227
10-19-78

sh. 627

LA-7327-MS

Informal Report

MASTER

MASTER

Some Corrosion Tests of Materials in UF_6

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663 Los Alamos, New Mexico 87545

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

LA-7327-MS
Informal Report

UC-25
Issued: September 1978

Some Corrosion Tests of Materials in UF_6

A. E. Florin*

---

*Consultant. 1499 44th Street, Los Alamos, New Mexico 87544.

SOME CORROSION TESTS OF MATERIALS IN UF_6

by

A. E. Florin

ABSTRACT

The corrosion by UF_6 of a number of metals, common structural alloys, ceramics, solders, plastics, and greases was determined at temperatures up to 700°C. Results are given in terms of weight gain (or loss) per cm^2, visual appearance of the corrosion products, and (in some cases) chemical analysis of the corrosion products. The results are useful in the selection of structural materials to be used in handling UF_6.

A selection of materials — noble metals, common metals, solders, ceramics, plastics (including the elastomer, Viton), composites of plastics and powdered metals, and greases — have been exposed to UF_6 gas at pressures to 1.33×10^4 Pa (100 torr) and temperatures to (for some of the materials) 700°C. Test times varied from 2 h to 168 h, and the results are given as appearance and weight changes. The purpose was to test for corrosion.

Passivation effects were observed but not systematically studied. The corrosion rates reported here are generally larger than those reported for studies of UF_6 corrosion on materials whose surfaces were passivated by buildup of a more or less impermeable fluoride layer in an initial treatment with fluorine gas before exposure to UF_6. On the other hand, it is felt that values reported here for materials having no prefluorination treatment are more representative of the inherent resistance to corrosion by UF_6 of the materials themselves.

Due to differences in the chemistry of the corrosion products, as in the $x UF_4 \cdot y UF_6$ series, absolute corrosion rates are beyond the scope of this work, and weight changes are useful here only to indicate relative rates within the confines of the individual experiments. For instance, NiF_2 and UF_4 are known to be corrosion products in the reaction of UF_6 and nickel. Uranium tetrafluoride can combine with additional UF_6 to give various intermediate fluorides including U_4F_{17}, U_2F_9, and UF_5 (two distinct crystal types known), the composition being dependent on the temperature and UF_6 pressure. If UF_4 or an intermediate fluoride remains on the corroding surface, the weight gain of the specimen could be 8 to 15 times higher than if the corrosion product were simply the fluoride of the surface material. Uranium pentafluoride becomes appreciably volatile at temperatures above 200°C, where the UF_5 vapor pressure is 0.13 Pa (0.001 torr) and where the UF_6 vapor pressure is sufficiently high [$>3.99 \times 10^3$ Pa (>30 torr)] to prevent disproportionation of the UF_5. At 250°C, the UF_5 vapor pressure is

5.3 Pa (0.04 torr), and the literature indicates the minimum UF_6 pressure to prevent disproportionation is 1.33×10^4 Pa (100 torr). The highest UF_6 pressure used in these experiments was 1.33×10^4 Pa (100 torr); therefore, 250°C would be expected to be the highest temperature at which we would observe UF_5 in these experiments. Copious evolution of uranium species from the furnace at temperatures to 700°C and depositions of UF_5, U_2F_9, and UF_4 in cooler regions outside the furnace during these runs would suggest that either unstable, volatile uranium oxyfluoride species are involved or the literature values reported for pressures of UF_6 necessary to stabilize UF_5 might be in error. Thus, it appears one might compare specimens corroded at lower and higher temperatures and find a smaller increase in weight for the more severely corroded, high-temperature specimen as a consequence of UF_5 volatilization. Some corrosion products, such as SnF_4, are volatile in themselves, and some may form double fluorides with uranium fluoride corrosion products. Since many materials were tested simultaneously, synergistic effects are possible but are thought to be unimportant except for a few instances that are noted. A complete understanding of the corrosion process would require a lengthy investigation with many chemical and metallurgical analyses.

While it is generally true that both fluorine and UF_6 behave comparably as corrosion agents, there are important differences. Notably, gold is consumed catastrophically in high-temperature fluorine, but gold is one of the most resistant (perhaps without equal) of all the materials tested in UF_6 at high temperatures.

A. Apparatus and Procedure

Most of the tests were conducted in a horizontal test tube-shaped, fused alumina (99.7% Al_2O_3) reactor, 4.4-cm (1 3/4-in.) i.d. by 61-cm (24-in.) long with 0.32-cm (1/8-in.) wall, heated in the central region by a 30.5-cm (12-in.)-long electric furnace. The open end of the reactor was capped by a Dural sleeve sealed to the exterior surface by a Viton O-ring and provided with a port for pump-out and entry of gases. A removable Fluorethene window with aperture equal to the full 4.4-cm reactor i.d. was O-ring-sealed to the end of the Dural sleeve. Cooling by a stream of compressed air kept the Fluorethene window and Viton O-rings at only slightly above room temperature. A telescope aimed through the window provided a magnified view of the specimens actively undergoing corrosion at high temperature during a run. In addition to natural emission of the materials themselves at high temperatures, illumination by a lamp could be directed through the window or the translucent wall of the reactor. After a run, specimens could be unloaded into weighing vials under protection from the room atmosphere by a flowing inert gas.

Test specimens were distributed along a 15.2-cm (6-in.) length of a 20-cm (8-in.)-long by 2.5-cm (1-in.) i.d. and 0.32-cm (1/8-in.) wall fused alumina (99.7% Al_2O_3) removable liner. Generally, metal foils 0.64-cm (1/4 in.) wide by 1.9-cm (3/4 in.) long and from a few to 127 μm (fifty-thousandths of an inch) thick were used as test specimens, but other shapes such as O-rings, dabs of grease, bellows, wires, and irregular, broken ceramic chips were used also, according to availability of the materials. As many as 20 specimens were run simultaneously.

As an unforeseen consequence of the reaction of UF_6 with the alumina tube used as the reactor for most of the experiments, oxygen gas appeared as a high concentration contaminant of the UF_6 in high-temperature runs of long duration, despite renewal of the UF_6 charge several times during the course of exposures. For oxygen gas to have been produced in the reaction of UF_6 with Al_2O_3, a uranium product with valence lower than six must also have been produced. A few experiments performed in platinum reactors at high temperatures did not suffer from this perturbation by oxygen.

Two additional reactors made of 30.5-cm lengths of platinum tubing of 0.64-cm and 0.32-cm diameter were used for additional tests of noble metals. The 0.32-cm-diam tube was equipped with a graded temperature furnace to permit wire specimens running the entire length of the tube to be exposed in a single experiment to all temperatures from 700°C to room temperature with no temperature gaps. A 0.64-cm-diam nickel tube was used as a reactor for tests of some electroplated specimens.

Pressures were measured by a 0-1.33×10^4 Pa Baratron capacitance diaphragm gauge. Weight gain of specimens and UF_6 loss by pressure measurements were inequivalent due to excessive consumption of UF_6 by the apparatus itself. A simple, low-resolution (unit resolution to mass 50) residual gas analyzer (trade name Farvitron) was used to monitor gas composition for some experiments, and served mainly to establish the presence of oxygen contaminant after long times with UF_6 in contact with Al_2O_3 at high temperature. Weighings were performed before and after exposure on a balance with 0.1-mg sensitivity. (Some small specimens were weighed on a semimicrobalance with 5-μg sensitivity.) Group CMB-1 provided microprobe analyses for a few residues. Group CMB-5 provided crystallographic x-ray analysis to identify UF_5, UF_4, and U_2F_9 in furnace-edge deposits.

Sample preparation was: "Lava" soap and water scrubbing, ultrasonic "Lava" soap cleaning, ultrasonic detergent cleaning, running water wash, acetone rinse, ultrasonic distilled water rinse, and drying in a nitrogen blast, with handling by tweezers after the soap wash. Some ceramics were not given any pretreatment as they appeared porous.

Depleted UF_6 was supplied by sublimation from the solid contained in a storage vessel. Before admitting to the reactor, HF impurity was removed by pumping while UF_6 was held at -80°C. Specimens were loaded into the reactor and heated in vacuum before exposure to UF_6. Initial UF_6 exposure was 1.33×10^2 Pa (1 torr) for a few minutes, followed by pump-down; then samples were exposed to 1.33×10^3 Pa (10 torr) of UF_6 for 5 min followed by pump-down. Finally, the specimens were exposed to 50- to 100 torr UF_6 followed by pump-down and renewal of UF_6 several times during the course of each run to remove any accumulation of gas other than UF_6. (As mentioned previously, oxygen was unexpectedly found in high abundance in the high-temperature runs in alumina reactors as a consequence of reaction between UF_6 and Al_2O_3. At 700°C, as much as 50% of the gas was oxygen after 24 h.) Hydrogen fluoride was produced by hydrolytic reactions, and peaks indicating possible SnF_4, VF_5, CF_4, SiF_4, and TaF_5 were detected, but the resolution was insufficient for positive identification of these, although the presence of these would be reasonable.

B. Results and Discussion

Materials in each group are ranked with the most resistant ranked first.

Group A, Noble Metals. The noble metals tested were gold, platinum, rhodium, palladium, and iridium. Results are presented on Charts A, B, C, and D.

1. Gold. Tests: [2 h, 550°C, 6.6×10^3 Pa (50 torr)] (2 h, 700°C, 6.6×10^3 Pa) (66 h, 700°C, 6.6×10^3 Pa) (112 h, 700°C to 25°C continuous range, 1.33×10^4 Pa). In no test was there any evidence that gold reacted with UF_6. Gold remained bright and shiny, with the crystal structure perhaps more apparent after a 66-h test. Some white thin coating and small clear crystals were AlF_3 by analysis. Weight gains of 0-60 μg/cm^2/h were attributed to AlF_3 deposit. In a 112-h run at 700°C and 1.33×10^4 Pa in a platinum reactor, gold wire became covered with both shiny smooth platinum and crystals or platinum in the region that had been between 500-700°C. By comparison, nickel, generally regarded as a material of

CHART A

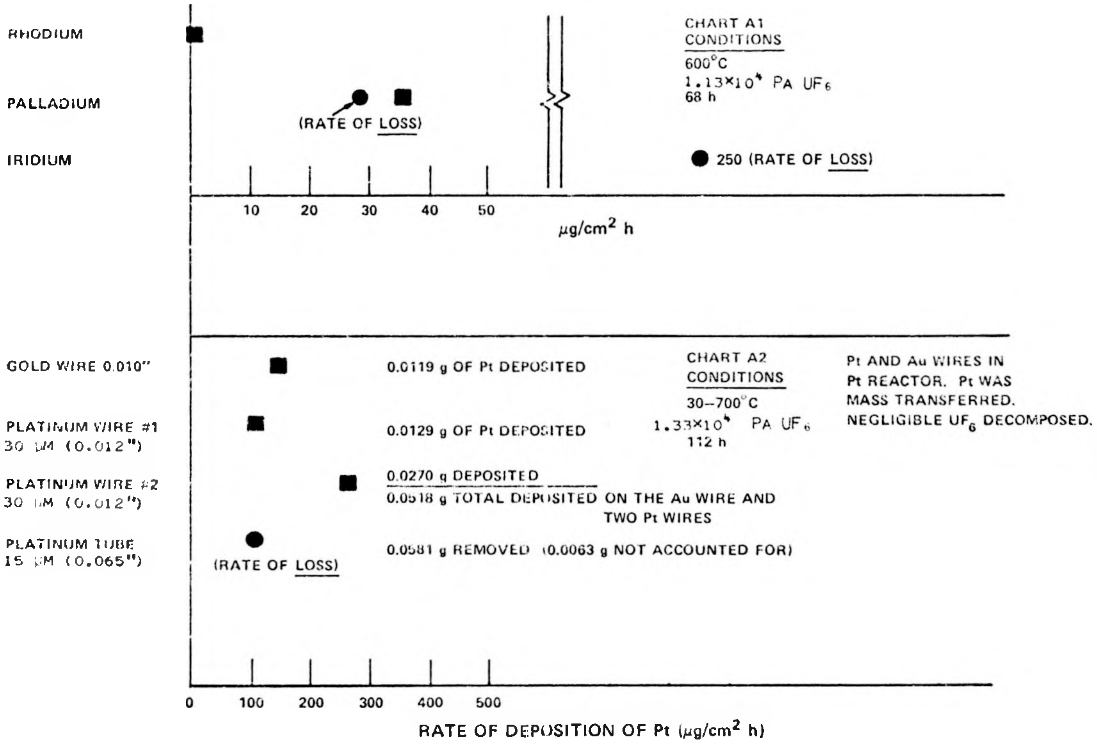


CHART B

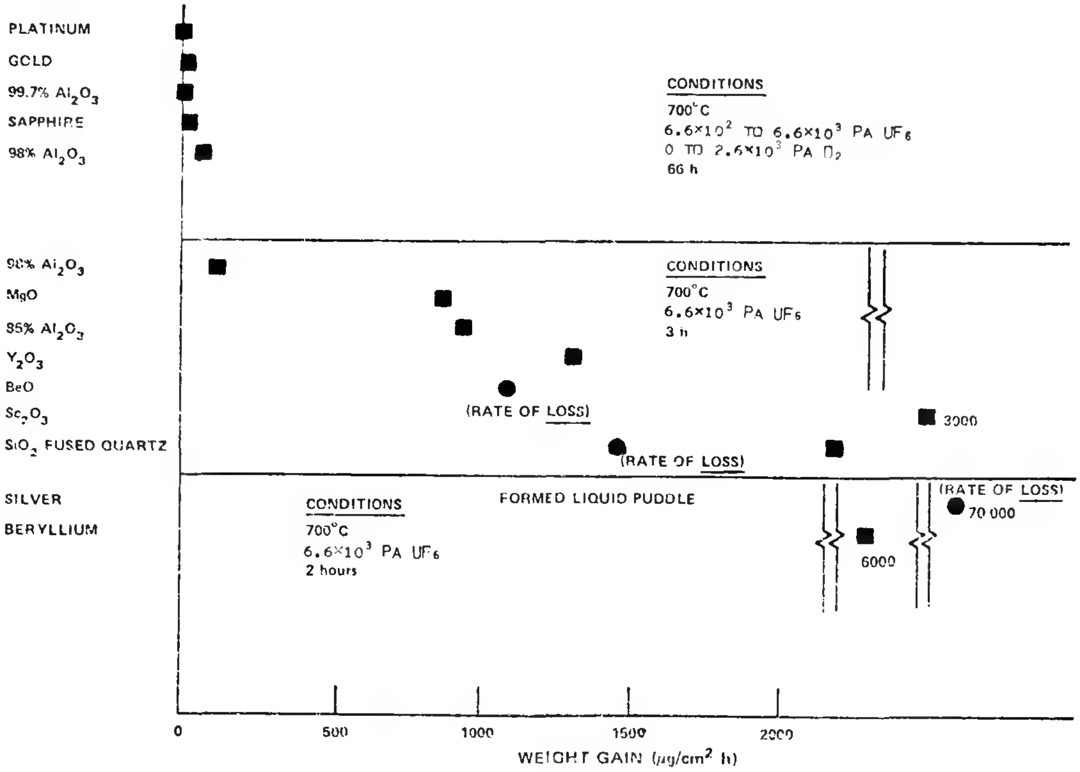
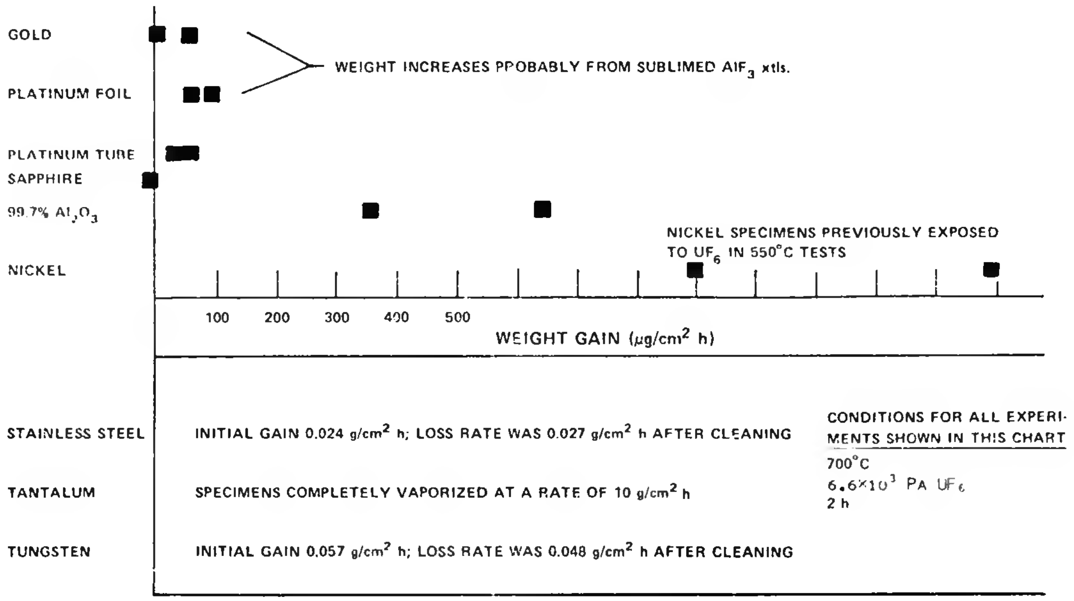


CHART C



WEIGHT INCREASES PROBABLY FROM SUBLIMED AlF_3 xtls.

NICKEL SPECIMENS PREVIOUSLY EXPOSED TO UF_6 IN 550°C TESTS

STAINLESS STEEL: INITIAL GAIN 0.024 g/cm² h; LOSS RATE WAS 0.027 g/cm² h AFTER CLEANING

TANTALUM: SPECIMENS COMPLETELY VAPORIZED AT A RATE OF 10 g/cm² h

TUNGSTEN: INITIAL GAIN 0.057 g/cm² h; LOSS RATE WAS 0.048 g/cm² h AFTER CLEANING

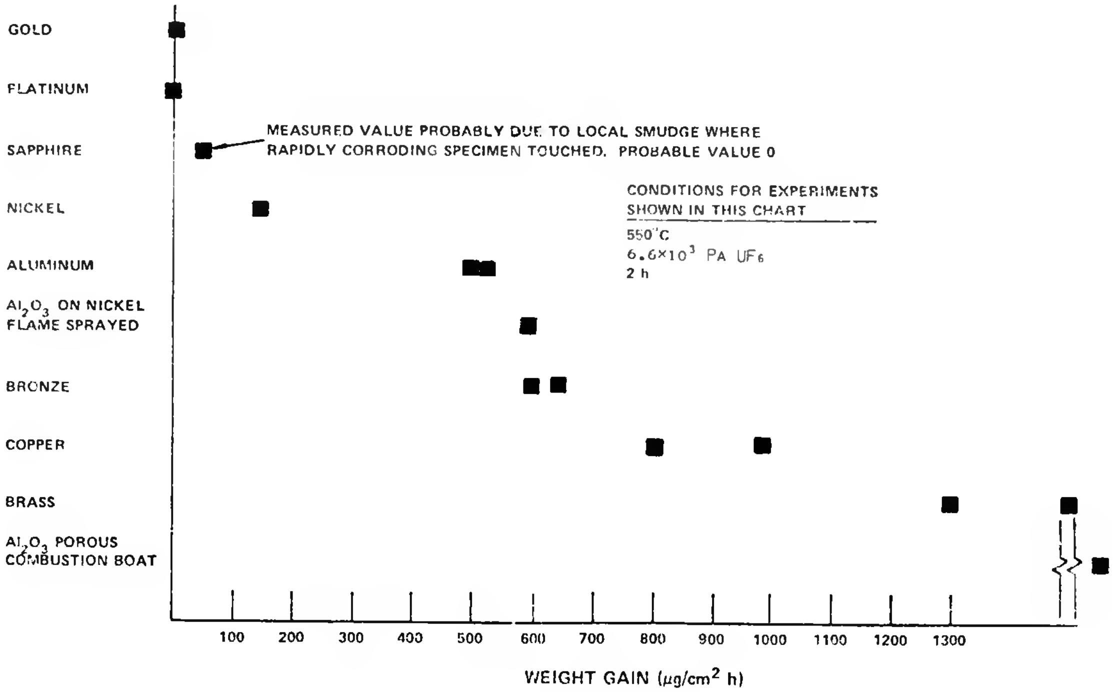
CONDITIONS FOR ALL EXPERIMENTS SHOWN IN THIS CHART

700°C

6.6×10^3 PA UF_6

2 h

CHART D



MEASURED VALUE PROBABLY DUE TO LOCAL SMUDGE WHERE RAPIDLY CORRODING SPECIMEN TOUCHED. PROBABLE VALUE 0

CONDITIONS FOR EXPERIMENTS SHOWN IN THIS CHART

550°C

6.6×10^3 PA UF_6

2 h

choice for UF_6 compatibility, corroded at a rate of 1000 $\mu g/cm^2/h$ at 700°C and 6.6×10^3 Pa, forming a thick, yellow-brown, blistering film. In these tests in UF_6, gold was more resistant than any other material tested. In previous tests, gold was observed to ignite in high-temperature fluorine.

2. Platinum. Platinum was also present in all the tests described for gold and the results were indistinguishable from those for gold except for the important difference that platinum suffered serious mass transfer in the single experiment at 700°C and 1.33×10^4 Pa for 112 h. Platinum and gold wires were contained in a 30.5-cm-long platinum tube having 0.16-cm i.d. A temperature gradient from 700°C at one end to 25°C at the other end provided a continuous range of temperatures for this test. At least 58 mg of platinum left the tube wall and redeposited as platinum metal on the gold and platinum wires contained in the tube in the temperature range 700-500°C. Deposits were in the form of both shiny smooth platinum metal and small cubic crystals in clumps radiating from the wires, some of which cemented the wires to each other and to the walls so they had to be forcibly separated. Undoubtedly, an amount of platinum larger than the 58 mg was involved in the mass transfer as some must have left the wall and redeposited on the wall and some must have left the wire and redeposited itself on the wire and wall; 58 mg measured only net loss from wall. Only a negligible amount of UF_6 was consumed in the run (3 mg) and 1 mg of this was found as isolated crystals of U_2F_9 among the platinum crystals. The minimum rate of mass transfer of platinum metal was 70 $\mu g/cm^2/h$. The mechanism of the platinum mass transfer was not explored. Perhaps a volatile platinum fluoride (PtF_6 is a possible candidate) formed at high temperature and diffused to a lower temperature region where it decomposed to metal. Such decomposition or disproportionation could be expected in the platinum fluoride system since PtF_6 is an endothermic compound. No easy decision could be made regarding possible liquid or vapor phases, but the well formed platinum crystals were probably vapor deposited. It would appear worthwhile to study the possible chemical vapor deposition of platinum via a platinum fluoride decomposition.* The mass transfer phenomenon was not observed in the runs in the alumina reactor also at 700°C. The lower UF_6 pressure (6.7×10^3 Pa compared to 1.33×10^4 Pa), the presence of oxygen impurity in the alumina reactor, or the reaction time (66 h compared to 112 h) are the known differences between the two cases. Platinum ignites at red heat in fluorine.

3. Rhodium. Rhodium appears to have excellent resistance to corrosion by UF_6 on the basis of a single experiment at 600°C and 1.13×10^4 Pa (85 torr) for 68 h. No weight change was suffered by a 70.6-mg specimen of rhodium. A slight, dull gray film appeared on the surface, which could be scratched away with forceps to reveal a bright metal surface underneath. Iridium and palladium, both of which corroded severely, were present along with the rhodium specimen and all were contained in a platinum tube for this single test of rhodium. Further testing could establish rhodium as possibly superior to platinum or even gold.

4. Palladium. Palladium is corroded rapidly by UF_6 at 1.13×10^4 Pa and 600°C on the basis of a single experiment in which both rhodium and iridium were also present in the same platinum tube reactor for 68 h. The palladium appeared black, and after standing awhile and examination under a microscope, a brown liquid layer was noted covering the black surface. Shiny metal could be seen underneath in a

---

*The literature refers to deposition of platinum from a platinum phosphorous fluoride, but the platinum thus obtained is contaminated with phosphorus.

few local areas. It is not known whether the brown liquid was present during the corrosion or formed after standing in the air. A weight increase amounting to 36 μg/cm^2/h was noted, but after cleaning by water wash to bright palladium metal a weight loss of 28 μg/cm^2/h was noted. Palladium is superior to many ordinary metals but is far less resistant than gold to UF_6.

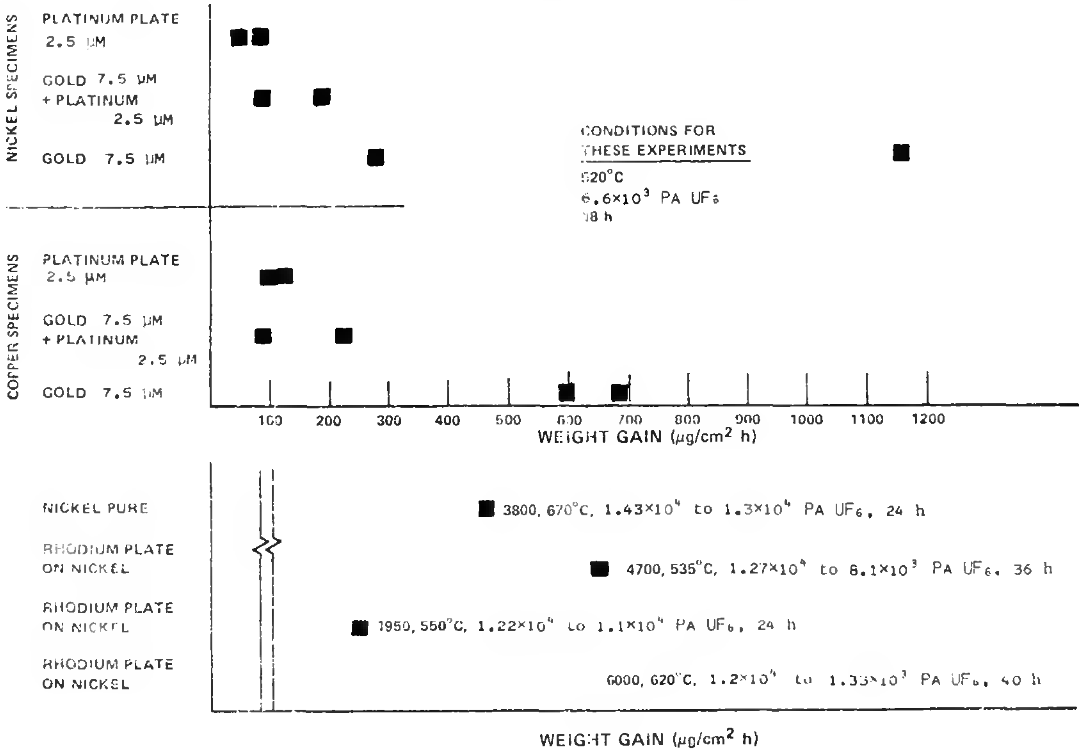
5. Iridium. Iridium is corroded rapidly by UF_6 at 1.13×10^4 Pa and 600°C on the basis of a single experiment in which both rhodium and palladium were also present in the same platinum tube reactor for 68 h. The iridium specimen came out of the reactor only after repeated hard banging. Crystals of UF_5 and U_2F_9 came out of the tube with the iridium. The iridium did not have any noticeable film covering but was less bright in its metallic luster. Weight loss was 250 μg/cm^2/h. The crystals of UF_5 and U_2F_9 contained no iridium, palladium, rhodium, or platinum by microprobe analyses.

6. Other noble metals. Osmium and ruthenium were available to us only as finely divided powders that were not tested. The project was terminated before a plan to have them arc-melted into massive metal could be carried out.

7. Electroplated noble metals. Because of the high cost and scarcity of noble metals, it was of interest to determine if a thin coating of these on ordinary metals could impart resistance to UF_6 corrosion. Electroplating was the only method attempted here of producing such thin coatings. Group CMB-6 prepared the specimens. Gold-, platinum-, and rhodium-electroplated specimens were prepared on various substrates, including copper, nickel, silver, and with some specimens having a gold plate first, followed by a platinum or rhodium electroplate. Specimens were tested at 550°C and 600°C at 1.2×10^4 Pa (90 torr) and times from 12 to 200 h. In only one out of six experiments was there any indication that the electroplated noble metals offered any protection to the metals underneath, but because that result could not be repeated and because there is a plausible reason to suggest an experimental flaw in that experiment, one must conclude that electroplating of noble metals was unsuccessful in preventing corrosion of the base metal. The flawed experiment was done in a horizontal platinum tube reactor that was not well anchored. It is believed the specimens, which had been loaded in at precise positions, were dislodged completely out of the hot zone of the tube as a result of vibrations caused by closing the furnace and sliding it into position. In those experiments where extensive corrosion was observed, the electroplated noble metals themselves were not corroded, but the plating was penetrated by pinholes and cracks through which UF_6 reached the base metal underneath, forming blisters and causing a peeling of the plated metal. Corrosion under the blisters appeared to be more severe than observed for the base metal unplated. Other methods of depositing noble metal coatings should be tried in the hope of achieving a continuous surface with no porosity and adequate bonding to the substrate. Results are shown on Chart E.

Group B, Common Metals. Common metals tested were nickel, aluminum, aluminum alloy 6061-T6, bronze, copper, brass, beryllium, stainless steel 316 (molybdenum), lead, stainless steel 347 (niobium), tungsten, silver, and tantalum. Aluminum oxide flame sprayed onto nickel and CaF_2-coated nickel were also tested. Testing covered the temperature range from 100-700°C with UF_6 pressures from 4×10^3 Pa (30 torr) to 1.33×10^4 Pa and times from 2 to 170 h. Although indium and titanium were not tested in UF_6, relevant fluorine corrosion observations are given.

CHART E
ELECTROPLATED SPECIMENS

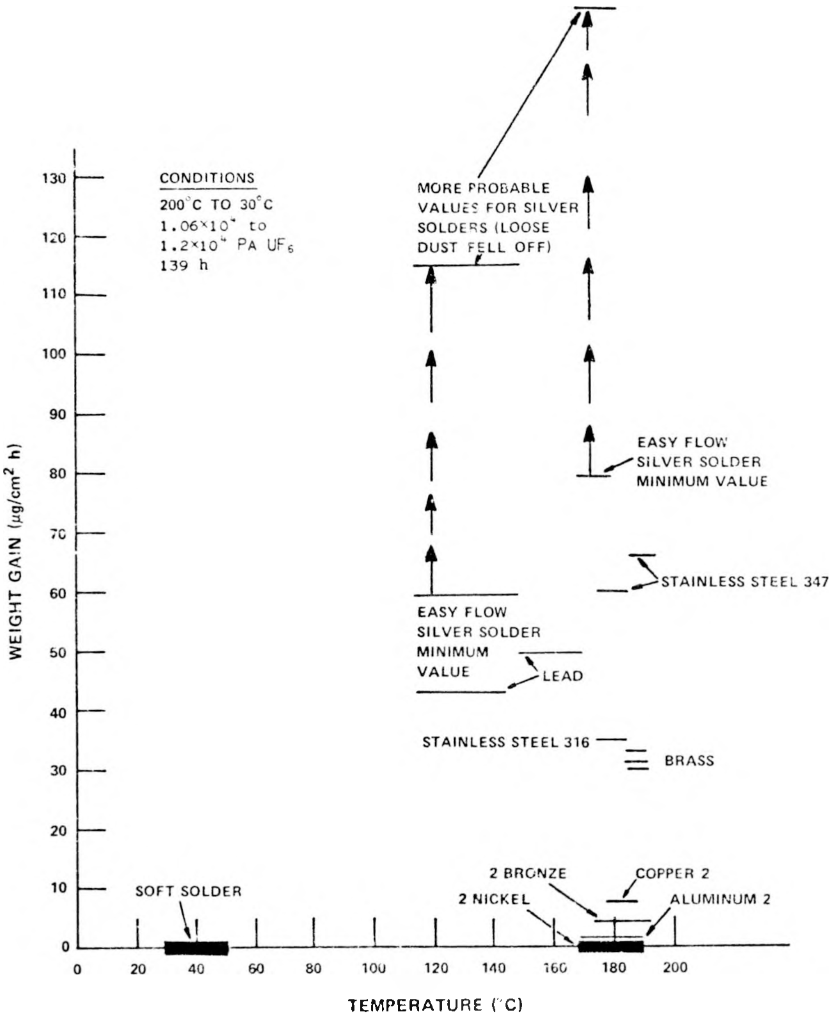


1. Nickel. Nickel's resistance to corrosion by UF_6 and fluorine is well known. In these tests it was clearly superior to any of the other common metals tested for temperatures above 500°C. At temperatures below 200°C, where the corrosion is very slow anyway, aluminum appears to be just as good as nickel or possibly better. Calcium fluoride coatings on nickel appeared to offer no advantage, and an Al_2O_3 coating, flame-sprayed onto nickel, was inferior to pure nickel. The noble metals, gold, platinum, and rhodium are impressively superior to nickel above 500°C. Sapphire and high-purity (99.8% Al_2O_3) nonporous alumina also show better corrosion resistance than nickel at high temperature. Nickel is compared with other materials in Charts C through G. At low temperatures the corrosion deposit was barely visible, but at 550°C a thin greenish film with many microscopic brown spots formed. At 700°C a thick, blistering, brown coating formed.

2. Aluminum. Pure aluminum foil and anodized aluminum alloy 6061-T6 are at least as resistant to corrosion as nickel at low temperatures (below 200°C) and possibly superior. By 550°C aluminum corrodes more than twice as rapidly as nickel when the two are compared at 6.7×10^3 Pa UF_6 pressure. Aluminum is compared with other materials in Charts D, F, and G. At high temperature a black, adherent deposit formed. At low temperature the original appearance was unchanged except for a few microscopic bunches of radiating needle crystals containing U, F, and O.

3. Bronze. As seen in Charts D and F, bronze (a type that contained no phosphorus) was more resistant to corrosion than copper but less resistant than aluminum at 550°C with 6.7×10^3 Pa UF_6 and at 180°C with 1.0×10^4 Pa (80 torr) to 1.2×10^4 Pa UF_6. The high-temperature tests produced a green coating and some loose, brown powder. The low-temperature tests produced a light color coating with many microscopic black spots —of good general appearance.

CHART F



4. Copper. As seen in Chart D, which lists materials exposed at 550°C to 6.7×10^3 Pa UF_6 for 2 h, copper under these conditions corroded about six times more rapidly than nickel, about two times more rapidly than aluminum, only about 50% faster than bronze, and slower than brass with a rate about two-thirds that of brass. At lower temperatures of near 200°C with 1.0×10^4 to 1.2×10^4 Pa UF_6 for 139 h, as seen in Chart F, the differences are larger; copper corroding about ten times faster than aluminum and at about one-fourth the rate of brass. The corrosion products were brown, and when formed at high temperature, very poorly adherent. The brown powder fell off the specimens without mechanical disturbance.

5. Brass. Data on Charts D and F show that brass corrodes at ten times the rate of nickel and 50% faster than copper in a test at 550°C and 6.7×10^3 Pa UF_6 for 2 h, and brass corrodes more than four times faster than copper, about fifty times faster than aluminum, but at about the same rate as stainless steel 316, about two-thirds the rate of lead and one-half the rate of stainless steel 347 in a test at just below 200°C with 1.0×10^4 to 1.2×10^4 Pa UF_6 for 139 h. The deposits resulting from the 200°C test were black and fairly hard with a sparkly appearance when broken and viewed in cross section. After exposure to room air for a time, the deposits changed to a green color. The deposits from the 550°C test were

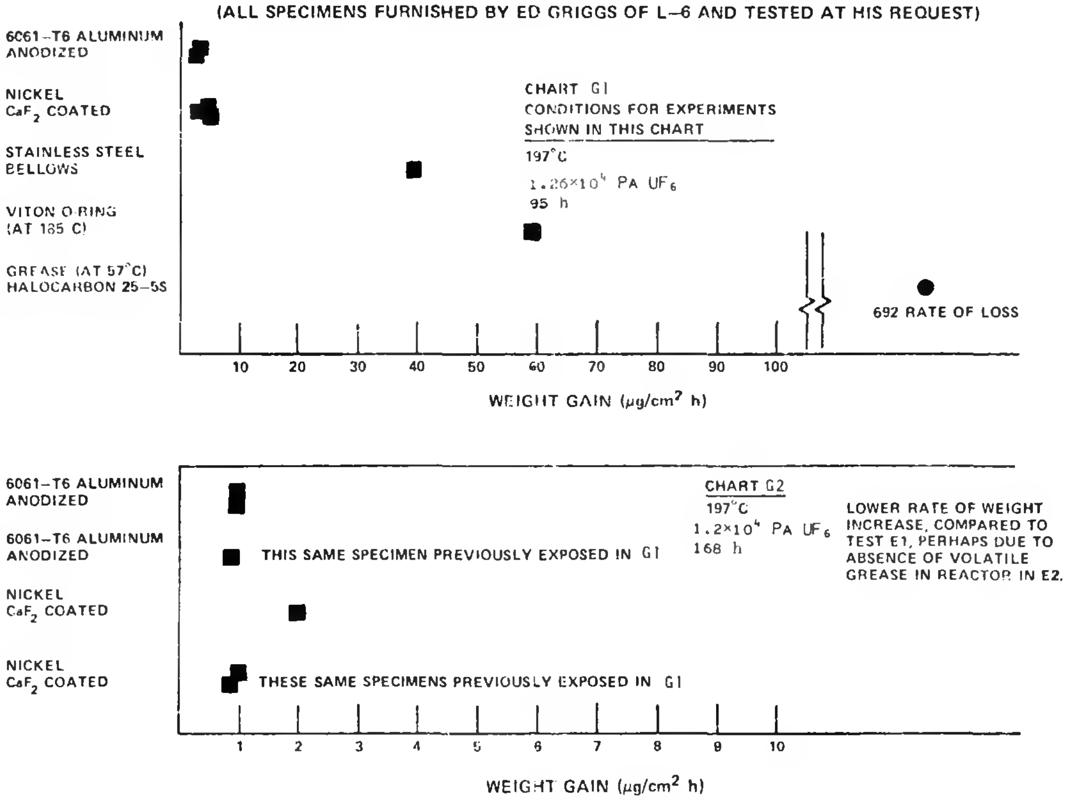
green, with some areas of whitish appearance; some of the green deposit fell from the specimens without external stimulation.

6. Beryllium. Only one test was run, at 700°C, 6.7×10^3 Pa UF_6 for 2 h. Our estimate of the resistance of beryllium to corrosion is therefore highly uncertain, except that it most certainly is more resistant than stainless steel, which was nearly destroyed in a test similar to this. The beryllium test was also complicated by a general contamination by liquid-phase silver fluoride resulting from extreme corrosion of a specimen of silver metal present in the same test. Weight change information is therefore highly unreliable, but it was clear the beryllium specimen had not disintegrated in the manner of stainless steel. It is conceivable beryllium should be classed close to nickel. Other work[1] has shown beryllium covered by a layer of BeF_2 consumes UF_6 more slowly by a factor of 6 than does Al-AlF_3 at 400°C. Results are shown on Chart B.

7. Stainless steel 316 (molybdenum). Stainless steel 316 corrodes slightly faster than does brass or about 50 times faster than aluminum in a test just below 200°C with 1.0×10^4 to 1.2×10^4 Pa UF_6 for 139 h as shown in Chart F. The corrosion product is black but with thin lines following evident striations or rolling marks, perhaps in the metal, that leave bright metal visible underneath. Needle-shaped crystals radiate from points scattered about the coating. After standing in air, the color of the product changes to green. Chart G includes data for a stainless steel bellows of unspecified composition. Though tested with other materials, at 200°C, 1.2×10^4 Pa UF_6 and 95 h, the rate was nearly that for stainless steel 316. Products also appeared similar.

8. Lead. Chart F shows corrosion data for lead at temperatures appreciably lower (by 30 to 60 degrees) than other metals simultaneously tested with 1.0×10^4

CHART G
(ALL SPECIMENS FURNISHED BY ED GRIGGS OF L–6 AND TESTED AT HIS REQUEST)



to 1.2×10^4 Pa UF_6 for 139 h. The corrosion rate, even at the lower temperature, is more rapid than the rate for 316 SS and is about 70 times faster than the rate for aluminum at the higher temperature. Crude extrapolation of the corrosion rate expected for temperatures just below 200°C where the aluminum was tested would give a rate of about 100 times faster than the aluminum rate and a rate very similar to the corrosion rate of 347 SS. The corrosion product on lead was black and rather brittle. It turned green on standing in air.

9. Stainless steel 347 (niobium). The corrosion rate for 347 SS is about 100 times faster than the rate for aluminum in a test at just under 200°C with 1.0×10^4 to 1.2×10^4 Pa UF_6 for 139 h, as shown in Chart F. The corrosion product had a velvety black appearance and a few needles appeared to be radiating from points on the surface. The color turned to green on standing in air.

10. Stainless steel (undesignated number). In a test of 700°C and 6.7×10^3 Pa UF_6 for 2 h, two specimens of this stainless steel corroded at a rate (shown on Chart C) about 20 times faster than a simultaneously exposed pair of nickel specimens. The destruction of the stainless steel was extensive. The original 38-µm (15-mil) thickness was reduced to about half that value after scraping away the voluminous corrosion product which displayed a prominent laminar or foliated structure with a large number of layers. The coating was white to light blue in color and some of it fell away before being disturbed, while the bulk of it could be removed by light scraping.

11. Tungsten. As shown on Chart C, tungsten reacted rapidly in a test at 700°C with 6.7×10^3 Pa UF_6 for 2 h. A dense, thick, black coating formed that could be easily dislodged from the metal by scraping. The original 38-µm-thick specimen measured 25 µm (10 mil) after removing the corrosion product.

12. Silver. The destruction of silver was catastrophic in 6.7×10^3 Pa UF_6 at 700°C for 2 h as shown on Chart B. A liquid silver fluoride formed quickly, and about one-half of the silver, originally 50 µm (20 mil) thick, survived at the bottom of the liquid puddle.

13. Tantalum. The most reactive of the metals tested, tantalum ignited and was completely consumed in a few seconds in the UF_6 at a pressure of about 1.33×10^3 Pa UF_6 at 550°C. Chart C indicates rates.

14. Indium. Although indium was not tested in UF_6 in these experiments, previous limited testing of indium exposed to fluorine would indicate good resistance of indium to UF_6 as a good possibility even above the melting point of indium at 156°C. Only slight coloration of the indium surface occurred in fluorine at 1 atm after several hours at room temperature. Heating with a torch to an unmeasured temperature well above the melting point (guessed at 250°C) produced sparks when the molten indium was jostled sharply, but there was no tendency to ignite in the fluorine, and the film seemed protective.

15. Titanium. Titanium wasn't tested in this work. It has been assumed that titanium does not form a protective fluoride film. However, G. L. Ericson et al. indicate some tendency for titanium to form a protective film during exposure to fluorine.[2]

Group C, Solders. Solders tested were Sil-Fos, soft solder of 60 wt % tin, 40 wt % lead composition, and Easy-Flo silver solder.

1. Sil-Fos. Compared with soft solder and silver solder, Sil-Fos had the lowest rate of corrosion over a range of temperatures below 200°C at 1.29×10^4 Pa (97 torr) UF_6 for 97 h. An anomalously high corrosion rate at a temperature of 137°C (as shown on Chart H) is considered to be an experimental error since rates at 123°C and at 153°C follow a rather smooth trend, and it seems improbable that a single temperature in such a narrow range would have a drastic effect on corrosion rate. In appearance, all specimens of Sil-Fos at 164°C and below had only a very thin black coating. Specimens at 168°C and 178°C had a very faint green coating and a few thicker black areas. The rate at 178°C would rank it between copper and brass in corrosion resistance.

2. Soft solder (60 wt % tin - 40 wt % lead). Soft solder corrodes only slightly more rapidly than Sil-Fos, as shown in Chart H. The specimens tested at low temperatures showed a very thin green coating, thickening some as temperature increased and exhibiting increasing numbers of blotches of thicker green as temperature increased. The coatings also tended to follow die markings through which the solder in wire form was extruded in manufacture. Brown blotches appeared on

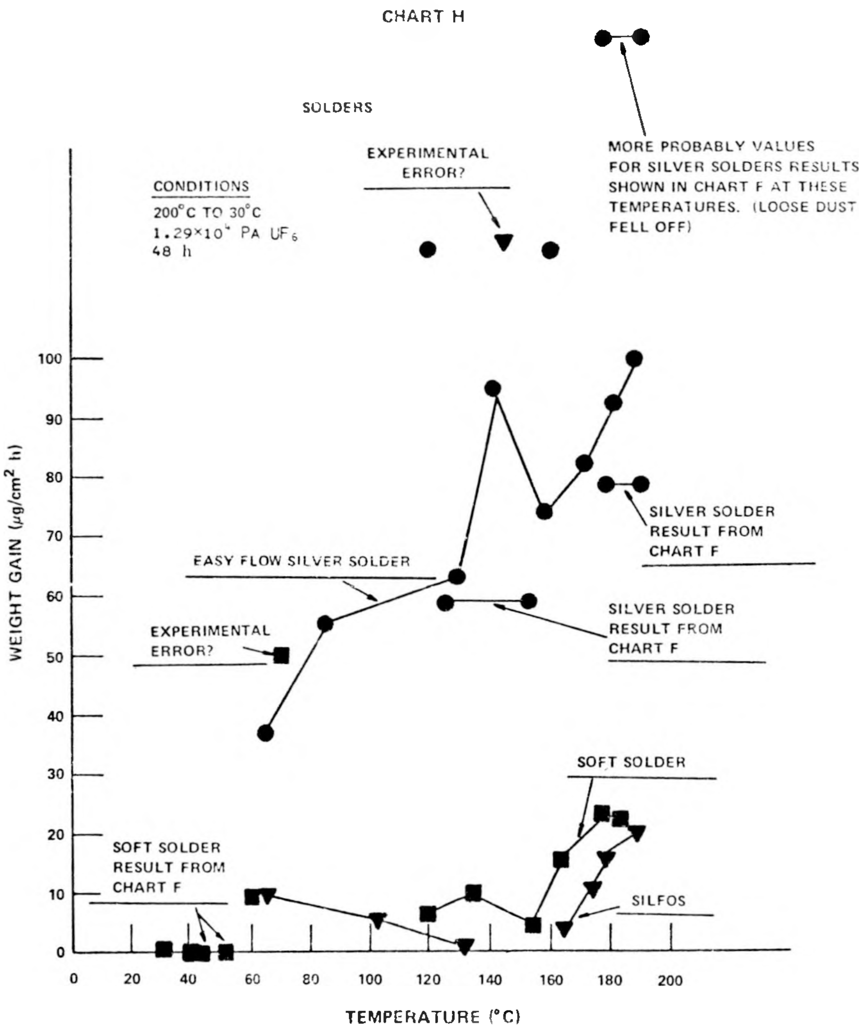


CHART H

SOLDERS

the 156°C specimen, and one-fourth of the area was covered with brown blotches in the 168°C specimen. One-half the area of the 173°C specimen was covered with thin black and brown blotches. In a separate experiment, soft solder in the temperature range 30 to 50°C was exposed to 1.0×10^4 to 1.2×10^4 Pa UF_6 139 h (Chart F). This specimen showed no weight increase, and only a thin surface dullness indicated the effect of UF_6.

3. Easy-Flo silver solder. From experience with fluorine, one would rank silver solder as more corrosion resistant than soft solder. Tests shown on Chart H, where Sil-Fos, soft solder, and silver solder are compared over a range of temperatures from 60 to 190°C in 1.29×10^4 Pa UF_6 for 48 h, show silver solder to be corroded at rates approximately 5 times faster than soft solder and Sil-Fos. It corrodes even more rapidly than 347 SS, and a separate experiment shown in Chart F, where silver solder was present simultaneously with 347 SS and other materials, confirms the high corrosion rate for silver solder. In appearance, the silver solder at 63°C had very light green, irregular deposits. Heavier, green, irregular deposits were formed at 86°C and 118°C with many furry hair-like growths appearing also on the 118°C specimen. Fewer hairs and black deposits appeared at higher temperatures, until at 178°C the deposit was a heavy black coating with very poor adherence, much of it falling off without external disturbance.

Group D, Ceramics. Five kinds of Al_2O_3 ceramics, MgO, Y_2O_3, BeO, Sc_2O_3, and SiO_2 as fused quartz were tested. Pure Al_2O_3 as sapphire had excellent resistance to corrosion by UF_6 even at temperatures of 700°C, although a clouding of the surface occurred at the high temperature so that use as a high-temperature window material would be compromised. Lower percentages of Al_2O_3 in other specimens resulted in higher corrosion rates even though the specimens were nonporous. A porous Al_2O_3 combustion boat had an extremely high corrosion rate.

1. Sapphire. Outstanding corrosion resistance as shown in Charts B, C, and D, puts sapphire in the class with the best noble metals. At 550°C a slight weight gain is attributed to smudge contributed by proximity to a rapidly corroding specimen being tested simultaneously. Slight cloudiness developed on the surface, and though it could be scraped off to restore perfect transparency, the surface was not the original surface, but an apparent cut beneath it. At 700°C, milky cloudiness was extensive, but weight gains were still not as large as for nickel.

2. Nonporous alumina (99.7% Al_2O_3). This material, available from LASL stock as tubes, was used as the reactor in which most of the corrosion experiments were run. While the corrosion rate by UF_6 is very low even at 700°C and 6.7×10^3 Pa UF_6, the large exposed area of the reactor resulted in consumption of UF_6 at a rate that prohibited using the consumption of UF_6 as a crosscheck with weight gain in the measure of reactivity of the specimens being studied. The reaction rate is nevertheless lower than the rate for nickel. A corrosion product with a light brown tint is produced; the original Al_2O_3 was white. The reaction is interesting in that O_2 gas is produced and, as a consequence, a reduction in the valence of uranium to a value below 6 must also be produced. Indeed, UF_5, U_2F_9, and UF_4 have been observed as crystalline deposits, lining the reactor just outside the hot zone. In addition, a whitish smoke (unidentified) was observed moving out of the furnace region toward the window at the end of the reactor where some of it deposited to reduce visibility through the window. This aerosol

material beautifully traced the motion of convection cells in the reactor in a pattern of fourfold symmetry, which would of itself be an interesting subject for aerodynamic research. The reaction between UF_6 and Al_2O_3 to produce oxygen was unexpected but simply reveals the lack of adequate thermodynamic studies, extensive though they have been, in the uranium, oxygen, fluorine system. An observation by Fried and Davidson,[3] noting that UF_6 and UO_2F_2 were produced by passing O_2 over UF_4 at high temperature, was later extended in work by Kirslis, McMillan, and Bernhardt[4] to show the existence of an unstable intermediate with unique crystal structure having the composition $UO_{1/2}F_4$. It seems likely that this or similar compounds are involved in the reaction encountered here. Understanding of such reactions and characterization of the chemical species would provide an important addition to our knowledge of uranium chemistry. Results are shown in Chart B.

3. Nonporous alumina (98% Al_2O_3, remainder Y_2O_3). This ceramic, obtained from Los Alamos Scientific Laboratory (LASL), CMB-6, Ceramics Section, ranked high in corrosion resistance but was not as resistant to UF_6 corrosion as the 99.7% Al_2O_3 specimen. Results are shown on Chart B for a test at 700°C, 6.7×10^3 Pa UF_6 for 3 h. Corrosion product was tinted light brown.

4. Magnesium oxide. High-purity MgO sintered and nonporous, was obtained from CMB-6 Ceramics Section. A test at 700°C, 6.6×10^3Pa UF_6 for 3 h, as indicated in Chart B, showed a high reactivity with UF_6, much greater than that of 98% Al_2O_3, but comparable with an 85% Al_2O_3 specimen. The corrosion product was pale yellow.

5. Nonporous alumina (85% Al_2O_3 — remainder mixed flux of ignited $CaCO_3$, $BaCO_3$, SiO_2, MgO). This material also was obtained from CMB-6 Ceramics Section. Performance depicted on Chart B shows the continual increase in corrosion rate as percentage of Al_2O_3 diminishes. Corrosion product was pale yellow.

6. Yttrium oxide. Nonporous yttria, also obtained from CMB-6, reacted more rapidly than 85% Al_2O_3 as shown on Chart B. The specimen, originally an olive-green color, came out of the reactor colored dark brown, purple, black, and white.

7. Beryllium oxide. This beryllia sample, also obtained from CMB-6, was unusual in that it showed a weight loss rather than weight gain. Volatility of beryllium fluoride is the probable cause. The result of a test at 700°C, as shown on Chart B, indicates the limited possible use of beryllia in UF_6 at high temperatures. The original white color was darkened after UF_6 exposure.

8. Scandium oxide. CMB-6 supplied this scandia specimen also. Tested at 700°C, and with the result shown in Chart B, the scandia reacted with UF_6 more extensively than the other ceramics tested except quartz. Originally white, the scandia was a light brown after UF_6 exposure.

9. Silicon dioxide. The specimen was a piece of fused quartz tubing. The results shown in Chart B at 700°C exposure indicate a high reaction rate but not the expected catastrophic destruction of the quartz. The corrosion produced a thick, flaky yellow and white coat with a few black areas. The coat was easily dislodged. The cleaned quartz was 97% of the original weight.

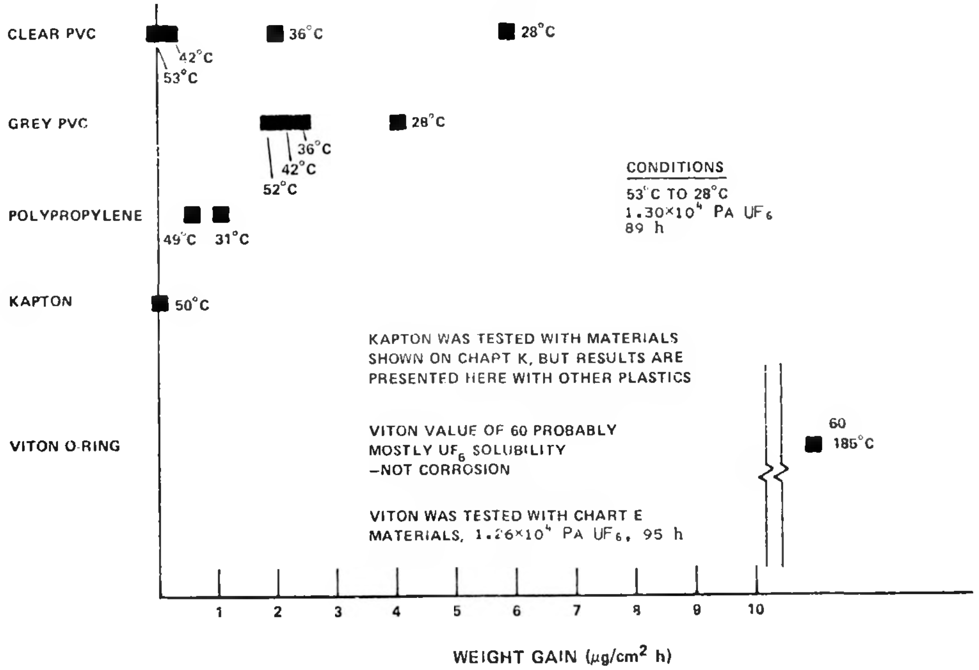
Group E, Plastics. The fluorocarbon plastics (Teflon) and the chlorofluorocarbon plastics (Kel-F) are well known for their resistance to corrosion by nearly everything, including fluorine and UF_6. Solubility of UF_6, particularly in Kel-F is not always appreciated but is not dealt with here; nor is the corrosion of these plastics by UF_6 treated, except for the elastomer, Viton, considered here and some composites of Teflon, powdered nickel, and powdered copper discussed in Group F. Surprisingly, polyvinyl chloride (PVC) of clear and gray varieties, polypropylene and Kapton, had very good resistance to corrosion by UF_6 at temperatures up to 50°C, the highest used for the plastics tests. Strangely, the weight gain was lower, progressively, for the samples tested at the higher temperature. This might be interpreted as better conditioning (by prior vacuum degassing of the specimens at the individual test temperatures, which would lower water content that would otherwise contribute to weight gains by way of hydrolytic deposits of UO_2F_2) or possibly as a phenomenon of solubility of UF_6 (the higher temperature corresponding to lower solubility) directly in the plastic without necessary reaction. If water is the source of the weight gain, it would imply that a vessel or window made of one of these plastics and intended for UF_6 use should be well dried before use and protected during use from diffusion of atmospheric moisture. A third possibility is that weight losses occurred in vacuum pretreatment, and these losses masked gains due to corrosion. A separate experiment established that weight losses by vacuum pretreatment were negligible. The PVC and polypropylene specimens and the Viton O-ring were supplied by Ed Griggs of L-6 and tested at his request. All tests except that on Viton were at 1.30×10^4 Pa UF_6 for 89 h with temperatures as individually noted and are shown on Chart I.

1. Clear PVC. Tests shown on Chart I were over a span of four temperatures from 28 to 53°C, and at the highest temperature, weight gain was zero. Weight gains increased monatomically as test temperatures of specimens decreased, although the specimen at lowest temperature, weighing 0.1592 g originally, gained only 0.0027 g. The pieces of PVC were 3 to 4 cm long, about 3/4 cm wide and 0.05 cm thick. Visual appearance of the specimens after testing showed progressively larger deviations from original appearance as test temperatures decreased, analogous to the weight change observations. The 53°C specimen showed only the very slightest, hardly detectable darkening of color compared to the original. The 42°C specimen had a definite though slight gray, smoky smudge. The 36°C specimen exhibited a general light gray-brown smudge. The 28°C specimen showed a general slight darkening and spotty, gray-brown smudge.

2. Polypropylene. Polypropylene specimens were tested at 48°C and 30°C. The specimens were about 5 cm long, 0.6 cm wide and 0.30 cm thick. The specimen tested at 48°C weighed 0.7849 g and gained 0.0006 g, and after test was visually indistinguishable from the original material. The specimen tested at 30°C, of similar dimensions and weight, gained 0.0009 g, and visual inspection revealed a very slight cloudy film.

3. Gray PVC. Gray PVC specimens were tested at the same temperatures as were the clear PVC specimens. The pieces were of similar dimensions to the clear PVC pieces except they were nearly three times as thick (0.14 cm) and they weighed about three times as much as the clear PVC specimens. The weight gains did not vary as much from the highest to the lowest temperatures as did the gains for the clear PVC's. The average weight gain per square centimeter for all the pieces was nearly the same as that quantity for the clear PVC's. The weight gains and appearances were distributed monatomically with temperature. In appearance, the piece tested at 53°C had a light general smudge on the surface. The piece tested at 42°C had a general light smudge but was very nearly unsmudged near the outer edge of the surface. The appearance of the piece tested at 36°C was identical to that of the piece tested at 42°C. The piece tested at 28°C had

CHART I
PLASTICS



only a slight smudge near the very center of the surface, and much of the surface near the edges looked like the original surface before exposure. The appearances were somewhat surprising for these samples in that those samples which showed the largest weight gains were those that showed the least appearance changes. Inspection of the clear PVC and polypropylene pieces under the microscope revealed thin films even on pieces that seemed clear by unaided eye. When the films were scraped away to reveal the underlying surface, residual smokelike coloring could be seen within the body of the plastic. This residual color was greater for the pieces tested at higher temperature than the pieces tested at lower temperature, but the surface film effects were greater for the pieces tested at lower temperature.

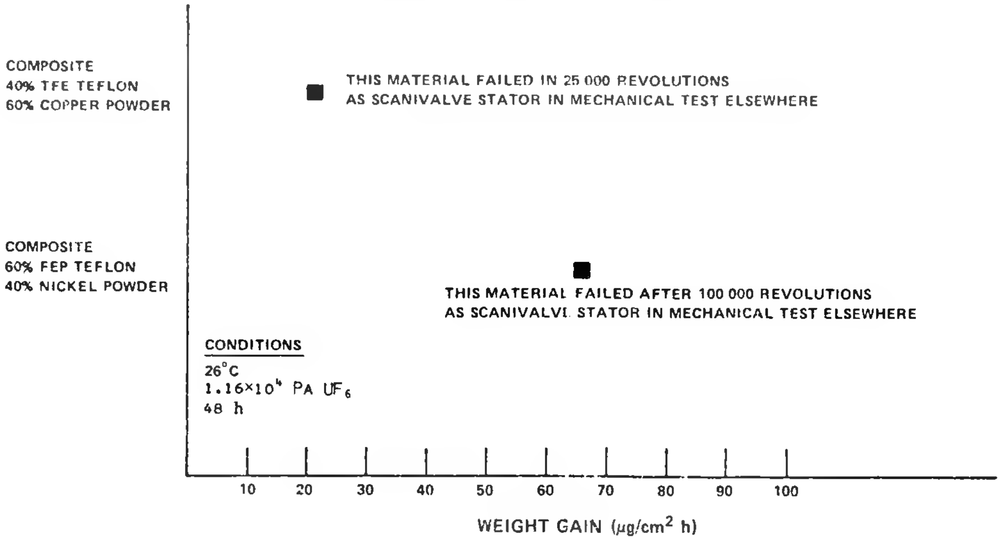
4. Kapton. Kapton was not tested simultaneously with the above materials, but the test conditions were similar for the single piece tested at 50°C. The Kapton piece was of similar area but much thinner (<0.01 cm) than the above plastics. The weight gain was within the weighing error of the balance (0.0001 g), and there was no appearance change after exposure to 1.25×10^4 Pa (94 torr) UF_6 for 97 h. Under the microscope a very thin film was detected. It could be readily scraped off to reveal the original surface.

5. Viton elastomer O-ring. This specimen was tested at the considerably higher temperature of 185°C at 1.27×10^4 Pa (95 torr) UF_6 for 95 h. Testing was with the materials shown on Chart G, and results reported there are also reported on Chart I. The considerable weight gain of 0.0997 g over the original weight of 2.5327 g probably was not due directly to corrosive action of UF_6 on the Viton. Rather it may have been due in large part to solubility of UF_6 in the Viton. The O-ring placed on a balance pan in room air continued to gain weight at the rate of about 0.001 g/min for several minutes after removal from the reactor. This is

likely to be a measure of the pickup of moisture from the room air and the reaction with UF_6 contained in the Viton. The Viton O-ring became stiffer as a result of the UF_6 exposure but was still quite elastic. There was a white bloom on the surface, in which small cracks could be seen. A few green flecks dotted the surface. The measured diameter was unchanged from the original 0.36 cm (0.142 in.).

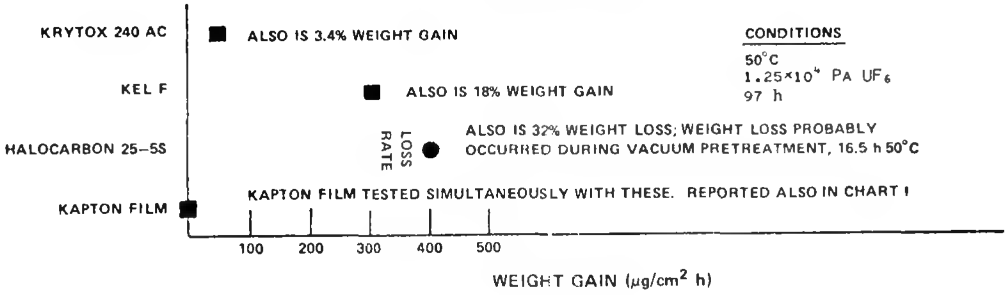
Group F, Composites of Fluorocarbon Plastics and Powdered Metals. Only two specimens are in this group. They were furnished by Scanivalve, Inc. (A Scanivalve is a small-volume multiple-port valve which connects a large number of ports alternately to a pressure transducer, for instance, on application of an electrical command signal.) Scanivalve, Inc. had worked with Milt Otey of the Paducah Plant in applying Scanivalves to UF_6 work. Direct use of the valve was unsuccessful due to swelling and hardening of internal parts that were required to make gastight seals while rotating to successive port positions. Internal parts made of either 40% TFE Teflon and 60% copper powder composite or 60% FEP Teflon and 40% nickel powder composite were tried as valve parts, but corrosion resistance to UF_6 had never been determined. Tests were conducted on chunks of both materials at 26°C and 1.16×10^4 Pa (87 torr) UF_6 for 48 h. The copper-TFE-composite that was mechanically inferior (failed after about 25 000 revolutions) was somewhat superior by a factor of about 3 in its ability to resist corrosion by UF_6. The FEP-nickel composite had failed after 100 000 revolutions in a mechanical test, but this material was found to be more severely corroded by UF_6. Results are shown in Chart J. Microscopic examination was necessary to detect changes. There was a slight furry, light-colored deposit on both pieces, but not on all surfaces of the pieces. It seemed possible that moisture or another component was coming to the surface of the pieces and there causing hydrolysis of UF_6. Use of the modified Scanivalve has never been adequately tested in UF_6. Our own interest declined and the Paducah people solved their problem by using a Scanivalve to program pneumatic operation of a series of small, specially built, UF_6-resistant valves.

CHART J
COMPOSITES – SUBSTITUTE PARTS FOR SCANIVALVES



Group G, Greases. Krytox 240AC, Kel-F, and Halocarbon 25-5S were tested at 50°C and 1.25×10^4 Pa UF_6 for 97 h. Results are shown in Chart K. The Krytox was superior, although it is uncertain that reaction of UF_6 occurred with any of the greases. Krytox suffered the least weight gain on exposure to UF_6, the least weight change on exposure to vacuum alone at room temperature and at 69°C, and the least appearance change. In vacuum, Krytox increased weight slightly and the increase may be attributed to absorption of a portion of a very large amount of volatile constituent evolving from the Halocarbon specimen present in the same vacuum chamber only 1 cm away. Kel-F also increased weight slightly in vacuum, probably from the same cause cited for Krytox. Exposure of Kel-F to UF_6 resulted in an 18% weight gain and a yellow-green color developed on the surface and throughout the body of the glob of grease. The weight gain and color were probably caused by UF_6 dissolved in the Kel-F. The Halocarbon grease lost an amazing 30% of its weight in the vacuum treatment, and the result of the UF_6 treatment (on a different sample but including vacuum pretreatment with unmeasured weight change for vacuum effect alone) was a 32% weight loss. Whether or not UF_6 reacted with the colloidal silica usually present in this Halocarbon was undetermined. The appearance of the Halocarbon was unchanged by the UF_6 exposure, but a different test with Halocarbon under similar conditions and shown in Chart E resulted in development of a yellow-green color in the Halocarbon grease. In that case weight loss was 20%.

CHART K
FLUOROCARBON GREASES



WEIGHT CHANGES IN VACUUM ALONE DETERMINED IN A SEPARATE TEST.

FIRST, VACUUM FOR 72 HOURS 25°C

0.40 g KRYTOX 240AC	GAIN 0.83%
0.45 g KEL F	GAIN 0.39%
0.53 g HALOCARBON 25–5S	LOSS 2.9%

NEXT, SAME SAMPLES LEFT 20.5 HOURS ADDITIONAL IN VACUUM, BUT AT HIGHER TEMPERATURE, NOW 69°C

KRYTOX	GAIN 0.05%
KEL F	LOSS 16.7%
HALOCARBON	LOSS 26.6%

OVERALL WEIGHT CHANGES FOR TOTAL VACUUM TREATMENT.

KRYTOX	GAIN 0.9%
KEL F	LOSS 16.3%
HALOCARBON	LOSS 29.5%

THE WEIGHT GAINS OF KRYTOX AND THE FIRST TEST WEIGHT GAIN OF KEL F ARE LIKELY DUE TO ABSORPTION OF MATERIAL RELEASED BY HALOCARBON.

REFERENCES

1. H. A. Bernhardt, W. Davis Jr., C. F. Hale, R. J. Heus, and R. H. Wiswall, Jr., "Consumption of F_2 and UF_6 by Aluminum and Beryllium near 400°C," Oak Ridge National Laboratory report K-239 (1948).

2. G. L. Ericson, W. K. Boyd, and P. D. Miller, "Corrosion of Titanium and Titanium Base Alloys in Liquid and Gaseous Fluorine," Battelle Memorial Institute, Titanium Metallurgical Laboratory, report NP-6729 (1958).

3. Joseph J. Katz and Eugene Rabinowitch, The Chemistry of Uranium (McGraw-Hill Book Company, Inc., New York, 1951), p. 401.

4. S. S. Kirslis, T. S. McMillan, and H. A. Bernhardt, "The Reaction of Uranium Tetrafluoride with Dry Oxygen," Oak Ridge National Laboratory report K-567 (1950).

☆ U.S. GOVERNMENT PRINTING OFFICE 1978—777-089/150