AECL EACL

CA9800247

AECL-11656

Corrosion of UN in Water

Corrosion du nitrure d'uranium dans l'eau

S. Sunder, N.H. Miller

October 1996 octobre

29-21

AECL EACL

CORROSION OF UN IN WATER

by

S. Sunder and N.H. Miller

Whiteshell Laboratories
Pinawa, Manitoba R0E 1L0
1996 October

AECL-11656

CORROSION OF UN IN WATER

by

S. Sunder and N.H. Miller

ABSTRACT

Corrosion of UN in water was investigated as a function of pH and temperature using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and by measuring the amount of ammonia formed due to its corrosion. The XPS results indicate that a freshly fractured surface of UN is quickly converted to UO_2 on exposure to liquid water or water vapours at ambient temperatures. These results show that UN is unstable in contact with water. The corrosion rate of UN is estimated to be $\geq 40\ \mu mol \cdot m^{-2} \cdot h^{-1}$ in deaerated water at ~92°C. There was no significant difference in corrosion rates measured in water at initial pHs of ~6 and ~10.3. These results contradict the literature reports stating that UN is stable in contact with boiling water. The implications of these results on the suitability of UN as a nuclear fuel for reactors are discussed.

Whiteshell Laboratories
Pinawa, Manitoba R0E 1L0
1996 October

AECL-11656

AECL EACL

CORROSION DU NITRURE D'URANIUM DANS L'EAU

par

S. Sunder et N.H. Miller

RÉSUMÉ

On a analysé la corrosion du nitrure d'uranium dans l'eau en fonction du pH et de la température en ayant recours à la spectroscopie de photoélectrons (XPS) et à la diffraction des rayons X, et en mesurant la quantité d'ammoniac produite. Les résultats de l'XPS indiquent qu'une surface de nitrure d'uranium récemment fracturée est transformée rapidement en UO_2 au contact de l'eau à l'état liquide ou de vapeur aux températures ambiantes. Ces résultats montrent que le nitrure d'uranium est instable au contact de l'eau. La vitesse de corrosion du nitrure d'uranium est évaluée à $\geq 40\ \mu mol \bullet m^{-2} \bullet h^{-1}$ dans l'eau dégazée à ~92 °C. Ces travaux n'ont permis de déceler aucune différence importante entre les vitesses de corrosion mesurées dans l'eau aux pH initiaux de ~6 et ~10,3. Ces résultats sont en contradiction avec la documentation scientifique où l'on énonce que le nitrure d'uranium est stable au contact de l'eau bouillante. On examine dans cette communication les conclusions qu'on peut tirer de ces résultats quant à l'utilisation éventuelle de ce matériau comme combustible nucléaire dans les réacteurs.

Laboratoires de Whiteshell
Pinawa (Manitoba) R0E 1L0
Octobre 1996

AECL-11656

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

Uranium mononitride, UN, has been considered as a potential fuel for advanced nuclear reactors (e.g., Dell et al. 1966, 1967; Sugihara and Imoto 1969; Matzke 1986, 1992; Richter and Sari 1991). It has a high melting point (~2850°C at 2.5 atm N_2 pressure (Dell et al. 1967)), high density (14.32 $g{\cdot}cm^{-3}$ (Bugl and Bauer 1964)) and high thermal conductivity. We are exploring its use as a fuel in advanced water-cooled reactors. Although UN has excellent nuclear properties, there are some uncertainties about its stability in contact with water. For example, several reports suggest that solid UN is stable in contact with liquid water, including boiling water (Sugihara and Imoto 1969), water at 300°C (Bridger et al. 1969), and water containing HCl, H_2SO_4 or NaOH (Sears 1970). On the other hand, several reports show that UN undergoes hydrolysis by superheated steam (Antill and Mayat 1966; Cragg et al. 1967; Dell et al. 1967; Sugihara and Imoto 1969; Rama Rao et al. 1991). It is essential to resolve this uncertainty about the stability of UN in aqueous environments if UN is to be considered as a fuel in a water-cooled reactor such as CANDU®. We have investigated the corrosion of UN in water using surface analytical techniques — X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) — in addition to monitoring the changes in the chemistry of water in contact with the UN samples. Results of these studies are reported here.

2. EXPERIMENTAL

2.1 MATERIALS

Uranium mononitride pellets were prepared at the Transuranium Institute, Karlsruhe, Germany. The pellets had a diameter of ~0.64 cm and a thickness of ~0.56 cm, and weighed about 2 g each. The pellets were black in colour, and polishing did not alter the colour. However, the colour of a freshly fractured surface was silver gray.

CANDU® is a registered trademark of Atomic Energy of Canada Limited (AECL).

The pellets used for XPS and XRD analysis and corrosion experiments were polished, using a 600-grit SiC paper, on all sides including the rim, to expose a fresh surface. The polishing was performed in an anaerobic chamber, to avoid surface oxidation by atmospheric oxygen, using deoxygenated water as a lubricant and dust collector. The water was purified using a Corning Mega-Pure System MP-3A. The pellets were stored in the anaerobic chamber, between different analyses, to minimize oxidation by atmospheric O_2.

Hydrolysis of UN by heated water vapour results in the formation of ammonia (Bridger et al. 1969), i.e.,

$$2UN + 4H_2O \rightarrow 2UO_2 + 2NH_3 + H_2 \qquad (1)$$

As ammonia is known to react with many metals to form complexes, we used glass vessels to conduct the corrosion tests so that we could monitor the formation of ammonia if the above reaction occurred in our experiments. Commercially available 25-mL Erlenmeyer flasks (Kimax, No. 26600, with ground glass joints (#16) to provide a greaseless seal) were used as the reaction vessels. The tops of the flasks were wrapped with parafilm (American National Can Company), to reduce evaporation for experiments conducted at room temperature.

The pH values of the solutions were measured using a Corning semi-micro combination pH electrode with a calomel reference and an Orion Research 601A pH meter. The electrode was calibrated using commercial buffers (obtained from Fisher) at pH 7 and 9.

The UO_2 disks used in the control experiments were obtained by cutting fuel pellets from an unused CANDU bundle.

2.2 CORROSION EXPERIMENTS

The UN pellets were weighed, before and after the experiments, to determine the changes in their weights during the corrosion experiments. The pellets were dried, before weighing, in an evacuated vacuum chamber and pumped for ~16 h.

Room-temperature experiments were conducted in an anaerobic chamber. Water (20 mL) was added to the reaction vessel containing a weighed pellet, and the vessel was sealed, as described above. The initial pH of the water was measured before adding it to the reaction vessel. At the end of the experiment (~1 or 2 weeks, Tables 1 and 2), the pellet was removed from the flask, dried and weighed. The pH of the solution was measured, and the solution was analyzed for NH_3 and U. Control experiments were conducted using UO_2 pellets in place of UN pellets, and without any pellets (Table 1). All experiments were conducted in duplicate.

To determine the effects of higher temperatures on UN corrosion, experiments were also conducted at 92°C. The reaction vessel was assembled and sealed in the anaerobic chamber, as described above, for the room-temperature experiments. The tops of the flasks were wrapped with Teflon tape for these experiments. The sealed vessel was placed in a heated sand bath in an oven at 92°C. At the end of the experiment, the vessel was taken out of the oven, allowed to cool to room temperature and brought into the anaerobic chamber for the retrieval of the pellet and the solution for analyses. Note that two sets of the high-temperature (92°C) corrosion experiments, (B1, B2; and C1, C2), were conducted using the pellets used in the preceding experiments without repolishing, Table 1. Pellets used in experiments B1 and B2 were from experiments Al and A2, and those in experiments C1 and C2 were from experiments B1 and B2, respectively, without repolishing.

High-temperature experiments were conducted in "pure water" and in water at an initial pH of 10.3, a value close to that for CANDU reactor primary coolant (Hemmings and Barber 1975). The higher pH was obtained by adding dilute LiOH solution, the chemical used to control CANDU coolant pH.

2.3 MEASUREMENT OF AMMONIA FORMED

For ammonia analysis, an aliquot (10 mL) of solution was transferred from the reaction vessel into a sample vial at the end of the experiment. The aliquot was acidified, by adding a small amount (0.0689 mL) of dilute (0.35 N) sulfuric acid, to retain ammonia in the solution. The concentration of ammonia was determined using a colorimetric method known as the "phenate method" (Clesceri et al. 1989). The method is based on the fact that an intensely blue compound, indophenol, is formed by the reaction of ammonia with hypochlorite and phenol. Concentration of the ammonia was determined by measuring absorption at 635 nm using a 1-cm cell and a Hach DR/3000 Spectrophotometer.

2.4 MEASUREMENT OF URANIUM DISSOLVED

After the sample for ammonia analysis was removed, the solution remaining in the vessel was used for uranium analysis. The volume of the remaining solution was measured, and a small amount (0.1 mL) of concentrated nitric acid was added to dissolve uranium colloids and keep the uranium in the solution. The concentration of uranium in the aqueous phase was determined by the standard addition method, using FLURAN (a buffered inorganic complexing agent) and the Scintrex Fluorescence Uranium Analyzer, Model UA-3 (Scintrex 1985).

2.5 X-RAY PHOTOELECTRON SPECTROSCOPY

The XPS spectra were obtained using a PHI-5300 ESCA system. A sample was mounted on an XPS specimen holder in the inert atmosphere chamber and was held on the specimen holder using copper clips. The sample was transferred from the inert atmosphere chamber to the evacuated compartment of the spectrometer without exposure to air, using a PHI vacuum transfer vessel (Sunder et al. 1990, 1992). The XPS spectra were excited using Mg Kα radiation filtered through an aluminum window. The energy scale of the spectrometer was calibrated using the line positions of the following noble metals: Au $4f_{7/2}$, 84.0 eV; Ag $3d_{5/2}$, 368.3 eV; and Cu $2p_{3/2}$, 932.56 eV (Wagner et al. 1979; McIntyre et al. 1981; Moulder et al. 1992).

2.6 X-RAY DIFFRACTION

X-ray diffraction (XRD) patterns of the UN pellets were obtained using a Rigaku Rotaflex X-ray diffractometer, equipped with a 12-kW rotating-anode Cu Kα X-ray source and a diffracted-beam graphite monochromator. The pellets were mounted in the sample compartment of the diffractometer using a brass holder, designed to accommodate a polycrystalline coupon as opposed to a powder sample. The diffractometer was calibrated using a silicon standard from the U.S. National Bureau of Standards (NBS)[1]. The diffractometer scanning rate was 1 min^{-1}. The data were acquired using a Rigaku IBM PC (Version 3.0, June 1992) data acquisition system and were analyzed using JADE+ software obtained from Material Data Inc. of Livermore, CA.

3. RESULTS AND DISCUSSION

3.1 X-RAY PHOTOELECTRON SPECTROSCOPY

Low-resolution survey spectra were recorded for the 0- to 1100-eV region to determine the elements present in the sample surface. High-resolution spectra were recorded for the U 4f, N 1s, O 1s and C 1s and the valence band region (0 to 20 eV) to determine the chemical state of these elements.

The XPS spectra of the as-received UN pellets showed strong peaks for C and O, but U peaks were very weak. N peak (N 1s) was not unambiguously seen in these spectra (see below). The pellets were polished (using 600-grit SiC) to remove the "impurity" layer, which may have been masking the U signal from UN; however, this increased only slightly the intensity of the U peaks. Therefore, one face of a UN pellet was subjected to aggressive polishing, using 1-µm Al_2O_3 powder, to remove the impurity layer. Although the aggressive polishing slightly increased the intensity of the U peaks, they were still quite weak. A significant increase in the U signal was achieved by recording the spectrum of a "fresh surface" obtained by fracturing a UN pellet in the anaerobic chamber. Figure 1 shows the survey spectra of a freshly fractured surface of a UN

---

[1] The present name of the NBS is National Institute of Standards and Technology (NIST).

pellet. Although the U/C signal ratio in this spectrum is still quite low, it is higher by a factor of >10 than that observed in the spectrum of a freshly polished UN pellet. The presence of strong C peaks in the XPS spectra of the polished and fractured UN pellets suggests that the carbon impurity is probably present in the pellets, and not only on the surface. Note that the fracturing does not remove the carbon impurity but prevents it from spreading on the surface (used for XPS analysis) and masking the UN signal. (A weak band, seen at about 338 eV, Figure 1b, is Cu LVV feature from the copper clips.)

Figure 2 compares the XPS spectrum for the region between 370 and 410 eV of a freshly fractured UN pellet with that of a freshly polished UN pellet. This region includes the U 4f level bands, the strongest bands of U (Moulder et al. 1992). The spectrum of a freshly polished UO_2 pellet, recorded under the same conditions, is also shown in this figure for comparison purposes. The peak maxima of the U 4f bands, shown in Figure 2, are listed in Table 3. This table also contains the literature values for the binding energies (BE) of these bands in UN and UO_2. There are two reports on the XPS spectra of the core level (U 4f) bands of UN. Both reports suggest that the BE of the U 4f bands in UN are lower than the corresponding bands in UO_2, by 1.2 eV according to Thibaut et al. (1979), and by ~2.7 eV according to Norton et al. (1980). (The literature spectra of UN were obtained from a surface obtained by fracturing and scraping a single crystal of UN in an ultra-high vacuum.) The binding energies observed for the UN pellets (Figure 2, Table 3) suggest that these pellets (polished or freshly fractured) are covered with a layer of UO_2. This suggests that UN reacts with liquid water (used in polishing) and water vapours (present in the anaerobic chamber atmosphere), at ambient temperatures, to form a UO_2 layer detectable by XPS. Note that fracturing of the pellet should produce a fresh UN surface. The UO_2 seen on the fractured surface most probably arises from a reaction of UN with water vapour. The reaction with O_2 is expected to be less important as the concentration of O_2 in the anaerobic chamber atmosphere is much less (~1 ppm) than that of H_2O.

The bandwidths that were observed for the U 4f bands in the spectra of the UN pellet, Figures 2a and 2b, are larger than those that had been observed for the corresponding UO_2 bands (Figure 2c). This indicates that the bands in the spectrum of the freshly fractured (or polished) UN pellet probably contain contributions from two or more uranium species. We believe that the larger bandwidths seen for the UN pellets are due to contributions not only from the UO_2 film (formed by the reaction of UN with water) but also from the underlying UN.

Figure 3 shows the curve resolution of the U $4f_{7/2}$ band in the spectrum of the fractured UN pellet into UO_2 and UN components. This resolution was carried out (after charge correcting and removing the contributions of the X-ray satellites) using a binding energy value of 379.8 ± 0.4 eV for UO_2 and of 377.9 ± 0.4 eV for UN. The binding energy value used for the UN is a mean of the two literature values for this band, Table 3. The analysis shown in Figure 3 indicates that ~30% of the intensity of the U $4f_{7/2}$ band in the spectrum of the fractured UN pellet arises from UN, and the remainder from UO_2. The presence of the UN signal suggests that the UO_2 layer formed on the surface of the freshly fractured UN pellet by its reaction with water vapour is thin, i.e., <3 nm. (This assumes a homogeneous surface layer of UO_2, instead of islands of UO_2, on UN surface (Rama Rao et al. 1991).) Note that there is no indication of the presence of any U(VI) species in the XPS spectra (for the U 4f region) of either the freshly polished or fractured UN pellets.

Figure 4 shows the spectrum of the O 1s band of the freshly fractured UN pellet. The oxygen signal is most probably from the UO_2 formed by the reaction of UN with the water vapours. This band has been resolved into H_2O, OH^- and O^{2-} components, according to the procedure discussed elsewhere (McIntyre et al. 1981; Sunder et al. 1992). (The H_2O, OH^-, and O^{2-} peaks in Figure 4 are at about 534.5 eV, 531.5 eV, and 529.3 eV, respectively.) This analysis shows that the intensity of the O 1s band arises mainly from the O^{2-} and OH^- moieties.

The strongest band of nitrogen in the XPS spectrum (N 1s) occurs at around 398 eV (Wagner et al. 1979; Moulder et al. 1992). The N 1s band is quite weak; its relative atomic sensitivity is lower than that of the U $4f_{7/2}$ band by a factor of about 15 (Wagner et al. 1979), and it occurs in the spectral region where both UN (Thibaut et al. 1979) and UO_2 (Verbist et al. 1976; Beatham et al. 1980) have satellite peaks. (The UO_2 shakeup satellite peaks can be seen at about 386.6 eV and 397.3 eV in its spectrum, c in Figure 2.) Therefore, it is difficult to locate the N 1s band unambiguously in the spectra of UN pellets. One can see a hint of the N 1s band in the spectrum of the fractured pellet of UN (a in Figure 2).

Figure 5 compares the spectrum for the valence band region (0-20 eV) of a freshly fractured UN pellet with that of a freshly polished UO_2 pellet. The spectrum of the UO_2 pellet shows a sharp band at ~1.2 eV. This band is assigned to the presence of valence electrons (U 5f) in UO_2 (Norton et al. 1980; McIntyre et al. 1981; Veal and Lam 1982; Allen et al. 1987). This band is less distinct in the spectrum of UN at room temperature (Rehl et al. 1982). The work of Norton et al. (1980) shows a band just above E_f (the Fermi level) for UN. This band is very weak in the spectrum of the freshly fractured (or polished) UN pellet. We believe that the near absence of the U 5f band in the spectrum of the fractured pellet is probably due to the fact that the spectrum in this region has significant contributions not only from the UO_2 film (suggested by the U 4f region spectrum) but also from the underlying UN. Note that the XPS signal in this region would arise from a "thicker layer" of the sample than that in the U 4f region, which is due to the higher kinetic energy (KE) of the photoelectrons in the valence region, i.e., ~1250 eV vs. ~860 eV. The mean free-path of electrons, with a KE of 1250 eV, is higher than those with a KE of 860 eV (Briggs and Seah 1983). Therefore, the contribution of UN, under the UO_2 film, is probably greater in the valence band region than that in the U 4f region.

3.2 X-RAY DIFFRACTION

The XRD patterns, for the 2θ range between 10° and 120°, were recorded for freshly polished UN pellets and for corroded UN pellets. Comparison of the observed X-ray diffraction pattern of the freshly polished UN pellets, Figure 6, with the literature patterns for UN (File #32-1397 of ICDD, 1994) showed that all major observed XRD peaks can be accounted by the pattern reported for UN. Computer analyses of the observed patterns also showed that the UN is the main phase in the polished pellets. UO_2 was seen as a trace impurity in the XRD patterns of the freshly polished UN pellets. No carbon compound was indicated by the XRD data. Therefore, we believe that the impurity giving rise to the strong C signal in the XPS spectra (Section 3.1) is present as an amorphous phase or as a thin adventitious surface layer.

The XRD results show that the UN pellets contain only a few weight percent of UO_2. Therefore, the UO_2 film on the surface of the freshly polished UN pellet, as indicated by XPS, most likely arose from its reaction with water. Note that the thickness of the sample analyzed in XPS is ~3 nm compared to ~3 µm in XRD. The XRD analysis of pellets corroded at room temperature did not show any significant increase in the thickness of the UO_2 layer. Figure 7 shows XRD pattern for a UN pellet corroded at 90°C for about a week, Experiment D1, Table 1. Formation of trace amounts of U_3O_7, and U_2N_3, in addition to a slight increase in the UO_2 signal, was indicated by the XRD patterns of the UN pellets corroded at ~90°C. There is also an indication of a very small trace of UO_3 and UN_2 in the XRD patterns of the pellets corroded at ~90°C. Formation of these phases (except that of U_3O_7) has been reported during the reactions of UN with super-heated steam or O_2 (Bridger et al. 1969; Rama Rao et al. 1991; Sood et al. 1993).

3.3 VISUAL OBSERVATIONS

Small gas bubbles formed on the UN pellets within 5 min of the addition of water to the reaction vessel in the room-temperature experiments. The bubbles escaped from the surface, at a very slow rate (a few per day), when they reached a diameter of about 1 to 2 mm. No noticeable change in the pellets was observed during these experiments.

Similar visual observations could not be made during the high-temperature experiments. Some of the water was lost due to evaporation during the high-temperature experiments, Table 2.

3.4 WEIGHT CHANGES AND URANIUM CONCENTRATIONS

Table 2 lists the changes in the weight of the UN pellets during the corrosion experiments. A decrease in the pellet weight was observed in all experiments, except one. A slight increase in weight should occur when UN is converted to UO_2 (reaction (1)). The decrease in the pellet weights indicates that some of the uranium oxide formed during the corrosion reactions is lost to the solution. This conclusion is supported by the increase in the uranium concentration in the aqueous phase, Table 2.

3.5 AMMONIA CONCENTRATIONS

Table 2 also lists the concentration of ammonia in the aqueous phase at the end of each experiment. These results show that detectable amounts of ammonia are formed, even at room temperature, during the corrosion of UN pellets in water. The uncertainty in ammonia measurements is estimated to be 40 µg/L, the concentration of ammonia in the control experiments without a UN pellet (A3 to A8, Table 2).

3.6 CORROSION RATES

We have calculated the corrosion rate of the UN from the concentration of ammonia seen in the aqueous phase according to reaction 1 and using the geometric area of the pellets, Table 2. We estimate the corrosion rate to be approximately 3 $\mu mol \cdot m^{-2} \cdot h^{-1}$ for UN in de-aerated water at ambient temperature, and ≥40 $\mu mol \cdot m^{-2} \cdot h^{-1}$ at 92°C.[#] These results are in conflict with the literature reports that claim that UN is stable in water under the conditions of the present experiments, e.g., Sugihara and Imoto (1969), Bridger et al. (1969). Our results show that UN reacts with water, even at ambient temperatures, to form a layer of UO_2. One possible explanation for the discrepancy between the results presented here and these literature reports is that the samples used in their experiments may have had coatings of UO_2. The XPS results, discussed above, show that UN pellets are covered by UO_2 by exposure to water vapour even at ambient temperature. Exposure to O_2 also results in the oxidation of a fresh surface of UN (e.g., Ikawa and Taketani 1970). It is well known that UO_2 has very low solubility in water (Parks and Pohl 1988; Grenthe et al. 1992; Shoesmith et al. 1994). Therefore, a UN sample covered with a UO_2 layer may appear unreactive in water.

In order to evaluate the potential of UN as a nuclear fuel, the corrosion rate of UN may be compared with that of U metal or other uranium compounds that are of interest as nuclear fuel.

[#] The geometric surface area of the pellets used in the rate calculations is 1.76 cm^2. We have not used the corrosion rates from experiments B1 and B2 to arrive at this rate. These rates are estimated to be the lower limit of the corrosion rates as some ammonia is lost during the experiments at ~90°C by evaporation, as indicated by a decrease in the final volume of the solution.

For U metal, we estimate a corrosion rate of ~0.12 $mol{\cdot}m^{-2}{\cdot}h^{-1}$ in water at 100°C (from Figure 3 in a report by Bourns (1968)). For uranium silicide, we estimate a corrosion rate of between ~4 $nmol{\cdot}m^{-2}{\cdot}h^{-1}$ and ~400 $nmol{\cdot}m^{-2}{\cdot}h^{-1}$ at ~100°C (Bourns 1967). (Note that U_3Si is used as fuel in research reactors which operate at lower temperatures than conventional power reactors.) Thus the corrosion rate for UN is much lower than that for U metal but higher than that of uranium silicide. The high corrosion rates of UN in water (at ~92°C) indicate that UN is not stable in the hot aqueous environment that a failed fuel bundle would encounter in a water-cooled reactor. See Appendix IV in a report by Bourns (1968) for a discussion of the tolerable corrosion rates of a fuel for use in a reactor.

4. SUMMARY AND CONCLUSIONS

The corrosion of UN in water was investigated at room temperature (~23°C) and at 92°C. Our studies show that UN quickly reacts with water and water vapour, yielding a UO_2 film on the uranium nitride specimens. The corrosion rate of UN in water increases with an increase in temperature. The corrosion rate of UN in water is estimated to be about 3 $\mu mol{\cdot}m^{-2}{\cdot}h^{-1}$ at ambient temperature and ≥ 40 $\mu mol{\cdot}m^{-2}{\cdot}h^{-1}$ at 92°C. Thus the use of UN as a fuel in water-cooled fission reactors is problematic. Also, "used UN fuel" will be a poor waste-form for permanent disposal in a geological disposal vault similar to that envisaged in the Canadian Nuclear Waste Management Program, because of its reactivity in an aqueous environment. Uranium mononitride may be a good fuel for a reactor that uses a non-aqueous coolant (one unreactive with UN) and is operated with a reprocessing option for the final disposal of its used fuel.

ACKNOWLEDGEMENTS

We thank Hj. Matzke for providing the UN pellets, and I. Muir, P. Taylor and R. Verrall for helpful discussions and comments on this report. Technical assistance provided by D.C. Doern for recording the XRD data is acknowledged.

REFERENCES

Allen, G.C., P.A. Tempest and J.W. Tyler. 1987. Oxidation of crystalline UO_2 studied using X-ray photoelectron spectroscopy and X-ray diffraction. Journal of the Chemical Society, Faraday Transactions I, 83, 925-935.

Antill, J.E. and B.L. Myat. 1966. Corrosion Science 6, 17-23.

Beatham, N., A.F. Orchard and G. Thornton. 1980. On the photoelectron spectra of UO_2. Journal of Electron Spectroscopy and Related Phenomena 13, 205-211.

Bourns, W.T. 1967. A literature survey of U_3Si corrosion. Atomic Energy of Canada Limited Report, AECL-2609.

Bourns, W.T. 1968. Corrosion testing of uranium silicide fuel specimens. Atomic Energy of Canada Limited Report, AECL-2718.

Bridger, N.J., R.M. Dell and V.J. Wheeler. 1969. Oxidation and hydrolysis of uranium and plutonium nitrides. In Reactivity in Solids, Proceedings of an International Symposium (J.W. Mitchell, editor), Wiley-Interscience, New York, NY, 389-400.

Briggs, D. and M.P. Seah (editors). 1983. Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy. J. Wiley & Sons, Chichester.

Bugl, J. and A.R. Bauer. 1964. Phase relations in the system uranium-nitrogen. Journal of American Chemical Society 47, 425-429.

Clesceri, L.S., A.E. Greenberg and R.R. Trussell. 1989. 4500-NH_3 D.Phenate method for ammonia analysis. In Standard Methods for the Examination of Water and Wastewater, 17th Edition, American Public Health Association, Washington, 4-120, 4-121.

Cragg, D.G., R.J. Dicker, J.D.L. Harrison, J.W. Isaacs, J.R. McLaren and W.G. Roberts. 1967. Reaction of oxygen and of water vapor at low concentration with UN, UC and (UPu) $C_{1-x}O_x$. Bullétin des Sociétés Françaises Ceramiques No. 77, 35-49.

Dell, R.M., V.J. Wheeler and E.J. McIver. 1966. Oxidation of uranium mononitride and uranium monocarbide. Transactions of the Faraday Society 62(12), 3591-3606.

Dell, R.M., V.J. Wheeler and N.J. Bridger. 1967. Hydrolysis of uranium mononitride. Transactions of the Faraday Society 63(5), 1286-94.

Grenthe, I., J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung and H. Wanner. 1992. Chemical Thermodynamics of Uranium, Volume 1, Chemical Thermodynamics (H. Wanner and I. Forest, editors). North Holland, Amsterdam.

Hemmings, R.L. and D. Barber. 1975. Design to nullify activity movement in heat transport systems. In Activity Transport in CANDUs, Atomic Energy of Canada Limited Report, AECL-5113.

ICDD. 1994. Powder diffraction files. International Center for Diffraction Data, Newton Square, PA, U.S.A.

Ikawa, K. and K. Taketani. 1970. Room temperature oxidation of uranium nitride powder. Journal of Nuclear Science and Technology 7(9), 433-8.

Matzke, H. 1986. Science of Advanced LMFBR Fuels. North Holland, Amsterdam, Holland.

Matzke, H. 1992. Radiation damage in nuclear materials. Nuclear Instruments and Methods in Physics Research, Section B B65, 30-39.

McIntyre, N.S., S. Sunder, D.W. Shoesmith and F.W. Stanchell. 1981. Chemical information from XPS - Applications to the analysis of electrode surfaces. Journal of Vacuum Science and Technology 18, 714-721.

Moulder, J.F., W.F. Stickle, P.E. Sobol and K.D. Bomben. 1992. Handbook of X-ray Photoelectron Spectroscopy (J. Chastain, editor). Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, U.S.A.

Norton, P.R., R.L. Tapping, D.K. Creber and W.J.L. Buyers. 1980. Nature of the 5f electrons in uranium nitride: A photoelectron spectroscopic study of UN, U, UO_2 ThN and Th. Physical Review B 21, 2572-2577.

Parks, G.A. and D.C. Pohl. 1988. Hydrothermal solubility of uraninite. Geochimica et Cosmochimica Acta 52, 863-875.

Rama Rao, G.A., S.K. Mukerjee, V.N. Vaidya, V. Venugopal and D.D. Sood. 1991. Oxidation and hydrolysis kinetic studies on UN. Journal of Nuclear Materials 185(2), 231-241.

Rehl, B., G. Hollinger and F.H. Himpsel. 1982. Angle-resolved photoemission and temperature dependence of 5f electronic states in uranium nitride. Journal of Magnetism and Magnetic Materials 29, 303-304.

Richter, K. and C. Sari. 1991. Investigation of the operational limits of uranium-plutonium nitride fuels. Journal of Nuclear Materials 184(3), 167-176.

Scintrex. 1985. Analytical Measurements and Instruments. Analytical Procedure for UA-3 Uranium Analysis, Application Brief 79-2, Concord, ON, Canada.

Sears, M.B. 1970. Reactions of uranium carbonitrides and uranium nitride with aqueous solutions of hydrochloric, sulfuric and nitric acids. Journal of Inorganic and Nuclear Chemistry 32, 2971-84.

Shoesmith, D.W., S. Sunder and W.H. Hocking. 1994. Electrochemistry of UO_2 nuclear fuel. In Electrochemistry of Novel Materials (J. Lipkowski and P.N. Ross, editors), VCH Publishers Inc., New York, NY, 297-337.

Sood, D.D., V. Venugopal, S.K. Mukerjee and V.N. Vaidya. 1993. Uranium nitride - Its preparation, oxidation and vaporization. Metal Materials and Processing 5, 13-22.

Sugihara, S. and S. Imoto. 1969. Hydrolysis of uranium nitrides. Journal of Nuclear Science and Technology 6, 237-42.

Sunder, S., G.D. Boyer and N.H. Miller. 1990. XPS studies of UO_2 oxidation by alpha radiolysis of water at 100°C. Journal of Nuclear Materials 175, 163-169.

Sunder, S., J.J. Cramer and N.H. Miller. 1992. X-ray photoelectron spectroscopic study of Cigar Lake uranium ore: A natural analog for used fuel. Materials Research Society Symposium Proceedings 257 (Scientific Basis for Nuclear Waste Management, XV), 449-457.

Thibaut, E., J. Verbist and R. Troc. 1979. Shape-up satellites in the U 4f ESCA spectra of NaCl-type uranium monocompounds: UN, UP, UAs and US. Journal de Physique 40, C4/77-C4/78.

Veal, B.W. and D.J. Lam. 1982. Photoemission spectra. In Gmelin Handbook of Inorganic Chemistry, Uranium, Supplement Volume A5, 8th Edition, Springer-Verlag, Heidelberg, 176-196.

Verbist, J.J., J. Riga, C. Tenret-Noel, J.J. Pireaux, G. d'Ursel, R. Caudano and E.G. Derouane. 1976. Bonding and valence in uranium compounds with oxygen: A study by X-ray photoelectron spectroscopy and electron paramagnetic resonance. In Plutonium and Other Actinides (H. Blank and R. Lindner, editors), North-Holland, Amsterdam, 409-419.

Wagner, C.D., W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg. 1979. Handbook of X-ray Photoelectron Spectroscopy. Perkin-Elmer, Eden Prairie, MN, U.S.A.

TABLE 1

UN CORROSION IN WATER: SUMMARY OF EXPERIMENTAL PARAMETERS

Experiment Number	Sample[a]	Temperature (°C)	Time (h)	pH	
				Initial	Final
A1	UN (1)	23	168	5.48	4.99
A2	UN (2)	23	168	5.48	5.30
A3	≠	23	168	5.48	4.88
A4	≠	23	168	5.48	5.36
A5	≠	23	168	5.48	5.04
A6	≠	23	168	5.48	4.94
A7	UO_2 (1)	23	168	5.48	5.11
A8	UO_2 (2)	23	168	5.48	5.13
B1	UN (1)	92	164	5.65	5.37
B2	UN (2)	92	164	5.53	5.32
C1	UN (1)	92	334	5.84	8.02
C2	UN (2)	92	334	5.84	5.76
D1	UN (1)	90	141	10.28	8.46
D2	UN(2)	90	141	10.28	8.40

[a] Number in parentheses denotes the pellet number. All pellets were freshly polished, except in experiments B1, B2, C1 and C2 (see text).

≠ No sample, just water.

TABLE 2

UN CORROSION IN WATER: SUMMARY OF EXPERIMENTAL RESULTS

Experiment Number	Sample[a]	Weight			Final Volume (mL)	(U) (µg/L)	(NH3) (µg/L)	Corrosion Rate (µmol•m^{-2}•h^{-1})
		Initial (g)	Final (g)	Change (mg)				
A1	UN (1)	1.88771	1.88760	-0.11	20.0	2160	125	5
A2	UN (2)	1.98689	1.98670	-0.19	20.0	2030	65	2
A3	≠				20.0	6	50	
A4	≠				20.0	12	40	
A5	≠				20.0	18	40	
A6	≠				20.0	9	50	
A7	UO_2 (1)				20.0	341	35	
A8	UO_2 (2)				20.0	764	35	
B1	UN (1)	1.88755	1.88715	-0.40	16.0	361	180	6
B2	UN (2)	1.98667	1.98628	-0.39	17.6	2470	400	14
C1	UN (1)	1.88715	1.88671	-0.44	17.4	1180	2530	44
C2	UN (2)	1.98628	1.98647	0.19	13.7	2550	3410	46
D1	UN (1)	1.86116	1.86091	-0.25	19.0	510	1180	53
D2	UN (2)	1.95614	1.95569	-0.45	17.0	1110	1140	46

[a] Number in parentheses denotes the pellet number. All pellets were freshly polished, except in experiments B1, B2, C1 and C2 (see text).

≠ No sample, just water.

TABLE 3

BINDING ENERGIES FOR THE U 4f BANDS IN THE XPS SPECTRA OF UN AND UO_2

Sample	U $4f_{7/2}$ (eV)	U $4f_{5/2}$ (eV)	Note
UN	378.4	389.2	a
"	377.3	388.0	b
UO_2	379.6	390.4	c
"	380.2	390.8	b
Polished UN Pellet	379.4	390.3	d
Fractured UN Pellet	379.4	390.2	d
Polished UO_2 Pellet	379.8	390.6	e

a Calculated from the results given by Thibaut et al. (1979) and Verbist et al. (1976).

b Measured from Figure 3 of Norton et al. (1980).

c From Verbist et al. (1976).

d UN sample covered with UO_2 film (see text, section 3.1).

e UO_2 was from an unused CANDU fuel pellet.

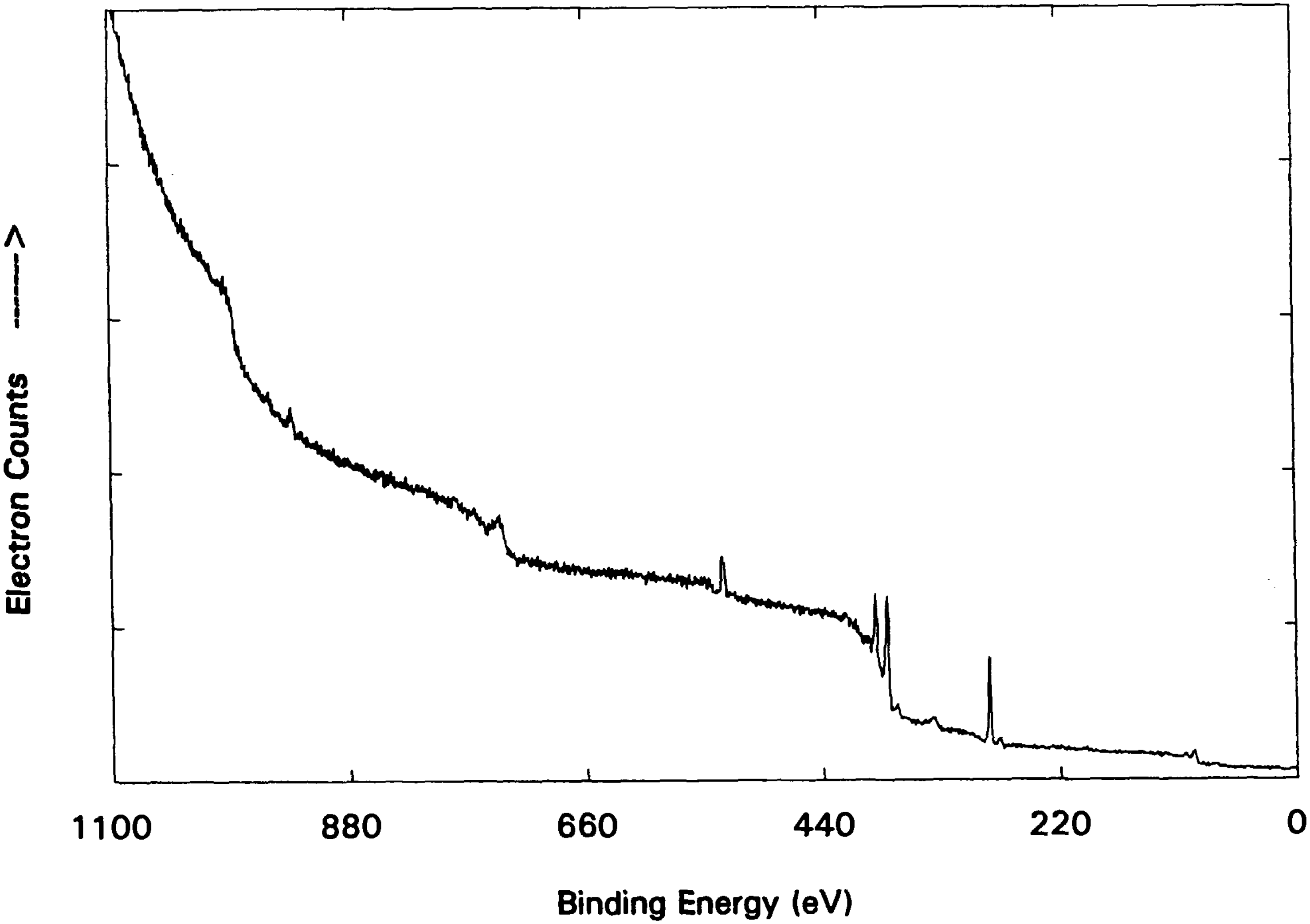

FIGURE 1a: Survey XPS Spectrum of a Freshly Fractured UN Pellet for the Region Between 0 to 1100 eV

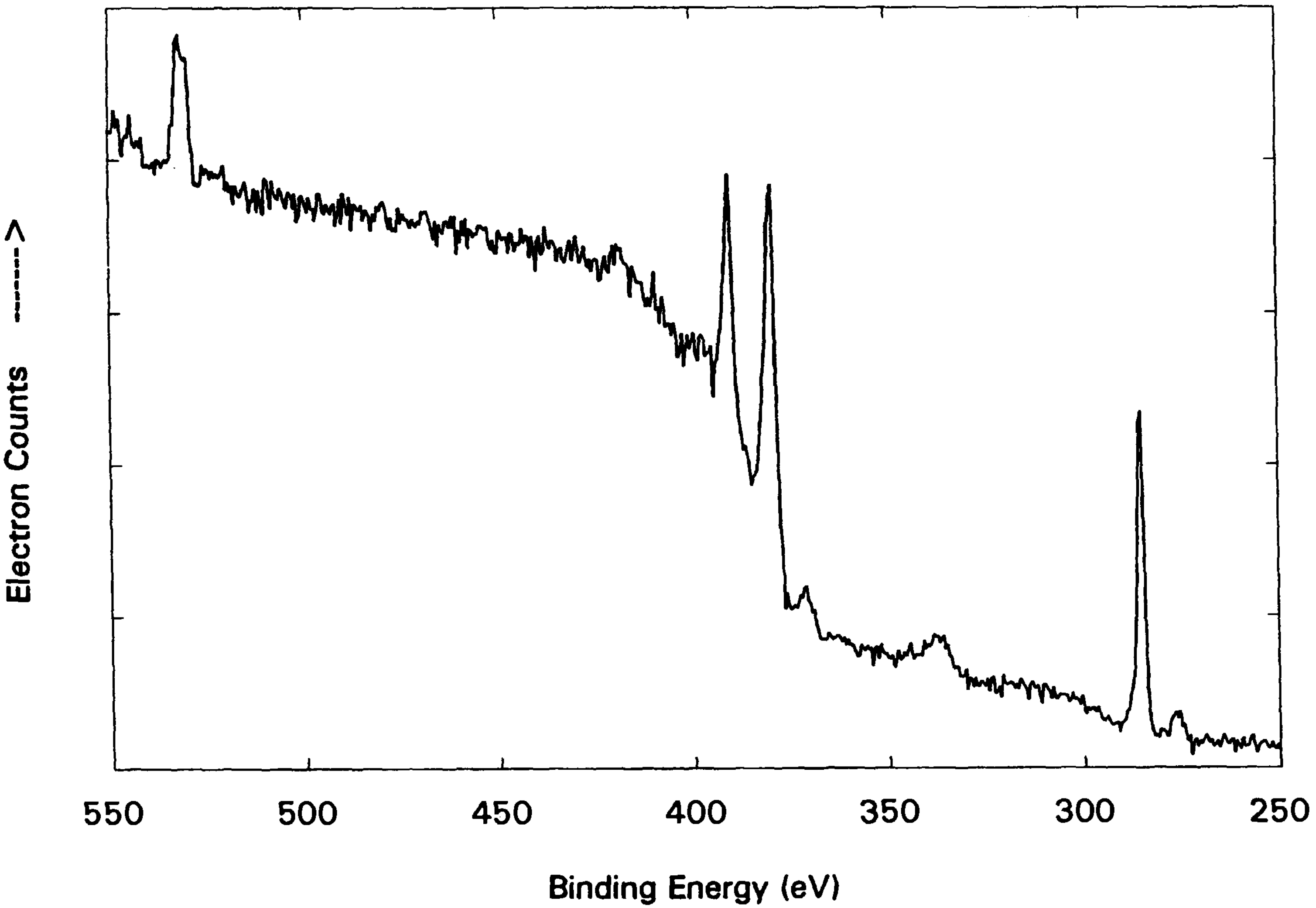

FIGURE 1b: Survey XPS Spectrum of a Freshly Fractured UN Pellet for the Region Between 250 to 550 eV

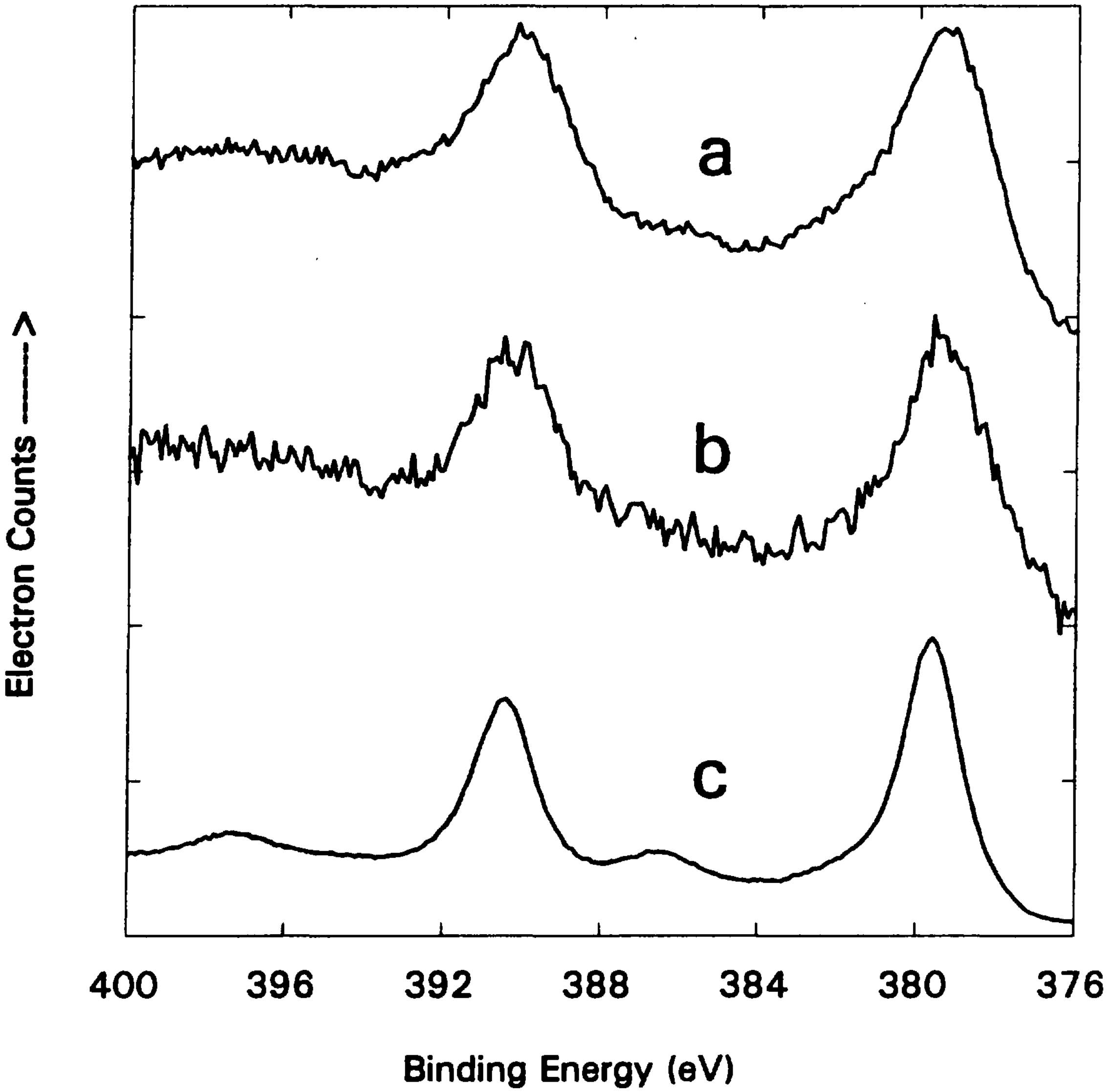

FIGURE 2: XPS Spectra for the U 4f Region of (a) a Freshly Fractured UN Pellet; (b) a Freshly Polished UN Pellet; and (c) a Freshly Polished UO_2 Pellet

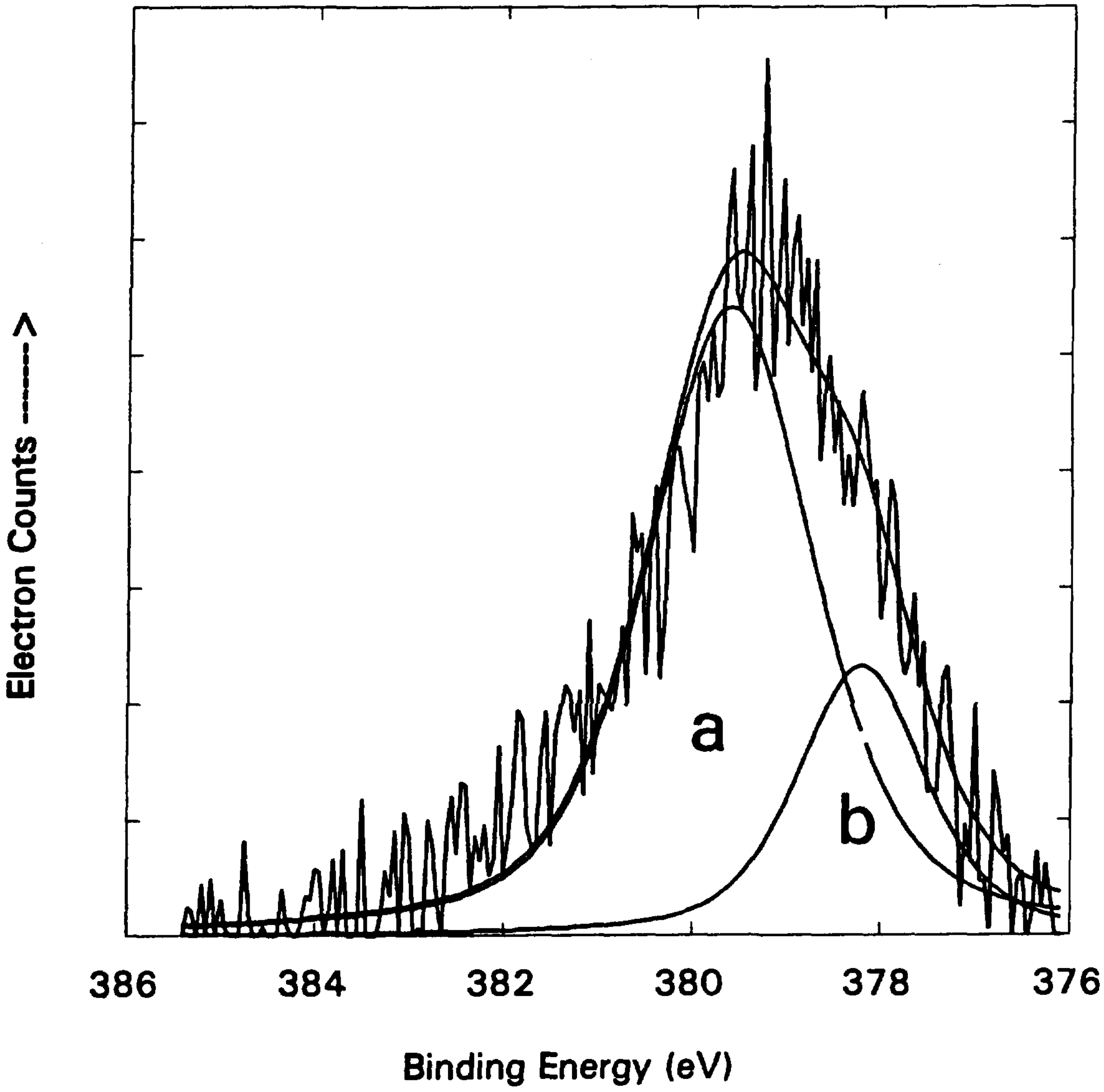

FIGURE 3: Resolution of the U $4f_{7/2}$ Band Seen in the XPS Spectrum of a Freshly Fractured UN Pellet into (a) UO_2, and (b) UN Components

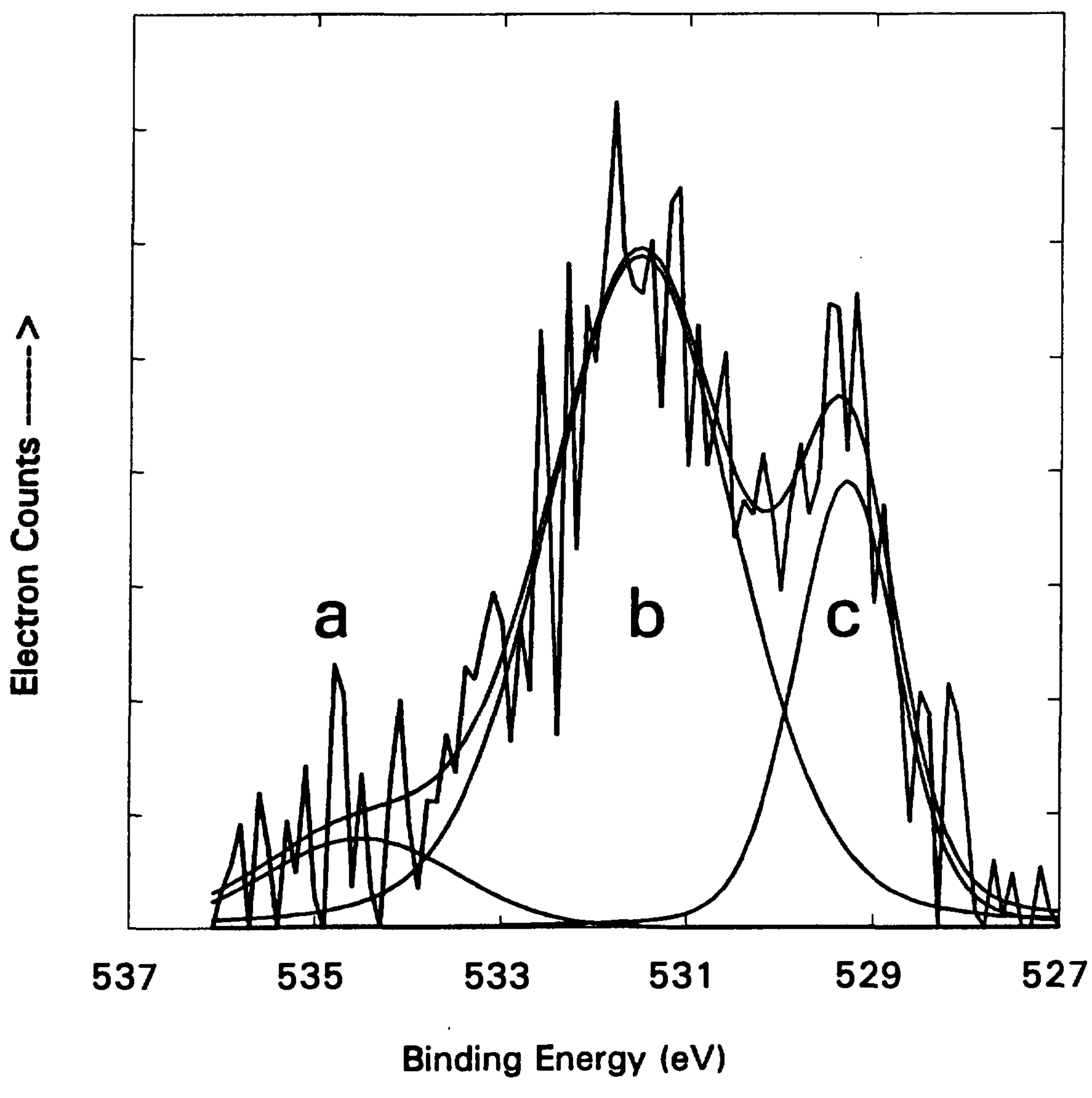

FIGURE 4: XPS Spectrum of a Freshly Fractured UN Pellet for the O 1s Region. The band has been resolved into (a) H_2O, (b) OH^-, and (c) O^{2-} components.

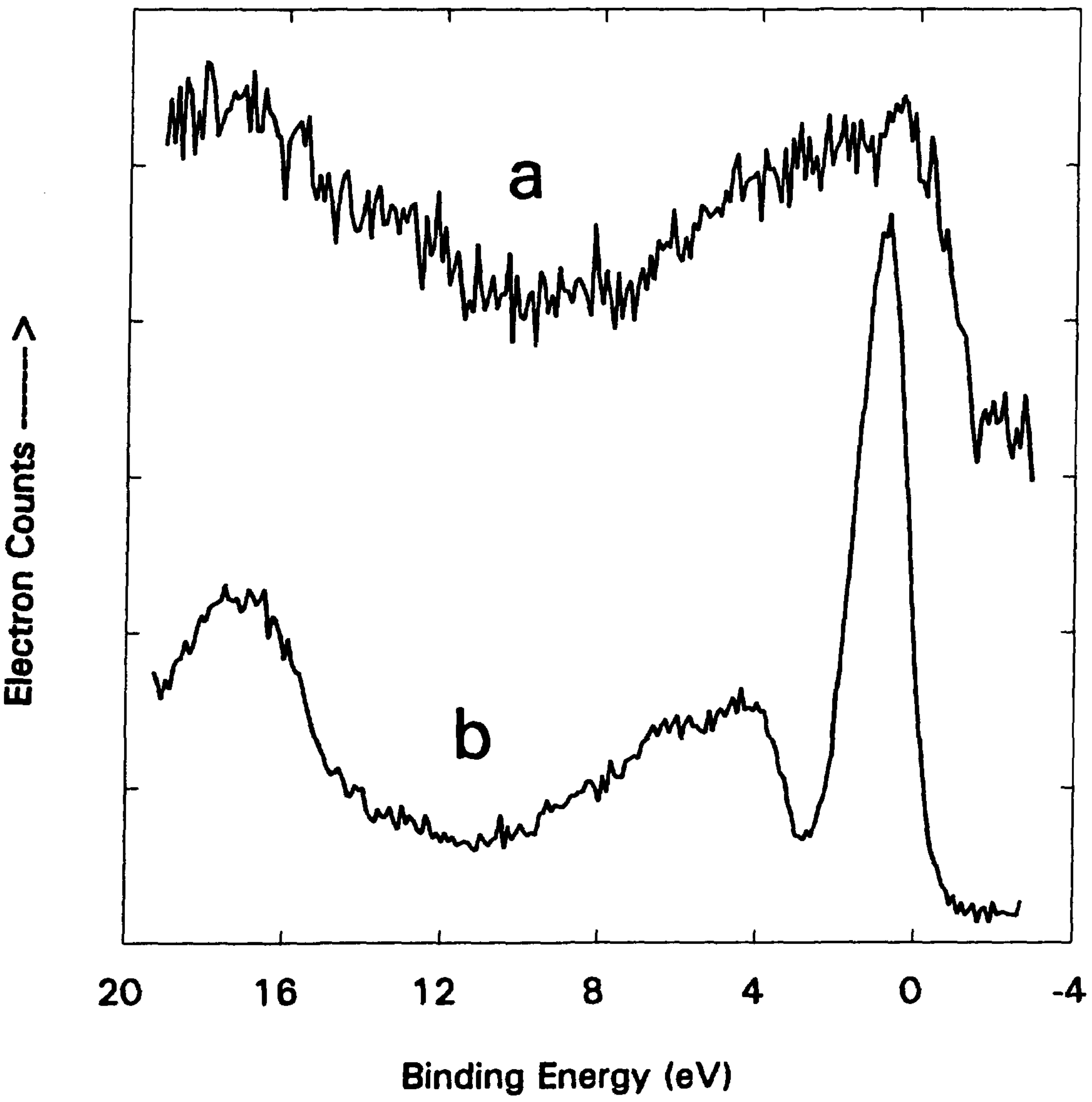

FIGURE 5: Valence Band Region in the XPS Spectra of (a) a Freshly Fractured UN Pellet (top), and (b) a Freshly Polished UO_2 Pellet (bottom)

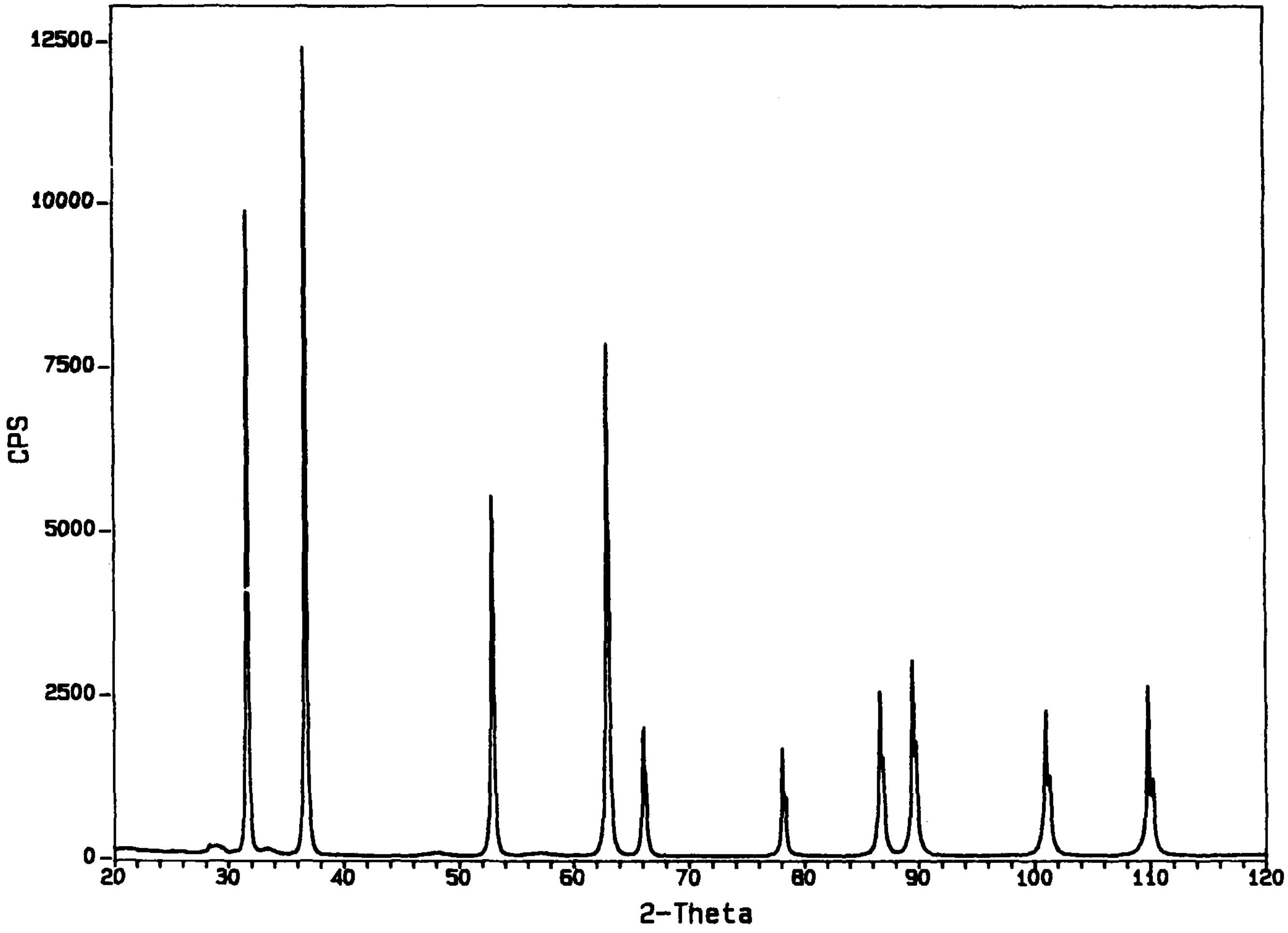

FIGURE 6: XRD Pattern of a Freshly Polished UN Pellet

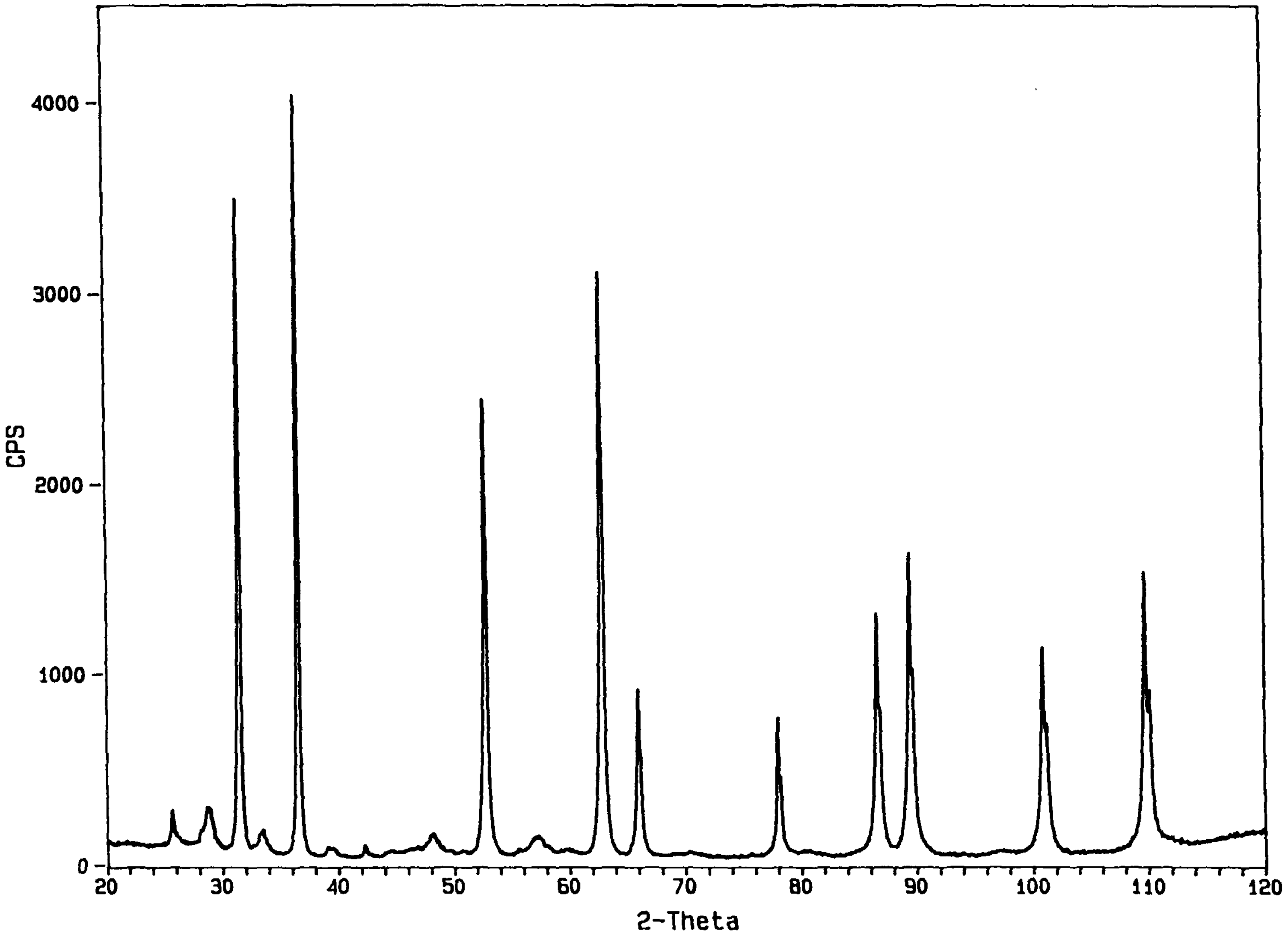

FIGURE 7: XRD Pattern of a UN Pellet Corroded in Water (initial pH = 10.3) for 1 Week at 90°C

Cat. No. / N° de cat.: CC2-11656E
ISBN 0-660-16662-3
ISSN 0067-0367

To identify individual documents in the series, we have assigned an AECL- number to each. Please refer to the AECL- number when requesting additional copies of this document from

Scientific Document Distribution Office (SDDO)
AECL
Chalk River, Ontario
Canada K0J 1J0

Fax: (613) 584-1745 Tel.: (613) 584-3311
ext. 4623

Price: A

Pour identifier les rapports individuels faisant partie de cette série, nous avons affecté un numéro AECL- à chacun d'eux. Veuillez indiquer le numéro AECL- lorsque vous demandez d'autres exemplaires de ce rapport au

Service de Distribution des documents officiels (SDDO)
EACL
Chalk River (Ontario)
Canada K0J 1J0

Fax: (613) 584-1745 Tél.: (613) 584-3311
poste 4623

Prix: A

Copyright © Atomic Energy of Canada Limited, 1996.

Printed on recycled paper with vegetable-oil-based inks