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AN INVESTIGATION OF URANIUM CORROSION
IN 100 C WATER AND 200 C STEAM
AT ATMOSPHERIC PRESSURE

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Material balance in atmospheric-pressure water and steam corrosion of uranium have been studied by examination of the phase composition and valence state of the corrosion product and by hydrogen-evolution measurements. The corrosion rates in atmospheric-pressure steam above 100 C are lower than those obtained in tests carried out in water with a hydrogen overpressure. The atmospheric-pressure-water corrosion product was found to be two phase: (1) an oxygen-rich oxide, $\text{UO}_{2.2}$, and (2) uncorroded metal particles. No hydride phase was detected, in contrast to previously reported evidence for hydride in uranium corrosion. The differences are explained on the basis of hydrogen pressure in the reaction vessel.

INTRODUCTION

The end product of the reaction of uranium with water or water vapor under degassed conditions is an oxide having a UO_2 -type structure. Several intermediate reactions may occur which influence the rate of reaction. It is generally believed that the following reactions can occur during the corrosion of uranium in water or steam:

In the presence of oxygen at temperatures below 70 C the oxide formed in Equation (1) is adherent and protects the underlying uranium from further attack by the water⁽¹⁾. At temperatures above 80 C in degassed or hydrogen-containing water uranium corrodes rapidly to form a voluminous loosely adherent oxide coating. It is believed⁽¹⁾ that atomic hydrogen migrates through the initial oxide film formed in Equation (1) and reacts with the uranium to form hydride as shown in Equation (2). This hydride layer is between the metal and the oxide and spoils the adherence of the oxide to the metal so that it no longer is protective⁽¹⁾. Water then reacts with the uranium hydride to form UO_2 as shown in Equation (3) and the hydrogen produced is free to react with the uranium, thus completing the cycle.

There is a fair amount of evidence to support the above theory. The reaction rate between uranium and hydrogen is reported to be considerably higher at all temperatures than that between uranium and steam⁽¹⁾. In some instances hydride has been detected beneath the oxide on samples corroded at 150 to 180 C.⁽¹⁾ Large quantities of UH_3 have been observed during bomb corrosion of uranium at 300 C⁽²⁾. In addition, collections of hydrogen evolved during corrosion have been less than the stoichiometric quantities

(1) References at end.

which should have been released assuming Equation (1) to be the corrosion reaction. This suggests that the missing hydrogen may be tied up as a hydride in the uranium.

Based on the above observations, it was believed that a more thorough study of the phase and chemical composition of the solid corrosion products and the material balances involved in uranium-water reactions might lead to a better understanding of the corrosion mechanism. Two arbitrary test temperatures, 100 C and 200 C, were selected. All tests were conducted at atmospheric pressure.

EXPERIMENTAL WORK

Test Procedures

The uranium used in this study was dingot material with nominal maximum impurities of 60 ppm carbon, 80 ppm nitrogen, 12 ppm oxygen, 4 ppm hydrogen, 20 ppm iron, and less than 5 ppm of tantalum, tin, titanium, and zirconium. Samples for the 200 C test were prepared by abrading under alcohol, were air-dried, weighed, and immediately immersed in alcohol and transferred to the reaction vessel. The voluminous corrosion product formed on specimens was easily wiped off, leaving an adherent tarnish film. Removal of the tarnish film in dilute nitric acid solutions did not increase weight losses appreciably.

Three methods of surface preparation were investigated for samples corroded in 100 C water: electropolishing*, abrading through 600-grit paper, and abrading followed by a HNO_3 pickle. The corrosion rates were independent of the method of surface preparation. After this preliminary work all of the samples were electropolished, rinsed in alcohol, and tested in boiled deionized water at atmospheric pressure. Pyrex glass containers were used throughout. A condenser was employed to prevent major losses of water during long-time tests.

A diagram of the reaction train employed in the 200 C tests is shown in Figure 1. Where possible, all components were constructed of Pyrex glass. The entire train was flushed with standard tank argon (A) for at least 1 hr before the alcohol-covered test samples were placed in the reaction chamber (B). The system was then flushed overnight with lamp-grade argon (C) of a 99.92 per cent purity (principal impurity is nitrogen). The water was degassed by boiling for at least 1 hr in a vessel (D) vented to the atmosphere. At the same time, the reaction vessel was brought to 200 C by means of a furnace or constant-temperature bath (E).

At the start of the run the argon flow was directed through the boiling water. The air vent to the degassing vessel (D) was closed. The moist argon, flowing at 100 ml per min, was passed through a preheater (F) before entering the reaction vessel. After passing through the reaction chamber, the bulk of the water was removed from the argon by means of a condenser (G). The remaining traces of water were removed in drying bottles (H). The hydrogen from the corrosion reactions reacted with copper oxide in a

*The electropolishing bath was 40 volume per cent H_2SO_4 , 40 volume per cent H_2O , 10 volume per cent $\text{C}_2\text{H}_5\text{OH}$, and 10 volume per cent H_3PO_4 . The open-circuit voltage was 10 v. A more uniform polish was obtained when the bath temperature was maintained below 15 C.

FIGURE 1. DIAGRAM OF REACTION TRAIN FOR URANIUM-STEAM REACTION STUDIES

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furnace (I) and the resulting water was collected in weighed drying bottles (J). The exit gas was passed through a mineral-oil trap (K) to avoid back diffusion of air.

Reaction times were 4 to 6 hr in duration. In tests designed to obtain corrosion rates, the reaction vessel was isolated from the rest of the system and was rapidly cooled. In other tests, the stopcocks to the water supply were closed and flowing argon was passed over the sample at 200 C to dry the oxide. After several hours of drying, the reaction vessel was isolated from the train, and the water condensed in a flask (L) (approximately 500 ml) was boiled to remove dissolved hydrogen. The condenser (G) and the flask (L) then were isolated from the system and drying of the sample with flowing argon was completed.

The increase in weight from water collected in drying bottles (J) was recorded at intervals and at the end of the tests. Hydrogen evolution was calculated from the weight increase of the drying bottles.

Analysis of the Corrosion Products

The solid corrosion products were analyzed by X-ray diffraction for phase composition, by X-ray absorption and chemical methods for the valence state of the uranium, and by ignition for the oxygen-to-uranium ratio. The latter analysis was carried out on vacuum-dried specimens in order to eliminate the effect of hydroxides or adsorbed water on the analysis. The evolved hydrogen was measured as described above. Metallographic examinations and hydrogen analyses were made on the uncorroded base metal to determine the amount of hydrogen pickup during corrosion.

The mean valence of the uranium in the loose corrosion product was obtained by dissolving the corrosion product in a 1N solution of AgNO_3 and NH_4F . The silver ion oxidized the uranium to the hexavalent state and silver was precipitated as in Equation (4):

The amount of reduced silver was measured gravimetrically and the amount of uranium determined by a weight-volumetric method, employing ceric sulfate. The valence state of the uranium in the major component (the oxide phase) of the corrosion product was studied by analysis of the X-ray absorption spectrum as described by Cahannes⁽³⁾. The L_{III} X-ray absorption edge of the corrosion product was compared with that of uranium, UO_2 , and UO_3 . It has been shown that the position and shape of the X-ray absorption edges are affected by the valence state of the element. These differences are small, of the order of 5×10^{-4} , and thus require precision wavelength measurements.

Test Results

Corrosion Rates

Corrosion rates were measured for the Dingot uranium to establish whether the wet argon supplied sufficient water to obtain a reasonable amount of attack. The

corrosion rates thus obtained are summarized in Table 1. Also included in Table 1 are hydrogen yields based on the assumption that $\text{UO}_{2.0}$ is the corrosion product.

TABLE 1. CORROSION RATES OF DINGOT URANIUM
IN ARGON PLUS WATER VAPOR

Temperature, C	Time, hr	Weight Loss, $\text{mg}/(\text{cm}^2)(\text{hr})$		Hydrogen Collected(a), per cent of theoretical
		Measured	Calculated	
100	6	2.9	2.2	None collected
150	5	7.7	7.3	95
150	6	7.0	6.1	87
200	4	53	48	91
200	4	58	55	95
200	6	61	54	89
200	5	45	42	93
200	5	70	57	82
200	6	36	31	86
200	5	37	33	89
200	6	35	32	91
400	4	328	355	108
400	6	212	190	90

(a) Based on the amount of hydrogen evolved and the equation $\text{U} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2 + 2\text{H}_2$.

The corrosion rates in wet argon were found to be linear with time in the temperature range of 100 to 400 C, indicating the formation of a nonprotective corrosion product. A temperature-dependency plot of the linear corrosion rates is presented in Figure 2. Also included in Figure 2 are results obtained at other laboratories for steam and water corrosion of uranium.

The corrosion rate of uranium in water at 100 C was also found to be linear. A variation in the corrosion rate between 2.7 and 3.5 $\text{mg}/(\text{cm}^2)(\text{hr})$ was measured, which is in good agreement with that obtained by other workers (Figure 2) and the results in argon plus steam at 100 C (Table 1). The effect of pressure and steam content of the gas at higher temperatures is seen in Figure 2, Curves A, B, and C. The differences between Curves A and C may be due to hydrogen overpressure in water tests, while the difference between Curves B and C may be the steam content of the corrodent.

The amount of hydrogen collected averaged about 90 per cent of the theoretical yield based on the assumption that $\text{UO}_{2.0}$ was the corrosion product. Hydrogen evolution was linear with time as shown in Figure 3. This would be anticipated since the corrosion rates for uranium also were linear. In four tests carried out in water at 100 C, the average amount of hydrogen evolved was 91.5 plus or minus 1.2 per cent of the amount calculated from weight loss, using Equation (1) above. In view of the lack of balance in the corrosion reaction, the solid corrosion products were analyzed for hydrogen and for the oxidation state of the uranium.

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FIGURE 2. TEMPERATURE-DEPENDENCY PLOT OF THE REACTION OF URANIUM WITH WATER AND WATER VAPOR

FIGURE 3. HYDROGEN COLLECTED DURING THE REACTION OF DINGOT URANIUM WITH STEAM-SATURATED ARGON AT 200 C

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Protective Action of Oxide Films

In contrast to the loose nonadherent nature of the oxide produced on uranium during corrosion, heat-tint oxide is very coherent. In order to evaluate the protective action of such coherent oxide films, a study was made of the corrosion rate of metal specimens preoxidized in oxygen at temperatures from 100 to 650 C.

Metal samples were heated in low oxygen pressures to form coherent oxide films prior to corrosion testing. Table 2 presents the results of short-term corrosion tests and the heat treatment employed. These data show that the protection of these films increases as the temperature of film formation is increased to 650 C. When the oxide film was removed by electropolishing, the corrosion rate was the same as that for unannealed samples, demonstrating that the increased corrosion resistance was due to a surface effect and not a bulk effect. When the films were formed at temperatures above the alpha-beta transformation (663 C), deep cracks appeared in the metal, producing discontinuities in the oxide film. All of the samples heated above the alpha-beta transformation corroded at the same rate as untreated samples. Figure 4 shows the results of longer tests on oxide-coated samples. All of the samples used in this test were held for 2 hr at 650 C in an oxygen atmosphere at a pressure of 5×10^{-4} mm of mercury. The oxide films were put on only two samples at a time in order to keep them well separated in the furnace. The samples that were coated together are enclosed by one circle in Figure 4. The spread observed is probably due to minor uncontrolled variations in the conditions used in forming the films. The oxide films failed after approximately 20 hr by developing a few small pits and undercutting. No inclusions were found at the site of the original failure. Failure probably occurred where the local stress level was sufficient to rupture the film. The oxygen-formed oxide films were nonprotective when formed at temperatures below 400 C. These results suggest that the lack of protective action of the aqueous corrosion product may be due to the mechanism of formation, to imperfections in the film caused by absence of diffusion and growth of the film at the lower temperatures, or by formation of other phases in the oxide layer.

Phase Studies on the Corrosion Products

Although X-ray diffraction patterns of the bulk corrosion product from 100 C water or 200 C steam-argon tests showed only broad diffraction lines which could be identified as the pattern of UO_2 , it should not be implied that minor phases are absent. The limit of detection of minor phases is particularly unsatisfactory, because of the high X-ray density of the major phase.

In order to account for the low hydrogen assay reported above, it would be advantageous to identify the minor phase or phases, such as UH_3 or metal, in the corrosion product. As a means of increasing the sensitivity for detection of the minor phase, its concentration by preferential dissolution of the oxide phase was investigated. It was found that dilute nitric acid (about 5 volume per cent) dissolved the oxide from partially oxidized uranium metal powder or UH_3 ; X-ray patterns of the residue were free of UO_2 . Therefore, several samples of the bulk corrosion product (100 C water test) were treated in this reagent to dissolve the oxide phase. In each case, the residue, consisting of feathery shaped particles, was identified by X-ray diffraction as metallic uranium. The presence of unreacted metal in the bulk corrosion product would account for the low hydrogen assay.

TABLE 2. CORROSION RESULTS ON PREOXIDIZED URANIUM

Sample	Condition of Oxide-Film Formation		Time in Corrosion Test, hr	Rate, mg/(cm ²)(hr)
	Temperature, C	Pressure, mm of mercury		
90	100	5×10^{-5}	4	2.93
91	100	5×10^{-5}	4	3.04
92	200	5×10^{-5}	4	3.26
93	200	5×10^{-5}	4	3.34
94	300	5×10^{-5}	4	2.78
95	300	5×10^{-5}	4	3.01
96	400	5×10^{-5}	4	3.00
97	400	5×10^{-5}	4	2.71
98	500	5×10^{-5}	4	1.56
99	500	5×10^{-5}	4	2.16
100	600	5×10^{-5}	4	0.68
101	600	5×10^{-5}	4	1.20
102	600	5×10^{-5}	4	1.24
103	600	5×10^{-5} (a)	4	3.10
104	600	5×10^{-5}	4	1.77
105	600	5×10^{-5} (a)	4	3.12
108	600	5×10^{-4}	4	Not detectable
109	600	5×10^{-4}	4	Not detectable
110	600	5×10^{-4}	4	Not detectable
111	600	5×10^{-4}	4	Not detectable
112	650	5×10^{-4}	21	0.06
113	650	5×10^{-4}	21	0.10
114	650	5×10^{-4}	21	0.09
122	600	1×10^{-3}	21	0.16
123	600	1×10^{-3}	21	0.28
124	600	1×10^{-3}	21	0.21

(a) Electropolished after film formation.

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FIGURE 4. EFFECT OF AN OXIDE FILM ON THE CORROSION OF URANIUM

Since it was possible that hydride would be present as a surface film, or as a dispersed phase in the metal surface, X-ray diffraction examinations of the metal surface, metallographic examinations of the surface layer and bulk metal, and hydrogen analyses were made on thin metal specimens after various time of exposure to 100 C water.

Using copper radiation, diffractometer traces of the sample surface were obtained after various times in water-corrosion test. Short-time tests showed alpha uranium and UO_2 . After the oxide had grown to such a thickness that it was no longer possible to obtain a diffraction pattern of the underlying metal, the loose oxide film was removed by directing a stream of alcohol or water against the sample. This removed enough oxide so that a metal pattern could be obtained from the specimen surface. Diffractometer traces of such samples also showed only metal and oxide. Metallographic examinations of the metal-oxide interface indicated no more hydride present at the interface than in the interior of the metal. Vacuum-fusion analyses also failed to detect any increase in the hydrogen content of the metal as corrosion progressed.

Assuming uranium hydride would be formed during uranium corrosion, according to Equation (2), some tests were carried out on the hydride. Beta UH_3 was prepared by reacting hydrogen with uranium metal at 200 C. This material was cooled and corrosion tested. If the powder was wetted at room temperature and then heated to boiling, hydride could be detected along with UO_2 by X-ray diffraction after 5 days. However, if the hydride was placed in hot water the reaction was violent. Metal samples which were hydrided on the surface were also corrosion tested. After 3 days in test at 60 C the hydride was readily detected under an oxide layer by both metallography and X-ray diffractometry, showing that if hydride is protected by an oxide film it is relatively stable in water.

It is concluded, therefore, on the basis of these phase studies that the 100 C water corrosion product consists of two phases, an oxygen-rich UO_2 plus unoxidized uranium particles. If a hydride phase were present, it should have been detected by the methods of examination employed.

Oxygen-to-Uranium Ratio

Uranium dioxide, prepared by hydrogen reduction of higher oxides, is frequently unstable in air, resorbing oxygen^(7,8,9). The oxygen-to-uranium ratio of oxide samples is generally determined by measuring the weight gain on ignition of the sample to U_3O_8 by heating it to 750 C for 15 min in air. This type of analysis cannot distinguish among oxygen, hydroxyl, and water. For this reason, when hydroxyl or water may be present, the valence of the uranium is not necessarily twice the oxygen-to-uranium ratio.

The apparent oxygen-to-uranium ratio of the dried 100 C or 200 C corrosion products, after air oxidation at room temperature, was 2.40. This is the maximum value obtained for active UO_2 samples prepared by different techniques and exposed to air or oxygen at room temperature⁽⁷⁾, but in the corrosion samples the ratios were probably excessively high because of air oxidation at room temperature, reabsorption of water, or retention of combined water.

Samples of the corrosion product, obtained after a 48-hr test, were transferred, without exposure to air, to a controlled-atmosphere differential thermal balance. The samples were dried overnight in vacuum (5×10^{-5} mm of mercury), weighed, heated to

constant weight at 750 C in vacuum, and then ignited in oxygen to U_3O_8 . A sample of Mallinckrodt oxide was exposed to boiling water for 48 hr and analyzed in the same manner. The latter sample lost 0.4 per cent of its weight on the heating cycle and had an oxygen-to-uranium ratio of 2.04, which shows that commercial oxide is not noticeably oxidized or hydrolyzed by boiling water in 48 hr. The corrosion-product samples lost 3.2, 1.6, and 4.2 per cent of their weight on the heating cycle. As this is an order of magnitude greater than the weight loss observed in an inert sample, it is evidently due to a loss of hydroxyl or water. These dehydrated corrosion products had oxygen-to-uranium ratios of 2.19, 2.24, and 2.19 (average, 2.21).

An experiment was conducted to determine the oxygen content in newly formed oxide from the corrosion of uranium by steam at 200 C. A thin sheet of uranium of known weight was completely converted to oxide by exposure in 200 C steam in a small reaction vessel. The vessel was packed with glass wool and was so constructed that oxide could not be carried over into the rest of the train. After the uranium was completely reacted (as indicated by no further weight change in the drying bottles), it was dried for 24 hr in flowing argon at 200 C. The reaction vessel was then removed from the train, cooled to room temperature, and weighed. Air was excluded from the reaction vessel during these operations. After weighing, the vessel was again inserted in the train and the system flushed for several hours with dried air at room temperature. Again the reaction vessel was weighed. As a final check to insure that no product escaped into the system, the oxide in the reaction vessel was ignited in oxygen to U_3O_8 . The drying bottles (J in Figure 1) were weighed after each step to account for the hydrogen evolved. The drying bottles (H in Figure 1) also were weighed after the air-oxidation and final-ignition reactions. The latter were weighed to determine whether water was a product of these reactions from the oxidation of adsorbed hydrogen or uranium hydride in the corrosion product.

The results of the above tests are presented in Table 3. Assuming that all weight increases were in the form of oxides, the oxide formed in steam at 200 C in the absence of oxygen had a composition of approximately $UO_{2.10}$, which approaches stoichiometric UO_2 . This oxide then oxidized to $UO_{2.40}$ when exposed to air. The latter composition agrees with analyses obtained earlier in the program in which no attempt was made to exclude air from the sample after its removal from the reaction chamber. Ignition analysis revealed an oxide having the composition $UO_{2.67}$ (U_3O_8), indicating that no corrosion product was lost in the experiment. The total hydrogen evolved in this experiment corresponds to a corrosion product of $UO_{2.24}$. This agrees very well with the $UO_{2.21}$ obtained on 100 C water corrosion products after dehydration in vacuum at 750 C.

Valence Analysis

The mean valence of uranium in the corrosion product was determined by the chemical method described previously on several samples from the 100 C test without exposure to air and on one sample from the 200 C test after exposure to air. In the case of the 100 C corrosion product, the mean valence of the uranium was found to be 3.70. However, when the loose corrosion product was allowed to drop into a cool zone (approximately 25 C), rather than remain in the proximity of the metal, the mean valence was found to be 3.16. A sample of corrosion product which was boiled 24 hr after the metal was removed from test had a mean valence of 3.87. These experiments indicate that oxidation continues after the "oxide" becomes detached from the metal.

TABLE 3. RESULTS OF SUCCESSIVE REACTIONS OF URANIUM WITH WATER VAPOR, AIR, AND OXYGEN

Run	Oxygen-to-Uranium Ratio As Calculated From Weight Data Obtained In The Steps Indicated					
	I. 200 C Steam Reaction		II. Room-Temperature Air Oxidation		III. 400 C Oxygen Reaction	
	Weight Gain in Reaction Vessel	Hydrogen Evolution	Weight Gain in Reaction Vessel	Hydrogen Evolution	Weight Gain in Reaction Vessel	Hydrogen Evolution
1	2.18	1.90	2.40	(a)	2.64	(a)
2	2.06	1.88	2.39	2.04 ^(b)	2.67	2.24 ^(b)

(a) Hydrogen from corrosion not measured.

(b) The additional hydrogen involved during air and oxygen oxidation indicates the possibility of some hydrides in this corrosion product. A second possibility would be incomplete corrosion of the uranium or UO_2 which might react with adsorbed water to produce hydrogen during subsequent oxidation. This experiment was not repeated.

A mean valence analysis was conducted on a 200 C steam corrosion product exposed to air (apparent oxide composition of $\text{UO}_{2.4}$). The results indicated a mean valence of 4.31 which would correspond to a uranium oxide having the composition $\text{UO}_{2.15}$. The higher valence obtained for this sample as compared with a mean valence of 3.70 for corrosion products obtained in the 100 C test may be due to oxidation on exposure to air or to a higher state oxidation of the corrosion product in 200 C steam.

In order to obtain an estimate of the uranium valence in the major component of the corrosion product, the X-ray absorption spectrum of the corrosion product was compared with that of uranium metal, UO_2 , and UO_3 . Spectrometer data were obtained over the range of X-ray wavelengths extending above and below the L_{III} absorption edge of uranium. Powders of the several samples in question were briquetted into absorption cells of about the same X-ray density. The corrosion samples were coated with water-soluble plastic before drying in an attempt to minimize air oxidation. The intensity versus wavelength over the absorption edge was analyzed mathematically for maximum, minimum, point of inflection, and band width. Results of this analysis for the four materials are given in Table 4. In all cases, except in band width, the characteristic values for the corrosion product are intermediate between those of UO_2 and UO_3 , suggesting a valence between 4 and 6 for the uranium. The nonuniform shift in the position of the maxima for UO_3 , UO_2 , and uranium is not understood. However, these results would tend to verify the oxygen-to-uranium ratio measurements and to indicate that Equation (1) should not be used to compute the amount of hydrogen that would be evolved in the corrosion of uranium in 100 C water. In particular, the oxide phase should not be considered as stoichiometric UO_2 .

TABLE 4. CHARACTERISTIC POINTS ON THE L_{III} X-RAY ABSORPTION EDGE OF URANIUM METAL, URANIUM DIOXIDE, URANIUM TRIOXIDE, AND URANIUM CORROSION PRODUCT

Sample	Maximum Absorption, A	Inflection Point, A	Minimum Absorption, A	Band Width, A
Uranium metal	0.72649	0.72253	0.71857	0.00791
UO_2	0.72679	0.72261	0.71841	0.00839
Corrosion product	0.72634	0.72232	0.71831	0.00802
UO_3	0.72631	0.72227	0.71824	0.00807

Note: The absorption-edge wavelength was calculated on the basis of a LiF analyzing crystal with a reported 2d spacing of 4.0275A.

DISCUSSION OF RESULTS AND CONCLUSIONS

The corrosion products formed when uranium reacts with 100 C water or 200 C steam at atmospheric pressure do not offer protection to the underlying metal. However, UO_2 films, produced on the metal at temperatures above 400 C in oxygen, temporarily protect the base metal against corrosion in 100 C water. Based upon ignition analyses of the water or steam corrosion products, their composition may be as high as

$\text{UO}_{2.2}$ and increase to $\text{UO}_{2.4}$ after exposure to air at room temperature. The amounts of hydrogen collected from the reaction at either 100 C or 200 C indicate that the solid corrosion products should have a composition of $\text{UO}_{1.9}$. Based upon valence studies, the corrosion product is at least two phase: (1) an oxygen-rich UO_2 -type phase with the CaF_2 type structure, and (2) a phase which has a valence of less than 4. X-ray absorption studies indicate that the bulk of the 100 C corrosion product is the oxygen-rich oxide, while X-ray diffraction analysis of separated residues shows that the low-valence material is actually metallic uranium particles incorporated in the corrosion product. The presence of uncorroded metal satisfactorily accounts for the low hydrogen assay, which was based upon Equation (1) going to completion. However, the premise that UO_2 is an end product [Equation (1)] was not verified in the present atmospheric corrosion tests, where the oxygen-to-uranium ratio approached 2.2.

Although no hydride was detected, its stability under the condition of the present tests was verified, and it is, therefore, likely that previous observations of a hydride phase in the corrosion layer were due to an increased hydrogen pressure in the reaction vessel. The corrosion rates observed in the present studies (Figure 1) at the higher temperature were lower than those reported by other investigators^(4,5,6). This may indicate that a different corrosion mechanism is operative. The major difference may be the formation of hydride, due to the hydrogen overpressure which must have been present in water corrosion tests at temperatures over 100 C⁽⁵⁾. It would be of interest to determine the hydrogen pressure required to form hydride in the presence of water or steam and its effect upon the corrosion rates.

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