CORROSION RESISTANCE OF (Th,U)O_2 FUEL IN WATER

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ABSTRACT

Dissolution and corrosion of (Th,U)O_2 fuel was investigated in near neutral and slightly acidic water (pH 3) at room temperature and near 100°C. X-ray photoelectron spectroscopy and X-ray diffraction were used to study oxidation of (Th,U)O_2 fuel during corrosion experiments. 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. These studies suggest that used (Th,U)O_2 fuel should be an acceptable waste form for direct geological disposal.

INTRODUCTION

Thoria-based nuclear fuels are being considered for use in CANDU reactors [1]. One reason for the resurgence of interest in thoria as a nuclear fuel is the potential of burning weapons' plutonium in a thoria-based matrix [2]. Also, the high relative abundance of thorium minerals compared with uranium minerals in certain countries makes the thorium fuel cycle attractive to such countries. The CANDU reactor has the capability to use a thorium fuel cycle because of its excellent neutron economy, channel design and on-power refueling, that results in an unsurpassed fuel-cycle flexibility.

As the thermal conductivity of ThO_2 is higher than that of UO_2 over a wide temperature range, ThO_2 fuel operating temperatures will be lower than those for UO_2 fuel [1]. Hence, the thermally activated processes in the fuel, such as diffusion of fission gas from the fuel, will occur at lower rates leading to lower fission gas releases from ThO_2 fuel than that from UO_2 fuel operating under similar ratings.

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(1) of used thoria fuel mainly consists of ^{233}U formed by the transformation of ^{233}Th. 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 - the used fuel may come in contact with water during storage and/or disposal conditions (see below). Thoria (ThO_2) is very

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[1] ^{233}U is formed by an absorption of a neutron by ^{232}Th, the main isotope of thorium, and subsequent beta-decay of ^{233}Th and ^{233}Pa. Although ^{233}U is a fissile isotope, its strong gamma activity makes it less amenable to recovery or diversion than plutonium [3].

insoluble in water and does not undergo oxidation beyond its +4 oxidation state. UO_2, however, 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 [4,5]. Although there are several studies on the dissolution of $(Th,U)O_2$ fuel in strongly acidic solutions [6] 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) [3]. 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).

EXPERIMENTAL

Two kinds of $(Th,U)O_2$ samples were used in this study - one from archived fuel pellets stored at the Whiteshell Laboratories of AECL (WL pellets) and the second from a recent production at the Chalk River Laboratories of AECL (CRL pellets) [7]. The WL pellets contained 2.4% natural UO_2 (0.7% ^{235}U) in ThO_2. The WL pellets were made by mixing ThO_2 and UO_2 powders, followed by cold pressing and sintering at 1700°C [5]. 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 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 was very high [7]. Therefore, we did not use electrochemical techniques, like those used in our studies on UO_2 corrosion [4,8] to study the corrosion of $(Th,U)O_2$. The corrosion of $(Th,U)O_2$ was investigated by studying changes in its surface stoichiometry and by measuring the amount of uranium dissolved during a corrosion test.

The pellets were cut to obtain ~4.5-mm thick disks for the corrosion experiments. The sample disk was mechanically polished on all sides, including the rim, to expose a fresh surface before all corrosion experiments. Corrosion experiments were carried out in purified water pH ~5.5, and in slightly acidic water, pH ~3, obtained by adding nitric acid to water.

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 $(Th,U)O_2$. Control tests were conducted using a UO_2 disk in place of a $(Th,U)O_2$ disk, and without any disk. Test conditions are summarized in Table 1. Additional details of test conditions and experimental methods are given in reference 7. All tests were carried out for a period of about 6 d. After this period, the reaction vessel was removed from the oven and cooled to room temperature on the laboratory bench. Sample disks were removed from the cooled solutions, and submitted for XPS and XRD analyses.

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 [7].

XPS spectra were recorded using a PHI-5300 ESCA system. The spectra were excited using Mg Kα X-rays and filtered through an Al window. 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.

RESULTS AND DISCUSSION

X-Ray Diffraction

XRD data were obtained only for tests carried out with the WL disks. The XRD data were recorded for diffraction angles (2θ) from 5° to 120°. A comparison of observed XRD pattern for $(Th,U)O_2$ with those in the literature for ThO_2 showed good agreement between the observed and the literature patterns [7]. Nearly all of the observed peaks could 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.

An analysis of all the observed diffraction peaks, with $60° < 2\theta < 120°$ (both $K\alpha_1$ and $K\alpha_2$) 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 [7]. The figure in parentheses is the estimated standard deviation 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 [9].

Cohen and Berman also determined values of unit-cell parameter for ThO_2, $a = 5.5975 \pm 0.0002$ 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. The calculated value for $(Th_{0.976}U_{0.024})O_2$ is in good agreement with the experimental value obtained above, as can be seen from Figure 1. This suggests that the WL $(Th,U)O_2$ disks are homogeneous solid solutions of the stated composition.

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 with a binding energy value of 284.8 eV was used to correct for charging effects [10].

Survey spectra of polished disks, from WL pellets, showed bands which were assigned to thorium, uranium, oxygen and carbon peaks [7,11]. The O 1s band, in the XPS spectrum of the freshly polished samples, suggests, that most of the intensity of this band arises from the oxide (O^{2-}) moieties, with a small contribution from OH^- and H_2O moieties present on the surface [7]. Analyses of the O 1s bands into O^{2-}, OH^- and H_2O components, according to the procedure described elsewhere [10], 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 or corroded $(Th,U)O_2$ samples were equal to those expected for ThO_2 [7,11]. 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. For example, the U $4f_{7/2}$ band occurs at ~379.9 eV in UO_2 and at ~381.2 eV in UO_3 [10]. 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 [7].

The relative amounts of U^{6+} and U^{4+} in the samples used in the tests were determined by the analyses of the U $4f_{7/2}$ bands (Table 1). 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 [4,5]. This conclusion is consistent with corrosion rate results discussed below.

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 [7]. (Thoria is very insoluble in water under the conditions of the experiments [3,7].) These rates were calculated using the following 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 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 [12]. 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 would be reduced by a factor of three.

The use of equation (1) to calculate the UO_2 dissolution rate assumes 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 [13]. 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 favorably with the results reported in the literature by different authors (Figure 2). The agreement between the dissolution rates of UO_2 obtained here and those reported in the literature gives confidence in the method used here to measure the dissolution rates of UO_2 from the sample.

The results listed in Table 1 show that the uranium dissolution rates increase with an increase in temperature of water (experiment C compared to experiments A and B, and experiments F and G compared to experiments J and K) and a decrease in water pH (experiment D compared to experiment E). These conclusions are in agreement with the literature on the solubility of UO_2 in water [4,10].

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 ~970 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). 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 [16] 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 minerals containing ThO_2 than those for uraninite minerals 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 [17]. 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 [3]. It should be noted, however, that the results obtained in this study (and those reported by Grandstaff [16]) 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 [18,19]. Therefore, it would be prudent to carry out selected experiments on the effects of water radiolysis on uranium dissolution from $(Th,U)O_2$ fuel.

SUMMARY AND CONCLUSIONS

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 dissolution rate from $(Th,U)O_2$ increases with an increase in water temperature.

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 direct disposal in a geological disposal vault.

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REFERENCES

1. BOCZAR, P.G., DYCK, G.R., SULLIVAN, J.D., ELLIS, R.J., JONES, R.T and TAYLOR, P., "A Fresh Look at Thorium Fuel Cycles in CANDU Reactors", Presented at IAEA Advisory Group Meeting on Thorium Fuel Cycle Perspectives (1997).

2. DASTUR, A.R., GRAY, A.S., GAGNON, N., BUSS, D.B., VERRALL, R.A., LUCUTA, P.G. and ANDREWS, H.R., "Annihilation of Plutonium in CANDU Reactors", Presented at the IAEA Technical Committee Meeting on "Unconventional Options for Pu Disposition", held at Obninsk, Russia, November (1994).

3. TAYLOR, P., HOCKING, W.H., JOHNSON, L.H., MCEACHERN, R.J. and SUNDER, S., "A Comparison of $(Th,Pu)O_2$ and UO_2 as Waste Forms for Direct Disposal", Nucl. Technol. **116**, 222-230 (1996).

4. SUNDER, S., and SHOESMITH, D.W., "Chemistry of UO_2 Fuel Dissolution in Relation to the Disposal of Used Nuclear Fuel", Atomic Energy of Canada Limited Report, AECL-10395 (1991).

5. GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C. and WANNER, H., "Chemical Thermodynamics of Uranium, Volume 1, Chemical Thermodynamics", H. WANNER and I. FOREST (eds.), North Holland, Amsterdam (1992).

6. DYCK, R.W., TAYLOR, R. and BOASE, D.G., "Dissolution of $(Th,U)O_2$ in Nitric Acid Hydrofluoric Acid Solutions", Atomic Energy of Canada Limited Report, AECL-5957 (1977).

7. SUNDER, S. and MILLER, N.H., "Corrosion of $(Th,U)O_2$ Fuel at Room Temperature and Near 100°C in Neutral and Acidic (pH ~3) water", Atomic Energy of Canada Limited Report, AECL-11967 (1998).

8. SUNDER, S., STRANDLUND, L.K. and SHOESMITH, D.W., "Anodic Dissolution of UO_2 in Slightly Alkaline Sodium Perchlorate Solutions", Atomic Energy of Canada Limited Report, AECL-11440, COG-95-461 (1996).

9. COHEN, I. and BERMAN, R.H., "A Metallographic and X-ray Study of the Limits of Oxygen Solubility in the UO_2-ThO_2 System", J. Nucl. Mater. **18,** 77-107 (1966).

10. SUNDER, S. and MILLER, N.H., "XPS, XRD and SEM Study of Oxidation of UO_2 by Air in Gamma Radiation at 150°C", Atomic Energy of Canada Limited Report, AECL-11351, COG-95-296 (1995).

11. MOULDER, J.F., STICKLE, W.F., SOBOL, P.E. and BOMBEN, K.D., "Handbook of X-ray Photoelectron Spectroscopy", CHASTAIN, J. (ed.), Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, Minnesota, U.S.A (1992).

12. SHOESMITH, D.W., TAIT, J.C., SUNDER, S., GRAY, W.J., STEWARD, S.A., RUSSO, R.E. and RUDNICKI, J.D, "Factors Affecting the Differences in Reactivity and Dissolution Rates Between UO_2 and Spent Nuclear Fuel", Atomic Energy of Canada Limited Report, AECL-11515, COG-95-581, (1996).

13. THOMAS, G.F. and TILL, G., "The Dissolution of Unirradiated UO_2 Fuel Pellets Under Simulated Disposal Conditions", Nucl. Chem. Waste Manag. **5**, 141-147, (1984).

14. SHOESMITH, D.W. and SUNDER, S., "An Electrochemistry-Based Model for the Dissolution of UO_2", Atomic Energy of Canada Limited Report, AECL-10488 (1991).

15. CASAS, I., GIMENEZ, J., DE PABLO, J. and TORRERO, M.E., "Dissolution of UO_2(s) in $MgCl_2$-Brines Under Different Redox Conditions", Materials Research Society Symposium Proceedings, **294**, 67-72, (1993).

16. GRANDSTAFF, D.E., "A Kinetic Study of the Dissolution of Uraninite", Economic Geology **71,** 1493-1506 (1976).

17. JOHNSON, L.H., LENEVEU, D.M., KING, F., SHOESMITH, D.W., KOLAR, M., OSCARSON, D.W., SUNDER, S., ONOFREI, C. and CROSTHWAITE, J.L., "The Disposal of Canada's Nuclear Fuel Waste: A Study of Postclosure Safety of In-Room Emplacement of Used CANDU Fuel in Copper Containers in Permeable Plutonic Rock, Volume 2:Vault Model", Atomic Energy of Canada Limited Report, AECL-11494-2, COG-95-552-2 (1996).

18. SUNDER, S., SHOESMITH, D.W., CHRISTENSEN, H., BAILEY, M.G. and MILLER, N.H., "Electrochemical and X-ray Photoelectron Spectroscopic Studies of UO_2 Fuel Oxidation by Specific Radicals Formed During Radiolysis of Groundwater", Mater. Res. Soc. Symp. Proc. **127**, 317-324 (1989).

19. SUNDER, S., SHOESMITH, D.W., CHRISTENSEN, H. and MILLER, N.H., "Oxidation of UO_2 Fuel by the Products of Gamma Radiolysis of Water", J. Nucl. Mater. **190**, 78-86 (1992).

TABLE 1
SUMMARY OF $(ThU)O_2$ CORROSION EXPERIMENTS

Exp't #	Sample	Conditions of Experiment	pH_i	pH_f	Dissolution Rate[a] mg m^{-2} d^{-1}	U^{6+}/U^{4+} Ratio from XPS[b]
	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	0.05	0.21
B	WL $(Th,U)O_2$	148 h, room temp, open air	3.01	2.97	0.07	0.14
C	WL $(Th,U)O_2$	144.5 h, 96°C, sealed bottle	3.11	2.98	0.34	0.35
D	CRL $(Th,U)O_2$	144.5 h, 95°C, sealed bottle	3.00	3.03	4.4	0.51
E	CRL $(Th,U)O_2$	143 h, 95°C, sealed bottle	5.55	4.69	0.9	0.33
F	UO_2, V3	140 h, 95°C, sealed bottle	3.02	3.20	350	0.59
G	UO_2, V25	140 h, 95°C, sealed bottle	3.02	3.15	310	0.57
H	Blank, #2	140 h, 95°C, sealed bottle	3.02	3.02		
I	Blank, #50	140 h, 95°C, sealed bottle	3.02	2.98		
J	UO_2, V3	141 h, room temp, sealed bottle	5.75	5.78	1.6	0.77
K	UO_2, V25	141 h, room temp, sealed bottle	5.75	5.85	1.5	0.57
L	Blank, #20	141 h, room temp, sealed bottle	5.75	5.76		
M	Blank, # 10	141 h, room temp , sealed bottle	5.75	5.76		

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[a] Dissolution rates calculated using geometric surface area, see text for the method for correcting for surface roughness. The relative precision (2s) of the uranium concentrations shown in Table 1 is ±20%.

[b] 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 the low concentration of uranium atoms) in these samples.

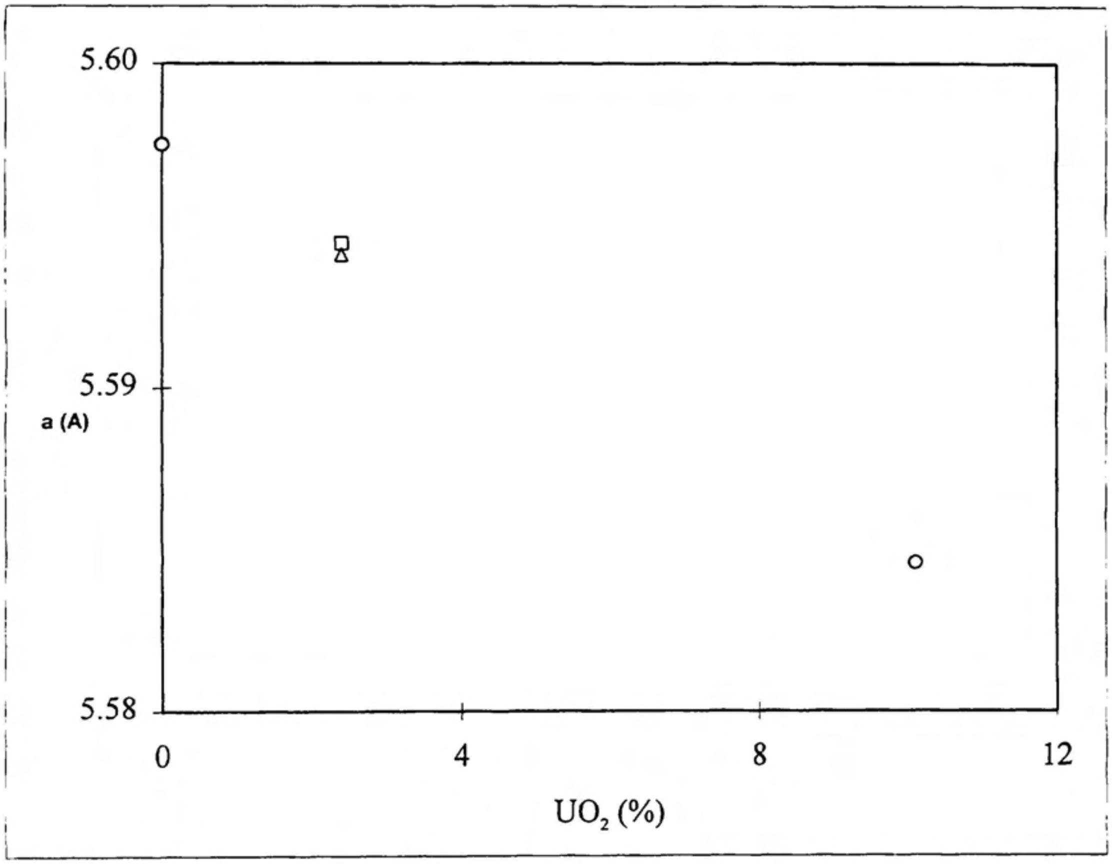

Figure 1: Lattice constant, *a*, of (Th,U)O_2 as a function of UO_2 concentration; (*i*) literature values (Cohen and Berman [9]),○; (*ii*) value calculated from literature values (see text), □; and (*iii*) value obtained in this work, Δ.

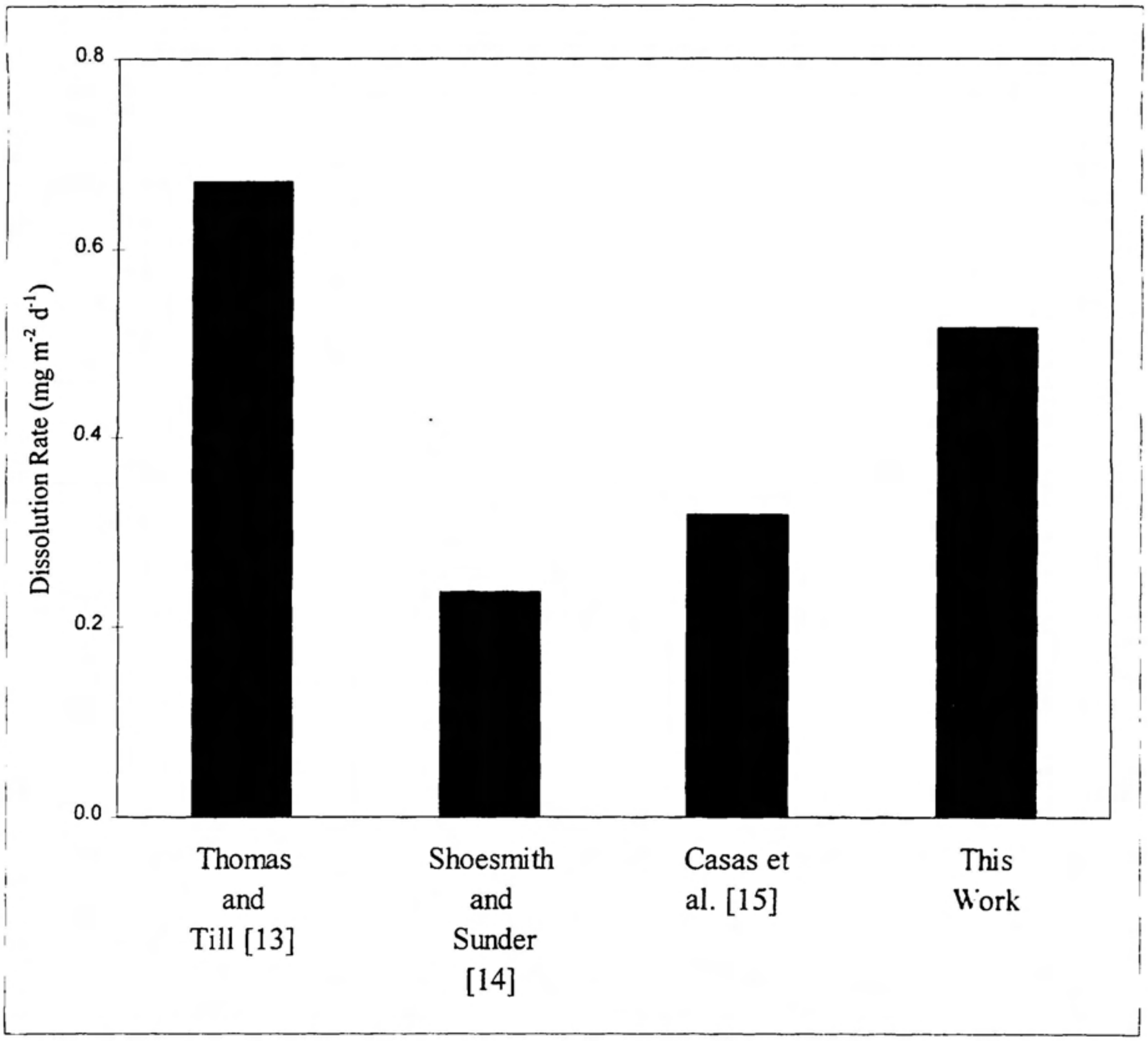

Figure 2: Comparison of dissolution rates of UO_2 fuel obtained by different workers in aerated, non-complexing, near neutral aqueous solutions at room temperature. The dissolution rates shown are for actual surface area of the fuel. Dissolution rates reported by Shoesmith and Sunder were obtained using electrochemical techniques [14], all other rates were obtained by the chemical analysis of the solution phase.