceeds the rated pressure, usually about 150 psig, the HF and unreacted UF_6 vent to the atmosphere. Because such a large source of UF_6 is present, every effort has been made during the design of autoclaves to minimize the amount of water held up, thereby minimizing the potential adverse consequences of a UF_6 and water reaction.

The UF_6 cylinders heated in autoclaves are limited to U^{235} enrichments of less than 5 percent. Uranium of this enrichment cannot be made critical without a moderator such as water. The UF_6 in the cylinders is of very high purity. Subcriticality in the large cylinders is assured by controlling or restricting the presence of moderators. If UF_6 is released from a cylinder into a steam-heated autoclave, moderation control is lost. To reduce the potential for criticality and to contain released UF_6, a number of systems have been developed and incorporated into autoclave design. These systems detect abnormal conditions and shut off the steam supply or place an autoclave in a "containment" mode. Figure 1 shows the systems in a typical autoclave. They include a high condensate level cutoff system, a UF_6 cylinder high pressure cutoff system, a UF_6 cylinder low pressure cutoff system, a UF_6 cylinder wall temperature cutoff system, an autoclave high pressure isolation system, an autoclave pressure relief system, and steam conductivity cells.

In 1989 an independent review was conducted to assess the risks of a criticality accident in UF_6 autoclave operations at the Portsmouth Gaseous Diffusion Plant(1). Subsequently, calculations were made to determine effective neutron multiplication factors of UO_2F_2 and water mixtures in a wide range of geometries and moderation ratios in steam-heated UF_6 autoclaves(2). In this paper, the results of that independent review are presented and evaluated.

A safety analysis generally assesses the risk of occurrence of some event. In this case, a nuclear criticality accident is the event of interest. The term "risk" is typically defined as the product of the probability of an event and the consequences of that event. The consequences of an accidental criticality are assumed to be relatively constant for the range of system failures considered in this analysis. This analysis qualitatively characterized the probability of a nuclear criticality accident. Thus, the magnitude of the risk changes in proportion to the magnitude of the probability of accidental criticality.

For a criticality accident to occur, material must be released from a UF_6 cylinder into an autoclave, and it must mix with a significant quantity of a hydrogenous moderator. The potential source of moderation in an autoclave is the steam that heats a cylinder. During normal operation, steam condenses on the cylinder and on the walls of the autoclave.

Tests were performed to determine the mass of water that could be retained within an autoclave if the drain valves and steam inlet valves are closed during an accident. These tests showed that a maximum of 100-140 pounds of water could remain in an autoclave. Therefore, this amount of water is available to react with and/or moderate any released UF_6. The greatest amount of water would be found in the largest (96-inch diameter) autoclaves.

ASSESSMENT OF RISK

The fault tree illustrated in Figure 2 was developed to evaluate the risk of a criticality accident. The fault tree assists in identifying and documenting combinations of events that could result in a critical configuration within an autoclave. The tree is particularly helpful in assessing whether the design of an autoclave satisfies the nuclear criticality safety double contingency criterion "that process designs should, in general, incorporate sufficient factors of safety to require at least two unlikely, independent, and concurrent changes in process conditions before a criticality accident is possible."(3)

Initiation of a Large Leak of UF_6

A substantial leak or rupture of a UF_6 cylinder in an autoclave is necessary for a criticality accident. This failure mechanism is shown on the left branch of the fault tree. The minimum critical mass of uranium enriched to 5 percent U^{235} is 3.7 pounds of U^{235}(4). This mass is equivalent to 110 pounds of UF_6. Historically, in autoclaves only a few releases of UF_6 greater than a few grams of uranium have occurred. Only one release approached the mass of material required for criticality. In that case, vibration caused the loosening of a connection between the cylinder valve and the safety valve. The resulting release from the cylinder was approximately one hundred pounds of UF_6. In all of the releases to date, the buildup of UO_2F_2 occurred at the leak point, resulting in self sealing and termination of the release.

Figure 3 shows the distribution of uranium following a UF_6 release. A defect in the weld at the valve-end circumferential, head-to-shell weld of a 10-ton UF_6 cylinder resulted in the formation of a hole approximately 1/32-inch in diameter. Ten pounds of UF_6 were released. The UF_6 reacted with the water vapor in the autoclave, and a light dust of UO_2F_2 covered the cylinder and other surfaces in the autoclave. A small mass of UO_2F_2 about 4 inches in diameter accumulated on the roller covering the hole in the cylinder. This

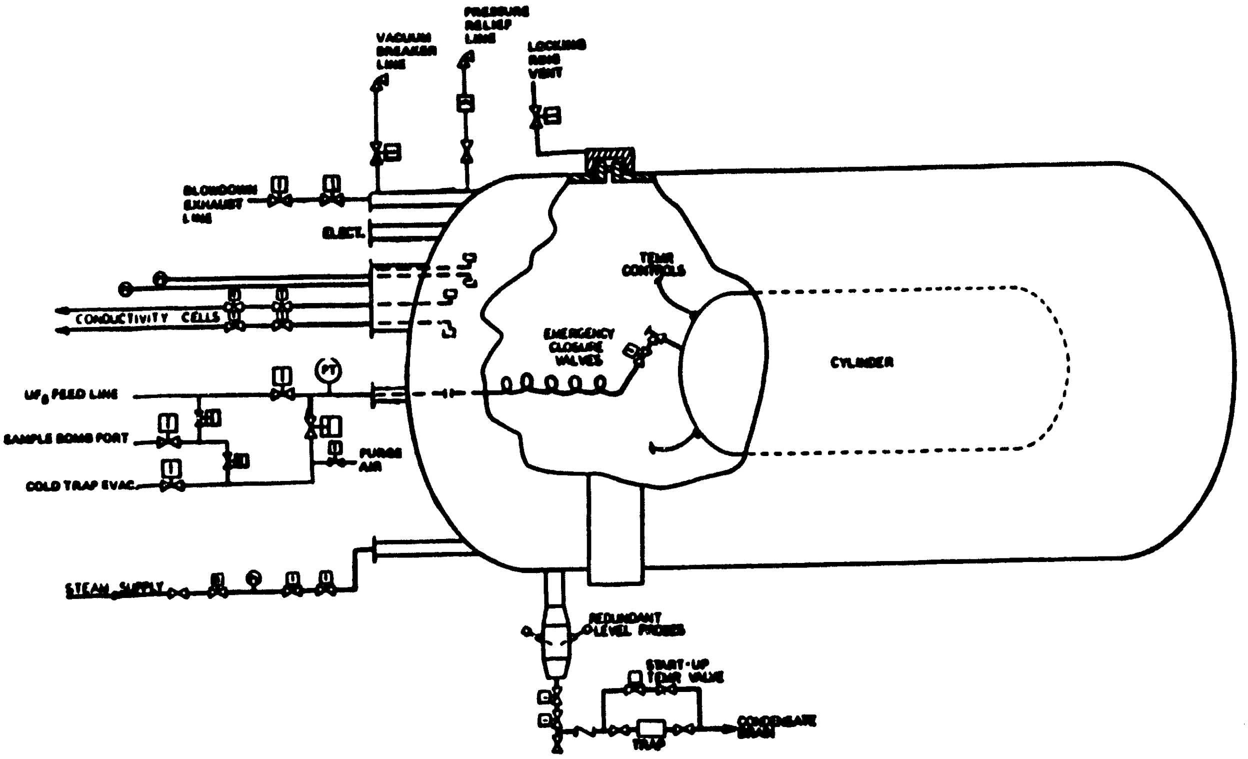

Figure 1. Diagram of a Typical Feed Autoclave

incident illustrates the phenomenon leading to the consumption of the moderator (water) through the formation of UO_2F_2 and HF and shows the widely dispersed deposition of the UO_2F_2 in the autoclave.

The rupture of a UF_6 cylinder or a major failure between the cylinder and the emergency closure "safety" valve are the two types of failures that can lead to a large release of UF_6 in an autoclave. The "safety" valve can be closed remotely.

A "pigtail" line is located between the cylinder's "safety" valve and manifold piping outside of the autoclave. The coils in the "pigtail" line provide flexibility to prevent large stresses from developing in UF_6 cylinder valves as a result of cylinder motion relative to the autoclave. In addition, the "pigtail" is more likely to fail than the interface between the two valves or the connection to the cylinder. A failure in the "pigtail" region can be isolated by closing the "safety" valve.

After a cylinder has been placed in an autoclave, no forces large enough to initiate a large leak or to rupture a cylinder are credible, provided the cylinder has not been overfilled. There are specific restrictions against moving large objects over cylinders in autoclaves. During the initial stages of heating, a low pressure cutoff assures that the valves and lines from the UF_6 cylinder are not closed or blocked. If the cylinder does not reach a pressure of 20 psia within one hour after initiation of heating, the steam supply is stopped. This system assures that the pressure monitoring system is truly monitoring the internal pressure of the cylinder. The steam supply is stopped if cylinder internal pressure limits are exceeded. Thus, the likelihood of a release of UF_6 greater than 125 pounds from a cylinder into an autoclave is very small (i.e., on the order of once per plant lifetime). To satisfy the double contingency criterion, however, all of the pathways on the right hand side of the fault tree in Figure 2 must also be unlikely.

Sufficient Water Present Prior to Leak

The fault tree in Figure 2 shows the two time frames for the addition of water to an autoclave during the course of an accident. In Branch 2.2 of the fault tree, water is present in the autoclave at the time the leak starts. In Branch 2.3, water

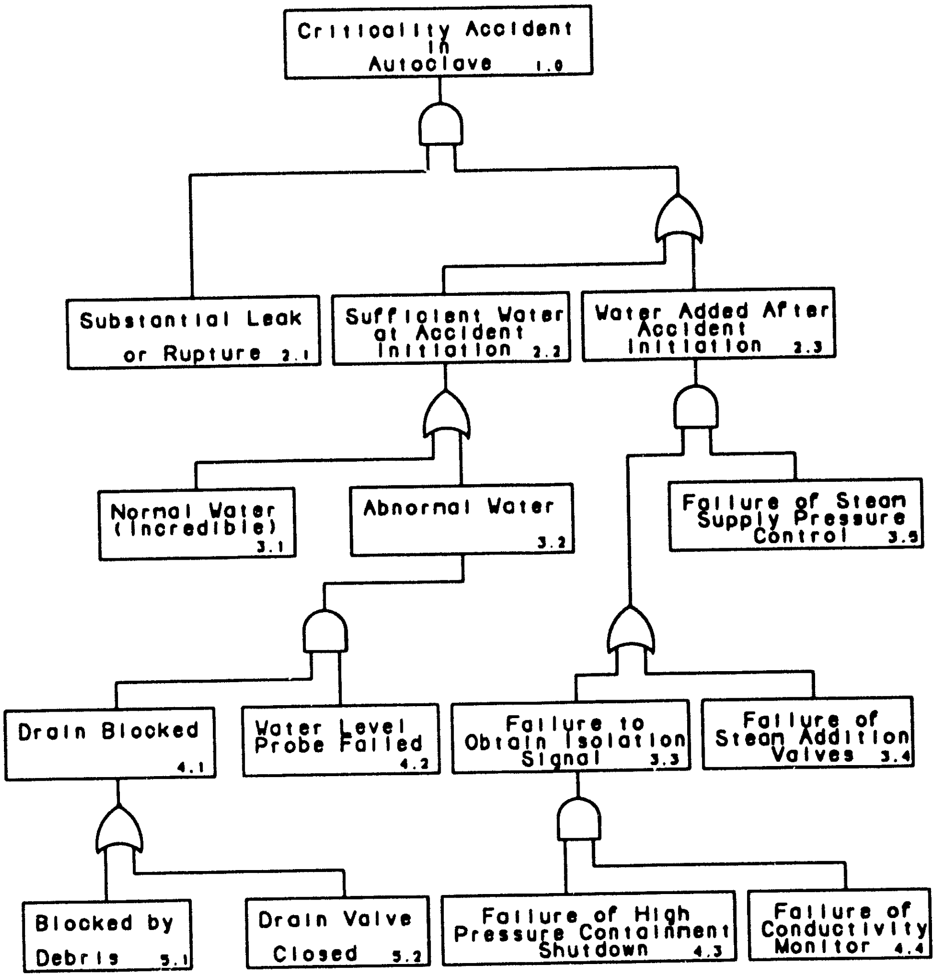

Figure 2. Autoclave Criticality Fault Tree

continues to be added subsequent to the initiation of a UF_6 leak.

The normal water inventory of an autoclave is less than 140 pounds. The minimum mass of water required for criticality of UO_2F_2 at 5 percent U^{235} enrichment is 48 pounds. Thus, sufficient water could be present in normal operating conditions to moderate a critical configuration if the appropriate geometry could be created. The appropriate geometry would be a sphere-like mixture of UO_2F_2 and water surrounded by a neutron reflector. The minimum critical radius of a reflected sphere of this material is about 7.9 inches. An optimally moderated UO_2F_2 and water mixture would be a solution. There are no structural components inside the autoclave large enough to contain a critical mass of a nearly spherical solution.

If the water spreads across the bottom surface of an autoclave, the depth of the resulting slab of water would be quite shallow (i.e., less than a couple of inches). The minimum critical thickness for an infinite slab of UO_2F_2 and water is 5.5 inches fully reflected or 9 inches unreflected. The amount of water required to fill a 96-inch diameter autoclave to this depth is approximately 1,500 pounds, an order of magnitude greater than the amount available.

A stream of UF_6 could impinge on a trough of water in the bottom of the autoclave. Of the 140 pounds of water potentially located in an autoclave at the time of an accident, 50 pounds would be in the form of steam. The rest of the water would be distributed as a surface film, in a shallow pool in the bottom of the autoclave, or in the drain line. The water in the form of steam would react rapidly with UF_6 vapor throughout the volume of the autoclave, producing HF and an aerosol of UO_2F_2. If the remaining 90 pounds of water were collected within a trough on the bottom of the

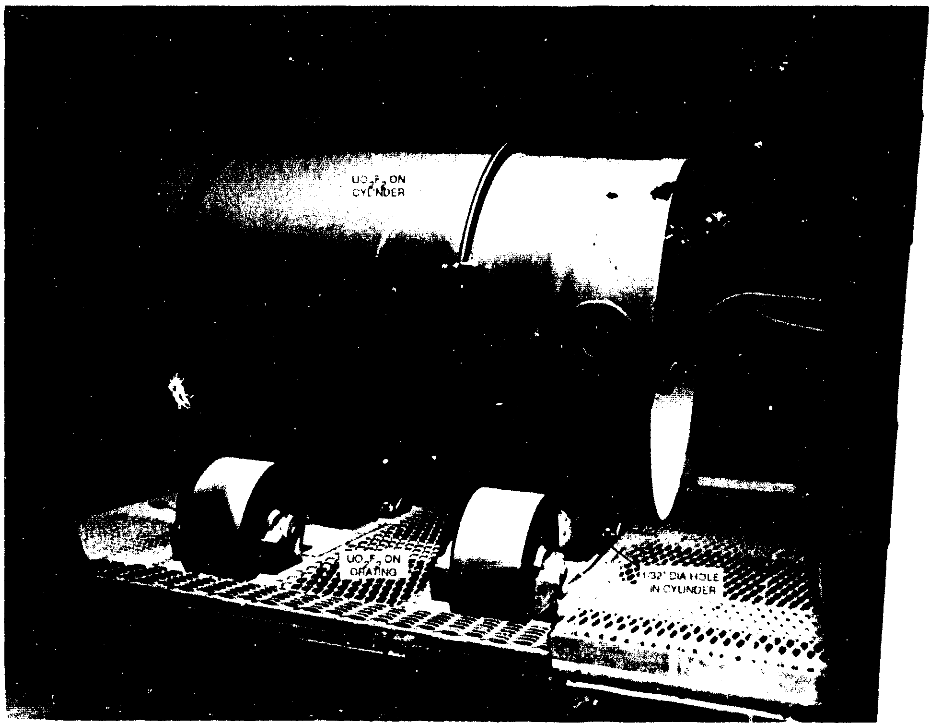

Figure 3. **UO_2F_2 Coating Cylinder and Grating Inside Autoclave Following Release of 10 Pounds of UF_6**

autoclave, the resulting pool would be approximately one-inch deep, 18 inches wide and 20 feet long.

As the UF_6 contacted the pool, it could react vigorously with the water to form UO_2F_2 and HF. The force of the stream of UF_6, the heat of the reaction, and the release of HF would provide agitation to facilitate dispersion. The UF_6 could continue to spread across the lower surface of the autoclave reacting with water wherever the UF_6 and water contacted. Because the reaction of UF_6 with water is exothermic, heat released from the reaction could boil residual water and make it unavailable as an interspersed moderator. The energy released in reacting a mole of UF_6 is approximately three times the amount required to boil a mole of water. Because of uncertainties in mixing, in the kinetics of the UF_6 and water reaction, and in the partitioning of the released energy to unreacted water, vaporization is not considered as a mechanism that reduces available moderator.

To achieve criticality with the water available requires a very localized, nearly spherical, solid ball of moderated uranium. The creation of such a critical geometry might occur in two ways. A well mixed configuration with water displaced from the drain could occur directly above the drain line. However, the three- to four-foot long 4-inch diameter drain pipe can hold only 16 to 23 pounds of water, not nearly enough for a criticality.

Given the distribution and amount of water available, it is not credible that a localized mass of moderated material could be formed of sufficient dimensions to be critical. Branch 3.1 of the fault tree thus represents an incredible means for criticality to occur.

Two failures must occur in order to get an abnormal quantity of water in an autoclave at the time a UF_6 leak starts (Branch 3.2). The drain must be blocked below the water level probes, and the water level probes must fail to indicate a high water level. High condensation rates during initial heating of cold UF_6 cylinders occasionally cause water to build up to the probe level in the drain. The redundant water level probes, upon sensing the buildup of water, cause the steam supply to be stopped. After the condensed water drains below the level probes, steam supply can resume.

Corrosion-generated debris collects in the autoclaves. Buildup of debris can reduce drainage by clogging the valve in the drain line (Fault 5.1). However, no evidence of such clogging exist. The drain valve could be left in a closed position prior to startup of the autoclave cycle (Fault 5.2). However, for water to accumulate, the redundant water level probes must fail to indicate high water level (Fault 4.2).

Blockage of the drain before the water level probes could lead to abnormally large quantities of water in the autoclave. If a large UF_6 cylinder is sufficiently empty, it could be buoyant. The cylinder movement could lead to failure of the "pigtail" and a UF_6 release could occur. However, the emergency closure "safety" valve can be operated remotely to terminate the release.

A potential common cause failure involves blockage of the drain upstream of the water level probes. This failure is discussed under "Potential for Common Mode Interactions". The drain screens that were the potential source of common mode failure were removed.

After UF_6 cylinder heating has started, the Operational Safety Requirements allow an autoclave to continue operating with only one water level probe for a limited time. Operating with only one probe potentially reduces the reliability of the system. However, there have been no problems with the water level probes resulting in extended periods of reduced reliability. Because two unlikely events, Branches 4.1 and 4.2, must occur to cause abnormally high water levels in an autoclave, the likelihood of Branch 3.2 is very small.

Water Addition Following Leak Initiation

Branch 2.3 of the fault tree illustrates the failure resulting in the continued addition of steam to an autoclave following the start of a UF_6 leak. The reaction of UF_6 with water produces HF and releases heat. If a large amount of UF_6 were released into an autoclave, the pressure in the autoclave would rise rapidly. Steam is normally added to an autoclave at a controlled pressure of 8 psig. High pressure in an autoclave would prevent the addition of 8 psig steam, even if the steam addition valves failed to close. To continue adding steam would require failure of the steam supply pressure controller by some unidentified mechanism (Branch 3.3). Both the high pressure containment shutdown system (Branch 5.3) and the conductivity monitors (Branch 5.4) should demand closure of the steam addition valves and condensate drain valves if UF_6 is released into an autoclave. There are no reported instances of failure of the steam addition valves to close on demand (Branch 4.4). Thus, the likelihood of adding significant amounts of water after a UF_6 leak starts is also very small.

A controlled addition of steam could be made during recovery following a UF_6 release in an autoclave. The steam would be added to react residual UF_6 gas prior to opening the autoclave. Such recovery activities would come under close scrutiny by the nuclear criticality safety staff.

Potential for Common Mode Interactions

Three potential common mode relationships between events in the fault tree in Figure 2 were identified. However, two of these sources of interdependency were rejected as insignificant. If a large release of UF_6 occurred, the ports that are used to monitor pressure and conductivity could be blocked. It was considered very unlikely that the safety function would be affected. Interaction between high water level and a hot cylinder could potentially lead to high stresses and induced leakage. Because the water pool would be at saturation temperature, high stresses would not result.

A third source of common cause failure could not be dismissed as insignificant. In some autoclaves, a removable drain screen is inserted in the top of the drain line above the water level probes. The purpose of the screen is to catch teflon gaskets that drop to the bottom of the autoclave. The potential common cause failure is plugging of the screen with rust or other debris and accumulation of water above the drain that cannot be monitored by the water level probes.

The removable drain screen has a one-inch diameter overflow pipe that should allow water to flow down to the level detectors even if the screen is blocked. However, the probability is substantially greater of blocking a one-inch diameter pipe than a four-inch diameter pipe. Use of the drain screens was discontinued. Other mechanisms are now used to prevent the teflon gaskets from entering the drain pipe.

Potential Added Safety Margin Provided by Raschig Rings

The current operation of the autoclaves satisfies the double contingency criterion. Early in the history of the autoclaves, additional safety margins were sought by placing borosilicate glass raschig rings in the bottom of the autoclaves. Boron is a good absorber of thermal neutrons.

After several years of experience, it was determined that a shallow layer of raschig rings provided little additional safety margin. The operational difficulties encountered by the use of the rings included additional holdup of debris, increased time to decontaminate following small releases (i.e., less than one pound) of UF_6, and possible increased holdup of water. These operational difficulties created by the raschig rings, coupled with their limited safety benefit, led to the discontinuing of their use.

CONCLUSIONS

Steam heated autoclaves used to heat cylinders of UF_6 were evaluated for nuclear criticality safety. A fault tree was developed to demonstrate that the double contingency criterion is met. The various branches in the fault tree were qualitatively reviewed. Only one potential problem was identified. This problem was the blocking of the drain line above the water level sensor. Drain screens that could cause this blockage were removed, and their use in the autoclaves was discontinued.

For UF_6 feeding, sampling, and transfer operations in steam-heated autoclaves, the risk of criticality is very small for U^{235} enrichments of up to 5 percent. Current operations satisfy the double contingency criterion used within the criticality safety community.

REFERENCES

1. Denning, R. S., McLaughlin, T. P., and Murray, R. L., "Autoclave Nuclear Criticality Safety Review", Portsmouth Gaseous Diffusion Plant, Martin Marietta Energy Systems, October 1989.
2. Davis, T. C. and Tayloe, R. W., "Autoclave Criticality Analysis", POEF-T-3544, Portsmouth Gaseous Diffusion Plant, Martin Marietta Energy Systems, February 21, 1991.
3. American National Standard for Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors, ANSI/ANS-8.1-1983. American Nuclear Society, LaGrange Park, Ill.
4. Paxton, H. C. and Pruvost, N. L., "Critical Dimensions of Systems Containing U^{235}, Pu^{239}, and U^{233}", LA-10860-MS 1986 Revision, Figure 22, p. 52, 1987.

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A PROBABILISTIC SAFETY ANALYSIS OF UF_6 HANDLING AT THE PORTSMOUTH GASEOUS DIFFUSION PLANT

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ABSTRACT

A probabilistic safety study of UF_6 handling activities at the Portsmouth Gaseous Diffusion Plant has recently been completed. The analysis provides a unique perspective on the safety of UF_6 handling activities. The estimated release frequencies provide an understanding of current risks, and the examination of individual contributors yields a ranking of important plant features and operations. Aside from the probabilistic results, however, there is an even more important benefit derived from a systematic modeling of all operations. The integrated approach employed in the analysis allows the interrelationships among the equipment and the required operations to be explored in depth.

This paper summarizes the methods used in the study and provides an overview of some of the technical insights that were obtained. Specific areas of possible improvement in operations are described.

INTRODUCTION

As part of its continuing efforts to limit the potential for releases of uranium hexafluoride (UF_6) at the Portsmouth Gaseous Diffusion Plant, Martin Marietta Energy Systems, Inc. undertook a probabilistic safety assessment of UF_6 handling activities. That study has been completed and is published in four volumes.(1) This paper summarizes the methods of the study and briefly describes some of the findings.

The primary objective of the study was a probabilistic analysis of all activities involving handling of liquid UF_6 at the Portsmouth plant. This study was to produce an understanding of the various ways in which a significant release of UF_6 could occur, including estimation of the nominal frequency of release associated with these scenarios.

BACKGROUND

The primary risk of concern at the plant is associated with the possible release of UF_6. The release of gaseous or liquid UF_6 is of concern due to the formation of reaction products when it interacts with moisture in the atmosphere. Chemical toxicity, rather than radiotoxicity, is the primary concern with these products.

The UF_6 is stored and transported as a solid, and there is little risk of release when the material is in this state. In the enrichment cascade, the diffusion process employs gaseous UF_6. There are no handling activities in this process, however, and the human interface is limited. Some of the other operations at the plant involve liquid UF_6. In these operations, the liquid is above atmospheric pressure and, if it were released to the environment, much of it would flash to the gaseous state. The principal source of concern for large releases that could affect the environment is, therefore, associated with the operations involving liquid UF_6.

A probabilistic analysis is complementary to the other forms of safety assurance. It is especially useful because it can provide a common basis for comparing different issues in a broader context, offering the opportunity for more efficient allocation of resources for safety improvements.

SCOPE OF THE ANALYSIS

The objectives listed above essentially define the scope of study. The analysis included the following types of events:

- Normal operations, including cylinder movements, autoclave operations, and the withdrawal process;

- Abnormal or infrequent operations, for example, movement of a cylinder with the safety valve attached;
- Unintended operations, for example, an inadvertent transfer (in violation of standard practice) by straddle carrier of a cylinder containing liquid UF_6; and
- External events, such as impact due to natural phenomena or vehicle accidents.

The models for these different activities are intended to cover all potential causes of release. Human error and equipment failures are considered both separately and in combinations. The models include other secondary causes for release that result in loss of cylinder or component integrity.

METHODS OF ANALYSIS

Probabilistic safety analysis methods have been used to study a large variety of engineered systems and operations. The methods used included tools such as fault trees and event trees which were assembled to optimize their usefulness in achieving the objectives of this study. A brief overview is provided below.

Models

The method used to determine the potential for a release during UF_6 handling operations employs a series of logic models. These logic models describe the specific ways in which a sequence of events can evolve and result in a release. Different types of logic models lend themselves more readily to different objectives. First, the activities involved in each handling operation are delineated in a systematic fashion. This is a prelude to the identification of release scenarios, and it also satisfies the objective of the study related to identifying all handling activities. By examining the handling activity steps, the possibilities for accidents that could result in a release are identified. Once a potential accident is identified, models must be developed to identify the specific ways in which the accident could occur. Following the development of causes of a release, the size and severity of the release must be established. The final step in the process is the integration and quantification of the models. Table 1 describes the analytical tools used in this study. The table identifies three basic types of models: event sequence diagrams, fault trees, and event trees.

Most of the risks not directly associated with operations (e.g., due to external events) were first assessed through simple screening analyses to determine if the release frequency could be significant relative to other causes. If the screening indicated minimal threat, the analysis was terminated; otherwise more detailed analysis was performed. The modeling of non-operational releases involved the same basic steps as for handling activities, although no ESDs were required.

Table 1. Summary of Analytical Techniques

Objective	Model	Description
Identify non-cascade UF_6 handling activities	Event sequence diagram (ESD)	Graphical, chronological display of the individual steps required to complete any UF_6 handling.
Identify deviations from normal UF_6 handling	ESD	Display of events that result in a deviation from normal handling.
Model the specific events that could lead to a deviation	Fault tree	Graphical display of the specific combinations of events that can lead to an undesired outcome.
Determine the release potential and the conditions	Event tree	Display of possible outcomes for various events that determine the size and severity of a UF_6 release.
Model the events that can shape the release, as defined in the event tree	Fault tree	Logic which describes how the conditions identified in the event tree can come about through combinations of failures or errors.

Data

In order to estimate frequencies for possible release scenarios, it is necessary to develop data for each of the events in the logic models. The first type of logic model is the ESD. The quantification of the frequency of the operations was generally straightforward, since the operations were part of the daily activity. Some of the ESDs describe off-normal or infrequent events. For these, plant records were reviewed for applicable data.

Equipment Failure Data

The fault-tree models describe the failures of various functions through the failures of individual pieces of equipment. The goal of the study was to quantify equipment failures with plant-specific data. This goal was accomplished with varying degrees of success, depending on the availability of plant information. Incident reports, safety system data sheets, and other sources were used to derive plant-specific evidence for failure rates.

The plant-specific data was supplemented with high-level data from other diffusion plants, particularly that related to significant incidents. While no component-level data was available, the experience from the other plants was used to consider the likelihood of significant events.

In general, plant records provided plant-specific input for most failure rates. There was not enough specific data available for a statistically rigorous estimation of failure rates for all components, however. A combination of plant-specific insights, generic data, and analyst judgment were therefore used in estimating the relevant probabilities.

Human Reliability

The models for potential release include many operator actions that must be quantified. Human reliability is a developing field that has not yet produced extensive raw data except for some very limited types of actions. The defense, aerospace, and nuclear industries have been addressing this problem, but no data base exists that is directly applicable. On the other hand, the Portsmouth plant has been operating for over 30 years, and other diffusion plants have similar amounts of experience. While this experience does not include a written record of success and failure for every type of human action, the experience proved extremely useful in estimating the reliability for many types of operator actions. The incident reports were the most useful sources of information.

For some events, the plant record was adequate for direct calculation of a reliability parameter. In most cases, the plant-specific record was used as one input that was then supplemented with data from other sources. The bulk of the human reliability estimates were derived through comparison to the quantification of analogous events. Thus although the plant record may not have included specific reference to an error of interest, the error could be compared to another for which sufficient data was available. Through this process it was possible to quantify human errors based on a relative scale, with the scale anchored to the plant record for specific actions.

Model Integration

The models represent the ways that normal UF_6 handling activities can deviate to become off-normal events, and the ways that those events can lead to different levels of release. Each deviation from the ESD is modeled by a fault tree. The combination of the ESD initial event and the fault tree is called an initiating sequence. These initiating sequences describe ways in which releases could occur. Each initiating sequence is then coupled with an event tree to identify the possibilities for release. The pathways through the event tree may also be modeled with fault trees. For each pathway through the event tree, the logic is assembled and combined with the initiating sequence.

The models account for dependencies, both hardwired and those related to human action. For example, the initiating sequences for the autoclaves include combinations of equipment and instrument failures. The event tree includes developments for other functions such as autoclave isolation. The fault tree models for the initiating sequence and the event tree must be solved together since there are dependencies between the cause of the accident and the response after the release is initiated.

The assembly of these models leads to a description of individual release scenarios. These are then quantified using the data discussed above. The results of the study include detailed listings of the ways that different releases can occur, along with the frequency of occurrence. Examination of the individual contributors provides the engineering insights concerning safety improvements.

The results of the study were categorized according to the severity of the release. Because there could be a whole spectrum of quantities involved, the potential releases were grouped into release classes. The classes represent discrete ranges of quantities that provide a simple perspective on the severity of the events. In addition to quantity, the release classes consider location, specifically whether the release would be isolated inside a building, leaking from an open building, or outside. The severity of release is also represented by size of the loss of integrity. Two categories were used, leak and rupture. Rupture refers to a release that would be essentially complete within 10 or 15 minutes of the initial leak. The leakage category refers to events in which the quantity would be released over a much longer time. The scope of the study did not include detailed assessment of later emergency response measures that could limit releases.

ESTIMATED FREQUENCY OF RELEASE

The overall release frequency is the sum of the estimated release frequencies for all of the facilities analyzed. The numerical results should not be the focus of the analysis, as the benefits of the study are derived from the analysis process itself and a thorough examination of the quantified results in a relative sense.

It is useful, however, to have a perspective on the overall results of the analysis and the estimated release frequencies and to compare the analysis estimates to actual release frequencies. In order to illustrate the analysis results in terms of frequency and release magnitude, a graph of all of the release classes was developed. As noted earlier, the release classes involve ranges of releases. The graph of the release frequency versus quantity was generated using simple histograms to represent the release classes according to their associated ranges of the quantity of material. The resulting graph is depicted in Figure 1. The figure illustrates the general trend of decreasing frequency versus increasing quantity. Also illustrated in Figure 1 is the Portsmouth plant experience for large releases. This is provided for comparison and to show that the results of this analytical study are consistent with experience.

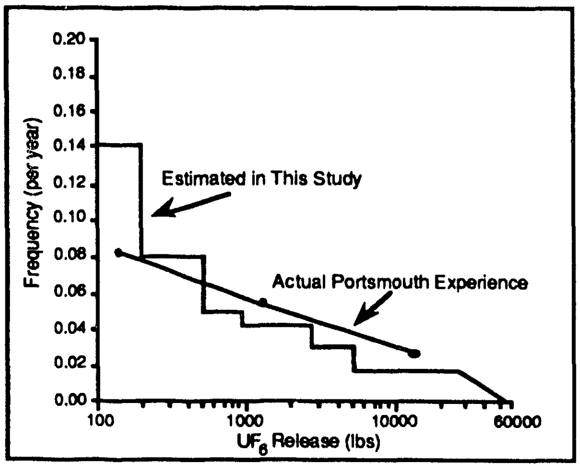

Figure 1. Comparison of Estimated Release Frequency to Plant Experience

Figure 1 cannot fully convey the understanding of the plant experience since the plant has changed over its operating history. The release experience depicted reflects events that occurred prior to 1978. There have been extensive efforts to reduce release frequency since 1978, and the last 12 years of experience suggests that those efforts have been successful. While the results of this study show some improvement over the earlier experience, it is the opinion of the authors that the actual situation is better yet because the modeling includes some conservatisms and simplifications that could lead to overprediction of the frequencies.

Release Frequencies for Different Facilities

The results in the previous section represent the integrated release frequencies for the five facilities studied in detail:

- Feed vaporization and sampling (X-343),
- Feed vaporization (X-342A),
- Toll enrichment services (X-344),
- Tails withdrawal station, and

- Low-assay withdrawal (LAW) station.

The contributions of the individual facilities to the various release class frequencies are discussed below.

Figure 2 illustrates the contribution of the individual facilities to the total frequency of the rupture release classes combined. The figure indicates that only X-342A has a negligible contribution, because there is very limited handling of liquid-filled cylinders at X-342A. For the total frequency of rupture, the risk of release is fairly evenly spread among the remaining facilities, although X-344 contributes the most, mainly because it has the largest number of operations involving liquid UF_6 of any of the facilities.

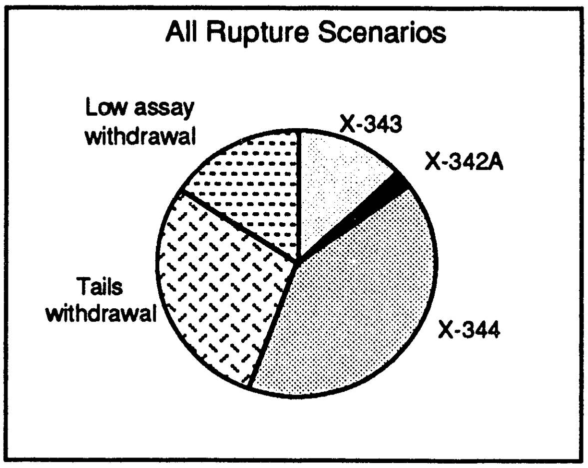

Figure 2. Contributions of Different Facilities to Total Frequency of Rupture

The contributions of individual facilities to the summed frequency of all leakage release classes are similar to those represented in Figure 2 for rupture events.

Contributions of Different Accidents

This section is analogous to the previous one in that the relative contributions to the total frequency are explored in more detail. In this case, the breakdown is by type of accident. The following categories of accidents are included:

- Crane accidents, including equipment failures and human errors.
- Autoclave accidents associated with the heating operations, including cylinder installation and removal and sampling.
- Straddle-carrier scenarios, in which a liquid-filled cylinder is inadvertently conveyed by straddle carrier.
- Transfer and withdrawal accidents, including all parent/daughter transfers and the filling of cylinders at tails and LAW.
- Compression system accidents, including equipment failures and human errors from the compressor to the manifold.
- Fire and system impact, which covers fires or accidental loss of integrity of the compression and condensation systems.
- Cooling cylinder storage accidents, including any type of accidental impact that results in the failure of a cylinder in a cooldown area.

The information is presented graphically for releases corresponding to the rupture of large (14-ton) cylinders in Figure 3. Crane accidents account for half the frequency. Storage and autoclave accidents also contribute. The other types of accidents are less important because there is a low probability that they would involve a 14-ton inventory.

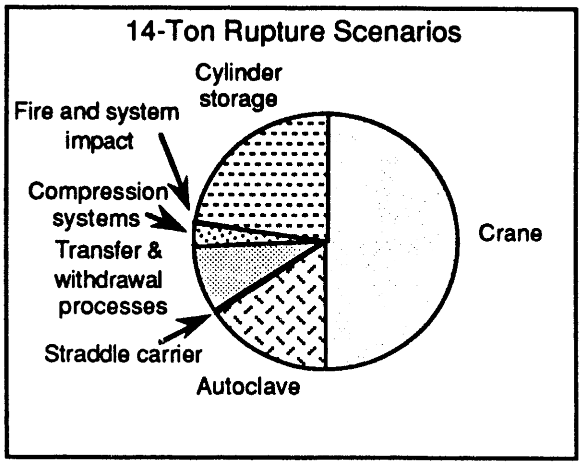

Figure 3. Contributions of Different Accidents to the 14-Ton Rupture Frequency

The 2.5-ton releases are primarily associated with the transfer and withdrawal processes, as indicated in Figure 4. Once again, however, several of the other types of accidents have non-negligible frequencies.

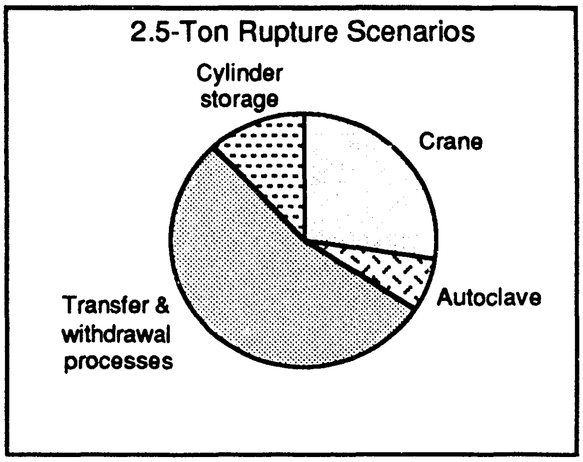

Figure 4. Contributions of Different Accidents to the 2.5-Ton Rupture Frequency

Individual Sequences

The models resulted in detailed delineation of potential accident scenarios. The results presented in the main report of the study (1) include listings of the most important scenarios for each facility. As noted previously, no one facility or type of sequence dominates the results. Hence, no detailed sequence type dominates the overall frequency. There are some insights to be gained from an examination of these detailed scenarios, however.

The most important observation is that all sequences that individually contribute 2% or more account for only 40% of the total frequency. The release frequency is therefore made up of a great many different scenarios that have very small relative contributions. This suggests that the operations have tended to reach a steady state and that any unique safety issues have been eliminated through plant improvements.

The single most frequent accident is associated with a hydrocarbon interaction in a daughter cylinder at X-344. This sequence accounts for 10% of the total rupture frequency. The rupture involving the largest inventory results from an inadvertent movement of a 10- or 14-ton cylinder by crane. The possibility of leaving one or more lifting chains attached to a cylinder followed by an accidental crane movement represents an important crane accident at each facility.

An examination of the individual sequences contributing to leakage release classes indicates that the same types of accidents are important at different facilities. Compressor seal failures at LAW and tails withdrawal account for about 20% of the total frequency. These failures involve a small total inventory. Valving errors account for about 15% of the total. Inadvertent crane lifts of cylinders without disconnecting the pigtail are also important, accounting for 7% of the total. Leakage scenarios can also occur as a result of failures of isolation boundaries during maintenance at tails withdrawal and LAW. The total of all maintenance-related leakage events is 14% of the leakage total.

DISCUSSION OF INSIGHTS

Examination of the release frequencies and the contribution of individual facilities and different types of accidents provides an understanding of the potential for UF_6 release. The insights derived from the study are summarized below.

Plant-Wide Frequency of Release

The results are consistent with plant data, although it is judged that limitations in data and methods lead to some conservatism in the estimates. Quantitative results alone should be used with caution, however, because they are subject to limitations associated with this type of study.

Another aspect of the results that should be recognized is that these release frequencies do not imply significant health risks, particularly to the public offsite. Large releases have occurred in the past without any significant adverse consequences. If these release frequencies were coupled with realistic models of atmospheric dispersion and health effects, a more accurate portrayal of public risk associated with plant operation would be obtained.

Importance of Individual Facilities

As described above, the results were calculated separately for individual facilities. The following findings apply:

- None of the facilities completely dominates the frequency of the important releases. Only X-342A has negligible risk compared to the others.
- Certain facilities are more important than others for some specific types of releases. For large inventory (14-ton) ruptures, tails withdrawal is the most important.

It was concluded that there are no facilities that pose undue risk compared to the others.

Relative Importance of Types of Accidents

The results provide insights regarding the makeup of the release frequency profile:

- For very large inventory releases, crane accidents account for about one-half the frequency. Accidents involving cooling cylinders account for nearly another 25%.
- Parent-daughter transfer operations account for more than half the frequency of rupture of a 2.5-ton inventory. Crane accidents are also important to this class.
- Compression system accidents account for about half the leakage frequency.
- Inadvertent straddle-carrier conveyance of a liquid-filled cylinder is not important.
- Autoclave malfunctions have limited impact on the overall results, although they do account for 15% of the very large inventory releases.
- Weather-related events did not contribute.

Specific Accident Scenarios

The analysis identified the specific types of accidents that are important to the potential for releases. The results sections include detailed listings of the specific types of contributors. A few of the important types of accidents are listed below:

- Hydrocarbon contamination of a daughter cylinder.
- Inadvertent movement of a cylinder by crane, due to failure to disconnect the cylinder after the previous operation.
- Straddle-carrier impact with a cooling cylinder at the LAW cooldown area.
- Collisions of the crane loads.
- For leakage scenarios, failure of the compressor seals.
- Valving errors that lead to leakage.
- Releases during disconnection of pigtails.
- Maintenance errors on the tails and LAW compression and condensation systems.

REDUCTION OF RELEASE FREQUENCY

While it is a desirable feature that no particular accidents dominate, it also implies that any attempts at reducing the frequency through improvements in any one area will have limited overall impact. It is believed that this conclusion is a product of the fact that the plant has had a long operating experience with continuous improvements.

The need for additional improvement is a management decision. While constant surveillance and marginal improvement continues to be a desirable process, the need for additional improvement through more significant changes is a function of cost versus benefit (and many other considerations). The consideration of risk reduction requires development of priorities concerning what types of risk to reduce.

In a quantitative sense these results suggest that there are no obvious measures to reduce the overall frequency of release. The qualitative aspects of the results should therefore be considered. The insights, when coupled with engineering judgment and other methods of safety review, may suggest areas for marginal improvement.

UNCERTAINTY AND LIMITATIONS

The analysis attempted to obtain a best-estimate of the frequency of release. There are limitations in the analysis that derive from the methodology as well as the scope of the evaluation. These limitations are discussed in appropriate sections of the report. It is important to recognize these uncertainties and limitations when using the output of the study. The quantitative output of the study should be used for perspective, but the frequencies should not override traditional engineering review, judgment, and decision-making.

USES OF THE MODELS AND RESULTS

The insights from the analysis can be folded into other plant efforts aimed at safety review and improvement. The models can be used for maintaining an understanding of the risks as changes are made to the plant and its operations, and as experience highlights other events with safety implications.

While there are limitations that must be recognized, the results of this study, when coupled with engineering judgment, offer a unique perspective on the safety of the plant.

REFERENCES

1. Boyd, G. J., Lewis, S. R., and Summitt, R. L., *Probabilistic Safety Study of UF_6 Handling Activities at the Portsmouth Gaseous Diffusion Plant*, POEF-2-X, Safety and Reliability Optimization Services (SAROS), Inc. for Martin Marietta Energy Systems, Piketon, Ohio, January 31, 1991.

A NUCLEAR CRITICALITY SAFETY ASSESSMENT OF THE LOSS OF MODERATION CONTROL IN 2½ AND 10-TON CYLINDERS CONTAINING ENRICHED UF_6

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ABSTRACT

Moderation control for maintaining nuclear criticality safety in 2½-ton, 10-ton, and 14-ton cylinders containing enriched uranium hexafluoride (UF_6) has been used safely within the nuclear industry for over thirty years, and is dependent on cylinder integrity and containment. This assessment evaluates the loss of moderation control by the breaching of containment and entry of water into the cylinders. The first objective of this study was to estimate the required amounts of water entering these large UF_6 cylinders to react with, and to moderate the uranium compounds sufficiently to cause criticality. Hypothetical accident situations were modeled as a uranyl fluoride (UO_2F_2) slab above a UF_6 hemicylinder, and a UO_2F_2 sphere centered within a UF_6 hemicylinder. These situations were investigated by computational analyses utilizing the KENO V.a Monte Carlo Computer Code. The results were used to estimate both the masses of water required for criticality, and the limiting masses of water that could be considered safe. The second objective of the assessment was to calculate the time available for emergency control actions before a criticality would occur, i.e., a "safetime," for various sources of water and different size openings in a breached cylinder. In the situations considered, except the case for a fire hose, the safetime appears adequate for emergency control actions. The assessment shows that current practices for handling moderation controlled cylinders of low enriched UF_6, along with the continuation of established personnel training programs, ensure nuclear criticality safety for routine and emergency operations.

NOMENCLATURE

H/U	Atomic ratio of hydrogen to uranium
K-eff	Effective multiplication factor, a measure of whether the number of neutrons in an assembly is increasing or decreasing from one generation to the next. A value of unity is a self-sustaining chain reaction or critical.
K-inf	Infinite multiplication factor, K-eff of an assembly of infinite size.

INTRODUCTION

Large 2½-ton, 10-ton, and 14-ton cylinders (i.e., Models 30B, 48X, and 48Y, respectively) are routinely used in the nuclear industry for handling, storing, and shipping low enriched UF_6. For criticality control, the filled cylinders must conform to both moderation limits and maximum uranium-235 (U-235) enrichment limits. However, moderation control can be compromised if a cylinder valve is broken off, or the cylinder wall is breached by a puncture or split. This paper presents the results of an assessment of breached cylinders which are exposed to various sources of water. The assessment was performed by the PAI Corporation of

Oak Ridge, Tennessee,(1) with supporting computer calculations performed by the Portsmouth Nuclear Criticality Safety Staff.(2)

BACKGROUND

Large 2½-ton, 10-ton, and 14-ton cylinders are not geometrically safe, and the uranium mass in a cylinder may greatly exceed the minimum critical mass for the U-235 enrichment. Thus, when these cylinders are used for enriched UF_6, both moderation control limits and maximum U-235 enrichment limits must be met. Moderation control for this purpose is defined as UF_6 having a purity of 99.5 percent or greater. This is equivalent to a hydrogen to uranium (H/U) atomic ratio of 0.088, or less. With moderation control, the DOE-ORO approved U-235 enrichment limits are 5.0% for the 2½-ton, and 4.5% for the 10-ton and 14-ton cylinders. Without moderation control, the maximum safe enrichment is 1% U-235.

If a cylinder were breached while the UF_6 is in the liquid state, the UF_6 vapor pressure would force the contents out of the cylinder and would prevent moisture or water from entering. Thus, this study considered only cylinders containing UF_6 in the solid state.

Subsequently, with its longitudinal axis horizontal, a cylinder containing liquid UF_6 undergoes a 5-day cool down period to allow the UF_6 to solidify. Thus, the typical expected conditions inside a cylinder during transportation and storage are a partial vacuum and a solid UF_6 mass located in the lower portion of the cylinder.

ANALYTICAL TECHNIQUE

On considering scenarios resulting in the loss of moderation control, it is evident that there are many possible situations that could occur within a large cylinder containing solid UF_6 when the valve is broken off, or the cylinder wall is breached and exposed to moisture or water. Both chemical reactions and the physical conditions must be considered.

The stoichiometry for the reaction between uranium hexafluoride and water is represented by:

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF\uparrow .$$

The uranyl fluoride (UO_2F_2) normally exists as a solid and the hydrogen fluoride (HF) normally exists as a gas.

The physical conditions depend upon several factors such as: the location and size of the puncture or opening, source and flow rate of the water into the cylinder, crystalline form and geometry of the solid UF_6 inside the cylinder, lapsed time since water entered the cylinder, etc. Further, a breach in the cylinder wall can occur above or below the upper UF_6 surface.

For a breach below the surface of the solid UF_6, the moisture or water would contact the solid UF_6 and possibly seal the hole by forming a solid plug of UO_2F_2 over the opening--at least temporarily. It is the authors' opinion that continued exposure of the solid UO_2F_2 plug to water would eventually result in an enlargement or growth, conservatively considered as a sphere of UO_2F_2 within the UF_6 inside the cylinder.

In the case of water entering a cylinder breached above the surface of the solid UF_6, the UO_2F_2 could form in a spherical configuration if the inleakage were at a slow rate; or, if the inleakage were at a faster rate, a layer or slab configuration could form at the upper surface of the solid UF_6.

Thus, calculations to investigate the spherical geometry would provide estimates for the minimum amounts of water for criticality, while the slab type geometry might be more realistic in particular situations. These two situations span the other possible geometries.

For these calculations, the UF_6 was considered to be moderated by HF to an atomic ratio of H/U = 0.088, which is equivalent to a density of 4.958 gmUF_6/cc.

The UO_2F_2 material was considered to be optimally moderated with water to give conservative results in the calculations. Consequently, two series of K-infinity calculations were run at various H/U values for both 4.5% U-235 and 5.0% U-235 enrichments using the CSAS1X control module in the KENO V.a computer code. The results are plotted in Figure 1.

The maximum K-infinity values occur at an H/U of 11 for 4.5% U-235, and 11.65 for 5.0% U-235 enrichments, and are the moderation values used for the KENO K-effective calculations. The equivalent densities were 2.327 $gmUO_2F_2/cc$ and 2.214 $gmUO_2F_2/cc$, respectively.

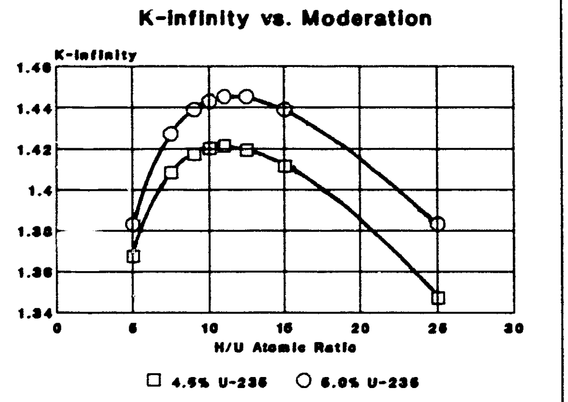

FIGURE 1. INFINITE UO_2F_2 SYSTEM

KENO computer code problems were run to investigate situations for masses of moderated uranium material in slab and spherical geometries in both 2½-ton and 10-ton cylinders. The 2½-ton cylinder was evaluated at 5.0% U-235. The 10-ton cylinder was evaluated at both the approved 4.5% enrichment limit and at 5.0% U-235 enrichment.

A 14-ton cylinder was not investigated since the results for the 10-ton cylinder using 4.5% U-235 enrichment can be conservatively applied to the 14-ton cylinder.

The 5.0% enrichment in the 10-ton cylinder was investigated because the Portsmouth Gaseous Diffusion Plant had requested, and has just recently received, DOE-ORO approval to withdrawal UF_6 up to 5.0% U-235 enrichment into 10-ton cylinders for on-site usage.

The slab geometry was modeled as an optimally moderated UO_2F_2 layer above a UF_6 hemicylinder inside a carbon steel cylinder which was reflected at the bottom by 12-inch thick concrete. The spherical geometry was modeled as an optimally moderated UO_2F_2 sphere located at the center of the UF_6 hemicylinder inside a carbon steel cylinder, similarly reflected.

For the spherical geometry, it was considered important that most of the 300 neutrons per generation be started near the location of the sphere. Thus, both cylinders were modeled lengthwise as three equal units so that the "cosine" neutron start type option could be used in the KENO calculations.

Representations of the KENO 10-ton cylinder model with a UO_2F_2 slab, and the 2-1/2-ton cylinder model with a UO_2F_2 sphere are shown in Figures 2 and 3.

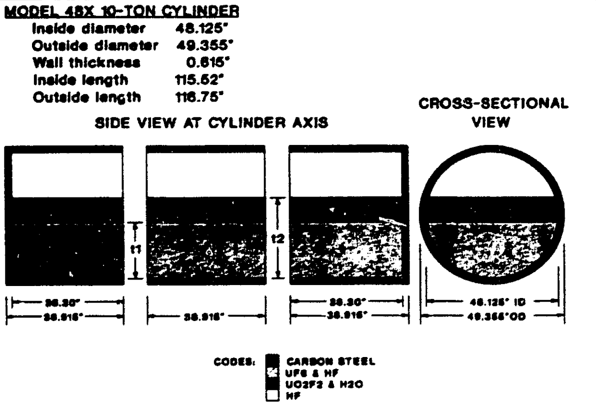

FIGURE 2. KENO 10-TON CYLINDER MODEL WITH UO_2F_2 SLAB

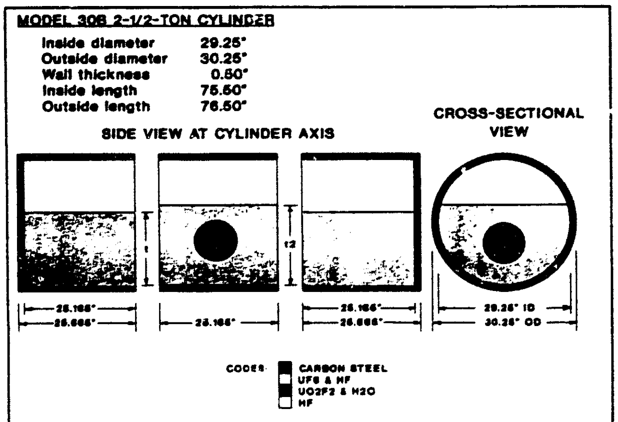

FIGURE 3. KENO 2-1/2-TON CYLINDER WITH UO_2F_2 SPHERE

Fortran programs for an IBM personal computer were written to calculate changes for the KENO input data as the thickness of the UO_2F_2 slab or sphere diameter was varied for a particular U-235 enrichment. As the volume of UO_2F_2 was varied, the volume of UF_6 was changed by an equivalent amount to simulate the UF_6

being converted to UO_2F_2 by reacting with water. Thus, the upper surface of the UF_6 hemicylinder, and the upper surface of the UO_2F_2 slab, as appropriate, were adjusted for each calculation so that the total uranium mass remained constant within the round-off error of the calculations. In the calculations involving the spherical geometry, only the UF_6 surface in the middle unit was changed. This was a choice in geometry modeling technique, and is not considered significant in these problems.

At least three KENO computer calculations were run for each of the six combinations of UO_2F_2 geometry, cylinder sizes, and enrichment values so that the calculated K-effective values spanned the range of interest.

RESULTS

The calculated K-effective values were plotted as a function of gallons of water for each particular geometry type and U-235 enrichment. Examples are shown in Figures 4 and 5.

The estimated critical and safe amounts of water for each situation were taken where the curves intersect the K-effective values of 1.0 and 0.95, respectively. These interpolated values were used as the estimated critical and safe amounts of water, and are presented in Table 1.

As stated previously, estimates for the 10-ton cylinder using 4.5% U-235 enrichment can also be conservatively applied to the 14-ton cylinder.

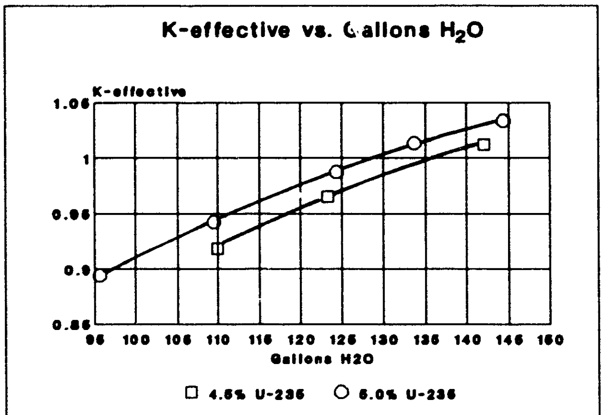

FIGURE 4. UO_2F_2 SLAB IN 10-TON CYLINDER

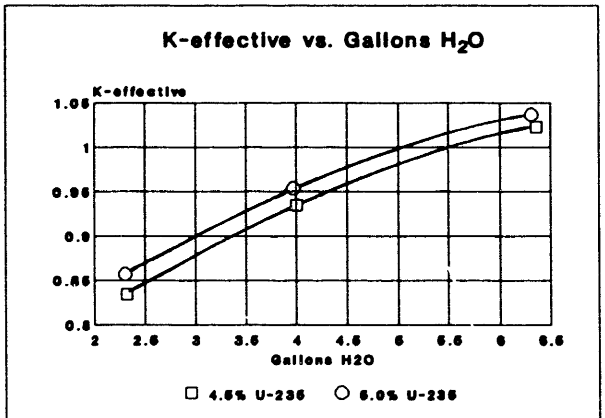

FIGURE 5. UO_2F_2 SPHERE IN 10-TON CYLINDER

TABLE 1. Estimated Critical and Safe Parameters

Cylinder Size	Wt % U-235	Geometry	Estimated Critical Pounds Water	Estimated Critical Gallons Water	Estimated Safe Pounds Water	Estimated Safe Gallons Water
10-ton	4.5%	Slab	1,133.8	136.0	992.1	119.0
10-ton	5.0%	Slab	1,075.5	129.0	933.7	112.0
2-1/2-ton	5.0%	Slab	479.4	57.5	429.4	51.5
10-ton	4.5%	Sphere	45.8	5.5	35.8	4.3
10-ton	5.0%	Sphere	41.7	5.0	32.9	3.95
2-1/2-ton	5.0%	Sphere	50.0	6.0	39.2	4.7

ASSESSMENT

In investigating loss of moderation control when wet air enters the various breached cylinders, it was assumed that the free volume inside a cylinder is 40% and is occupied by the wet air. An ambient temperature of 80 degrees Fahrenheit and a relative humidity of 82% was assumed; under these conditions wet air has a mass of 0.0013 lbs H_2O per cuft of air.

Even if all the moisture in the air above the UF_6 were available for moderating the uranium, no criticality would occur since the quantity of water would be insufficient to reach critical conditions. In reality, a portion of the hydrogen would be forced out of the cylinder by the formation of HF gas in the hydrolysis of UF_6.

Should a breached cylinder remain open for an extended period of time, the cylinder could undergo temperature cycles and experience "breathing" which could introduce additional moisture into the cylinder. Depending on the size of the opening, the effect of breathing of wet air could be short term, since small openings self seal due to the formation of UO_2F_2. As the hole size increases, the HF and UO_2F_2 tend to escape which would be noticed by operating personnel so that corrective action could be taken.

In order to approach criticality, the breathing cycle must be repeated in excess of 1,000 times for both Model 48 and Model 30 cylinders. Obviously, the safetime in this situation might be quite long, or could terminate by changing to a different type situation as described below.

When the source of moderation is a liquid such as rainfall, or water from fire-fighting or fire-protection systems, the situations are more complex. The safetimes for these situations are based upon the time required for 3.95 gallons of water, the minimum estimated safe amount taken from Table 1, to enter a cylinder from the particular water source. These calculated safetimes are presented below in Table 2.

Some simplifying assumptions were required in calculating the safetimes; flow rates were assumed to be 50 gal/min over 225 sqft for the sprinkler head and 100 gal/min over 5 sqft for the 1-1/2 inch hose.

By comparing the potential for water entry through various size openings and from various water sources, time periods have been identified during which corrective action can be taken before the occurrence of a criticality.

However, it is apparent that when a high pressure hose stream is directed toward even a small opening, the safetime for emergency control could be relatively short. Therefore, a specific prohibition in regard to the use of these hose streams around moderation control cylinders is incorporated into emergency procedures.

TABLE 2. Estimated Safetime for Emergency Action

Water Source	Cylinder Size	Safetime Opening Diameter (in) 1	 3	 6
1 in/hr Rainfall	10-ton	132 hr	13 hr	3.3 hr
	2-1/2-ton	157 hr	16 hr	3.9 hr
Sprinkler Head	10-ton	55 hr	6 hr	90 min
	2-1/2-ton	65 hr	7 hr	107 min
1-1/2 inch Hose	10-ton	6 hr	4 min	1 min
	2-1/2-ton	7 hr	5 min	1 min

For the case of a Model 48X cylinder at 5% U-235 enrichment, when the water source is a sprinkler head and the opening is 6 inches in diameter, the safetime to reach the safe water volume of 3.95 gallons and to take emergency action is about 90 min. If the opening is smaller and/or the water flow is smaller, the safetime becomes significantly greater. Conversely, larger openings and/or greater water flow would reduce the safetime.

CONCLUSIONS

Based upon the results of this assessment, the following conclusions apply to cylinders under moderation control:

1. A criticality can occur if the containment is breached and a sufficient quantity of water enters the cylinder.
2. Prompt emergency actions in a safe, orderly manner can prevent a criticality. For example, a breach in a cylinder could be covered temporarily with a tarpaulin or an HF- and UF_6-resistant material to seal the opening until more permanent repairs can be made.
3. If flooding is imminent, a damaged cylinder should be transferred to a dry area immediately.
4. Storage areas should have satisfactory drainage and not be subject to flooding.
5. Fire hose streams should not be used in areas where moderation controlled UF_6 cylinders are stored.

REFERENCES

1. W. A. Pryor and R. L. Newvahner, "Nuclear Criticality Safety Assessment of Loss of Moderation Control in Large Cylinders Containing Low U-235 Enriched Uranium Hexafluoride," PAI Corporation, Oak Ridge, Tennessee, and Martin Marietta Energy Systems, Inc., Portsmouth Gaseous Diffusion Plant, March, 1990.

2. R. L. Newvahner, "Nuclear Criticality Safety Study of Loss of Moderation Control in 10-ton and 2-½-ton UF_6 Cylinders by KENO V.a Computer Code Analyses," POEF-T-3495, Martin Marietta Energy Systems, Inc., Portsmouth Gaseous Diffusion Plant, December, 1989.

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Cylinders:
Storage and Maintenance

THE ULTIMATE DISPOSITION OF DEPLETED URANIUM

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ABSTRACT

Depleted uranium (DU) is produced as a by-product of the uranium enrichment process. Over 340,000 MTU of DU in the form of UF_6 have been accumulated at the U.S. government gaseous diffusion plants and the stockpile continues to grow. An overview of issues and objectives associated with the inventory management and the ultimate disposition of this material is presented.

INTRODUCTION

Large quantities of depleted uranium are generated as a by-product of the uranium enrichment process. In natural uranium, the concentration or assay of the fissile isotope, U-235, is only 0.7% of the total uranium. Natural uranium also contains a minute amount of U-234, but is made up primarily of the most stable isotope (over 99%) U-238. For most military and commercial applications, the uranium must be enriched - i.e., the concentration of the U-235 isotope must be increased. Enriching uranium involves robbing or depleting U-235 from the bulk of the feed material in order to concentrate it in the enriched stream. For commercial enrichment levels (up to 5% U-235), 5 to 10 kgs of DU are generated for every kg of enriched uranium produced. Higher enrichments generate much higher proportions of DU.

Significant quantities of DU have been used for various commercial and military applications in the past. However, DU generation has far outstripped demand so large stockpiles of DU have been accumulated and are growing rapidly. This paper explores options for inventory management and the ultimate disposition of surplus DU.

The only commercial production process for uranium enrichment in the USA is the gaseous diffusion process. This process utilizes uranium hexafluoride for the process medium. Feed materials are received at the gaseous diffusion plants (GDP's) in the UF_6 chemical form and shipments of both enriched and depleted uranium to customers are in the UF_6 form. Current practice is to maintain all inventories as UF_6 for cost minimization and flexibility. In general, the enriched and depleted UF_6 products are converted to uranium metal or uranium dioxide after they have been shipped to commercial facilities for a customer.

About 340,000 MTU of depleted UF_6 have been accumulated at the US government GDP sites. Most of this stockpile is stored in standard 14-ton thin wall cylinders (Type 48G). The stockpile contains more than 40,000 cylinders, some of which have been in storage for more than 20 years. (Figure 1. DU Storage at the Paducah Enrichment Facility--Aerial View of Cylinder Yards)

Storage of DU in UF_6 cylinders is expected to continue for many years. An important objective of the DU inventory management program is to maintain the UF_6 cylinders in serviceable condition and prevent any accidental release which could adversely affect the environment or the health and safety of plant workers and the public. The DU cylinders are stored outside in two-tier rows where they are subject to external corrosion and sometimes to mechanical damage. (Figure 2. Cylinder Handling in Storage Yards--Cylinder Stacker and Straddle Carrier in Action) The ongoing cylinder integrity program includes cylinder yard inspections, corrosion studies, and maintenance/upgrading activities. Other conference papers discuss these programs in detail (see "An Update on Corrosion Monitoring in Cylinder Storage Yards" by H. M. Henson and "UF_6 Cylinder Inspections at PGDP" by G. W. Lamb and W. N. Whinnery).

+ Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

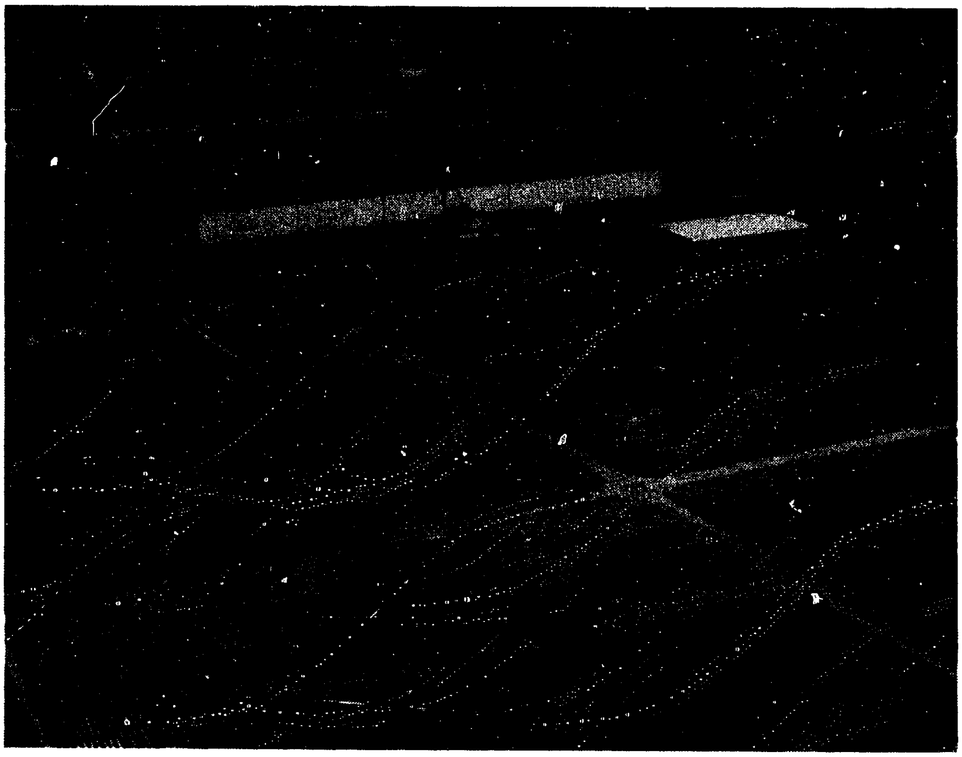

Figure 1. Cylinder Storage at Paducah GDP

Figure 2. Handling and Stacking of DU Cylinders

DU management planning must address near-term economic goals as well as the long-term disposition of excess DU. Near-term goals are to utilize the partially depleted uranium as feed for the uranium enrichment program for further stripping of the U-235 isotope when economic conditions warrant while avoiding any unnecessary chemical conversion costs. Long-term, it is expected that excess DU will be converted to oxide for permanent storage or disposal after the U-235 has been fully depleted.

UF_6 CYLINDER STORAGE

The total DU-UF_6 inventory at the end of September 1991 was approximately 340,000 metric tons of uranium (MTU). The DU cylinder inventory at the three U.S. diffusion plant sites included about 40,000 standard 48-inch cylinders. In addition, a few thousand nonstandard cylinders were included in the inventory. All of the cylinders are located in outside storage yards where they are exposed to the elements.

The principal DU-UF_6 storage container is a 48-inch-diameter thin-wall cylinder of 14-ton capacity designated as Type 48G (working pressure rating of 100 psig, with a wall thickness of 5/16 inch). Several minor design variations have been fabricated such as Models 48 H and 48 X, Model O, and Model M.

Most of these cylinders are stacked in two-high arrays, in double rows, with the plug ends of the cylinders separated by about one foot and the valve ends by three to four feet. DU cylinders are nominally spaced at 62-inch centers. In an infinite array (i.e., ignoring dead space at the edges), this gives an area requirement of 38 ft^2 per cylinder, exclusive to the area for manipulation of the cylinder handling equipment. About 40 acres are currently dedicated to DU storage yards at the three GDP sites. The DU-UF_6 stockpile is increasing at the rate of about 20,000 MTU per year, requiring about 2500 new cylinders and 2.2 acres of new storage space each year. Although costs for the new DU storage run to several million dollars per year, these costs are minor compared to total UE program costs.

The geometric arrangement currently used for DU cylinder storage was intended only to facilitate inventory and accountability requirements, with no consideration for other monitoring or inspection needs. Many rows of cylinders are butted together on the plug end so that thorough visual inspection would require special equipment. As cylinders are restacked to replace saddles and correct other deficiencies, rows will be spaced to provide easy access to both ends of the cylinders. This will increase storage yard areas by a small amount.

Corrosion studies have shown that solid UF_6 is very compatible with the bare steel inner surface of the cylinders used for handling and storage. Cylinder life is limited only by exterior corrosion or mechanical damage. The only short-term corrosion problems have been pitting where moisture is more or less continually present or chemical corrosion where containment has been breached due to mechanical damage. At present, nearly all of the DU cylinders are stored on either concrete-paved or compacted-gravel yards. The lower tier of cylinders utilizes creosote-treated wood or concrete saddles for above-ground support. However, some early yard preparation proved to be inadequate. Wooden saddles deteriorated in many cases and some sank below the surface of the yard leaving the bottom cylinder in ground contact. Pit corrosion has rendered a few cylinders unserviceable in these instances. The only known instances of breach of containment have been two cylinders at Portsmouth which apparently suffered cracked cylinder walls from rough handling and subsequently had holes formed in the cylinder walls by chemical corrosion. Dr. E. J. Barber has prepared a conference paper on these incidents (see "Chemical Aspects of Cylinder Corrosion and a Scenario for Hole Development").

A protective coating on the exterior surface of DU cylinders could extend cylinder life indefinitely. Cylinders have generally been procured with a painted exterior surface. However, the paint has not been protective in outside storage and is not resistant to steam in the autoclave cycle; so the storage life of an unprotected cylinder in outside storage is limited by the effects of atmospheric corrosion. The net effect of the initially specified paint coating is to extend the cylinder life by a few years at best, not a significant amount in the estimated 50-60 year storage service life of a thin-wall steel cylinder. Preparing the steel cylinders, which would <u>not</u> require emptying, for extended storage in order to essentially eliminate atmospheric corrosion would require cleaning all surfaces to bare metal by abrasive blasting and then priming and painting them. Presently, available paint systems have life expectancies in outdoor service that may exceed 25 years, and with spot repair and effective monitoring, use of such systems would reduce atmospheric corrosion losses to zero. Reconditioning the once-painted cylinder would be less costly since the initial abrasive blast preparation step would not have to be repeated. High quality protective coatings are currently being evaluated.

Extensive storage yard upgrading has been evaluated. In an idealized storage configuration, every cylinder would be accessible and well-protected. The ultimate upgrade would be indoor storage in a secure facility with humidity control to eliminate corrosion and with equipment to monitor for possible releases. Single tier rows (no stacking) or rack storage with sophisticated handling equipment would minimize the risk of mechanical damage. However, this level of upgrade would escalate costs dramatically and such cost increase is not justified in light of the excellent track record for outside storage. A lower level of upgrading which could include paved surfaces with run-off monitoring, concrete aprons, security fencing, lights, and more space for handling equipment should be sufficient.

DU INVENTORY MANAGEMENT

DU has accumulated at enrichment facilities because it currently has no feed value to uranium enrichment customers and demands for other applications have been limited. Established practice is to provide only the lowest assay DU (nominal 0.2%) to any customer requesting their tails for enriching services, even when the transaction tails assay is much higher. DOE will accept title and responsibility for the tails associated with any enrichment transaction if the customer elects not to take the calculated quantity of tails at the 0.2% U-235 assay. Almost all customers elect to let DOE keep the tails from their enrichment service.

Demands for uranium for other applications are relatively small so nearly all of the tails generated is being stockpiled by DOE. Other applications include government and military uses for such things as radiation shielding and high penetration projectiles. Commercial applications such as special counterweights take negligible quantities of DU.

Some, perhaps all of the DU stockpile has the potential for acquiring value as feed material as time progresses. This will result when excess supplies of natural uranium are worked off and the price of natural feed material escalates rapidly relative to the cost of enrichment. An insight to this phenomenum can best be gained by reviewing the economic trade-off between the feed cost and the enrichment cost of the uranium enrichment customer.

The economic objective of uranium enrichment customers is to minimize the overall cost of enriched uranium production by striking an optimum balance between feed and separative work costs. This balance is quantified as the optimum or break-even tails assay, at which the total cost of enriched product is minimized.

The total cost of enriched product is the sum of two component costs; feed cost and enrichment cost. For a given enriched product requirement, feed cost increases and enrichment cost decreases as the transaction tails assay is increased, and vice versa.

The total cost of the enriched product will reach a minimum at the optimum tails assay. The optimum tails assay can be calculated by determining the tails assay for which the derivative of the total cost equation is equal to zero. A derivation of this equation is shown in Table 1.

Note that for a given feed assay, the expression for calculating optimum tails assay is simply a function of the unit costs for feed and separative work. The optimum X_w is completely **independent** of the enriched product assay. A plot of the optimum transaction tails assay versus the ratio of unit costs for feed and separative work is shown in Figure 3 for natural uranium feed (assay 0.711% $_{235}$U). The absolute values of the feed and SWU costs are not important--only the cost ratio.

The ratio of unit costs for feed and SWU in recent years has been on the order of 0.5 which leads to an optimum tails assay of about 0.3%. In this environment, the existing DU stockpile is essentially worthless as feed for uranium enrichment. If feed and SWU unit costs increase by the same percentage (e.g., due to inflation), the optimum X_w is unchanged. However, if the cost ratio escalates to 1.3 or above, the optimum X_w

Table 1. Calculation of Optimum Tails Assay

Total Cost of Enriched Product, C_T = Feed Cost + Enrichment Cost

$$\text{Feed Cost} = U_F F = U_F\, P(F/P) = U_F P\ \frac{x_P - x_W}{x_F - x_W}$$

and,

$$\begin{aligned}\text{Enrichment Cost} &= U_{SWU}\, V = U_{SWU}\, [P\upsilon(x_P) + W\upsilon(x_W) - F\upsilon(x_F)] \\ &= U_{SWU} P\, [\upsilon(x_P) + W/P\ \upsilon(x_W) - F/P\ \upsilon(x_F) \\ &= U_{SWU}\, P \left[\upsilon(x_P) + \left(\frac{x_P - x_F}{x_F - x_W}\right) \upsilon(x_W) - \left(\frac{x_P - x_W}{x_F - x_W}\right) \upsilon(x_F) \right]\end{aligned}$$

where:

P, F, and W = Product, feed, and tails quantities, respectively, in kg U;

x_P, x_F, and x_W = Product, feed, and tails assays, respectively, in wt fraction U-235;

U_F = Unit cost of feed, \$/kg U;

U_{SWU} = Unit cost of separative work, \$/SWU;

V = Separative work requirement (total SWU) for product quantity P in kg U;

$\upsilon(x)$ = Value function = $(1-2x)\ell n \left(\frac{1-x}{x}\right)$

Combining:

$$C_T/P = U_F \left(\frac{x_P - x_W}{x_F - x_W}\right) + U_{SWU} \left[\upsilon(x_P) + \left(\frac{x_P - x_F}{x_F - x_W}\right) \upsilon(x_W) - \left(\frac{x_p - x_w}{x_f - x_w}\right) \upsilon(x_F) \right]$$

Taking the derivative of C_T with respect to x_W and setting it equal to zero, we obtain:

$$\frac{U_F}{U_{SWU}} = (1-2x_F)\ \ell n \left[\frac{x_W(1-x_F)}{x_F(1-x_W)}\right] + \left(\frac{1-x_F}{x_W}\right) \left(\frac{2x_W - 1}{1 - x_W}\right)$$

Which will yield the optimum x_W when solved by trial and error for any U_F/U_{SWU} cost ratio.

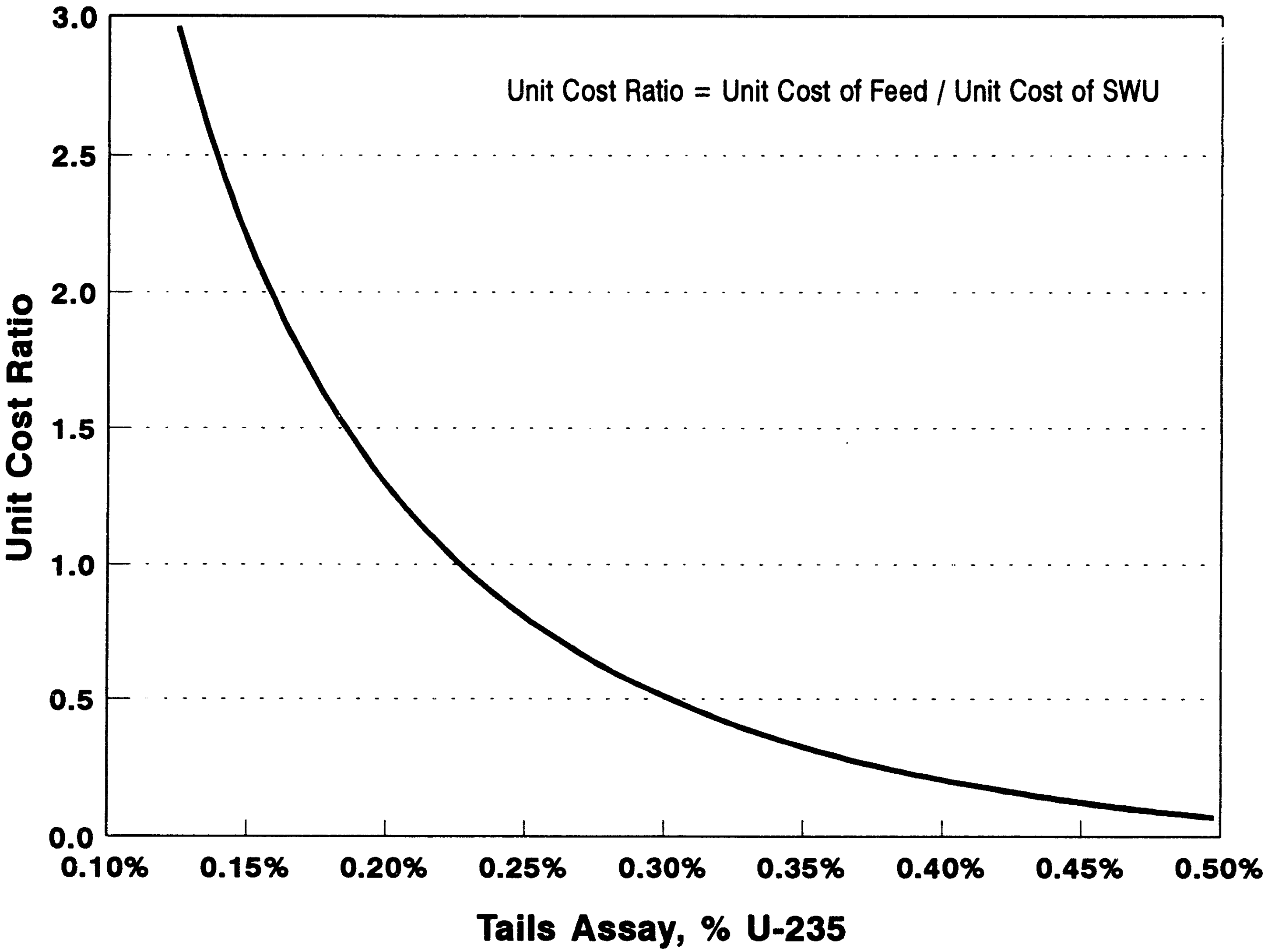

Figure 3. Optimum Tails Assay

will drop below 0.2% and all of the existing DU stockpile would have feed value. This would make it profitable to recycle the DU material if no chemical conversion or other major costs are incurred.

The DU material can be recycled in the existing commercial enrichment processes (gaseous diffusion and centrifuge) for nominal handling costs as long as the stockpile remains in the UF_6 form. Chemical conversion costs would be an important factor in determining the economic viability of DU recycle in the AVLIS process. Whether rapid escalation of the feed/SWU cost ratio will occur before or after the gaseous diffusion and centrifuge processes are replaced by AVLIS or another process utilizing a different chemical form of uranium is a matter of sheer speculation at this time. Therefore, a prudent decision on chemical conversion of the DU stockpile cannot be made until a replacement technology is deployed and the economics are known.

ULTIMATE DISPOSITION OPTIONS

The only major long-term use for uranium stripped of all economically recoverable ^{235}U which has been identified to date is for target material in a breeder major energy source. It follows that fully depleted uranium should be converted to a stable chemical type of nuclear reactor. It will be decades, perhaps even hundreds of years, before breeders become a form for ultimate disposition.

Common chemical forms used for open storage of uranium in industry are: UF_4, metal, and oxide. Of these, U_3O_8 is the most stable form and is the form of uranium found in nature. UF_4 decomposes in a moist environment, emitting HF. Uranium metal readily oxidizes. This leaves U_3O_8 as the obvious choice for "permanent" storage.

If a program of converting fully depleted uranium to U_3O_8 is adopted in the future, two waste minimization objectives of interest would be to develop a conversion process which permits recovery/recycle of all fluorine and which utilizes the UF_6 cylinders as storage vessels for the oxide. This would eliminate disposal costs for these materials plus reap the economic benefit for the new applications. Development work would be required to achieve either of these objectives and this development work should be initiated well in advance of the initiation of engineering design work on conversion facilities.

REFERENCES

1. T. R. Lemons et al., The Ultimate Disposition of Depleted Uranium, K/ETO-44, Martin Marietta Energy Systems, Inc., ORGDP, December 1990.

AN UPDATE ON CORROSION MONITORING IN CYLINDER STORAGE YARDS*

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ABSTRACT

Depleted uranium, from U.S. uranium isotope enrichment activities, is stored in the form of solid uranium hexafluoride (UF_6) in A285 and A516 steel cylinders designed and manufactured to ASME Boiler and Pressure Vessel Code criteria. In general, storage facilities are open areas adjacent to the enrichment plants where the cylinders are exposed to weather. This paper describes the Oak Ridge program[1] to determine the general corrosion behavior of UF_6 cylinders, to determine cylinder yard conditions which are likely to affect long term storage of this material, and to assess our cylinder storage yards against these criteria.

This program is targeted at conditions specific to the Oak Ridge cylinder yards. Based on (a) determination of the current cylinder yard conditions, (b) determination of rusting behavior in regions of the cylinders showing accelerated attack, (c) monitoring of corrosion rates through periodic measurement of test coupons placed within the cylinder yards, and (d) establishment of a computer base to incorporate and retain these data, we are working with the enrichment sites to implement an upgraded system for storage of this material until such time as it is used or converted.

INTRODUCTION

Uranium hexafluoride (UF_6) throughout the nuclear fuel cycle is handled and stored in cylinders which are designed, manufactured, and maintained in accordance with the ASME Boiler and Pressure Vessel Code for unfired pressure vessels (Section VIII). Cylinders for the storage of partially depleted material, in 10 and 14 ton sizes, are 48 inches in diameter and are constructed of mild steel. There are presently more than 40,000 of these cylinders within the DOE complex currently used for the storage of isotopically depleted solid UF_6. Approximately 5000 of these cylinders are stored at the Oak Ridge K-25 Site; some of these are over 35 years old.

Oak Ridge cylinder storage facilities are open areas adjacent to the former enrichment plant, where the cylinders are exposed to weather. Some cylinder degradation is expected to have taken place, primarily from exposure to the environment. Atmospheric corrosion of mild steel varies from less than 1 to over 10 mils per year; UF_6 corrosion at the inside wall surface is expected to be less than 0.1 mil per year.[2,3] This atmospheric corrosion of the exterior surface of the cylinders indicated the need for the monitoring of cylinders in storage to provide assurance that they have not deteriorated to the extent that they no longer meet wall thickness requirements for shipping and handling.

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*Based on work performed at the Oak Ridge K-25 Site managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy.

At one time, feed materials were transported exclusively in cylinders rated for 200 psi working pressure, the same design utilized for product (enriched) material. In frequent use in the fuel cycle, they were subjected to periodic cleaning, inspection, and hydrostatic testing. Present practice, however, allows one-time use of a new 100 psi cylinder for UF_6 transport, after which it is used for UF_6 storage at its destination. The cylinder yards are therefore occupied by two populations of storage cylinders:

1. Obsolete feed cylinders code-rated at 200 psi working pressure with 5/8 inch nominal wall thick ness.
2. Cylinders code-rated for 100 psi working pressure, designed and built as storage cylinders with 5/16 inch nominal wall thickness, or cylinders built as one-time use feed cylinders, then diverted to depleted solid UF_6 storage at the receiving site. These two types of cylinders were built to the same specifications.

The cylinders in the second category continue to be the primary focus of the Oak Ridge monitoring work. The programs ongoing at the K-25 Site include (1) determination of the current conditions of cylinders in outside storage by improved inspection methods and procedures, including ultrasonics, (2) measurement of corrosion rates through use of ASTM corrosion test coupons and commercial corrosion probes, and (3) provision of quality assurance documentation through a complete data base meeting NQA-1 requirements.

CYLINDER YARD SURVEILLANCE

Inspection of the Oak Ridge cylinder yards during the summer of 1990 revealed both storage defects and adverse valve conditions, and surveillance of storage yards on a semi-annual basis was initiated. While original inspection criteria for the cylinders focused mainly on the valve area, the revised Oak Ridge inspection program will address safe storage in a comprehensive manner, so that some inspections will include thorough documentation of the condition of both cylinder and storage environment. Regions of the cylinder where accelerated corrosion might be expected, such as welds, contact points, damp regions, crevices, dissimilar materials points, and ground contact are of particular interest; however inspection of many of these areas presents a particular challenge, since access is often difficult. Techniques developed for these evaluations include microscopic sampling. However, in addition to periodic inspections, the revised program includes provision for evaluation during stacking operations. More details on these revisions are presented in a paper by G. W. Lamb and W. N. Whinnery entitled "*UF_6 Cylinder Inspections at PGDP.*"[4]

Periodic visual inspections of the cylinder yards are being supplemented by microscopic sampling, field metallography, and ultrasonic testing of a statistically determined sample of the cylinders in storage. Field testing will emphasize those regions of the cylinders that have been identified for special attention.

Ultrasonic determination of cylinder wall thickness continues at Oak Ridge, as well as at the other enrichment sites. Laminar discontinuities within the steel cylinder wall can give false thickness readings using the small portable instrumentation previously described; the use of beta-scans can differentiate between these discontinuities and actual wall thinning.

The use of commercially available indicating tape for detection of HF vapor in the cylinder yards is expected to provide further confirmation of cylinder integrity. This tape is currently undergoing field trials at the Oak Ridge K-25 Site; it changes colors at HF levels of less than 10 ppm.

MEASUREMENT OF CORROSION RATES

ASTM corrosion monitoring has been in progress for over two years at the K-25 Site, in order to accurately predict environmental degradation of cylinder steel in the Oak Ridge area. Similar programs are in place at Paducah and Portsmouth. Sets of well-characterized standard coupons placed in racks at the three sites are removed periodically for evaluation. The preparation of the coupons and racks and the collection of data are being performed following American Society for Testing and Materials (ASTM) standards. Three sets of steel coupons were chosen for the study, (1) ASTM A285 to represent cylinders pre-1975, (2) ASTM A516 to represent cylinders post-1975, and (3) ASTM A36 steel to encompass all material conditions of cylinder corrosion. The work will continue for a 16 year period.

Initial data confirms a low rate of overall thinning in Oak Ridge. Measured rates for initial two-year exposures of a cleaned surface ranged from 0.8 to 1.2 mils per year. This rate is expected to decrease with exposure, as the corrosion products provide surface protection, so that overall thinning is expected to progress at a rate of less than 1 mpy under current conditions.

Determination of changes in storage environment has received considerable attention as well. Weathering attack depends on the presence of surface moisture; corrosion rate is, therefore, influenced markedly by relative humidity. Surface temperature will affect both the corrosion kinetics and the presence of surface moisture. Retention of moisture in contact with the steel surface, particularly where the moisture contains mineral salts, can increase attack rates by a factor of 10 or more. Time-of-wetness probes have been evaluated, and are being deployed in Oak Ridge, to monitor the presence of moisture (rainfall, dew, fog or snow) on steel surfaces in the cylinder yards in accordance with ASTM guidelines.

Commercially available transducers by Epitek Electronics, Inc. and UNIDATA America have been selected. The probes which have been found to give the most reliable data have a grid size ranging from approximately 2 in. by 3 in. to 3 in. by 4 in. A Starlog Data Logging System, Model 6003B with the vendor provided software package is used for acquisition and logging of the data from the time-of-wetness probes.

Probes are adhesively bonded to the surface being measured and are being placed on the ASTM rack coupons as well as representative cylinders from top, bottom, inner and outer rows. Monitoring will include those special areas (e.g., junction of the cylinder head and the skirt where water and debris are expected to accumulate for time periods much greater than that of the bulk surface area of the remainder of the cylinder). Temperature probes are also being placed in the same areas as the time-of-wetness probes. This data will be used to more closely relate the information obtained from the study of the coupons to the actual condition of the cylinders.

Another commercially available instrument which is expected to rapidly (real-time) verify corrosion conditions at the Oak Ridge K-25 Site is a system of electrical resistance corrosion probes manufactured by Cortest Instrument Systems, Inc. One monitoring instrument (Petrolite® Electrical Resistance Portable IN-8000) is used with electrical resistance probes installed at multiple locations. The sensing element housed within the electrical resistance probe is a metallic conductor whose electrical resistance depends on the thickness of the element. Thinning of an environmentally exposed measuring element is compared to that of a reference element which is protected from the environment and retains its original thickness and resistance. This measuring element reacts continuously with the environment; portable instrumentation can detect very small changes in corrosion rate.

Initial results with this system were not positive. A single probe, consisting of a 10 mil solid metal strip element of AISI 1018 mild steel encased in epoxy failed completely after seven days of exposure, due to separation of metal strip and epoxy. The element now in the field testing is a thin-walled (10 mil), cylindrical element (XCEL) fabricated from AISI 1018 mild steel.

DOCUMENTATION

Revision of the initial data base developed for documentation of corrosion data is currently underway to reflect the integration of corrosion data with other storage concerns. The new database will be entered on a mainframe computer system, but will still follow guidelines set forth in ANSI/ASME NQA-1 *Basic Requirement No. 17 - Quality Assurance Records*. The cylinder manufacturing data, service history, inventory , and inspection records are included; records will be flagged for cylinders identified as requiring special handling. Data from the mainframe may be transferred to a personal computer for authorized modification and presentation.

SUMMARY

The corrosion monitoring program at the Oak Ridge K-25 Site has undergone considerable modification during the past several years. Current work reflects an integrated effort, with planned safe storage recognized as an important part of Site operations. Field techniques have been evaluated for cylinder examination and commercially available instrumentation and existing techniques identified as suitable for use in the cylinder yards. Revised criteria for periodic inspection and ultrasonic measurement have been developed. Initial data obtained indicates overall cylinder wall thinning in the Oak Ridge area is progressing at a very low rate. This work is continuing, while more emphasis is now being placed on the monitoring of cylinder yard conditions to assure continued responsible custody of isotopically depleted material.

REFERENCES

1. Henson, H.M., Barlow, C.R., Frazier, J.L., and Ziehlke, K.T., Uranium Hexafluoride - Safe Handling, Processing and Transportation: Conference Proceedings, "Monitoring of Corrosion in ORGDP Cylinder Yards.", Oak Ridge, TN, May 24-26, 1988.

2. Barber, E.J. and Ritter, R. L. , Personal communication to Helen M. Henson, Oak Ridge K-25 Site.

3. Kimmerly, E. Y., Personal communication to J. O. Dodson, Oak Ridge K-25 Site, Oct. 27, 1982.

4. Lamb, G.W. and Whinnery, W. N., Second International Uranium Hexafluoride Handling Proceedings, "*UF_6 Cylinder Inspections at PGDP*", Oak Ridge, TN, Oct. 29-31, 1991 (In publication).

UF_6 CYLINDER INSPECTIONS AT PGDP

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ABSTRACT

Routine inspections of all UF_6 cylinders at the Paducah Gaseous Diffusion Plant have been mandated by the Department of Energy. A specific UF_6 cylinder inspection procedure for what items to inspect and training for the operators prior to inspection duty are described. The layout of the cylinder yards and the forms used in the inspections are shown. The large number of cylinders (>30,000) to inspect and the schedule for completion on the mandated time table are discussed. Results of the inspections and the actions to correct the deficiencies are explained. Future inspections and movement of cylinders for relocation of certain cylinder yards are defined.

RADIATION DOSE RATES FROM UF_6 CYLINDERS

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ABSTRACT

This paper describes the results of many studies, both theoretical and experimental, which have been carried out by Urenco over the last 15 years into radiation dose rates from uranium hexafluoride (UF_6) cylinders. The contents of the cylinder, its history, and the geometry all affect the radiation dose rate. These factors are all examined in detail. Actual and predicted dose rates are compared with levels permitted by IAEA transport regulations.

NOMENCLATURE

d density of steel
k decay constant = 0.6932/half life
m mass absorption coefficient
R radiation dose rate
t time
w thickness of cylinder wall

INTRODUCTION

Many studies, both theoretical and experimental, have been carried out by Urenco over the last 15 years into radiation dose rates from UF_6 cylinders. This subject is increasingly of importance because of greater emphasis world-wide on controlling people's exposure to radiation and because Urenco will shortly be enriching recycled uranium in substantial quantities, with associated higher radiation fields.

SOURCES OF RADIATION

Radiation from a cylinder can in practice originate only from those radioactive species in the UF_6 which yield a high energy gamma radiation, since alpha and beta radiation would be fully absorbed by the cylinder wall, and low energy gamma would be mainly absorbed. For natural uranium and low enriched product and depleted tails made therefrom, the main radiation source is Protactinium 234 (Pa234) which is the daughter of Thorium 234 (Th234), itself the daughter product of U238. Uranium 235 is itself a gamma emitter (186 keV), and this will give a small contribution to the radiation dose rate from a full cylinder. Radiation from U235 daughters is insignificant, as it is easily absorbed by the cylinder wall.

Recycled uranium also contains U232, and substantial radiation emanates from one of its daughters, Thallium 208 (Tl208). Of the fission products present in recycled Uranium, Ruthenium 106 decays to Rhodium 106, which is a gamma emitter. Quantitatively however, this contributes little to the radiation dose from a UF_6 cylinder, even at the ASTM specification level for fission products.

Table 1. Sources of Radiation

	Units	U232	U235	U238
Daughter		Th228	Th 231	Th 234
Half Life	Days	698	1.07	24.1
Decay Constant	$(days)^{-1}$	0.000993	0.650	0.029
Decay Constant	$(yr)^{-1}$	0.362	237	10.5
Main Radiation Source		Tl 208	Th 231	Pa 234
Main Photon Energy	MeV	2.6	0.08	1.0
Mass Absorption Coefficient	cm^2/g	0.04	0.48	0.06

FACTORS AFFECTING DOSE RATES

The factors affecting radiation dose rates from UF_6 cylinders are listed in Table 2 and described in turn in the paper.

Table 2.
Factors Affecting Dose Rates

Content:	Full or Emptied U232 concentration
History:	Storage time before emptying Storage time after emptying Speed of emptying
Geometry:	Cylinder size Cylinder wall thickness Location on cylinder Distance from cylinder

FULL/EMPTIED CYLINDERS

Full UF_6 cylinders have a low dose rate because the uranium is self-shielding, and it largely absorbs the radiation from the daughter products in the UF_6. However, when the cylinder is emptied by gassing off the UF_6, the non-volatile daughter products remain behind in the remaining "heel" without any self-shielding. The radiation dose increases by a factor of about 12 for a freshly emptied 48" cylinder, and a factor of about 6 for a 30" cylinder. The dose rate increases steadily during the emptying process, as shown in Figure 1.

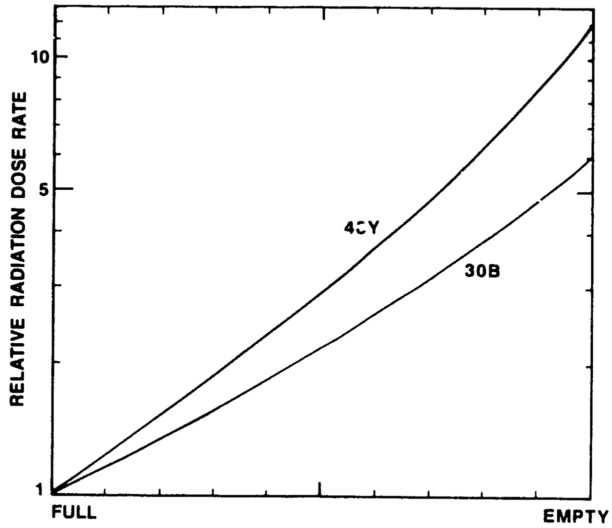

Figure 1. Increase in Radiation Level on Emptying

On filling a freshly - emptied cylinder with UF_6, the radiation dose rate only reduces by a factor of up to 2. The daughter products in the heels clearly remain mainly on the inside wall of the cylinder and there is little self-shielding.

U232 CONTENT

All recycled uranium contains U232 along with consequent daughter products. For spent LWR fuel, the typical U232 content is currently 1 ng/gU (ie 1 part per billion, or ppb). The oxide recycled uranium used by Urenco to date has had U232 contents in the range 0.6 to 1.3 ppb. However, as fuel burn-ups increase then so will the U232 content of spent fuel, although the ASTM specification limit of 5 ppb is expected only for very high burn-up fuel (greater than 50 GWd/tU) which is not expected to be reprocessed until well after the year 2000.

Enriched recycled uranium has a greatly increased U232 content, typically by a factor of 5 to 10 for LWR reload fuel with product assays in the range 3-4% U235. Thus the U232 content of enriched recycled UF_6 is currently 5 to 10 ppb and could approach the ASTM specification limit of 50 ppb in time.

In the UK, the Magnox reactors (natural uranium fuel, graphite moderated, CO_2 gas cooled) operate with much lower fuel burn-up - 3 to 6 GWd/tU. The resulting reprocessed spent fuel (Magnox Depleted Uranium, or MDU) has a correspondingly low U232 content, with an average of 0.06 ppb and a maximum of 0.15 ppb for current MDU production. On enrichment, the U232 content increases by a factor of about 20, therefore enriched MDU has a U232 content of 1 to 3 ppb.

STORAGE TIME BEFORE EMPTYING

When a cylinder is initially filled with UF_6, it contains very few uranium daughter products and the radiation from the cylinder is very low. The daughter products grow in with a time constant of the half-life of the thorium daughter, as given in Table 1. The radiation dose rate after storage for time t is given by formula 1 and is shown in Figure 2.

$$R_t = R\ (1 - e^{-kt}) \tag{1}$$

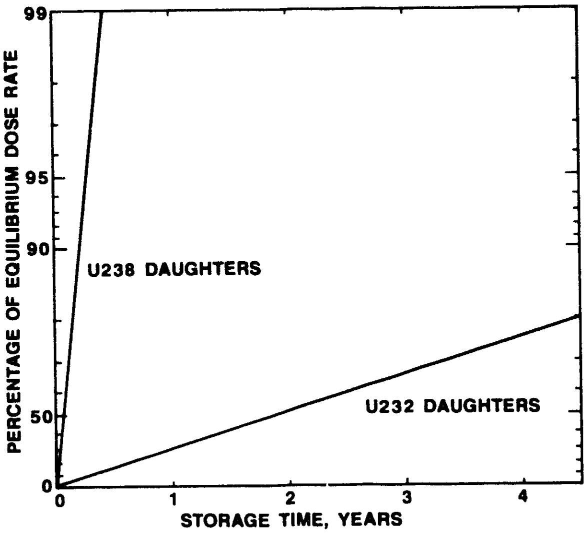

Figure 2. Grow-in of uranium daughters

Because the daughter products of U238 grow in with a 24 day time constant, the equilibrium dose rate from natural UF_6 is reached within a few months. For example, the dose rate from cylinders of 3 months' old natural UF_6 is 93% of the equilibrium dose rate from cylinders of fully aged UF_6. Natural UF_6 feed will normally be stored for 6 to 12 months before feeding to enrichment plants, and thus the UF6 will usually be fully-aged.

However, U232 daughters grow in much more slowly (with a 1.9 year time constant) and for example are only 30% of equilibrium value after one year of storage. This is critically important as it means that if cylinders of recycled uranium are used promptly, radiation dose rates are much reduced.

STORAGE TIME AFTER EMPTYING

After a cylinder of UF_6 is emptied by gassing-out the contents, the uranium daughter products stop being produced (as their parents, the uranium isotopes have been removed) and decay with the half lives shown in Table 1. The radiation dose at time t after emptying is given by formula 2 and is shown in Figure 3.

$$R_t = R_o \ e^{-kt} \qquad (2)$$

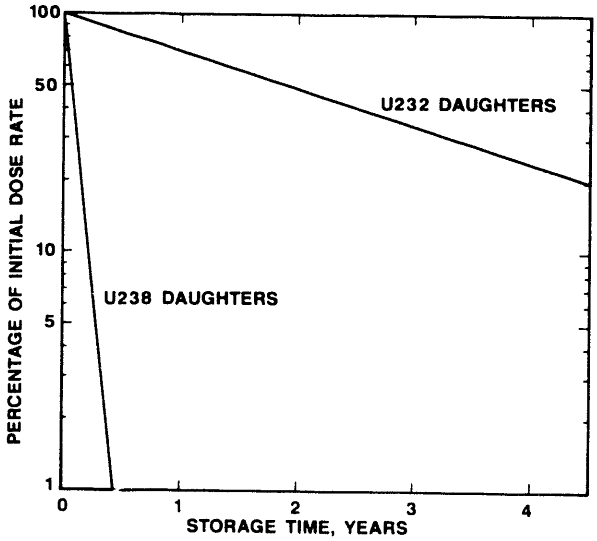

Figure 3. Decay of uranium daughters

Storing an emptied ex-natural UF_6 cylinder for a few months before re-using or transporting it will dramatically reduce the radiation dose from it, and this is a fairly low cost way of reducing personnel radiation exposure. For example, after 80 days' storage, the radiation dose is reduced by a factor of 10.

However, the long half-life of U232 daughters means that several years' storage would be needed to reduce dose rates from emptied cylinders of recycled uranium. This is not likely to be a practical option, other than when an emptied feed cylinder is re-filled with tails depleted UF_6, which would then normally be stored for many years.

SPEED OF EMPTYING

The U238 daughter products decay whilst a cylinder is being emptied, and there will therefore be less remaining behind in a cylinder which is emptied slowly. The radiation dose rate of a freshly emptied cylinder reduces with emptying time t as given by formula 3 and shown in Figure 4. The corresponding feed rate for a 48Y cylinder is also shown.

$$R_t = \frac{Ro}{kt}(1 - e^{-kt}) \qquad (3)$$

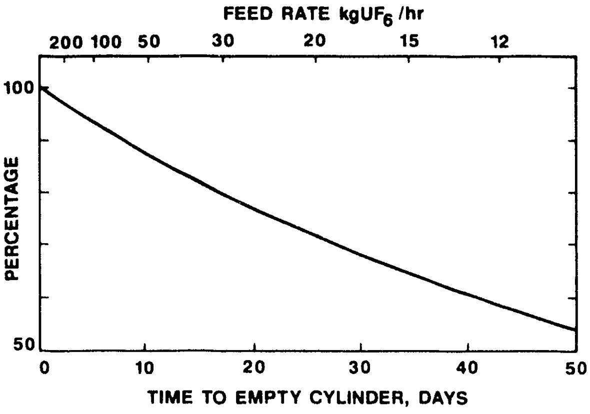

Figure 4. Radiation from freshly emptied cylinder

Usually UF6 cylinders are emptied in under 15 days. The decay of U238 daughters during this period is small. The decay of U232 daughters during this period is even smaller.

The spatial distribution of daughter products within the cylinder is affected by the speed of emptying, as explained later.

CYLINDER SIZE

As described earlier, the larger the cylinder is, the greater its ratio of volume to surface area, and hence the larger the concentration per unit surface area of daughter products in an emptied cylinder. The ratio of volume to surface area for a 48Y or G cylinder is twice that of a 30A or B. A larger cylinder will also present a larger source of radiation and hence at any given distance away from it, the radiation dose rate will be higher than from a smaller cylinder, as described later. Radiation dose rates will therefore be higher for larger cylinders, although the radiation dose rate per tU will be lower.

CYLINDER WALL THICKNESS

Bulk UF_6 cylinders are made of steel of between 1/4" and 5/8" thickness. The low-energy gamma radiation (less than 100 keV photons) from Thorium 234 and Thorium 231 is almost fully attenuated, and can be ignored. However, the high energy gamma photons from Pa234 and Tl208 are attenuated much less. The transmission through the cylinder wall of thickness w is given by formula 4 and shown in Figure 5. The comparative surface dose rates measured on different types of cylinders are in good agreement with this model.

$$R_W = R_o e^{-mdw} \quad (4)$$

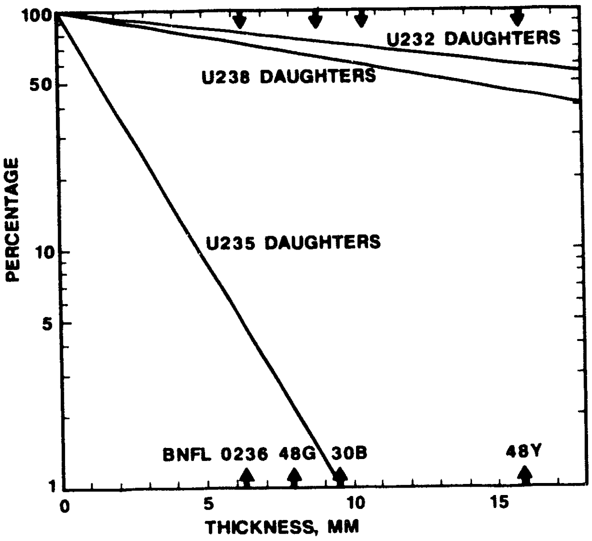

Figure 5. Transmission through cylinder wall

LOCATION ON CYLINDER

The radiation dose rate from a full cylinder is fairly even over the whole surface, reflecting the uniform distribution of daughter products. However, when emptied, the heels and daughter products tend to lie along the base of the cylinder and hence the radiation dose is higher there. This effect is much greater when the cylinder is emptied by evaporation of liquid rather than solid UF_6 because the daughter products tend to dissolve in liquid UF_6 and remain behind in a narrow strip along the bottom of the cylinder when the UF_6 has all evaporated. The effect is greater at higher feed rates as there is less time for the daughter products to migrate to the cylinder wall, by diffusion or convection. Figure 6 shows typical readings at the cylinder base for freshly emptied 48Y cylinders of natural UF_6.

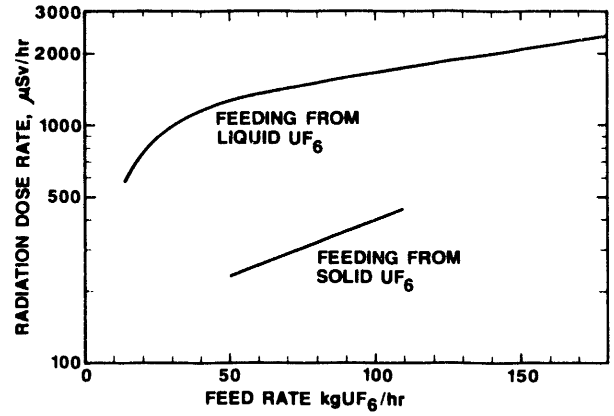

Figure 6. Radiation Dose at Cylinder Base

DISTANCE FROM THE CYLINDER

The dose rate at a given point will be proportional to the fractional solid angle subtended by the cylinder. For distances (d) less than the cylinder diameter, the dose rate will vary as $^1/_d$, and at large distances, the dose rate will vary as $^1/d^2$. This theory is well borne out by measurements. The dose rate will decline with distance more quickly for a 30" than for a 48" cylinder, and more quickly if the cylinder is viewed end-on than side-on. Figure 7 shows how rapidly the dose rate declines with distance from the side of a 48Y cylinder.

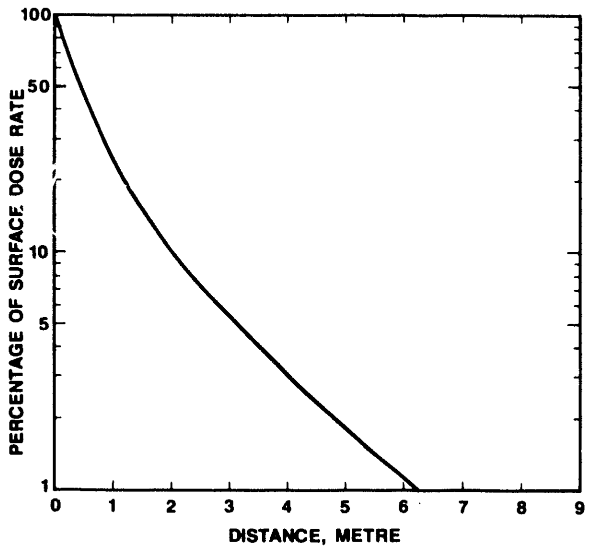

Figure 7. Radiation Decline with Distance

MEASURED DOSE RATES

The average measured surface dose rates at the centre, side of full and freshly emptied cylinders of fully aged natural origin UF_6 are given in Table 3. Individual cylinders have dose rates that lie within -30% to +50% of these average values.

Table 3. Surface Dose Rates, uSv/hr

	Full	Freshly Emptied
30B	17	100
48Y	15	170
48G	22	260*
BNFL 0236	27	350

* Estimate

Cylinders of recycled uranium have an <u>additional</u> radiation level equivalent to 120% of the values in Table 3 for 1 year aged UF_6 with a

U232 content of 1ppb. For example, a freshly emptied 48Y cylinder having contained 1 year aged UF_6 with U232 at 1.3 ppb has a surface dose rate of 435 uSv/hr (= 170 (1 + 1.2 x 1.3)).

TRANSPORT REGULATIONS

The radiation limits in the IAEA transport regulations are very complex, and for any given type of shipment, the regulations (1) will need to be examined. The main limits likely to apply to shipment of UF_6 cylinders are given in Table 4.

Table 4. Radiation Limits, uSv/hr

Location	Exclusive Use	
	Yes	No
Surface of package	10000	2000
Vehicle outer surface	2000	2000
1m from package	1000	100
2m from vehicle	100	100
In driver's cab	20	20

Please note the following:

- The drivers cab dose rate limit does not apply if the driver is a classified worker and thus uses a film badge (in which case his total radiation exposure is controlled under other regulations).
- An example of an "exclusive use" shipment would be where an UF_6 cylinder is shipped door-to-door in an ISO freight container. Cylinders shipped on open trailers would not count as exclusive use.
- A complex set of "Transport Index" limits might place restrictions on the number of cylinders that can be carried in (or on) a single vehicle, freight container, or ship.
- IAEA transport regulatory limits are to be reviewed (2) following the recent reduction (by a factor of 2.5) in ICRP recommended personnel exposure. The implications of any changes will need to be assessed.

ACTUAL AND PREDICTED DOSE RATES IN TRANSPORT

Radiation dose rates incurred in transport will depend on the nature of the packages shipped (cylinder types, whether in overpacks, cylinder contents and history) and the geometry of the vehicle/freight container (eg size of vehicle, and positioning of packages). As one example, for a 48Y feed cylinder shipped by road on a standard 8 foot wide lorry, expected radiation dose rates are given in Table 5.

Table 5. Calculated Dose Rates

Position	Dist. from Cylinder m	Relative Dose Rate %
Surface of 48Y	0.0	100
Side of Vehicle	0.6	40
1m from Cylinder	1.0	25
2m from Vehicle	2.6	7
In driver's Cab	2 - 8	0.5 - 10

Actual measurements bear out the above relationship. An analysis of shipments of emptied 48Y natural UF_6 feed cylinders leaving Capenhurst in 1989 and 1990 showed an average dose rate at the cylinder surface of 20 uSv/hr and an average cab dose rate of 0.6 uSv/hr - ie 3% of the surface dose rate. For emptied cylinders of oxide recycled Uranium, radiation dose rates can be much greater, as explained earlier. For example, two emptied 48Y cylinders of oxide recycled feed shipped from Capenhurst in 1986 had average dose rates of 200 uSv/hr at the cylinder surface, 70 uSv/hr at the sides of the vehicle and 11 uSv/hr in the driver's cab. Comparing Tables 4 and 5 indicates that the critical radiation limits are likely to be:

- for non-exclusive use:
  100 uSv/hr at 1m from cylinder. This limit can be exceeded even for freshly emptied natural feed - at the cylinder base.

- for exclusive use:
  100 uSv/hr at 2m from vehicle. This limit may be exceeded for long stored recycled uranium with high U232 levels.

MEASURES TO REDUCE PERSONNEL EXPOSURE

The following low-cost measures can be taken, to reduce personnel radiation exposures:

- store emptied natural feed cylinders for about two months before moving them, eg before return shipment to the conversion plant.

- coordinate closely with converters and fuel fabricators to schedule prompt use of feed and product from oxide recycled uranium.

- if a cylinder has a high surface dose rate, position it near the rear of a lorry to reduce the radiation dose rate in the driver's cab.

- When people work close to a cylinder, carry out such operations speedily.

CONCLUSIONS

1. Radiation dose rates from UF_6 cylinders depend on their contents, geometry and history.

2. For natural uranium, dose rates are normally well within IAEA transport regulation limits.

3. For oxide recycled uranium, dose rates can be much greater, and IAEA transport regulations may place restrictions on the use of cylinders.

ACKNOWLEDGEMENTS

I thank R Mueller and K H Sorgalla (Uranit) and F Irons (ex-Urenco (UK)), who have done much theoretical work in this area and R Abbink (Urenco NL) and J Chalmers (Urenco UK) who have obtained much experimental data.

REFERENCES

1. IAEA, Regulations for the Safe Transport of Radioactive Material, Safety Series no 6, Section IV, 1985 (as amended 1990)

2. Selling H.A. "The Long Way to a New Comprehensive Edition of the IAEA Transport Regulations". I Nuc Eng. 2nd International Conference on Transportation for the Nuclear Industry, Bournemouth, May 1991.

RADIATION LEVELS ON EMPTY CYLINDERS CONTAINING HEEL MATERIAL

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ABSTRACT

Empty UF_6 cylinders containing heel material were found to emit radiation levels in excess of 200 mR/hr, the maximum amount stated in ORO-651. The radiation levels were as high as 335 mR/hr for thick wall (48X and 48Y) cylinders and 1050 mR/hr for thin wall (48G and 48H) cylinders. The high readings were found only on the bottom of the cylinders. These radiation levels exceeded the maximum levels established in DOT 49 CFR, Part 173.441 for shipment of cylinders. Holding periods of four weeks for thick-wall cylinders and ten weeks for thin-wall cylinders were established to allow the radiation levels to decay prior to shipment.

INTRODUCTION

This paper details a study conducted at the Paducah Gaseous Diffusion Plant (PGDP) on the radiation levels emitted from empty UF_6 cylinders containing heel material. This issue is addressed in ORO-651, "Uranium Hexafluoride: Handling Procedures and Descriptions," where it is stated that radiation levels up to 200 mR/hr may be experienced on the exterior surface of the cylinder. Data collected at PGDP show that the radiation levels often exceed 200 mR/hr after a cylinder is emptied. Valves have been observed as high as 1050 mR/hr for 48G cylinders and 335 mR/hr for 48X cylinders. The 200 mR/hr surface radiation valve is important because it is the maximum allowable value for shipment on open-bed trailers as stated in Department of Transportation (DOT) Regulation 49 CFR, Part 173.

BACKGROUND

The radiation emitted from empty UF_6 cylinders results from Th-234 and Pa-234m, the first two daughter products in the U-238 decay chain. The half-lives and equilibrium concentration for Th-234 and Pa-234m are listed in Table 1.

Table 1. Properties of Th-234 and Pa-234m

	Th-234	Pa-234m
Half-Life	24.1 days	68 seconds
Equil. Conc. (ppb)	0.0145	4.9E-7

After a cylinder has been filled with UF_6, the daughter products begin to form at a rate governed by their half-lives until they have reached their equilibrium concentrations. The daughter products are present in the form of non-volatile fluoride compounds. When the cylinder is liquified prior to being emptied, the daughter products accumulate on the bottom and remain in the cylinder heel with little uranium to provide shielding. The radiation emitted from the cylinder heel will decrease relative to the half-life of Th-234.

CONCLUSIONS

The purpose of the study performed at PGDP was to determine the time necessary for the radiation levels to decay below 200 mR/hr so they would meet the requirements of DOT 49 CFR, Part 173 shipment. In this study, ten 48X and five 48G cylinders were emptied and the radiation levels monitored until they decayed below 200 mR/hr. The radiation levels immediately after feeding ranged from 335 to 195 mR/hr for the 48X cylinders and 735 to 421 mR/hr for th 48G cylinders. It should be emphasized that these surface radiation levels are only on the bottom of the cylinders. Readings collected on the tops, sides, heads, and ends of cylinders are consistently below 20 mR/hr. Based on data collected from this study, a holding period of four weeks was established for thick-wall cylinders and ten weeks for thin-wall cylinders to allow for radiation levels to decay below 200 mR/hr. Since the holding periods have been established, approximately 98 percent of the cylinders have been below 200 mR/hr upon their receipt in the shipping area.

SUMMARY

Radiation emitted from heel material contained in empty UF_6 cylinders has been found to exceed 200 mR/hr on the bottom exterior surface of the cylinder. Holding times of four weeks for thick-wall cylinders and ten weeks for thin-wall cylinders have been established at PGDP to allow the radiation levels to decay below 200 mR/hr. This is necessary to meet shipping requirements as stated in DOT 49 CFR, Part 173.

REFERENCES

1. Benedict, M., Pigford, T. H., and Levi, H. W., *Nuclear Chemical Engineering*, Second Edition, McGraw Hill, New York, p. 218, 1981

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Cylinders:
Regulations and Testing

THE LEGAL STATUS OF UF_6-CYLINDER TESTING AND LICENSING IN GERMANY (AND EUROPE)

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ABSTRACT

New german and european transport regulations for road and rail transport of UF_6-cylinders are presented, in particular those provisions which have direct impact on the majority of cylinders used in shipments touching ADR and RID member states. First experiences and difficulties in it's application are highlighted taking into account experiences of a forrunning german regulation. A summary of research efforts on the behaviour of cylinders in fire environments concludes the paper.

INTRODUCTION

In the Federal Republic of Germany, even prior to the "Mont Louis" event in 1984, it was recognized, that the design, inspection and testing of UF_6-cylinders for transport purposes was characterized by a considerable technical standard, oriented in the handling and opertion on one hand but by some technical and legal deficiencies with respect to transportation on the other hand. This was the reason to apply to the International Atomic Energy Agency (IAEA) already in may 1982 to amend it's transport regulations (IAEA-Safety Series No. 6) /1/ with respect to the "subsidiary" chemical risks. (The proposal was part of the 3rd Draft Revision of the 1984 rev. Edition, distributed in may 1983).
Though too late for the last revision process, it was the starter for continued efforts of the IAEA to complete it's world-wide harmonized and accepted transport regulations. Levin and Wieser reported on these efforts during the last conference /2/. Meanwhile the schedule of the Agency for the establishment of a "regulatory" document has repeatedly been delayed. The last meeting of the superiour advising committee SAGSTRAM in December 1990 recommended, "contrary to earlier recommendations, the publication of the document again as a TECDOC, representing a statement of the work done in this area. SAGSTRAM considered that the prevailing uncertainties, in particular those concerning the release criteria during the projected fire test, preclude publication as a Safety Guide, and that a Co-ordinated Research Programme under the auspices of the Agency should provide the necessary input to resolve the remaining problems. Since the intention to incorporate the provi-ions on UF_6 in the next major re-

vision (1996) of the IAEA Regulations and the supporting documents still stands, the text in this document has been split into regulatory, advisory and explanatory material. Any additional information arising from experience gained in the use of this TECDOC should then be taken into account."

This lengthy procedure to establish worldwide accepted recommendations on that topic (it took two Technical Committee Meetings, three Consultant Service Meetings and three rounds of comments by Member States, so far, was not to be expected in the beginning of the process. This is why it seemed justified to prepare - in parallel - regulations on the european level. Last but not least, it was the "Mont Louis" event which fostered this procedure.

A joint working group of the rule setting bodies for road and rail transport in Europe, charged with the adoption of the 1985 revised edition of IAEA Safety Series No. 6 into the "ADR" and "RID", the conventions for international shipments of dangerous goods in Europe /3, 4/, prepared also provisions to cover the "subsidiary" chemical hazard of UF_6. These provisions were taking into account the status of recommendations as developped by the IAEA at that time. The completion of the IAEA-deliberations was not awaited - this is why the ADR/-RID regulations are now not in line with all detail of the latest IAEA--TECDOC 608 /4/ and probably any further IAEA-recommendation on that issue.
After the approval of these ADR/RID provisions by the boards, the national transport regulations of the Federal Republic of Germany for road and rail transport of dangerous goods were amended accordingly in December 1987.
In view of the very limited domestic shipments of UF_6 this had only a minor effect on the users and shippers of UF_6-cylinders.

NEW REGULATIONS

The amended ADR and RID regulations came into force January 1st, 1990. The provisions on the packaging and transport of Uranium hexafluoride are part of the section on "Radioactive Materials Having Other Hazardous Properties", to make clear, that these are to be complied with in addition to the provisions, written under radiological and criticality safety aspects (in accordance with IAEA Safety Series No. 6). The provisions are annexed, using text and structuring of the ADR.

EXPLANATIONS

As to be seen, the character of the text is of regulatory nature, summarizing general requirements on the design, fabrication and testing in general terms and performance oriented. The majority of provisions is in line with the existing technical standard and the american standards ANSI N14.1 and ORO-651, such as service and test pressures, service temperature range, establishment of volume, maximum fill, inservice and reinspection program).

However, there are some paragraphs, where the need for some explanations is apparent:

a) Provisions opening the door for new technical solutions:

- Generally spoken, the nature of the provisions now allows new cylinder designs, new materials and constructions, no longer bound to the rigid US-Standards. (However, it's well understood, that any new design must be acceptable to the plants and its competent authorities). The key design figures are set forth such as to garantee the same safety level.

- Leackage test
  This test is opecified by sensitivity rate (0.1 $Pa \cdot l \cdot s^{-1}$), which now allows the replacement of the "air test" by other leakage test methods, working safer and faster.

- The option to replace the hydraulic test as part of the reinspection test program by "any other equivalent non-destructive examination procedure" also brings in more flexibility, taking into accont the state of the art in pressure vessel reinspections.

b) Provisions, additional to the status of the US-standards, but keeping the actual technical standard:

- Shipment after storage times longer that five years, now does presuppose an examination with a program approved by the competent authority.
  To the estimate of the german competent authority, this program shall include not only a "visual inspection for degradation of the cylinder wall "but, essentially and on a random basis, the same elements as for the regular five years reinspection program. This seems justified in the interest of public safety during shipment, the concealing effects of repaints for visual inspections and,in particullar, the ever more increasing storage times (the paper by R. Christ also adresses this subject).

- Approval by the competent authority is also required for the inservice and reinspection test programms, alternative, maintenance and repair programs but, above all, for the design of all cylinders, with the exemption of those for less than 10 kg of UF_6. Because of the fact, that the compliance of existing ANSI/ORO-cylinders with the ADR/RID provisions has not yet been demomonstrated in all points, this will need, at least, some administrative efforts.

c) Provisions, additional to the status of the US-standards with the implication of technical improvements:

- For cylinders with a capacity of more than 450 l (i.e. 30′ and 48′-cyl.) leakproofness is required after the performance of the Type A-drop test in the most damaging impact orientation. This requirement will, in view of available test results foster the development of new valve protectors, exept in case, where outer protective packagings are used from other reasons.

- Fire resistance capability is not required. With reference to the ADR/RID safety standard for receptacles with a comparable potential risk and the test criteria still pending, no fire resistance requirement was included.

d) Grandfatherclause

   Standard UF_6-cylinders according to ANSI N14.1 - 1982 (not 1987!) or aquivalent, may be continued to be used by the agreement of the competent authority. By reference to the specific issue of the standard, 48 G-cylinders are not subject to this clause!

EXPERIENCES

From the view point of the competent authority the following experiences and conclusions could be obtained:

- The flexibility of the new provisions is wellcomed by the concernded industry, in general.
- There is no urgent need for new designs of cylinders and structural equipments so far and as long the grandfatherclause is applied.
- In particullar, the possibility to apply alternative test methods and procedures for reinspections is used.
- International agreement is necessary in those cases, where consent of the competent authority is required.
- The grandfatherclause need to be time - limitted in order to put the new provisions really into function.
- The new provisions will have to take into account the progress made with the IAEA.

RELATED RESEARCH EFFORTS

In context with the increased interest of the regulaters for the safety in shipment and storage of UF_6 some research studies are to be seen.

At Bergische Universität Wuppertal calculations have been performed, sponsored by the Federal Ministry for Environment, Nature Protection and Reactor Safety, on the behaviour of UF_6-cylinders, filled with the maximum amount of UF_6, under fire exposure conditions corresponding to IAEA-requirements for type B-packages, using the design characteristics of the 48Y-cylinder.

The calculations have been based on:
1.) Fouriers's equation on instationary thermal state,
2.) a rotationally symmetrical distribution of UF_6 in all its phases in the vessel, **Fig.1,**
3.) on thermal and material data given in **Table 1** and **Table 2,**
4.) the application of the programme-system THEL /6/.

Fig. 1: Rotationally symmetrical UF_6 distribution and 5 layers (grid) of the liquid and solid phase

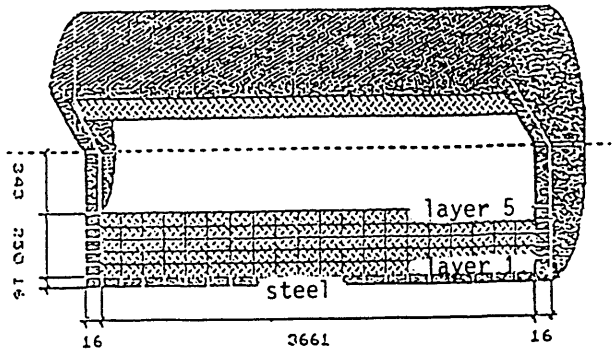

Table 1: Thermal data of UF_6

specific heat, solid	475 kJ · kg^{-1} K^{-1}
specific heat, liquid	542 kJ · kg^{-1} K^{-1}
specific heat, gaseous	429 kJ · kg^{-1} K^{-1}
transformation energy (solid-liquid)	54,15 kJ · kg^{-1}
transformation energy (liquid-gaseous)	53,39 kJ · kg^{-1}
heat radiation coefficient, fire	0,9
heat radiation coefficient, steel	0,8

Table 2: Thermal conductivity and mass density for steel and UF_6 phases

	$W \cdot m^{-1} K^{-1}$	$kg \cdot m^3$
steel	62	7,850
UF_6, gas	0,001	11
UF_6, solid	4	5,000
UF_6, liquid	366	3,600

Results being obtained from this first approach are: 1.) The temperature of the wall comes up to 200 °C about 5 minutes fire exposure. 2.) The UF_6 was not melted completely within the time of exposure (30 minutes), because the temperature of the inner layer (layer 5, Fig. 1) raised only slightly by about 5 °C.

It can be concluded: The 48 Y-vessel will presumably fail after about 5 minutes after fire exposure because of the melting point of the tin-lead solder in the valve area is about 200 °C.

The vessel will leak considerably. Bursting of the vessel can be encluded within the time of exposure to fire over a period of 30 minutes at least.

Continuation of these efforts in cooperation with other ingaged institutions on that issue is our intention.

REFERENCES

/1/ International Atomic Energy Agency, "Regulations on the Safe Transport of Radioacitve Materials", IAEA-Safety Series No. 6, 1985 Edisiton, Vienna, Austria, 1985

/2/ Levin, I. and Wieser, K., "The IAEA Recomendations for Providing Protection During the Transport of Uranium Hexafluoride", Proc. of Conf. "Uranium hexafluoride - Safe Handling, Processing and Transporting, Oak Ridge, TN, USA, p. 187 ff, May 1988.

/3/ United Nations, Economic Commission for Europe, "European agreement concerning the international carriage of dangerous goods by road (ADR) and protocol of signature", Annex A, as amended, NY, USA, 1990

/4/ Office Central De Transport Internationaux Par Chemin De Fer, "Règlement concernant le transport international ferroviaires des marchandises dangereuses" (RID), Attachment 1, as amended, Bern, Switzerland, 1990

/5/ International Atomic Energy Agency, "Interim guidance on the safe transort of uranium luxafluoride", IAEA-TECDOC-608, Vienna, Austria, June 1991

/6/ Lipa, P.; Ortmann, L.; Sprack, P.; Weber, F.: THEL. User's Guide, Ingenieurbüro Peter Lipa, Castrop-Rauxel, Germany, 1988

Annex

RADIOACTIVE MATERIAL HAVING OTHER HAZARDOUS PROPERTIES

3770 ...

(4) Packagings for uranium hexafluoride shall be designed, constructed and used in accordance with the provisions of marginal 3771.

Provisions for the packaging and transport of uranium hexafluoride

3771 (1) Packagings for uranium hexafluoride shall be designed as pressure vessels and manufactured from an appropriate carbon steel or other appropriate alloy steel.

(2) (a) The packagings and their service equipment shall be designed for working temperatures of at least -40 °C up to 121 °C and for a working pressure of 1.4 MPa (14 bar).

(b) The packagings and their service and structural equipment shall be so designed as to prevent any leakage or permanent deformation when they are subjected for five minutes to a hydraulic test pressure of 2.8 MPa (28 bar).

(c) The packagings and their structural equipment (if this is permanently attached to the packaging) shall be so designed as to withstand an external gauge pressure of 150 kPa (1.5 bar) without permanent deformation.

(d) The packagings and their service equipment shall be so designed as to remain leakproof so that the limit specified in paragraph (4) (f) is observed.

(e) Pressure relief valves are not permitted and the number of openings shall be as few as possible.

(f) Packagings with a capacity of more than 450 l and their service and structural equipment (if this is permanently attached to the packaging) shall be so designed that they remain leakproof when they are subjected to the drop test specified in marginal 3742.

(3) After manufacture, the inside of the pressure bearing parts shall be throughly cleaned of grease, oil, scale, slag and other foreign matter by an appropriate procedure.

(4) (a) Every manufactured packaging and its service and structural equipment shall,

either jointly or separately, undergo an inspection initially before being put into service and periodically thereafter. These inspections shall be performed and certified by agreement with the competent authority.

(b) The initial inspection shall consist of a check of the design characteristics, the strength test, the leakproofness test, the water capacity test and a check of satisfactory operation of the service equipment.

(c) The periodic inspections shall consist of a visual inspection, the strength test, the leak proofness test and a check of satisfactory operation of the service equipment. The interval for periodic inspections shall be not more than five years. Packagings which have not been inspected within this five-year period shall be examined before transport in accordance with a programme approved by the competent authority. They shall not be refilled before completion of the full programme for periodic inspections.

(d) The check of design characteristics shall demonstrate compliance with the design type specifications and the manufacturing programme.

(e) The strength test before first being put into service shall be conducted by means of a hydraulic test with an internal pressure of 2.8 MPa (28 bar). For the periodic inspections, any other equivalent non-destructive examination procedure recognized by the competent authority may be applied.

(f) The leakproofness test shall be performed in accordance with a procedure which is capable of indicating leakages in the containment system with a sensitivty of 0.1 Pa.l/s (10^{-6} bar·l/s).

(g) The water capacity of the packagings shall be established with an accuracy of +0.25% at a reference temperature of 15 °C. The volume shall be stated on the plate described in paragraph (6).

(5) With the exception of packagings for less than 10 kg of uranium hexafluoride, the competent authority of the country of origin shall, for every design type uranium hexafluoride package, confirm that it complies with the provisions of this

marginal and issue an approval. This approval may be part of the approval for a Type B package and/or for a package with fissile contents in accordance with Section IV of this Appendix.

(6) A plate made of non-corroding metal shall be durably attached to every packaging in a readily accessible place. The method of attaching the plate must not impair the strength of the pakkaging. The following particulars, at least, shall be marked on the plate by stamping or by an other equivalent method:

- approval number;
- manufacturer's serial number;
- maximum working pressure (gauge pressure) 1.4 MPa (14 bar);
- test pressure (gauge pressure) 2.8 MPa (29 bar);
- contents: uranium hexafluoride;
- capacitys in litres;
- maximum permissible filling mass of uranium hexafluoride;
- tare mass;
- date (month, year) of the initial test and the most recent periodic test;
- stamp of the expert who performed the test.

(7) (a) The uranium hexafluoride must be in solid form when transported.

(b) The degree of filling shall only be such that the capacity is not more than 95 % filled at 121 °C.

3771 (contd)

(c) The cleaning of pakkagings shall be performed only by a suitable procedure.

(d) The execution of repairs is permissible only in accordance with design and manufacturing programmes laid down in writing. Repair programmes require the prior approval of the competent authority.

(e) Uncleaned empty packagings shall be as tightly closed, during transport and intermediate storage, as when full.

(f) For maintenance, a programme approved by the copetent authority shall be operated.

(8) Packagings constructed in accordance with the united States Standard ANSI N 14.1 - 1982 [12] or equivalent, may be used, with the consent of the competent authority concerned,

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[12] ANSI N 14.1 - 1982 published in 1982 and obtainable from the American National Standards Institute, 10430 Broadway, New York, Ny 10018.

if the tests specified in these standards have been performed by the expert named therein and continue to be performed and certified in agreement with the competent authority in accordance with paragraph (4) c).

FIRE TESTING OF BARE URANIUM HEXAFLUORIDE CYLINDERS

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ABSTRACT

In 1965, the Oak Ridge Gaseous Diffusion Plant (ORGDP), now the K-25 Site, conducted a series of tests in which bare cylinders of uranium hexafluoride (UF_6) were exposed to engulfing oil fires for the U.S. Atomic Energy Commission (AEC), now the U.S. Department of Energy (DOE).[1] The tests are described and the results, conclusions, and observations are presented. Two each of the following types of cylinders were tested: 3.5-in.-diam × 7.5-in.-long cylinders of Monel (Harshaw), 5.0-in.-diam × 30-in.-long cylinders of Monel, and 8-in.-diam × 48-in.-long cylinders of nickel. The cylinders were filled approximately to the standard UF_6 fill limits of 5, 55, and 250 lb, respectively, with a U-235 content of 0.22%. The 5-in.- and 8-in.-diam cylinders were tested individually with and without their metal valve covers. For the 3.5-in.-diam Harshaw cylinders and the 5.0-in.-diam cylinder without a valve cover, the valves failed and UF_6 was released. The remaining cylinders ruptured explosively in time intervals ranging from about 8.5 to 11 min.

INTRODUCTION

The AEC's Operating Arm, now the U.S. Department of Energy, and Regulatory Arm, now the U.S. Nuclear Regulatory Commission (NRC), and the U.S. Interstate Commerce Commission (ICC), now the U.S. Department of Transportation (DOT), adopted parts of the 1961 International Atomic Energy Agency (IAEA) Regulations for the Safe Transport of Radioactive Materials. The effective date of the rules was July 1, 1968. The concept of what are now Type B packages, which were required to meet the condition of the hypothetical accident (see Appendix), was introduced. Fissile material which includes UF_6 enriched to greater than 1% U-235 would require Type B packaging. In 1964, the ORGDP initiated a test program to develop a family of UF_6 packages which could qualify as Type B packages. Earlier tests with bare cylinders involved drops from heights of 30 ft (9 m) onto an "unyielding surface," drops from 40 in. (1 m) onto a piston, and hydrostatic tests to failure at ambient temperatures.[2] The fire tests were conducted to determine the mode of cylinder failure, time available for fire fighting, and the contamination from this type of UF_6 release. Results indicate that the UF_6 can be released both with and without an explosion. It appears due to the limited time available before the explosion occurs when a bare cylinder is engulfed in an oil fire, fire fighting is not feasible. On the other hand, if the cylinder is <u>not</u> so engulfed, fire fighting could be initiated. While some contamination, both airborne and surface, was detected after the tests, the bulk of uranium was widely disseminated and was not readily detectable.

TEST FACILITY

The tests were conducted at a site which is located within the DOE reservation in Oak Ridge, Tennessee. Equipment included the following:

+ Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

1. Two concentric open-top tanks, 8½ ft and 10½ ft diameter and 30 in. deep. Test cylinders were positioned on the center tank with their longitudinal center lines parallel to the ground. Diesel fuel was used in both tanks, with the oil in the outer tank to provide better temperature control. The fire was also more engulfing.

2. A roofed viewing stand was installed about 200 ft from the oil tanks. It was constructed of ¼-in.-thick steel plate welded to railroad rails. Supports were embedded in concrete in 4½-ft-deep holes.

3. A 15-ft-wide barricade consisting of railroad rails and heavy steel grating and welded to inclined rail supports was positioned adjacent to the tanks and between the tanks and the observation barricade. A smaller barricade was positioned between the tanks and the nearby woods to prevent hot fragments from entering the woods. Steel panels also protected instrumentation and the power supply.

4. A manned fire pumper was available to extinguish the oil fire at the completion of each test. Later a foam generating system was successfully used to extinguish fires.

SAFETY CONTROL

The test location was selected due to its remote location from other Oak Ridge installations. Access was controlled by the AEC Patrol. Radio contact was maintained with the plant facilities and the AEC Patrol. The number of personnel at the viewing site was limited for each test. Other visitors and personnel assisting were at sites at least 800 ft away. Advance notice was provided to ensure that no activities which would be affected by the tests were underway near the site. Gas masks and safety helmets were required for test personnel.

TEST PROGRAM

Table 1 summarizes the test program and results.

OBSERVATIONS/CONCLUSIONS

1. The fire tests confirmed that base UF_6 cylinders up to 8 in. diameter can rupture with explosive force when exposed to a thermal source.

2. When a bare UF_6 cylinder is exposed to an engulfing fire, there is probably insufficient time for fire fighting.

3. The explosions from UF_6 are probably no more severe or hazardous than those due to similar chemical or gas explosions.

4. Health physics monitoring indicated that UF_6 and its reaction products were widely dispersed by the resultant explosion and heat.

   Contamination patterns are influenced by the magnitude of the fire and wind velocity and direction shifts.

5. For cylinders up to 30 in. in diameter and containing U-235–enriched UF_6, protection is required to preclude loss of containment for the regulatory thermal exposure at 1475°F for 30 min.

SUMMARY

The fire testing programs of bare UF_6 cylinders were useful in establishing packaging for safe transport in order to meet regulatory requirements. Limitations on fighting fires involving bare UF_6 cylinders were determined. In event of an explosion, the UF_6 and its reaction products are expected to be widely disseminated.

APPENDIX

The Type B requirements (hypothetical accident test series from AEC Manual Chapter 0529, Safety Standards for the Preparation of Radioactive and Fissile Material for Transportation, August 22, 1966) were as follows:

1. Free drop of 30 ft onto a flat, essentially unyielding horizontal surface.

2. Free drop of 40 in. striking the end of 6-in.-diam piston mounted on an essentially unyielding horizontal surface.

3. Exposure for 30 min within a source of radiant heat having a temperature of 1475°F and an emissivity coefficient of 0.9 or equivalent.

4. Immersion in water for 24 h to a depth of at least 3 ft.

REFERENCES

1. Mallett, A. J., ORGDP Container Test and Development Program Fire Tests of UF_6-Filled Cylinders, Report K-D-1894, January 12, 1966.

2. Mallett, A. J. and Wheatley, S. J., Fissile Material Container and Packaging Development and Testing Program, Report K-1661, April 1, 1966.

Table 1. Fire Tests of Bare UF_6 Cylinders

Test No.	Cylinders No.	Dimensions (in.)	Quantity UF_6 (lb)	Failure Time (min)	Failure Mode
1	2	3.5 × 5.7	5	(A) 4 (B) 6	Valve* Valve**
2	1	5.0 × 30***	55	10	Explosion
3	1	8.0 × 48***	249	10½	Explosion
4	1	5.0 × 30****	53	10	2 Valves*****
5	1	8.0 × 48****	245	8½	Explosion

* Plastic Valve Seat
** Metal Valve Seat
*** With Valve Cover
**** Without Valve Cover
***** Both Valves failed; Part of Valve Eroded; Stem & Cap Missing

MODELLING OF THE THERMAL BEHAVIOUR OF 48 INCH CYLINDERS

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ABSTRACT

This paper describes the current state of the analytical models being developed by BNFL to improve the understanding of the response of Uranium Hexafluoride containers engulfed in a fire. Details are given of the modelling methods used and physical processes simulated, together with some predictions from the models. Explanations for the differences between the predictions are presented as well as an outline for future development of the models.

INTRODUCTION

Uranium Hexafluoride (UF6) is an intermediate in the fuel cycle and is transported by many international nuclear companies including BNFL. It is transported in large capacity type 30 or 48 containers. The type 48 container is a steel pressure cylinder, about 1.2m diameter and 2.4m length, containing 12,500 kg of UF6. The cylinders are carried on flat bed trailers or in ISO containers. Natural, depleted and enriched UF6 is transported by BNFL to and from the Springfields and Capenhurst sites to Europe, the USA, Russia and Japan.

The offsite movements are currently regulated by the IAEA, International Modal Documents and ANSI design Standards, amongst others. During 1987 the IAEA initiated a review of the current regulations that cover the chemical hazards of an accidental release of UF6, and made recommendations for additional regulatory requirements and research into aspects of the transport operations. Of the recommendations, further work into the response of the containers to a fire test was suggested.

Under the auspices of the IAEA, an international collaborative programme is being organised with the objective of arriving at an agreed thermal model of the response of UF6 containers to a fire test. The programme includes theoretical and experimental work. Small scale experiments, to be carried out in the US, are aimed at determining UF6 behaviour/properties and the effects of the fire on the container filling/emptying valve. It is planned to conduct near full scale tests on a section of a type 48 container filled with UF6 and exposed to fire temperatures in a facility being constructed in France.

In order to demonstrate compliance with the proposed revised regulations and as part of the collaborative programme, BNFL are developing calculational models of the container, including prediction of temperature transients in the UF6 and the consequent phase changes and pressure transients. UF6 exhibits complex physical and phase behaviour. Melting of the solid is accompanied by an abnormally large reduction in density (about a third reduction) and consequent increase in volume. Models of the container and UF6 are being developed using both finite element and analytical methods taking into account the sublimation, vaporisation and melting processes. The finite element modelling is refined by adaptive remeshing, where automatic mesh refinement follows the progress of the melt front.

Associated studies include the important aspect of the integrity of the container. Tests have been conducted in the US to determine failure pressures of different container designs by pressurising them at ambient temperature - this data has been extrapolated to higher temperatures using finite element modelling methods. Using the internal pressure transient and container materials data, the potential failure of a container in a fire test can be predicted. The planned near full scale practical tests will provide valuable supporting validation data.

OVERVIEW OF CURRENT ASSESSMENT

Complex problems are posed by the behaviour of UF6 when it is contained within a sealed vessel and exposed to the high heat fluxes of an engulfing fire.

The heat transfer, internal pressure generation and mechanical failure of the vessel are all aspects that must be addressed by an assessment. Each aspect exhibits some degree of dependence on the others; for example, the pressure generated within the vessel is a function of the UF6 temperature which itself is pressure dependent since the heat transfer processes used in its evaluation include the value of vapour density. In addition to the difficulties involved in producing a mathematical model of the various processes, there are uncertainties in our understanding of the physics of the problem and also uncertainties in the physical properties of UF6. It was decided that to attempt a fully coupled model solution would be an unrealistic objective at present, and so a group of computer models are being developed to handle the aspects of heat transfer and pressure generation separately from vessel failure. These models, together with additional experimental data, provide a means of gaining an insight into the problem and form a good basis for a more comprehensive solution.

The thermal response of the UF6 vessel is largely independent of any distortion or failure of the containment shell. In view of this, three preliminary assessment models have been developed. Two independent thermal models, determining the transient temperature and pressure response to the fire, are used. The first of these, BURST2, is a semi-analytical code that incorporates all the known physical processes in a simplified geometrical representation of the container. This code is used to investigate the uncertainties in the physics of the model and in the material properties.

The second thermal model was initiated to provide more detailed information on container shell temperatures, (needed in the failure assessment model), and the implications of using simplifying geometrical transformations in the lumped parameter model. This second model is a two dimensional finite element simulation using an adaptive meshing code and is also intended to form the basis for the final assessment strategy.

The pressure and shell temperature results from the thermal models are used, in the vessel failure calculation, to produce the container yield, *(burst)* pressure values. These burst pressures are continuously compared with the container pressures - as predicted by the model - and container failure occurs when the burst pressure and container pressure become equal. An alternative failure mode, caused by the expansion of UF6 on melting, is that of hydraulic over-pressurisation, which occurs when the vapour space vanishes

STRUCTURAL MODELS

The calculation of container burst pressure is fundamental to the analysis of Uranium Hexafluoride containers. The problem of defining container burst pressure has been addressed by several people and has produced a variety of answers. Some typical predictions of burst pressure generated within BNFL are shown in figure 1. These indicate the wide range of values and the importance of accurately representing the temperature profile around the container. For the work reported in this paper, the container failure criterion has been taken as the onset of membrane yield stress and the yield stress used is that defined by ASME 8 for A516 steel, grade 65.

Initial estimates for the bursting pressure of a UF6 container were calculated using a simplistic finite element model of a plain cylinder at uniform temperature. Over the temperature range 25°C to 700°C the model predicted yield as indicated by curve A in figure 1.

Minor refinement of the uniform temperature model, by incorporation of temperature dependent material properties and the application of a realistic, circumferentially-varying temperature profile to the container, produced values for the onset of yield depicted by points B and C in figure 1.

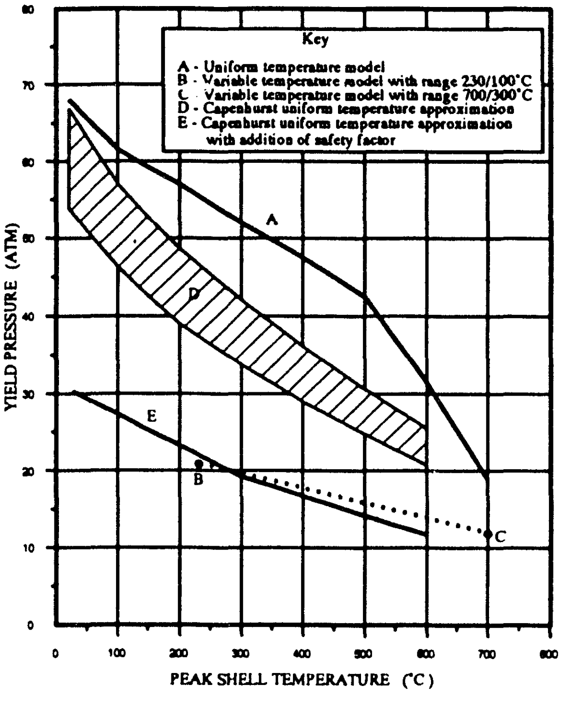

Figure 1. Predictions of container burst pressure

Finite element model. For essentially the same initial conditions, the thermal response predicted by the finite element program is similar to that predicted by the lumped parameter model. Initially, heat input from the fire causes the solid to sublime with liquid formed at a later stage in the transient. However, sublimation is predicted to terminate much sooner than in the lumped parameter simulation so that the container wall temperature does not rise above the critical value before liquid is formed. Consequently, the liquid wets the wall and nucleate boiling heat transfer is predicted. Because the code models conduction only, nucleate boiling and the convection within the liquid are both simulated by a conductivity enhancement factor. The nucleate boiling process enables substantially more heat to enter the container and around 88% of the solid UF6 is melted by the end of the fire transient. The pressure transient for this case is shown in figure 6 and it can be seen that, although the pressure predictions from the two models are almost numerically equal at 20 minutes into the transient, the finite element model predicts an almost exponential rise after that time whereas the lumped parameter model shows only a slight increase in the rate of pressure rise.

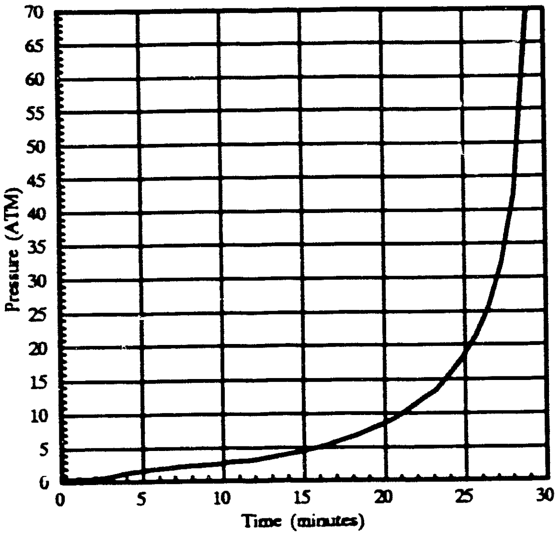

Figure 6. Pressure prediction from finite element model

Additionally, the finite element model has been used to investigate the sensitivity of the solution to some of the heat transfer methods and formulations used. From the results produced so far, the most significant parameter affecting the predicted vapour pressure is the enhancement factor applied to the liquid conductivity. For example, if liquid convection is simulated by enhancing the liquid conductivity by 10 rather than 100, then after 30 minutes of heating, the absolute pressure generated within the container is approximately ten times the previously predicted value.

Other parameters influencing the pressure predictions to a lesser degree are the radiation and convection across the ullage space. Without this heat transfer mechanism, the mean liquid surface temperature is reduced and the predicted vapour pressure, 20 minutes into the transient, is only 25% of that when radiation and convection heat transfer across the ullage are simulated.

Rupture results. Both heat transfer models currently predict container vapour pressures that cause failure due to over pressurisation within the heating phase. However, because of the uncertainties in the models an accurate failure time can not be given, and it is possible that the container may survive the fire. The prudent view, at present, is of a failure to meet the fire requirement.

GENERAL DISCUSSION

BNFL have not modelled UF6 containers previously and in order to participate fully in any collaborative venture need to be conversant with the problems inherent in modelling the physical phenomena occurring within heated UF6 containers. The analytical models presented in this paper have therefore been developed with the aim of testing the mathematical methods and initiating the BNFL modellers into the intricacies of UF6, rather than producing definitive solutions to the thermal response of a UF6 container. As the models are still being developed, this paper represents only a progress report and any conclusions stated or implied should be treated with caution.

Notwithstanding the above, the information derived from the analyses to date has indicated the requirement to model the initial heating stage, say over the first 50 seconds, with great care. The presence or absence of a small gap between the container wall and the solid UF6 is crucial in determining the outcome of the ensuing transient. By explicit inclusion of the gap in the lumped parameter model, the poor heat transfer properties of the gap allow high container temperatures to develop before melting begins. When melting starts, the high wall temperatures produce a film-boiling condition which persists throughout the fire.

However, in the finite element model where the vapour gap is not explicitly defined, sufficient heat is transferred into the solid to enable liquid to form early in the heating transient. Once liquid has formed and is in contact with the wall, nucleate boiling can transfer sufficient heat to maintain the wall below the critical value. As the liquid level extends up the wall sufficient heat is extracted to bring the wall temperature below critical and allow continued nucleate boiling.

It has also been noted during the development of these models that even though a container may be predicted to survive the 30 minute fire transient without bursting, the period of hazard has not ended. In fact it is possible, dependent on initial fill level, to cause a hydraulic rupture of the container some 10 minutes after the fire source is removed. This is due to the continued melting of solid UF6 (with volume increase) by heat stored in the liquid UF6.

FUTURE DEVELOPMENTS

As part of the continuing programme of extension and refinement of the calculational tools developed so far, a more comprehensive investigation into the differences between the predictions of the two thermal models is to be undertaken. Where suitable test data is available, experimental conditions will be simulated using the mathematical models with a view to validating the computational methods and assumptions.

The temperature variation around the container wall, especially near the liquid/vapour interface, can now be obtained from the finite element model. Incorporation of this temperature profile into the current stress model will maximise the information that can be extracted. The potential for providing more detailed stress distributions by conversion of the plain cylinder stress model to three dimensions so that the stiffening ribs and end effects can be incorporated will be investigated.

Development of the lumped parameter model to include a heat transfer mechanism on the underside of the container or conversion to a cylindrical geometry will remove one of the most significant deficiencies of this current model. Other potential developments identified are the absorption of heat by the solid and the inclusion of condensation on the inside of the container during cool-down. In the finite element model, consideration will be given to separating the liquid film heat transfer coefficient from the convection process within the bulk liquid. This will enable differing conduction enhancement factors to be applied.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. R W Lewis, R W Sze, Y Zheng, H C Huang and D T Gethin of the University College of Swansea for their collaboration in development of the finite element modelling programme and B Creswell of BNFL Capenhurst for his collaboration and guidance in the development of the lumped parameter modelling programme.

HIGH TEMPERATURE EXPERIMENTS ON A 4 TONS UF6 CONTAINER

TENERIFE PROGRAM

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ABSTRACT

The paper presents an experimental program (called TENERIFE) whose aim is to investigate the behaviour of a cylinder containing UF6 when exposed to a high temperature fire for model validation.

Taking into account the experiments performed in the past, the modelization needs further informations in order to be able to predict the behaviour of real size cylinder when engulfed in a 800°C fire, as specified by the IAEA regulation.

The main unknowns are related to (1) the UF6 behaviour beyond the critical point, (2) the relationship between temperature field and internal pressure and (3) the equivalent conductivity of the solid UF6.

In order to investigate these phenomena on a representative way it is foreseen to perform experiments with a cylinder of real diameter, but reduced length, containing 4 tons of UF6. This cylinder will be placed in an electrically heated furnace.

A confinement vessel prevents from any dispersion of UF6. The heat flux delivered by the furnace will be calibrated by specific tests. The cylinder will be changed for each test.

I - INTRODUCTION

Over the past few years, the International Atomic Energy Agency has been working on establishing regulation for UF6 transportation which should take into account chemical and radiological hazards. This action took a concrete form with the guide TEC - DOC 587-2 published by the IAEA in 1989 and which will serve as a basis for the next issue of the IAEA regulation for the transport of radioactive materials (Safety Series N° 6), planned for 1995.

This guide specifically provides that packagings for the transport of non-fissile products (enrichissment less than 1%), such as the type 48Y cylinder, must be able to resist in the fire conditions identical to these related to containers for radioactive materials of type B, 800°C for half an hour, which has not yet been unequivocally demonstrated. This is the reason for which we consider that studies are needed to develop a model for the thermal behaviour of UF6 and for which an experimental program (called TENERIFE)

II - OBJECTIVES

To know the input of the future thermo-mechanical code we have to get a better understanding of the thermo-physical evolution of the UF6 which pressurizes the container. This evolution is function of :
a) the heat transfer rate from the fire to the container
b) the UF6 behaviour in the container

The first point may proceed from the type B regulation requirements (about 54 kW/m^2) or real heat flux during experimental fire (120 kW/m^2 in ref (1)). Though this external boundary conditions are not specific to UF6 it is a very important unknown of the problem.

The actual main incertitude is more related to the second point which concerns heat transfer itself inside the cylinder depending on the phenomenology of UF6 liquefaction and vaporization.

Malett experiments ref (2) are the only UF6 heating in a fire. The analysis and extrapolation to a 48Y container in fire during 30 minutes gives a great scattering in the results in terms of time and cause of rupture :
. Williams ref (3) 28 mn hydraulic rupture
. Park ref (4) 22 mn rupture due to vapor pressure
. Shiomi and al ref (5) and (6) no rupture
. Duret ref (7) and (8) no rupture (hydraulic rupture at 40 mn)

This dispersion come from the scale effect from 100 kg of UF6 to 12 tons.

It is the main reason for which we decide to respect two important parameters in the TENERIFE experiment :

a) external temperature level

b) realistic internal diameter

a) external temperature level

At the beginning the heat transfer to UF6 material is limited by the presence of a gap between the steel wall and the UF6. In order to get a picture of the events we will make use of a calculation based on our model developped for a 48Y container ref (8) These calculations indicate that the steel temperature is higher than 500°C.

The transfer will come from conduction heat transfer (unknown : the contact surface) and also by radiation (unknown: the internal emissivity). On the other hand, this temperature level is much higher than the critical temperature of UF6 : thus the liquid UF6 should not wet the hot steel and a vapour film may separate the liquid UF6 from the steel surface.

If this vapour film is stable, this film acts as a thermal resistance and will delay the heating up and the melting of UF6. Thus the time to rupture would be increased,

If not, the heat transfer to UF6 should be increased, which reduces the time to rupture.

The stability of this film will, in fact, depend on the time at which UF6 will really start to melt. This will depend on the quality of the heat transfer in the solid UF6. If transverse conduction in the solid UF6 is taken into account, the temperature distribution in the solid will not be uniform and the melting temperature will be reached near the steel wall sooner as precalculated with the assumption of uniform temperature distribution (which is in the model we developed).

b) Realistic internal diameter

Solid UF6 is porous and UF6 has a high vapour pressure ; therefore heat transverse exchange in solid UF6 is related not only to conduction but also to vapour convection (evaporation in hot sites and condensation in cold sites). It is a matter of fact that the experiments give "equivalent conductivities" which are much higher than the conductivity of the pure solid.

But what is the validity of the known "equivalent conductivity" derived from low temperature low diameter experiments when real cases (high steel temperatures, high diameters) are considered ? It is possible that phenomena like porosity occlusions may appear for high diameters which may not exist for lower diameters.

III - DESCRIPTION OF THE EXPERIMENTAL PLANT

III.1 Working principle

The experimental container which contains about 4 tonnes of UF6, is put inside a radiant furnace. It is heated under vacuum, in a fast transient, for a pre-defined time or until previously established thresholds are reached. The made measurements will lead to better understanding of heat transfers towards UF6 under these conditions.

To confine UF6 in case of a leak on the experimental container (1st barrier), container and furnace are enclosed in a vessel (2nd barrier) which is leak tight, under primary vacuum and under an absolute pressure equal to 6 bars (case of UF6 release). This vessel is equipped with facilities designed to recover any UF6 accidentally released in this volume (figure 5).

The third barrier consists of caisson J of a building 346, where the entire experimental rig is situated.

The test is run by remote control, from the caisson J control room, using fundamental test parameters which are associated with known threshold values :

- strain measured on the container surface, threshold of which corresponds to elastic limit of used steel,
- maximal temperature in UF6 mass with a threshold equal to 150°C,
- the pressure inside the container with a threshold equal to 14 bars.

III.2 Experimental container

The experimental container is used for filling, emptying, transport of UF6, and for carrying out the thermal tests.

It is planned to use one container for each thermal test. Each of them will be placed inside the experimental furnace where it is secured by its bottom jackets.

The container will be fabricated and checked as in the last edition of ANSI N 14-1 1987 (American National Standard Institute Inc : Packaging of Uranium Hexafluorure for Transport).

The experimental container consists of a cylindrical sleeve and of pressed ends (large radius cross section), both made of steel A 516 grade 70. The thickness is equal to 16 mm. Its minimal capacity is 1400 litres. Its external walls undergoes the same surface treatment (sand blasting and painting) as for 48Y containers.

the container (see figure 1) is equipped with :

- a stiffening ring

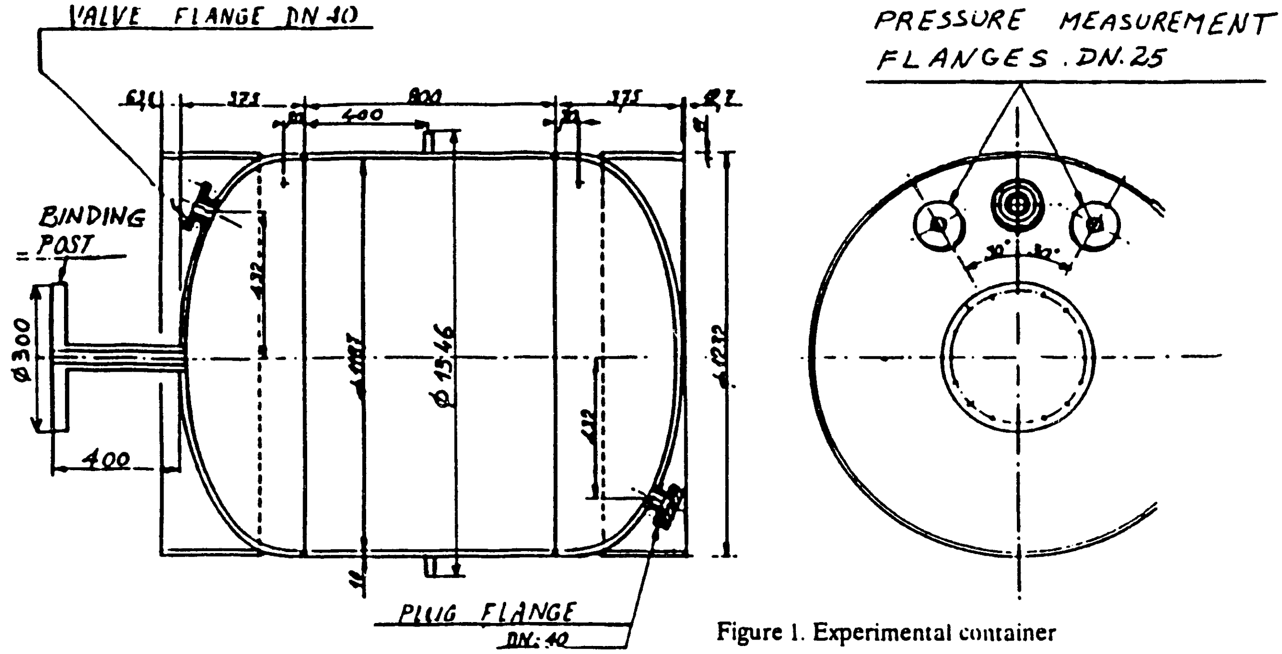


Figure 1. Experimental container

- bottom jackets, in which oblong holes are provided for handling,
- two protection hoods for instrumentation devices and valves during handling and transport.
- a flange on one of the two curved faces, for thermocouple crossing,
- two flanges for pressure measurements,
- one valve for filling and one for emptying and cleaning.

The maximale relative pressure is 14 bars and the calculated temperatures are + 120°C and - 40°C.
The proof pressure is 28 bars.

Its dimensions are :
- inside diameter : 1217 mm,
- length : 1550 mm (excluding flanges and curved face jackets).

III.3 Furnace

The furnace function is to apply to external walls of the UF6 container, heat fluxes of the order of 30 to 50 kW.m-2, under vacuum atmosphere.
It answers to the following working specifications :
- a fast transient (1000°C within about 4 minutes),
- four heating zones
  - . zone A or lower cylindrical part of the container,
  - . zone B or upper cylindrical part,
  - . zone C or front face,
  - . zone D or back face.

The furnace is positionned horizontally and consists of two half-shells which are fitted together along a median horizontal plane. A sketch is given on figure 2.

Its dimensions are :
- outside diameter : 2000 mm,
- length : 2400 mm.

The electrical power requirements is 500 kW which will be independantly regulated for each of the four zones by means of one or more sensitive probes for each zone.

Gas flow can be directed inside the space between container and furnace by mean of the cooling at the end of the test.

A calibration test will be performed to know the most precisely as possible the external heat low coming from the furnace.

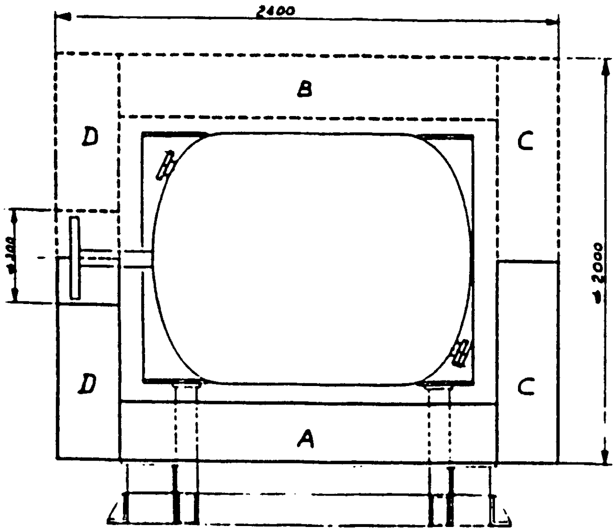


Figure 2. Furnace

For this a special container will be constructed. Similar to the UF6 container, externally painted, but empty, it will be simply rigged with about twenty thermocouples in the thickness of the wall. After that, it will be putted through different thermal conditions in the furnace.

From each thermocouple the temperature increasing measurements will give the heat flow with following method :

For example : if Te is the regulation temperature of the furnace, Fp the local heat flow at the point p depends on Te and Tp the steel temperature at p.

$Fp = r . Cp . e . dTp/dt$

e : steel thickness

r,Cp : density and thermal capacity

The transient measurements of Tp and dTp/dt will permit to obtain the external heat flow, which we will write eventually as :

$Fp = Eeq.S. ((Te+273)^4-(Tp+273)^4)$

Where Eeq (equivalent emissivity) is adjusted in order to reproduce the measured heat flow (if we establish that Eeq stays constant, or may be a function of Tp).

For inner emissivity, it seems necessary that wall has been in contact with UF6 in order to create the normal fluorure coating. We propose to cut a steel piece after a test with UF6 and perform a classical emissivity measurement on the sample at differents temperatures.

III.4 Instrumentation

Experimental measurements include those which are performed on the container to control the strain level and to measure temperature inside UF6 mass.

The number and position of the different measuring devices are as follows :

- 20 strain gauges and 10 thermocouples placed at locations on the external surface of the container (2 strain gauges in the quarter of a bridge) according to the results of a structural analysis.
- 2 pressure gauges connected to the flanges in the upper part of the container by mean of heated tubes in order to avoid solidification of UF6 inside (measuring range : 0-100 psia to 0-250 psia).
- 40 thermocouples installed inside the container as indicated on the figure 3 :

. 24 thermocouples (circles on figure 3) positionned on the middle right section of the container to measure temperature gradients near the wall and inside UF6.

. 16 thermocouples (arrows on figure 3) positionned against the wall to verify heating homogeneity.

Thermocouples will be positionned in the container before welding of the last bottom. In order to avoid any deformation during melting of UF6 they will be held vertically by mean of combs and grooved tubes, as described on figure 4.

Inside thermocouples come out of the container through a small diameter tube where they are brazed. There are connected, with the outside thermocouples, strain gauges and pressure gauges, on a binding-post which is offset from the container bottom at a distance of about 40 cm. With this arrangement, the heat transfer to the bottom of the container is only slightly modified.

Additional measurement devices are needed for plant thermodynamic state monitoring and for running the tests. These will include :

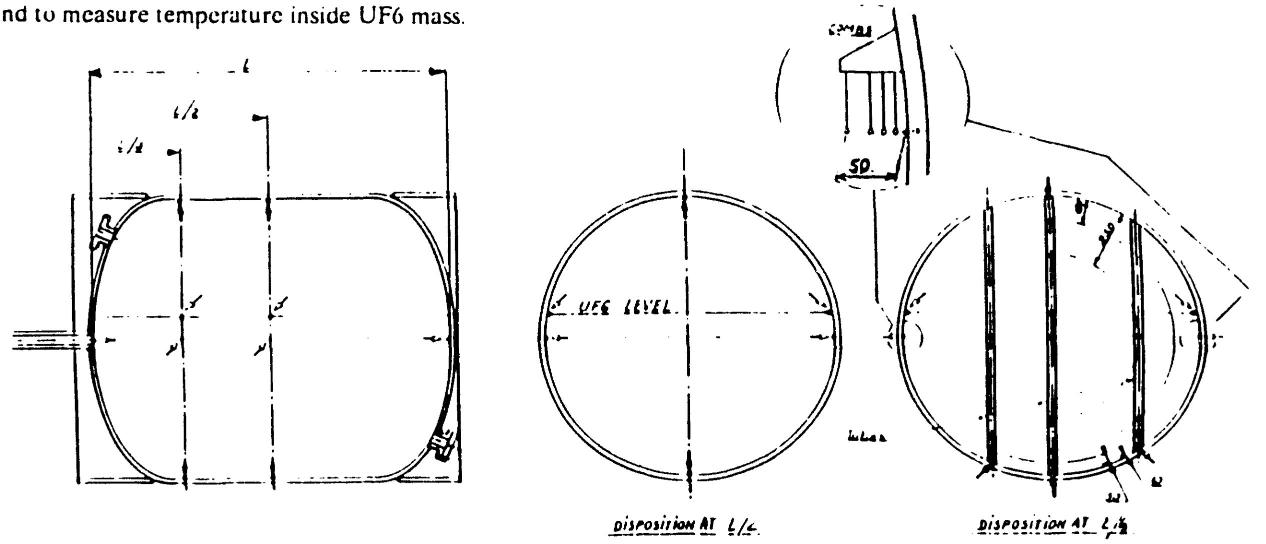


Figure 3. Measurement locations

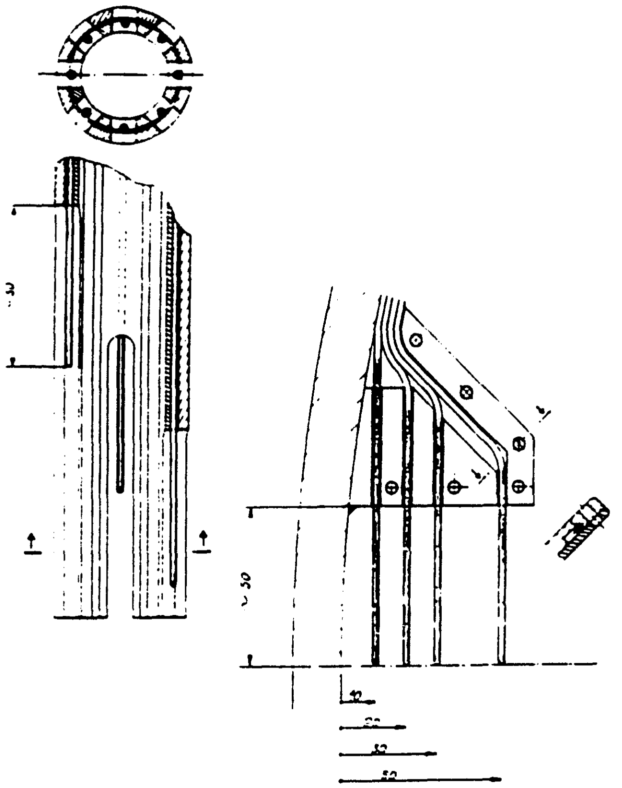


Figure 4. Thermocouple's supports

- thermocouples to control furnace operation,
- thermocouples dispersed in the free atmosphere inside the vessel,
- pressure gauges connected to the internal vessel volume.

During the UF6 filling of each container the previous thermocouples will be used; on an other hand the internal UF6 aspect and the level visualisation will be performed with a fiberscope after the cooling and aslo after every test in the furnace.

III.5 Experimental Vessel

Its function is to maintain UF6 confined in the case of a leak of the container . It is a plain steel vessel, 3,85 m long and 3.00 in diameter, consisting of a horizontal cylindrical sleeve and two curved ends ; its internal volume is about 21 m3 (figure 6).

The cover consisting of one of the curved ends, can be dismantled and is movable. Moving the cover involves completely opening the vessel to insert the experimental container and upper half-shell of furnace, and extracting them out between tests.

The vessel is designed to withstand an absolute pressure of 6 bars, reached in case of container rupture, and a primary vacuum of 1.10^{-2} to 5.10^{-1} torrs, required during thermal tests, and to support wall temperatures up to 200°C.

Measurements devices for plant thermodynamic state monitoring and running the tests, include thermocouples located in the free atmosphere inside the vessel, wall probes on the outside wall of the vessel, pressure gauges connected to the internal volume and a α detector connected with the vessel volume.

III.7 Caisson J

This experimental room, made of reinforced concrete, can withstand wall temperature equal to 130°C and an overpressure equal to 1 bar. Its walls are 1 meter thick and the dimensions are : 20mx15mx12mx = 3600m^3.

For thermal tests planned, ventilation outlet circuit which includes a very high efficiency filter box, is used to maintain an under-pressure of a few millibars inside the room. Gas temperature, pressure are measured inside the caisson, α detection devices are located inside the room and on the outlet circuit.

III.7 UF6 Recovery

Container burst with dispersion of all the UF6 quantity inside the vessel or UF6 smaller leak are detected by pressure increase or by means of an α detector. For the recovery of UF6, two principles are applied :

UF6 gaseous transfer by hot point cold point method, from the vessel to the 48Y container which is kept at about 15°C ;

residual UF6 hydrolysis with a large quantity of water : after which, gas and liquid effluents are neutralized with a potassium carbonate solution.

It is constituted of two parts :

. a 48Y container, connected to the vessel by means of a heating pipe with adjustment or shut off valves,

. an hydrolysis circuit with, above the vessel, wet air supply system, and below the vessel, released gas treatment and liquid efluents recovery.

These facilities will not be used during normal operation of the rig. However, as they are connected with the vessel, some of its components are taken into account during operation of the rig for the thermal tests.

III.8 Plant Control And Monitoring System

Test remote control and measurement recording

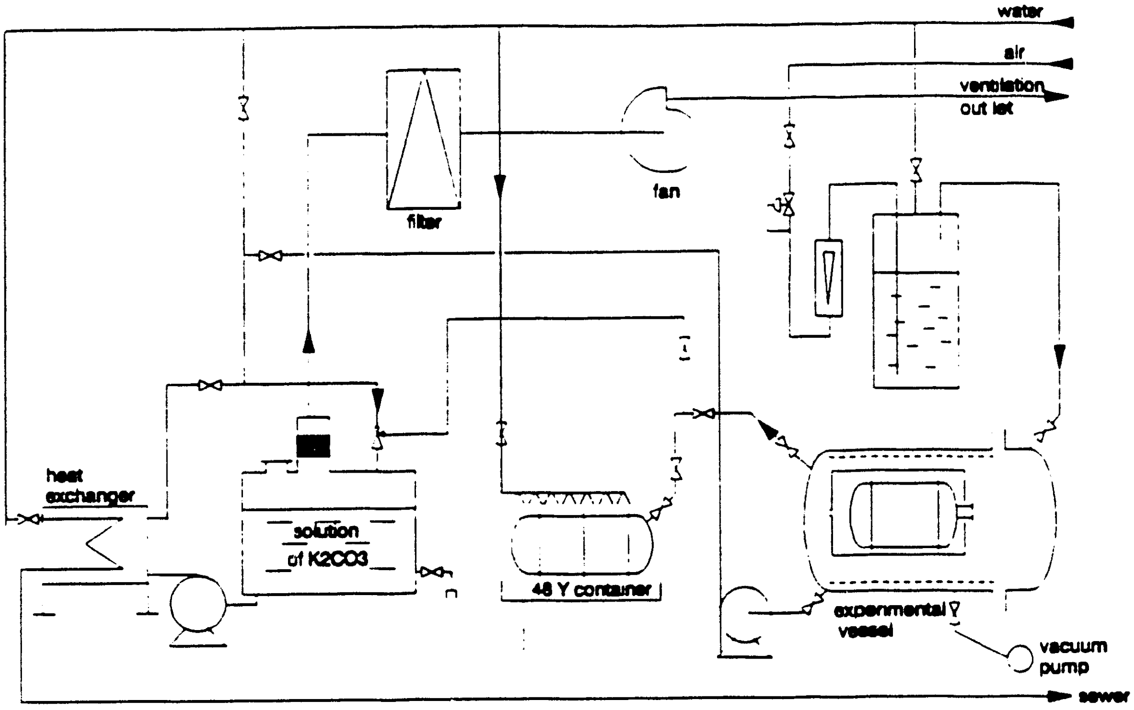
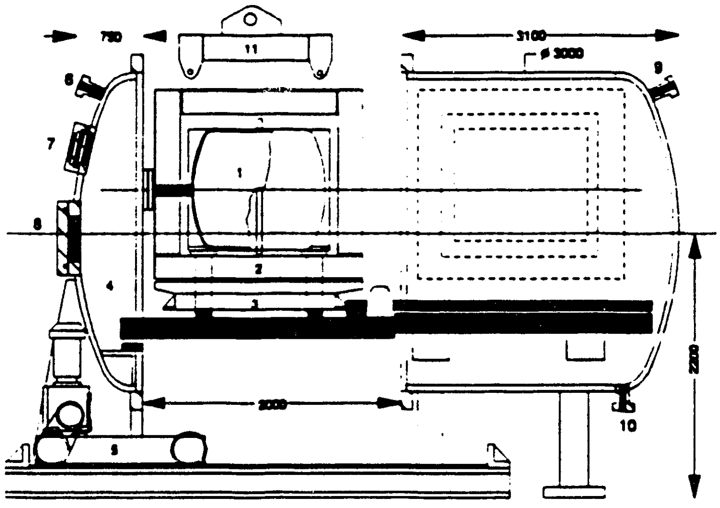


Figure 5. Schematic of experimental facilities



1 experimental container 2 electrical furnace 3 supporting structure 4 movable cover
5 truck for cover moving 6 to wet air supply system 7 view hole 8 tape for tight crossings
9 to 48Y container and effluents recovery circuit 10 to pump 11 rocking lever

Figure 6. Experimental vessel

are performed by means of a data recorder, which is situated in the monitor room of caisson J, and of mimic boards of the plant.

There are 120 readings including 88 temperatures, 10 strains and 5 pressures. Experimental readings are recorded at time intervals less than or equal to 1 second.

On the test mimic board, monitoring of test parameter are displayed :

- strain measured on the container surface, temperature in UF6 mass, the pressure inside the container,
- furnace temperature,
- temperature and pressure inside the experimental vessel,
- the signal from UF6 detection system inside the vessel.

III.9 Test Matrix

Test matrix (table 1) includes six tests :

- the first test is a calibration one with an empty cylinder which aims to determine the heat flux received by the experimental cylinder,
- the second test aims to investigate the general behaviour of the experimental container fed with liquid UF6 with total surface heating at 800°C, with special attention paid to "overshoot" effect at the end of heating time ; its consists of several separate heating phases with increasing duration ;
- two tests are performed with a container fed with liquid UF6, with total surface heating at 800°C ; heating durations are determined from second test results analysis ;
- one test aims to analyse the "end" effect and is performed with a container fed with liquid UF6, with cylindric surface heating at 800°C and with insulated curved ends ;
- one test is carried out with a container equipped with protective covers.

Optional tests are considered to investigate :

- The behaviour of the valve,
- the effect of filling with gaseous UF6 which changes initial distribution of matter inside the container, - the effect of the filling rate.

Tests at higher temperature (1000°C) would also be possible.

Detailed studies of the project began in 1991 ; realization of the experimental facilities will last two years and the first test will be performed at the beginning of 1994.

Table 1. Test matrix

Test number	Furnace tempera-ture °C	Heating duration minutes	type of filling	heated surface	remark
1			empty container		calibration test
2	800	5 10 15 X	liquid	total	
8	800	X/2	liquid	total	
4	800	X	liquid	total	
5	800	X	liquid	cylindric	
6	800	X	liquid	total	with protectives covers

REFERENCES

(1) J.J Gregory N.R Keltner thermal measurements in a large pool fires Trans of the ASME Vol. 111, May 1989 pp 446 to 454

(2) A.J MALLETT ORGDP Container test and development program : Fire tests of UF6 filled cylinders Union Carbide Corporation, K D 1894 Oak Ridge, Tennessee, January 1966

(3) W.Reid Williams Investigation of UF6 behaviour in a fire. UF6 Safe Handling Processing and Transporting CONF 880558 - May 24-26, 1988 Oak Ridge, Tennessee

(4) S.H Park Personnal communication

(5) H. Yamakawa S. SHIOMI Safety evaluation of the transport container for natural UF6 under fire accident CONF 880558 - May 24-26, 1988 Oak Ridge, Tennessee

(6) H. Abe and al. The integrity verification tests and analyses of a 48Y cylinder for tansportation of natural UF6 PATRAM 1989, Washington June 11 16 1989

(7) B. Duret J. Bonnard Behaviour of Uranium Hexafluoride Package in Fire - comparaison of calculations with Fire Experiment. PATRAM 83

(8) B. DURET P. WARNIEZ Thermal tests on UF6 containers and valves modelisation and extrapolation on real fire situations. UF6 Safe Handling Processing and Transporting CONF 880558 - May 24-26, 1988 Oak Ridge, Tennessee

Poster Sessions

UF_6 CYLINDER FIRE TEST

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With the increasing number of nuclear reactors for power generation, there is a comparable increase in the amount of UF_6 being transported. Likewise, the probability of having an accident involving UF_6-filled cylinders also increases. Accident scenarios which have been difficult to assess are those involving a filled UF_6 cylinder subjected to fire. A study is underway at the Oak Ridge K-25 Site, as part of the U.S. DOE Enrichment Program, to provide empirical data and a computer model that can be used to evaluate various cylinder-in-fire scenarios. It is expected that the results will provide information leading to better handling of possible fire accidents as well as show whether changes should be made to provide different physical protection during shipment. The computer model being developed will be capable of predicting the rupture of various cylinder sizes and designs as well as the amount of UF_6, its distribution in the cylinder, and the conditions of the fire.

The empirical data is to be obtained in a series of experiments involving an instrumented 12-inch cylinder filled to the design fill level with UF_6. Heat will be applied to the bottom of the cylinder when it is in the vertical position and then in the horizontal position. Heat transfer coefficients will be determined from surface and internal temperature profiles at various heat fluxes as a function of time. The two position heating tests should provide information to determine the effect of liquid UF_6 on the heat transfer rate and to show the porosity of the solid UF_6 structure. The thermal tests will be conducted in an autoclave which will serve as a containment vessel in the event of any possible UF_6 leakage.

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DEVELOPMENT OF A UF_6 CYLINDER TRANSIENT HEAT TRANSFER/STRESS ANALYSIS MODEL

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ABSTRACT

A heat transfer/stress analysis model is being developed to simulate the heating to a point of rupture of a cylinder containing UF_6 when it is exposed to a fire. The assumptions underlying the heat transfer portion of the model, which has been the focus of work to date, will be discussed. A key aspect of this model is a lumped parameter approach to modeling heat transfer. Preliminary results and future efforts to develop an integrated thermal/stress model will be outlined.

ACKNOWLEDGEMENTS

Other participants in the development of this model include J. C. Anderson, C. P. Kerr, and G. H. Llewellyn of the Energy Systems Analysis Department and B. W. Reimer of the Structural Analysis Department of Process Engineering.

CYLINDER MONITORING PROGRAM

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Cylinders containing depleted uranium hexafluoride (UF_6) in storage at the Department of Energy (DOE) gaseous diffusion plants, managed by Martin Marietta Energy Systems, Inc., are being evaluated to determine their expected storage life. Cylinders evaluated recently have been in storage service for 30 to 40 years. In the present environment, the remaining life for these storage cylinders is estimated to be 30 years or greater. The group of cylinders involved in recent tests will continue to be monitored on a periodic basis, and other storage cylinders will be observed as on a statistical sample population. The program has been extended to all types of large capacity UF_6 cylinders.

Two methods of determining cylinder longevity are presently being employed: 1) nondestructive ultrasonic thickness (UT) measurements on selected in-service UF_6 cylinders, and 2) corrosion studies on coupons made from unserviceable storage cylinders.

Ultrasonic thickness measurements are taken on a statistically significant number of large capacity storage cylinders while they contain depleted material (i.e., in-service cylinders). Measurements for each cylinder consist of 36 readings; (16 readings on the shell, and 10 readings on each head). These measurements are taken in specific locations where high corrosion rates have been observed in long-term storage. Each location is prepared by sanding an approximate one-inch diameter area to facilitate precise reproducible UT readings. The corrosion rate is first determined by subtracting the lowest actual thickness from the base line (original) thickness and dividing by cylinder age (years). The remaining life in years is then determined by subtracting the minimum required wall thickness allowable from the lowest actual wall thickness and dividing by the calculated corrosion rate. The minimum required wall thickness is obtained from the American National Standards Institute, (ANSI), N14.1 "Uranium Hexafluoride Packaging for Transport," and from ORO-651, "Uranium Hexafluoride: Handling Procedures and Container Descriptions," which require cylinders to be removed from service when their shell thickness has decreased below a specified value, depending on the type of cylinder.

Coupon corrosion studies are designed to determine corrosion rates of cylinder steels exposed to long-term atmospheric weathering. The coupons involved in these tests, steel ASTM A285 and A516 are being obtained from existing UF_6 storage cylinders. Grade A36 coupons are cut from structural steel plates. The test coupons are situated in direction-oriented environmental racks in present storage yard locations at each of the DOE-managed gaseous diffusion plant sites. These coupons are used to study the effects of surface chemistry and microstructure on the weathering of exposed samples to determine reaction kinetics and metallurgical effects. The tests are accomplished in accordance with the provisions of ASTM G15-85a, "Standard Terms and Definitions Relating to Corrosion and Corrosion Testing." Sample coupons in sizes of four-inch x six-inch and three-inch x five-inch are to be monitored for periods of up to 16 years, which will require the periodic removal of coupons for evaluation. Each coupon is prepared and weighed prior to setting in racks, and removals are scheduled at intervals of 1 year, 2 years, 4 years, 8 years, and 16 years. Corrosion rates will be determined by weighing the exposed coupons for material loss through weathering and oxidation.

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REACTIONS OF ALUMINUM WITH URANIUM FLUORIDES AND OXYFLUORIDES

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ABSTRACT

Every 30 to 40 million, operating hours a destructive reaction is observed in one of the –4000 large compressors that move UF_6 through the gaseous diffusion plants. Despite its infrequency, such a reaction can be costly in terms of equipment and time.

Laboratory experiments reveal that the presence of moderate pressures of UF_6 actually cools heated aluminum, although thermodynamic calculations indicate the potential for a 3000-4000°C temperature rise. Within a narrow and rather low (<100 torr; 1 torr = 133.322 Pa) pressure range, however, the aluminum is seen to react with sufficient heat release to soften an alumina boat.

Three things must occur in order for aluminum to react vigorously with either UF_6 or UO_2F_2.

1. An initiating source of heat must be provided. In the compressors, this source can be friction, permitted by disruption of the balance of the large rotating part or by creep of the aluminum during a high-temperature treatment. In the absence of this heat source, compressors have operated for 40 years in UF_6 without significant reaction.

2. The film protecting the aluminum must be breached. Melting (of UF_5 at 620 K or aluminum at 930 K) can cause such a breach in laboratory experiments. In contrast, holding Al samples in UF_6 at 870 K for several hours produces only moderate reaction. Rubbing in the cascade can undoubtedly breach the protective film.

3. Reaction products must not build up and smother the reaction. While uranium products tend to dissolve or dissipate in molten aluminum, AlF_3 shows a remarkable tendency to surround and hence protect even molten aluminum. Hence the initial temperature rise must be rapid and sufficient to more reactants into a temperature region in which products are removed from the reaction site.

INTRODUCTION

The Uranium-235 isotope is enriched by passing the gaseous uranium hexafluoride through many barriers (in a cascade) in such a fashion that the lighter isotope is concentrated at one end of the plant. The heavier isotope, U-238, is, conversely, concentrated at the bottom of the plant. The gas, UF_6, is a potent fluorinating agent and can, thermodynamically, react with a large evolution of heat which can be very destructive of the equipment, and consequently costly, in terms of dollars and potential harm to personnel and environment.

Such a destructive reaction is infrequent, however. In the 43 years since the first of the three plants went on stream, only 40 incidents have been counted that were related to interaction of the UF_6 with the aluminum construction material. Translated into operating hours of the compressors, the average time between incidents is 30-40 million compressor hours. Understanding the manner in which these reactions can occur and propagate is a first step in their prevention, and this is the reason for the reported research.

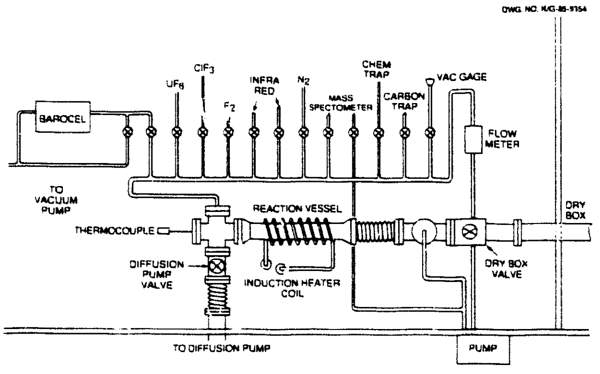

Fig. 1. Experimental system.

EXPERIMENTAL PROCESS

Figure 1 shows the system in which the experiments were performed. Surrounding the system was an insulated box that was maintained at 100°C (373 K) during the experiments. Gas could be added to the system as desired, or the system could be maintained at high vacuum both before and during heating. Heating was by induction. Samples were sometimes small chips of aluminum, usually an alloy (214-X), and in this case the temperature was measured by placing a thermocouple over the boat. This imprecise measurement, used to detect a plasmalike reaction, was replaced by a thermocouple within a slug or crucible during later experiments. Flow was provided by a metal bellows pump, and pressure was maintained during a reaction by a differential pressure measuring device that also admitted gas as required. At pressures below 20 torr, the differential pressure device could not control the pressure, and manual control was necessary. Temperatures were measured by means of a chromel-alumel thermocouple. Temperatures measured by the system at the ice point deviated by less than one degree. Melting temperatures of aluminum varied several degrees from the reported melting point, caused both by a lag in the measurement and by impurity-lowering of the melting point, as well as by inherent thermocouple error. Pressures were measured by means of digital readout. A maximum deviation of 0.4 torr was seen at zero pressure; however, deviations cause by the action of the metal bellows pump were larger. An infrared pyrometer was used on some measurements; it was uncalibrated except by comparison with the thermocouple during an experiment, as described later. The uncertainties in these calibrations are much less than the uncertainties in the chemistry of the system. Values from the readout devices were obtained several hundred times a second during some of the fast reactions and the data stored in computer memory during an experiment. Data could be retrieved subsequently and plotted.

When boats were used rather than an eddy current concentrator, samples unexposed to ambient air could be obtained by sliding the boat into an adjoining dry box at less than 1 ppm moisture. In this way, X-ray samples of moisture sensitive materials could be obtained. Debye-Scherrer patterns were obtained for identification.

Samples used were high-purity aluminum, aluminum alloy 214-X, 200-mesh atomized aluminum powder, and aluminum capsules of 1100 alloy. The high-purity aluminum was obtained from a vendor and stated to be 99.99% aluminum. Scanning electron microscope (SEM) examination of reacted material revealed no foreign material in the high-purity aluminum, but the material was not further analyzed. The 214-X alloy contains Mg, Si, and Fe, primarily, as alloying elements. The Mg and Si are added in approximately the proportion necessary to form Mg_2Si as a strengthening agent at the grain boundaries of the Al. The iron is added as a fluidizing agent to help in casting. The iron is present in the solid alloy as $Fe_{13}Al_4$ (ASTM Card 29-42) and was identified by electrolytic extraction and X-ray diffraction. the Mg_2Si was identified in the same manner. The UO_2F_2 was formed on the walls of a tube by interaction of UF_6 and H_2O. This compound forms adducts both with HF and with H_2O. Water contamination was removed by heating in UF_6, and any HF contamination was removed by heating the system to 100°C and evacuating the system by means of a diffusion pump. The aluminum capsules were made of 1100 aluminum, and the primary impurity found was a small quantity of iron. The aluminum powder had been obtained as "high purity" some years ago. SEM examination failed to reveal any second phase, but an oxide layer must have been present on the surface. The 214-X alloy was used both as chips and as slugs. The chips were machined coarsely, about 1 to 2 mm thick, about 3 to 5 mm wide, and of varying length. All the slugs, both of high purity and of 214-X alloy, were about 9 mm dia and 18 mm long. The capsules were of the same outer dimensions, with a 1.5 mm wall thickness.

Reacted samples for scanning electron microscope examination were mounted in epoxy plastic immediately after being removed from the system because the reaction products are themselves sensitive to moisture. The samples were ground to a midplane in air, and then polished in Freon by use of a vibratory polisher. A final polish was made by use of 0.5 micrometer diamond paste.

RESULTS AND DISCUSSION

UF$_6$–Al Reaction at High Temperatures

Even at temperatures near the melting point of aluminum, gaseous UF$_6$ reacts slowly with the metallic aluminum. Figure 2 shows micrographs of the results of a 30-min heating of aluminum alloy 214-X in 60 torr (1 torr = 133.322 Pa) UF$_6$ at 863 K. The micrograph on the right shows a layered structure of AlF$_3$ on the aluminum substrate, and a layer of UF$_4$ (the brighter layer) can be seen between the two components. The mechanism of reaction is most likely diffusion of UF$_6$ through the layers of AlF$_3$ to the reductant (aluminum) and reaction to produce a layer of UF$_4$ and one of AlF$_3$

$$2Al(s) + 3UF_6(g) = 2AlF_3 + 3UF_4(s). \qquad (1)$$

The AlF$_3$ is protective, up to a point. When the mismatch between the layers stresses the AlF$_3$ layer beyond its tensile strength, fracture results. The UF$_6$ can then react with the UF$_4$, producing a volatile pentafluoride, UF$_5$. Successive steps produce the layered structure.

The micrograph on the left of Fig. 2 reveals that this is not the whole story, however. Reaction occurs in some places and not in others, and large differences are seen only a few micrometers apart. Clearly, some regions of the alloy are protected more than others. A line has been drawn across the micrograph, estimating the initial position of the polished surface of the starting sample. The protection is akin to the protective oxide layer on the aluminum cookware, but the specific mechanism of the protection—and its variation—has not been identified.

More than 100 laboratory experiments have been performed, heating aluminum and alloys of it in UF$_6$ at temperatures in excess of 600 K but below the melting point of aluminum without obtaining what might be called a destructive reaction. These experiments confirm the experience of more than 40 years that, kinetically, aluminum and its alloys are stable in gaseous UF$_6$.

Furthermore, Fig. 3 shows the UF$_6$ can actually cool hot aluminum. When UF$_6$ (20 torr) is admitted to a system containing a small

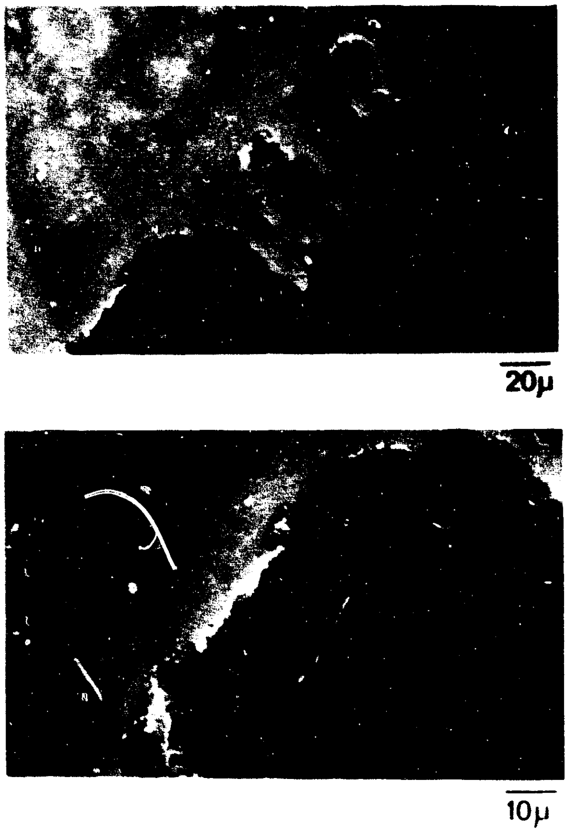

Fig. 2. Micrograph showing reaction extent on aluminum in 30 min at 590°C (863 K) and 60 torr UF$_4$ (1 torr = 133.322).

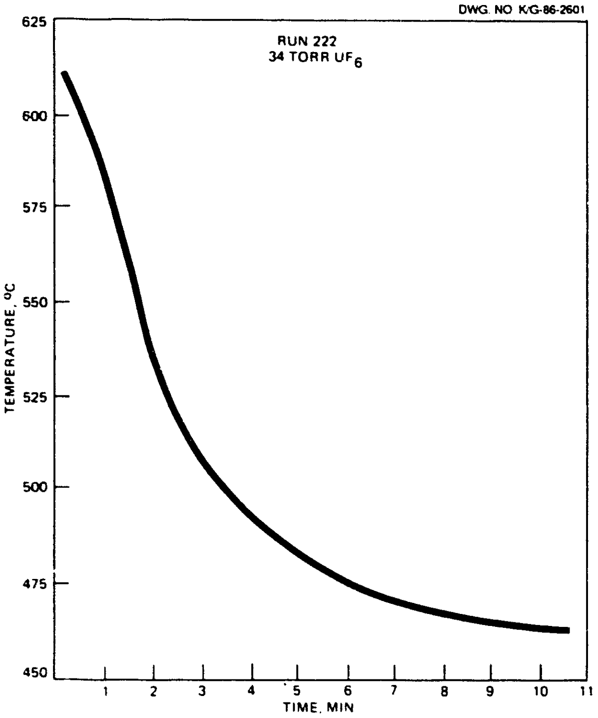

Fig. 3. Cooling of aluminum in UF_6 at constant power.

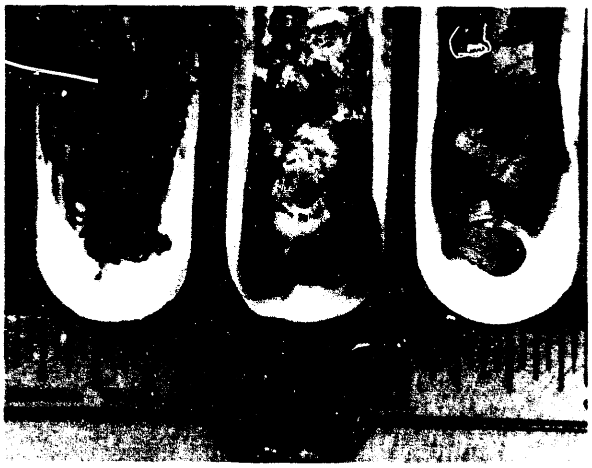

Fig. 4. Reaction of aluminum alloy 214-X chips in increasing pressures of UF_6.

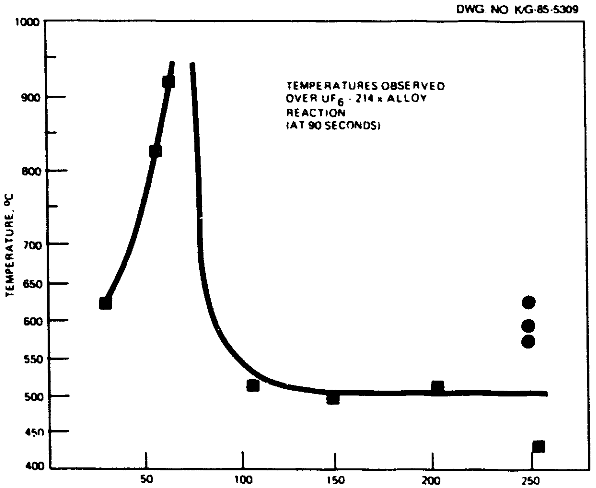

Fig. 5. Measured temperatures over boats of aluminum alloy chips as a function of UF_6 pressure.

aluminum slug at 600°C (873 K), the temperature of the slug is observed to steadily decrease, even though the power to the induction heater is kept constant.

Reaction of Aluminum Chips with UF_6

Heating of the aluminum alloy chips inductively in UF_6 gave results which were pressure dependent. Figure 4 compares samples that were heated at three different pressures: 25, 100, and 200 torr, shown left to right. In the boat heated at 25 torr, sagging of the alumina boat can be detected in the upper left. (Alumina melts at approximately 2345 K.) The remarkable difference shown is somewhat deceptive. The photographer showed only the ends of the boats, and some reaction was seen in the center of the boat on the right, although by no means as much as in the center or leftmost boat.

The effect of the UF_6 pressure on the temperature measured over the boats of aluminum at 900 s after heating began is shown in Fig. 5. While this is an imprecise measurement of temperature, there is a clear trend with UF_6 pressure, which is in agreement with the observations recorded in Fig. 4. Higher pressures of UF_6 clearly interfere with reaction.

The UF$_6$ can actually cool the reaction, as shown in Fig. 3, which can only be true when the UF$_6$ temperature is cooler than the temperature at the reacting surface. Further, the heat-producing reaction cannot take place rapidly if protective layers, as shown in Fig. 2, interfere with the reaction. Thus, the conclusion seems to follow that protective layers, coupled with actual cooling by UF$_6$ prevent or slow reaction except under special circumstances.

Reaction with UO$_2$F$_2$

Admission of moisture, even in small amounts, to the cascades results in the formation of oxyfluorides of uranium in a reaction that may be satisfactorily considered for our purposes as

$$UF_6(g) + 2H_2O(g) = UO_2F_2(s) + 4HF(g). \qquad (2)$$

The possible contribution of this reaction to destructive reactions in the cascades was of interest.

One gram of UO$_2$F$_2$ was mixed with 0.1 g of 200-mesh aluminum powder and packed in a small aluminum capsule. The capsule and its contents were placed within an eddy current concentrator, the system was evacuated, usually overnight, and the surrounding box was heated to 100°C (873 K).

In initial experiments samples were heated to 600°C (873 K), both in vacuum and in a partial atmosphere of UF$_6$. No significant reaction was ever detected in the six experiments that could be attributed to reaction of aluminum with UO$_2$F$_2$. An interesting reaction did occur on initial admission of UF$_6$ to the system. Figure 6 records the rise in temperature, both as measured by a thermocouple in the interior of the capsule and an infrared pyrometer focused on the surface of the capsule, observed when UF$_6$ is admitted to the system at 500°C (773 K). Figure 7 records the pressure of the UF$_6$ that appears to rise erratically because admission was performed by hand. Note that the surface temperature reading takes an immediate drop, which is ascribed to a change in surface emissivity. Note also that the surface temperature rises only very slightly, whereas the temperature measured by the thermocouple is rising to about 525°C. This portion of the experiment was repeated numerous times, and results were erratic. Sometimes the interior temperature rose more than 50°C, whereas other times the temperature rose hardly at all on first admission of UF$_6$ at about 500°C. This difference is ascribed to subtle differences in the surface of the aluminum, but further investigation was not successful. Extensive examination in the SEM failed to reveal any reaction in the system that could not be ascribed to simple reaction of aluminum with UF$_6$.

Only when the melting point of aluminum was exceeded during this series of experiments was a significant, exothermic reaction observed. Figure 8 records the abrupt rise in temperature as the aluminum melting point is exceeded at about 655°C (928 K). The infrared pyrometer fails to note an abrupt temperature rise until the central thermocouple records above 1050 K, whereupon it also rises rapidly. (The pyrometer is calibrated at the initial point of these experiments by fixing its temperature equal to that observed on the chromel-alumel thermocouple. It should be noted that the thermocouple is stainless steel jacketed and the reaction of the jacket is not only expected, it has been observed. However, the stainless steel-UF$_6$ reaction rate is slow and does not change dramatically as one passes the melting point of aluminum. Thus, one can conclude that the strong effects are related to the system being studied, rather than being an artifact of the thermocouple.

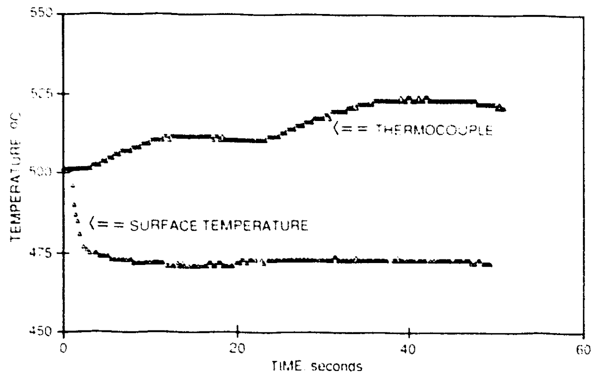

Fig. 6. Rise in temperature on admission of UF$_6$. Crucible contained UO$_2$F$_2$ and aluminum powder.

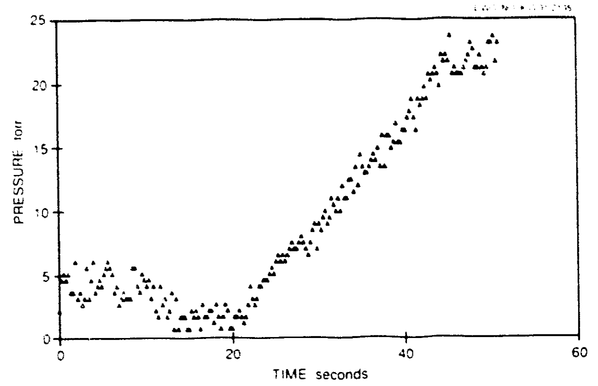

Fig. 7. Rise in pressure on admission of UF_6. Same as Fig. 6.

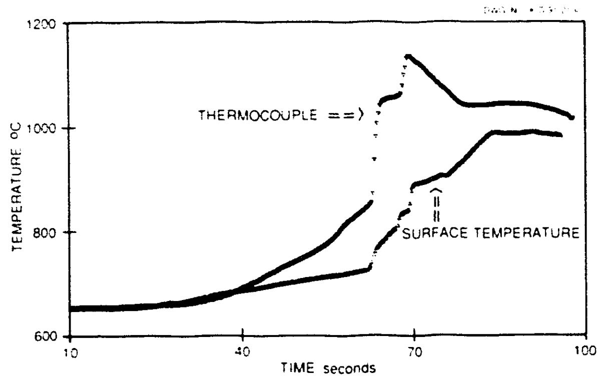

Fig. 8. Rise in temperature as capsule passes through melting point of aluminum. Same run as Figs. 6 and 7.

Figure 9 is an SEM micrograph, with elemental dot maps of the elements of interest, of a partially reacted aluminum powder particle in a matrix of what used to be UO_2F_2. The AlF_3 coating around the particle can be most clearly seen in the F dot map. That uranium-containing particles exist within the aluminum particle can be readily deduced from the U dot map, as well as from the Al dot map. Note the absence of F dots both within the aluminum particle and within the "UO_2F_2" matrix.

Figure 10 reveals the morphology of uranium-containing regions, both within the aluminum powder particles and within the aluminum capsule. The morphology indicates the uranium phase is precipitating on matrix planes during cooling, probably as UAl_4. Transmission electron microscopy could reveal which planes were being decorated.
That more than one U-Al phase is present in the aluminum particles can be deduced from the evidence in Fig. 11. The varying shades of the blocky precipitates in the SEM micrograph, as well as the varying intensity in both the U- and Al-dot maps, indicate a different composition. That these were formed at high temperatures is argued by the blocky shape, which indicates the two phases are probably UAl_3 and UAl_2. The phase which precipitated on cooling is also visible in the micrograph and is probably UAl_4, the most aluminum-rich compound.

A number of reaction products were identified during the study, and a number of others were deduced.

Effects of Impurities

Previously, the suspected effect of impurities in aluminum on reaction with UF_6 was noted. A more direct measure is seen in Figs. 12 and 13. Figure 12 compares the temperature rise of a cylinder of high-purity (99.99%) aluminum with that of aluminum alloy 214-X as the separate samples pass through melting.

High-purity aluminum showed very little reaction, whereas the alloy showed a sharp temperature rise. Further, the visual appearance of the samples after reaction (Fig. 13) shows a dramatic difference. Incidentally, both samples were easily removed from the supporting thermocouple after melting and reaction, again indicating the temperature rise is related to the aluminum rather than to thermocouple-UF_6 interaction.

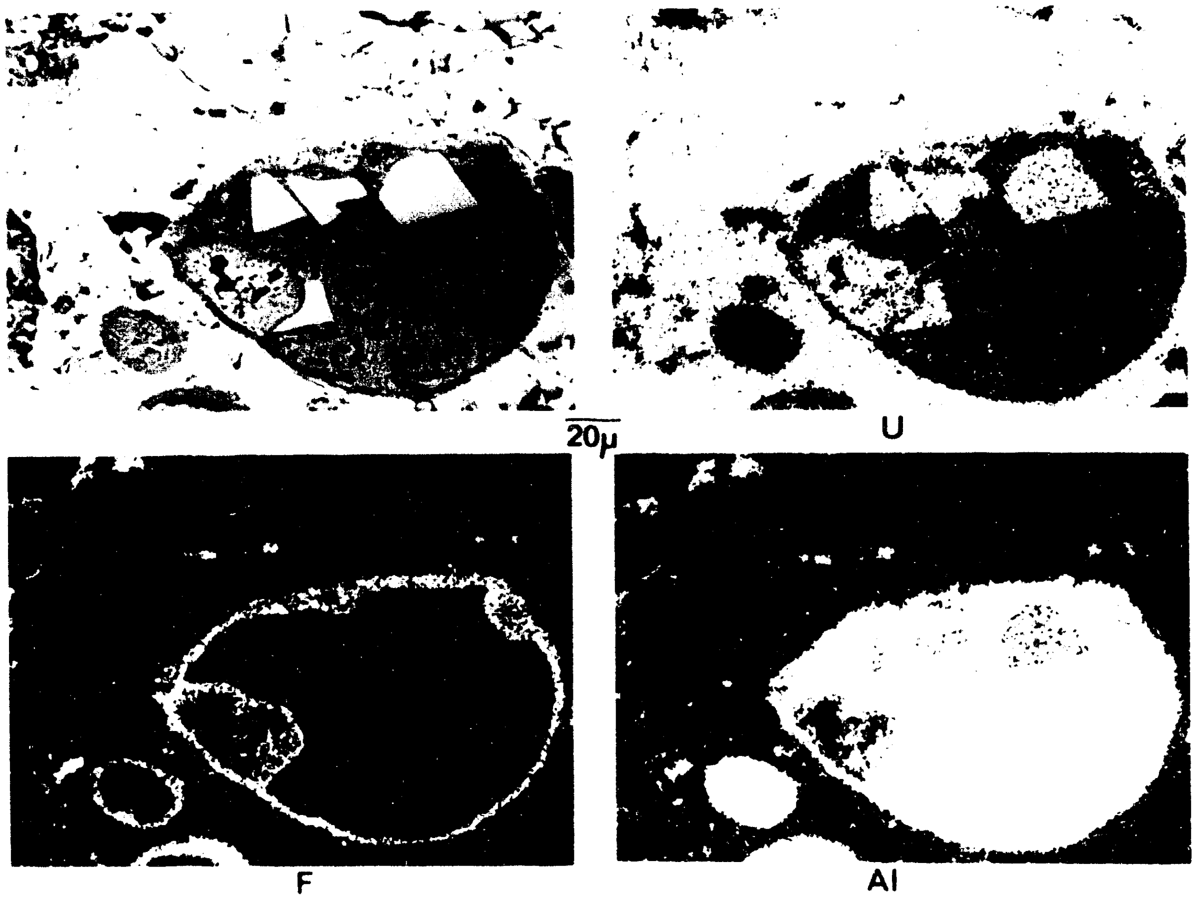

Fig. 9. Aluminum particle partially reacted with UO_2F_2 + UF_6. Similar experiment as shown in Fig. 8.

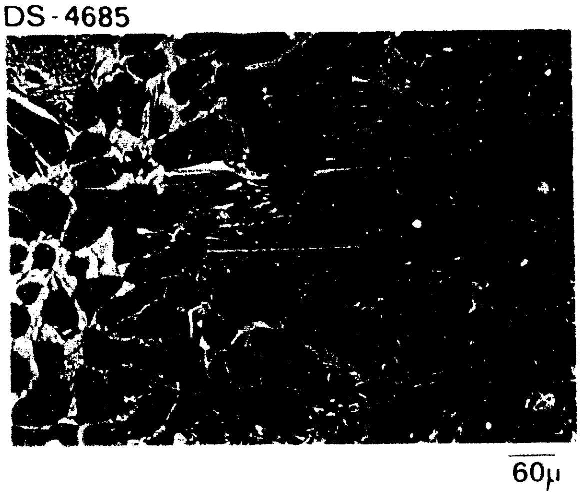

Fig. 10. Morphology of U-Al phase precipitated during cooling.

Lack of reaction of pure aluminum in UF_6 must be related to a protective coating on the aluminum that prevents attack. The attack on the impure aluminum must, therefore, be related to partial destruction of the protective nature of this coating, an area that needs further investigation.

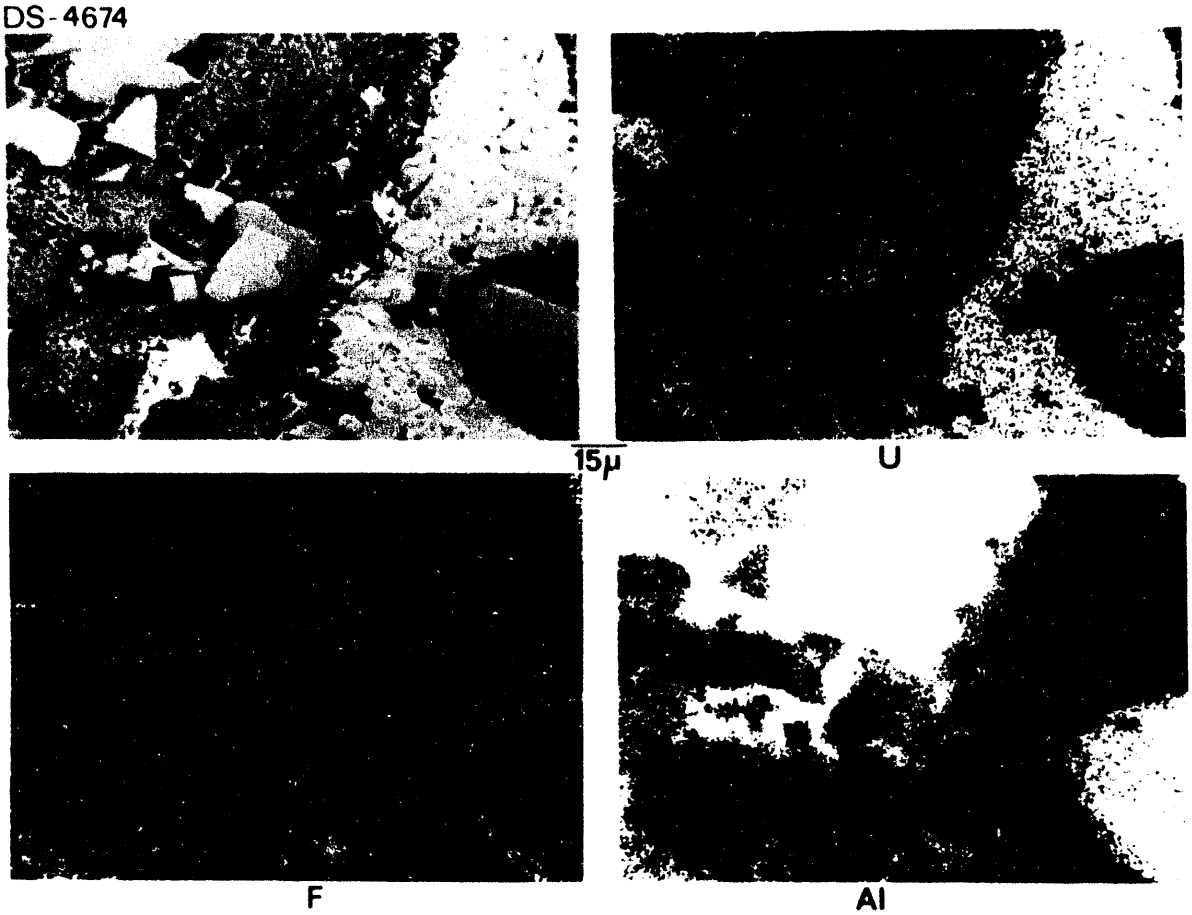

Fig. 11. Evidence for several U-Al phases within aluminum particles.

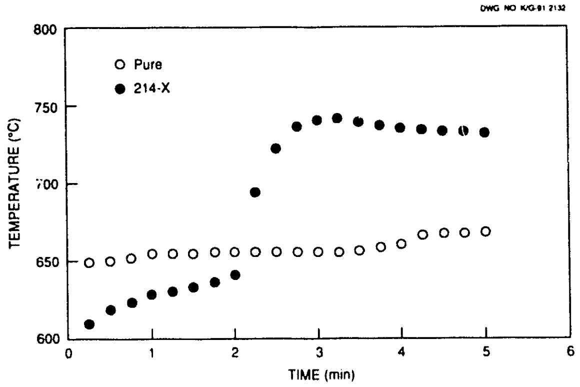

Fig. 12. Comparison of temperature change in high purity and alloyed aluminum as sample pass through melting point of aluminum in UF_6.

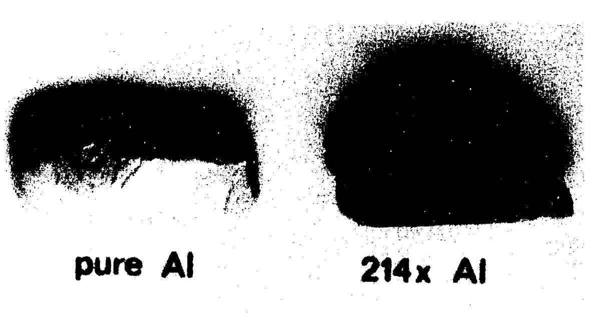

Fig. 13. Visual comparison of samples from experiment shown in Fig. 12.

More on Reaction with Aluminum Chips

Even at high pressures of UF_6, reaction occurred in the boats with aluminum chips. Subsequent to the experiments, examination of the residue in the boats revealed the presence of UF_5 condensed in the colder regions of the boats. The UF_5 can be easily recognized by its needle-like morphology, and this recognition was confirmed by X-ray diffraction of the crystals. Thus, a mechanism for rapid reaction of UF_6 with the chips can be surmised. If UF_5 can be deposited in the boat, as was demonstrated, and if this deposition was present among the aluminum chips as they reached the melting point of UF_5, then the molten UF_5 could serve as the mechanism for disrupting the protective film on the aluminum. This provides a plausible explanation for the observed reaction of the chips in UF_6.

SUMMARY

In reactions of UO_2F_2 with aluminum, only when the surface layer on the aluminum was breached by melting was reaction vigorous. Reaction of UF_6 with pure aluminum was also slow, even with melting. Alloyed aluminum, however, reacted more vigorously with UF_6 when melting occurred. The coating on pure aluminum is more protective than the coating on alloyed aluminum. Gaseous UF_6 reacts slowly with solid, alloyed aluminum and large rate variations are observed within short distances. Clearly, the outer layer is protective at some times and not at others—an observation that is probably related to impurity content in the surface layer.

Since disrupting the surface layer allows an increased reaction rate, low melting compounds or elements might be expected to increase reactivity. Deposition of UF_5, for example, could provide a low melting (620 K) compound to disrupt the protective layer on aluminum.

The effect of UO_2F_2 on the destructive reactions in a compressor is analogous to trash piled in the corner of a building. Both contribute to the problem once the conflagration is well under way.

ACKNOWLEDGMENT

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FIRE TESTING OF BARE URANIUM HEXAFLUORIDE CYLINDERS

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ABSTRACT

In 1965, the Oak Ridge Gaseous Diffusion Plant (ORGDP), now the K-25 Site, conducted a series of tests in which bare cylinders of uranium hexafluoride (UF_6) were exposed to engulfing oil fires for the U.S. Atomic Energy Commission (AEC), now the U.S. Department of Energy (DOE).[1] The tests are described and the results, conclusions, and observations are presented. Two each of the following types of cylinders were tested: 3.5-in.-diam × 7.5-in.-long cylinders of Monel (Harshaw), 5.0-in.-diam × 30-in.-long cylinders of Monel, and 8-in.-diam × 48-in.-long cylinders of nickel. The cylinders were filled approximately to the standard UF_6 fill limits of 5, 55, and 250 lb, respectively, with a U-235 content of 0.22%. The 5-in.- and 8-in.-diam cylinders were tested individually with and without their metal valve covers. For the 3.5-in.-diam Harshaw cylinders and the 5.0-in.-diam cylinder without a valve cover, the valves failed and UF_6 was released. The remaining cylinders ruptured explosively in time intervals ranging from about 8.5 to 11 min.

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METAMORPHOSIS: PHASES OF UF_6

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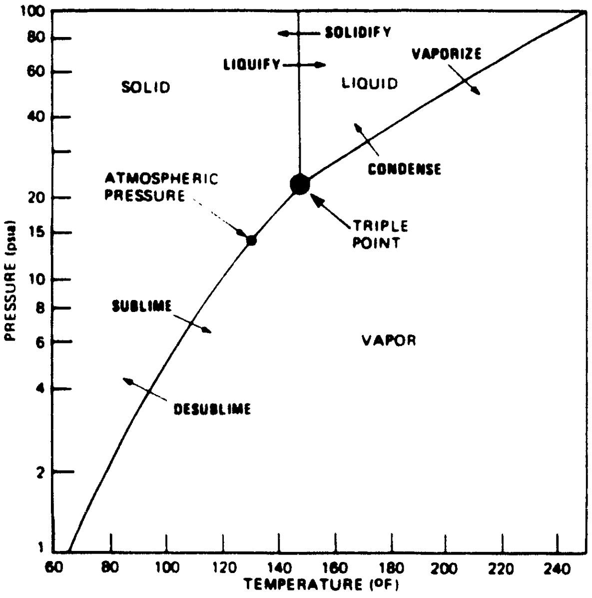
A 15-minute videotape is presented. The subject matter is 150 grams of UF_6 sealed in a glass tube. Close-up views show the UF_6 as phase changes are effected by the addition or removal of heat from the closed system. The solid-to-liquid transition is shown as heat is added, both slowly and rapidly. The solid phases which result from freezing and from desublimation are contrasted.

In the solid state, uranium hexafluoride is a nearly-white, dense crystalline solid. The appearance of this solid depends on whether it is formed by freezing from the liquid or by desublimation from the vapor phase. If frozen from the liquid, the solid particles take the form of irregularly shaped coarse grains, while the solid product of desublimation tends to be a rather formless mass without individually distinguishable particles. The changes in state are presented in terms of the UF_6 phase diagram.

Arrangements for obtaining copies of the tape may be made at the conference.



PHASE DIAGRAM OF UF_6

FIRE EXPOSURE OF EMPTY 30B CYLINDERS

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Cylinders for UF$_6$ handling, transport, and storage are designed and built as unfired pressure vessels under ASME Boiler and Pressure Vessel Code criteria and standards. They are normally filled and emptied while UF$_6$ is in its liquid phase. Transport cylinders such as the Model 30B are designed for service at 200 psi and 250°F, to sustain the process conditions which prevail during filling or emptying operations. While in transport, however, at ambient temperature the UF$_6$ is solid, and the cylinder interior is well below atmospheric pressure. When the cylinders contain isotopically enriched product (above 1.0 percent U-235), they are transported in protective overpacks which function to guard the cylinders and their contents against thermal or mechanical damage in the event of possible transport accidents.

Two bare Model 30B cylinders were accidentally exposed to a storage warehouse fire in which a considerable amount of damage was sustained by stored materials and the building structure, as well as by the cylinder valves and valve protectors. The cylinders were about six years old, and had been cleaned, inspected, hydrotested, and re-certified for service, but were still empty at the time of the fire. The privately-owned cylinders were transferred to DOE for testing and evaluation of the fire damage.

OBSERVATIONS

Visual Examination

When the cylinders were received at the Oak Ridge enrichment plant site (K-25), they were observed to be covered with a semi-adherent oxide, presumably a result of the fire exposure or the fire-fighting efforts. Portions of each cylinder were coated with a black asphaltic material, evidently the roofing material that rained down after the warehouse roof ignited. One of the cylinders had been located with the 10 o'clock position uppermost, judging from the patterns of the asphalt residue. The valve cover on this cylinder lacked one of the two attachment bolts, and it had sagged out of position under the influence of heat from the fire. Both valves were heavily oxidized and were covered with a loosely adherent, flaking bluish scale. The packing nuts were cracked and the top disc sections had separated from the nut bodies. The Teflon packing had melted and the extruding material was charred.

A group of photographs of the fire scene were submitted by the cylinder owner, for use in the damage assessment. Study of these photographs by the K-25 Fire Protection Engineering staff concluded that floor-area temperatures had reached in excess of 1000°F, and roof-area temperatures may have approached 2000°F prior to roof penetration. These temperatures were of short duration, in the range of 30 minutes to one hour.

The damaged valves were removed from the cylinders for laboratory examination and to prepare the cylinders for hydrostatic testing. It was observed that both cylinders were under vacuum, although this pressure could not be measured. Following cleaning, inspection, and hydrostatic testing, UF$_6$ cylinders are normally evacuated to $<$ 5 psia (26 cm Hg) for subsequent filling. A pressure check to verify this pressure serves as a quality check on cylinder and valve integrity for all new/cleaned cylinders received for filling at the gaseous diffusion plants.

Rupture Testing

Both cylinders were hydrostatically tested to failure. Rupture occurred at 2250 and 2350 psi, with a substantial volume expansion, about 30

[+] Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

percent, prior to rupture. The failures were fully ductile, and were longitudinal in orientation, located near cylinder mid-length.

Microstructural Examinations

Metallographic sections taken through the packing nuts showed the failures to be intergranular. The failures were probably caused by the hydraulic pressure of the molten Teflon packing, and laboratory tests on similar packing showed melting accompanied by charring (as observed on the valves) at about 1000°F. This temperature corresponds to the so-called equicohesive temperature for the aluminum bronze valve alloy, the temperature at which the tensile failure mode changes from ductile transgranular to brittle intergranular fracture.

The valve protector was made from a mild steel with a carbon content estimated at 0.05 to 0.10 percent. Available creep data for mild steels suggests that the observed deformation must have occurred at a temperature well above 1400°F. The observed partial recrystallization of the ferritic microstructure is consistent with a temperature of about 1600°F.

No microstructural features noted in the body of the cylinder indicated anything other than the expected hot-rolled plate structure. The partially charred asphalt on the cylinder surfaces indicates that this portion of the cylinders did not exceed a temperature of 700-800°F.

CONCLUSIONS

From the physical evidence associated with the two fire-exposed cylinders, it is concluded that

- Portions of the valve protectors reached temperatures as high as 1600°F.
- The valves reached 1000°F at the time of failure of the packing nuts. The primary seal at the valve seat remained intact during and after the fire.
- The cylinder bodies reached temperatures no higher than about 800°F during the fire.
- Although the valves were no longer serviceable, the cylinder bodies were not damaged by the fire exposure.

It is also noted that the observed burst pressures are about eleven times greater than the nameplate working pressure for the Model 30B cylinder. Both the burst pressure and the 30 percent expansion prior to rupture give a substantial margin of safety and an assurance of containment integrity in the event of transport accidents. It should be pointed out in this regard that when this cylinder contains enriched product, it is always contained in a protective overpack except for plant-site operations involving filling or emptying. The overpack provides added assurance of safety in transport.

RUPTURE TESTING PROGRAM

The Model 30B and all of the Model 48 cylinders for UF_6 containment are made from ASTM A516 pressure vessel plate steel. Smaller cylinders for shipment of higher isotopic enrichment levels are made from nickel or Monel plate, sheet, pipe, or tube. The safety of these cylinders is assured by

- the very conservative design practices employed by the ASME code.
- the use of properly qualified welders and welding procedures, developed and administered by the codes and monitored by state-licensed inspectors.
- inspection during fabrication prior to acceptance by the buyer.
- hydrostatic testing at twice the design pressure prior to affixing the code stamp to the new cylinder.
- establishment of well-defined fill limits.
- user inspection for damage before filling, before shipping, and upon receipt prior to filling or emptying.
- use of protective shipping packages for all handling procedures except filling and emptying, and

- cleaning, internal inspection, and repeat hydrostatic testing at 5-year intervals during their service life.

In addition, an ongoing program of design improvements is based on service and manufacturing experience and on rupture testing of cylinders removed from service. Significant accomplishments of this program, in addition to demonstrating the inherent conservatism in cylinder design with respect to the nameplate working pressures, include:

- the development of the Model 30B design.
- upgrading the Model 48 cylinders from ASTM A285 to ASTM A516 steel to assure good low-temperature properties for year-round shipments.
- upgrading A516 steel to a low-sulfur grade for improved resistance to handling damage.

The program has included all of the cylinder sizes used in transport of UF_6, from fuel materials at all levels of enrichment to normal and partially-depleted feed in interplant shipments. The table summarizes the results of these tests.

RUPTURE TEST DATA FOR UF_6 CYLINDERS

CYLINDER TYPE	MATERIAL	WALL THICKNESS inch	WORKING PRESSURE psi	RUPTURE PRESSURE psi	VOLUME INCREASE %
5A	MONEL	1/4	200	8250	–
5A	MONEL w/NICKEL COUPLING	1/4	200	7950 (Avg. of 3 Tests)	21
8A	MONEL	3/16	200	2950	–
8B	NICKEL	3/16	200	2450	–
12A	NICKEL	0.200	200	2400	30
12B	MONEL	0.250	200	2260	53
30A*	A285 STEEL	13/32	250	1250 (Avg. of 2 Tests)	20**
30B	A516 STEEL	1/2	200	2320 (Avg. of 2 Tests)	34
48OM	A285 STEEL	5/16	100	870	9
48Y	A516 STEEL	5/8	200	1770	6
48A	A285 STEEL	5/8	200	1285	6
48A	A285 STEEL	5/8	200	1432	16
48G	A285 STEEL	5/16	100	975	17

*OBSOLETE

**VOLUME INCREASE DUE TO INVERSION OF CONCAVE HEADS AT INTERNAL PRESSURE OF 900-1,000 psi

CONCEPTUAL DESIGN FOR PSP MOUNTING BRACKET

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ABSTRACT

Protective structural packages (PSP's or overpacks) used to ship 2½-ton UF_6 product cylinders are bolted to truck trailers. All bolts penetrate two longitudinal rows of wooden planks. Removal and replacement is required at various intervals for maintenance and routine testing. A conceptual design is presented for mounting brackets which would securely attach PSP's to trailer frames, reduce removal and replacement time, and minimize risk of personnel injury.

NOMENCLATURE

30A	Obsolete model 2½-ton UF_6 product cylinder.
30B	Current model 2½-ton UF_6 product cylinder.
PSP	Protective structural package.
21PF-1	Type of protective structural package used to enclose Model 30A and 30B UF_6 product cylinders.

EXISTING PRACTICE

Model 30A and 30B UF_6 product cylinders are enclosed in DOT model 21PF-1A or 21PF-1B protective structural overpacks (PSP's) for shipment by commercial truck. The axes of the enclosed cylinders and overpacks may be longitudinal or transverse with respect to the trailer. As shown in Figure 1., packages are mounted longitudinally, on dedicated, customer owned trailers, at the Portsmouth Gaseous Diffusion Plant. Two bolts at each overpack corner are inserted from the top through holes in wood trailer planks. These bolts are retained by a small back-up plate and two nuts. Because all eight bolts penetrate two longitudinal rows of wood planks, several overpacks may be attached to only two planks.

Overpacks must be removed and replaced regularly for weight verification, and as required for maintenance or repair. During replacement, it is difficult to align overpack mounting holes with existing holes in the wooden planks. Two people, one underneath the trailer, and one on top with an impact wrench, are required to manipulate each nut and bolt. Due to the awkward position and sound amplification, the person under the trailer is exposed to a high risk of physical injury and hearing loss.

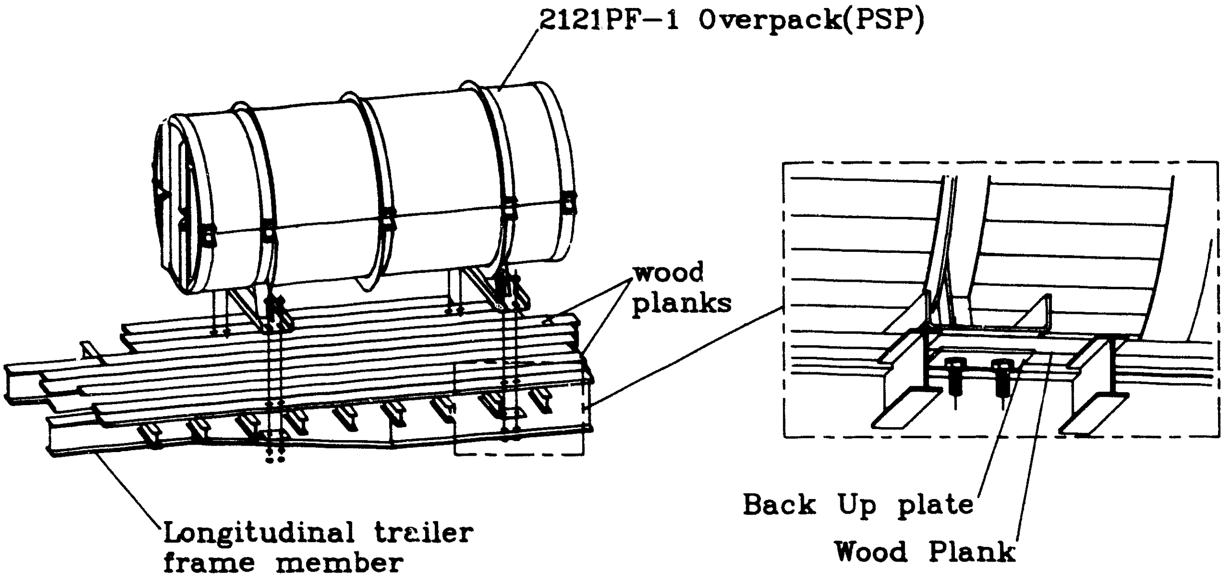
PROPOSED DESIGN

Figure 2. shows a proposed design for mounting brackets to be permanently attached to the owner's trailers. Overpacks would be bolted to these brackets which in turn would transfer all load directly to the trailer frame for more secure retention. The proposed brackets contain two sets of mounting holes and slots to match both existing hole spacings on 21PF-1 overpacks.

After initial installation, overpacks could be removed as necessary with the mounting brackets always remaining in place. Only one person, working from the top, would be required to install fasteners joining overpacks to the brackets. Hole alignment and fastener manipulation would be easier and result in faster turnaround. Since no work would be regularly required beneath the trailer, risk to personnel would be minimized.

REFERENCES

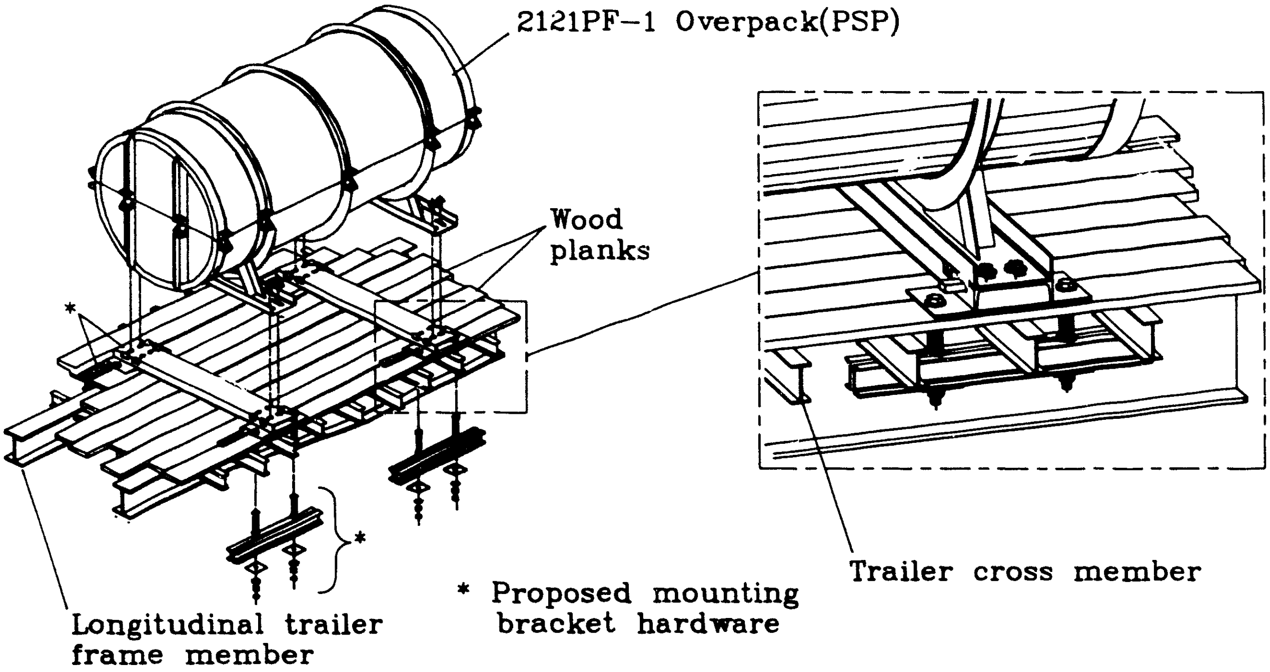
1. ORO-651, Rev. 5, (DE87014088) *Uranium Hexafluoride: Handling Procedures and Container Descriptions*, Martin Marietta Energy Systems, Oak Ridge, Tennessee, 1987.



a) Overall view showing a typical trailer section and existing mounting hardware.

b) Detail of existing mounting hardware showing attachment to a single wooden plank.

Figure 1. Existing overpack mounting arrangement.



a) Overall view showing a typical trailer section, proposed mounting bracket and PSP.

b) Detail of mounting bracket showing positive clamping to trailer cross members.

Figure 2. Proposed overpack mounting arrangement.

REFURBISHMENT AND MODIFICATION OF EXISTING PROTECTIVE SHIPPING PACKAGES (FOR 30-INCH UF_6 CYLINDERS) PER USDOT SPECIFICATION NO. USA-DOT-21PF-1A

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ABSTRACT

This paper addresses the refurbishment procedures for existing shipping containers for 30-inch diameter UF_6 cylinders in accordance with DOT Specification 21PF-1 and the criteria used to determine rejection when such packages are unsuitable for refurbishment.

INTRODUCTION

In 1982 several incidents involving water leakage from 30-inch UF_6 cylinder overpacks highlighted the need for improving existing overpacks. In September, 1988, the US Department of Transportation issued Specification No. 21PF-1A to cover such modifications. These new regulations required that all existing overpacks be dried, refurbished, and modified to meet Specification 21PF-1A by March 31, 1991.

The dryness requirement is that each overpack half (top and bottom) contain no more than 25 pounds of water. Primary refurbishment steps include sand blasting to remove old paint and rust, repair of broken welds, dents, punctures, etc., repainting, and installation of new vent plugs, pads and gaskets. Modification requirements include installation of metal cover plates over the wood in the bottom half of each overpack, the use of plastic cap plugs in the vent holes, replacement of neoprene gaskets with silicone gaskets, and the use of RTV silicone caulking to seal vent plugs, metal to wood seams in the top half of the overpack, and spaces between intermittent welds attaching reinforcing bars and angle. A most important final step is the establishment of an accurate new tare weight for each overpack so that future water inleakage can be determined simply by weighing.

As the major manufacturer of 21PF-1 overpacks, Nuclear Containers, Inc. quickly became the major refurbisher of such overpacks. Since September, 1988, NCI has received approximately 600 overpacks for refurbishment and modification, and others are still being received every month. Of the overpacks already received, about 400 have been dried, refurbished, and modified to meet 21PF-1A Specification requirements; the remainder have been rejected as candidates for modification and will be scrapped. Some owners of overpacks have elected to scrap some or all of their existing overpacks without attempts at refurbishment and modification. Some of the scrapped overpacks have been replaced with new, upgraded stainless steel models, ie. the DOT-21PF-1B or the NCI-21PF-1.

Prior to September, 1988, there were two to three thousand 21PF-1 overpacks in existence throughout the world. Many of these overpacks were ten to twenty years old, and only about 25% of them will be modified for continued use. The remainder have been removed from service and are being replaced with new stainless steel overpacks; so far about 500 new overpacks have been placed into service such that today there are only about 1000 overpacks in service.

REFURBISHMENT & MODIFICATION PROCESS

Upon receipt of a package for refurbishment a complete and thorough visual inspection is completed and ultrasonic thickness readings are taken in suspect areas (i.e. corners, ends and pad areas). Acceptable thickness requirements are given in the modification drawings (SIE-3156-J1 Rev. D). After this inspection, the following procedures are observed:

(a) all gaskets and pads are removed;
(b) each vent is drilled to ¼" diameter and 2 ⅜" drain holes are drilled in each of the 3" x 3" x ¼" angle braces on the bottom of each package;
(c) a pre-drying weight is taken;
(d) the package is placed in a drying oven operating at 200° F for approximately four weeks; and
(e) the package is removed and checked by a moisture meter inserted through each of the vent holes.

A package found to be wet is placed back in the oven for additional drying. When the package is dry, a post drying weight is taken and recorded in order to determine the amount of water loss. Some packages have lost in excess of 400 pounds per half, but typical weight loss has been 100 to 200 pounds per package.

Packages are then sand blasted to clean the metal (Figure 1) and given a complete visual inspection for deterioration and any needed weld repairs.

All exposed wood is coated with intumescent fire retardant paint. Prior to painting, wooden step joints are inspected to assure flatness within 1/16" in order to ensure a good fit between the top and bottom halves.

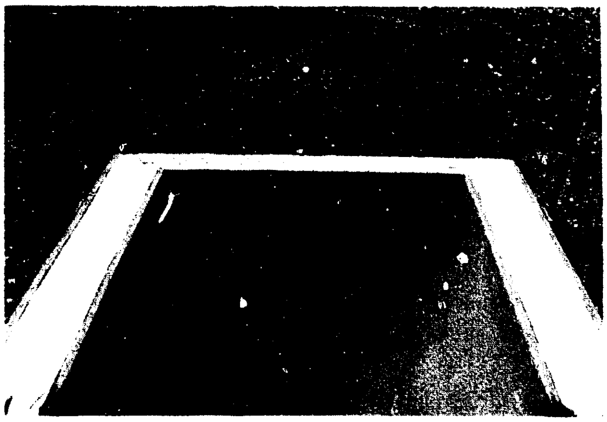

Figure 1 Package after sand blasting

Weld repairs are made and damaged metal repaired as required by either welding or by filling small dents and punctures with auto body putty. (Putty is used because welding over foam is not recommended.)

Metal cover plates are installed to encase the wood in the bottom half of the package using the approved welding process (Figure 2).

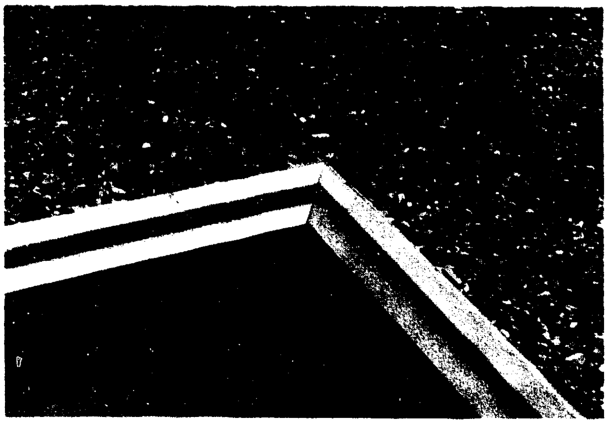

Figure 2 Metal cover plates installed

Each package half is then painted with one coat of zinc chromate epoxy primer and two coats of automotive urethane enamel. Gaskets and pads are then installed using silicone RTV adhesive (Figures 3 & 4) and a coat of intumescent fire retardant paint is applied to the bottom metal cover and to the exposed wood in the top half.

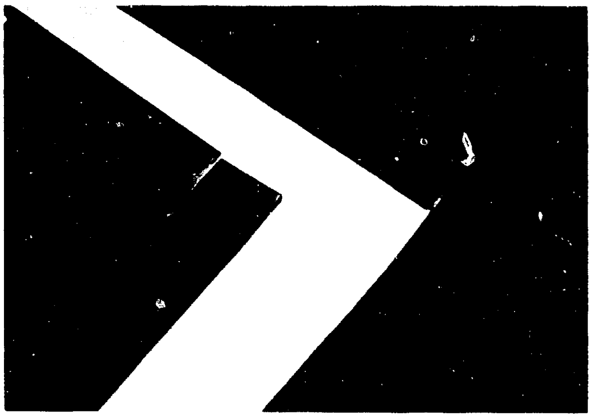

Figure 3 Bottom gaskets

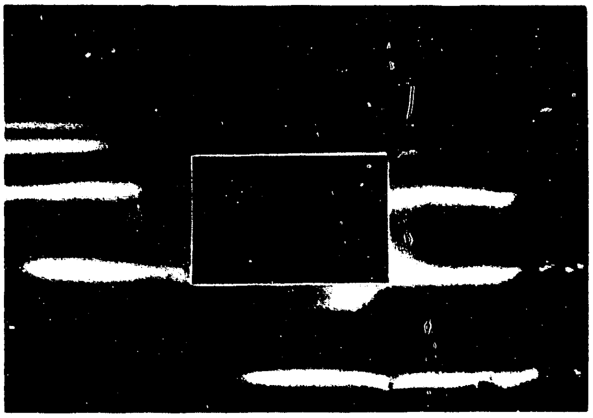

Figure 4 Inner shell pads

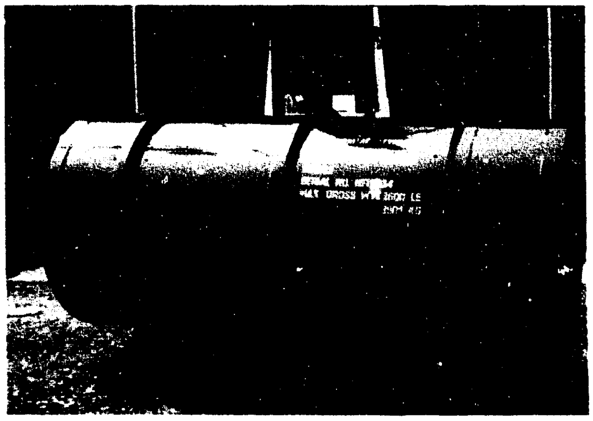

Figure 5 Finished Exterior

Cap plugs are installed in all vent holes by filling the hole with silicone RTV caulking, inserting the plug, then removing excess caulking. All seams between the wooden rails and metal flanges of the cover, and all skip welds (seen in Figure 5) joining reinforced angles and bars to the outer shells where water may accumulate are also sealed.

Each half is then weighed as required including all bolts, nameplates and shackles. The package is then assembled using B7 bolts, 2H nuts, flat washers and cotter pins.
The refurbished package is weighed (Figure 6) and the weights are recorded on the QA Inspection Report.

A new nameplate is installed showing the newly established tare weights from which future judgements can be made in reference

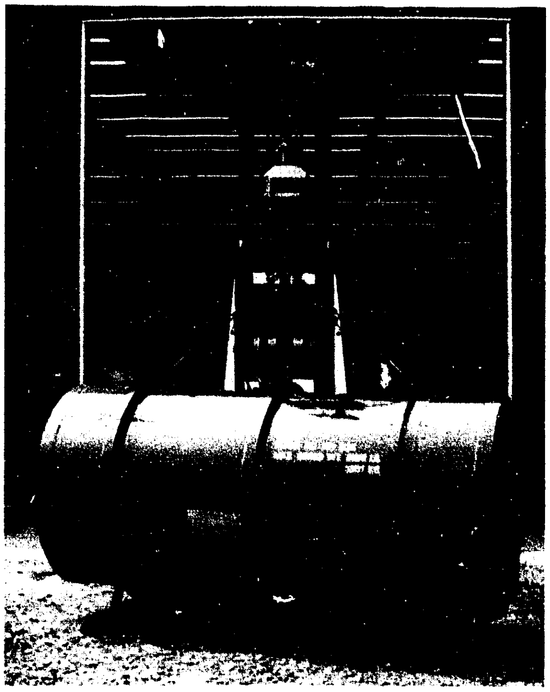

Figure 6 Weight recorded for QA Inspection Report

to the 25 pound weight gain per half as mandated by DOT.

To this date approximately 400 packages have been refurbished and modified to meet the requirements of DOT 21PF-1A.

REJECTION

The primary causes for rejection of overpacks for refurbishment and modification to 21PF-1A Specification requirements are as follows:

(a) Serious damage or punctures that require welding over the foam insulation; to ensure sound welds over foam is virtually impossible.

(b) Excessive corrosion in areas where patching with sheet metal is impractical such as those areas which would require welding over foam. Typical areas for such corrosion include surfaces under the rubber pads (Figure 7), sheet metal near and under angle reinforcements and corner welds, and sheet metal which has been in constant contact with wet wood or foam (Figure 8).

Figure 7 Corrosion under pad

(c) Excessive deterioration and rotting of wooden components other than exposed wooden rails which can be replaced. Such deteriorated wood cannot be removed without serious damage to the overpack.

Figure 8 Corrosion from contact with wet foam

In addition, some overpacks which were manufactured abroad were never in compliance with 21PF-1 Specification requirements to begin with. Typical deficiencies found in such overpacks included:

(1) Wooden rails which were spliced together from small pieces of wood (Figure 9); some were obviously made with wood other than oak or hard maple.

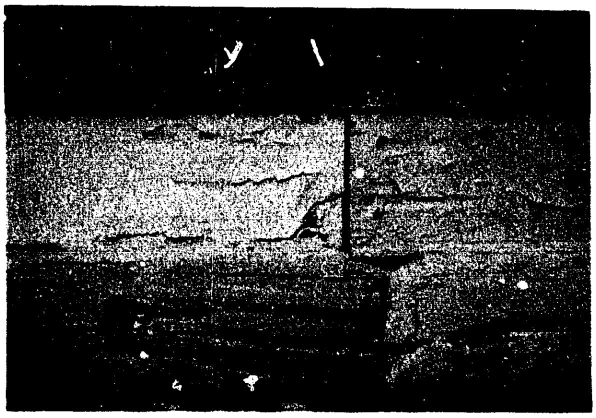

Figure 9 Spliced wooden rails

(2) Improperly installed foam as indicated by large voids in the foam and large areas of incomplete filling with foam. Upon

dismantling some of these overpacks for scrapping, the foam itself has been found to be suspect in that it is much more flammable than the SP-9 phenolic foam specified for these overpacks.

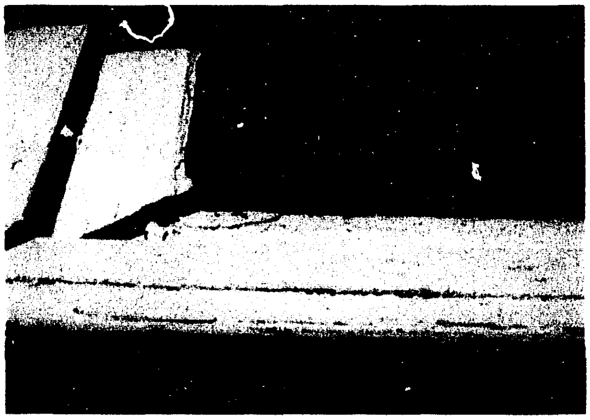

Figure 10 Inner shell separation

(3) Upon drying, many of these overpacks which were manufactured abroad experience separation of the inner shells from the body of the overpack (Figure 10); this can only happen if the inner shells were initially improperly installed.

None of the above deficiencies are practical to repair and all such overpacks have been rejected with the recommendation that they be scrapped.

So far NCI has rejected about 200 out of approximately 600 overpacks received for refurbishment and modification. Some overpacks, those which have received proper care and maintenance over the years, are still in excellent condition after as much as 20 years service. However, there seems to be a general relationship of overpack age to rejection rate as shown in Figure 11 which covers all overpacks r eived by NCI.

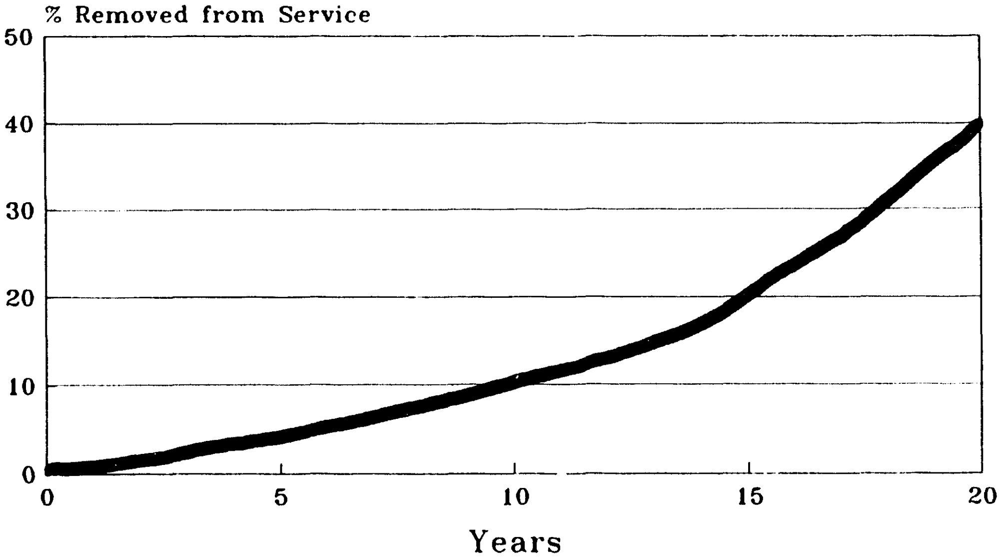

Figure 11 Relationship between age of packages and rejection and removal from service

UF$_6$ TIEDOWNS FOR TRUCK TRANSPORT — RIGHT WAY/WRONG WAY

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ABSTRACT

Tiedown systems for truck transport of UF$_6$ must be defined and controlled to assure the least risk for hauling the material over the highways. This paper and an associated poster display will present the current status of regulatory criteria for tiedowns, analyze the structural stresses involved in tiedowns for two major UF$_6$ packaging systems, the 21PF series of overpacks and the 48 in. diameter shipping cylinders, and will present photographs showing some "right ways" and some "wrong (or risky) ways" currently used for tiedown systems. Risky tiedown methods must be replaced with safer less risky methods to insure the safe transport of UF$_6$.

INTRODUCTION

Safe shipments of uranium hexafluoride (UF$_6$) by truck transport are an essential part of the nuclear power industry in the United States and in many countries of the world. Safe packaging is being improved, package maintenance is being much improved with requirements for periodic inspections, and a new ANSI Standard (N14.30) for properly designed and maintained semitrailers for transport of UF$_6$ is nearly a reality. The issue of tiedowns (attaching the packages to the transport vehicle) remains a concern in upgrading to a safe and reliable transport system. ANSI N14.2 defining tiedown design criteria is currently being promulgated.

REGULATORY REQUIREMENTS

Three federal regulatory agencies have published requirements for certifying packaging and for designing tiedowns for truck transport of radioactive materials when being hauled over the nation's highways. The Nuclear Regulatory Commission[1] (NRC), the Department of Energy[2] (DOE), and the Department of Transportation[3] (DOT) each specify certain requirements for these packages and for tiedowns to the transport vehicle. Also the International Atomic Energy Agency[4] (IAEA) has published requirements for tiedowns which must be complied with for international shipments and for shipments in states where IAEA regulations have been adopted.[5]

The American National Standards Institute (ANSI) has recognized a need for standards defining tiedown requirements[6] and defining requirements for design, fabrication, and maintenance of semitrailers[7] to assure an acceptable level of risk in transporting certain radioactive materials. Although these ANSI standards are not regulatory requirements, they very likely will be adopted by the regulatory agencies. Applicable regulatory requirements for NRC, DOE, DOT and IAEA will be provided in the poster displays.

[+] **Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.**

AMERICAN NATIONAL STANDARDS INSTITUTE (ANSI)

ANSI has assigned a writing group to develop ANSI Standard N14.2 defining tiedowns for truck transport of UF_6.[6] The standard is being refined and is close to being completed. The design load factors for tiedowns have been a controversial issue but have been established now at:

Direction	Design Loads
Longitudinal	2.3 X package weight
Transverse	1.6 X package weight
Vertical	2.0 X package weight

The tiedowns require a preload sufficient to eliminate slack.

The foregoing factors are slightly more stringent than the factors for current regulatory requirements and a little less stringent than tiedown attachment points for the semitrailers in ANSI N14.30[7]. These are the factors that will be used in calculating tiedown loads.

Calculations for tiedown loads of 21PF-1A and 1B overpacks.

Maximum gross weight of loaded overpack - 8600 lb.

In accordance with ANSI N14.2[6], tiedown system load factors are:

Direction	Design Loads
Longitudinal	2.3 X package weight
Transverse	1.6 X package weight
Vertical	2.0 X package weight

The overpacks are placed on the truck bed one of two ways, with the longitudinal axis of the package parallel or transverse to the direction of travel of the truck. The worst case for the tiedown system is with the longitudinal axis of the overpack transverse to the direction of truck travel. The resultant tiedown loads are shown in Fig. 1.

The maximum tensile load for each bolt is 1970 lb. and the maximum shear load for each bolt is 2473 lb. The bolts can withstand these loads very well. The main concern is to attach the packages to the transport vehicle at a point sufficiently strong to withstand the loads. Generally if a package is attached only to the wooden deck, weathering of the wood and corrosion of attachments of the wood to the truck framing can reduce its capability below the required strength. This type attachment is forbidden in the DOE tiedown requirement. If the package is attached to the metal framing, sufficient strength and reliability can be assured. Photograph set A depicts a semitrailer with four 21PF-1 packages mounted and attached to the badly weathered wood deck. The framing below is badly corroded. This has very questionable structural strength and is inadequate for UF_6 shipments. Photograph set B depicts a semitrailer with four 21PF-1 packages mounted and attached to the main framing members with bolts, heavy plates, and welded joints. This tiedown system provides adequate structural strength with good reliability – a right way for tiedowns of UF_6 shipments.

Calculations for tiedown loads of a 14-ton UF_6 cylinder

Total weight of a filled model 484 cylinder is 32760 lb.

These cylinders are always loaded on a transport vehicle with the longitudinal axis parallel to the direction of travel. The tiedown load factors from ANSI N14.2 are defined in the foregoing discussion. The resultant tiedown loads for one transport system (by Davis Transport Co., Paducah, KY) for 14-ton cylinders are shown in Fig. 2.

The maximum tensile load to each tiedown strap is 8190 lb. and occurs when the 2.0 X weight vertical force is applied to the cylinder. The maximum shear load of 75348 lb. from the 2.3 X weight longitudinal force is resisted by the stiffening ring against the saddle and has little effect on the tiedown straps. Photograph set C depicts part of a dedicated semitrailer loaded with an empty 10 ton UF_6 cylinder which illustrates how the tiedown straps are applied to the cylinder and attached to the semitrailer main frame. The 14-ton cylinder would be attached similarly, but a third tiedown strap is used providing a larger safety factor. Each tiedown strap is made of nylon with a certified minimum breaking strength of 20000 lb. providing a safety factor above the 8190 lb. required. The straps are attached to a hook on one end and a winch on the other. The hooks and winches are each welded to the semitrailer main frame thereby transmitting the tiedown loads directly to the main frame. A small preload on the straps required to eliminate slack applies an insignificant additional load to the 8190 lb. tensile load.

SUMMARY

Safe shipping of UF_6 by truck is an essential part of the nuclear power industry, and proper tiedowns on the conveyance are essential to that shipping system. The industry must use tiedown methods with the least risk to minimize the possibility of a transport accident. The nuclear industry is encouraged to support adequate and effective tiedown standards as well as the other safety measures for packages and semitrailers.

CALCULATIONS FOR TIEDOWN OF 21PF-1A OR -1B OVERPACKS,

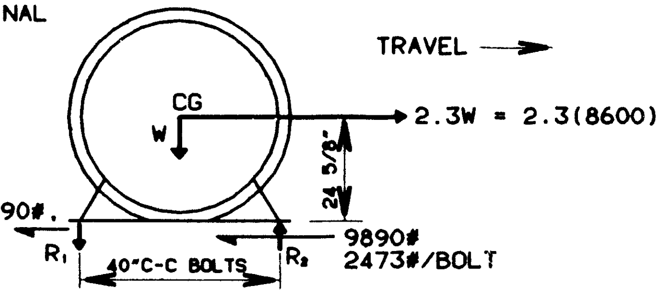
USING ANSI N14.2 REQUIREMENTS (REFERENCE 6)

WT OF 21PF-1A OR-1B=8600 LBS. WITH A FILLED CYLINDER

LOADS IN TIEDOWNS: LONGITUDINAL: 2.3 X PACKAGE WEIGHT
(LOADS APPLIED AT CG) LATERAL: 1.6 X PACKAGE WEIGHT
VERTICAL: 2.0 X PACKAGE WEIGHT

WORST CASE: PACKAGE MOUNTED WITH AXIS TRANSVERSE TO DIRECTION OF TRAVEL.

TIEDOWN LOAD = 2.3W LONGITUDINAL



$\frac{2.3(8600)}{2} = 9890\#.$
OR 2473#/BOLT

$\Sigma MR_2: 40R_1 = 2.3(8600)24\frac{5}{8} - \frac{8600(40)}{2} = 315083$

$R_1 = \frac{315083}{40} = 7877$ FOR 2 SUPPORT FEET

$\frac{R_1}{2} = \frac{7877}{2} = 3939$ PER SUPPORT FOOT (2 BOLTS)

OR $\frac{3939}{2} =$ 1970 LB. TENSION PER BOLT (CONTROLS)

LOAD IN SHEAR: $\frac{9890}{4} = 2473$ LB PER BOLT

TIEDOWN LOAD = 2W VERTICAL: 2(8600)-8600 = 8600

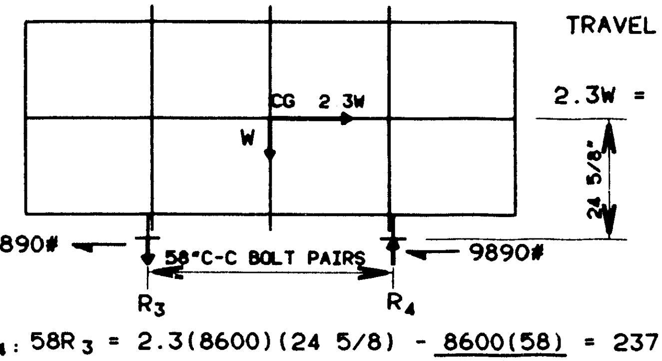
$\frac{R_1}{2} = \frac{8600}{4} = 2150$ PER SUPPORT FOOT (2 BOLTS)

TENSION LOAD: $\frac{2150}{2} = 1075$ LB. PER BOLT < 1970

FOR A325 OR A449 BOLTS, 3/4" DIA.: PER AISC, ALLOWABLE TENSION = 19400 LB. > 1970 OK.
ALLOWABLE SHEAR = 7510 LB. > 2473 OK.

2ND CASE: PACKAGE MOUNTED WITH AXIS PARALLEL TO DIRECTION OF TRAVEL.

TIEDOWN LOAD = 2.3W LONGITUDINAL



$\frac{2.3(8600)}{2} = 9890\#$

$\Sigma MR_4: 58R_3 = 2.3(8600)(24\ 5/8) - \frac{8600(58)}{2} = 237{,}683$

$R_3 = \frac{237683}{58} = 4098$ FOR ONE BASE WITH 4 BOLTS
= 1025 LB. PER BOLT < 19400 OK.

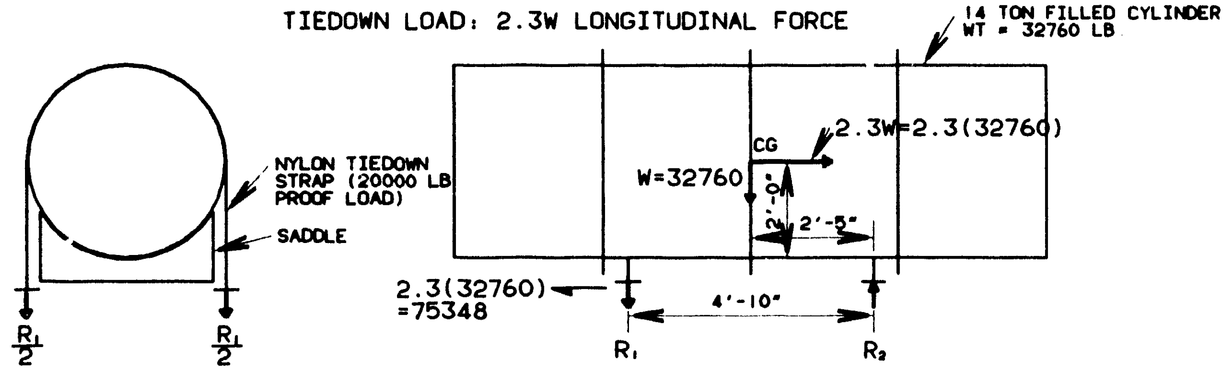
LOAD IN SHEAR: $\frac{9890}{4} = 2473$ LB PER BOLT < 7510 OK.

TIEDOWN LOAD = 2W VERTICAL: SEE ABOVE, TENSION LOAD = 1075 LB. PER BOLT < 19400 OK.

FIGURE 1. TIEDOWN LOADS FOR 21PF-1A OR -1B OVERPACKS.

CALCULATION OF TIEDOWN LOADS FOR 14 TON UF_6 CYLINDER

USING ANSI N14.2 TIEDOWN REQUIREMENTS



ΣMR_2 2.3(32760)(2.)−4.83R_1 −(32760)(2.42)=0

4.83R_1 = 2.3(32760)(2) − (32760)(2.42)=71417

$R_1 = \frac{71417}{4.83}$ =14786 LB.

$\frac{R_1}{2} = \frac{14786}{2} =$ 7393 LB. = LOAD TO TIEDOWN STRAP

SHEAR LOAD AT BOTTOM OF CYLINDER IS RESISTED BY THE STIFFENING RING AGAINST THE SADDLE AND HAS LITTLE EFFECT ON TIEDOWN STRAPS.

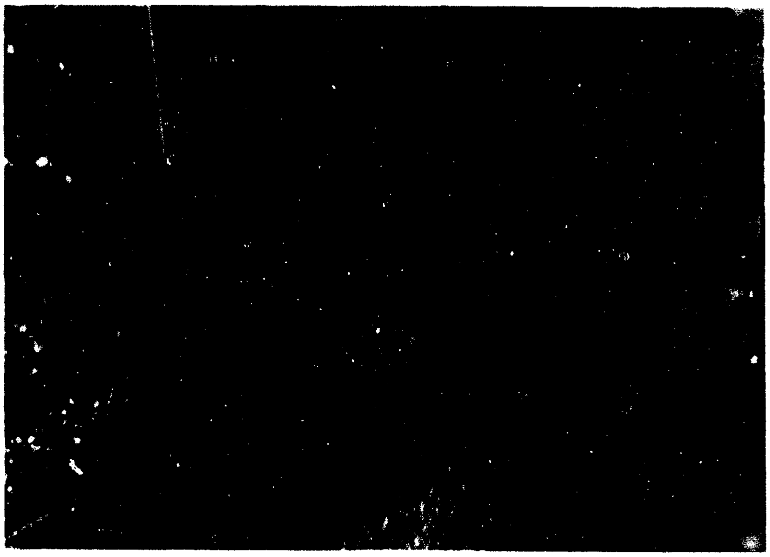
TIEDOWN LOAD: 2W VERTICAL FORCE

2(32760)−32760=32760

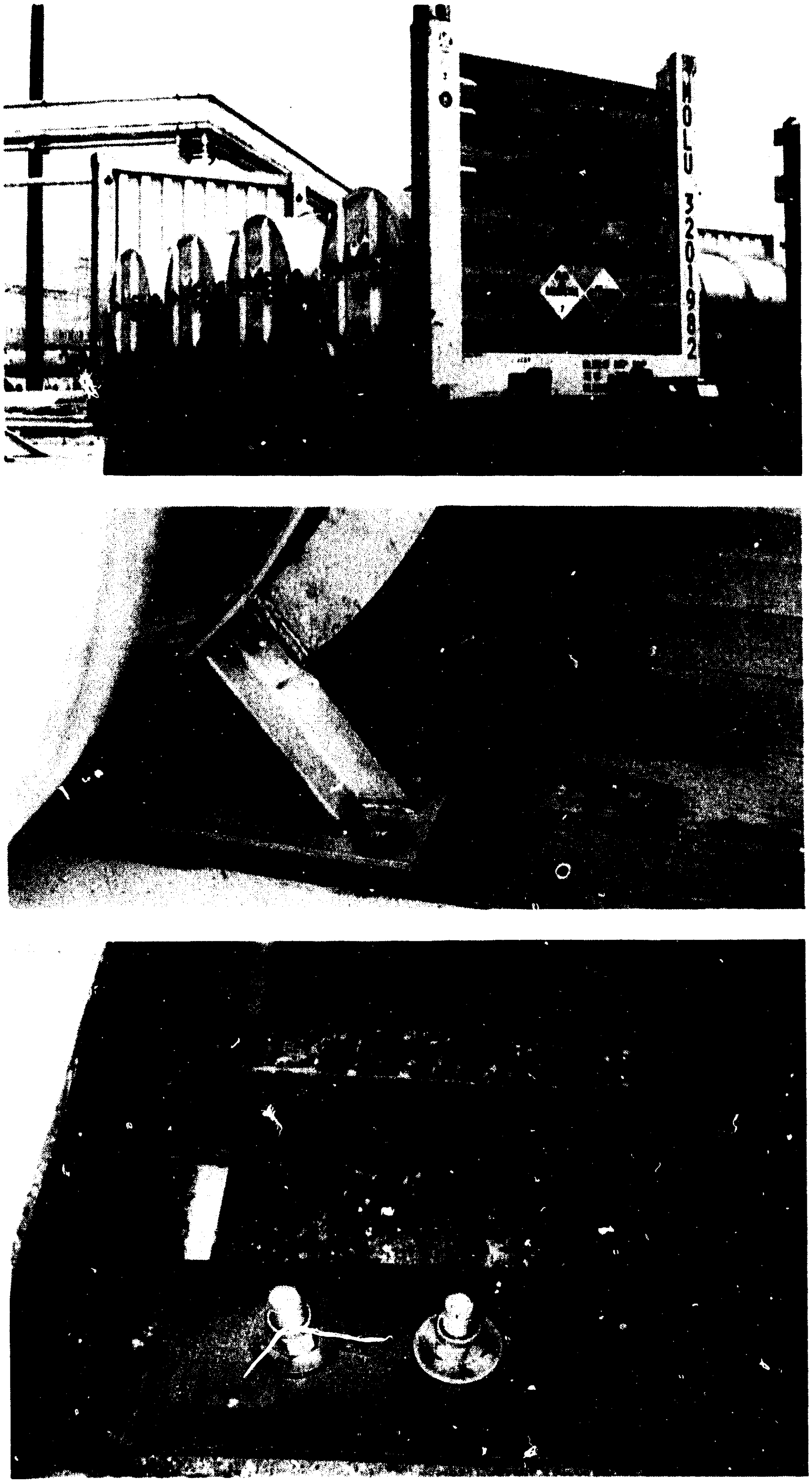
$\frac{R_1}{2} = \frac{32760}{4}$ = 8190 LB. LOAD TO TIEDOWN STRAP (CONTROLS)

20000 LB. STRAP ADDS AN EXTRA FACTOR OF SAFETY

FIGURE 2. TIEDOWN LOADS FOR 14 TON UF_6 CYLINDER



SET A



SET B

SET C

ACKNOWLEDGMENTS

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REFERENCES

1. *"Packaging and Transportation of Radioactive Materials"* Code of Federal Regulations, Title 10, Part 71, U.S. Government Printing Office, January 1991.

2. *"Materials Transportation and Traffic Management,"* DOE Order 1540-1, U.S. Department of Energy, Washington, D.C., July 1990.

3. *"Parts and Accessories Necessary for Safe Operation."* Code of Federal Regulations, Title 49, Part 393, U.S. Government Printing Office, Washington, D.C., October 1990.

4. *"Advisory Material for the IAEA Regulations for the Safe Transport of Radioactive Material"* (1985 edition, amended 1990), Safety Series No. 37, International Atomic Energy Agency, Vienna, Austria, 1990.

5. D. L. Becker, *"Uranium Hexafluoride Packaging Tiedown Systems Overview at Portsmouth Gaseous Diffusion Plant, Piketon, Ohio,"* WHC-MR-0233, Westinghouse Hanford Company, Richland, Washington, March 1991.

6. *"Proposed American National Standard Tiedown for Truck Transport of Radioactive Materials"* American National Standards Institute, ANSI N-14.2, New York, New York, April 1990, Draft.

7. *"Proposed American National Standard for the Design, Fabrication and Maintenance of Semitrailers Employed in the Transport of Weight-Concentrated Radioactive Loads,"* American National Standards Institute, ANSI N14.30, New York, New York, October 1989, Draft.

IMPLEMENTATION OF CONDUCT OF OPERATIONS AT PADUCAH URANIUM HEXAFLUORIDE (UF_6) SAMPLING AND TRANSFER FACILITY

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ABSTRACT

This paper describes the initial planning and actual field activities associated with the implementation of "Conduct of Operations." Conduct of Operations is an operating philosophy that was developed through the Institute of Nuclear Power Operations (INPO). Conduct of Operations covers many operating practices and is intended to provide formality and discipline to all aspects of plant operation. The implementation of these operating principles at the UF_6 Sampling and Transfer Facility resulted in significant improvements in facility operations.

Cylinders:
Valve Studies

ONE-INCH VALVE FOR UF_6 CONTAINERS PACKING-NUT FAILURE: CAUSE OF THE PROBLEM AND SUGGESTED SOLUTION

Jean Pierre Richer
President
Descote S.A.
Feyzin, France

Paper will be distributed at conference.

CYLINDER VALVE PACKING NUT STUDIES

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ABSTRACT

The design, manufacture, and use of cylinder valve packing nuts have been studied to improve their resistance to failure from stress corrosion cracking. Stress frozen photoelastic models have been analyzed to measure the stress concentrations at observed points of failure. The load effects induced by assembly torque and thermal expansion of stem packing were observed by strain gaging nuts. The effects of finishing operations and heat treatment were studied by the strain gage hole boring and X-ray methods. Modifications of manufacturing and operation practices are reducing the frequency of stress corrosion failures.

INTRODUCTION

The current design of the one-inch cylinder valve originated in the early 1950's when the Chlorine Institute initiated a design and materials study to correct serious problems with the two-piece copper-zinc alloy valve body used by the chlorine producers and the U.S. enrichment plants. Details of the investigations conducted at Oak Ridge are described in References 1 and 2. Valve body failures were eliminated with the adoption of the one-piece body and a single phase aluminum bronze alloy. The production and use of tens of thousands of these valves has revealed only isolated quality problems that have been investigated and corrected by the uranium enrichment industry. Instances of stress corrosion cracking failures of the one-inch cylinder valve packing nut have been observed since the current valve design and alloy (C63600) was adopted. With only a few exceptions these failures were considered to be of a random nature. The failures usually occurred at the top of the nut through the intergranular network of the alloy, Figures 1 and 2. The intergranular failures were ascribed to a stress corrosion mechanism. The following paper describes studies undertaken to control the causes of the infrequent failures of the one-inch packing nut.

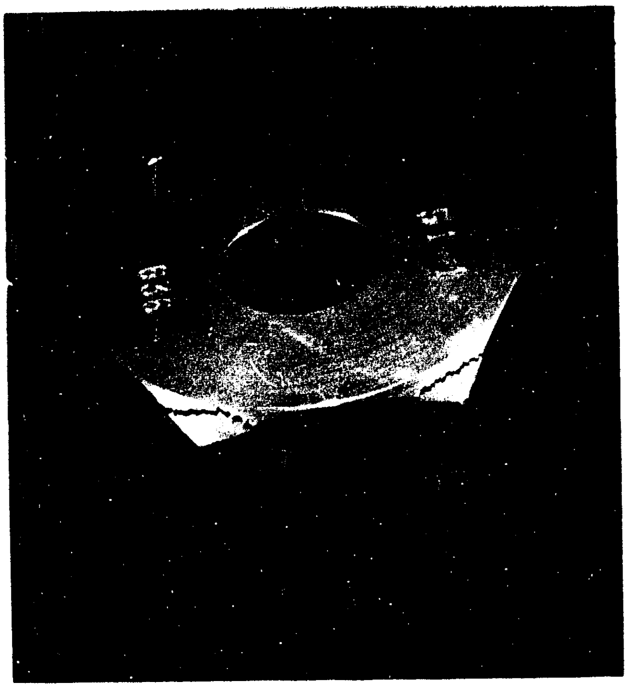


Figure 1. Stress corrosion failure of cylinder valve packing nut.

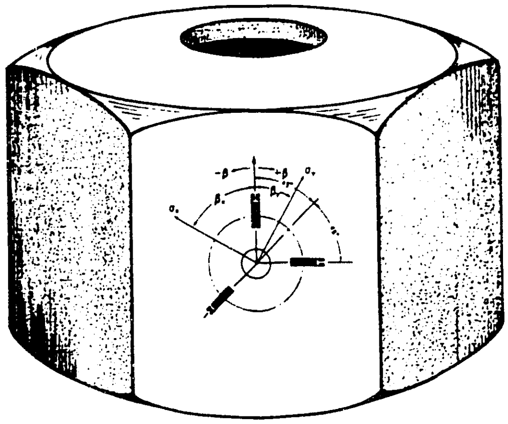
Figure 2. Cross section of intergranular fillet crack.

EFFECT OF RESIDUAL STRESSES

Residual stress appears to play a significant role in the corrosion cracking of the cylinder valve packing nut.[3] These stresses are introduced during the straightening of mill stock or machining and finishing operations of the nut. The influence of residual stresses and the beneficial effect of controlling them can be seen in the comparison of the instance of cracking after inspection of storage yards containing depleted material. In a yard of 7,000 cylinders, mostly filled before the stress relief treatment was required, 0.3% of the valve nuts were cracked. In a larger yard of 35,000 cylinders, 60% filled after initiation of treatment, only 0.03% of the nuts were cracked, and in a yard of 12,000 cylinders, the cracking incidence was zero where all valve nuts were either produced after the treatment was specified or removed and stress relieved.

RESIDUAL STRESS MEASUREMENT

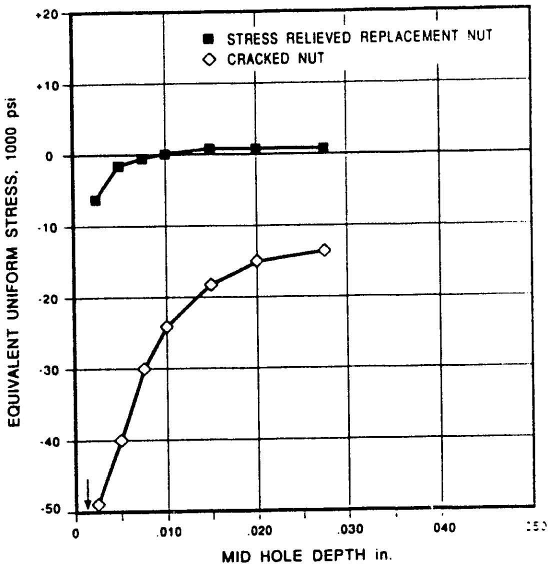
Residual stresses are measured to monitor the effect of stress relief treatments and investigate service failures. The measurements are usually made by the hole-drilling method (ASTM E837) using special rosette strain gages bonded to the side of the nut, Figure 3. The center of the gages are drilled at incremental depths of 5 mils and the strain data is converted to equivalent stresses.[4] In one of the investigations, cracked nuts were discovered when new valves were taken from their original packing boxes. For an unknown reason, the surfaces of the nuts had been sanded. High compressive stresses were found in and below the sanded surface, Figure 4. Another sanded nut was analyzed after it had been stress relieved at 700°F. The treatment significantly reduced the level of residual stress. Similar tests of samples from a shipment of replacement nuts confirmed that they had been stress relieved.



(ROSETTE NOT TO SCALE)

STRAIN GAGE ROSETTE ARRANGEMENT FOR DETERMINING RESIDUAL STRESSES

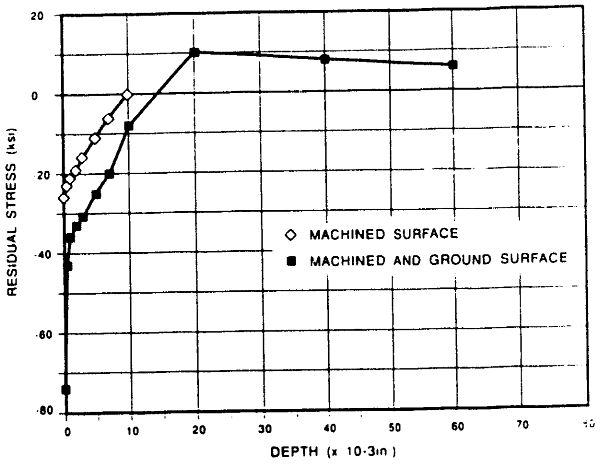
Figure 3.



MEASUREMENT OF RESIDUAL STRESSES BY THE HOLE-DRILLING STRAIN GAGE METHOD

Figure 4.

The compressive stresses near the external surface should be balanced by residual tensile stresses at a lower depth. This was confirmed when the residual stress level was measured by the X-ray method at successive depths after the surface had been chemically removed, Figure 5. The residual stress induced when the nut was machined from a mill shape intensified when the sides were sanded. Since the depth of the analyzed material is only a fraction of a mil, the profile of residual gradients can be accurately detected. The incremental removal of surface material also permits detection of changes of the sign of subsurface stresses. The internal tensile stresses will be intensified by concentration points such as thread roots and the fillet between the side wall and top of the nut.



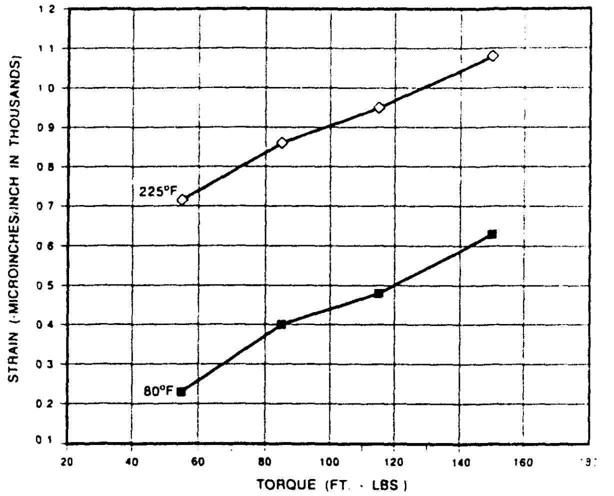
AXIAL RESIDUAL STRESS DISTRIBUTION BY X-RAY METHOD

Figure 5.

OPERATIONAL PRACTICE

Manufacturing and operational practices such as assembly of the valve, retightening the nut, and heating the valve produce stresses in the nut and result in stress corrosion cracking if they are not limited. Strain gages were mounted on a side face of the nut at a location where external compressive stresses are produced by the upward deflection of the top. This location was chosen because it was impossible to apply gages on the inside surface where the nut was yielding and the cracks were initiating. Experimentation indicated that the maximum longitudinal compressive stress was approximately 1.30 inches above the bottom edge of the nut. The instrumentated nut was put on a valve and the strain gage signal was recorded as the torque was increased. Photoelastic analysis of models of the nut have indicated that the interior tensile stresses in the fillet and root of the first thread are three times the magnitude of the external recorded compressive strain that is generated by the upward deflection of the top of the nut.

The level of tensile stress (about 15 ksi) in the fillet after typical torque of 150 ft-lbs would be only a small fraction of the yield strength of the extruded stock used for packing nuts. The stresses that induce the corrosion cracking failures and deform the nuts are generated by sources such as residual stresses and the thermal expansion of the teflon packing against the packing follower that is in contact with the top of the nut. The effect of a typical thermal cycle, such as autoclave heating, was investigated by assembling valves with strain gaged nuts and heating them in a laboratory oven.[5] The increase in the compressive strain was constant over a range of assembly torque, Figure 6. At the interior stress concentration points, the tensile stress may exceed 50 ksi and permanent deformation of softer nuts may occur.

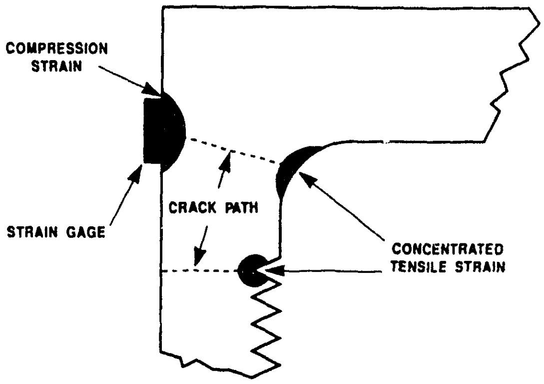


COMPRESSIVE SURFACE STRAIN AS A FUNCTION OF ASSEMBLY TORQUE AT 80°F AND THERMAL EXPANSION OF PACKING AT 225°F

Figure 6.

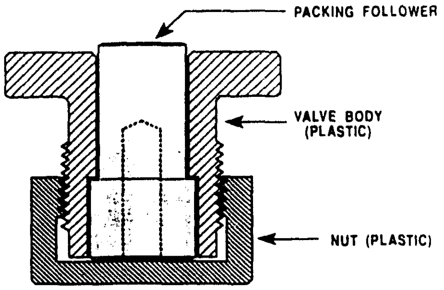
DESIGN ANALYSIS

Service failures of packing nuts originate at the internal stress concentrations shown in Figure 7. Because of the inaccessibility to the concentration points, the traditional tools of experimental stress analysis such strain gages or photoelastic coatings cannot be used to measure strains at crack initiation sites. Strain measurements of the external surface will only record the compressive strains generated as the top bends upward. In order to overcome this problem, photoelastic models are being used to locate and measure the tensile strains on the internal surface. Full-scale models are machined from a special epoxy formulated for the stress freezing method and stressed with the loading fixture show in Figure 8. Analysis of slices from stress frozen models of the standard nut indicate that the stress concentrations in the fillet and root of the first thread are about equal and the tensile stresses are approximately three times the absolute value of the maximum external compressive surface strain.

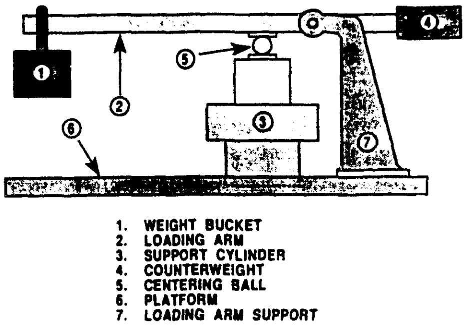


STRESS CONCENTRATIONS AND CRACK PATHS

Figure 7.



PLASTIC NUT AND SUPPORT/LOADING SYSTEM



PHOTOELASTIC LOADING FRAME

Figure 8.

The compressive stress levels measured on the side faces of nuts are indicative of 14 to 16 ksi tensile stresses in the fillet and thread root at a nut torque level of 150 ft-lbs. This is an insignificant stress representing only about 25% of the yield strength of the packing nut stock. However, residual stresses in unrelieved stock could be intensified to the material's yield point after the nut is machined to shape. The strains generated by the thermal expansion of the packing will also be magnified in the fillet and thread root. The investigation of photoelastic models is to be extended to include designs that might reduce the stress concentrations at both the fillet and first thread root.

CORRECTIVE ACTIONS

The investigations of residual, assembly, and thermal induced stresses have prompted the introduction of changes which are reducing the incidences of failures of the one-inch packing nut. The manufacturing specification has been revised to require a 700°F stress relief of the manufactured nut. This treatment will remove 75% of the maximum stress without softening the alloy below 80HRB. The maximum torque that can be used to retighten the packing nut has been reduced to less than 100 ft-lbs. Lower torque levels can also be used if the leak tightness of a valve can be verified before the initiation of a material transfer. Acceptable leak tightness can be achieved at 60 ft-lbs.

CONCLUSION

The susceptibility of the one-inch packing nut to failure from stress corrosion cracking can be reduced by limiting the total stress that a material element may experience at any point in it's life cycle. Experience gained through the investigation of cracked nuts and the analysis of working stresses has indicated that thermal stress relief of both mill stock and finished nuts and reduction of assembly and retightening torque should control the failure rate to the extent that cracking of the nuts manufactured from C6360 is virtually eliminated. With the adoption of a 700°F heat treatment and a lower torque limit for retightening nuts, the U.S. diffusion plants are presently operating without reports of new failures. However, it must be emphasized that the selection of any material and control of manufacturing and operational procedures will not fully eliminate the possibility of failure. Inspection and operational testing programs must be established and followed to minimize the failure of a component like the packing nut.

REFERENCES

1. M. Schussler, "Minimizing Stress Corrosion Cracking of Cylinder Valves," *Corrosion, 11*, March, 1955.
2. M. Schussler and D. S. Napolitan, "Dealuminization of Aluminum Bronze," *Corrosion, 12*, March, 1956.
3. S. C. Blue, *UF_6 Cylinder Valve Packing Nuts*, KY/L-1468, Martin Marietta Energy Systems, Paducah Gaseous Diffusion Plant, December, 1987.
4. "Measurement of Residual Stresses by the Hole-Drilling Strain Gage Method," TECH NOTE, TN-503-3, Measurements Group, Inc., Raleigh, NC, 1988.
5. S. J. Davis and D. E. Underwood, *Cracking of 1-Inch UF_6 Cylinder Valve Packing Nuts: The Effects of Packing Nut Torque on Stem Seal Leakage and Packing Nut Stress Due to Thermal Expansion of the PTFE Stem Seal Rings*, KY/L-1549, Martin Marietta Energy Systems, Paducah Gaseous Diffusion Plant, August, 1989.

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TESTING OF ONE-INCH UF_6 CYLINDER VALVES UNDER SIMULATED FIRE CONDITIONS

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ABSTRACT

Accurate computational models which predict the behavior of UF_6 cylinders exposed to fires are required to validate existing firefighting and emergency response procedures. Since the cylinder valve is a factor in the containment provided by the UF_6 cylinder, its behavior under fire conditions has been a necessary assumption in the development of such models. Consequently, test data is needed to substantiate these assumptions.

Several studies cited in this document provide data related to the behavior of a 1-inch UF_6 cylinder valve in fire situations. To acquire additional data, a series of tests were conducted at the Paducah Gaseous Diffusion Plant (PGDP) under a unique set of test conditions. This document describes this testing and the resulting data.

INTRODUCTION

At the "Uranium Hexafluoride—Safe Handling, Processing, and Transporting Conference" of 1988, the need for UF_6 cylinder fire tests at temperatures near 800 °C was identified in a report by B. Duret and P. Warniez (1). They indicated that the leakage of the cylinder valve should be measured as a part of this proposed testing. Others at that conference, including M. Suzuki et al., (2), W. Williams (3), and H. Yamakawa et al., (4), also reported on related UF_6 fire studies. The cylinder valve was of secondary concern in these studies, and it was obvious that additional data regarding its behavior at high temperatures was needed. Consequently, PGDP implemented high temperature testing of UF_6 cylinder valves in April of 1990. These tests were conducted in support of a UF_6 cylinder fire study by S. Park at the Oak Ridge K-25 site. The objective of such testing was to determine the leakage and behavior of cylinder valves when exposed to temperatures near 1450° F and pressures up to 2000 psig.

TEST SYSTEM

Figure 1 provides photographs of PGDP's UF_6 cylinder valve test system. The basic components of the test system include: (1) a 14-foot run of high pressure piping, terminated at one end by a coupling for attachment of a 1-inch UF_6 cylinder valve, and terminated at the opposite end by connections for the high pressure nitrogen cylinders which feed the system; (2) the high pressure nitrogen cylinders; (3) a turbine-type flowmeter and pressure transducer located near the nitrogen cylinder end of the piping; (4) a hot-wire type flowmeter which is employed at pressures below 250 pounds per square inch gage (psig); (5) a tube furnace for heating the cylinder valve; and (6) a datalogger. Sets of dual thermocouples are attached to the cylinder valve outlet port cap and other areas of the test system to provide a means of measuring and controlling the temperatures of testing.

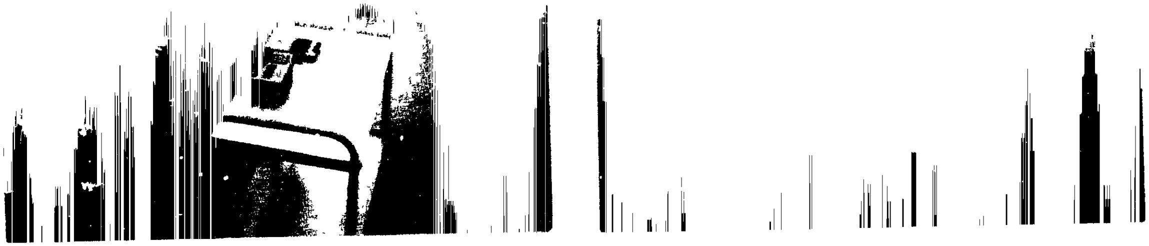

Figure 1. PGDP Test System.

GENERAL TEST PROCEDURES

A new 1-inch cylinder valve was used to initiate each test series described herein. Prior to testing, all Teflon materials (packing and outlet cap seal) were removed from each cylinder valve, after which the packing nut and outlet port cap were reinstalled hand-tight. Each valve was installed in the test system coupling with 200 to 400 foot-pounds (ft-lbs) of torque and a thread engagement of 7 to 12 threads. Before initiation of a test series, each valve was also seated with 55 ft-lbs of torque applied to the stem. Due to the gross leakage of the cylinder valve at 1450°F and the cooling effects this produced, pressurization of the test system piping with high pressure nitrogen was generally limited to the time span required to obtain a stable reading from the system's flowmeters. The nitrogen feed was also interrupted when the cooling effects of leaking nitrogen dropped the cylinder valve temperature below the 1300°F level.

TEST SERIES I - VALVE LEAKAGE AT 1450°F

The intent of this series was to determine cylinder valve leakage at pressures ranging from 50 to 2000 psig, while maintaining the cylinder valve temperature relatively constant between 1450°F 1300°F. Cylinder valve leakage is defined as the sum of leakage through the valve seat and leakage through the tinned threads of the valve's inlet port. This paper reports such leakage in units of standard cubic feet per minute (scfm). This particular series was conducted twice, with the installation of a new cylinder valve initiating each series, and the results were similar. In each case, leakage appeared to be limited to 10 scfm nitrogen, until gross deformation and complete failure of the cylinder valve outlet port cap occurred as pressures were incremented past the 1000 psig level. Just prior to complete failure of the cylinder valve outlet port cap, leakage ranged from 20 to 40 scfm. The maximum leakage after failure of the cap was 102 scfm. Figure 2 provides data from this series of tests. Figure 3 provide a photograph of a failed outlet port cap.

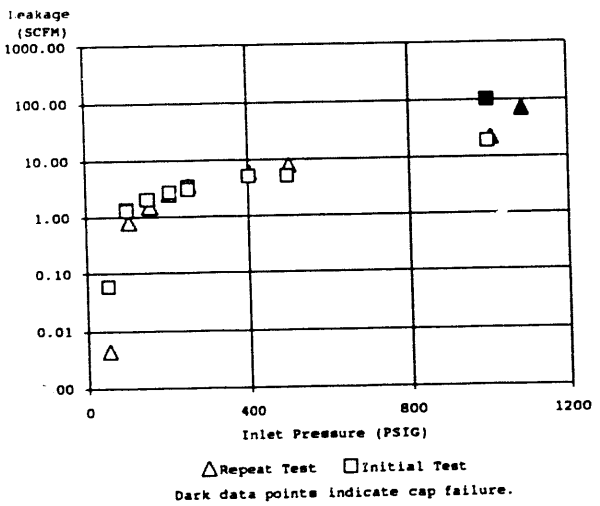

Figure 2 Test Series I data.

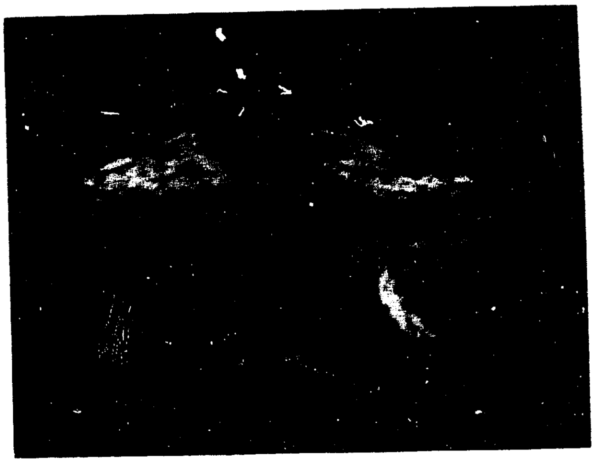

Figure 3. Failed outlet port cap.

The failure of the cylinder valve outlet cap had not been anticipated, but the fact that it did fail provided rather significant information. In a fire which exposes the cylinder valve to the pressures and temperature extremes of the described testing, the cylinder valve outlet port cap will probably be the first component to experience total failure. Also, the significant increase in leakage after outlet cap failure indicates that the valve seat is not the primary factor in limiting leakage at test conditions; it is the outlet cap which limits leakage. Another deduction arising from the outlet cap failure concerns the mating Acme threads of the valve stem and valve body. In order for there to be a pressure build-up in the valve body sufficient to fail the outlet cap, these mating threads must seal effectively at high temperatures.

TEST SERIES II - VALVE LEAKAGE FROM 200°F TO 1600°F

The intent of this series was to determine leakage at temperatures which ranged from 200°F to 1600°F. A test pressure of 250 psig was used throughout this series. This series was only conducted once. Table 1 provides selected data from this series. Note that significant increases in leakage occur near 800°F and 1200°F. A maximum leakage of 10.26 scfm occurred at 1387°F.

It may be important to note that this data does not indicate any increase in leakage as the temperature exceeds the 421°F liquidus temperature of the 50/50 lead-tin solder used to tin the valve's inlet port threads. This implies that leakage through the inlet port threads at elevated temperatures may be only a small percentage of total leakage.

Table 1. Test Series II Data

Elapsed Time (min.)	Valve Temp. (F)	Leak-age (scfm)	System Press. (psig)
0	207	.052	247
8	416	.057	246
16	595	.059	246
46	780	.431	226
65	1003	.509	249
73	1214	7.87	248
92	1416	9.32	229
102	1601	5.12	257

TEST SERIES III - VALVE BEHAVIOR AT 1450°F AND 2000 PSIG

The intent of this test series was to determine the effect of 1450°F and 2000 psig on the cylinder valve body. Due to outlet cap failures, no valve had actually experienced the combined pressure and temperature extremes of the planned testing. One of the effects anticipated was that the lead-tin solder used to tin the valve body's threaded inlet port would fail the body by liquid metal embrittlement. In order to provide a valid test of this hypothesis, it was essential that a cylinder valve be exposed to the test extremes. This test series was conducted only once.

In order to sustain test pressures near 2000 psig, a new cylinder valve was equipped with a special steel outlet cap that incorporated a soft copper gasket. This valve was subjected to a sequence of test cycles, which consisted of heating the valve to 1450°F, introducing nitrogen until the system pressure reached 2000 psig, and holding this pressure until the valve temperature dropped to 1300°F due to the cooling effect of the leaking nitrogen. After valving-off the nitrogen and allowing the valve to recover to 1450°F, the test cycle was repeated. Generally, 1300°F occurred within 30 seconds after the introduction of nitrogen.

After a total of eight cycles in which leakage increased from the 40.00 scfm level to the 90.00 scfm level, the test was discontinued due to the accelerated cooling rate of the valve. Examination of the valve revealed gross deformation of the valve body. This destroyed the effectiveness of the soft copper gasket which sealed the valve outlet. Figure 4 provides data from this test. Figure 5 provides photographs which illustrate the valve body's gross deformation.

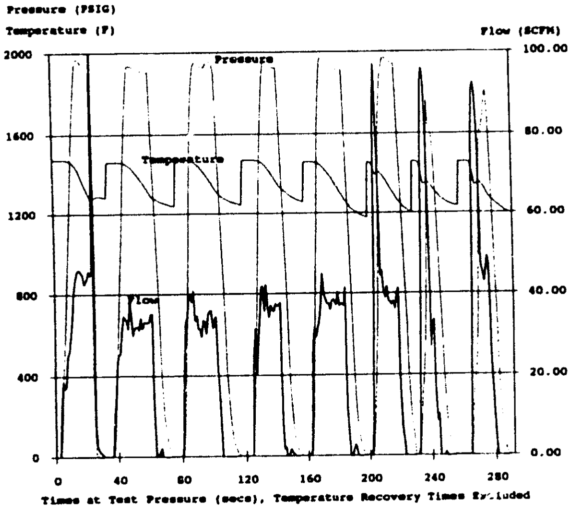

Figure 4. Test Series III data.

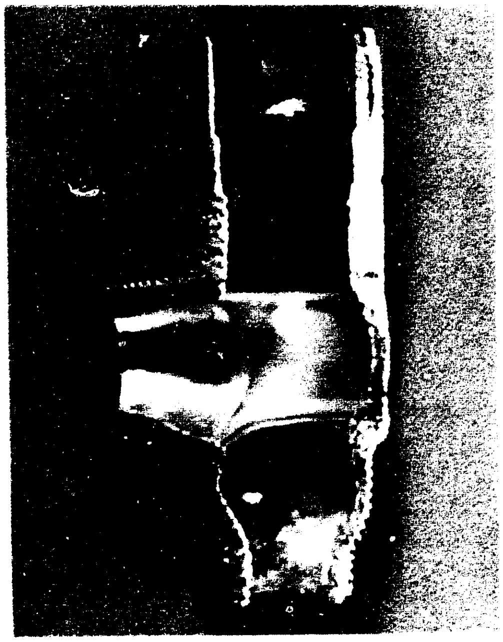

Figure 5. Deformed valve body.

The CDA 636 aluminum bronze alloy valve body did not fail due to liquid metal embrittlement. Metallurgical examination revealed that there was weakening of the valve body's grain structure by solder penetration, but the body remained intact. A photomicrograph which illustrates the typical nature of this solder penetration is provided by Figure 6.

Figure 6. Solder penetration. (Thread Crest—175X)

TEST SERIES IV - STRESS ANALYSIS OF OUTLET PORT CAP

The outlet port cap failures of Test Series I aroused interest in the stress levels being experienced by this cap. As a result, strain gages (90-degree biaxial) were applied to the top dead center of the cap of a new valve, and the valve was subjected to a series of room temperature pressurizations. Figure 7 provides a comparison of stress data from this test series with known tensile strengths of CDA 636 alloy at various temperatures (5). Lab analysis verified that the cap material was CDA 636 alloy.

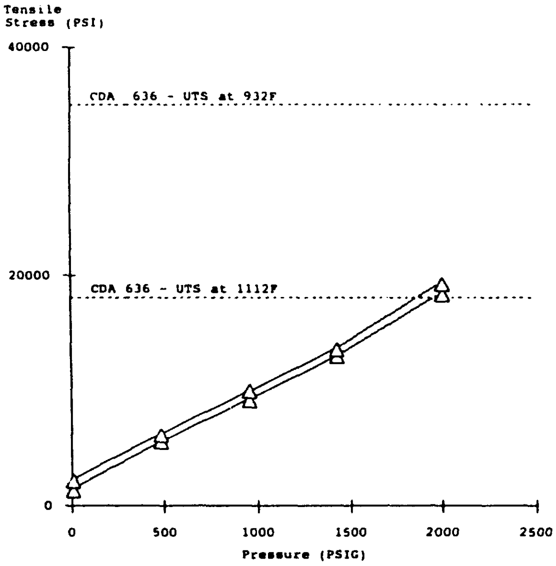

Figure 7. Outlet cap stresses.

TEST SERIES V - STUDY OF SEAL FORMED BY STEM/BODY ACME THREAD

As previously noted, the mating Acme thread of the stem and valve body must form an effective seal at high temperatures. A test was conducted to determine if the forming of this seal could be associated with some threshold temperature. A new valve with the previously described steel outlet cap and soft copper gasket was utilized for this test. A test pressure of 250 psig was utilized throughout the test, as temperatures were increased from room temperature to 1400°F over a 60-minute period.

The test was inconclusive with regard to the sealing of the Acme thread. A leak between 3.0 and 4.0 scfm initiated as the temperature exceeded 400°F, and remained in this range throughout the test. Possibly, leak initiation near 400°F is related to the liquidus temperature of the solder used to tin the inlet port threads. There was a very slight decrease in leakage and increase in system pressure during the test, which may be indicative of the sealing of the Acme thread. Figure 8 provides data from this test.

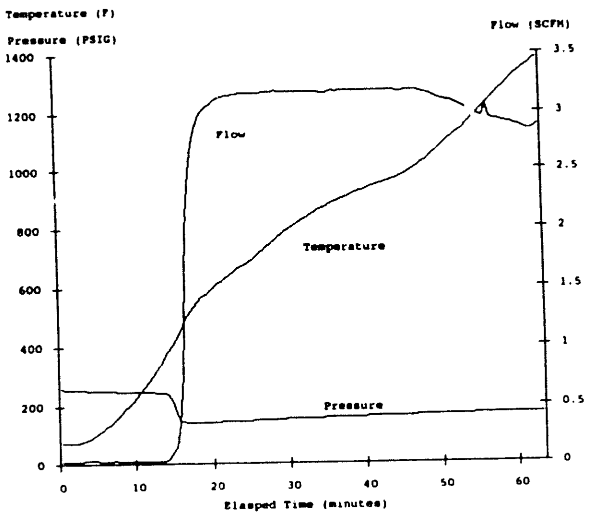

Figure 8. Test Series V data.

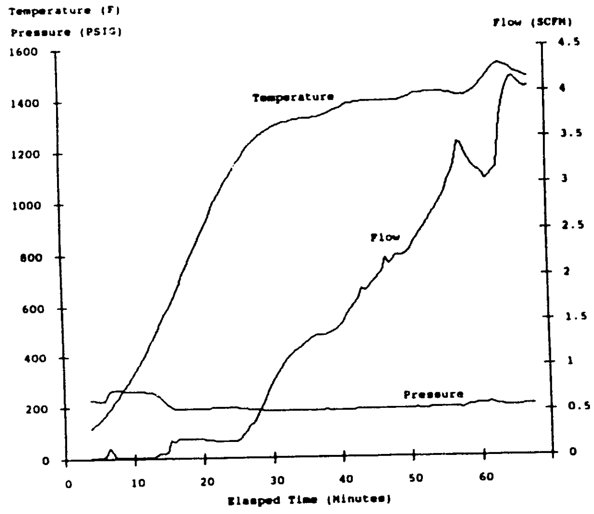

Figure 9. Test Series VI data.

TEST SERIES VI - STUDY OF LEAKAGE THROUGH THREAD OF VALVE INLET PORT

A single test was conducted in an effort to isolate and measure the leakage that occurs through the valve inlet port thread. As before, a new valve was equipped with a steel outlet cap and copper gasket. In addition, the stem was removed and a similar steel capping arrangement was employed to seal the packing cavity of the valve. Leakage was measured as the valve temperature was incremented up to 1600°F, with a test pressure of 250 psig being applied at each temperature increment. The test was inconclusive in that leakage through the inlet port thread could not be distinguished from total valve leakage. Figure 9 provides data from this test.

SUMMARY

The basic objective of the PGDP testing of 1-inch UF_6 cylinder valves was to acquire additional data concerning their leakage and behavior when subjected to 1450°F temperatures and internal pressures up to 2000 psig. This objective was achieved.

Based on data from the testing, an in-service 1-inch UF_6 cylinder valve may perform in the following manner if exposed to a fire which heats it to 1450°F and subjects it to internal pressures above 1000 psig. As pressure and temperature rise, the UF_6 leakage (liquid or gaseous) of the cylinder valve will approach the equivalent of 10 scfm nitrogen. Test data indicates that this leakage rate may be established between 250 and 500 psig when the valve temperature is above 1000°F. This leakage rate will continue until the outlet cap material experiences a combination of pressure and temperature which fails the cap by a rapid creep mechanism. At this point, the outlet port cap will deform to the extent that it is blown off the cylinder valve body, and the UF_6 leakage rate will increase to the equivalent of near 100 scfm nitrogen.

The need for additional testing to fully define the specific combinations of temperature and pressure which result in outlet cap failure is evident.

There is also a need for more extensive testing to thoroughly investigate the seal formed by the mating Acme threads of the stem and valve body. Similar testing is also needed to fully determine the nature of leakage through the valve's inlet port thread.

ACKNOWLEDGMENTS

The author thanks R. I. Reynolds and his cohorts in the PGDP Plant Engineering Division for their efforts in assuring the successful design and fabrication of the cylinder valve test system. R. A. Hobbs of the PGDP Quality Programs Division also provided excellent service and advice with regard to the planning and procedural aspects of the testing.

REFERENCES

1. Duret, B., and Warniez, P., "Thermal Tests on UF_6 Containers and Valves—Modelisation and Extrapolation on Real Fire Situations," Uranium Hexafluoride—Safe Handling, Processing, and Transporting Conference Proceedings, Oak Ridge, Tennessee, May 24-26, 1988, CONF-880558, pp. 89-95, 1988.

2. Suzuki, M. et al., "An Experimental Study on Heat Transfer of a UF_6-Filled Vessel," Uranium Hexafluoride—Safe Handling, Processing, and Transporting Conference Proceedings, Oak Ridge, Tennessee, May 24-26, 1988, CONF-880558, pp. 89-95, 1988.

3. Williams, W. R., "Investigation of UF_6 Behavior in a Fire," Uranium Hexafluoride—Safe Handling, Processing, and Transporting Conference Proceedings, Oak Ridge, Tennessee, May 24-26, 1988, CONF-880558, pp. 89-95, 1988.

4. Yamakawa, H. et al., "Safety Evaluation of the Transport Container for Natural Uranium-Hexafluoride Under Fire Accident," Uranium Hexafluoride—Safe Handling, Processing, and Transporting Conference Proceedings, Oak Ridge, Tennessee, May 24-26, 1988, CONF-880558, pp. 89-95, 1988.

5. Blue, S. C., furnished from personal files, data attributed to Bridgeport Brass Company, July 25, 1991.

Transportation:
Operations and New Standards

OVERSEAS SHIPMENTS OF 48Y CYLINDERS

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ABSTRACT

This paper describes experiences with two incidents of overseas shipments of uranium hexafluoride (UF_6) cylinders. The first incident involved nine empty UF_6 cylinders in enclosed sea containers. Three UF_6 cylinders broke free from their tie-downs and damaged and contaminated several sea containers. This paper describes briefly how decontamination was carried out.

The second incident involved a shipment of 14 full UF_6 cylinders. Although the incident did not cause an accident, the potential hazard was significant. The investigation of the cause of the near accident is recounted. Recommendations to alleviate future similar incidents for both cases are presented.

HISTORY

Commercial production of UF_6 started in the early 1970's and Cameco has been shipping UF_6 cylinders since that time. A transport forwarder is contracted to supply all the necessary freight containers and equipment for both land and sea transport. The forwarder has primarily used wooden cradles, steel straps, and 6 metre heavy-duty flat rack sea containers to support and tie down UF_6 cylinders for transatlantic shipments (Figure 1). ISO approved standard open top containers are sometimes used, but the floor must be reinforced to ensure proper weight distribution.

In the twenty years that Cameco has been shipping UF_6 cylinders overseas, we have not had a serious incident until May, 1989.

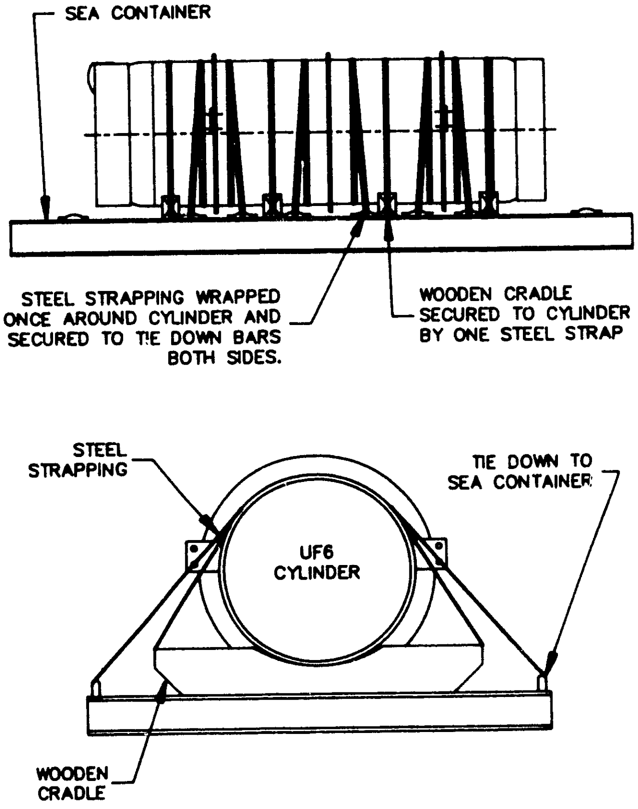

Figure 1. UF_6 **cylinder tie-down**

INCIDENT I

On May 23, 1989, Cameco was advised by the Port Authorities in Montreal, that a shipment of empty 48Y UF_6 cylinders being returned from Europe was damaged and had contaminated other sea cargo. The vessel encountered a severe storm of force 8 and rolled 32 degrees each side.

This shipment consisted of nine empty UF_6 cylinders stowed in three 12 metre closed sea containers and placed above deck of the sea vessel. All three sea containers, as well as a fourth container loaded with hospital equipment, sustained external damage and contamination. The UF_6 containers had side wall tears with openings as great as 516 cm^2 (Figures 2 & 3). Detectable contamination was present on most external surfaces of these containers and white dust was present throughout the interior of one UF_6 container. All three UF_6 cylinders in this container had broken their tie-downs and ejected from the floor cradles (Figure 4). It was apparent they had rolled about during the severe storm, puncturing the side walls as well as the walls of the adjacent containers. Two valve covers were distorted and displaced from the valve area. One valve was sheared and another was pulled out causing the contamination. About one-third of the wooden floor was torn up. The four sea containers were offloaded from the ship and placed in a secured area at the Port. All damage debris was cleaned up on ship and placed in one of the Port's garbage dumpsters.

Figure 3. Container sidewall tears

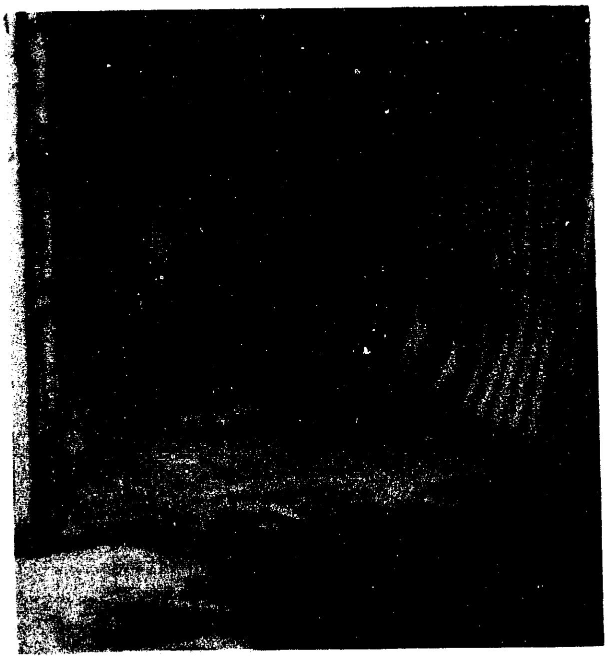

Figure 2. Damaged sea container

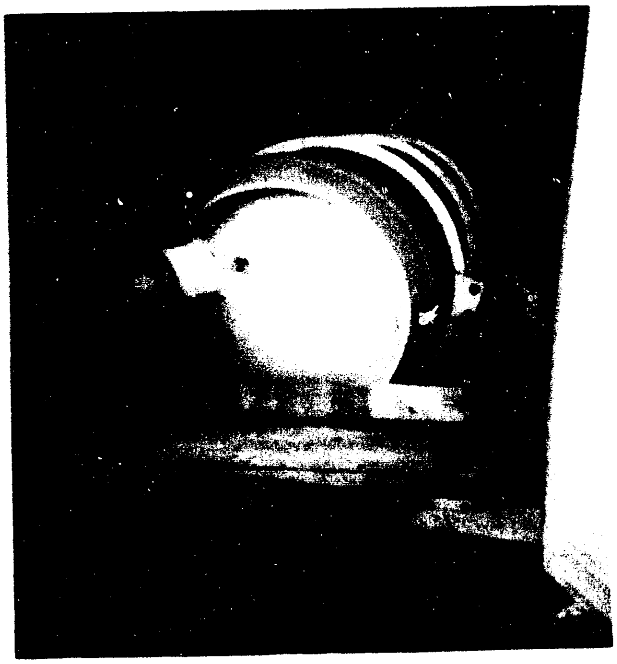

Figure 4. Ejected wooden cradles

ACTION TAKEN

Immediately after being notified of the incident, Cameco dispatched two specialists, a Radiation Officer and a Materials Handling Specialist, to co-ordinate and supervise the clean up and decontamination operations. The following action plan was formulated in conjunction with the Atomic Energy Control Board and the Harbour Master.

a. All decontamination work must be done in secured area.

b. Sea containers and cylinders are to be decontaminated in inverse order of damage to expedite removal from secured area, leaving garbage dumpster and hospital equipment container to the end.

c. Unload UF_6 cylinders from sea containers, decontaminate, and move to normal Port storage area.

d. Obtain authority from owner to enter sealed hospital container and decontaminate equipment.

e. All contaminated materials must be packed in drums and kept in secured area until approval is received by authorities to transport drums to our facility for disposal.

The Radiation Officer's main functions were to:

a. Identify the extent and degree of contamination and to maintain zone control.

b. Define methods of decontamination for items affected by the UF_6 product so that environmental clean-up crews could achieve decontamination standards of 0.5 Bq/cm^2 for non-porous material and 5.0 Bq/cm^2 for asphalt.

c. Remove the UF_6 cylinders and medical equipment from the sea containers for monitoring and decontamination.

The radiation survey disclosed that, three containers, six UF_6 cylinders, 109 pieces of medical equipment, and a waste container of wood from the floor of the damaged sea containers were above the standard.

Various decontamination methods were employed. These were acid, and soap and water scrub washing of UF_6 cylinders, high pressure washing of stubborn areas, sand blasting (wet and dry), cutting, removing wooden container floor with a power saw, oxyacetylene cutting of metals. All contaminated waste, cleaning items, sand, water, wood and metal were placed into drums and shipped back to Cameco's Port Hope facility for disposal. No quantitative measurements of contamination were recorded. This approach was strictly go/no-go basis. The decontamination process was slow -- especially when field innovated modifications were needed. When all the items were decontaminated, the area used for decontamination was cleaned with a high pressure wash before returning the area for normal use. Any area (total less that $1m^2$), exceeding 5.0 Bq/cm^2 was acid washed and rinsed. 99% of the area was less than 1 Bq/cm^2 and no area exceeded 3.7 Bq/cm^2.

This incident generated 96 drums of low level radioactive waste and three scrap sea containers.

CONCLUSIONS

a. The primary cause of the damage was improper stowage. Although the UF_6 cylinders were mounted in the sea containers on wooden cradles, the cradles were not secured to the cylinders or to the container floor. The rope ties were inadequate security for transport, Figure 5.

b. Two cylinders were stowed valve-to-valve configuration, increasing the damage effects on valve covers and valves, Figure 6.

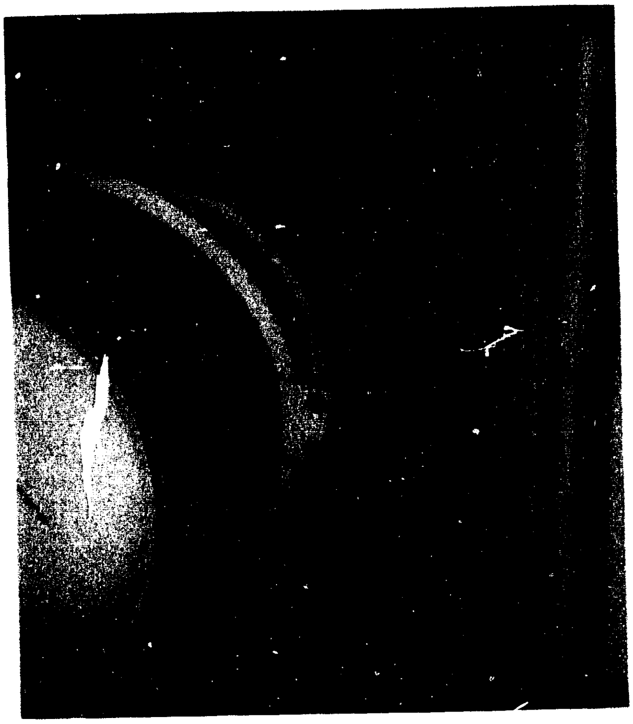

Figure 5. Tie-down

Figure 6. Sheared valve cylinder

c. Cylinder movement within one container caused puncturing of side walls and contamination to three other containers.

d. The extent of contamination was increased by procedures used in unloading the ship when clean material was mixed with damaged contaminated debris.

e. Since the UF_6 cylinders were empty, environmental impact was minimal.

RECOMMENDATIONS

a. Closed sea containers must not be used because UF_6 cylinders are not designed to be pulled out using lateral force on the cylinder lift lugs. Only open top sea containers must be used so that cylinders can be handled by sling or overhead lift devices, always coupling to the cylinder lift lugs.

b. UF_6 cylinders must be placed on not less than four wooden cradles with the cylinder valve at the 12 o'clock position. Each cradle is secured to cylinder with steel strapping.

c. This cylinder/cradle assembly must be secured to the container floor using not less than 6 steel straps, as shown in Figure 7.

d. Ensure valve covers are in place and tightened properly.

e. Response procedures must be reviewed, particularly shipboard methods, to minimize the spread of contamination.

f. Forwarding agent should certify compliance to packaging and transport standards.

Figure 7. Steel strap tie-downs

INCIDENT II

A second incident, which happened earlier this year, involved full cylinders. A shipment of 14 UF_6 cylinders left the Port of Montreal on February 13, 1991, destined for the Port of Felixstowe, UK. Concerns were raised about the handling, packaging and inspection procedures used for this shipment.

Normally, a UF_6 cylinder is placed on not less than four wooden cradles with the cylinder valve at the 12 o'clock position. Each cradle is secured to the cylinder with one steel strap and a single crimp joint. This assembly (UF_6 cylinder tie-down to cradles), is secured to the sea container floor using not less than six steel straps and secured with double crimp joints at all connections, as shown in Figure 1.

On February 21, Cameco was notified that an inspection by the Port of Felixstowe Safety Officer revealed that cylinders were unstable because of slack steel strapping and poorly fitting wooden cradles, which had too large a radius. This resulted in all stress to be taken up by the steel straps, causing the straps to stretch. Some straps were broken on two of the cylinders. A Health Physicist was dispatched to check for direct radiation and surface contamination. No contamination was evident and the radiation levels were 15-17 microsieverts per hour, which are normal readings for full cylinders of natural UF_6. The cylinders were secured properly and shipped by rail to the enrichment plant.

Although there was no accident, the potential for one was great because the cylinders could have broken loose during sea or rail transport causing a full-scale nuclear accident. Cameco investigated this incident with the forwarder and Port of Montreal authorities, as well as the Atomic Energy Control Board and Transport Canada. The result of the inquiry was that, the use of improperly fabricated wooden cradles, cut to the wrong radius, was the main contributor that allowed the cylinders to rotate and cause steel strapping to stretch or break, Figure 8.

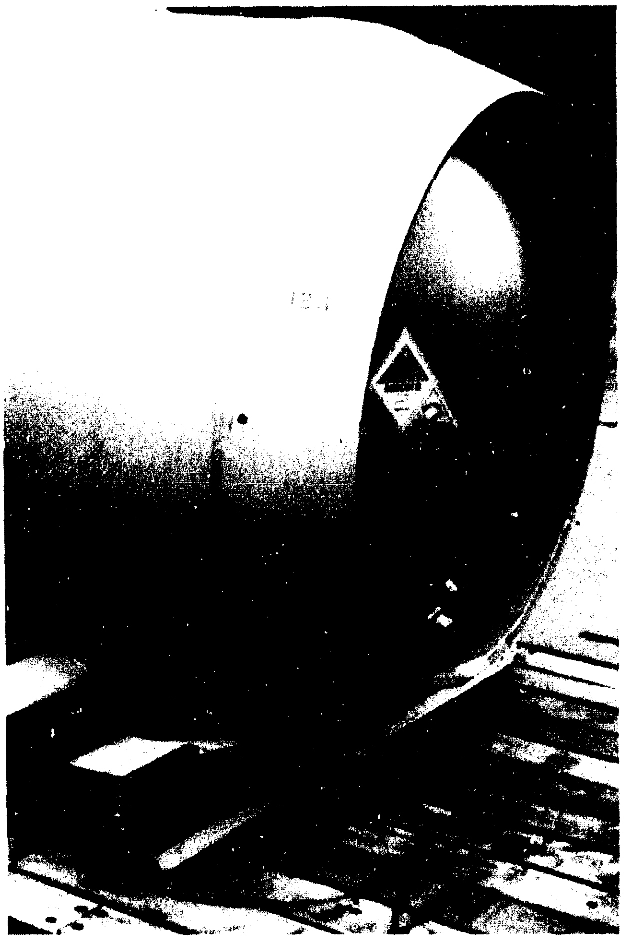

Figure 8. Large radius wooden cradles

The following conclusions were also noted from our investigation:

a. The wooden cradles were not constructed from a solid piece of hardwood. Two strips of softwood (5 cm x 3.8 cm), which probably compressed during transit due to the weight of the cylinder, were nailed to the bottom of these cradles. This caused the cylinder stiffening rings to rest on the sea container floor, and accelerated cylinder rotation (as shown in Figures 9 and 10).

b. ISO open-top containers were used but were not properly reinforced to ensure proper weight distribution.

c. There was no inspection by any Port of Montreal authorities. Manpower and time constraints, a result of a strike at the Port, could have contributed to this.

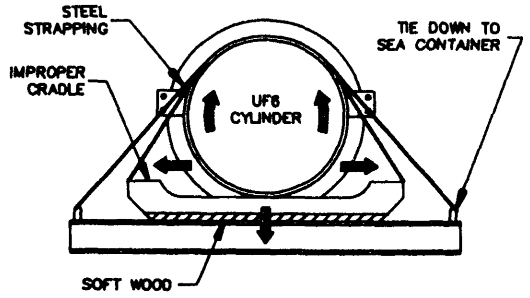

Figure 9. Cylinder rotation

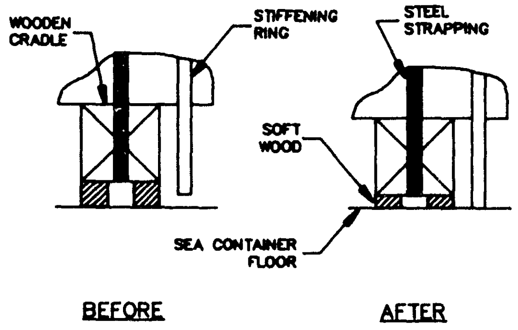

Figure 10. Compressed wooden cradles

A result of this incident is that one of the shipping companies has issued a directive that UF_6 cylinders, on fixed metal cradles only, will be allowed on their vessels. A typical composite of an exclusive skid with metal cradles is shown in Figure 11.

Cameco feels that the present UF_6 cylinder preparation method, using wooden cradles and steel strapping, is safe when proper equipment and inspection procedures are followed; however, Cameco is presently reviewing this matter in view of the directive issued by the shipping company.

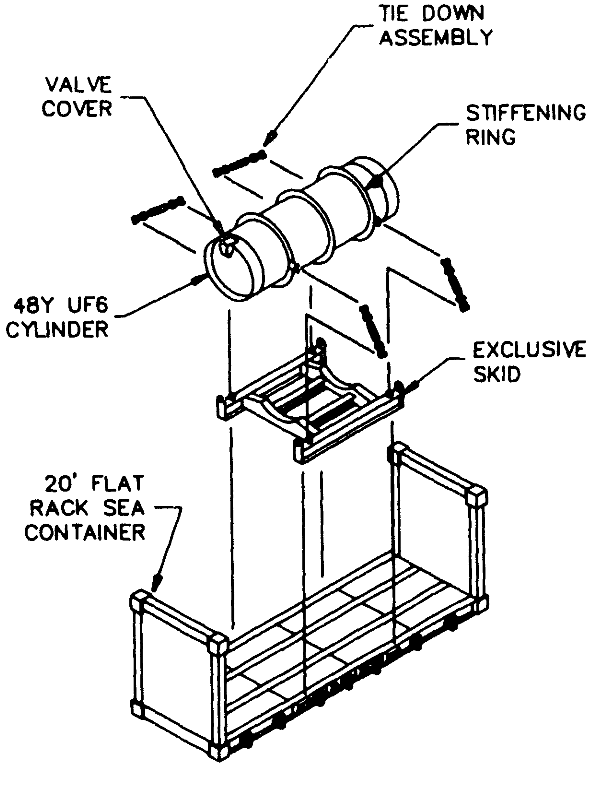

Figure 11. Exclusive metal cradle skid

THE DESIGN, FABRICATION AND MAINTENANCE OF SEMI-TRAILERS EMPLOYED IN THE HIGHWAY TRANSPORT OF WEIGHT-CONCENTRATED RADIOACTIVE LOADS

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ABSTRACT

Transportation of weight-concentrated radioactive loads by truck is an essential part of a safe and economical nuclear industry. This proposed standard presents guidance and performance criteria for the safe transport of these weight-concentrated radioactive loads. ANSI N14.30 will detail specific requirements for the design, fabrication, testing, in-service inspections, maintenance and certification of the semi-trailers to be employed in said service. Furthermore, guidelines for a quality assurance program are also enumerated. This standard would apply to any semi-trailer that may or may not be specifically designed to carry weight-concentrated loads. Equipment not suitable per the criteria established in the standard would be removed from service. The nature of the nuclear industry and the need for a positive public perception of the various processes and players, mandates that the highway transportation of weight-concentrated radioactive loads be standardized and made inherently safe. This proposed standard takes a giant step in that direction.

INTRODUCTION

"The public perceives the potential risks of the transportation of radioactive and hazardous materials and wastes at a far greater magnitude than the estimated risks calculated by scientists and engineers."[1] "Little is accomplished by a good tiedown if the semi-trailer is inadequate for the load."[2] These two statements, alone, provide a legitimate basis for the creation of a national standard for the "Design, Fabrication, and Maintenance of Semi-Trailers Employed in the Highway Transport of Weight-Concentrated Radioactive Loads" - ANSI N14.30.

Even though there has never been a fatality or, for that matter, a major incident involving the highway transportation of radioactive materials, the nuclear industry can not be complacent about its record. The general public still perceives any activity involving radioactive materials to be extremely hazardous and, typically, demands that extreme safety measures be taken in preparing for and executing said activity. The nuclear industry has a perceived mandate, therefore, to exercise prudence in the transportation of all radioactive substances.

It is apparent that much has been accomplished, for instance, in the packaging of radioactive matter for transport, but there are no standards or consensus criteria for the design and care of vehicles to carry these packages. This is the purpose of ANSI N14.30.

The following paper will discuss the background encompassing the creation of a writing group to draft the standard, the activities of this writing group and the environment as N14.30 was developed, detail the contents of the draft standard, and summarize its current status.

BACKGROUND

The nuclear industry was aware that no design, fabrication, or maintenance standard existed for semi-trailers transporting radioactive loads, but there was also no concerted effort to establish one, until R. H. Towell of DuPont de Nemours and Company submitted a letter - dated October 16, 1986 - to the N14 Management Committee. He was, at the time, the chairperson of the ANSI N14.2 Writing Group which was preparing a standard for tiedowns. It became apparent to that committee that adaquate tiedowns were useless unless the vehicle was capable of coping with the subsequent forces. Mr. Towell then recommended to the management committee that a new standard be developed for the "selection of vehicles for transporting radioactive packages.[3]

At the annual meeting of the N14 Management Committee in October 1986, the decision was made to approve the development of N14.30. M. D. Kosmider of Allied Signal - Metropolis Works - was chosen to chair the writing group and, subsequently, prepared the Nuclear Standard/Project Initiation Notice and Data Sheet, which was transmitted to ANSI in June 1987. ANSI submitted the Data Sheet to approximately 150 individuals from industry, government, technical committees and societies, etc. The results of the survey demonstrated a need for the proposed standard - January 1988. The writing group was, subsequently, formed in February 1988.

In the Spring of 1988, D. S. Huffman of Allied Signal - Metropolis Works - replaced Mr. Kosmider as the writing group chairperson. The first meeting of the committee to draft the standard met on June 16, 1988 at Oak Ridge, TN. Meanwhile, several independent events had already occurred that supported the need for developing a standard for vehicles transporting radioactive loads and, therefore, added legitimacy to the efforts of the ANSI N14.30 Writing Group. Examples include:

- A letter (dated May 9, 1988) was written to Mr. John Arendt, Chairperson of the N14 Management Committee, by M. Cynthia Douglas, Director of the Research and Special Programs Administration, U.S. Dept. of Transportation (DOT). This letter commended the N14 Management Committee for tasking a writing group to prepare a standard for vehicle selection for the transport of radioactive packages. Ms. Douglas stated that most accidents involving radioactive packages were due to vehicle failure or human error. She commented that a consensus standard, suitable for incorporation by reference, could become federal regulation.

- On March 11, 1988 a tractor/trailer carrying empty fuel casks, overturned at the Rocketdyne Santa Susana Field Laboratory near Chatsworth, California. The trailer owned by the Department of Energy (DOE) buckled while turning a 25 foot radius corner. Probable cause for semi-trailer failure was the combination of cracks in the main structural beam and the high center of gravity of the cask on the trailer. The semi-trailer was not designed to carry the intended load.

- The Transport Insurance Company in a letter (dated October 2, 1987) to the President of Davis Transport, Inc. stated that unless there are standards for equipment (referring to trailers) design, operation, and maintenance the insurers are forced to exercise their best judgment in evaluating the risks of a carriers operation. Likewise, the American Nuclear Insurers/Mutual Atomic Energy Liability Underwriters (ANI/MAEL-U) in May 1986 developed engineering inspection criteria for nuclear liability insurance. Included in this criteria is a section dealing specifically with the inspection of vehicles employed to transport radioactive material. The insurance industry is obviously desiring performance standards for semi-trailers and other vehicles handling nuclear cargo.

- In May 1988, F. M. Kovac, Traffic Department Supervisor, Martin Marietta Energy Systems, Inc., Portsmouth Gaseous Diffusion Plant presented a paper at the first UF_6 Safe Handling, Processing, and Transporting Conference. In this paper he made reference to the many instances where the semi-trailers arriving at the Portsmouth Plant for transporting overseas shipments had "shoddy" and defective equipment - rotten flooring, bald tires, no brakes, broken springs, etc. Many of these semi-trailers had to be rejected by the Portsmouth Plant. At the same conference, Bert Jody, President of Davis Transport, Inc. offered a paper detailing the exemplary safety record of vehicles designed and dedicated to transporting weight-concentrated radioactive loads. As of May 1988,

> these first generation special purpose vehicles had traveled more than 1,700,000 miles without incident or failure.

The first draft of the standard was completed in January 1989 and a second meeting of the writing group was held in February of the same year to deal with the comments to said draft. The second draft of N14.30 was submitted at the end of March 1989. At the same time, a bill was introduced in the U.S. Senate (sponsored by Senators Danforth and Bond of Missouri and Senator Kassenbaum of Kansas) to make sweeping changes in the DOT regulations regarding shipments of radioactive materials. Among the provisions of this bill, all shipments of radioactive materials would be inspected on a regular basis and shippers could only use DOT approved carriers. This action in the Senate gave the committee a green light to expedite their labors. If the industry doesn't agree to acceptable standards, then the government will do it for us.

A third meeting of the N14.30 Writing Group was called in mid-April of 1989, and the resultant third draft of the proposed standard was mailed to the committee for ballot. This balloting was concluded September 15, 1989 with only one "No" vote out of the twenty that were cast. The proposed standard was then presented to the N14 Management Committee at the end of October 1989 for balloting.

The N14 Committee ballot was taken between November 10, 1989 and February 15, 1990. Forty-nine official votes were cast (74% of the eligible voters); the tally indicated "Yes" - 39, "No" - 9, and 1 "Not Voting". At this point the draft standard could have been published. However, there were many constructive editorial comments that added clarity to the proposed N14.30. Subsequently, the draft was reworked and mailed to the writing group for their consideration in August 1990. Meanwhile, in February 1990 the DOE established a Motor Carrier Evaluation Program (WHC-EP-0336) to assist the DOE field offices and their contractors in selecting carriers to transport DOE owned hazardous and radioactive materials. This program required the shippers, among other things, to measure the quality of the equipment utilized by the carriers, as well as the carrier's maintenance program(s). With ANSI N14.30 in place, shippers of radioactive substances could readily and reliably determine the acceptability of carriers and their equipment.

The revised draft (January 1991) was then mailed to the N14 Committee for a second ballot. This process will be completed in mid August of this year.

SCOPE AND DEFINITIONS

Early in the process of drafting this standard it became apparent that the writing group must agree upon a scope for N14.30 and, likewise, clearly define certain key terms. Once these tasks were accomplished, the remainder of the document could, generally, be easily assembled. The scope as instituted by the committee is:

> "...establishes the requirements for the design, fabrication, testing, and maintenance of semi-trailers used in the highway transport of weight-concentrated radioactive loads...also provides detailed procedures for inservice inspections, testing, and quality assurance of these semi-trailers..."

Two definitions are critical to the focus of the proposed standard - "semi-trailer" and "weight-concentrated radioactive load".

> A semi-trailer is a "load carrying vehicle equipped with one or more axles and constructed so that its front end is supported on the fifth wheel of the truck tractor that pulls it".

> A weight-concentrated radioactive load is "any radioactive live load(s) and its (their) package(s), in contact with the loadbearing portion of the semi-trailer, that exceeds 1000 pounds for any linear foot of length or width at the point of delivery of the load to the structure of the semi-trailer. Certain loads will only become weight-concentrated after stacking".

Radioactive for the purposes of this text is "any material having a specific activity greater than 0.002 microcuries per gram (μCi/g)".

ANSI N14.30 is, therefore, bounded by the above scope and definitions and will initially apply only to those experiences within the purview of these limits.

DESIGN, FABRICATION, TESTING AND CERTIFICATION

The design criteria outlined in the proposed standard is, for the most part, generic. The writing group intends to permit the owner and the manufacturer to mutually arrive at the specific engineering details. The proposed standard will only remind the designer/manufacturer that certain pertinent factors must be understood and applied as the semi-trailer is designed and fabricated. Besides, it would be almost impossible to generate specific design criteria for all of the many potential semi-trailer configurations for transporting weight-concentrated radioactive loads.

Such considerations as lateral stability, operating environment, center of gravity, torsional stress, stress concentrations, materials of construction, static loads, cyclic and dynamic load factors, etc. shall be factored into the design calculations. All ancilliary components - axles, suspension, brakes, tires, rims, landing gear, etc. - must also be capable of supporting the maximum intended load(s). Even the welding process is crucial to an acceptable semi-trailer.

The proposed standard stipulates that the structure of the semi-trailer must be designed and assembled to withstand 2.5 times the aggregate of the maximum "live" and "dead" loads without exceeding the minimum yield strength of the material(s) of construction. Likewise, a 120% safety margin is applied to the design of the structural members to avoid structural failure or fatigue from the influence of cyclic and dynamic loading. After the cumulative application of all dynamic and cyclic loading factors, the yield point of the materials of construction must not be reached.

The designer must specify all fabrication procedures. All welding shall be accomplished by qualified welders using qualified welding procedures as defined in ANSI/AWS D1.1, D1.2, etc. Furthermore, it is imperative that the complete fabrication process be well documented. Design, fabrication, testing, and inspection documents are required for the semi-trailer to be certified.

After fabrication the semi-trailer must be thoroughly inspected for possible defects and to insure compliance with the designer's specifications. Next, the vehicle will undergo a static load test using a package weight of twice the maximum intended "live" load and, then, be inspected again. Following the static load test, the semi-trailer will be subjected to a dynamic test, as it travels through several "normal" operating maneuvers, while it is carrying a package equal to the maximum intended "live" load. The semi-trailer must then be inspected a third time.

All inspections must be performed by personnel qualified for the methods employed. Structural components will be inspected by a licensed professional engineer experienced in semi-trailer manufacturing and design. As a minimum, all non-destructive inspections will include:

1. A visual inspection of the main load carrying members for delaminations, cracking, and deformation.

2. A visual inspection of the 5th wheel upper coupler assembly for deformities and a dye penetrant inspection of the welds joining these members.

3. A magnetic particle or dye penetrant inspection of the welds joining the primary structural members and the primary strucutral members to secondary members.

4. A dye penetrant and visual inspection of the welds joining the suspension to the semi-trailer structural members.

Certification is the responsibility of the manufacturer. The certification process involves several activities, some of which include:

1. A verification that the welders, inspectors, and their procedures are qualified/certified per ANSI/AWS.

2. An examination of mill test certificates for all the materials of construction.

3. A review of all drawings, design calculations, manufacturing procedures, and designer acceptance criteria.

4. A verification of the load rating of all ancillary components.

5. A review of the static and dynamic load tests.

After certification the manufacturer will position an ANSI N14.30 Identification Plate on the semi-trailer and, subsequently, stamp the date of certification on the plate. See Figure No. 1 for a sample ANSI N14.30 ID Plate. The proposed standard permits the certification of semi-trailers not originally designed for use in transporting weight-concentrated radioactive loads, providing the vehicle has the appropriate documentation to verify the designed load rating of its structural members and component parts, as well as a detailed history of all maintenance and repair activities.

A shipper has only to check the ANSI 14.30 Identification Plate to verify that a semi-trailer is designed and certified to haul a given "live" load. Of course, the shipper must confirm that the vehicle is being maintained in agreement with ANSI N14.30.

INSPECTION, MAINTENANCE, REPAIRS, AND MODIFICATIONS

The bulk of this section of the proposed standard is taken from recommended practices suggested by the Truck Trailers Manufacturers Association. The requisites in the standard are intended to augment those promulgated by regulation and those required by the manufacturer. In no way will guidelines in this standard supersede those of the manufacturer or the regulatory agencies.

There are four levels of inspections: Pre-trip, Post-trip, Level 1, and Level 2. Pre-trip and Post-trip inspections are common. The Level 1 inspection in this standard will be performed monthly for semi-trailers in regular service, and includes scrutinizing the electrical system, the air system and brakes, the landing gear and supports, the tires and rims, the suspension, and the structural members.

The Level 2 inspection will be accomplished every two years or 100,000 miles for vehicles in normal service. Specifically, this level requires everything in a Level 1 plus a detailed inspection of axles and brakes, a non-destructive test of the welds on the structural members, and recertification of the semi-trailer, if major repairs or modifications are made to it. All semi-trailers which are built/modified and certified for service under N14.30 must be recertified after five years or 500,000 miles (whichever comes first).

Of course, all inspection, maintenance, and repair reports must be kept for designated periods of time. Furthermore, a "Trailer Inspection Due Date Panel" will be affixed to the front of the semi-trailer. This panel will offer to the shippers and regulators quick confirmation that maintenance inspections are current.

QUALITY ASSURANCE

A Quality Assurance (QA) Program will be mandated for each manufacturer and owner/carrier. The proposed standard presents generic guidelines for establishing a QA program, which includes all the necessary attributes. The writing group realizes that it would be untenable for the standard to prescribe specific criteria for a QA program to each of the parties adhering to N14.30.

CURRENT STATUS OF ANSI 14.30

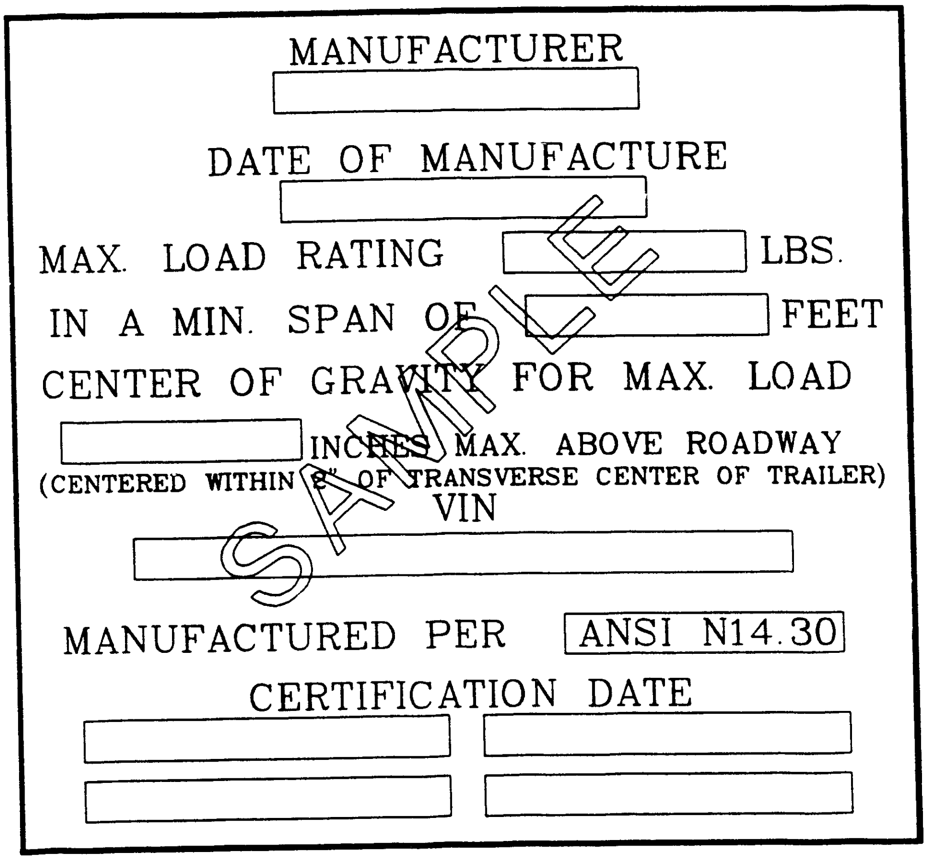
If the vote of the N14 Management Committee is positive and meets the ANSI criteria for a consensus, then this standard can be submitted for publication. At the earliest, the published document will be available around the first of 1992.

REFERENCES

1. Boness, G.O., Maxwell, J.E., and Portsmouth, J. H., "Motor Carrier Evaluation Program", prepared for U.S. Department of Energy by Westinghouse Hanford Company, WHC-EP-0336, February 1990.

2. Towell, R.H., "Recommendation for New Standard Selection of Vehicle for Transporting Radioactive Packages", letter to ANSI N14 Management Committee, October 16, 1986.

3. Towell, R.H., "Recommendation for New Standard Selection of Vehicle for Transporting Radioactive Packages", letter to ANSI N14 Management Committee, October 16, 1986.



MANUFACTURER

DATE OF MANUFACTURE

MAX. LOAD RATING LBS.

IN A MIN. SPAN OF FEET

CENTER OF GRAVITY FOR MAX. LOAD

INCHES MAX. ABOVE ROADWAY

(CENTERED WITHIN 2" OF TRANSVERSE CENTER OF TRAILER)

VIN

MANUFACTURED PER ANSI N14.30

CERTIFICATION DATE

TYPICAL ANSI IDENTIFICATION PLATE

FIG. NO. 1

QUALITY ASSURANCE IN THE TRANSPORT OF UF_6

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Edlow International's primary business is the international transportation of radioactive materials. Therefore, Edlow has the responsibility to ensure that shipments are performed in compliance with regulatory requirements. In this regard, Edlow maintains a Quality Assurance (QA) Program. A major part of this Program is the establishment and use of QA Procedures.

This paper addresses QA procedural requirements and how they are applied to a routine international shipment of low enriched UF_6.

Only the major requirements for scheduling shipments will be addressed. These items are:

- Export Licensing
- Permits
- Notifications
- Packaging
- Regulations
- Documentation
- Inland Carrier Selection
- Ocean Carrier
- Insurance
- Emergency Response
- Export Fees/Taxes

EXPORT LICENSE

Some organizations have bulk U.S. NRC export licenses which allow for multiple shipments over an extended period of time. For various reasons, it is not always possible to obtain bulk licenses for all shipments. In these situations, it is necessary to obtain individual shipment export licenses.

Some items which should be addressed in QA procedures, that have the potential to cause shipment delays, are:

- Submission of incomplete or erroneous information in the export license application.
- A request for an insufficient volume of material or enrichment level. Always remember to add DOE's fluctuation factor of plus or minus 0.05% for enrichment and 0.5% for volume.

Now the NRC has a Full Cost Recovery program ($3,600 per LEU export license), errors will equal additional costs.

PERMITS

Except for routine shipments, it is difficult to incorporate all permit requirements into QA procedures. Edlow, therefore, maintains information on permit requirements by U.S. state and local jurisdictions as well as foreign countries and ports.

The best procedure to follow in this regard is to investigate permit requirements for each shipment well in advance of the planned shipment.

Do not assume that steamship lines actually call at all ports shown in their schedule; delivery to a port shown in a schedule may involve trans-shipment.

Do not assume that the steamship line schedule includes all foreign ports of call.

When possible, use the steamship line with the fewest intermediate ports of call in order to reduce the number of permits required.

NOTIFICATIONS

Some of the entities which may require advance notification and associated QA procedural considerations are:

--Receiver--
There may be permit, import license or notification requirements imposed upon the receiver. Provide the receiver with planned shipment data well in

advance. Never ship until written acceptance of the proposed schedule is received.

--U.S. NRC--
Submit a ten(10) day advance shipment notification to the NRC. This is required for compliance with U.S. NRC regulations established to ensure physical protection as required by the Convention on the Physical Protection of Nuclear Material.

--Local Jurisdictions--
Investigate and comply with all local jurisdictional regulations. In most cases, compliance only requires a basic notification.

--Intermediate Countries--
Investigate and comply with the regulations of all intermediate countries. When possible, investigate specific country and port requirements with nuclear transport organizations located within the intermediate country. They usually have an understanding of both regulatory requirements and policy within their respective countries.

--Inland and Ocean Carriers--
Inland carriers can usually accommodate transportation needs with relatively short notice. This is not always the case with ocean carriers. In some cases, ocean carriers must obtain several approvals before they are allowed to accept the cargo. In order to maintain a planned shipment schedule, one must provide the ocean carrier with shipment data and desired routing details as quickly as possible. In the case of fissile materials via the Panama Canal, carriers are required to provide Canal Authorities with a minimum of 30 days advance notice.

PACKAGING

Routine shipments of low enriched UF_6 require Model 30B cylinders and Protective Shipping Packages (PSPs).

--Cylinders--
A good QA procedure when shipping 30B cylinders from U.S. DOE consists of a summary of the requirements specified in ORO-651 and a checklist for compliance, by cylinder. Other QA procedures must address timely placement of the cylinders, recycle agreements and empty transports.

--PSPs--
As we have all learned over the past 2 or 3 years, PSPs provided for shipment from U.S. DOE must be in suitable condition for the planned transport. When PSPs are used for international shipments, several months may pass without an opportunity to inspect them. Additionally, some users of PSPs do not secure them to steamship containers or highway trailers, they ship them as loose cargo. When PSPs are shipped as loose cargo, one can assure that they will be damaged. For international shipment, PSPs should always be shipped containerized, and on an exclusive use basis. With conditions such as these in mind, QA procedures for PSP maintenance is a must.

REGULATIONS

Most regulations and QA Procedural requirements associated with the international transportation of UF_6 are contained in the following publications:

- U.S. DOT's CFR Title 49
- U.S. NRC's CFR Title 10
- International Maritime Dangerous Goods Code (IMDG)
- International Atomic Energy Agency (IAEA)
- Regulations of Countries Enroute and Destination

DOCUMENTATION

Some of the required documentation items are listed below. Samples of these and all documentation should be included with QA procedures. Some of the documentation requirements for this sample shipment are:

- Inland U.S. Bill of Lading
- Emergency Response Data and Contact Information
- Export Declaration
- Packing List
- Customs Invoice
- Copy of U.S. NRC Export License

INLAND CARRIER SELECTION

We have QA Procedures in place involving the selection of inland carriers. These include items such as insurance coverages, driver training requirements and so forth. Edlow believes in maintaining a routine and has worked with some carriers for over twenty years. Occasionally, carriers must be changed at a specific port. Before accepting a replacement carrier, a visit is in order. A preliminary visit lets the potential carrier know that we have a genuine interest in how they handle our cargo. Additionally, one can tell a lot about a trucking company by observing their equipment and how they keep house.

OCEAN CARRIER

At this point, carriers willing to accept fissile radioactive material shipments <u>at reasonable prices</u> are fairly well established. Therefore, our QA procedures address matters such as:

- Does the carrier have the required equipment?
- Does the carrier have chassis?
- Is the equipment supplied by the carrier usually in good condition?
- If the carrier accepts a shipment, can they really transport it?

In some situations, we are more aware of a carrier's ability to accept and transport radioactive material shipments than the carrier. In this regard, Edlow is obligated to do all possible to prevent difficulties for ocean carriers. If an ocean carrier accepts cargo and then learns after the ship departs that they will not be allowed to enter a specific port, or other major problems develop, not only does the carrier have major problems, but the carrier will probably refuse to accept radioactive material shipments in the future.

INSURANCES

In addition to the insurance requirements relating to inland and ocean carriers, QA Procedures must address other insurance considerations. They are as follows:

- Nuclear Liability Insurance
- Loss and Damage Insurance and War Risk Insurance

--Nuclear Liability Insurance--
Considerations in this regard usually relate to the shipment origin, intermediate ports of call and destination. The Price-Anderson Act provides for nuclear liability insurance on shipments to, or from DOE facilities while the shipment is in the U.S. territorial limits. Edlow, as well as the receiving facilities also have nuclear liability insurance coverage. QA Procedures must be established which address all segments of the transport route, and which ensure that thorough coverage is provided.

--Loss and Damage Insurance and War Risk Insurance--
As with Nuclear Liability insurance, QA Procedures must be established with address the possible need for Loss and Damage and War Risk insurance coverages. We must let our customers know of the consideration and make the coverage available if desired.

EMERGENCY RESPONSE

QA Procedures must address the DOT requirement which states that shippers of hazardous materials include emergency response information with shipments and that all arrangements be in place for 24-hour emergency response assistance. QA Procedures must outline the method by which an organization implements and maintains compliance with this requirement.

EXPORT FEES/TAXES

QA Procedures must address the following charges which are collected by U.S. Customs:

--Harbor Maintenance Tax--
This charge applies to both import and export shipments and is based upon the value of the UF_6. The current rate of charge is 0.125% of the declared value.

--Customs User Fees--
This charge applies to import shipments only and is charged at the current rate of 0.17% of the cargo value with a maximum charge of $400 per shipment.

QA procedures for these items, as well as the new NRC full cost recovery program, must address accounting procedures as well as operational procedures.

Lessons Learned

UF_6 PRESSURE EXCURSIONS DURING CYLINDER HEATING

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ABSTRACT

As liquid UF_6 inside a cylinder changes from a liquid to a solid, it forms a porous solid which occupies approximately the same volume as that of the liquid before cooling. Simultaneously as the liquid cools, UF_6 vapor in the cylinder ullage above the liquid desublimes on the upper region of the inner cylinder wall. This solid is a dense, glass-like material which can accumulate to a significant thickness. The thickness of the solid coating on the upper cylinder wall and directly behind the cylinder valve area will vary depending on the conditions during the cooling stage. The amount of time lapsed between UF_6 solidification and UF_6 liquefaction can also affect the UF_6 coating. This is due to the daily ambient heat cycle causing the coating to sublime from the cylinder wall to cooler areas, thus decreasing the thickness. Structural weakening of the dense UF_6 layer also occurs due to cylinder transport vibration and thermal expansion. During cylinder heating, the UF_6 nearest the cylinder wall will liquefy first. As the solid coating behind the cylinder valve begins to liquefy, it results in increased pressure depending upon the available volume for expansion. At the Paducah Gaseous Diffusion Plant (PGDP) during the liquefaction of the UF_6 in cylinders in the UF_6 feed and sampling autoclaves, this pressure increase has resulted in the activation of the systems rupture discs which are rated at 100 pounds per square inch differential.

BACKGROUND

Solid uranium hexafluoride is heated in containment autoclaves in order to liquefy the UF_6 for liquid sampling, feed to the enrichment cascade, or toll transfer between cylinders. U^{-235} assay and UF_6 purity are obtained through liquid sampling. The UF_6 cylinder valve is connected to the autoclave manifold using a copper pigtail which is approximately 6 feet long. The UF_6 cylinders are heated to approximately 220°F using steam. At this temperature, a UF_6 vapor pressure of 68 pounds per square inch absolute (psia) is generated within the cylinder and manifold system. Each autoclave is equipped with safety systems to prevent overpressuring the UF_6 cylinder, UF_6 manifold, and associated piping. The safety systems used at PGDP to prevent overpressuring the UF_6 systems are listed in Table 1.

Table 1. UF_6 Pressure Control Safety Systems

System	Limit
Cylinder Low Pressure Control	24 psia*
Cylinder High Pressure Control	90 psia
Cylinder Relief System (Rupture Discs)	100 psid**

*One hour and 45 minutes after initiating heat to cylinder.

**Pounds per square inch differential.

The low cylinder pressure alarm safety system is provided to guard against overpressure of a UF_6 cylinder while heating due to a closed cylinder valve, a plugged valve or pigtail. A timer is integrated into the cylinder pressure monitoring system which will close the autoclave inlet steam block valve and cause alarms if the internal cylinder pressure has not reached 24 psia within a time limit of 1 hour and 45 minutes.

The second safety system is a high cylinder pressure safety system which is used to protect UF_6 cylinders from overpressuring. Redundant pressure sensors monitor the cylinder pressure and activate a safety system to close the autoclave steam inlet valve should the cylinder pressure exceed 90 psia.

The third safety system as shown in Figure 1 is a dual rupture disc system. This system consists of two 100 psid rupture discs in series with a cavity between the primary and secondary discs which is monitored using a pressure transmitter. The rupture discs are a reverse buckling type utilizing four knife blades located in the safety head assembly. They are a Teflon coated Monel material rated to actuate at 100 psid ± 2% at 200°F. If the pressure between the discs fluctuates 2 pounds per square inch (psi) above or below atmospheric pressure, alarms are sounded which indicate a possible leak in the rupture disc. If the UF_6 cylinder or manifold pressure should exceed 100 psig, the rupture discs will rupture and relieve the pressure to relief drums.

The activation of any of these safety systems requires prompt notification to the Department of Energy (DOE) and an investigation as to the root cause of the pressure excursions.

Rupture disc systems for UF_6 pressure relief have been used at PGDP for approximately 40 years. During this period of time, there have been only a small number of times while heating UF_6 cylinders that the rupture disc systems have been activated. During the fall of 1990 and winter 1991, PGDP began to experience pressure spikes within the first 20 minutes after valving in steam heat on UF_6 cylinders. The pressure spikes ranged from approximately 20 psig to greater than 100 psig, and on four occasions, the pressure spike activated the rupture disc safety system. Also, the high pressure safety system was activated shutting off steam to the autoclaves.

A summary of the four incidents are shown in Table 2. A separate investigation was performed on each of the incidences.

Table 2. Summary of Safety System Activations

Date	Location	Cylinder Type	UF_6 Assay
10/15/90	C-360	48G	PGDP Tails
12/07/90	C-337-A	48G	Customer Toll Normal
1/20/91	C-337-A	48Y	Customer Toll Normal
2/26/91	C-360	48G	PGDP Tails

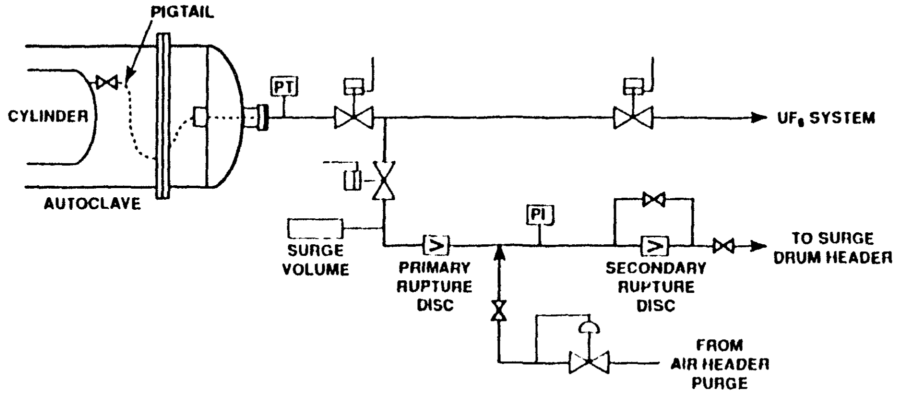

Figure 1. UF_6 Pressure Relief System

DISCUSSION OF CAUSE OF UF_6 PRESSURE EXCURSIONS

When a liquid UF_6 filled cylinder is placed in the cylinder yard to cool, the liquid level is about 1-5 inches below the cylinder valve. As the liquid changes phase (from liquid to solid), it forms a porous solid which occupies approximately the same volume as that of the liquid before cooling. Simultaneously as the liquid cools, UF_6 vapor in the ullage above the liquid desublimes on the upper region of the inner cylinder wall. This solid is a dense, glass-like material which can accumulate to a significant thickness as depicted in Figure 2. Complete solidification leaves a void in the upper portion of the cylinder. The solidification process was filmed in laboratory demonstrations using UF_6 filled glass vials at the Oak Ridge K-25 Site and later at the Portsmouth Gaseous Diffusion Plant. These experiments were directed by R. H. Dyer, DOE.

A study was conducted at PGDP in 1971 concerning the effects of ambient temperature on the shape and location of the void volume in UF_6 cylinders[1]. In this study, two scale models of 10-ton UF_6 cylinders were constructed and filled in the horizontal position with liquid UF_6 to the same relative fill limits as a full 10-ton cylinder. One of the cylinders was frozen quickly in ice water at 32°F while the second cylinder was cooled from 200°F to room temperature over a period of 15 hours. Both cylinders were then frozen in solid carbon dioxide and sectioned for observation. In both cylinders, the major cavities were lengthwise in the top half of the cylinder. All surfaces were covered with solid UF_6 including the inlet openings. One important difference was noted between the two cylinders. The cylinder which was frozen rapidly contained a much larger cavity and the UF_6 was hard and dense. UF_6 in the slow cooled cylinder was flaky and contained many small voids which should offer localized relief for expansion during liquefaction. The thickness and density of the solid UF_6 coating on the upper cylinder wall and the cylinder valve area will vary depending on the conditions during the cooling stage. The ambient temperature, the daily change in ambient temperature, and wind direction will all cause variation in the coating thickness. The amount of time lapsed between UF_6 solidification and UF_6 liquefaction can also affect the UF_6 coating. This is due to the daily heat cycle causing the coating to sublime from the cylinder wall to cooler cylinder areas, thus decreasing the thickness. Structural weakening of the dense UF_6 layer also occurs due to transport vibration and cracking due to thermal expansion.

The most plausible explanation for the excessive manifold pressure, which caused the actuation of rupture discs, resulted from the liquefaction of solid UF_6 confined by a dense, solid UF_6 barrier existing behind the cylinder valve.

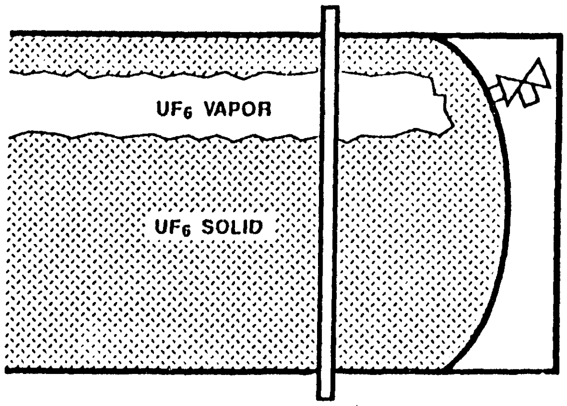

Figure 2. UF_6 Solidification

During cylinder heating, the material nearest the cylinder wall will liquefy first. As the solid coating behind the cylinder valve begins to liquefy, UF_6 liquid will fill the manifold. The manifold has a volume of approximately 0.32 cubic feet (ft^3). On many cylinders, a coating remains intact behind the cylinder valve when the manifold volume is filled. Any increase in liquid temperature will result in an increase in pressure in the manifold. Pressure will continue to increase in the heated manifold until the remaining coating behind the cylinder valve fractures, thus relieving the pressure to the void within the cylinder or the rupture disc rating is exceeded.

An evaluation of the heat transfer characteristics of heating a UF_6 cylinder in an autoclave was performed by PGDP Technical Services Division personnel[2]. The evaluation (based on the heat flux to the cylinder and assuming that 10 percent of the liquid UF_6 generated is localized in the area of the cylinder valve) indicated the entire UF_6 manifold volume would be generated in 12.25 minutes. (The calculated value was in agreement with the observed time of the pressure spikes during the UF_6 cylinder heat cycle.) Additionally, the evaluation (based upon the coefficient of thermal expansion provided in K/ET-194(3) of 65.3 psi/°F at the triple point) indicated a temperature rise of only 2.3°F of the liquid held within the manifold would account for a 150 psia pressure increase.

The maximum manifold pressure attained will depend on the thickness of the coating behind the valve. If the coating is thin, there will be only a small pressure spike or no spike at all. However, if the coating is sufficiently thick, the pressure spike will grow quite large before breaking through the solid UF_6 coating. In the four recent cases, the solid thickness behind the valve was sufficient to withstand the pressure required to actuate the rupture discs.

The four cases of very high pressure spikes occurred between October 1990 and February 1991. During this cold weather period, lower level pressure spikes occurred frequently during the heating of other cylinders. However, the pressure spikes were limited to PGDP UF_6 tails cylinders and to one customer's Toll UF_6 cylinders. The customer's Toll Normal UF_6 cylinders had been previously heated in the PGDP C-360 toll transfer facility with no pressure spikes observed. (Most of the cylinders had been in storage at PGDP for approximately 2 years.) The next time these cylinders were heated in C-337-A shortly after being heated in C-360, pressure excursions were observed. Similarly, the PGDP UF_6 tails cylinders were being heated for liquid sampling with a much shorter time between filling the cylinders and the liquid sampling process. This was caused by an increased emphasis on assay data due to studies being performed on UF_6 tails assay fluctuation during cascade power fluctuations. This commonality substantiated the relationship of lapsed time between heating cylinders shortly after UF_6 solidification as a contributing factor in the rupture disc activation.

Many root cause theories were evaluated during the investigation of the four separate occurrences of high pressure spikes. Other possible scenarios explored for the high pressure problem were the presence of organic contaminants, uranium deposits in UF_6 manifolds and the presence of improperly rated rupture disc. These theories were ruled out after further testing and chemical analysis.

CONCLUSION

UF_6 pressure excursions have occurred at PGDP within the first twenty minutes of heating of UF_6 cylinders. This was caused by the thermal expansion of liquid UF_6 in the autoclave UF_6 manifold. The elevated pressure levels occur only when a combination of two factors takes place in the following sequence. First, the liquid UF_6 filled cylinder cools in cold weather, typically less than 40°F which increases the magnitude and density of the UF_6 directly behind the cylinder valve. Secondly, the UF_6 cylinder is heated shortly after the UF_6 solidification process without sufficient time for the breakdown of the UF_6 solid in the cylinder valve area. The rupture disc and high UF_6 pressure safety systems functioned as designed and limited the UF_6 pressure excursions in PGDP's C-337-A and C-360 facilities.

REFERENCES

(1) Otey, M. G., "Voids in UF_6 Cylinders," letter to C. W. Walter, February 24, 1971.

(2) Kreitz, P. B., "Response Regarding the Actuation of Rupture Discs, C-337-A Vaporizer," letter to J. R. Elrod, February 25, 1991.

(3) Sternberg, E. O., Relationship of Pressure to Temperature Rise in Overfilled Cylinders, K/ET-194, Supplement 3, May 18, 1979.

INCIDENTS OF CHEMICAL REACTIONS IN CELL EQUIPMENT

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ABSTRACT

Strongly exothermic reactions can occur between equipment structural components and process gases under certain accident conditions in the diffusion enrichment cascades. This paper describes the conditions required for initiation of these reactions, and describes the range of such reactions experienced over nearly 50 years of equipment operation in the U.S. uranium enrichment program. Factors are cited which can promote or limit the destructive extent of these reactions, and process operations are described which are designed to control the reactions to minimize equipment damage, downtime, and the possibility of material releases.

INTRODUCTION

In the U.S. uranium enrichment program, the principal isotopes of uranium, of atomic weights 235 and 238, are separated by the gaseous diffusion process. The slight differences in atomic weight make it possible to separate the two isotopes by diffusion through a porous membrane. In the process medium (uranium hexafluoride gas), the lighter species, $U^{235}F_6$, has a slightly higher velocity than the heavier molecule of $U^{238}F_6$, and as a consequence, it comes into contact with the diffusion membrane wall with somewhat higher frequency. Control of the pore size in the diffusion membrane optimizes the separative capacity by permitting diffusion through the membrane while limiting molecule-to-molecule collisions which tend to negate separation by deflections away from or out of the membrane pores. Even so, the single-stage separation factor is so small as to require the operation of many such stages in series, in a cascade configuration, in order to effect the desired separation, or enrichment.

Operating parameters are maintained to force about half of the stage feed through the diffusion membrane as the isotopically enriched stream, while the remainder passes along the membrane tubes as the isotopically depleted stream. Cascading is effected by feeding the enriched stream to the next upstream diffuser for further enrichment, while the depleted stream is fed back to the next downstream stage for additional stripping (Figures 1 and 2). A sufficient number of

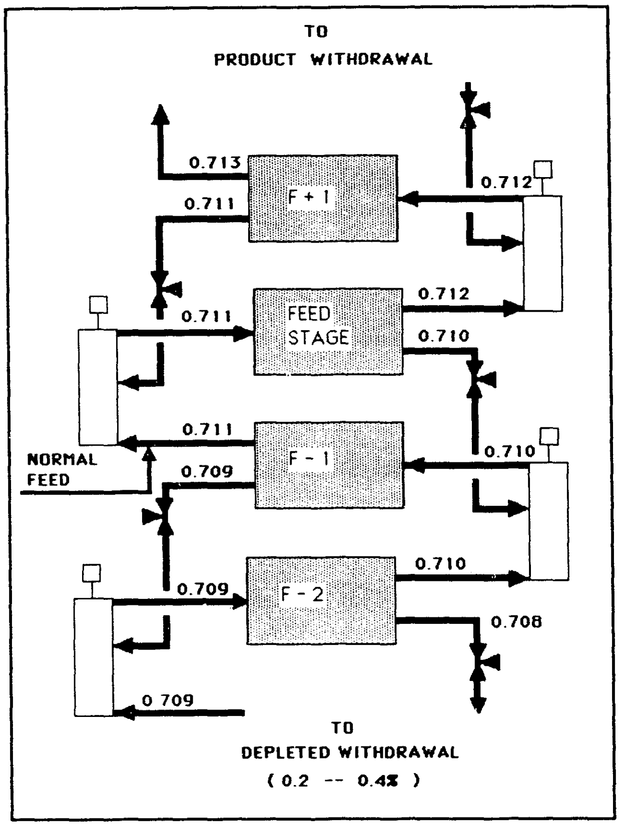

Figure 1. Gaseous Diffusion Stage "Cascading."

[+] Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

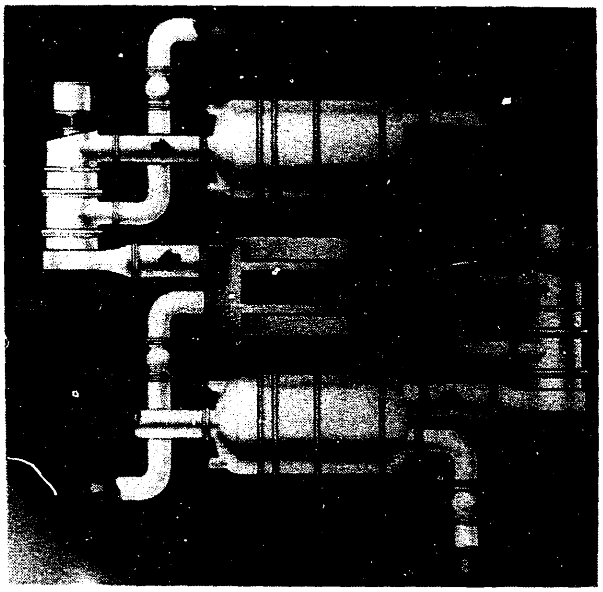

Figure 2. Stage Arrangement

stages are operated above the feed point to obtain the desired enrichment, and sufficient stages below the feed point assure the desired tails assay (Figure 3).

To meet the needs of the U.S. enrichment program at its maximum capacity, nearly 11,000 separative stages were employed at one time in three independent diffusion plants. Changing schedules, plant improvements, and finally reduced demand for enrichment services resulted in gradual phase-out of older portions of the original K-25 cascade and then shut-down of the Oak Ridge enrichment facility in 1985. The present Paducah and Portsmouth cascades contain about 6,000 separative stages. Each of these stages includes, in addition to the diffuser, a compressor and drive motor, a gas cooler, a flow-regulating control valve, and associated piping. In order to permit isolation of small portions of the cascade without adverse effect on overall operations, small numbers of stages are grouped into cells. Each cell may be isolated from the rest of the cascade by closing a few block valves, so that equipment can be repaired or replaced to correct failures or malfunctions.

GAS-METAL REACTIONS

About 300,000 stage years of operating experience have been accumulated in the three diffusion enrichment plants since the start-up of the K-25 cascade in 1945. Over that time period, there have been about 50 reported incidents of gas-metal reactions involving compressors, diffusers, or gas coolers, in various combinations. Although uranium hexafluoride is regarded as a stable compound, it is, under the right circumstances, a powerful fluorinating agent, reacting vigorously with aluminum and its alloys, and, at higher temperatures with nickel, copper, and even steel. Similar reactions have also been observed with the cell treatment gases, fluorine and chlorine trifluoride. Each of the incidents had a common feature: rubbing contact in the stage compressor initiated the reaction or generated molten metal which served as an ignition source within the compressor or at a downstream location. Thus sustained reactions have been observed in compressors, in gas coolers, and in diffusers. Hot metal reacts with process gas to form metal fluorides with the evolution of large amounts of heat. The reaction accelerates as additional molten metal surfaces are made available to additional supplies of process gases. If a gas cooler is breached, the coolant, Freon 114, also enters into the reaction. Flashing and expansion of the coolant can force the reactants into adjacent stages, and it is considered likely that without measures to control the reactions, they are capable of spreading throughout a cell, and possibly even into adjacent cells.

OPERATING EXPERIENCE

Gas-metal reactions that have been experienced in compressors have ranged from a minimal involvement of a few blade tips (Figure 4) to some which have resulted in loss of several inches of rotor length or a large hole burned through the rotor or the stator shell. Such reactions may confine themselves to the compressors in which they initiated, but in some cases the hot gases or burning masses of molten metal may be carried into the adjacent diffuser, where they may ignite structural components to further extend the damage. The finned gas coolers and the diffuser tube bundles are at particular risk in such events since they present large surface areas to sustain the reactions.

An incident which occurred in the Oak Ridge K-29 plant in 1982 illustrates a number of factors that may be involved in initiating and propagating destructive gas-metal reactions.

Figure 3. "000" Unit Configuration

The K-29 portion of the Oak Ridge enrichment cascade went on-stream in 1951. Ten diffusion stages constitute a cell in K-29, and gas movement is effected by multi-stage axial flow compressors with die cast aluminum blades mounted in cast aluminum stators and rotors. Loss of rotor-end clearance had been noted in early plant operations, and this was found to be due to changes in the metallurgical structure of the cast aluminum-copper alloy rotors. A program of heat-treatment (overaging) and re-machining to restore the drawing-specified clearances was carried out in the mid-1950s.

On March 1, 1982, K-29, Unit 2, Cell 7, had undergone a ClF_3 treatment following a seal change on the Stage 7 compressor. In the initial phase of recharging UF_6 into the cell, the stage motor loads appeared normal. During the UF_6 charging process, however, the Stage 7 and Stage 8 compressors began to surge. In addition, the Stage 7 high side pressure was lower and the Stage 8 high side pressure was higher than expected. Approximately 15 minutes after placing the cell onstream, the cell pressures began to decrease rapidly, suggesting a destructive reaction within the cell, and the Stage 7 diffuser was observed to be cherry red at the bottom of the inlet nozzle.

The cell was isolated and standard procedures were followed to insure confinement of the reaction. Since the cell coolant system operates at high internal pressures, rupture of a gas cooler could overpressure the cell, therefore, the initial response to the cell reaction was to dump the cell coolant into storage tanks and valve off the system. Since some mixtures of coolant and process gases are highly reactive, draining the coolant also removes a possible reactant from the system. Shutting off the cell supply of lube oil removed another potential hazard. Cell isolation from the rest of the cascade limited the supply of UF_6 to that contained within the cell volume, so that the reaction with molten metal would starve as this gas was consumed.

These emergency measures for confining a gas-metal reaction are covered in a standard operating procedure, SOP 100.7, "Destructive Chemical Reactions in K-29." Radiation surveys and chemical samples taken after the occurrence indicated that no systems were opened to the atmosphere and no uranium compounds were released.

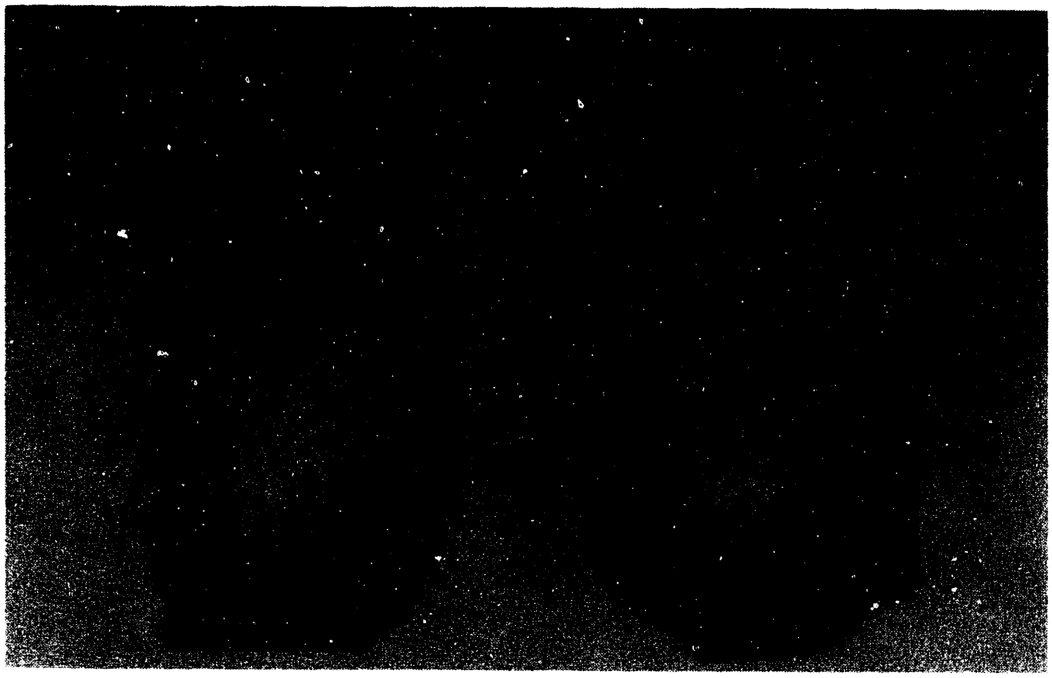

Figure 4. Limited Reaction Caused By Blade Tip Rubbing.

Examination of the equipment after removal and disassembly showed that severe end rubbing had occurred in the Stage 7 compressor, and the B-rotor barrel had debladed (Figure 5). The compressor interior surfaces and the inlet and discharge nozzles were coated with a powdery reaction product, and some of the turning vanes in the discharge nozzle had been damaged. The Stage 8 compressor components were also lightly coated with a reaction product and the Stage 6 pump also showed a dusting of similar material. Reaction products were distributed as far as the Stage 9 diffuser. The Stage 7 diffuser, where the principal reaction occurred, showed major damage. The shell in the heated area collapsed (Figure 6) because of the pressure drop that resulted from UF_6 consumption by the reaction, and a portion of the tube bundle was destroyed. The gas cooler remained intact and structurally sound, although some tube fins had melted.

The incident investigation concluded that the reaction was triggered by the rotor end rubbing that occurred as a result of the surging that took place during cell pressurization with UF_6. It was not determined whether additional growth of the rotor had occurred after the 1954 stabilization heat treatment, although such growth is possible and would make the compressor more susceptible to rubbing because of surge operation.

SUMMARY

- Strongly exothermic reactions can occur between process gases and metals in the diffusion enrichment cascades.
- Ignition depends on a heat source, generally rubbing in a compressor.
- Reactions can spread by ejection of burning molten metal from the compressor. Diffusers have been ignited by this mechanism.
- In-place operating procedures are available to limit the extent of these reactions.
- Destructive chemical reactions are infrequent. Only about 50 have been observed in some 300,000 stage years of operation in the U.S. enrichment program.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the work of C. L. Sherman, Portsmouth Gaseous Diffusion Plant, and M. G. Otey, Paducah Gaseous Diffusion Plant, in compiling histories of exothermic reactions which have occurred at their respective facilities.

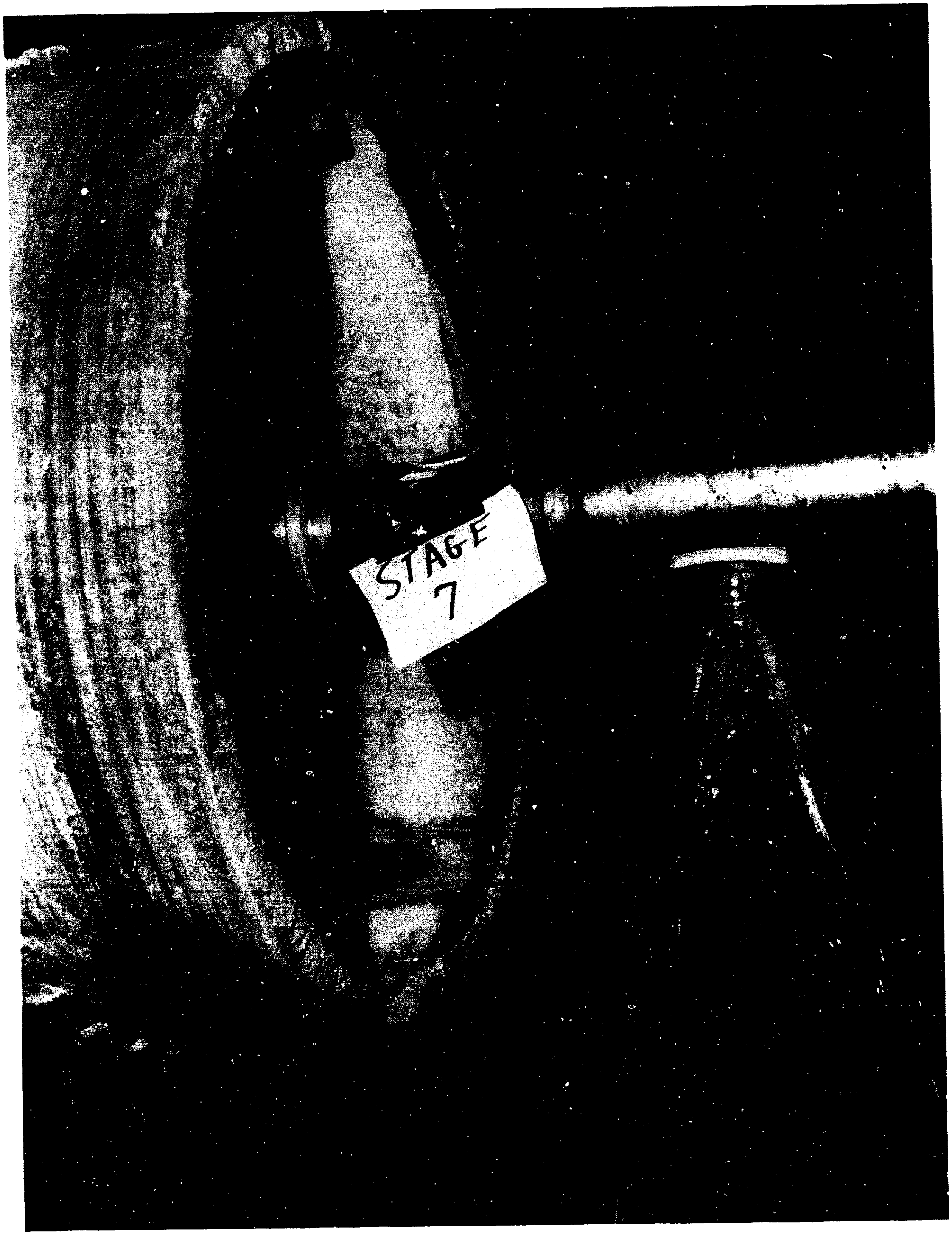

Figure 5. Rotor End Damage from Exothermic Gas-Metal Reaction

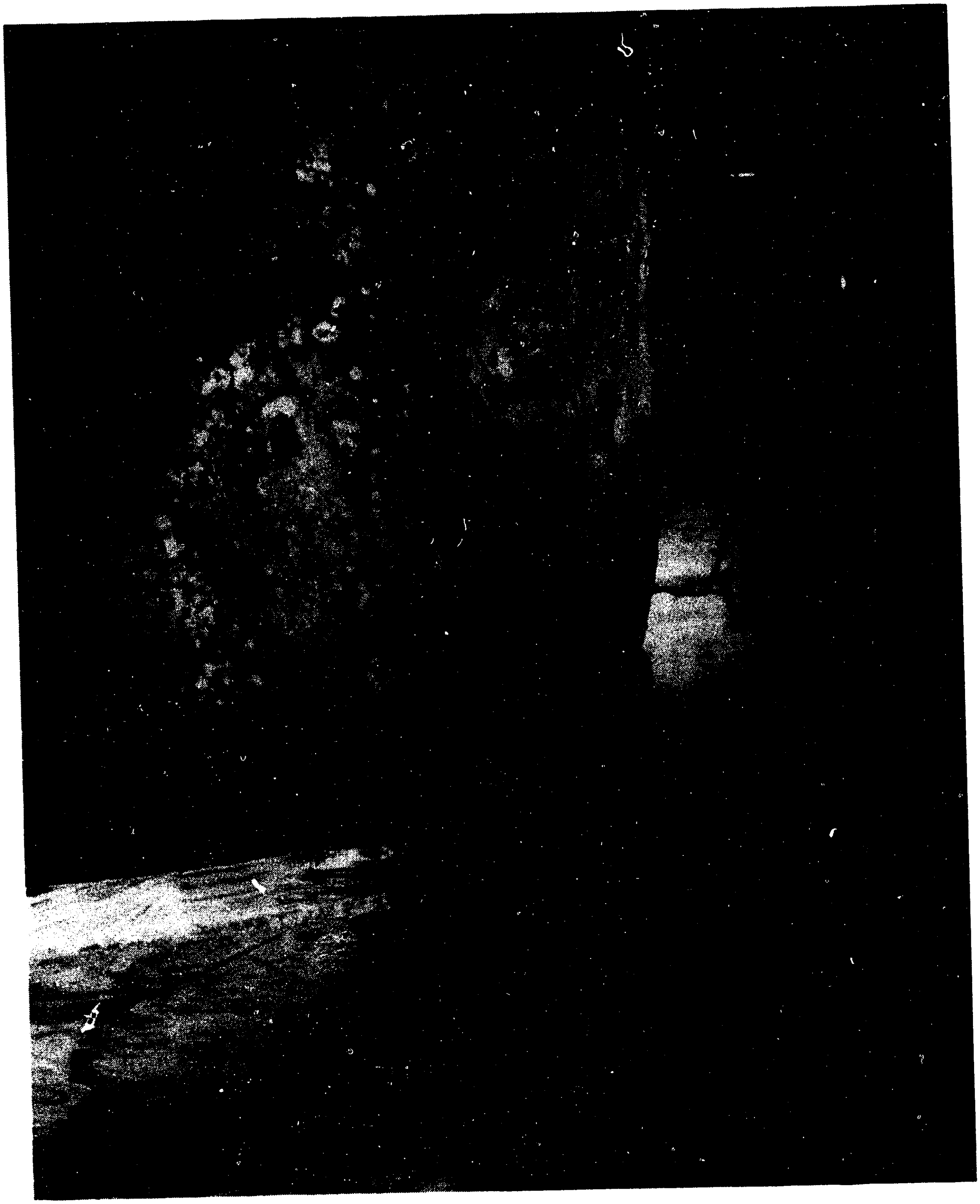

Figure 6. Diffuser Shell Collapse in Region of Gas-Metal Reaction.

BREACHED CYLINDER INCIDENT AT THE PORTSMOUTH GASEOUS DIFFUSION PLANT

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ABSTRACT

On June 16, 1990, during an inspection of valves on partially depleted product storage cylinders, a 14-ton partially depleted product cylinder was discovered breached. The cylinder had been placed in long-term storage in 1977 on the top row of Portsmouth's (two rows high) storage area. The breach was observed when an inspector noticed a pile of green material along side of the cylinder. The breach was estimated to be approximately 8-inches wide and 16-inches long, and ran under the first stiffening ring of the cylinder. During the continuing inspection of the storage area, a second 14-ton product cylinder was discovered breached. This cylinder was stacked on the bottom row in the storage area in 1986. This breach was also located adjacent to a stiffening ring.

This paper will discuss the contributing factors of the breaching of the cylinders, the immediate response, subsequent actions in support of the investigation, and corrective actions.

INVESTIGATION OF BREACHED DEPLETED UF6 CYLINDERS

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ABSTRACT

In June 1990, during a three-site inspection of cylinders being used for long-term storage of solid depleted UF_6, two 14-ton cylinders at Portsmouth, Ohio, were discovered with holes in the barrel section of the cylinders. An investigation team was immediately formed to determine the cause of the failures and their impact on future storage procedures and to recommend corrective actions.

Subsequent investigation showed that the failures most probably resulted from mechanical damage that occurred at the time that the cylinders had been placed in the storage yard. In both cylinders evidence pointed to the impact of a lifting lug of an adjacent cylinder near the front stiffening ring, where deflection of the cylinder could occur only by tearing the cylinder. The impacts appear to have punctured the cylinders and thereby set up corrosion processes that greatly extended the openings in the wall and obliterated the original crack. Fortunately, the reaction products formed by this process were relatively protective and prevented any large-scale loss of uranium. The main factors that precipitated the failures were inadequate spacing between cylinders and deviations in the orientations of lifting lugs from their intended horizontal position.

After reviewing the causes and effects of the failures, the team's principal recommendation for remedial action concerned improved cylinder handling and inspection procedures. Design modifications and supplementary mechanical tests were also recommended to improve the cylinder containment integrity during the stacking operation.

INTRODUCTION

Depleted uranium hexafluoride (UF_6) produced at the uranium enrichment gaseous diffusion plants has been stored in steel cylinders since the diffusion plants first went into production more than 40 years ago. As the number of cylinders became significant, each of the three diffusion plants created outdoor storage yards as long-term depleted UF_6 repositories. These yards consist of concrete or compacted gravel storage pads, with lower cylinders positioned on wooden or concrete saddles and a second level of cylinders supported by the lower level. In June 1990, during inspections at Portsmouth, Ohio, two steel cylinders, each containing 14 tons of depleted UF_6, were discovered with holes in the barrel section of the cylinders. The holes in both cylinders appeared to have originated very close to the stiffening ring nearest the valve end. An investigating team was appointed and, in association with Portsmouth personnel, developed action plans to permit detailed examinations of the cylinders and their contents, as well as an assessment of the environmental impact of the incidents on the storage yard and neighboring cylinders. Evidence was gathered through the process of removing the failed cylinders from the storage yard, checking their internal pressure, analyzing gas and salt samples, emptying one cylinder, and sampling internal reaction products from the other cylinder. Details of the procedures followed in these examinations and related problems are described in a companion paper presented at this Conference (1). Another companion paper (2) presents the chemical findings uncovered in these examinations and their general implications for continued cylinder storage. The present paper discusses the failure cause and the associated lessons learned that can be applied to improvements in cylinder design and cylinder storage practices. Members of the investigation team who were instrumental in the failure analysis consisted of Energy Systems personnel (Jack DeVan, Chairman, John Barker, John Googin, Tim Butler, and Mike Taylor) and Department of Energy representatives Bob Dyer and Joe Russell. An interim final report covering their investigation was issued in September 1991 (3).

INVESTIGATION STRATEGY

The lesser damaged of the two cylinders was investigated first, since it was hoped that the initial cause of failure would be less obscured by subsequent exposure of the cylinder contents to the ambient atmosphere. To access this cylinder, over 200 stacked cylinders had to be moved with the Raygo Wagner loader. Several nearby cylinders were observed to be dented at, or near, the location where both failures had occurred. These other cylinders were examined for cracks; however, none was found. Once access had been gained, the cylinder was pressure checked and a gas sample taken for chemical analysis. As would be the case for an undamaged cylinder, the internal pressure was still less than atmospheric (-4 psig at 85°F), and the gas analysis showed negligible oxygen or nitrogen contamination. The cylinder was then patched, removed from the storage yard, and valved at ambient temperature into the cascade. After removal of the UF_6, the breached area was X-rayed and the internal cylinder surface in the area of the hole was imaged in the X-705 annex using a miniature video camera mounted on a flexible cable. Presently, this cylinder is in storage awaiting sufficient radioactive decay to allow removal and evaluation of the material still plugging the hole and metallographic examination of the cylinder wall.

To clear a path to the cylinder with the larger hole, 60 neighboring cylinders had to be moved. The pressure in this cylinder was above atmospheric (+8 psig at 85°F) and contained elevated concentrations of HF. The hole was covered by an aluminum patch, and core samples of the salt underlying the hole were taken through two ports in the patch for chemical analyses. The cylinder was weighed for accountability and then valved into the cascade. Evacuation was begun in the same manner as for the cylinder with the smaller hole and was continuing at the time of this report.

DESCRIPTION OF FAILURES

The larger of the holes found in the two breached cylinders at Portsmouth is pictured in Fig. 1. The area of salt exposed by the breach was approximately 9 in. along the axis of the cylinder and 13 in. from top to bottom. Viewed from the valve end, the hole was centered at the 9 o'clock position and extended under the nearest stiffening ring. The upper corner of the lifting lug of the adjacent cylinder was positioned at the approximate center of the hole. A green-colored, jagged, fluoride salt layer covered the exposed hole area slightly below the original solid UF_6 surface, and a similarly colored layer of salt covered areas below the hole and on the underlying cylinder. Some loose, green salt deposits were also found on the top of the underlying cylinder and on the concrete pad directly under it. Removal of the salt deposit from the underlying cylinder revealed a series of vein-like grooves etched into the cylinder surface. The grooves were relatively widely spaced and shallow near the top of the cylinder but converged into a much deeper groove over the right-hand quadrant of the cylinder, where it reached a maximum depth of .13 in. None of the other neighboring cylinders showed any evidence of corrosion.

Fig. 1. Appearance of large hole. Width is 9 in. and length is 13 in.

The smaller of the two holes is pictured in Fig. 2. The hole lies at the 3 o'clock position when the cylinder is viewed from the valve end. Like the larger hole, it was positioned at a point close to the front stiffening ring and again was located directly under the top corner of the lifting lug of an adjacent cylinder. The upper circular section of the hole (Fig. 2) was approximately 2 in. in diameter and was concentric with the juxtaposing lifting lug corner. A lower tear drop section extended approximately 2 in. below the

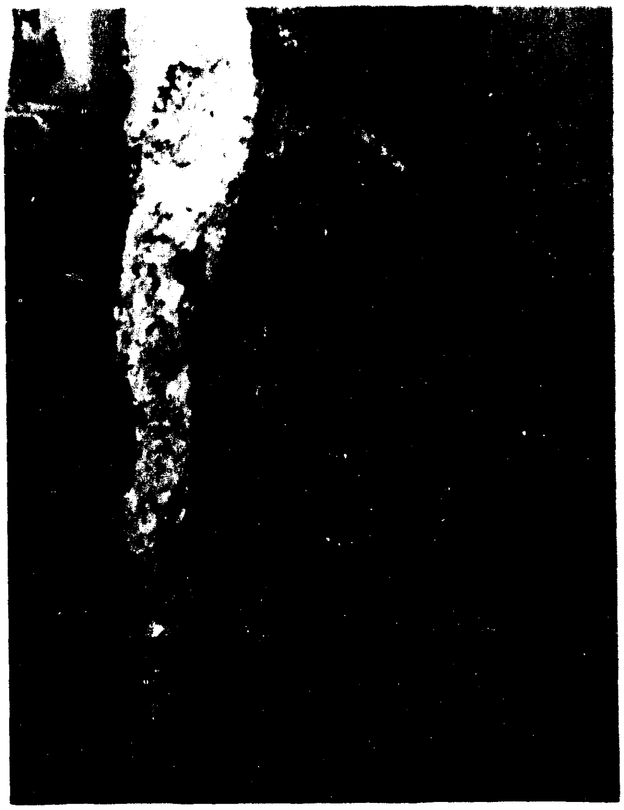

Fig. 2. Appearance of smaller hole. Width is 2 in. and length is 4 in.

circular section. Green salt deposits covered the lifting lug and completely obscured the hole until the lug was pulled away. (Because the green salt deposit closely matched the color of the paint covering the cylinder, very careful inspection was required to spot the hole when viewed from the front of the cylinder). There were no salt deposits on the underside of this cylinder and only a small green spot (about the size of a dime) on the concrete pad directly under the hole. Although examinations of neighboring cylinders showed no effects directly resulting from this failure, several of the neighboring cylinders did show minor mechanical damage attributable to improper spacing (overcrowding) and misalignment of lifting lugs.

PROBABLE FAILURE CAUSES

The team's analysis indicated that the smaller of the two holes had been initiated by a through-wall crack that occurred at the time of stacking. The crack resulted from the impingement of the upper corner of the lifting lug of an adjacent cylinder, which deformed the shell of the subject cylinder in the immediate vicinity of the front stiffening ring. Because of the restraint afforded by the 1-in.-thick stiffening ring, this deformation led to tearing of the shell along the fusion line of the weld joining the shell to the stiffening ring. Conditions contributing to the puncture were: (1) an insufficient separation distance between the cylinders, which resulted from too tight a spacing of the wooden saddles under the cylinders, and (2) the offending lifting lug being placed at a position of 7 o'clock rather than the desired 9 o'clock position. Although the original breach had been largely obliterated by the extensive wastage of the shell associated with the exposure of UF_6 to air and moisture (Fig. 2), evidence for the initial failure cause was afforded by examinations of neighboring cylinders, which indicated a relatively high incidence of dents caused by the lifting lugs of adjacent cylinders. In most cases, these dents were sufficiently far away from an unyielding stiffening ring that they could be accommodated by dimpling of the shell rather than tearing. The small-hole cylinder sustained such a dent at the end opposite from where the hole occurred. Although the degree of indentation here appeared to be of the same order as that which occurred at the failed end, the indent was not restrained by the stiffening ring and there was no indication of cracking in this location. In the few instances where lugs were found to have impinged much closer to the stiffening ring, the degree of indentation was insufficient to have caused failure. However, in these cases the indents in fact appeared as small tears.

Other support for the stated failure mode comes from drop tests performed on similarly designed cylinders at Paducah. A consistent observation in these tests has been the susceptibility of the cylinder shell to tearing when it was impacted next to the stiffening ring (4). The tests also showed that the 5/16-in. A516 steel plate used in the manufacture of the small-hole cylinder was particularly prone to lamellar tearing along the fusion line of the stiffening ring weld. Failures by this mode were already on record for at least two other cylinders made from this particular grade of steel. The first occurred in March 1978 when a cylinder was accidentally dropped onto a wooden saddle and the second, in March 1982, by an indeterminate cause during shipping on a railroad flatcar. It was shown by Blue (4) that sulfide inclusions in this steel adversely affected its impact properties transverse to the rolling direction – a problem that is exacerbated by welding, which concentrates the inclusions along the weld fusion line. Based on these findings, the allowable sulfur content was reduced in the specifications for all cylinders subsequently built with A516 steel components.

In common with the smaller hole, the larger hole is located in the region of a stiffening ring with the corner of the lifting lug of the adjacent cylinder again positioned near the center of the hole. Again, the spacing between the failed and adjacent cylinder was less than the desired minimum. However, unlike the small-hole cylinder, physical measurements at the outer circumference of the large hole showed that a small gap had actually existed between the corner of the opposing lifting lug and the original outer circumference of this cylinder. Thus, while the positions of the two failures, with respect to the stiffening ring and lifting lugs, are quite similar and point to a common failure mechanism, any impingement of the lifting lug on the large-hole cylinder must have occurred before, not after the cylinder reached its rest position. This caveat seems reasonable given the stacking situation for this cylinder. Unlike the small-hole cylinder, which was at ground level and supported by wooden saddles, the large-hole cylinder was in the second tier and was therefore positioned in a crease formed by two underlying cylinders. If either this cylinder or the one opposing it had been lowered and released into a position that was slightly away from the lowest point of the crease, a rolling motion would be set up as the cylinder moved to its rest point. Given the tight spacing, only a slight movement past the rest point would be required to make contact with the adjacent cylinder and, because of the relatively close position of the lifting lug to the stiffening ring, to initiate the type of tearing fracture discussed above. Operators at Portsmouth, who have experience in stacking these cylinders, confirm that difficulties in visual perception and in steadying the cylinders make this sequence of events entirely plausible.

The shell of the larger-hole cylinder was fabricated of a different grade of steel than the smaller-hole cylinder. The former was made of A285 and the latter of grade A516. A change from A285 to A516 occurred shortly before the smaller-hole cylinder was built because the fracture toughness properties of the latter grade were nominally better at low temperatures (≤0°C). However, given the probable temperature of the cylinder and its contents at the time of stacking, the A285 cylinder should not have been any more vulnerable to fracture than one constructed of A516. In fact, based on drop tests of cylinders built with the A285 grade, this material has even better toughness properties than the particular A516 heat used in constructing the small-hole cylinder. Nevertheless, experience during shipping and handling of these cylinders has shown that tearing near the stiffening rings can occur with even the best of these materials.

As discussed in a companion paper (2), corrosion played a major role in these failures once the cylinders had been breached. However, the investigation team could find no evidence that corrosion might have contributed to the initial break in the wall. Wall thickness measurements were performed at numerous points around both failed cylinders, and there were no indications of wall thinning at any point other than in the immediate vicinity of the holes. Even at crevice regions, which are the most susceptible to atmospheric corrosion, there were no indications of localized attack or pitting.

ENVIRONMENTAL IMPACT

Analysis of an air sample taken near the large hole showed approximately 1 ppm HF. Contamination surveys of the concrete pad in the vicinity of the large-hole cylinder showed negligible contamination, except in the area directly under the hole and along a short track where water runoff had deposited traces of UF_4. This area was successfully decontaminated without removing any of the pad surface. Contamination of cylinder surfaces in the immediate vicinity of the leaking cylinder was minor except where there were visible traces of UF_4. Surfaces of four neighboring cylinders (in addition to the failed cylinder) required decontamination, which again was completed using conventional swabbing techniques. Before decontaminating the area around the cylinder, approximately 15 lbs of UF_4-containing salt were collected from the pad under the cylinder and as loose deposits on the cylinder directly under the failed one. In the case of the small-hole cylinder, contamination surveys showed negligible contamination, except in the immediate vicinity of the hole, and smears of the pad under the cylinder showed negligible alpha/beta readings.

One of the soil samples checked when preparing the roadway to access the large-hole cylinder indicated contamination above background levels. Several samples were then surveyed from soil debris left by road construction. One sample had a maximum activity of 12 picocuries/gram, and the rest were below 8 picocuries/gram. (A level of 30 picocuries/gram is permitted for landfill disposal.) The source of this activity appeared to be water runoff from the cylinder, which crossed the concrete pad and entered the ground at the edge of the pad where the new road attached.

An analysis of the chemical processes accompanying the formation and growth of the cylinder holes was used to estimate the mass of UF_6 that could have escaped the cylinders as unrecovered material. Lower bounds were determined from comparisons of the pre- and post-failure cylinder weights together with recovered solid and gaseous products. Upper bounds were estimated from a corrosion model (2) that predicted the reaction paths for UF_6 and the masses of uranium reaction products not necessarily accounted for in the weight measurements. The unrecovered mass of UF_6 from the longer-term failure (13 years) was estimated to be between 17 and 109 lbs. In the case of the shorter-term failure (4 years), the unrecovered UF_6 was below measurable limits but possibly amounted to 4 lbs.

IMPLICATIONS OF FAILURES ON PRESENT STORAGE POLICIES

Cylinder Design Faults - Based on the overall failure statistics for the 14-ton, depleted UF_6 cylinders, the mechanical design has proved generally reliable and well suited to the required filling and handling operations. Nevertheless, an obvious design change that could reduce the probability for the type of failures observed here is to round the upper corner of the lifting lug. Other modifications that would divert impacts away from the area of the stiffening ring weld include welding a band around the outside diameter of the stiffening ring or devising removable shields (bumpers) that can be placed on the lifting lugs during stacking. These failures also point to a need for qualification testing that would assess mechanical properties in the context of storage requirements, where external pressures acting on the cylinders need to be addressed as well as internal pressure. Paducah personnel responsible for qualification testing of the cylinders have indicated (5) that mechanical tests could be included in their test program to evaluate the effects of external loads typical of lifting lug impacts, particularly forces required to penetrate the cylinders. Without such tests, there is currently no methodology for recommending design changes to the shell that would make it more resistant to handling mishaps, such a as sharp impacts, or to movements induced by ground tremors or shifting between cylinders.

An issue related to cylinder design is the selection of the material to be used as the pressure boundary. The selection process for the steel for these cylinders has been very exacting, with input from a relatively long history of acceptance tests and a large service data base. The A516 grade currently specified for the 14-ton cylinders was adopted because minimum toughness properties could be included in the acceptance test requirements for this grade. It replaced the A285 grade, which had no toughness requirements as part of the purchase specification. Although both grades are considered acceptable in terms of their toughness properties at the expected cylinder service temperatures, A516 is obviously preferred for quality assurance reasons. Metallurgical tests at Paducah (5) have indicated that the heat of A516 steel used to fabricate the smaller-hole cylinder probably contained segregated sulfide inclusions, which may have increased the risk for the type of damage (tearing) that ultimately occurred. However, current specifications for this steel call for a lower sulfur level to avoid the sulfur segregation problems, so this issue is not relevant to cylinders being manufactured today. Furthermore, the failure in the larger-hole cylinder, which is made of A285 steel, indicates that, even without sulfide inclusions, tearing can result from an impact near the stiffening ring. Thus, the failures observed here appear endemic to the cylinder design and cannot be tied to insufficiencies in the types of steels specified.

Integrity of Neighboring Cylinders - The heat of A516 steel used in the manufacture of the smaller-hole cylinder has been shown to be more vulnerable to a tearing failure along the stiffening ring weld than steels used before or since. It is particularly important that other cylinders made from this same heat of A516 be fully inspected and kept under surveillance if evidence of mechanical damage near the stiffening ring is found. Furthermore, in the unstacking of cylinders to gain access to the subject failed cylinders at Portsmouth, cylinders were identified that have dents near the stiffening ring weld. Although subsequent non-destructive examinations of these cylinders showed no detectable cracks and they, therefore, were restacked, the affected cylinders should be kept under surveillance and periodically inspected. The same requirement should be extended to cylinders for which mechanical defects have been noted or which are obviously vulnerable to impingement by a neighboring cylinder.

The cylinder directly below the large-hole cylinder was corroded by

HF-containing reaction products to a maximum depth of 0.13 in. Although the resultant loss of wall thickness posed no problems in moving the cylinder, the thickness was below that allowed for liquid feeding back to the diffusion plant, and warm feeding will have to be used to empty this cylinder. Based on the experience here, it must be accepted that failure of a neighboring cylinder could be induced by breached cylinders, provided that the neighboring cylinder is in the line of movement of HF-containing reaction products. Such an induced failure could have potentially serious consequences if: (1) the damaged area was so extensive that it precluded patching or moving the cylinder or (2) it formed near the top of the cylinder where there was very little solid UF_6 available to act as a plug to prevent the spread of contamination. The latter scenario reinforces the importance of early detection of failures of the type incurred here and emphasizes the need for inventorying and maintaining surveillance on any damaged cylinders currently in storage.

Potential Accident Scenarios and Remedial Actions - Until the present failures, the primary concern with the existing thin-wall cylinder design for long-term storage was corrosion. This stemmed from the assumption that, once the cylinder had been transported to the cylinder yard and stored, corrosion should be the only factor to reduce mechanical integrity. These failures indicate that mechanical factors can have an influence on cylinder lifetime even after stacking. One problem stems from mechanical damage induced at the tail end of the stacking sequence, which has remained undetected by prevailing inspection procedures Another problem stems from damage that can occur even after the cylinders are stacked .due to one cylinder resting on another or the shifting of one cylinder relative to another. These failures also emphasize the vulnerability of the cylinders to impact damage by projectiles and jostling from earthquakes. Inspections of the cylinder storage yards at all three diffusion plants, conducted in the course of this failure analysis, indicated that the sequence of events leading to these two failures has a relatively low probability of occurrence and does not reflect a generic problem. Nevertheless, some of the circumstances contributing to the failures, such as insufficient spacing between adjacent cylinders and improperly oriented lifting lugs, are common among several of the storage sites. Thus, the possibility that additional cylinders may have sustained damage by the same means, while considered quite small, cannot be completely ruled out because not all cylinders can currently be viewed in their entirety. In some yard locations at all three sites, cylinder rows are stacked too closely for a thorough visual inspection. Because of the effective plugging by the reaction products of the two exposed areas, the contamination from any unidentified cylinders damaged from the same cause should be minimal as was the case with these two failures. Nevertheless, a concerted effort is needed to identify and empty such cylinders.

The information gained from the present failures provides significant insight into the effects of cylinder failures that occur below the solid-vapor interface of the cylinder. The environmental effects associated with the smaller-hole cylinder failure (which went undetected for 4 years) were minimal, and the cylinder was moved and emptied with little difficulty. Even in the case of the larger hole, formed over a period of 13 years, the environmental insult was minimal as it existed on the site at the time of discovery. Unfortunately, the present failures do not allow a full assessment of breaches which occur nearer the top of the cylinder, i.e., in the vapor space. Scenarios have been proposed in which extreme conditions could lead to a steam-driven expulsion of contaminated liquid and HF from the cylinder, although this situation appears unlikely if the breaches are small, i.e., detected in a reasonable time span(≤1 to 2 years). In any case, an experimental effort should be directed at examining the long-term effects of a hole nearer the top of the cylinder with water introduced under controlled conditions.

To counter the causes and effects of the present failures, the most important remedical action involves improved handling and inspection procedures. Routine inspections of all stockpiled cylinders can effectively limit the impact of potential future failures by a similar cause. Inspections of the cylinders at the time of stacking should be instituted to verify that no mechanical defects exist and that the spacing between cylinders is adequate. Where inspections reveal that mechanical defects exist, or that determinations of such defects are precluded because of poor access to the suspect areas, such situations should be noted and covered by surveillance procedures.

CONCLUSIONS AND RECOMMENDATIONS

An examination of the two failed cylinders, together with inspections of neighboring cylinders, indicated that the failures most probably resulted from mechanical damage that occurred at the time that the cylinders had been placed in the storage yard. In both cylinders evidence pointed to the impact of a lifting lug of an adjacent cylinder near the front stiffening ring, where deflection of the cylinder could occur only by tearing the cylinder (the exact force to fracture a thin-wall cylinder is unknown). The impacts appear to have punctured the cylinders and thereby set up corrosion processes that greatly extended the openings in the wall and obliterated the original crack. Fortunately, the reaction products formed by this process proved to be relatively protective and prevented any large-scale environmental insult or loss of uranium.

Factors that facilitated the failures were inadequate spacing between cylinders and deviations in the orientations of lifting lugs from their intended horizontal position. In both failure cases, neighboring cylinders were crowded and lugs were misaligned to the point where dents due to impinging lugs could be found. Thus, although the current cylinder design is particularly vulnerable to punctures near the stiffening rings, the present failures stem more from handling and stacking procedures than from design inadequacies. However, design changes that could be beneficial involve rounding the lifting lug profile and modifying the present paint scheme to a color that contrasts with that of UF_4. An assessment of the failures experienced here indicates that the associated environmental impact can be greatly reduced by a more rigorous visual inspection during the stacking operation and routine inspections thereafter. In the four years that elapsed in forming the smaller hole, there was no measurable quantity of unrecoverable uranium lost. With adequate inspection and monitoring, both of these incidents most likely would have been detected early enough to have avoided any significant impact on the environment or loss of inventory. However, the inherent difficulty of visually inspecting stacked cylinders for dents and possible cracks will require a high level of awareness training of the personnel responsible for inspecting the cylinders.

The team's survey of the cylinder yards at the three diffusion plants showed that the factors that led to the failures were not unique to the Portsmouth site. The frequency of these factors at other sites appeared less. Yet, the possibility that a similar accident sequence could have occurred for other cylinders now in storage cannot be completely ruled out, and further efforts will be required at all three sites to examine those cylinders whose spacing has prevented a complete visual inspection.

In view of the size of the holes produced and the length of time that corrosion processes operated (13 years in one case), these failures approach the "worst-case" scenario of what can accrue when a storage cylinder is breached in an area backed up by solid UF_6. Fortunately, the effects appear to have been minimal in terms of the inventory of uranium and fluorine lost to the environment and the overall physical damage to the cylinders. However, it is not known whether a failure closer to the top of the cylinder (i.e., in the vapor space) would have resulted in the same environmental effects, since the reaction products formed may not be as protective as those formed in the present failures. Accordingly, a study of the effects of a break into the gas space of the cylinder will be required before the maximum credible incident associated with the mechanical failure during storage can be absolutely defined.

REFERENCES

1. Boelens, R. A., *Breached Cylinder Incident at the Portsmouth Gaseous Diffusion Plant*, Proceedings of this Conference.

2. Barber, E. J., *Chemical Aspects of Cylinder Corrosion and a Scenario for Hole Development*, Proceedings of this Conference.

3. Barber, E. J., T. R. Butler, J. H. DeVan, J. M. Googin, M. S. Taylor, R. H. Dyer, and J. R. Russell, *Investigation of Breached Depleted UF_6 Cylinders*, ORNL/TM-11897, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., September 1991.

4. Blue, S. C., "Fracture Control of Steel UF_6 Cylinders", *Uranium Hexafluoride - Safe Handling, Processing, and Transporting*, Conference Proceedings, CONF-880558, Martin Marietta Energy Systems, Inc., Oak Ridge Gaseous Diffusion Plant, May 1988.

CRACKED LIFTING LUG WELDS ON TEN-TON UF_6 CYLINDERS

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ABSTRACT

Ten-ton, Type 48X, UF_6 cylinders are used at the Portsmouth Gaseous Diffusion Plant to withdraw enriched uranium hexafluoride from the cascade, transfer enriched uranium hexafluoride to customer cylinders, and feed enriched product to the cascade. To accomplish these activities, the cylinders are lifted by cranes and straddle carriers which engage the cylinder lifting lugs. In August of 1988, weld cracks on two lifting lugs were discovered during preparation to lift a cylinder. The cylinder was rejected and tagged out, and an investigating committee formed to determine the cause of cracking and recommend remedial actions. Further investigation revealed the problem may be general to this class of cylinder in this use cycle.

This paper discusses the actions taken at the Portsmouth site to deal with the cracked lifting lug weld problem. The actions include inspection activities, interim corrective actions, metallurgical evaluation of cracked welds, weld repairs, and current monitoring/inspection program.

INTRODUCTION

The daily operation of the Portsmouth Gaseous Diffusion Plant necessitates the handling (lifting) of ten-ton heavy-wall, Type 48X, cylinders (Figure 1). These cylinders are used in the toll enrichment cycle to withdraw low-assay product from the cascade, and are subsequently processed at the sampling and transfer facility to fill customer orders. The ten-ton cylinders are also used to supply UF_6 to the cascade at the feed facility. These operations all require routine heating in steam heated autoclaves, as well as lifting of the cylinders.

The most common method of lifting cylinders at the Portsmouth site employs cranes fitted with special lifting fixtures that attach to the cylinder lifting lugs. The cylinders are lifted using cranes at the feed facility, the sampling and transfer facility, and at the product withdrawal facilities. The other method of moving UF_6 cylinders is by straddle carrier. This type of equipment, which lifts the cylinder using the bottom flats of the cylinder lifting lugs, is used to move the solid-UF_6 cylinders between facilities.

In August 1988, while conducting a pre-operational visual inspection of a full ten-ton cylinder, an operator observed apparent weld cracks in two of the lifting lugs. The cylinder was rejected and tagged out-of-service pending an investigation. The apparent cracks occurred along the horizontal weld between the lifting lug and the cylinder stiffening ring. Code Inspection and Quality Control performed a preliminary investigation and confirmed the presence of two cracks. The visual inspection of the welds was hampered by the cylinder paint and the rusted condition of the cylinder surfaces.

Two formal investigating committees were assigned to define and resolve the problem. One committee (chaired by the DOE) was charged with determining the cause of the weld cracking and the magnitude of the problem. The second committee (the standing Uranium Handling and Safety Committee) was assigned the responsibility of determining technically sound and safe methods to handle cylinders with the weld cracks, and also to identify methods to repair the cylinders.

INTERIM ACTIONS

Inspection of all ten-ton cylinder lifting lug welds prior to transfer operations was initiated using dye penetrant inspection techniques and qualified inspectors. The initial inspection of 88 cylinders resulted in 50 rejected cylinders (57% rejection

Material compositional analysis was performed using electron microprobe techniques in conjunction with sulfur and carbon analyses using wet chemistry techniques. The results of these tests and the microstructural analysis indicated that the material conformed to an ASTM A285 steel which is in agreement with the Type 48X cylinder specification in place at the time the cylinder was manufactured.

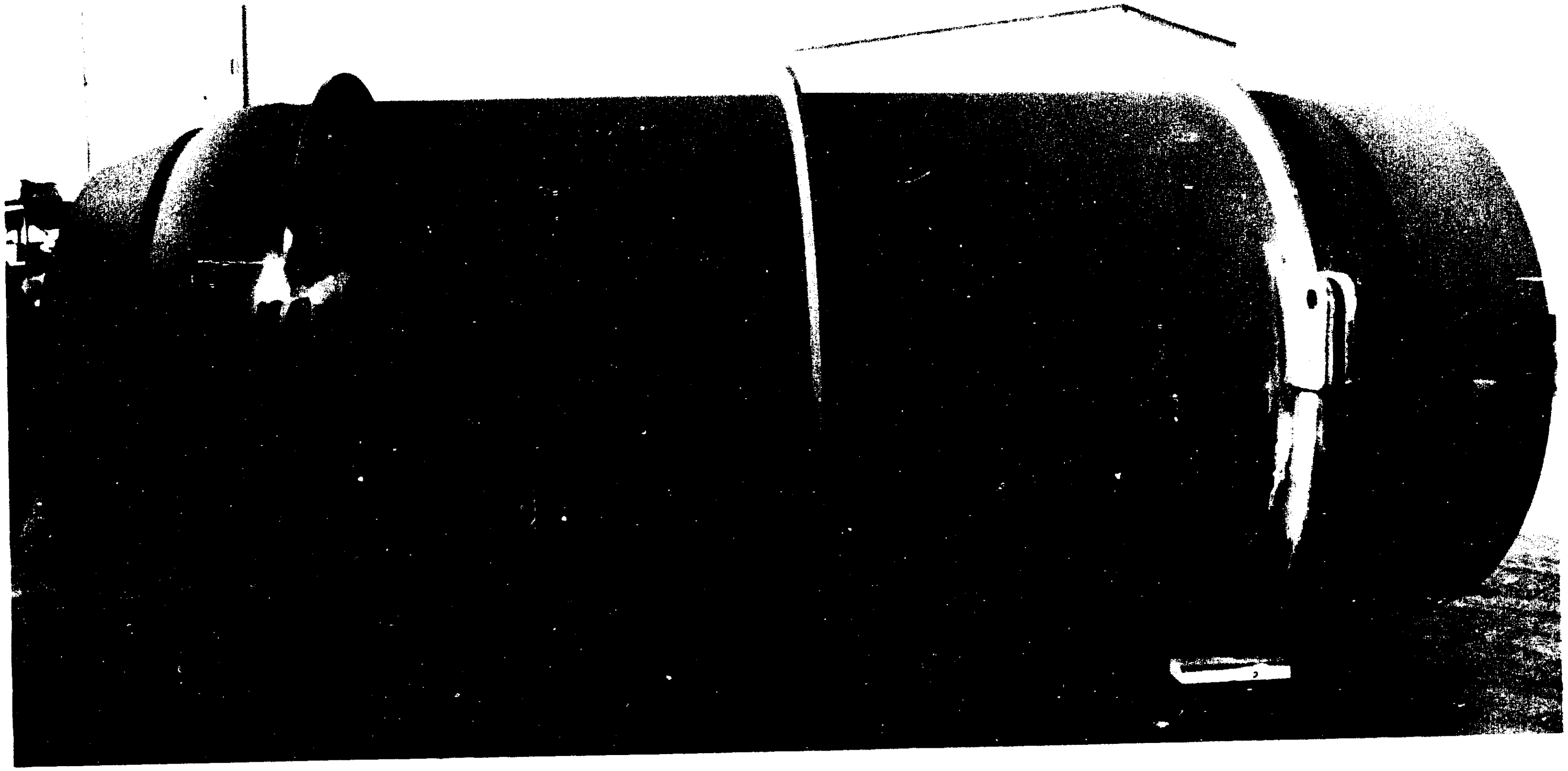

FIGURE 1
Ten-Ton, Type 48x, Product Cylinder
Type 48x Found to Have a Cracked Lifting Lug-to-Stiffening Ring Weld in the Area Indicated by the Arrow. (0.07X)

rate), with many having more than one cracked lifting lug weld. Figure 2 shows the typical indication observed using the dye penetrant inspection technique. Similar inspections were initiated at the Paducah Gaseous Diffusion Plant, and yielded similar results thereby confirming that the problem existed throughout the uranium enrichment complex.

The dye penetrant inspection of the lifting lug welds necessitated the removal of the paint and the oxidized surfaces using a glass-bead blasting technique. This cleaning technique generated concerns that small cracks could escape detection. Therefore, magnetic particle inspection was employed and found to be more sensitive. In addition, the magnetic particle technique could also detect subsurface cracks and flaws that the dye penetrant technique could not.

Special handling procedures were issued to permit handling of the cylinders requiring repair. The cylinders that had cracked lifting lugs were evaluated to determine if sufficient weld remained to permit the safe movement of the cylinder. In cases where extensive weld cracking was found, the cylinder was lifted using "belly bands".

Procedures were also written and implemented to field-repair the cracked horizontal welds. The repair procedures required the removal of the cracked weld, replacement of the weld (monitoring heat input to the cylinder), and seal welding between the lifting lug and the stiffening ring (vertical weld), if feasible. The procedures also required dye penetrant inspection to assure that all of the crack had been removed and that the new weld was acceptable.

METALLURGICAL EVALUATION

Two cracked lifting lug-to-stiffening ring welds from a ten-ton cylinder were evaluated to aid in determining the cause of the weld cracking. Initial rough cutting of the lifting lug from the cylinder revealed a large amount of corrosion by-products between the stiffening ring and lifting lug, Figure 3. The crack was then propagated to failure by cooling in liquid nitrogen and impact loading, resulting in an induced brittle fracture zone.

Examination of the crack surface indicated that the crack extended through about 75% of the weld. The crack surfaces were heavily oxidized which destroyed the fracture features. Scanning electron microscopy analysis of the fracture surfaces revealed some isolated gas pockets in the weld, but they were not considered to be significant contributing factors in the cracking.

Metallographic examination of the cross sectional surface revealed a typical weld microstructure consisting of a heat affected zone and a dendritic weld structure. The corrosion attack was more pronounced in the weld and heat affective zone regions than it was in the bulk material. The fillet weld displayed good fusion and adequate penetration.

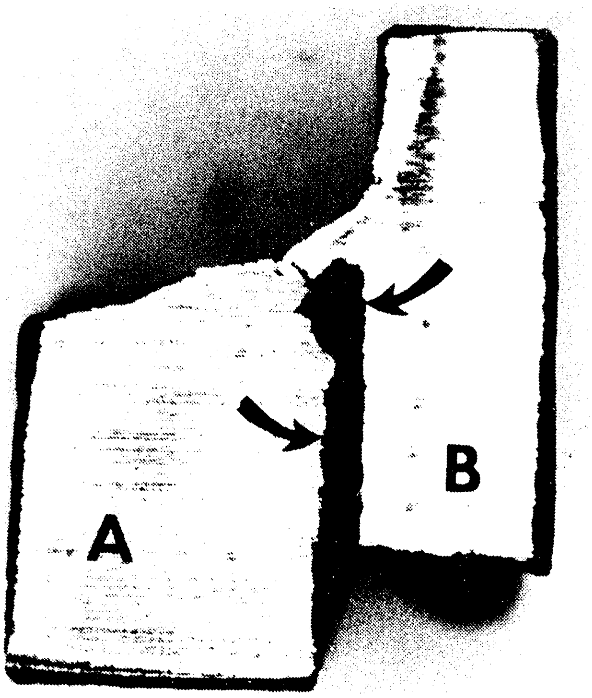

FIGURE 3
Rough Cut Stiffening Ring (A) To Lifting Lug (B) Weld Showing a Cracking of the Weld and Location of Corrosion Products (Arrows).

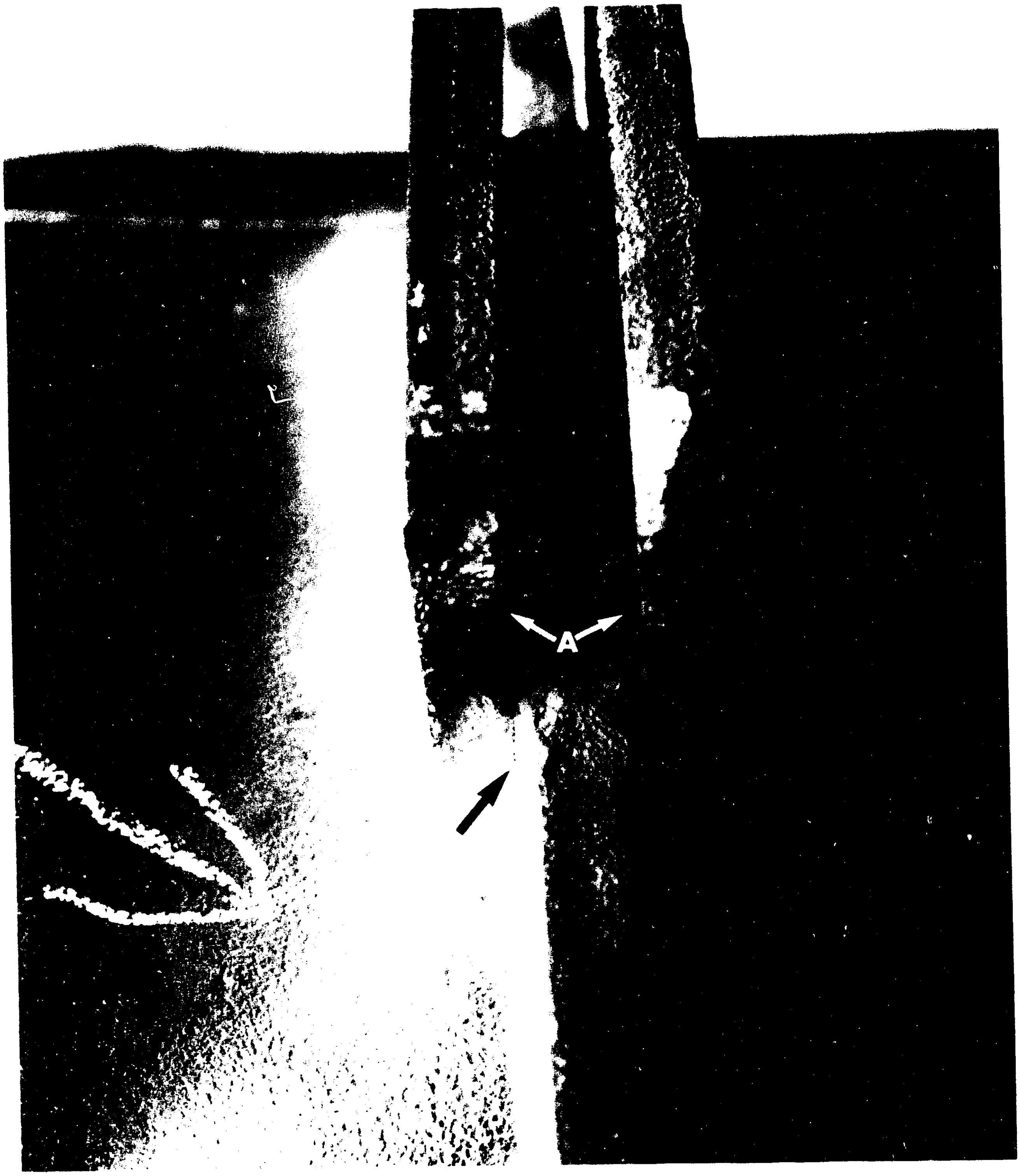

FIGURE 2
Lifting Lug Stiffening Ring Assembly Containing a Crack in the Horizontal Weld (Black Arrow). The Location of the Lifting Lug/Stiffening Ring Seal Weld is Given by Arrow A. (0.65X)

Metallographic examination of a second horizontal lifting lug-to-stiffening ring weld indicated a partial crack in the weld root, Figure 4. This crack would not have been found by visual or dye penetrant inspection techniques, and probably was too deep for magnetic particle technique detection. This crack was wider in the middle than on either end, suggesting a hot crack or internal weld flaw that later propagated through the root. A weld hot crack generally occurs as a result of excessive heat input due to a large root gap (poor fit up) requiring more filler metal. The entire length of the crack including the crack tip displayed a buildup of deposits which were found to be high in iron and oxygen. The surface oxidization had destroyed most of the fracture features. The tip of the crack appeared to consist of an intergranular fracture mode.

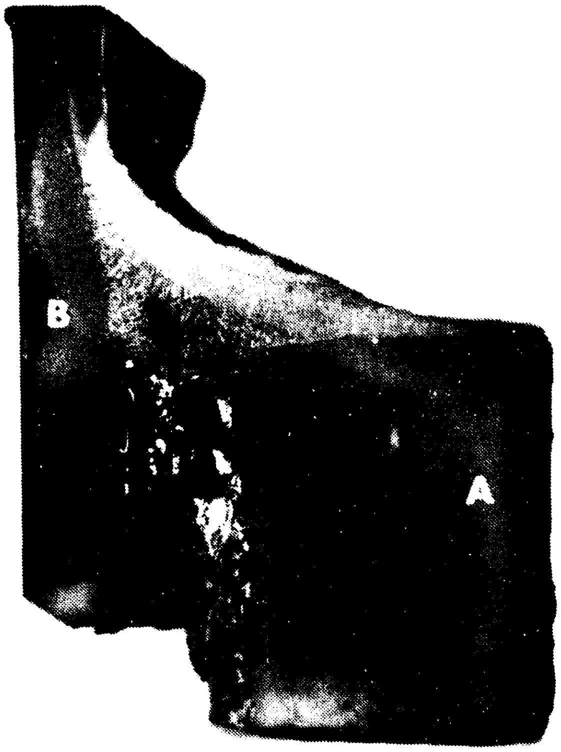

FIGURE 4
Etched (3% Nital) Surface of a Cylinder Lifting Lug (A) to Stiffening Ring (B) Weld. Note the Crack Located in the Weld Root (Arrow). A large Amount of Corrosion Products Fill the Wide Gap Left from Poor Fit.

METALLURGICAL EVALUATION CONCLUSIONS

The cause of the lifting lug to stiffening ring horizontal-weld cracking in ten-ton cylinders was attributed to corrosion resulting from repeated autoclave steam heating. The corrosion reduced the cross sectional area of the weld fillet, resulting in a stress concentration, and more significantly produced corrosion product which stressed the weld joint by applying a force between the lifting lug and stiffening ring. Another contributing factor was the poor fit of the lifting lug to the stiffening ring. The poor fit (large gap) required more heat and filler metal, and resulted in hot cracks in the weld root during cooling.

It was concluded that the current weld repair procedures should be continued, including the seal welding to prevent moisture buildup between the lifting lug and the stiffening ring. It was also concluded that a periodic inspection of these welds prior to processing of the cylinders program should be established. A time frame of one to two years between inspections was deemed adequate to detect the presence of weld cracking.

CURRENT STATUS

The lifting lug to stiffening ring weld cracking on ten-ton cylinders has been brought under control at the Portsmouth site. The most recent magnetic particle inspection of 510 cylinders indicated that the rejection rate has dropped to 24%. None of the welds that were previously repaired were found cracked. Since seal welding of some of the cylinders is not practical, a continual inspection program is in place to assure that the weld cracking problem remains in check.

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