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FOR PROTECTION OF URANIUM

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ALUMINUM AND POLYMERIC COATINGS
FOR PROTECTION OF URANIUM*

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INTRODUCTION

It is desirable to reduce the corrosion of uranium in storage to less than 1 μ m oxide thickness (spallation thickness) in 25 years. A typical storage environment would consist of dry nitrogen with 0.1 Torr $H_2O(v)$ and ~ 1.0 Vol.% O_2 at an average storage temperature of 30°C. Thus, we have undertaken a project whose objective is to protect uranium using metallic and polymeric coatings, applied under conditions such that the uranium surface temperature would not exceed 95°C.

Several methods have been studied to protect uranium against corrosion by water vapor and/or oxygen. They are: 1) aluminum ion plating coatings; 2) magnetron-produced aluminum coatings; 3) polymeric coatings (Kel F-800, Saran F-310, a chlorinated polyolefin, viton, and phenoxy); and, 4) a combination of an aluminum film plus a polymer overcoat.

The chosen protection techniques have been evaluated using small coupons as well as large uranium samples. The results of these studies, and the calculational techniques used to predict the extent of oxidation in 25 years, will be discussed in detail.

*Presented at the 11th DOE Compatibility Meeting, Sandia National Laboratories, Livermore, California, October 18-20, 1983.

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FAB

EXPERIMENTAL

Depleted uranium coupons of two different sizes and large uranium samples having a surface area of 1500 cm^2 were used for corrosion testing. The flow-apparatus used to test the coupons in oxygen-free water has been described in detail elsewhere.⁽¹⁾ We chose oxygen-free water vapor to be the test atmosphere in order to obtain results in a short time, since these conditions produce the fastest oxidation of uranium. An all-metal apparatus provided with a source of water vapor was used to test the large samples as shown in VG-1. Data in the form of weight gain per unit area ($\Delta W/A$, mg/cm^2) as a function of time resulted from the flow-system, and hydrogen generated (moles) as a function of time from the apparatus used to test the large samples.

Uranium was coated with aluminum by the ion plating technique. The process parameters and the resulting film thickness range are defined in VG-2, while the characteristics of this type of coating are shown in VG-3. Initial corrosion results on Magnetron-produced (sputtering techniques) coatings were encouraging, but this type of coating has not been fully evaluated yet.

Screening tests were carried out with uranium coupons coated with phenoxy, chlorinated polyolefin, Viton A, Saran F-310, and Kel F-800 (Copolymer of polyvinylidene fluoride (25%) and chlorotrifluoroethylene (75%)). The solvent for this screening test was methyl-ethyl ketone. In subsequent experimentation with Kel F-800 ethyl acetate was used as the solvent.

(1) C. A. Colmenares, D. R. McKenzie, and T. E. Shell, J. Phys. E: Sci. Inst., 6 1121-4(1973)

EXPERIMENTAL EQUIPMENT TO TEST LARGE SAMPLES

ION-PLATING PARAMETERS

(TYPICAL)

1. REMOVAL OF SURFACE OXIDES BY SPUTTERING
-4KV, 12-15 μ AR, 15 MIN OR 650C U-TEMPERATURE
2. ALUMINUM DEPOSITION
-3 KV, 1.4 μ AR
-40 MA FILAMENT CURRENT RAISED UNTIL AL MELTS
-250 $\frac{\text{\AA}}{\text{s}}$ DEPOSITION RATE
-0.0003 TO 0.001 IN. THICK FILM (COINCIDES WITH COMPLETE AL
DEPLETION IN FILAMENT)
3. CHAMBER VENTED TO ~ 127 TORR DRY-AIR AND PART ALLOWED TO
COOL TO 600C

AL-COATED URANIUM BY ION PLATING

- ALUMINUM FILMS ARE COLUMNAR IN STRUCTURE AND HAVE LARGE POROSITY
- WATER VAPOR IS EASILY TRANSPORTED THROUGH PORES TO CORRODE URANIUM
- URANIUM OXIDE GRADUALLY FILLS THE PORES IN THE ALUMINUM FILM AND BECOMES OBSERVABLE ON THE SURFACE OF THE ALUMINUM
- COMPLETE SEPARATION OF THE ALUMINUM FILM FROM URANIUM HAS NOT BEEN OBSERVED
- THIS TYPE OF FILM DOES NOT MEET THE REQUIREMENTS FOR 25 YEAR STORAGE

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RESULTS AND DISCUSSION

The oxidation of bare uranium at 100 Torr $H_2O(v)$ and $81^\circ C$ for the two types of samples (Grades B and D) used in this test are shown in VG-4. Grades A and C, representing extremes in purity, are shown for comparison. Grade D should have had an intermediate value between grades B and C; the low value shown may have been caused by loss of hydrogen through an O-ring seal in the support for the large sample. The corrosion of uranium in oxygen-free water vapor is linear as shown in VG-5.

The results obtained in the screening test, using several polymers to coat uranium, are summarized in VG-6. It shows that Kel F-800 is the best candidate to use as a water vapor barrier to protect uranium against corrosion. Other good qualities of Kel-F are ; 1) long term stability in high explosives use; 2) good radiation resistance; and 3) low reactivity with uranium below $100^\circ C$. Based on these results it was decided to study Kel F-800 as the prime candidate for uranium protection. Some of the pertinent properties of Kel-F are shown in VG-7.

To evaluate Kel F-800 as a water vapor barrier it is necessary to know its permeation characteristics as a function of temperature. Unfortunately, these are not well known and the only data available to serve as a guide are the water permeation values for Kel F-81 (chlorotrifluoroethylene) as shown in VG-8. Permeability values for Kel-F 800 have been calculated using corrosion data from coated uranium coupons as shown in VG-9. These data tell us that there is no change in permeability between 69 and $100^\circ C$ within the experimental limits of error. A comparison of permeability values measured at LLNL and Y-12 is presented in VG-10.

Kel-F 800 in direct contact with uranium has been found to react to produce UF_3 and some oxyfluorides at the uranium-Kel-F interface after treatment at $\sim 80^\circ C$, which is the temperature used to remove the ethyl acetate solvent. The presence of these fluorides/oxyfluorides was found by examination of Kel-F films removed from corroded uranium coupons using x-ray photoelectron spectroscopy. UO_2 was also found from the reaction of uranium with water vapor. The effect that this UO_2/UF_3 layer may have on the water permeability in Kel-F and uranium reactivity has not been determined.

The calculational scheme to predict uranium oxide thickness in coated coupons exposed to water vapor is shown in VG-11. It involves obtaining corrosion data for bare and coated uranium (VG-5, VG-12, and VG-13) at the same temperature and water vapor pressure, and calculating the permeability constant (P) of the polymer film at the experimental temperature. Using an activation energy of 10 kcal/mole it is possible to estimate P at $30^\circ C$. We have previously shown that the pressure dependence of the reaction rate constant (k , $mg/hr\text{-}cm^2$) for the $U\text{-}H_2O$ reaction is,

$$k(\text{bare}) = ap^{1/2} \quad (1)$$

where,

a = is a function of temperature ($\exp(-E/RT)$) with $E = 10$ kcal/mole

p = water vapor pressure

Applying equation (1) a value of "a" for $30^\circ C$ can be calculated. Then, since the water transport through the polymer film controls the process and uranium can react with all this water, it is possible to estimate an interface pressure, p_i , at $30^\circ C$. Applying equation (1) again one arrives at the value of $k(30^\circ C, p_i)$ representative of storage conditions. From this value it is

OXIDATION OF URANIUM

IN 100 TORR $H_2O(v)$ AT $81^{\circ}C$

I.D.	SAMPLE	CORROSION RATE MG./H-CM ²
GRADE A	Y-12 HIGH PURITY (~ 50 PPM TOTAL IMPURITIES)	4.90×10^{-2}
GRADE B	LLNL DERBY	6.70×10^{-2}
GRADE C	LLNL (1000 PPM IMPURITIES)	7.67×10^{-2}
GRADE D	LARGE SAMPLE	1.63×10^{-2} *

* LOW DUE TO LOSS OF HYDROGEN THROUGH RUBBER O-RING

CORROSION OF BARE URANIUM

(COUPON DATA)

GRADE B
100 TORR H₂O(V)

CORROSION OF COATED URANIUM IN

100 TORR H₂O(v) AT 100°C

SAMPLE	CORROSION RATE MG./H-CM ²	APPROXIMATE POLYMER FILM THICKNESS IN.
BARE URANIUM (GRADE C).	0.205	--
PHENOXY COATED	0.193	0.005
CHLORINATED POLYOLEFIN	0.083	0.005
VITON	0.081	0.002
SARAN	0.019	0.006
KEL-F 800	0.009	0.003

KEL-F 800

CO-POLYMER OF:

O POLYVINYLIDENE FLUORIDE (25%)

O CHLOROTRIFLUOROETHYLENE (75%)

LL DSC scan of Kel F-800, lot 552.

KEL-F 81*

O CHLOROTRIFLUOROETHYLENE

$$T_G = 54^{\circ}\text{C} \quad T_M = 218^{\circ}\text{C}$$

* REFERENCE MATERIAL. PERMEATION DATA FOR WATER IS KNOWN AS A FUNCTION OF TEMPERATURE

PERMEATION OF WATER VAPOR IN KEL-81 (3M DATA)

T, °C	PERMEABILITY CONSTANT
	<u>CM³ H₂O (STP)-MM/S-CM²-CM H_g</u>
25	1 x 10 ⁻¹⁰
50	10 x 10 ⁻¹⁰
75	28 x 10 ⁻¹⁰
100	100 x 10 ⁻¹⁰

- THE ACTIVATION ENERGY FOR PERMEATION CALCULATED FROM THE VALUES ABOVE IS:

$$E_p = .13.2 \pm 5.3 \text{ KCAL/MOLE (95\% CONFIDENCE LEVEL)}$$

WATER PERMEATION IN KEL-F 800

RUN NO	T, °C	K _I MG.O/H-CM ²	K _F MG.O/H-CM ²	P, MG.O-MM/H-CM ² - TORR	
				BASED ON K _I	BASED ON K _F
275-3	67	2.22 x 10 ⁻³	3.67 x 10 ⁻³	5.3 x 10 ⁻⁷	8.4 x 10 ⁻⁷
275-4	67	2.15 x 10 ⁻³	3.61 x 10 ⁻³	5.0 x 10 ⁻⁷	8.8 x 10 ⁻⁷
270-3	80	N.A.	1.83 x 10 ⁻³	--	10.2 x 10 ⁻⁷
270-4	80	N.A.	1.76 x 10 ⁻³	--	8.1 x 10 ⁻⁷
267-3	100	N.A.	2.19 x 10 ⁻³	--	9.46 x 10 ⁻⁷
267-4	100	N.A.	2.13 x 10 ⁻³	--	9.20 x 10 ⁻⁷

Av. = 9.03 x 10⁻⁷/**

- THERE IS NO CHANGE IN PERMEABILITY BETWEEN 69⁰ AND 100⁰C WITHIN EXPERIMENTAL ERROR
- THIS BEHAVIOR MAY BE CAUSED BY THE PROXIMITY OF THE MEASUREMENTS TO THE MELTING POINT (99⁰C*). CADY* REPORTS THE ONSET OF KEL-F 800 MELTING TO BE BETWEEN 64⁰ TO 83⁰C (MOLDED, ANNEALED SHEETS).

* W. E. CADY AND L. E. CALEY, "PROPERTIES OF KEL-F 800 POLYMER,"
UCRL-52301, JULY 21, 1977.

**EQUIVALENT TO 3.5 x 10⁻⁹ CM³ (STP) - MM/S-CM² CM HG

WATER PERMEATION IN KEL-F 800

● LLNL

- $P = 3.5 \times 10^{-9} \text{ CM}^3 \text{ (STP) - MM/S-CM}^2\text{-CM HG}$ 67-100°C
 $P(\text{EST.}) = 4.5 \times 10^{-10} \text{ CM}^3 \text{ (STP) MM/S-CM}^2\text{-CM HG}$ 30° (10 KCAL/MOLE)
- CONSTANT PRESSURE (100 TORR)

● Y-12*

- $P = 3 \times 10^{-9} \text{ CM}^3 \text{ (STP) - MM/S-CM}^2\text{-CM HG}$ 25°
 $P = 2 \times 10^{-9} \text{ CM}^3 \text{ (STP) - MM/S-CM}^2\text{-CM HG}$ 45°
- NO PRESSURE DEPENDENCE (1, 5, 10 TORR)

* YDA-8673, AUG. 1983

AT STEADY STATE, CONSTANT P_g , AND CONSTANT T :

$$Q = k$$

$$\frac{P(P_g - P_i)}{x} = a P_i^{1/2}$$

CORROSION OF KEL-F 800 COATED URANIUM

(COUPON DATA)

100 TORR H₂O

0.0018 IN. KEL-F

DW/A
MG/CM²

CORROSION OF KEL-F 800 COATED URANIUM

0.001 IN. KEL-F

87 C, 100 TORR H₂O(V)

then possible to calculate the amount of reaction in 25 years and thus, the thickness of the oxide formed. This type of calculation is demonstrated in VG-14 and VG-15. Since the value of the activation energy (E_p) for water permeation in Kel-F 800 is not known well, the effect of E_p on the uranium oxide thickness formed in 25 years is shown in VG-16.

For uranium coated with a 0.0018" thick film of Kel F-800 it takes 62 years to build an oxide layer 1 μ m thick (VG-15). The oxide thickness in 25 years is 0.4 μ m (VG-15). Thus, we must conclude that Kel F-800 will meet the requirements for a good water barrier to protect uranium for 25 years in storage.

Aluminum coatings on uranium were of a columnar structure that permitted the free-flow of oxidant to the uranium-aluminum interface. The oxidation of an aluminum-coated surface was manifested by the appearance of innumerable, small, black-spots of uranium oxide on the surface of the aluminum. Therefore, the effect of aluminum coating by ion-plating was to reduce the bare uranium area available for corrosion. Addition of a Kel F-800 layer on top of the aluminum produced what appeared to be a further "effective reduction" in reactive area; however, this effect really represented a reduction in the rate of corrosion due to the reduced water transport to the available bare uranium area after coating with aluminum. These effects are illustrated in VG-17 and 18.

Large uranium samples were also coated with 0.003" of Kel-F and corrosion tested in 25 Torr of H_2O (v) at 75°C (see VG-19). The rates of hydrogen generated shown are approximately twice of what the expected rates should be as determined from coupon data (VG-12 and VG-13). SEM pictures have shown that this is due to pores made by escaping solvent in the Kel-F film,

ESTIMATE OF CORROSION IN 25 YEARS
BASIS OF CALCULATIONS

1. WE WILL USE 69°C AND 100 TORR H₂O(V) AS A BASIS FOR OUR CALCULATIONS

$$\bar{K}_{\text{BARE}} = 3.61 \times 10^{-2} \text{ MG.O/H-CM}^2$$

$$\bar{K}_{\text{COATED}} = 1.67 \times 10^{-3} \text{ MG.O/H-CM}^2 \text{ (HNO}_3\text{-H}_2\text{O CLEANING)}$$

0.0018" THICK KEL-F 800

2. WE WILL IGNORE THE INTIAL CORROSION PERIOD

OXIDATION OF KEL-F COATED URANIUM

IN 25 YEARS (30°C, 0.1 TORR H₂O)

$$\text{FOR K(30°C, } 2.23 \times 10^{-7} \text{ TORR)} = 2.54 \times 10^{-7} \text{ MG/O/H-CM}^2$$

$$\text{CORROSION IN 25 YEARS} = 0.43 \text{ MG. UO}_{2.2}\text{/CM}^2$$

$$\rho(\text{UO}_{2.2}) \sim 11.000 \text{ MG/CM}^3$$

$$\text{OXIDE THICKNESS} = \frac{0.43}{11.000} = 3.93 \times 10^{-5} \text{ CM} \approx 0.40 \text{ }\mu\text{M.}$$

(62 YEARS TO BUILD A LAYER 1 μM THICK !)

OXIDE THICKNESS IN 25 YEARS

0.1 TORR H₂O (V), 30 C

KEL-F 800

CORROSION TESTS, P(CH₂O)=23 TORR, 75 C

(FULL SCALE TESTS)

LARGE SAMPLE CORROSION TESTS

(~23 TORR H₂O(V), 750C)

UNIT	RATE OF H ₂ GENERATION MOLE/HR	TIME FOR ONSET OF FAST REACTION HOUR	EFFECTIVE U AREA ATTACKED CM ²
BARE U	$1.52 \times 10^{-3} *$	0	1500
AL-COATED	2.1×10^{-4}	500	240
AL + KEL-F- 800 **	1.34×10^{-4}	800	134

* EQUIVALENT TO 1.0×10^{-6} MOLES H₂/H-CM² $\equiv 1.62 \times 10^{-2}$ MG./H-CM²

** UNEVEN KEL-F COATING: THIN AT ONE END AND THICK AT THE OTHER.

and to a scalloped morphology, with cracks and pores resulting from the plastic application process, on a large portion of the film. Use of Kel-F 800 directly on uranium is not recommended for storage use at this time until the effect of uranium fluoride formation at the plastic-uranium interface is evaluated.

The conclusions for the full scale tests are summarized in VG-20. Further work is now in progress to determine the permeability constant for water vapor in Kel F-800 as a function of temperature.

CORROSION OF KEL-F 800 COATED URANIUM

$P(\text{H}_2\text{O}) = 25 \text{ TORR}$, $T = 75 \text{ C}$

0.003 IN. KELF

$K(\text{BARE})/K(\text{COATED}) = 8.4$

CONCLUSIONS

1. ION-PLATED ALUMINUM FILMS ON URANIUM WILL NOT PROVIDE ADEQUATE PROTECTION FOR 25 YEARS
2. MAGNETRON-PLATED ALUMINUM FILMS ON URANIUM ARE MUCH BETTER THAN ION-PLATED ONES
3. KEL-F 800 FILMS ON URANIUM CAN PROVIDE ADEQUATE PROTECTION FOR 25 YEARS. THEIR USE IN PRODUCTION MUST BE DELAYED UNTIL THE FOLLOWING FACTORS ARE SORTED OUT:
 - WATER PERMEABILITY IN KEL-F 800 MUST BE DETERMINED BETWEEN 30⁰ AND 60⁰C
 - THE EFFECT OF UF₃, AT THE KEL-F/METAL INTERFACE, ON THE PERMEABILITY OF WATER MUST BE ASSESSED
 - THE EFFECT OF CRYSTALLINITY ON WATER PERMEABILITY MUST BE EVALUATED
4. APPLYING KEL-F FILMS ON ALUMINUM ION-PLATED URANIUM PROVIDES A GOOD INTERIM SOLUTION FOR LONG TERM STORAGE.