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Corrosion of (Th,U) O_2 Fuel at Room Temperature and Near 100°C in Near Neutral and Acidic Water (pH 3)

Corrosion du combustible (TH,U) O_2 à la température ambiante et à près de 100°C dans l'eau presque neutre et acide (pH 3)

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CORROSION DU COMBUSTIBLE (TH, U)O_2 À LA TEMPÉRATURE AMBIANTE ET À PRÈS DE 100 °C DANS L'EAU PRESQUE NEUTRE ET ACIDE (pH 3)

par

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RÉSUMÉ

La dissolution et la corrosion du combustible (Th, U)O_2 a été étudiée à la température ambiante et à une température de près de 100 °C dans de l'eau presque neutre et acide (pH 3) pour évaluer l'aptitude de la thorine dopée à l'UO_2 irradié en tant que forme de déchet pour le stockage direct en formation géologique. La spectroscopie de photoélectrons et la diffraction des rayons X ont été utilisées pour étudier l'oxydation du combustible (Th, U)O_2. L'uranium à la surface du combustible (Th, U)O_2 est soumis à l'oxydation semblable à celle observée dans le combustible à UO_2 dans des conditions semblables. Toutefois, la vitesse de dissolution de l'uranium du combustible (Th, U)O_2 dans des solutions aérées est bien inférieure à celle du combustible à UO_2 dans des conditions semblables.

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ABSTRACT

Dissolution and corrosion of $(Th,U)O_2$ fuel was investigated at room temperature and near 100°C in near neutral and acidic water (pH 3) to evaluate the suitability of irradiated UO_2-doped thoria as a waste form for direct geological disposal. X-ray photoelectron spectroscopy and X-ray diffraction were used to study oxidation of $(Th,U)O_2$ fuel. The uranium in the surface of $(Th,U)O_2$ fuel undergoes oxidation similar to that observed in UO_2 fuel under similar conditions. Nevertheless, the dissolution rate of uranium from $(Th,U)O_2$ fuel in aerated solutions is much lower than that from UO_2 fuel under similar conditions.

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1. INTRODUCTION

Thoria based nuclear fuels are being considered for use in CANDU reactors (Boczar et al. 1997). The reason for the resurgence of interest in thoria as a nuclear fuel is the potential of burning weapons' plutonium in a thoria-based matrix (Akie et al. 1994, Dastur et al. 1994). Also, the high relative abundance of thorium minerals compared to uranium minerals in certain countries (e.g., Turkey) makes the thorium fuel cycle attractive to such countries.

Natural thorium does not have a fissile isotope. Therefore, thoria is generally mixed with another actinide oxide, containing a fissile isotope (e.g., $^{235}UO_2$ or $^{239}PuO_2$), for its use as a fuel in a nuclear reactor. The majority of the ^{235}U or ^{239}Pu isotopes present in the thoria fuel are "burned-out" during its stay in the reactor. The fissile component of the used thoria fuel mainly consists of ^{233}U formed by the transformation of ^{233}Th. ^{233}Th is formed by an absorption of a neutron by ^{232}Th, the main isotope of thorium. Therefore, if thoria fuel is to be used as a nuclear fuel one needs to know the behaviour of $(Th,U)O_2$ in contact with water.

Thoria (ThO_2) is very insoluble in water and does not undergo oxidation beyond its +4 oxidation state (Langmuir and Herman 1980, Lemire and Garisto 1989, Taylor et al. 1996). However, UO_2 does undergo oxidation beyond its +4 oxidation state, and uranium oxides with U in the higher (+6) oxidation state have higher solubility than UO_2 (Lemire and Garisto 1989, Sunder and Shoesmith 1991, Grenthe et al. 1992). Although there are several studies on the dissolution of $(Th,U)O_2$ fuel in strongly acidic solutions (e.g., Dyck et al. 1977), very few experimental results are available on the behaviour of $(Th,U)O_2$ fuel in near neutral conditions expected during used nuclear fuel storage (in a water pool) or disposal (in a geologic vault). Here, we describe the results of our experiments on the dissolution of $(Th,U)O_2$ fuel in pure water and in slightly acidic water (pH 3). Changes in the surface oxidation of $(Th,U)O_2$ samples used in these tests were investigated using X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD).

2. EXPERIMENTAL

2.1 Materials

Two kinds of $(Th,U)O_2$ samples were used in this study - one from archived fuel pellets stored at the Whiteshell Labs (WL pellets) and the second from a recent preparation at the Chalk River Labs (CRL pellets).

The WL pellets, inventory code FMIC # A2263, contained 2.4% UO_2 in ThO_2, and were prepared by Canadian General Electric (Dyck et al. 1977). The UO_2 used in the WL pellets was natural UO_2, i.e., 0.7% ^{235}U. WL pellets were made by mixing ThO_2 and UO_2 powders, followed by cold pressing and sintering at 1700°C. These pellets had density ~9.64 g cm^{-3}, diameter ~14.5 mm, height ~14.5 mm, average weight ~22.5 g, and were beige-gray in colour. The CRL pellets (Reference # FFP-1340-121, PS # 195507) contained 1.5% UO_2 (93% ^{235}U) in ThO_2. The CRL pellets were also beige-gray in colour with flecks of darker gray and white matter. UO_2 pellets used in reference experiments were obtained from an unused CANDU fuel bundle and were uniformly dark gray in colour.

The electrical resistance of all the $(Th,U)O_2$ pellets obtained for this study (10 WL pellets and 3 CRL pellets) was measured in order to select suitable electrochemical techniques for corrosion studies. The resistance of all the $(Th,U)O_2$ pellets was very high - the average resistance of $(Th,U)O_2$ pellets was >2 GΩ, compared to 200 kΩ for UO_2 pellets with similar dimensions. Therefore, we did not use electrochemical techniques, like those used in our studies on UO_2 corrosion (Sunder et al. 1981, 1996, 1997, Shoesmith et al. 1994), to study the corrosion of $(Th,U)O_2$. The corrosion of $(Th,U)O_2$ was investigated by studying changes in its surface chemistry and by measuring the amount of uranium dissolved during a corrosion test.

The pellets were cut with a diamond saw to obtain ~4.5-mm thick disks for the corrosion experiments. (The XPS spectrometer used in this study, Section 2.3, cannot accommodate samples of the dimensions of the uncut $(Th,U)O_2$ pellets.) Water was used as the lubricant and coolant in the cutting process. The sample disk was mechanically polished on all sides, including the rim, using a 600-grit SiC paper to expose a fresh surface before all corrosion experiments. Polishing was carried out using water as the lubricant and dust collector. The disk was washed with water and methanol to remove the loose particles and organic film that may have formed on the surface during polishing.

The water used for washing and corrosion tests was purified by passing distilled water through a Millipore milli-R06+ unit with organic and inorganic removal cartridges. The purified water had a specific resistance of 18.2 MΩ cm and a pH of ~5.5 - from CO_2 dissolved from the air. The methanol used was of analytical reagent grade purity, obtained from AnalaR, BDH Inc. Corrosion experiments were carried out in purified water pH ~5.5, and in slightly acidic water, pH ~3. The lower pH solution was obtained by adding a small amount of nitric acid, Fisher Scientific Reagent ACS grade, to water. The pH was measured using a Fisher Accumet pH meter 25 - calibrated using buffer solutions of pH 7.0 and 4.0, obtained from Fisher.

2.2 Corrosion Experiment

Room temperature, open air, corrosion tests were carried out using 50 mL-Pyrex beakers as the reaction vessels. The reaction vessel was placed in a larger beaker, partially filled with water, that was covered with a carton standing on three rubber bungs. This allowed a constant supply of fresh, clean air without causing significant loss of water from the reaction vessel by evaporation.

High temperature (~95°C) tests were carried out using wide-mouth Teflon bottles (capacity 90 mL) as the reaction vessels. The Teflon bottles were cleaned by sealing in them ~25 mL of pH 3 solution and heating at ~95°C for ~120 h in an oven. This cleaning step was carried out after each test to remove any uranium adsorbed on the inside surfaces of the bottles. For corrosion tests with water only, the cleaning step was repeated using water, after cleaning with pH 3 solution.

Corrosion tests were started by adding 10 mL of water (or water containing nitric acid) to the reaction vessel containing a polished, washed, dried and weighed disk of $(Th,U)O_2$. Teflon bottles were sealed using a screw cap and Teflon-tape to reduce water loss during the test. The sealed bottle was placed in a heated sand bath in an oven at ~95°C (Sunder and Miller 1996). Control tests were conducted using a UO_2 pellet in place of a $(Th,U)O_2$ pellet, and without any pellet. All tests were carried out for a period of about 6 d (Table 1). After this period, the reaction vessel was removed from the oven and cooled to room temperature on the laboratory bench. The sample disk was removed from the cooled solution, mounted on an XPS sample holder, pumped down to degas, and analyzed using XPS (Section 2.3). The sample disk was weighed immediately after the XPS analysis to determine the weight change during the corrosion test. There was a very small decrease (less than a few tenths of a milligram) in the weight of the disk during the corrosion tests. The sample disk was submitted for XRD analysis (Section 2.4) after weighing.

The pH and volume of solution remaining in the reaction vessel were measured and the solution analyzed for uranium. Uranium concentration in the solution was determined by the standard addition method using FLURAN (a buffered inorganic complexing agent) and a Scintrex Fluorescence Uranium Analyzer UA-3 (Scintrex 1985).

2.3 X-Ray Photoelectron Spectroscopy

XPS spectra were recorded using a PHI-5300 ESCA system. The sample disk was mounted on an XPS specimen holder using copper clips and brought into the side-arm of the spectrometer where it was pumped for >10 min before introducing it into the spectrometer. The sample was pumped in the side arm to reduce excessive degassing from the sample in the spectrometer. The spectra were excited using Mg Kα X-rays (generated by operating the anode at 15 kV and 20 mA, i.e., at a power of 300 W) and filtered through an Al window. The binding energy scale of the spectrometer was calibrated using known energies of bands in the spectra of noble metals (Sunder and Miller 1995, 1996).

2.4 X-Ray Diffraction

A Rigaku Rotaflex X-ray diffractometer, equipped with a 12-kW rotating-anode Cu Kα X-ray source and a diffracted-beam graphite monochromator, was used to obtain the XRD patterns (Sunder and Miller 1995, 1996). The sample disk was placed in a specially designed brass sample-holder to record the XRD data from its surface. XRD data were obtained from the same surface as that used for the XPS analysis. The XRD data were obtained using a scanning rate of $1°min^{-1}$. XRD data were obtained only for the

WL pellets as the XRD analysis of the CRL pellets is planned to be carried out at the Chalk River Labs.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction

The XRD data were recorded for diffraction angles (2θ) from 5° to 120°. Figure 1 shows the XRD pattern of a polished disk of $(Th,U)O_2$, from a WL pellet, used in experiment A (Table 1). The bottom part of this figure compares the observed pattern of $(Th,U)O_2$ with the literature pattern of synthetic ThO_2 (ICDD 1994). There is good agreement between the observed pattern for $(Th,U)O_2$ and the literature pattern for ThO_2. Nearly all of the observed peaks could be assigned to the ThO_2 pattern. Only one extremely weak feature, observed at $2\theta = 13.71°$ ($d = 6.45$ Å) in the XRD pattern (Figure 1), could not be assigned to the ThO_2 pattern. Distinct peaks for uranium oxides were not seen in the XRD pattern. The information about the oxidation state of uranium in the test specimens was obtained using XPS (Section 3.2).

An analysis of all the observed diffraction peaks, with $60°<2\theta<120°$ (both $K\alpha_1$ and $K\alpha_2$) in Figure 1, gave the value of the unit-cell parameter $a = 5.5941(3)$ Å for the WL pellet containing 2.4% UO_2 in ThO_2. The figure in parentheses is the estimated standard deviations in the last significant figure. Similar analyses were carried out on five different UO_2 specimens and gave values of the unit-cell parameter a ranging between 5.4700 and 5.4704 Å. Our experimental values of unit-cell parameter a for UO_2 are in excellent agreement with the literature value of 5.4704±0.0003 Å reported by Cohen and Berman (1966).

Cohen and Berman (1966) also determined values of unit-cell parameter for ThO_2, $a = 5.5975\pm0.0002$ Å; and for $(Th_{0.899}U_{0.101})O_{2.00}$, $a = 5.5846(3)$ Å. One obtains a value of unit cell parameter $a = 5.5944$ Å for $(Th_{0.976}U_{0.024})O_2$ by interpolating between the values of UO_2 and ThO_2, or by interpolating between the values for $(Th_{0.899}U_{0.101})O_{2.00}$ and ThO_2. This calculated value for $(Th_{0.976}U_{0.024})O_2$ is in good agreement with the experimental value obtained above. This suggests that the $(Th,U)O_2$ disk used in experiment A is a homogeneous solid solution of the stated composition.

3.2 X-Ray Photoelectron Spectroscopy

XPS spectra of the $(Th,U)O_2$ disks were recorded before and after the corrosion experiments. Low-resolution survey spectra, for the 0-1100 eV region, were recorded to determine the elements present in the pellet surface. High-resolution spectra were recorded for C 1s, O 1s, Th 4f, Th 5d, U 4f, and the valence region (0-20 eV) to determine the chemical state of these elements. (The C 1s band arises from the ubiquitous hydrocarbons present on solid surfaces.) The XPS spectra of $(Th,U)O_2$ disks showed severe charging owing to the non-conducting nature of the sample (Section 2.1). The

C 1s band with a binding energy value of 284.8 eV was used to correct for charging effects (Sunder and Miller 1995).

Figure 2 shows a survey spectrum of a polished disk, from a WL pellet, used in experiment A (Table 1). The bands seen in this spectrum can be assigned to thorium, uranium, oxygen and carbon peaks (Moulder et al. 1992). Figures 3, 4, 5, 6 and 7 show typical high-resolution spectra for C 1s, O 1s, Th 4f, Th 5d and U 4f regions, respectively, for the same disk. Note the Figures 2-7 are plotted using a charge correction of 6.4 eV obtained from the spectrum of the C 1s band, as discussed above. The O 1s band in the spectrum of the freshly polished sample (Figure 4) suggests that most of the intensity of this band arises from the oxide (O^{2-}) moieties, i.e., from a peak centered around 529.8 eV. The weak shoulders seen on the high binding energy side of this band most probably arise from OH^- and H_2O moieties present on the surface. Analyses of the O 1s bands into O^{2-}, OH^- and H_2O components, according to the procedure described elsewhere (Sunder and Miller 1995), showed that the fraction of the OH^- and H_2O species was much higher in the spectrum of a corroded sample than in the spectrum of the freshly polished sample.

The binding energies of the Th 4f bands and Th 5d bands in the freshly polished (Figures 5 and 6) or corroded $(Th,U)O_2$ samples were equal to those expected for ThO_2 (Moulder et al. 1992, Wagner et al. 1979). However, the binding energies of the U 4f bands were slightly higher in the spectra of the corroded samples than those in the spectrum of a freshly polished sample. The binding energies of U 4f bands are very sensitive to the chemical state of the uranium atom and increase with an increase in its oxidation state. (Figure 7 shows the spectrum for the U 4f bands for a freshly polished $(Th,U)O_2$ sample.) For example, the U $4f_{7/2}$ band occurs at ~379.9 eV in UO_2 and at ~381.2 eV in UO_3 (Sunder and Miller 1995 and references therein). Therefore, the increase observed in the binding energies of the U 4f band of the samples, after the corrosion tests, indicates that the uranium present in the surface of these samples underwent some oxidation during the tests.

We have developed a procedure to obtain the relative amounts of U^{6+} and U^{4+} in the surface of a sample containing uranium oxides from an analysis of its U $4f_{7/2}$ band (Sunder et al. 1981, 1990 and Sunder and Miller 1995). This procedure was used to determine the relative amounts of U^{6+} and U^{4+} in the samples used in the tests. The results of these analyses are summarized in Table 2. This table also contains U^{6+}/U^{4+} ratios for freshly polished $(Th,U)O_2$ and UO_2 disks for comparison purposes. In general, there was an increase in the U^{6+}/U^{4+} ratio during corrosion of $(Th,U)O_2$ disks in aerated solutions. The average value of the U^{6+}/U^{4+} ratio is about 0.3 in acidic solutions (pH ~3) and about 0.6 in near neutral (pH ~5.5) solutions. We believe that the lower values of the U^{6+}/U^{4+} ratio, for the samples corroded in acidic water, is due to the increased dissolution of U^{6+} species in acidic solutions (Grenthe et al. 1992). This conclusion is consistent with corrosion rate results discussed below.

3.3 Corrosion Rates

Corrosion rates of $(Th,U)O_2$ and UO_2 disks in different tests were calculated from the amount of uranium released into the solution during the corrosion tests, Table 1. These rates were calculated using equation:

$$DR = (U_f \cdot V_f \cdot k \cdot 24) / (t \cdot A \cdot 100) \qquad (1)$$

where

DR = dissolution rate ($mg \cdot m^{-2} \cdot d^{-1}$),
U_f = uranium concentration ($\mu g \cdot L^{-1}$),
V_f = final volume (mL),
t = time of corrosion test (h),
A = area of the disk (cm^2), and
k = conversion factor to calculate dissolved UO_2 from measured amount of uranium, i.e., = (270/238) = 1.1344.

The dissolution rates are calculated in units of $mg \cdot m^{-2} \cdot d^{-1}$ to facilitate a comparison of uranium dissolution rates obtained in this work with the recent studies on UO_2 fuel dissolution carried out for the nuclear waste management program (e.g., Shoesmith et al. 1996, 1997, and references therein). The relative precision (2s) of the uranium concentrations shown in Table 1 is ±20%. Note, for the CRL fuel, with 93% ^{235}U, the precise value of k is 1.1360, ((0.93*235 + 0.07*238) +32) /(0.93*235 + 0.07*238)), i.e., the difference from the k value given above for natural UO_2 (and used to calculate dissolution rates) is less than 0.15%.

The dissolution rates given in Table 1 were calculated using the geometric area of the sample disk, i.e., 5.35 cm^2. To obtain the *actual* area of a solid the geometric area is multiplied by the roughness factor . The roughness factor for UO_2 disks is believed to be ~3 (Shoesmith et al. 1989, 1996). If one were to use the same roughness factor for $(Th,U)O_2$ as that for UO_2, the dissolution rates shown in Table 1 will be reduced by a factor of three.

The use of equation (1) to calculate the UO_2 dissolution rate implies that the final uranium concentration in the aqueous phase is still unsaturated with respect to solid U-containing phases, i.e., there is no significant re-precipitation of dissolved uranium (Thomas and Till 1984). This is a reasonable assumption for tests with the $(Th,U)O_2$ samples because of the low uranium concentrations seen in these tests (Table 1). It may be noted here that the dissolution rates obtained in this work for UO_2, in aerated water at room temperature (experiments J and K), compare favourably with the results reported in literature by different authors (e.g., Shoesmith et al. 1996, 1997, Tait and Luht, 1997 and references therein). Figure 1 in the report by Shoesmith et al. (1997) gives a concise summary of the recent literature on UO_2 dissolution rates in aerated solutions.

A comparison of the dissolution rates for $(Th,U)O_2$ and UO_2 samples in pH ~3 solution at ~95°C (Table 1) shows that the rate of uranium dissolution from $(Th,U)O_2$ is much lower than that from UO_2. In particular, the dissolution rate of uranium from WL $(Th,U)O_2$ is lower by a factor of ~9700 than that from UO_2 under these conditions, experiment C compared to experiments F and G. As the UO_2 concentration in the solid sample used in experiment C is 2.4%, the reduction in the uranium dissolution rate is about 25 times greater than that expected solely from the decrease in the uranium concentration in the solid phase. We have not attempted a similar quantitative comparison of uranium dissolution rates from $(Th,U)O_2$ and UO_2 at room temperature because of the exceedingly low uranium dissolution rates from $(Th,U)O_2$ at pH ~3, Experiments A and B in Table 1. UO_2 solubility is lower at pH 5.5 than that at pH 3 (Grenthe et al. 1992). It is clear from the data shown in Table 1 that the uranium dissolution rates in water are much lower from $(Th,U)O_2$ than those from UO_2. These results are in agreement with the results of Grandstaff (1976) who carried out an extensive study on the dissolution of uraninite minerals in water. Grandstaff observed much lower (about 2 to 3 orders of magnitude) uranium dissolution rates in aerated water for uraninite mineral containing ThO_2 than those for uraninite mineral with little ThO_2.

The results obtained in this work show that the uranium dissolution rate from $(Th,U)O_2$ fuel, with UO_2 present as a solid solution in ThO_2 matrix, will be much lower than that from UO_2 fuel. The release rate of fission products (FP) from used fuel into liquid water is governed by the dissolution rate of the fuel as >90% of the FP are present within the fuel grains (Johnson et al. 1996). Therefore, the release of most of the radioactive FP would be much lower from used $(Th,U)O_2$ fuel than that from used UO_2 fuel. Hence, the used $(Th,U)O_2$ fuel should be a suitable waste form for direct geological disposal. These results support the conclusions of Taylor et al. (1996), obtained from a literature review, that the used $(Th,Pu)O_2$ fuel will be a suitable waste-form for direct geological disposal. However, it may be mentioned here that the results obtained in this study (and those reported by Grandstaff (1976)) were obtained from experiments carried out in solutions containing dissolved oxygen as the oxidant and do not take into account the effects of water radiolysis on UO_2 dissolution from $(Th,U)O_2$ fuel. We have shown that the radical oxidants formed during water radiolysis are much more effective, in increasing the uranium oxidation and dissolution rates from UO_2 fuel, than dissolved oxygen (Sunder et al. 1989, 1992). Therefore, it would be prudent to carry out selected experiments on the effects of water radiolysis on uranium dissolution from $(Th,Pu)O_2$ fuel.

The uranium dissolution rate from the CRL $(Th,U)O_2$ sample is also lower than that from UO_2 (experiment D compared to experiments F and G). However, the dissolution rate from the CRL $(Th,U)O_2$ sample is greater than that from the WL $(Th,U)O_2$ sample. This is a bit puzzling as the CRL pellets contain nominally less uranium than the WL pellet (i.e., 1.8% UO_2 in CRL pellets compared to 2.4% UO_2 in WL pellets). Additional tests are needed to confirm this difference and determine its cause(s).

4. SUMMARY AND CONCLUSION

It is possible to prepare $(Th,U)O_2$ pellets that behave like *solid solutions* by mixing ThO_2 and UO_2 powders, followed by cold pressing and sintering at 1700°C.

The uranium in the surface of $(Th,U)O_2$ specimens undergoes oxidation as if it was present in *pure* UO_2. However, the leach rate of uranium from a properly prepared $(Th,U)O_2$, i.e., with UO_2 present as a solid solution in ThO_2 matrix, is reduced by a factor greater than that expected solely from a decrease in the uranium concentration in the solid phase.

A properly prepared $(Th,U)O_2$ fuel can be an acceptable waste-form for permanent geological disposal. Studies on the effects of water radiolysis on the uranium dissolution rates from $(Th,U)O_2$ are recommended to confirm the above conclusions.

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TABLE 1

SUMMARY OF $(ThU)O_2$ CORROSION EXPERIMENTS

Exp't #	Sample	Conditions of Experiment	V_i	V_f	pH_i	pH_f	$[U]_f$	Dissolution Rate[a]
			mL	mL			$\mu g\ L^{-1}$	$mg\ m^{-2}\ d^{-1}$
A	WL $(Th,U)O_2$	150 h, room temp, open air	10.0	6.7	3.04	2.87	23	0.05
B	WL $(Th,U)O_2$	148 h, room temp, open air	10.0	6.7	3.01	2.97	31	0.07
C	WL (Th,U)O2	144.5 h, 96°C, sealed bottle	10.0	9.5	3.11	2.98	100	0.34
D	CRL $(Th,U)O_2$	144.5 h, 95°C, sealed bottle	10.0	9.6	3.00	3.03	1300	4.4
E	CRL $(Th,U)O_2$	143 h, 95°C, sealed bottle	10.0	9.8	5.55	4.69	260	0.9
F	UO_2, V3	140 h, 95°C, sealed bottle	10.0	9.8	3.02	3.2	97000	350
G	UO_2, V25	140 h, 95°C, sealed bottle	10.0	9.8	3.02	3.15	88000	310
H	Blank, #2	140 h, 95°C, sealed bottle	10.0	10	3.02	3.02	1	
I	Blank, #50	140 h, 95°C, sealed bottle	10.0	9.8	3.02	2.98	1	
J	UO_2, V3	141 h, room temp, sealed bottle	10.0	10	5.75	5.78	430	1.6
K	UO_2, V25	141 h, room temp, sealed bottle	10.0	10	5.75	5.85	410	1.5
L	Blank, #20	141 h, room temp, sealed bottle	10.0	10	5.75	5.76	19	
M	Blank, # 10	141 h, room temp , sealed bottle	10.0	10	5.75	5.76	10	

[a] Dissolution rates calculated using geometric surface area, see text for the method for correcting for surface area.

TABLE 2

$(Th,U)O_2$ CORROSION EXPERIMENTS: XPS RESULTS

Exp't #	Sample Disk	Conditions of Experiment	pH_i	pH_f	U^{6+}/U^{4+} Ratio from XPS[a]
	UO_2, V25	Freshly polished			0.07
	CRL $(Th,U)O_2$	Freshly polished			0.09
A	WL $(Th,U)O_2$	150 h, room temp, open air	3.04	2.87	0.21
B	WL $(Th,U)O_2$	148 h, room temp, open air	3.01	2.97	0.14
C	WL $(Th,U)O_2$	144.5 h, 96°C, sealed bottle	3.11	2.98	0.35
D	CRL $(Th,U)O_2$	144.5 h, 95°C, sealed bottle	3.00	3.03	0.51
E	CRL $(Th,U)O_2$	143 h, 95°C, sealed bottle	5.55	4.69	0.33
F	UO_2, V3	140 h, 95°C, sealed bottle	3.02	3.2	0.59
G	UO_2, V25	140 h, 95°C, sealed bottle	3.02	3.15	0.57
J	UO_2, V3	141 h, room temp, sealed bottle	5.75	5.78	0.77
K	UO_2, V25	141 h, room temp, sealed bottle	5.75	5.85	0.57

[a] The uncertainty in the U^{6+}/U^{4+} ratio values is estimated to be ±10% for UO_2 samples and ±20% for $(Th,U)O_2$ samples. The higher uncertainty for the $(Th,U)O_2$ samples is because of the lower signal-to-noise ratio of uranium bands (resulting from low concentration of uranium atoms) in these samples.

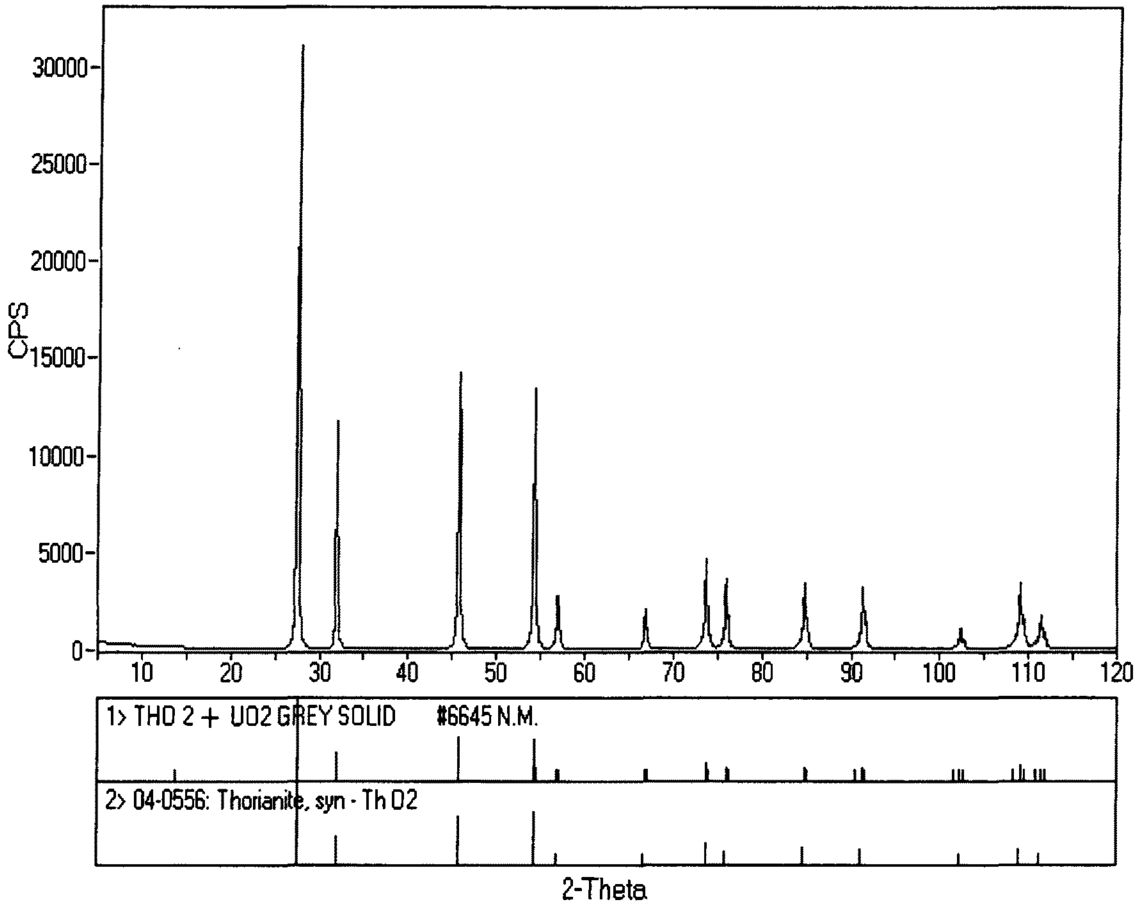

Figure 1: XRD pattern of a freshly polished $(Th,U)O_2$ disk containing 2.4% UO_2, (File # z0317, sample # 6645 N.M.), top; and comparison of the observed pattern with the literature pattern for synthetic thorianite, ThO_2, bottom.

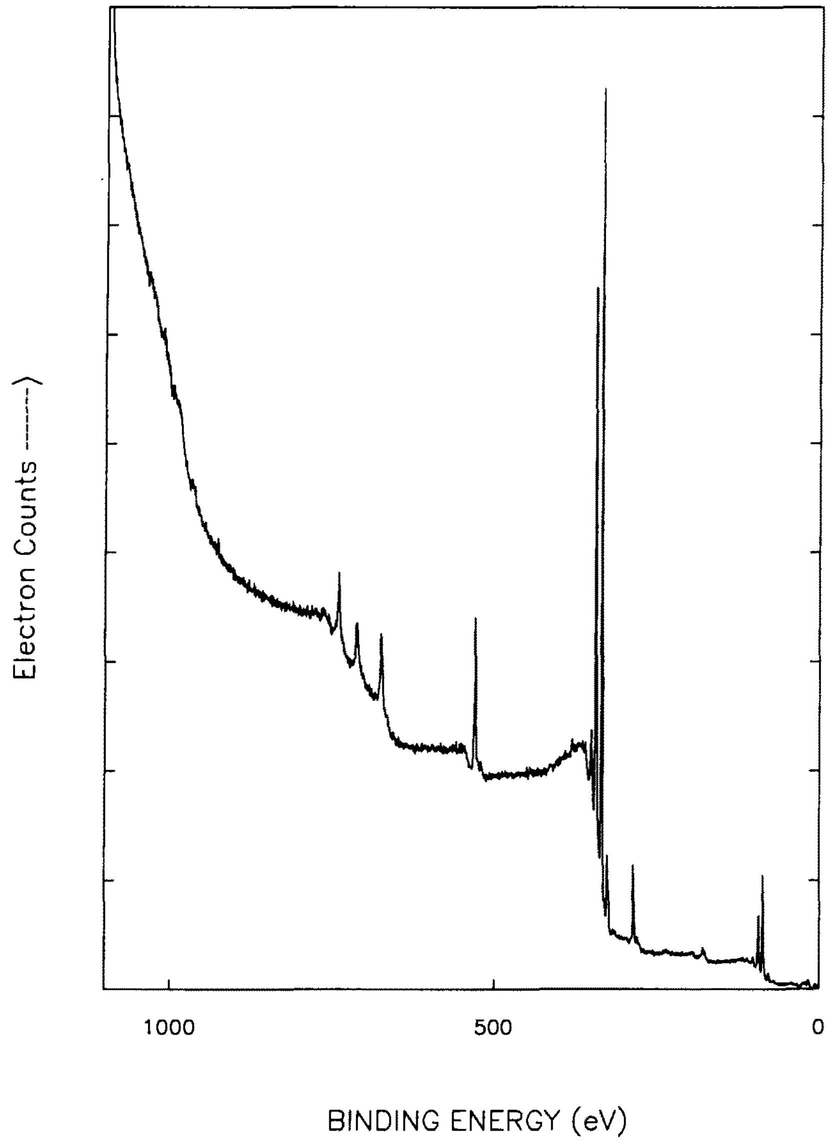

Figure 2: Survey XPS spectrum of a freshly polished (Th,U)O_2 disk containing 2.4% UO_2 (File # ma0797t22).

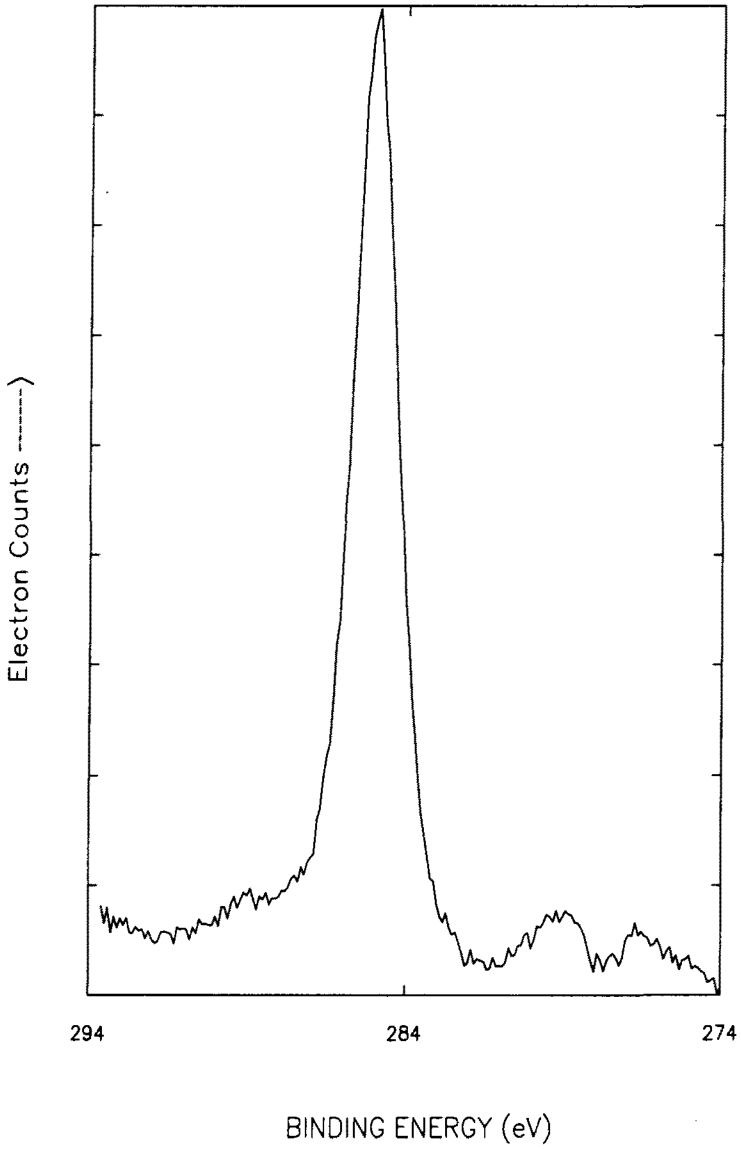

Figure 3: High-resolution XPS spectrum for the C 1s region of a freshly polished (Th,U)O_2 disk containing 2.4% UO_2 (File # ma0797t21).

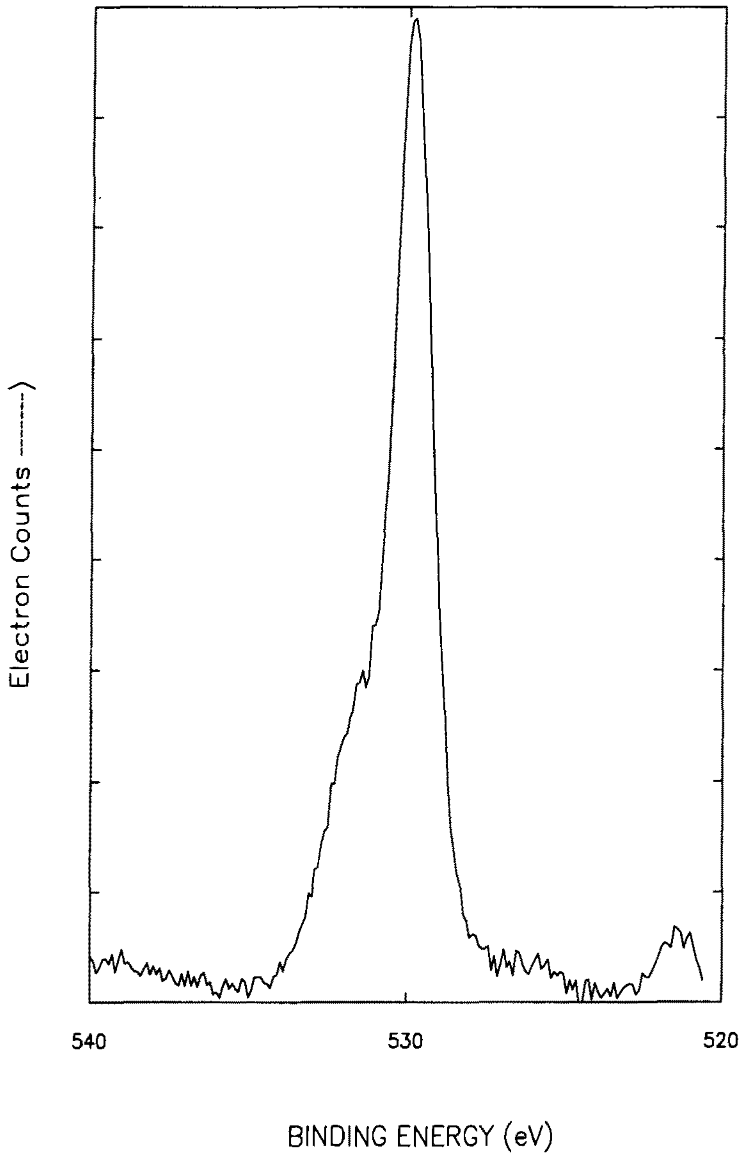

Figure 4: High-resolution XPS spectrum for the O 1s region of a freshly polished (Th,U)O_2 disk containing 2.4% UO_2 (File # ma0797t21).

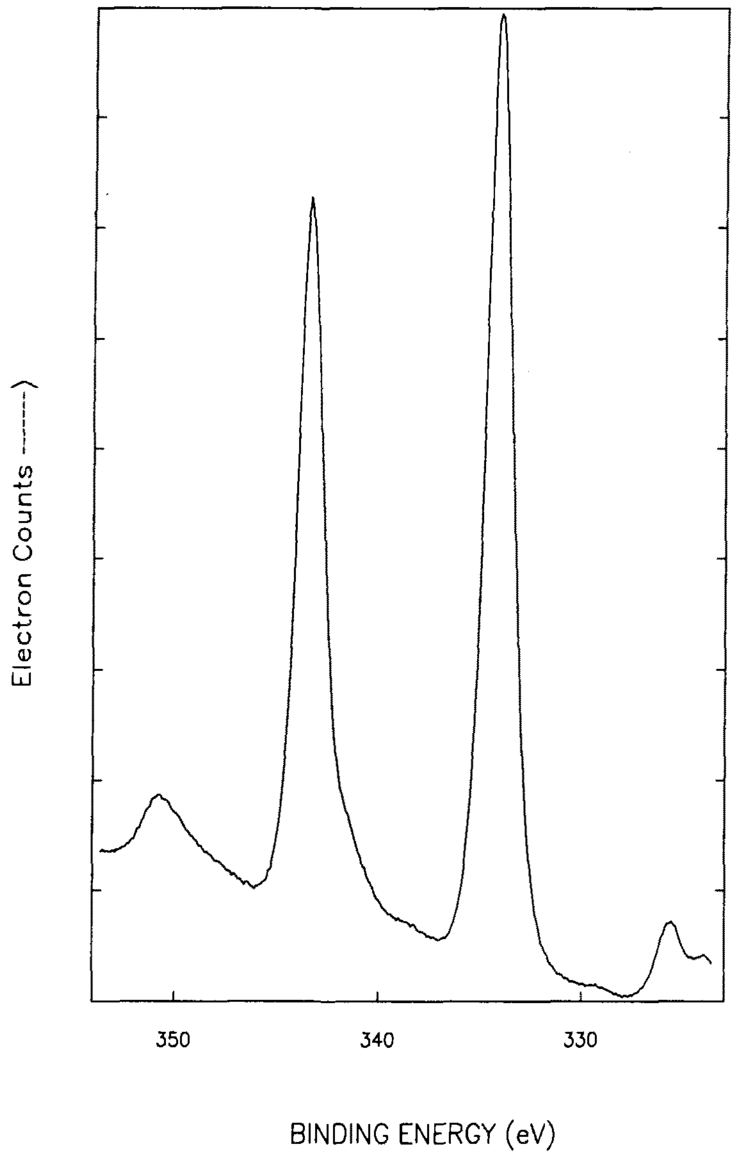

Figure 5: High-resolution XPS spectrum for the Th 4f region of a freshly polished (Th,U)O_2 disk containing 2.4% UO_2 (File # ma0797t21).

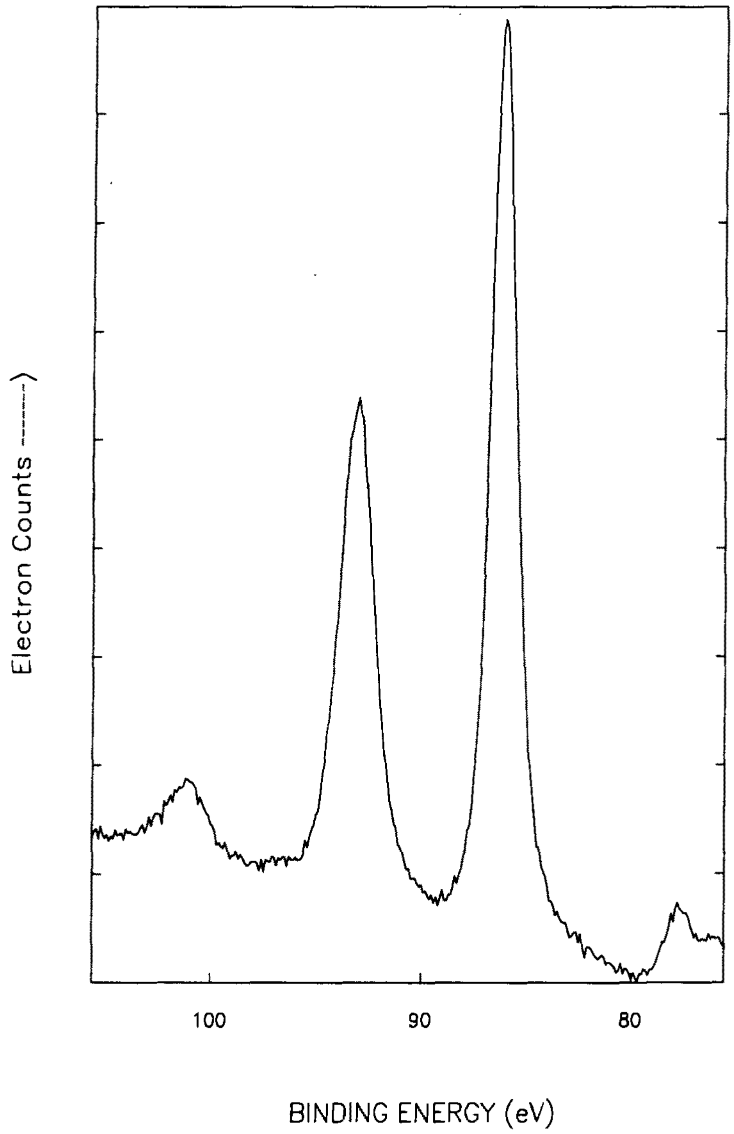

Figure 6: High-resolution XPS spectrum for the Th 5d region of a freshly polished $(Th,U)O_2$ disk containing 2.4% UO_2 (File # ma0797t21).

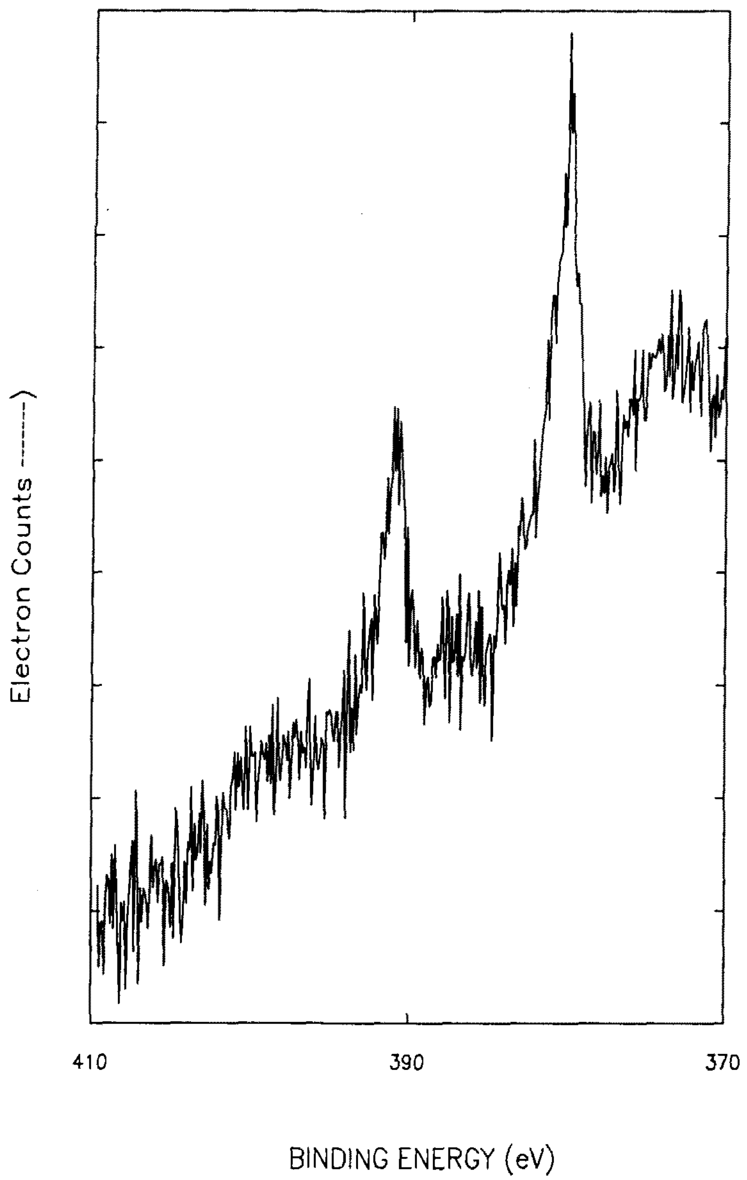

Figure 7 : High-resolution XPS spectrum for the U 4f region of a freshly polished (Th,U)O_2 disk containing 2.4% UO_2 (File # ma0797t21).

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