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URANIUM OXIDATION: CHARACTERIZATION OF OXIDES
FORMED BY REACTION WITH WATER

E. L. Fuller, Jr.
N. R. Smyrl
J. B. Condon
M. H. Eager

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April 1983

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Oak Ridge y-12 Plant
P. O. Box Y, Oak Ridge, Tennessee 37830

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ABSTRACT

Three different uranium oxide samples have been characterized with respect to the different preparation techniques. The results show that the water reaction with uranium metal occurs cyclically forming laminar layers of oxide which spall off due to the strain at the oxide/metal interface. Single laminae are released if liquid water is present due to the prizing penetration at the reaction zone. The rate of reaction of water with uranium is directly proportional to the amount of adsorbed water on the oxide product. Rapid transport is effected through the open hydrous oxide product. Dehydration of the hydrous oxide irreversibly forms a more inert oxide which cannot be rehydrated to the degree that prevails in the original hydrous product of uranium oxidation with water.

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I. INTRODUCTION

Extensive studies and reviews of the kinetics and mechanism of uranium oxidation show that the complex process depends on a number of factors⁽¹⁾. The synergistic relationship between moisture (relative humidity), oxygen concentration, and pressure are well documented⁽²⁾. There is considerable interest at present in the details of oxide formation from both experimental and theoretical standpoints^(3,4). The global model must consider both the chemical and mass transfer processes as well as the physical state of the metal⁽⁵⁾, substrate, and the adherent, as well as the released oxide⁽⁶⁾. This study was carried out at the Oak Ridge Y-12 Plant* to evaluate the use of infrared^(7,8) and colloid and surface chemical techniques^(9,10) for characterizing uranium oxide.

II. EXPERIMENTAL

Sample Preparation

A very reactive form of uranium can be prepared by hydriding high-purity uranium metal and subsequently dehydriding to a highly dispersed form of the metal. A finely divided oxide is formed when the activated metal is exposed to water vapor (4.6 torr) at 300°K for a prolonged period (ca 2 weeks). The hydrogen formed in the process was allowed to diffuse from the reaction chamber through a palladium metal disc. The highly dispersed nature of the oxide is noted in Figure 1. There is little or no discernable

* Operated by the Union Carbide Corporation, Nuclear Division, for the U.S. Department of Energy.

Figure 1. a.

Scanning Electron Micrograph of UO_2 (C) Powder — The highly dispersed material is shown to be rather uniform when viewed at low magnification. (one millimeter full scale)

Figure 1. b.

Magnification of 1.a. — The dispersed powder of $\text{UO}_2(\text{C})$ is shown to be composed of varying degrees of agglomeration. (300 μm full scale)

Figure 1. c.

Magnification of 1.b. — Showing further the complex nature of the aggregation. (100 μm full scale)

Figure 1. d.

Magnification of 1. c. — Emphasizing the contrasting size of the aggregates and the composite units. (30 μm full scale)

Figure 1. e.

Magnification of 1. d. — Shows that the composites are formed of globular metamict, noncrystalline material. (10 μm full scale)

crystallinity noted at the magnification of these micrographs. The X-ray diffraction studies showed only very broad diffuse patterns characteristic of small crystallites and/or nearly metamict UO_2 . Figure 2 is a stereomicrograph showing that there is little or no restricted porosity that would lead to hysteretic retention of condensed phases. The globules of oxide appear to be loosely adhering to each other forming interparticulate porosity. Pendular condensation will flex the agglomerates and lead to hysteretic retention.

In contrast, UO_2 can be formed, albeit much more slowly, by reaction of water vapor with a freshly milled bar of high purity uranium metal. This reaction proceeds with impeded diffusion of H_2O into and H_2 out from the metal through the adherent oxide layer. This process continues until the strain becomes great enough that the product oxide spalls off and away from the metal substrate. This cyclical process continues as the diffusion barrier periodically increases and spalls away. A record of the cycles of this process is noted in the laminar nature of the oxide as recorded in the micrographs of Figure 3 and Figure 4. These figures graphically show the periodic laminae where twenty to several hundred are formed before the spalling process occurs. The laminae are probably filled with hydrating (adsorbed) water initially.

Figure 2.

Stereophotomicrograph of $\text{UO}_2(\text{C})$ showing that agglomerates form a randomly undulating surface and there exists internal volume enclosed by loosely agglomerated metamict entities. (30 μm full scale)

Figure 3. a.

Scanning Electron Photomicrographs of $\text{UO}_2(\text{A})$ showing the shards that spalled away from the metal/oxide interface. (500 μm full scale)

Figure 3. b.

Magnification of 3. a. — Emphasizes the wide variety of sizes both perpendicular and parallel to the planes of laminae formed by the cyclical oxidation process. (250 μm full scale)

Figure 3. c.

Magnification of 3. b. — shows how the material is comprised of relatively flat laminae sequentially formed by the oxidation process. (50 μ m full scale)

Figure 3. d.

Magnification of 3. c. — Shows a minor component of fine material adhering to the shards. (20 μm full scale)

Figure 3. e.

Magnification of 3. d. — Where the laminae are noted to be rather open with rather large holes in the plane of the laminae. (11 μm full scale)

Figure 3. f.

Magnification of 3. e. — Further shows that the solid portion of the laminae are composed of grains of oxide. (7 μm full scale)

Figure 4. a.

Scanning Electron Micrograph of UO_2 (A) — Showing the wide range of sized and shapes of the laminar shards that spalled from the oxide/metal interface during the course of the reaction. (500 μm full scale)

Figure 4. b.

Magnification of 4. a. — the laminar structure due to the cyclical reaction of the water vapor is evident. Thick multilaminar material spalls away from the metal substrate.

Figure 4. c.

Magnification of 4. b. — To reveal more of the fine structure of the laminae and the curling associated with the termination of the laminae.
(50 μm full scale)

Figure 4. d.

Magnification of 4. c. — Shows that the curls are comprised of fine meta-
Oict material with no crystallinity evident. (20 μm full scale)

Figure 4. e.

Magnification of 4. d. — Indicates that there has been subnucleation at virtually every exposed laminae. (11 μm full scale)

Figure 4. f.

Magnification of 4. e. — Shows the metamict, globular, noncrystalline nature of the secondary deposits. (7 μm full scale)

The same cyclical process is noted when the high purity uranium metal is allowed to react with liquid water. A much faster reaction rate is noted and the spalling process is accelerated by the generation of bubbles of hydrogen and by the prizing action of the liquid water which tends to relieve the strain earlier and generate thinner laminar shards as recorded in Figure 5. These are the shards that were deposited in the bottom of the cell by gravity flow through the liquid water phase. It is quite evident that the shards are only made up of a few, 1 to 3, laminae and that there are undulations of the surfaces due to either deposition of additional UO_2 or to interlaminar distortion in the laminar plane prior to or during the exfoliation process. In contrast, finer, smoother, flatter, and more angular fragments are carried to the surface of the liquid water by a "froth flotation" process of adhesion to the hydrogen bubbles that are generated in the oxidation reaction. The details of the separated (floated) portion, which comprises a minor fraction of the oxide product, are shown in Figure 6.

The purpose of this study is to characterize these oxide preparations in terms of colloid and surface chemistry with two major goals. One is to understand the mechanism of oxidation in order to prevent and/or control the process as the situation may demand. The other is to generally tailor the oxide as a useful sorbent and/or catalyst. For convenience,

Figure 5. a.

Scanning Electron Photomicrograph of $\text{UO}_2(\text{B})$ — This powdered material spalled from the oxide/metal interface and fell through the liquid water reaction medium. (300 μm full scale)

Figure 5. b.

Magnification of 5. a. — Showing the wide range of sizes and shapes.

(100 μm full scale)

Figure 5. c.

Magnification of 5. b. — Shows this material to be shards of one to three laminae thick. (30 μm full scale)

Figure 5. d.

Magnification of 5. c. — Showing that the laminae surfaces appear crenelated and that since they are composed of even finer laminae and amorphous entities. (10 μm full scale)

Figure 6. a.

Scanning Electron Micrographs of $\text{UO}_2(\text{B})$ — Which had been entrained by the evolved hydrogen and swept to the top of the liquid water reaction medium. (300 μm full scale)

Figure 6. b.

Magnification of 6. a. — Partial agglomeration of the floated fines is noted. (100 μm full scale)

Figure 6. c.

Magnification of 6. b. — Shows the variety of flat angular fragments that form the agglomerate. (30 μm full scale)

Figure 6. d.

Magnification of 6. c. — Shows that these are quite smooth, small, flat, and distinct shards of one to three laminae. (10 μm full scale)

these three samples are denoted (A), (B), and (C) for the products of direct reaction with water vapor with metallic uranium formed by dehydriding of uranium hydride, respectively.

B. Nitrogen Sorption

Nitrogen sorption analyses were used to study the surface chemistry and morphology of these materials using proven techniques and theories⁽¹⁰⁻¹³⁾. This approach is chosen in deference to many of the current electronic techniques that cannot be readily used nondestructively on finely divided insulator substrates such as we have here. The techniques of sorption analysis are quite well developed and, with due caution to avoid erroneous assumptions and theoretical interpretations, can be used to evaluate details related to surface chemistry morphology, porosity, etc., that are virtually impossible to obtain by any other means.

C. Infrared Analyses

Diffuse reflectance infrared spectroscopy of surfaces has become a very informative method for direct observation of infrared active sorbates and sorbents^(8,11-13). The techniques and theoretical considerations have been given previously⁽¹⁴⁾. Here we can observe the spectral information inherent in diffusely reflected light while minimizing the specularly reflected component⁽¹⁵⁾. The system works

well for qualitative chemical speciation and in many cases quantitative analyses over a wide range of temperature (300°K to 800°K) and pressure (10^{-5} torr to 10^3 torr)^(14,16).

A schematic drawing of the Diffuse Reflectance Infrared Fourier Transform (DRIFT) cell is given in Figure 7.

III. RESULTS

Nitrogen Sorption

The nitrogen sorption isotherms for sample $\text{UO}_2(\text{B})$ are given in Figure 8. They are generally of the classical sigmoidal shape that is characteristic of physical sorption on a heterogeneous surface. The high pressure uptake is marked due to multilayer formation and capillary condensation in pores. The hysteresis, which is abruptly absent below $\text{ca } 0.5P_0$, is very characteristic of slit-shaped pores^(17,18) and is consistent with the periodic laminae of Figures 3 through 6. Furthermore, the very high pressure data conclusively shows that the sintering process wrought by the 16-18 hours in vacuo at 600°C did little to alter the total sorption capacity even though the "monolayer" capacity (generally assumed to be the amount sorbed at the knee, ca $0.05 P_0$ to $0.1 P_0$) showed a threefold decrease. Such an analyses is a quantitative measure of the unique sintering process where there is a conservation of sorption volume (Gurvich volume in some texts)⁽¹⁹⁾ during the sintering process which also closes the slits that are responsible for the abrupt hysteresis at ca $0.5P_0$. The ΔT curves were derived by interpolation of the adsorption

Figure 7.

Diffuse Reflectance Cell for Infrared Reflectance Measurements. The optical path is incident and exits from the sample stage at ca 50° avoiding specular reflection components. The environmental gases are controlled and monitored, and accurate temperature control and measurements are maintained.

Figure 8.

Nitrogen Sorption on $\text{UO}_2(\text{B})$ at 77°K. Heating in excess of 500°C decreases the amount of surface by closing interlaminar spaces and leaving the total sorption space unaltered.

and desorption branches and, subsequently, evaluation of the difference at precisely fixed internals of P/P_0 . The resultant hysteresis curve for the 600° C outgassed sample is a smooth continual function emanating from the characteristic 0.5 P_0 . This use of the ΔI curves is equally informative in evaluating the nature of the porosity of $UO_2(C)$ as shown in Figure 9. Here the flexing structure model is quite valid where limited flexure is allowed to the degree dictated by the limit of 0.8 P_0 for the vapor pressure of the imbibed liquid nitrogen. Sintering at 600° C in vacuo is accompanied by interparticulate adhesion to form a rigid array that does not flex to allow liquid penetration. This sintering also decreases the maximum uptake by decreasing the total volume. It is worthy of note that the 500°C sintering actually leads to an increase in the total volume at the higher pressures, again showing the "volume conservation" phenomena with more sorption above ca 0.98 P_0 and less sorption below 0.98 P_0 . One must conclude that there is a trade off with the loss of surface being compensated by a corresponding increase in interparticulate and for intraparticulate volume.

The computer-controlled sorption system routinely calculates classical BET surface area, adjustable parameter (C), and other parameters related to the calculated porosity of the samples based on oversimplified models. For instance, the pores are all considered to be cylindrical and the thickness

Figure 9.

Nitrogen Sorption on $\text{UO}_2(\text{C})$ at 77°K. Sintering to 500°C leads to surface area loss by interparticulate sintering with a constant total volume; 600°C in vacuum leads to material transport and markedly decreases the porosity.

of sorbed multilayers (t) is taken to be a somewhat unrealistic "statistical average approximation" even in the realm of only a few such layers⁽¹¹⁾. These techniques have become so common that one is virtually forced to calculate these parameters to compare them to the works of others. Calculated results are listed in Table I, which also includes some of the results of the applications of the potential theory of sorption where the dimensionless sorption potential is given by:

$$\frac{\epsilon}{RT} = -\ln(P/P_o) \quad (1)$$

and, as Polanyi pointed out⁽²⁰⁾, there exists a functionality between the amount adsorbed, Γ , and the sorption potential:

$$\Gamma = f(\epsilon) \quad (2)$$

It remains for the investigator to deduce the nature of this functionality. The following form was chosen:

$$\frac{\epsilon}{RT} = \frac{\epsilon_o}{RT} \text{EXP}(-\alpha\Gamma) \quad (3)$$

This can be cast into a rectilinear form with respect to Γ :

$$\ln\left(\frac{\epsilon}{RT}\right) = \ln\left(\frac{\epsilon_o}{RT}\right) - \alpha\Gamma \quad (4)$$

and defines the data quite well, as noted in Figure 10. The relevant parameters, Σ^* and ϵ_o are given in Table I.

B. Infrared Analyses

Figure 11, shows the spectra obtained when $\text{UO}_2(\text{C})$ was placed in DRIFT.

TABLE I. CALCULATED SURFACE AREA AND POROSITY.

	<u>M</u>	<u>$\Sigma(\text{BET})$</u>	<u>C(BET)</u>	<u>V(A)</u>	<u>$\Sigma(\text{C,A})$</u>	<u>V(D)</u>	<u>$\Sigma(\text{C,D})$</u>
<u>°C</u>	<u>gm</u>	<u>m²/g</u>	<u>—</u>	<u>$\mu\text{L/g}$</u>	<u>m²/g</u>	<u>$\mu\text{L/g}$</u>	<u>m²/g</u>
<u>UO₂(B)</u>							
65	10.2900	6.334	161	11.4	5.80	13.1	6.50
120	10.3210	6.509	169	11.5	5.91	13.4	6.56
200	10.3443	6.513	184	11.1	5.76	13.0	6.32
335	10.3283	5.888	158	10.6	5.31	12.1	6.01
500	10.3263	5.5176	143	10.9	5.28	12.8	5.90
600	11.1311	2.027	93	7.4	2.26	10.2	2.58
<u>UO₂(C)</u>							
65	7.7330	10.704	138	35.8	13.29	44.1	15.14
120	7.7129	10.971	123	36.2	13.68	45.1	15.46
200	7.6889	11.196	115	36.1	13.92	45.0	15.63
335	7.6751	10.971	107	35.9	13.69	45.5	15.54
500	7.6751	8.7608	106	30.6	10.60	40.5	12.09
600	7.7086	3.040	108	8.0	3.21	12.2	3.37

Figure 10.

Rectilinear Presentation of Nitrogen Sorption on UO_2 (B) and UO_2 (C) at 77°K. All data seems to fit the linear relation indicating that the mode of preparation and subsequent heating produces material with little or no microporosity ($1 < 2.0 \mu\text{m}$).

DRIFT SPECTRA: URANIUM OXIDE (C)

Figure 11.

Diffuse Reflectance Spectra for Dehydration of UO_2 (C). Cursory observation shows a loss of hydrogen-bonded OH species, some molecular water, and three bands associated with the UO_2 substrate.

spectra cell and subsequently subjected to the time, pressure and temperature conditions given in Table II. For clarity some of the spectra are not shown graphically although they are incorporated in the numerical analyses described henceforth. It is quite evident that the sorbed hydrogen bonded hydroxyl entities are removed and that some of this bound species exists as molecular water characterized by the bending mode at ca 1600 cm^{-1} . Three persistent bands exist which are currently attributed to the UO_2 substrate. One of these bands overlaps the HOH bend mode and somewhat complicates quantitative analyses. Figure 12 is an expanded view to further show the details of the overlap and the tenacious retention of hydrating species with respect to prolonged vacuum and sample temperature. The "negative" features at 2300 to 2400 cm^{-1} and those above 3600 cm^{-1} and at $1600 \pm 200\text{ cm}^{-1}$ are due to over compensation for residual water vapor and carbon dioxide which exist in the dry argon purge. Prolonged purge and evacuation of the light path within the cell cause this effect which is not due to the sample.

Figure 13 shows the results of exposure to highly deuterated water (ca 95% D_2O). The general features are those of surface rehydration (sorption of water) on the oxide surface with bond assignments as noted. Intensity analyses can be carried out as noted by the shaded areas of Figure 14 for semiquantitative work. A second evacuation removes the sorbed water entities as shown in Figure 15, and some additional retention of hydrogen-bonded species is noted.

TABLE II. DIFFUSE REFLECTANCE SPECTRA SEQUENCEY $\text{UO}_2(\text{C})$

<u>Sequence</u>	<u>Vapor Phase</u>	<u>P</u> <u>Torr</u>	<u>T</u> <u>°C</u>	<u>t</u>	<u>Date</u>
1	Air	730	28	9:35 a.m.	May 21
2	Air	99.6	28	9:50 a.m.	May 21
3	Air	29.9	28	10:00 a.m.	May 21
4	Air	11.0	28	10:10 a.m.	May 21
5	Air	3.4	28	10:23 a.m.	May 21
6	Air	1.2	28	10:33 a.m.	May 21
7	Air	0.40	28	10:42 a.m.	May 21
8	Air	0.15	28	10:54 a.m.	May 21
9	Air	0.011	28	11:03 a.m.	May 21
10	Air	0.006	28	11:15 a.m.	May 21
11	Vacuum	2×10^{-6}	28	1:05 p.m.	May 21
12	Vacuum	4×10^{-6}	80	1:22 p.m.	May 21
13	Vacuum	4×10^{-7}	80	9:45 a.m.	May 22
14	Vacuum	3×10^{-7}	29	10:47 a.m.	May 22
15	D_2O	8×10^{-3}	29	10:55 a.m.	May 22
16	D_2O	0.188	28	11:08 a.m.	May 22
17	D_2O	0.456	28	11:21 a.m.	May 22
18	D_2O	0.777	27	11:41 a.m.	May 22
19	D_2O	2.401	27	11:59 a.m.	May 22
20	D_2O	4.777	27	12:13 p.m.	May 22
21	D_2O	10.493	27	12:28 p.m.	May 22
22	D_2O	7.335	25	8:15 a.m.	May 26

<u>Sequence</u>	<u>Vapor Phase</u>	<u>P</u> <u>Torr</u>	<u>T</u> <u>°C</u>	<u>t</u>	<u>Date</u>
23	D ₂ O	11.826	26	9:15 a.m.	May 26
24	D ₂ O	18.14	27	10:30 a.m.	May 26
25	D ₂ O	19.61	27	1:00 p.m.	May 26
26	D ₂ O	2.870	27	3.42 p.m.	May 26
27	D ₂ O	0.050	27	5:06 p.m.	May 26
28	D ₂ O	1.5×10^{-3}	27	6:20 p.m.	May 26
29	Vacuum	8.0×10^{-7}	25	8:10 a.m.	May 27
30	Vacuum	7×10^{-7}	26	9:14 a.m.	May 27

DRIFT SPECTRA URANIUM OXIDE (C) TEMPERATURE EFFECTS

Figure 12.

Diffuse Reflectance Spectra of UO_2 (C) in vacuum. There is overlap for the HOH band and the UO_2 band. Some OH is retained in vacuum and some thermal lability is evident. Subsequent cooling shows that the thermal effect involves volatile loss.

DRIFT SPECTRA: URANIUM OXIDE (C)

Figure 13.

Diffuse Reflectance Spectra for Rehydration of UO_2 (C). Band assignments are relatively straight forward and the vapor phase OD is detected at higher pressure in the head space above the sample.

DRIFT SPECTRA: URANIUM OXIDE (C)

Figure 14.

Diffuse Reflectance Spectra for Second Dehydration of UO₂ (C). Band assignments are given and some hydrocarbon is removed incompletely in vacuum.

DRIFT SPECTRA D_2O SORPTION BY UO_2 (C)

Figure 15.

Intensity Evaluation for Diffuse Reflectance Spectra of UO_2 (C). Three general features preclude accurate evaluation: (1) the general background curve is ill-defined, (2) the periodic undulations are a problem, and (3) there is considerable overlap of HOH bands and substrate bands.

More detail and quantitative information can be obtained if all of the data are normalized to one curve and changes with respect to this state, are evaluated. In this way, the intensity changes of chemical interest free of the distracting background effects due to invariant physical phenomena (Rayleigh scattering, refractive index variation, instruments artifacts, etc.) and fixed substrate composition (UO_2 , bulk impurities, etc.) as shown in Figure 16. This operation of actually subtracting the data (point-by-point, 3200 times) is possible only with the aid of a digital computer data management system. This is a direct (unity or 1:1) subtraction since it is the same sample, free from spurious effects that accompany separate samples and/or matrix, and supporting media which often require multiplicative weighing of the reference spectrum to compensate for the curved background, undulating background, and invariant (UO_2) absorption bands. The net result is the same as if spectrum number 25 were referenced to spectrum number 14 directly instead of recording each with respect to a third reference (powdered KBr or a mirror in this case). The relevant features of the sorbed entities is much more apparent, and subtle effects such as the D_2O retention are obvious as shown in Figure 17. The band and frequency assignments are less ambiguous as noted in Figure 18. Furthermore, the intensity analyses are much simpler with much less question as to line breadths and

DRIFT COMPARISON SPECTRA: D₂O ON UO₂ (C)

Figure 16.

Comparative techniques for Diffuse Reflectance Spectra of UO₂(C).
Point-by-point numerical subtraction showing the changes wrought
in rehydration (25) of the vacuum state (14) of UO₂(C).

DRIFT SPECTRA: D₂O RETENTION ON UO₂ (C)

Figure 17.

Spectra Comparison to Show Irreversible Retention of Deuterated Water on UO₂(C). Numerical evaluation of spectral differences showing the additional amount of irreversible retention of deuterated water after rehydration of UO₂(C).

DRIFT COMPARISON SPECTRA: D₂O ON UO₂(C)

Figure 18.

Band Assignments for Diffuse Reflectance Spectra for Sorption of D₂O on UO₂(C). The speciation is much simpler when the comparative spectra are employed.

background curves as shown graphically in Figure 19. Again, the data management system is invaluable in numerically evaluating the integrated areas for each of the regions noted in Figure 19 and listed in Table 3.

In retrospect, the results comparing the initial evacuation to the vacuum state are informative as shown in Figure 20. Conclusions from these results are:

1. An additional transient feature at ca 2490 cm^{-1} is prominent only at intermediate pressures. This is not due to a carbonate species since no exposure to air was allowed. The oxide was formed in H_2O vapor and transferred to the sealed cell in an argon glove box specifically to avoid exposure to CO_2 or O_2 .
2. An intriguing effect is noted involving the " UO_2 " bonds that overlap the HOH bond. This DRIFT technique can observe these transient metastable states which actually show that the amount of this " UO_2 " decreased through a minimum and then increased to the vacuum concentration measure by the reference spectrum (#14).
3. This method of analyses also conclusively shows that there is a loss of absorbance between 800 and 1100 cm^{-1} that has the suspiciously characteristic shape of an infrared-active vibrational mode and that the

DRIFT INTEGRATION: D₂O ON UO₂ (C)

Figure 19.

Integration Limits for Integrated Intensity Analyses for D₂O Sorbed on UO₂(C). Band integration is now easier and more reliable with the use of the comparative spectra; even the choice of integration limits are less ambiguous. The data management computer is used to perform the integration numerically.

TABLE #3. Integrated Infrared Band Intensities for Uranium Oxide (C).
All numerical values quoted in units of cm^{-1} .

	A	B	C	D	E	F	G
Maximum	3700	3000	2800	2770	1810	1510	1300
Minimum	<u>2700</u>	<u>2800</u>	<u>2770</u>	<u>1810</u>	<u>1510</u>	<u>1300</u>	<u>1100</u>
1	152.3			0.0	(9.6)*		
2	149.3			0.0	(11.4)		
3	143.1			0.0	(11.6)		
4	135.9			0.0	(11.3)		
5	113.6			0.0	(10.2)		
6	102.2			0.0	(9.0)		
7	81.9			0.0	(7.5)		
8	56.6			0.0	(5.7)		
9	35.0			0.0	(3.9)		
10	19.6			0.0	(2.8)		
11	4.3			0.0	(1.3)		
12	7.6			0.0	(1.5)		
13	2.8			0.0	(4.4)		
14	<<< Reference State Spectrum >>>						
15	7.42	0.2	0.0	0.9	-0.1	0.3	0.0
16	8.6	0.2	0.0	1.6	0.9	1.0	0.0
17	10.6	0.3	0.0	2.7	1.7	1.7	0.0
18	11.7	0.2	0.0	4.4	1.7	1.7	0.0
19	12.0	0.3	0.0	9.5	2.1	2.1	0.1
20	14.0	0.2	0.0	13.2	2.4	2.7	0.9
21	16.3	0.5	0.0	20.7	2.7	3.6	1.4
22	31.4	0.6	0.0	43.2	4.3	6.3	2.3
23	29.3	0.7	0.0	49.6	4.3	6.3	2.7
24	28.6	1.4	0.8	52.0	4.1	6.9	4.0
25	24.2	1.2	0.11	59.2	4.0	6.3	4.6
26	19.4	1.4	0.07	61.4	4.7	6.0	4.7
27	21.5	0.9	0.05	59.5	4.6	5.8	4.3
28	21.5	0.8	0.01	55.4	3.9	5.1	3.9
29	-0.9	0.5	-0.02	12.4	-0.0	0.6	0.7
30	-1.7	0.3	0.02	9.4	-1.3	0.7	0.0

* Parenthetic values questionable due to spurious effects.

DRIFT SPECTRA: ATMOSPHERIC SPECIES SORBED ON $\text{UO}_2(\text{C})$

Figure 20.

Comparative Diffuse Reflectance Spectra for Initial Dehydration of $\text{UO}_2(\text{C})$. These results reveal several features not discernable in the original spectra. Even the "negative" absorption is informative in evaluating the restructuring of the substrate on dehydration.

population of the composite entities were greatly decreased. Such a conclusion can be deduced from Figure 11; but, with much less confidence, the lack of increased absorbance on rehydration (Figure 19) is due to either an isotope shift or to the fact that the initial drying of the oxide actually proceeds through a metastable intermediate and that the process is irreversible because this state is not regenerated by rehydration. The latter conclusion is bolstered by the lack of the additional deuterated counterpart of (1) in Figure 19.

IV. DISCUSSION

A. Reaction of Uranium with Water

Previous works^(21,22) have shown the temperature variation of the reaction rate to follow Arrhenius behavior as noted in Figure 21. Linear relations are common and the slopes of the lines vary somewhat depending on the techniques employed and the purity of the metal being oxidized. The simplest experiments are performed at the equilibrium vapor pressure of water (generally ranging from 10 to 100 torr) as reported in Figure 21. The pressure effects are evaluated at constant temperatures to further aid in elucidating the kinetics and mechanisms, and results such as those given in

Figure 21.

Temperature Effects for the Reaction of Water with Uranium Metal.

Classical Arrhenius Behavior is Noted in the Linearity. Different slopes arise for various techniques and uranium purity.

Figure 22 are usually noted⁽²³⁾. The results are not as straightforward as one might like. Two general trends are shown. The low pressure trend, possibly giving way discontinuously to a general linear trend, might be inferred from Figure 22. Alternatively, a general sigmoidal behavior seems to fit the data also as one might suspect if the rate controlling step involves sorbed water. In such a case Equation (4) should be applicable and indeed a rather good rectilinear relation does exist as shown in Figure 23. A general linear adherence is noted for a wide range of rates and relative humidity. Furthermore, the general trend is limited and a much lower rate enhancement factor is noted at $P > 0.8 P_0$.

As seen earlier, the potential theory notes a linear relationship between sorbed concentration $\Gamma(H_2O)$ and $\ln (E/RT)$ as defined by equation (4). There is a general relation between $\Gamma(H_2O)$ and discrete layer, $\Gamma(m, H_2O)$, coverages for nonporous surfaces such that:

$$\Gamma (C, H_2O) = 1.50 \quad \Gamma(m, H_2O) \quad (5)$$

when

$$\epsilon = RT \quad (6)$$

and

$$\ln (\epsilon/RT) = 0 \quad (7)$$

thus, the magnitude of the coverage as shown in the right

Figure 22.

Pressure Effects for the Rate of Reaction of Water with Uranium Metal.

There is considerable question related to whether a linear and/or sigmoidal behavior prevails.

ordinate of Figure 23. The results would lead us to conclude that the reaction rate is linearly dependent upon the sorbed concentration up to three (3) discrete layers where a much (ca 3 fold) lesser enhancement factor is noted:

$$\frac{d(UO_2)}{dt} = k_1 \theta(H_2O) \quad \text{for } \theta(H_2O) < 3.0 \quad (8)$$

$$= k_2 \theta(H_2O) \quad \text{for } \theta(H_2O) > 3.0 \quad (9)$$

This model is quite plausible if the rate will increase when the reservoir of bound (sorbed) water is increased. The additional water above $\theta(H_2O) = 3$ is physically separated from the substrate and can only make a lesser contribution through the intervening layers.

The preceding discussion allows us to evaluate ϵ_o to be ca - 4480 cal/mole, based on the intercept of Figure 23. One can note 115°C data is not generally following this trend and a value of $\epsilon = -6680$ cal/mole seems to be more favored as shown in Figure 24. These values to correlate well with the E_o values measured for nonporous lunar regolith⁽²⁴⁾, (-7600 cal/mole) and nonporous coal⁽²⁵⁾, (-4600 cal/mole).

B. Interaction of Water with Uranium Oxide

The complex irreversible changes wrought in the initial

Figure 23.

The Rate of Reaction of Water with Uranium Metal Related to the Sorbed Concentration of Water on the Oxide. The majority of the data indicates a rectilinear logarithmic relation which undoubtedly prevails for the H₂O sorbent concentration at the oxide/metal interface.

Figure 24.

Water Reaction Rates at low Pressures. The rectilinear logarithmic relation defines the data quite well over the range of the reported data.

dehydration of the oxide formed by the reaction of uranium is shown in Figure 25. Two distinct rectilinear trends are noted for the initial exposure to incrementally decreased pressure. The irreversibility is also seen in the decreased sorption capacity when rehydration is instigated. These data are given in table 3; the interpretation assumes, with a high degree of probability, that equal extinction coefficients exist for hydrogen bonded O-H and O-D. Also, a 4-day exposure is more than adequate to account for any isotopic kinetic differences. The amount of molecular water present is monitored, as shown in Figure 26, and we see that there is appreciable, if not complete, exchange for the initial stages of the rehydration process and the concentration of D-O-D does not appear until higher levels of exposure. Thus, we note that the first coverage process is dissociative, and that molecular water (D_2O) is then subsequently bound to the hydroxyl entities. This same phenomenon is noted when the data are replotted in Figure 27 with total O-H and O-D represented on the ordinate and the total molecular species represented on the abscissa. Thus, we see the initial adsorption to be virtually completely dissociative.

The entire process is much akin to the well-documented case of the stoichiometric dehydration of the surfaces of thorium oxide⁽²⁶⁻²⁸⁾:

DRIFT INTENSITY: INITIAL DRYING OF $\text{UO}_2(\text{C})$ AND READSORPTION

Figure 25.

Diffuse Reflectance Intensity Related to Sorption Potential. The intensities associated with the OH stretch (OH and OD for 16 through 23) are proportional to the surface concentration and vary in a rectilinear logarithmic manner.

Figure 26.

Relative Amounts of Molecular Water as Measured by Infrared Diffuse Reflectance. The integrated intensities associated with bending mode of the molecularly adsorbed entities are quite well defined by the rectilinear logarithmic relation to the chemical potential for sorption.

Figure 27.

Infrared Diffuse Reflectance Spectral Intensities Showing Dissociative Adsorption of Water on $\text{UO}_2(\text{C})$. The initial increase in the ordinate with only a small change in the abscissa is a direct result of the dissociative sorption of water as noted by increase in OH with not much HOH.

Each of these steps can be reversed (i.e. rehydration of the surface) under distinct realms of temperature and pressure. By analogy, the uranium oxide surface is hydrated by a very similar reaction involving three sequential steps: (1) the bare oxide surface is hydroxylated by a dissociative process;

This process is followed by (2) bridging hydration of these surface hydroxyls;

forming the surface analog of a bulk entity (i.e. $\text{NaOH} \cdot \frac{1}{2}\text{H}_2\text{O}$). The data all seem to indicate that there is another step, that is, (3) addition of the stoichiometric additional water to each site;

on each site to form the surface analog of hydrated base (i.e. $\text{NaOH} \cdot \text{H}_2\text{O}$). The overall stoichiometric balance additoin effect etc., is then noted involves one site (adjacent-bridged metal ions)

which conforms very well to the three monolayers (3θ) that contribute to the rate of oxide formation initially seen (see Figure 23 and section IV. A.).

C. Kinetic and Mechanistic Models

This study of the morphology and reactivity of uranium oxides is useful in evaluating the models of the oxidation process per se⁽²⁹⁾. The results of this work lends strong credence to the perfusive — precipitation model⁽³⁰⁾ for the reaction of water with uranium metal as represented by the overall reaction:

The mechanistic evaluation involves understanding the individual steps of Reaction (15) on a molecular scale. Our results favor a model that involves very rapid adsorption of water onto the oxide which is adherent to the metal substrate:

The amount of water present is thermodynamically controlled by the relation of Equation (4), and surface transport is very rapid⁽³⁰⁾ over the entire oxide surface even up to oxide/metal interface. The rate of the overall reaction is then controlled at this interface by a direct proportionality to the surface concentration adsorbed water:

The metal/water intermediate state (activated complex) then reacts to form a semioxide (or pseudohydroxide):

This species further reacts with the replenished sorbed water:

and the stepwise release of hydrogen continues to form a metastable analog of uranyl hydroxide:

with subsequent reaction to form the stable oxidation state (+4),

In each case the active hydrogen ($\text{H}\cdot$) eventually associates to form the evolved H_2 gas. However, there is good evidence⁽³¹⁾ that some of this active form actually diffuses into the metal and aids in the further reaction (possibly by a mechanism akin to the hydrogen embrittlement process so common in a wide range of metals). There is also quite a body of data⁽³²⁾ showing that even minor traces of gaseous oxygen markedly impede the water reaction rate by scavenging the active hydrogen:

Thus, we see that the "oxygen inhibition" is actually a diminution of the "hydrogen enhancement" in this context. An actual

inhibition probably exists since the UO_2 formed by reaction of oxygen is not hydrated and is rather impervious to further vapor transport to the metal/oxide interface.

Our results favor the model in which the initially formed oxide is in a somewhat active hydrated state akin to the product shown in Equation (21) and that a vacuum drying process irreversibly dehydrates this material to a more common oxide as represented stoichiometrically by:

Once this dehydration is effected, the oxide does not possess the high permeability⁽³⁰⁾ that it had when it was originally formed by water oxidation (and simultaneous hydration). This result shows why stoichiometry can often be found for stable hydroxides that are formed by hydration reactions based on water evolution from the fresh products (subsequent hydration of activide oxides to stoichiometric hydroxides is difficult if not impossible). This material is difficult to distinguish from solids composed of finely dispersed oxides⁽³³⁾.

The merits of the diffuse reflectance infrared techniques are obvious. Few other techniques are capable of providing the combined features of:

1. Nondestructive Observation — the small thermal effects of the beam impinging upon the sample are not great enough to alter the sample appreciably.
2. Chemical Specificity — chemical entities can be observed

based on classical infrared selection rules. The use of several bands (i.e. HOH bend and OH stretch delineates molecular water from other hydroxyl entities.

3. Isotopic Exchange — the marked infrared isotopic shift associated with hydrogen isotopes allows good delineation and band assignments. Kinetics and magnitude of exchange reactions are discernable.
4. Direct Observation — the sample is free of the encumbrances, chemical interactions, and physical barriers used for classical infrared transmission analyses. This allows insight observation of the effects of changing the sample environment over a wide range of temperatures and pressures.
5. Alternate Data Analyses — using a single sample, several options are available which are readily implemented with a good computer-based data management system.

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Figure 1. a.

Scanning Electron Micrograph of $\text{UO}_2(\text{C})$ Powder — The highly dispersed material is shown to be rather uniform when viewed at low magnification. (one millimeter full scale)

Figure 1. b.

Magnification of 1.a. — The dispersed powder of $\text{UO}_2(\text{C})$ is shown to be composed of varying degrees of agglomeration. (300 μm full scale)

Figure 1. c.

Magnification of 1.b. — Showing further the complex nature of the aggregation. (100 μm full scale)

Figure 1. d.

Magnification of 1. c. — Emphasizing the contrasting size of the aggregates and the composite units. (30 μm full scale)

Figure 1. e.

Magnification of 1. d. — Shows that the composites are formed of globular metamict, noncrystalline material. (10 μm full scale)

Figure 2.

Stereophotomicrograph of $\text{UO}_2(\text{C})$ showing that agglomerates form a randomly undulating surface and there exists internal volume enclosed by loosely agglomerated metamict entities. (30 μm full scale)

Figure 3. a.

Scanning Electron Photomicrographs of $\text{UO}_2(\text{A})$ showing the shards that spalled away from the metal/oxide interface. (500 μm full scale)

Figure 3. b.

Magnification of 3. a. — Emphasizes the wide variety of sizes both perpendicular and parallel to the planes of laminae formed by the cyclical oxidation process. (250 μm full scale)

Figure 3. c.

Magnification of 3. b. — shows how the material is comprised of relatively flat laminae sequentially formed by the oxidation process. (50 μ m full scale)

Figure 3. d.

Magnification of 3. c. — Shows a minor component of fine material adhering to the shards. (20 μ m full scale)

Figure 3. e.

Magnification of 3. d. — Where the laminae are noted to be rather open with rather large holes in the plane of the laminae. (11 μ m full scale)

Figure 3. f.

Magnification of 3. e. — Further shows that the solid portion of the laminae are composed of grains of oxide. (7 μ m full scale)

Figure 4. a.

Scanning Electron Micrograph of UO_2 (A) — Showing the wide range of sized and shapes of the laminar shards that spalled from the oxide/metal interface during the course of the reaction. (500 μ m full (scale)

Figure 4. b.

Magnification of 4. a. — the laminar structure due to the cyclical reaction of the water vapor is evident. Thick multilaminar material spalls away from the metal substrate.

Figure 4. c.

Magnification of 4. b. — To reveal more of the fine structure of the laminae and the curling associated with the termination of the laminae. (50 μ m full scale)

Figure 4. d.

Magnification of 4. c. — Shows that the curls are comprised of fine metamict material with no crystallinity evident. (20 μ m full scale)

Figure 4. e.

Magnification of 4. d. — Indicates that there has been subnucleation at virtually every exposed laminae. (11 μm full scale)

Figure 4. f.

Magnification of 4. e. — Shows the metamict, globular, noncrystalline nature of the secondary deposits. (7 μm full scale)

Figure 5. a.

Scanning Electron Photomicrograph of $\text{UO}_2(\text{B})$ — This powdered material spalled from the oxide/metal interface and fell through the liquid water reaction medium. (300 μm full scale)

Figure 5. b.

Magnification of 5. a. — Showing the wide range of sizes and shapes. (100 μm full scale)

Figure 5. c.

Magnification of 5. b. — Shows this material to be shards of one to three laminae thick. (30 μm full scale)

Figure 5. d.

Magnification of 5. c. — Showing that the laminae surfaces appear crenelated and that since they are composed of even finer laminae and amorphous entities. (10 μm full scale)

Figure 6. a.

Scanning Electron Micrographs of $\text{UO}_2(\text{B})$ — Which had been entrained by the evolved hydrogen and swept to the top of the liquid water reaction medium. (300 μm full scale)

Figure 6. b.

Magnification of 6. a. — Partial agglomeration of the floated fines is noted. (100 μm full scale)

Figure 6. c.

Magnification of 6. b. — Shows the variety of flat angular fragments that form the agglomerate. (30 μm full scale)

Figure 6. d.

Magnification of 6. c. — Shows that these are quite smooth, small, flat, and distinct shards of one to three laminae. (10 μm full scale)

Figure 7.

Diffuse Reflectance Cell for Infrared Reflectance Measurements. The optical path is incident and exits from the sample stage at ca 50° avoiding specular reflection components. The environmental gases are controlled and monitored, and accurate temperature control and measurements are maintained.

Figure 8.

Nitrogen Sorption on $\text{UO}_2(\text{B})$ at 77°K. Heating in excess of 500°C decreases the amount of surface by closing interlaminar spaces and leaving the total sorption space unaltered.

Figure 9.

Nitrogen Sorption on $\text{UO}_2(\text{C})$ at 77°K. Sintering to 500°C leads to surface area loss by interparticulate sintering with a constant total volume; 600°C in vacuum leads to material transport and markedly decreases the porosity.

Figure 10.

Rectilinear Presentation of Nitrogen Sorption on UO_2 (B) and UO_2 (C) at 77°K. All data seems to fit the linear relation indicating that the mode of preparation and subsequent heating produces material with little or no microporosity ($1 < 2.0 \mu\text{m}$).

Figure 11.

Diffuse Reflectance Spectra for Dehydration of UO_2 (C). cursory observation shows a loss of hydrogen-bonded OH species, some molecular water, and three bands associated with the UO_2 substrate.

Figure 12.

Diffuse Reflectance Spectra of UO_2 (C) in vacuum. There is overlap for the HOH band and the UO_2 band. Some OH is retained in vacuum and some thermal lability is evident. Subsequent cooling shows that the thermal effect involves volatile loss.

Figure 13.

Diffuse Reflectance Spectra for Rehydration of UO_2 (C). Band assignments are relatively straight forward and the vapor phase OD is detected at higher pressure in the head space above the sample.

Figure 14.

Diffuse Reflectance Spectra for Second Dehydration of UO_2 (C). Band assignments are given and some hydrocarbon is removed incompletely in vacuum.

Figure 15.

Intensity Evaluation for Diffuse Reflectance Spectra of UO_2 (C). Three general features preclude accurate evaluation: (1) the general background curve is ill-defined, (2) the periodic undulations are a

problem, and (3) there is considerable overlap of HOH bands and substrate bands.

Figure 16.

Comparative techniques for Diffuse Reflectance Spectra of $\text{UO}_2(\text{C})$. Point-by-point numerical subtraction showing the changes wrought in rehydration (25) of the vacuum state (14) of $\text{UO}_2(\text{C})$.

Figure 17.

Spectra Comparison to Show Irreversible Retention of Deuterated Water on $\text{UO}_2(\text{C})$. Numerical evaluation of spectral differences showing the additional amount of irreversible retention of deuterated water after rehydration of $\text{UO}_2(\text{C})$.

Figure 18.

Band Assignments for Diffuse Reflectance Spectra for Sorption of D_2O on $\text{UO}_2(\text{C})$. The speciation is much simpler when the comparative spectra are employed.

Figure 19.

Integration Limits for Integrated Intensity Analyses for D_2O Sorbed on $\text{UO}_2(\text{C})$. Band integration is now easier and more reliable with the use of the comparative spectra; even the choice of integration limits are less ambiguous. The data management computer is used to perform the integration numerically.

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Y-12 Central Files (5)

Paducah Gaseous Diffusion Plant

Walter, C. W.

Pennsylvania State University

Bradt, H. D.

Walker, P. L.

Portland State University

Emmett, P. H.

Rockwell International - Rocky Flats

Larson, D. T.
Stakebake, J. L.

Sandia National Laboratories - Albuquerque

Goodman, W.
Houston, J. E.
Madden, H. H.
Mail Service Station
Rye, R.

Sandia National Laboratories - Livermore

Felton, T. E.
Leider, H. R.
Technical Library

Solar Energy Research Institute

Czanderna, A. W.

Standard Oil Research Center

Mahajan, O. P.

University of Tennessee
College of Engineering

Stansberry, E. E.

University of Denver

Smith, D.

Virginia Polytechnic Institute

Wightman, J.