AECL-5957

ATOMIC ENERGY   **L'ÉNERGIE ATOMIQUE**
OF CANADA LIMITED   **DU CANADA LIMITÉE**

DISSOLUTION OF (Th,U)O$_2$ IN NITRIC ACID-HYDROFLUORIC ACID SOLUTIONS

by

R.W. DYCK, R. TAYLOR and D.G. BOASE

Whiteshell Nuclear Research Establishment

Pinawa, Manitoba

December 1977

ATOMIC ENERGY OF CANADA LIMITED

DISSOLUTION OF $(Th,U)O_2$ IN NITRIC ACID-HYDROFLUORIC ACID SOLUTIONS

by

R.W. Dyck, R. Taylor and D.G. Boase

Dissolution de $(Th,U)O_2$ dans des solutions d'acide
nitrique et d'acide fluorydrique

par

R.W. Dyck, R. Taylor et D.G. Boase

Résumé

La dissolution de combustibles mélangés d'oxyde de thorium et d'uranium dans des mélanges d'acide nitrique et d'acide fluorydrique a été étudiée pour faciliter la conception des équipements et des méthodes de retraitement. On a constaté que le taux de dissolution dépend de la concentration des acides et de la température et qu'une dissolution quasi-optimale se produit dans 13 mol$\cdot$L^{-1} HNO$_3$/0.05 mol$\cdot$L^{-1} HF bouillant. Les échantillons réduits en poudre se sont dissous plus rapidement que les pastilles de combustible intactes. La gaine de combustible en Zircaloy s'est également dissoute dans une certaine mesure comme le combustible, mais dans les conditions typiques du tronçonnage du combustible à l'échelle industrielle et des procédés de dissolution, cela a eu un effet insignifiant sur le taux de dissolution de $(Th,U)O_2$. Le nitrate d'aluminium ajouté pour réduire la corrosion de la cuve par le dissolvant n'a eu qu'un effet limité sur le taux de dissolution du combustible. On a noté des différences dans le taux de dissolution pour divers lots de fabrication du combustible. Plusieurs explications possibles ont été recherchées mais aucune conclusion n'a pu être tirée. On commente les tentatives faites pour intensifier le taux de dissolution. Des essais comparatifs effectués avec des échantillons de combustible UO$_2$ ont montré des taux de dissolution plus élevés que pour les échantillons de combustible $(Th,U)O_2$ dans des conditions semblables. Le combustible $(Th,U)O_2$ irradié s'est dissous plus rapidement que le combustible inirradié par suite de l'effritement du combustible durant la dissolution. Une petite quantité de résidus fortement radioactifs est restée non dissoute.

DISSOLUTION OF $(Th,U)O_2$ IN NITRIC ACID-HYDROFLUORIC ACID SOLUTIONS

by

R.W. Dyck, R. Taylor and D.G. Boase

ABSTRACT

The dissolution of mixed thorium-uranium oxide fuel in nitric acid/hydrofluoric acid mixtures was studied to assist the design of equipment and procedures for reprocessing. The dissolution rate was found to depend upon the acid concentrations and the temperature, with near optimum dissolution occurring in boiling 13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF. Powdered samples dissolved more rapidly than intact fuel pellets. The Zircaloy fuel sheathing also dissolved to some extent along with the fuel but, under conditions representative of industrial scale fuel chopping and dissolution procedures, this had an insignificant effect on the $(Th,U)O_2$ dissolution rate. Aluminum nitrate, added to reduce dissolver vessel corrosion, had only a small effect on the fuel dissolution rate. Differences in rate for various fuel fabrication lots were observed. Several possible explanations were investigated, but no conclusions could be drawn. Attempts to enhance the dissolution rate are discussed. Comparative tests with UO_2 fuel samples showed higher dissolution rates than for $(Th,U)O_2$ fuel samples under similar conditions. Irradiated $(Th,U)O_2$ fuel dissolved more rapidly than unirradiated fuel, due to crumbling of the fuel during dissolution. A small amount of highly radioactive residue remained undissolved.

CONTENTS

1. INTRODUCTION

Future development of the CANDU* reactor system in Canada may focus, in part, on the use of thorium-based fuels[1-3], to provide more flexibility in reactor fuelling and to offer more efficient utilization of nuclear fuel resources. A requirement of the thorium fuel cycle is recovery and recycle of fissile material from irradiated fuel. The fuels are expected to be sintered mixed oxides of thorium with uranium and/or plutonium. After irradiation, the fuel will be dissolved in a nitric acid medium and the fission products, thorium, uranium and plutonium separated using solvent extraction with tributylphosphate. Information on the dissolution of thorium oxide fuel is required for the design of dissolving equipment and procedures.

Earlier studies have shown that the most effective solvent for mixed thoria-urania fuel, compatible with the extraction process, is nitric acid with fluoride ion added[4,5]. The rate of dissolution in the absence of fluoride is impractically slow. This report describes laboratory scale experiments conducted at Whiteshell Nuclear Research Establishment (WNRE) to determine the optimum conditions of acid composition and temperature, and to determine the effects of fuel particle size and fuel irradiation. The effect of zirconium on the dissolution rate was of particular interest because the fuels in CANDU reactors are normally clad in Zr alloys which also would be at least partially dissolved by the nitric acid/fluoride reagent. It is known that Zr forms strong complexes with fluoride in solution and therefore could influence the $(Th,U)O_2$ dissolution rate. The effect of aluminum nitrate was also studied, as it can be added to the acid in a reprocessing plant to complex the fluoride ion and reduce corrosion of the stainless steel dissolver vessel.

---

* CANDU – CANada Deuterium Uranium

Several comparison tests of UO_2 fuel dissolution are also described.

2. EXPERIMENTAL

2.1   APPARATUS AND TEST PROCEDURES

The dissolution tests were conducted in Pyrex round bottom flasks fitted with an air reflux condenser. The flasks were heated from the bottom using a combination hotplate-stirrer, and Teflon-coated magnetic stirring bars were used for agitation. In most tests, the ratio of starting acid volume to fuel weight was chosen to give a final Th concentration of approximately 1 $mol \cdot L^{-1}$. Typically, 5 g of $(Th,U)O_2$ was dissolved in 16 mL of a nitric acid/hydrofluoric acid mixture, using a 25 mL flask.

To check that the glass apparatus had no effect on the $(Th,U)O_2$ dissolution rate, several comparative tests were carried out in polycarbonate plastic and in Teflon containers. No differences in the dissolution rates were detected, in agreement with the work reported by Schuler[6]. Other workers[7,8] have also used glass apparatus for thorium oxide dissolution studies with no apparent effect on the rates compared with other materials.

Most tests were conducted with vigorous agitation. In this manner, experimentally reproducible rate data were obtained. Good agitation also eliminates bulk solution diffusion as being rate determining[9,10], and allows the kinetics of the surface reactions to be determined. In tests at the boiling point, the boiling action itself provided good agitation, and no rate differences were noted with additional stirring. The dissolution experiments with large pellets in boiling acid were therefore conducted with

no additional stirring. Hyder[4] also found that vigorous mechanical agitation caused no increase in rate for tests at the boiling point if the vessel was heated from the bottom. Side heating of the vessel, however, did not provide as efficient agitation, even in large-scale dissolver tests.

The fuel dissolution rate was monitored by periodic sampling of the solution and determination of the Th concentration by titration with EDTA* using xylenol orange indicator[11]. The sample was added to 50 mL of water and buffered to pH 2.5-3 with sodium acetate before titration. In tests where Zr was present, excess EDTA was added to the sample followed by back titration with bismuth nitrate[12]. Ammonium sulfate was then added to preferentially complex Th, and the EDTA released was again titrated with Bi. The Zr was determined by difference. In some tests, the $(Th,U)O_2$ and Zr dissolution rates were determined by weight loss measurements. The experimental results were expressed either graphically as percent dissolution of the sample versus time, or by calculation of the reaction rate in $mg \cdot cm^{-2} \cdot min^{-1}$. The latter was normally calculated after a two hour dissolution time, at which point approximately 30% of the sample had dissolved. The initial geometric surface area of the sample was used in the calculation. Some rates were calculated after only 10% sample dissolution and these values were generally 50% higher. For comparison of one sample with another, either calculation method was satisfactory. In general, the data were reproducible to within ± 10%.

The Th to U ratio in solution was monitored throughout a dissolution test to determine if there was preferential leaching of the U or the Th from the fuel. No change was observed, establishing that the Th analysis is a representative parameter of the overall fuel dissolution rate.

Tests with irradiated $(Th,U)O_2$ fuel were conducted remotely in a shielded hot cell facility. The apparatus and procedures were similar to those described for unirradiated fuel. Small quantities of the dissolver

---

*EDTA - Ethylenediamine-tetraacetate

solution were withdrawn periodically and analyzed in a shielded laboratory fumehood.

2.2   MATERIALS

The various types of oxide fuel used in this study are described in Table 1. The fuels were prepared by Canadian General Electric, by mixing ThO_2 and UO_2 powders, followed by cold pressing into cylindrical pellets and sintering at 1700°C. The pellets were approximately 1.4 cm in diameter and 1.4 to 2.1 cm long. The impurity concentrations are given in Table 2.

Several forms of fuel were used, including powders, irregular shaped fragments, half discs and whole pellets. Chopped fuel is likely to be a mixture of intact pellets, fragments and powder. The particular form is indicated with the data. It was demonstrated that the dissolution data for single whole pellets could be extrapolated to batches of multiple pellets, for example, curves of the percent sample dissolution versus time for single pellets and batches of 5 pellets were found to be essentially identical.

The fuel designated WR1-947 was the only material for which both irradiated and unirradiated specimens were available. However the impurity levels of this material (see Table 2) are somewhat higher than would be permitted by the most recent fuel specifications[13]. The fuels designated DME-166, DP-14 and FDO-680 are for the most part within the specifications, and are thought to be most representative of currently produced material. The H1 and H2 fuels were prepared as part of the WNRE fuel development program and were not designed for reactor use. The fuels designated Series I and II were prepared specifically for the present dissolution study (see Section 3.5) and were also not intended for reactor use.

TABLE 1

(Th,U)O$_2$ FUEL TYPES USED IN DISSOLUTION STUDIES

Fuel Designation*	UO$_2$ Content wt.%	^{235}U Enrichment	Irradiation	Density mg/m^{-3}	Comments
1. WR1-947	3.9	93%	Unirradiated	9.75	
2. WR1-947	3.9	93%	2.16 GJ/g	-	
3. W1	2	Natural	Unirradiated	9.68	Not designed for reactor use
4. W2	4	Natural	Unirradiated	-	Not designed for reactor use
5. DME-166	1.6	93%	Unirradiated	10.04	
6. DP-14	1.2	93%	Unirradiated	9.95	
7. FDO-680	4	93%	Unirradiated	9.97	
8. Series I	(See Note 2)				
X	2.4	93%	Unirradiated	9.53	
Y	2.4	50%	Unirradiated	9.63	
Z	2.4	10%	Unirradiated	9.77	Not intended for reactor use
A	2.4	Natural	Unirradiated	9.64	
9. Series II	(See Note 3)				
A	2.4	Natural	Unirradiated	9.64	0 µg F/g
B	2.4	Natural	Unirradiated	9.65	5 µg F/g Not intended for reactor use
C	2.4	Natural	Unirradiated	9.65	25 µg F/g
D	2.4	Natural	Unirradiated	9.65	100 µg F/g
E	2.4	Natural	Unirradiated	9.64	300 µg F/g

NOTE: 1. All fuel types were sintered at a nominal temperature of 1700°C.

2. Series I prepared with 93% ^{235}UO$_2$ and natural UO$_2$ to a constant UO$_2$ content.

3. Series II prepared with various fluoride contents, by addition of UF$_4$ to the fuel before sintering.

* For convenience, the internal WNRE fuel designation numbers are used.

TABLE 2

ANALYSIS OF IMPURITIES OF $(Th,U)O_2$ FUELS

Fuel Designation[*]	IMPURITY (µg/g)											
	Si	Mn	Cr	Fe	Al	Ca	Ni	Zn	Mg	Sn	B	Cd
WR1-947	175	26	200	510	250	550	<5	<10	<5	<1	<1	<2
DME-166	53	<1	52	100	10	125	32	<10	<5	<1	<1	<2
DP-14	20	<1	18	20	5	125	15	<10	<5	<1	<1	<2
FDO-680	64	<1	80	120	20	125	150	<10	<5	<1	<1	<2
H1	190	2.5	2	430	250	75	<5	<10	<5	<1	<1	<2
H2	10	<1	<1	20	<5	10	<5	<10	<5	<1	<1	<2
Series I-X	15	<1	<5	25	<5	35	5	<10	<5	<1	<1	<2
-Z	15	<1	<5	12	<5	35	5	<10	<5	<1	<1	<2
Series II-A	18	<1	<5	45	<5	25	5	<10	<5	<1	<1	<2
-C	12	<1	<5	12	<5	35	5	<10	<5	<1	<1	<2
-E	18	<1	<5	16	<5	40	5	<10	<5	<1	<1	<2
Specification[**]	100	20	40	100	50	50	50	10	30	5	0.5	0.3

[**] Data taken from reference 13.

[*] For convenience, the internal WNRE fuel designation numbers are used.

3. RESULTS AND DISCUSSION

3.1   DISSOLUTION OF UNIRRADIATED $(Th,U)O_2$

3.1.1 HNO_3 Concentration

The effect of HNO_3 concentration on the dissolution rate of unirradiated $(Th,U)O_2$ in mixtures of HNO_3/HF is shown in Figures 1 and 2. The HF concentration in these tests was constant at 0.05 $mol \cdot L^{-1}$. The initial reaction rate, based on the weight loss of the sample in a 2 hour period and using the initial geometric surface area, increases with starting HNO_3 concentration to a maximum at 14-15 $mol \cdot L^{-1}$ HNO_3 (Figure 2). The complete dissolution curves in Figure 1 show little difference in the overall time to dissolve the sample at acid concentrations of 13 and 14 $mol \cdot L^{-1}$, with longer dissolution times above 14 $mol \cdot L^{-1}$ HNO_3. A starting concentration of 13 $mol \cdot L^{-1}$ appears optimum and is in agreement with previous work[4,5]. This concentration was chosen for most tests in this study.

In the range 8-13 $mol \cdot L^{-1}$ HNO_3, the apparent order of the reaction with respect to HNO_3 concentration is approximately equal to unity. This is in agreement with the work of Bond[5] and Farrell and Isaacs[14]. However at lower concentrations of 2-6 $mol \cdot L^{-1}$ HNO_3, Bond found the rate was approximately proportional to the third power of the acid concentration.

Approximately four moles of acid are consumed per mole of ThO_2 dissolved.

$$ThO_2 \ + \ 4 \ HNO_3 \ \longrightarrow \ Th(NO_3)_4 + 2 \ H_2O$$
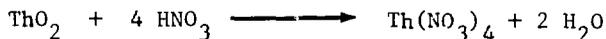
For example, for a starting HNO_3 concentration of 13 $mol \cdot L^{-1}$, the acid concentration decreases to approximately 9 $mol \cdot L^{-1}$ in the batch dissolution of

1 mol of $(Th,U)O_2$ in one litre of acid. Both the decrease in HNO_3 concentration and increase in Th concentration contribute to the lower rates towards the end of the dissolution.

3.1.2   HF Concentration

Figures 3 and 4 illustrate the effect of fluoride ion concentration on the rate of $(Th,U)O_2$ dissolution. In the range $0.001 - 0.01$ $mol \cdot L^{-1}$ HF, the rate increases with increasing fluoride concentration, with an apparent reaction order of approximately 0.5 (Figure 4). However, in the range $0.02 - 0.2$ $mol \cdot L^{-1}$ HF, the reaction rate is essentially independent of the fluoride concentration (zero order). These results are in close agreement with previous work[4,5,9,15], although Ferris and Kibbey[15] noted a decrease in rate above 0.07 $mol \cdot L^{-1}$ HF which they attributed to the formation of insoluble ThF_4 at the thoria surface. The dissolution rates measured by Bond[5] at the 3 hour mark were independent of fluoride concentration in the range of $0.01 - 0.50$ $mol \cdot L^{-1}$. Shying[10] found that the order of reaction with respect to fluoride decreased from approximately unity at very low fluoride levels ($\sim 2 \times 10^{-4}$ $mol \cdot L^{-1}$) to approximately 0.6 at 0.006 $mol \cdot L^{-1}$ HF. A reaction order of 0.5 was obtained by Farrell and Isaacs[14] in the range $0.001 - 0.05$ $mol \cdot L^{-1}$ HF.

The dissolution of $(Th,U)O_2$ in nitric acid proceeds extremely slowly if fluoride ion is not present. For several specimens of WR1-947 fuel, a rate of 0.3 $mg \cdot cm^{-2} \cdot min^{-1}$ was obtained in boiling 13 $mol \cdot L^{-1}$ HNO_3, compared with values of 15-20 $mg \cdot cm^{-2} \cdot min^{-1}$ with 0.05 $mol \cdot L^{-1}$ HF present. Bond[5] also found the dissolution in the absence of fluoride to be very slow and obtained a rate of 0.09 $mg \cdot cm^{-2} \cdot min^{-1}$. An increase in rate of 100 times was observed by Farrell and Isaacs[14] upon the addition of 0.001 $mol \cdot L^{-1}$ HF compared to tests without fluoride.

It is advantageous both in experimental dissolution studies and in a plant, to use an HF concentration above 0.02 $mol \cdot L^{-1}$ where the rate is

independent of the HF concentration, yet maximum, so that precise control
of the fluoride is not important. However, in a stainless steel plant, too
high a value could lead to excessive corrosion of the dissolver. A concen-
tration of 0.05 $mol \cdot L^{-1}$ HF was considered to be a reasonable compromise and
was used almost exclusively.

Takeuchi and co-workers[9] have proposed a reaction mechanism
in which thoria surface sites react with HF to form a surface fluoride which
in turn adsorbs molecular HNO_3. The rate determining step, they suggest,
involves the reaction of the adsorbed HNO_3 with the surface fluoride to form
soluble ions. The derived rate expression is a function of both the fluoride
and HNO_3 concentrations and is valid for conditions up to 0.035 $mol \cdot L^{-1}$ HF
and 6 $mol \cdot L^{-1}$ HNO_3. At this acidity, the HF is largely undissociated and it
was also considered that undissociated HNO_3 was involved in the reaction.
Our studies show that the rate is only dependent on the fluoride concentration
below 0.01 $mol \cdot L^{-1}$.

Shying[10,16] found the dissolution kinetics dependent on both
the fluoride adsorbed on the oxide surface and the fluoride in solution.
The mechanism was considered to involve initial reaction of the oxide with
water or a protonated species to form surface hydroxyl compounds. These
compounds dissociate in acid solution to provide positively charged surface
sites, followed by adsorption of fluoride onto these sites. The reaction
of the flourinated surface compounds with fluoride ions in solution and
nitric acid is rate controlling, and the thorium fluoride complex desorbs
from the surface. Shying's studies of the kinetics with respect to fluoride
showed a large decrease in solution fluoride concentration due to adsorption
on the thoria surface, and showed that both adsorbed fluoride and fluoride
in solution governed the dissolution rate. However, Shying's work was con-
ducted at very low fluoride concentrations (10^{-4} $mol \cdot L^{-1}$). The studies
described in this report were generally conducted at higher fluoride con-
centrations in which, as expected, no decrease in solution fluoride concen-
tration due to adsorption was detected.

3.1.3   Fuel Particle Size

The dissolution rates of $(Th,U)O_2$ powders of various particle size are compared to those of pellets in Figure 5. As mentioned earlier, the fuel geometry likely to occur in a reprocessing dissolver is a composite of powder and pellets, with the overall dissolution rates intermediate between the two. The powders dissolve very much more rapidly than the pellets and the rates increase with a decrease in the particle size. Only 1-3 hours are required to completely dissolve powders, compared with approximately 30-40 hours for pellets. The rate increase with decreasing particle size is not limited even down to powders of 38 µm average diameter, and illustrates that, under the experiment conditions, the dissolution rates are governed by the thoria surface reactions and not by bulk solution diffusion.

3.1.4   Temperature

The increase in dissolution rate with temperature in the range 70°C to the boiling point is shown in Figure 6. The apparent activation energy is 54.4 kJ·mol^{-1} (13.0 kcal·mol^{-1})(Figure 7). Values reported previously[9,14,16] range from 44-80 kJ·mol^{-1} (10.5-19 kcal·mol^{-1}), but in general they were obtained at lower HNO_3 and HF concentrations and at lower temperatures.

Since the highest practical dissolution rates are desired, most tests in this study were conducted at the acid boiling point of approximately 118°C. Experimentally, this allowed easy control of the temperature and the boiling action gave good agitation.

3.1.5   Effect of Al Addition

Severe corrosion of stainless steel dissolver vessels may occur with HNO_3/HF solutions if the fluoride ion remains uncomplexed. It is normal practice to add aluminum ion to the dissolver acid to complex the fluoride and reduce the corrosion rate[4,7]. Corrosion tests at WNRE[17] have shown

that the optimum concentration of aluminum nitrate for the reduction of corrosion of 304L stainless steel is 0.125 $mol \cdot L^{-1}$.

Reports of the effect of Al addition to the $(Th,U)O_2$ dissolution rate are somewhat varied. Hyder[4] reported no adverse effect of 0.1 $mol \cdot L^{-1}$ $Al(NO_3)_3$ on the dissolution of powdered samples in boiling 13 $mol \cdot L^{-1}$ HNO_3/ 0.05 $mol \cdot L^{-1}$ HF. Ferris and Ullman[7] observed only a 10% reduction in the amount of $(Th,U)O_2$ powder dissolved in a 7 hour test at 0.1 $mol \cdot L^{-1}$ $Al(NO_3)_3$, and almost no effect at 0.04 $mol \cdot L^{-1}$. On the other hand, Farrell and Isaacs[14] reported a reduction in the initial rate of almost a factor of two at Al concentrations of 0.1 $mol \cdot L^{-1}$, and very much larger effects at higher concentrations up to 0.85 $mol \cdot L^{-1}$. In the present study, no adverse effect was noted at 0.1 $mol \cdot L^{-1}$ $Al(NO_3)_3$, and only a 5-10% reduction in rate at 0.125 $mol \cdot L^{-1}$ $Al(NO_3)_3$ (Figure 8). At 0.5 $mol \cdot L^{-1}$ $Al(NO_3)_3$, the rate reduction was less than a factor of two, a smaller effect than reported by Farrell and Isaacs.

3.1.6   Effect of Stainless Steel Surfaces

Stainless steel (304L) is a candidate material of construction for a reprocessing plant dissolver vessel. To determine if a steel surface, or dissolved iron, influences the $(Th,U)O_2$ dissolution rate, coupons of stainless steel were added to a number of dissolution tests. The ratio of the surface area of the coupon to that of the fuel and the acid volume was chosen to represent a typical dissolver design. No effects on the dissolution were detected. In another test, stainless steel turnings were added to provide a large surface area and higher dissolved iron concentration ($\sim$ 0.004 $mol \cdot L^{-1}$). Again no change was observed in the dissolution rate, using a pellet sample of DP-14 fuel in 13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF. Stainless steel surfaces and low concentrations of dissolved iron therefore do not appear to have any influence on the dissolution of thorium oxide fuels.

3.1.7   Comparison with UO_2 Fuel Dissolution

It is of interest to compare the dissolution rates and reaction mechanisms of $(Th,U)O_2$ fuels with those of conventional UO_2 fuels. Several unirradiated specimens of each were dissolved under similar temperature and acid conditions (Figure 9). Sintered pellets ($\sim 1700°C$) of natural UO_2 were used.

In 8 $mol \cdot L^{-1}$ HNO_3 at 80°C, conditions which approach the optimum for UO_2 dissolution[18], the UO_2 dissolution rate was 15 to 25 times greater than for samples of WR1-947 $(Th,U)O_2$ fuel in 8-13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF at the same temperature. However, the $(Th,U)O_2$ rates in 13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF at the boiling point were only 3-7 times slower than the UO_2 rates at 80°C, depending on the type of $(Th,U)O_2$ fuel used. Only the data for samples of WR1-947 are shown.

The dissolution of UO_2 in nitric acid is autocatalyzed by nitrite ion, produced by the decomposition of nitric acid in the UO_2/HNO_3 reaction[18]. The dissolution rate is decreased by increasing the degree of agitation, for example by mechanical means, sparging, or by boiling. For $(Th,U)O_2$, the dissolution mechanism differs, in that the rate is maximum at the acid boiling point, as discussed earlier, and therefore the nitrite ion does not appear to have an influence. To test this conclusion further, small amounts of UO_2 were added periodically to a $(Th,U)O_2$ dissolution to increase the concentration of nitrite present. No acceleration of the rate was observed, although the extent of the nitrite concentration increase was not known.

3.2   DISSOLUTION OF UNIRRADIATED $(Th,U)O_2$ IN THE PRESENCE OF ZIRCONIUM

The effect of zirconium on the $(Th,U)O_2$ dissolution rate was of particular interest in this work, because CANDU fuels are normally sheathed in zirconium alloys, and the sheathing is expected to be partially dissolved during fuel dissolution. Previous reports have indicated that the $(Th,U)O_2$ dissolution rate was diminished in the presence of dissolved zirconium, but

that the effect was not large[19,29]. It was also reported that zirconium added as a solution to the acid had a greater effect than when added as a metal[21]. It was important to the present study to determine if the presence of zirconium would inhibit the $(Th,U)O_2$ dissolution rate to an unacceptable degree and in general to examine the chemical interrelationships between Th,Zr,Al and fluoride.

Zirconium (Zircaloy-4) was added to the dissolution tests in the form of coupons cut from sheath (nominally 1 cm x 1 cm x 0.04 cm) or as finely divided turnings or powder. It was normally added at a 1 to 10 ratio by weight with respect to $(Th,U)O_2$ approximating the ratio existing in CANDU fuel. The coupons were considered to be representative of the cladding fragments resulting from a chop-leach dissolution process. Relatively small quantities of Zircaloy fines are expected to be produced during chopping[19].

The results, given below, show that the effect of Zr depends on the degree of subdivision of both the $(Th,U)O_2$ fuel and the sheath. No effect on the dissolution rate of either powdered or pellet fuel was observed in the presence of Zr coupons. However finely divided turnings or powdered zirconium retarded the dissolution of fuel in either form. Some zirconium also dissolved, the amount depending on the fluoride concentration. The variation of the $(Th,U)O_2$ dissolution rate with fluoride concentration was similar to that described previously when zirconium was absent.

3.2.1   Effect of Zr Sheath Coupons

Figure 10 compares the dissolution of whole intact pellets of DP-14 fuel at the boiling point with and without Zr present. No significant difference in the $(Th,U)O_2$ dissolution rates was detected. The Zr sheath dissolved rapidly for the first hour, but the rate then decreased quickly so that only 20% of the zirconium was dissolved at the point of complete $(Th,U)O_2$ dissolution. The final concentration of dissolved zirconium was about 6 $g \cdot L^{-1}$. Similar results were obtained for irregular fragments of WR1-947 fuel, with 10-15% of the Zr being dissolved.

With powdered DP-14 fuel (Figure 11), no significant change in the dissolution rates occurred in the presence of Zircaloy sheath, and only ∿ 3% of the Zr was dissolved. With powdered WR1-947 fuel dissolved at 80°C in various concentrations of HF, again no effect of Zr was observed but the quantity of Zr dissolved increased with increasing fluoride concentrations. With 0.1 $mol \cdot L^{-1}$ $Al(NO_3)_3$ present, the amount of Zr dissolved was only 1% or less and fuel dissolution was not affected.

Separate tests of the dissolution of zirconium in the absence of fuel showed an apparent reaction order of one with respect to fluoride concentration, and two-thirds with respect to nitric acid concentration.

3.2.2   Effect of Zr Turnings or Powder

In the presence of finely divided Zr, the dissolution rate of powdered or half disc fuel specimens was lower by about a factor of two. Specimens of DP-14 fuel were tested at the boiling point, and WR1-947 fuel at 80°C. The results for DP-14 are given in Figures 11 and 12. Somewhat more Zr dissolved in these tests, to give a final concentration of 5-10 $g \cdot L^{-1}$. In tests where the fuel was added to a solution of previously dissolved zirconium at 8 to 12 $g \cdot L^{-1}$, a similar factor of two decrease in rate was observed, compared with the rates in the absence of zirconium. This demonstrates that the small decrease in fuel rate is related to Zr species in solution and not to processes on the Zr metal surface.

The dissolution data for half disc specimens of DP-14 at various HF concentrations are shown in Figure 13 and are compared with the data with no Zr present (from Figure 4). In the range 0.01 to 0.2 $mol \cdot L^{-1}$ HF, the rates are roughly a factor of two lower in the presence of Zr. Below 0.01 $mol \cdot L^{-1}$ HF, the rate increases markedly with increasing fluoride concentration, but between 0.01 and 0.20 $mol \cdot L^{-1}$ HF, the rates show little increase. The corresponding Zr dissolution curves are given in Figure 14 and are again characterized by rapid reaction for the first hour or so, with essentially no further reaction thereafter.

The observations described show there is a kinetic competition between Th and Zr for the available fluoride ion. Initially the Zr dissolves rapidly, until the dissolved Th concentration is sufficiently high to complex the fluoride effectively and inhibit its role in Zr dissolution. When the Th concentration reaches 0.2 ~ 0.3 mol·L^{-1}, the Zr reaction essentially ceases (zirconium dissolution is completely inhibited in solutions of 1 mol·L^{-1} Th). The final amount of Zr dissolved appears to depend on the relative initial dissolution rates of the Th and Zr. With finely divided Zr, the quantity of Zr dissolved is sufficiently high to complex the fluoride itself and inhibit the $(Th,U)O_2$ dissolution. In effect, the free fluoride concentration available for $(Th,U)O_2$ dissolution is decreased below the range where zero order reaction kinetics apply (Figure 4). Coupons of Zr are dissolved to a lesser extent and the fluoride is not complexed sufficiently to affect the fuel dissolution kinetics.

Since aluminum also forms fluoride complexes, it was thought that the addition of aluminum ion may reduce the amount of Zr dissolved, particularly in the finely divided form, and thus minimize any effect on the fuel dissolution. The results given in Figure 8 show little improvement in the fuel dissolution rate upon the addition of $Al(NO_3)_3$ up to 0.5 mol·L^{-1} although less Zr by a factor of two was dissolved in these tests. It is apparent, however, that Th in solution is more effective than Al in reducing the amount of Zr dissolved. Therefore it may be beneficial to maintain a certain Th concentration in the dissolver acid of a reprocessing plant during the addition of fresh fuel. In this manner, the dissolution of the cladding would be reduced and the Zr effect on fuel dissolution would be minimized.

3.3   DISSOLUTION OF DIFFERENT TYPES OF UNIRRADIATED $(Th,U)O_2$

Tests were conducted to determine the reproducibility of the dissolution data in boiling 13 mol·L^{-1} HNO_3/0.05 mol·L^{-1} HF acid for various fabrication lots of $(Th,U)O_2$. These tests arose in part from the observation that the dissolution rates of two lots of $(Th,U)O_2$ (designated H1 and H2) were markedly lower than for other fuel. This difference was noted with both

powdered samples and pellets. As noted in Section 2.2, the DP-14, DME-166
and FDO-680 fuels are considered to be most representative of reactor grade
fuel, whereas the H1 and H2 fuels were prepared for fuel development test
purposes only. The dissolution curves are shown in Figure 15 and the rates
are given in Table 3.

TABLE 3

DISSOLUTION RATES OF $(Th,U)O_2$ FUEL PELLETS

FUEL	DESCRIPTION		DISSOLUTION RATE* + $(mg \cdot cm^{-2} \cdot min^{-1})$
WR1-947	3.9% UO_2	93% enriched	15-20
DP-14	1.2% UO_2	93% enriched	6.1
DME-166	1.6% UO_2	93% enriched	5.9
FDO-680	4.0% UO_2	93% enriched	6.1
H1	2% UO_2	Natural	0.7 - 1.5
H2	4% UO_2	Natural	1.8

* Calculated on the basis of weight of $(Th,U)O_2$ pellet dissolved in a
   2 hour test, and using the initial geometric surface area.

\+ In boiling 13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF.

3.3.1   Fuel Examination

Wide variations in dissolution rates have been reported previously
for $(Th,U)O_2$ prepared by different techniques or from different sources[4,15,22].
These variations were largely attributed to differences in fuel density or to
the temperature at which the fuels were sintered. In our case the latter were
not sufficiently well known to allow a correlation. However, several other

methods of inspection and analysis were used in an attempt to elucidate the reasons for the differences in dissolution behaviour.

Metallographic examination of each fuel showed differences in grain structure and in porosity. The DP-14, DME-166 and FDO-680 fuels showed similar properties to H1 and H2, whereas the WR1-947 fuel was markedly different. In the former, the average grain diameter was approximately eight times larger, and the number of pores was greater than in WR1-947 fuel. However, these differences could not be correlated with the fuel dissolution rates.

Ferris and Kibbey[15] noted that the variable with the greatest effect on $(Th,U)O_2$ dissolution was the pellet density, with an order of magnitude difference in dissolution rate possible. No correlation could be found with our fuel density data, given in Table 1.

Analysis for impurity elements by emission spectrography (see Table 2) did not reveal any single impurity which could explain the differences in fuel dissolution rates. Traces of carbon in the form of thorium carbide were found on the outermost surface of the fuel by x-ray photoelectron spectroscopy, but its role in the dissolution is not clear.

As shown in Table 3, the fuels fabricated using natural UO_2 (H1 and H2) were slower to dissolve than other conventional fuel lots fabricated using enriched $^{235}UO_2$ (WR1-947, DP-14, etc.). Since the enriched $^{235}UO_2$ is derived from a process involving uranium hexafluoride, it was thought that traces of fluoride which could be present in these fuels might cause a higher reactivity towards dissolution acids. Several attempts to determine the fluoride content of the $(Th,U)O_2$ fuel specimens were unsuccessful. Therefore an alternative approach to test this possible explanation was explored. Two types of experimental fuel were fabricated, one containing varying amounts of $^{235}UO_2$ (Series I), and a second containing varying amounts of fluoride, added initially as UF_4 (Series II). The results of dissolution tests with these fuels are summarized in Table 4. Although the rates of the Series I fuel as a group fell somewhat below that of most of the fuels tested earlier, there was no correlation between rate and $^{235}UO_2$ concentration. With the

Series II fuels, a small increase was apparent in the initial dissolution rate with increasing fluoride content. Although these tests were somewhat inconclusive, they do not rule out the possible rate-enhancing effects of trace fluoride in fuel. Further tests were suspended until reliable methods to measure the fluoride content of $(Th,U)O_2$ fuel are developed.

TABLE 4

DISSOLUTION RATES OF SERIES I AND II EXPERIMENTAL FUEL PELLETS

FUEL	DESCRIPTION	DISSOLUTION RATE*+ $(mg \cdot cm^{-2} \cdot min^{-1})$
SERIES I	Varying $^{235}UO_2$	
X	2.4% UO_2 93% enriched	3.1
Y	2.4% UO_2 50% enriched	4.9
Z	2.4% UO_2 10% enriched	4.9
A	2.4% UO_2 Natural	3.6**
SERIES II	Varying UF_4	
A	2.4% UO_2 0 µg/g F^- added	3.6**
B	2.4% UO_2 5 µg/g F^- added	4.1
C	2.4% UO_2 25 µg/g F^- added	4.9
D	2.4% UO_2 100 µg/g F^- added	5.2
E	2.4% UO_2 300 µg/g F^- added	6.5

* Calculated on the basis of weight of $(Th,U)O_2$ pellet dissolved in a
  2 hour test, and using the initial geometric surface area.

** These fuel specimens and data are the same.

+ In boiling 13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF.

3.3.2   Tests to Enhance Dissolution Rate

Several attempts were made to increase the rather slow dissolution rates of $(Th,U)O_2$ fuels by changing the chemical composition of the acid and the physical condition of the fuel. The dissolution of PuO_2 in HNO_3/HF mixtures is known to be enhanced by the addition of sulfuric acid[23]. When 0.1 mol· L^{-1} H_2SO_4 was added to tests with our $(Th,U)O_2$ fuels, a somewhat lower dissolution rate was obtained. Ferris and Kibbey[15] reported a similar result and explained this as due to the formation of an insoluble film of thorium sulfate on the $(Th,U)O_2$ surface. Farrell and Isaacs[14] found that some thorium sulfate was precipitated from solution upon sulfate addition and that fluoride was incorporated in the precipitate. They attributed the decrease in dissolution rate to the removal of fluoride ion from solution rather than to any passivation effect of a thorium sulfate film on the fuel.

The effect of the UO_2 content of the fuel was considered. If the UO_2 were preferentially dissolved, reaction pathways leading into the sample interior could result. In the range 0 to 4.0 wt. % UO_2 in the fuels tested, no differences in dissolution rate were observed. Similarly Ferris and Kibbey found no effect of UO_2 concentration up to 10%[24]. As discussed in Section 3.1, the autocatalytic effect evident with UO_2 fuel was also ruled out as a factor in $(Th,U)O_2$ dissolution.

An increase in the dissolution rate by approximately 50% was reported upon the addition of 0.5 mol· L^{-1} $Fe(NO_3)_3$ to the acid[15]. Farrell and Isaacs[14] also indicated that the addition of small quantities of certain metal ions, provided they do not form too strong a complex with fluoride, may assist in dissolution by preventing the formation of a ThF_4 film on the oxide surface at high fluoride concentrations. In addition to ferric ion, they reported that divalent beryllium ion also appeared to have a beneficial effect. In the present work, tests in the presence of $Fe(NO_3)_3$ at concentrations of 0.005 mol· L^{-1} and 0.5 mol· L^{-1} showed no significant increase (< 5%) in the dissolution rate. For example, a reaction rate of 6.3 mg· cm^{-2}· min^{-1} for a pellet of DP-14 was obtained in the presence of 0.5 mol· L^{-1} $Fe(NO_3)_3$, compared with a value of 6.1 mg· cm^{-2}· min^{-1} in the absence of ferric ion.

The effect of preheating the (Th,U)O$_2$ to high temperatures in air was investigated. Potentially, some of the UO$_2$ could be oxidized to lower density U$_3$O$_8$, thus cracking the sample and providing a larger surface area for reaction. However, the dissolution rate of a sample of DME-166 fuel heated to 900°C for 16 hours was in fact reduced (Figure 16). Visually, the sample was not altered by the heat treatment, but it was possible that additional sintering had occurred. In contrast, heating the sample to 1000°C followed by rapid quenching in cold water showed a rate increase of up to a factor of four for DME-166 and H1 fuel specimens. In these cases, the samples crumbled quickly to powder during dissolution, apparently the result of heavy cracking from the thermal shock (Figure 16). These results coincide with those discussed previously for powdered fuel compared to pellets (Section 3.1).

The "heel" technique is commonly used to decrease the overall time for fuel dissolution[7]. In this technique, the fuel is only partially dissolved when the acid is drained and a fresh charge of fuel and acid is added. The "heel" is defined as the percentage of fuel not dissolved that is present at the beginning of each reaction cycle, and is typically 10-15%. A similar technique of acid replenishment was tested in the present work. A partial charge of acid was introduced initially, and then removed when the Th concentration had reached 0.5 mol·L^{-1}. Another partial charge of acid was added to the fuel, and so on until all the fuel was dissolved. In this manner the decrease in the instantaneous dissolution rate with decreasing acidity and increasing Th concentration[5] is partly overcome. For the conditions chosen, using 6 acid charges, about a factor of two reduction in the overall time required for complete fuel dissolution was achieved (Figure 17).

3.4   DISSOLUTION OF IRRADIATED (Th,U)O$_2$

Samples of WR1-947 fuel irradiated to 2.16 GJ/g (600 MW·h/kg) were dissolved at temperatures in the range of 80°C to the boiling point, with and without Zr present. This fuel lot was the only one for which both unirradiated and irradiated specimens were available for comparison. The fuel was highly

cracked after irradiation and broke into pieces upon cutting (sawing) of the
sheath. The degree of fuel subdivision resulting is shown in Figure 18. It
consisted of fine powder and irregular fragments up to 8 mm in cross section,
but with the major portion as 4-5 mm fragments. Three of the latter pellet
fragments each weighing approximately 1.5 g were selected and combined for
each dissolution test (total weight ∿ 5 g) and fragments of similar geometry
were taken from unirradiated WR1-947 $(Th,U)O_2$ fuel for comparison.

The irradiated specimens dissolved more rapidly than the unirradi-
ated, by up to a factor of two (Figure 19), probably because of the presence
of microcracks in the irradiated specimens and further crumbling during the
dissolution. The degree of cracking and subdivision is likely to increase
with fuel burnup. Therefore low burnup fuel may react more like unirradiated
fuel. Fuels of different irradiation levels were not available for this study.
Goode and Flanary[8] have also observed higher dissolution rates for irradiated
$(Th,U)O_2$ in the range 270 to 1530 MJ/g (75 to 425 MW·h/kg). On the average,
irradiated pellets were completely dissolved in 24 hours, compared with 75
hours for unirradiated fuel. Other authors[4,22,25] report little difference
between irradiated and unirradiated specimens.

The dissolution rate of irradiated $(Th,U)_2$ can be conveniently
monitored using the fission product activity in the dissolver solution. Samples
of the dissolver liquid were removed periodically, and the activities were
determined and converted to percent sample dissolution by normalization, using
the final activity of the solution when all the fuel was dissolved. Figure 20
compares data obtained by counting the γ activity of several radioisotopes with
that obtained by the normal EDTA titrimetric Th determination. Good agreement
was obtained with the ^{144}Ce isotope, and to a lesser degree with ^{95}Zr and ^{137}Cs.
Other radioisotopes, ^{134}Cs, ^{106}Ru, and ^{125}Sb showed larger deviations.
This method of monitoring the progress of the dissolution is rapid and not
subject to chemical interferences and may be useful for future engineering
scale tests of the dissolution process.

3.4.1 Effect of Zr

The presence of Zircaloy sheath coupons had only a small effect on the irradiated fuel dissolution rate (Figure 21). In tests at the boiling point, only 3.5% of the Zircaloy was dissolved at the point of complete oxide dissolution. Generally the Zr effect with irradiated fuel was essentially the same as for unirradiated fuel.

3.4.2 Undissolved Residue

A small amount of highly radioactive residue remained undissolved in the tests with irradiated fuel. The residue weight was obtained in one case and was approximately 0.25% of the original fuel sample. Analyses showed it was mainly Mo, Ru, Tc and Rh, with some Pd, all highly insoluble noble metal fission products. The sample activity was due mainly to the isotopes ^{103}Ru, ^{106}Ru and ^{95}Nb. Residues of similar composition have been observed previously with $(Th,U)O_2$ fuels[8].

4. SUMMARY

An initial acid composition of 13 mol·L^{-1} HNO$_3$/0.05 mol L^{-1} HF is near optimum for dissolution of mixed thorium-uranium oxide fuel. Approximately four moles of HNO$_3$ are consumed per mole of $(Th,U)O_2$ dissolved, and the rate is first order with respect to HNO$_3$ concentration. In the range 0.001 to 0.01 mol·L^{-1} HF, the rate is half order with respect to HF, but is constant in the range 0.02 to 0.20 mol·L^{-1} HF. In nitric acid with no fluoride present, the dissolution is extremely slow.

The dissolution rate increases with temperature to a maximum at the acid boiling point of ∿ 118°C (E$_{act}$ ∿ 54.4 kJ/mol). The rate may be increased by subdivision of the fuel, either by mechanical means or by thermal shocking.

Addition of 0.125 mol·L^{-1} Al(NO$_3$)$_3$ to the acid, to reduce dissolver vessel corrosion, causes only a 5-10% reduction in the $(Th,U)O_2$ dissolution rate. Tests in the presence of 304 L stainless steel, a candidate material of

construction for a reprocessing plant dissolver, showed no change in the rate, compared with the laboratory tests in glass apparatus.

Zircaloy fuel sheathing also partially dissolves during fuel dissolution. If finely divided, sufficient Zr dissolves to reduce the $(Th,U)O_2$ rate by up to a factor of two. However, when present as Zircaloy sheath coupons, the most probable form produced by a fuel chopping procedure, no significant effect on the oxide dissolution rate was observed.

A wide variation was observed in the results for different fabrication lots of $(Th,U)O_2$ fuel. However the reasons could not be established and further investigation is required. The presence of trace fluoride in the fuel may have an effect on the dissolution rate but this was not proven. Additives such as sulfate or ferric ion caused no increase or decrease. A dissolution technique involving multiple acid charging reduces the overall dissolution time by a factor of two.

Comparative tests with UO_2 fuel showed markedly higher dissolution rates than for $(Th,U)O_2$ fuel. The dissolution of UO_2 in nitric acid is autocatalyzed by nitrite ion, but this is not the case for $(Th,U)O_2$ fuel. Changes in the UO_2 content of thorium fuels in the range 0 to 4 wt % did not affect the rate.

The dissolution rate of fragments of irradiated $(Th,U)O_2$ with a burnup of 2.16 GJ/g was approximately twice that of similar specimens of unirradiated fuel. This was attributed to cracking of the fuel which occurs during irradiation, and to the fuel subdivision which occurs during sheath removal and dissolution. The determination of fission product [144]Ce in solution by γ spectrometry provided a convenient means of monitoring the dissolution rate. A small quantity of highly radioactive residue consisting of mainly noble metal fission products (Mo, Ru, Tc, Rh and Pd) remained undissolved.

The total time to dissolve whole intact pellets of unirradiated $(Th,U)O_2$, considered representative of low burnup reactor fuel, was approximately 30-40 hours, but the highly fragmented irradiated fuel (2.16 GJ/g) required only 5 hours for complete dissolution.

ACKNOWLEDGEMENTS

5. REFERENCES

1.   A.J. Mooradian, Atomic Energy of Canada Limited Report, AECL-5516 (1976).

2.   W.B. Lewis, M.F. Duret, D.S. Craig, J.I. Veeder and A.S. Bain, Atomic Energy of Canada Limited Report, AECL-4445 (1973).

3.   E. Critoph, S. Bannerjee, F.W. Barclay, D. Hamel, M.S. Milgram and J.I. Veeder, Atomic Energy of Canada Limited Report AECL-5501 (1976).

4.   M.L. Hyder, W.E. Prout and E.R. Russell, Du Pont de Nemours (E-I) and Co. DP-1044 (1966).

5.   W.D. Bond, Oak Ridge National Laboratory, ORNL-2519 (1958).

6.   F.W. Schuler, F.L. Steahly and R.W. Stoughten, U.S. Atomic Energy Commission, AEC TID-5223 (1952).

7.   L.M. Ferris and J.W. Ullmann, Oak Ridge National Laboratory, ORNL-TM-867 (1964).

8.   J.H. Goode and J.R. Flanary, Oak Ridge National Laboratory, ORNL-3725 (1965).

9.   T. Takeuchi, C.K. Hanson and M.E. Wadsworth, J. Inorg. Nucl. Chem. 33 1089 (1971).

10.   M.E. Shying, T.M. Florence and D.J. Carswell, J. Inorg. Nucl. Chem. 32 3493 (1970).

11.   A. Brueck and K.F. Lauer, EURATOM EUR-4714 (1971).

12.   G.W.C. Milner and J.W. Edwards, Anal. Chim. Acta 20, 31 (1959).

13.   H.R. Lee, unpublished information.

14.   M.S. Farrell and S.R. Isaacs, Australian Atomic Energy Commission, AAEC/E143 (1965).

15.   L.M. Ferris and A.H. Kibbey, Oak Ridge National Laboratory, ORNL-2934 (1960).

16.   M.E. Shying, T.M. Florence and D.J. Carswell, J. Inorg. Nucl. Chem. 34 213 (1972).

17.   E.V. Murphy, WNRE, private communication.

18.   R.F. Taylor, E.W. Sharratt, L.E.M. de Chazal and D.H. Logsdail, J. Appl. Chem. 13, 32 (1963).

19.   J.T. Roberts, L.M. Ferris, E.L. Nicholson, R.H. Rainey and C.D. Watson, Oak Ridge National Laboratory, ORNL-TM-1139 (1965).

20. E.L. Nicholson, L.M. Ferris, J.R. Flanary, J.H. Goode, B.A. Hannaford, J.W. Landry, J.G. Moore, R.H. Rainey, C.D. Watson and H.O. Witte, Proc. Second Int. Thorium Fuel Cycle Symposium (1966) (Conf-660524).

21. Gulf Atomic Quarterly Progress Report, Gulf Atomic GA--A13366 (1975).

22. C.E. Stevenson and D.M. Paige, Power Reactor Technology and Reactor Fuel Processing 10, 152 (1967).

23. C.H.H. Chong, T.W. Crockett and J.W. Doty, J. Inorg. Nucl. Chem. 31, 81 (1969).

24. L.M. Ferris and A.H. Kibbey, Oak Ridge National Laboratory, ORNL-3143 (1961).

25. L. Kuchler, L. Schafer and B. Wojtech, Kerntechnik 12, 327 (1970).

CONDITIONS: DP-14   single pellets
Various $HNO_3/0.05$ mol·L^{-1} HF
Boiling Point
300 mg $(Th,U)O_2$/mL acid
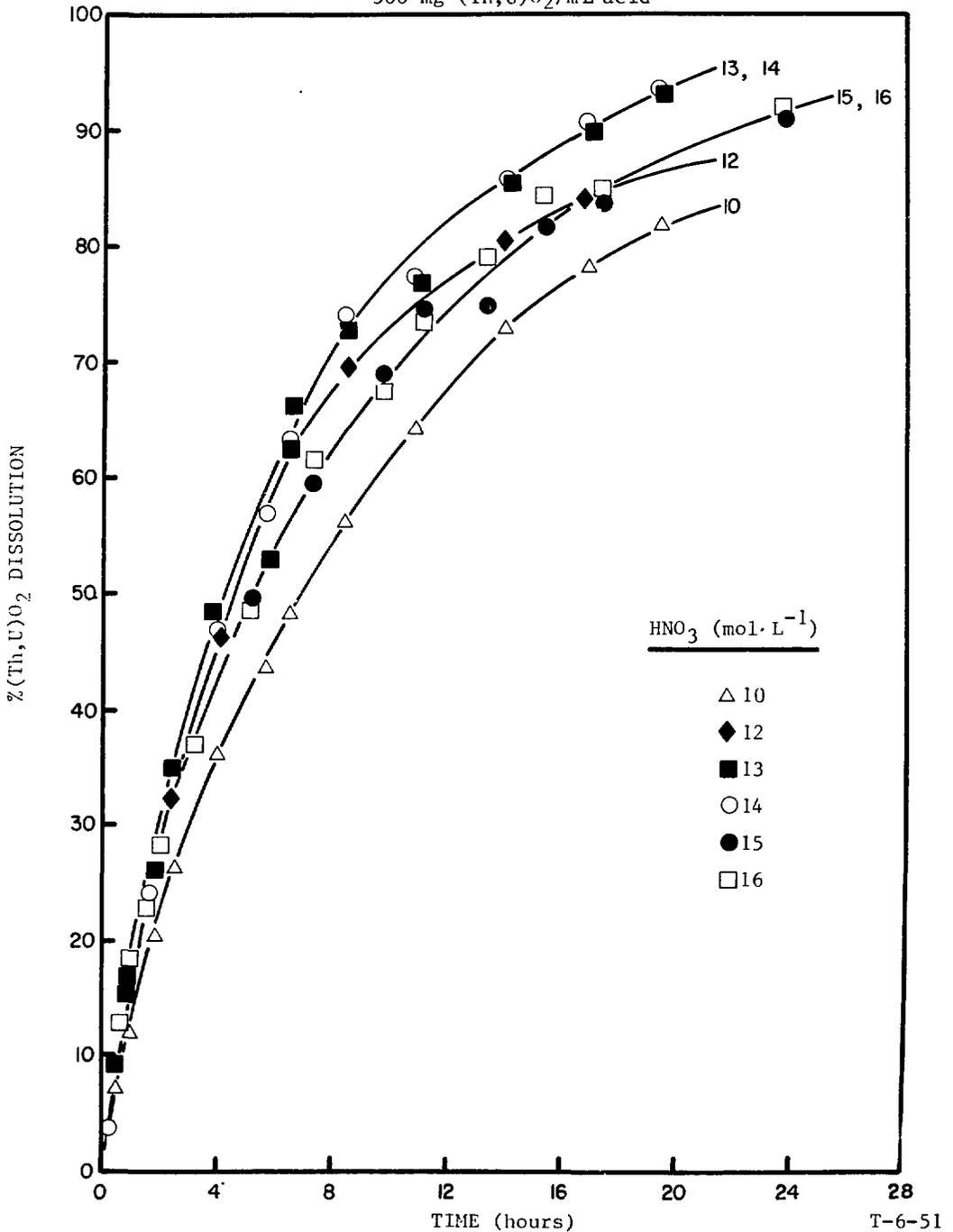
FIGURE 1.   EFFECT OF HNO_3 CONCENTRATION ON THE DISSOLUTION
OF $(Th,U)O_2$.

CONDITIONS: DP-14   single pellets
Various HNO_3 0.05 mol L^{-1} HF
Boiling point
300 mg$(Th,U)O_2$/mL acid
Rates calculated after 2 hours

Slope ≈ 1.2

DISSOLUTION RATE (mg $\cdot$ cm^{-2}min^{-1})
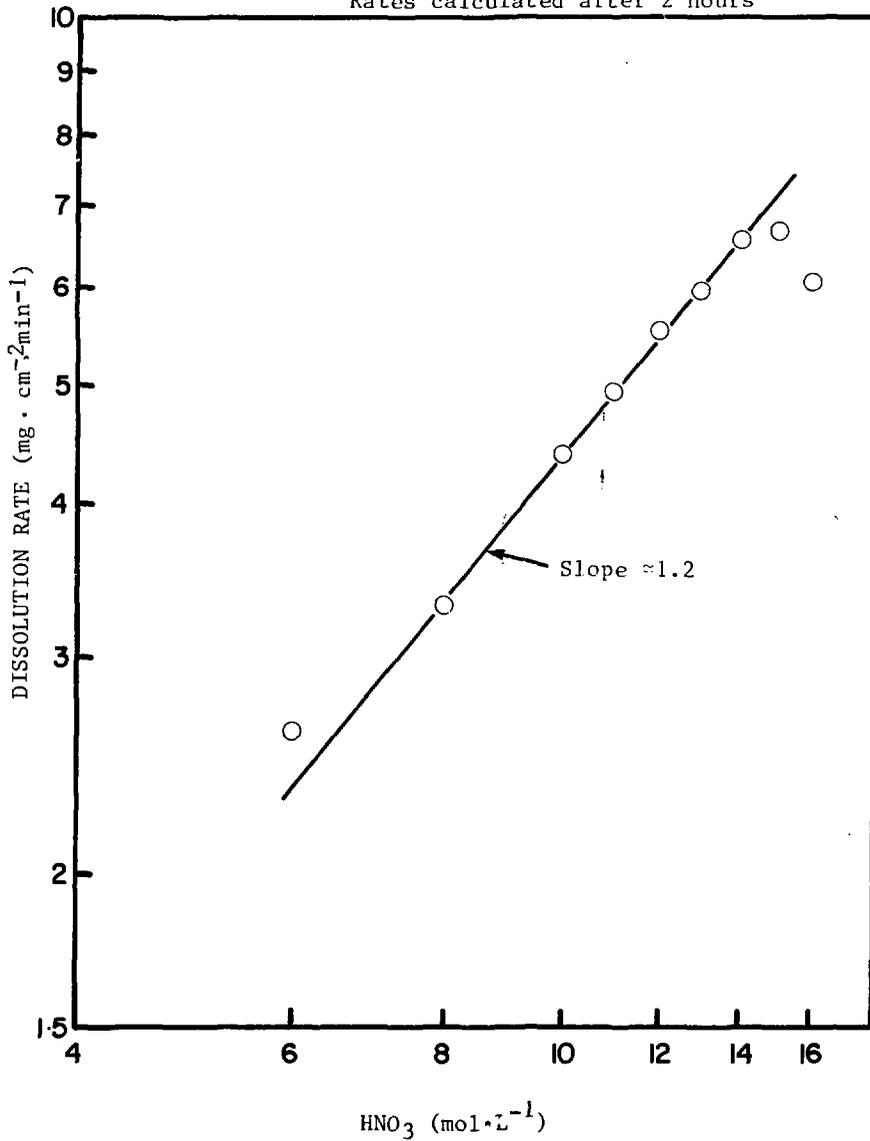
HNO_3 (mol$\cdot L^{-1}$)

T-6-52

FIGURE 2.   DETERMINATION OF THE APPARENT ORDER OF REACTION
WITH RESPECT TO HNO_3 CONCENTRATION

CONDITIONS: DP-14 half discs
13 mol·L^{-1} HNO$_3$/various HF
Boiling Point
300 mg (Th,U)O$_2$/mL acid
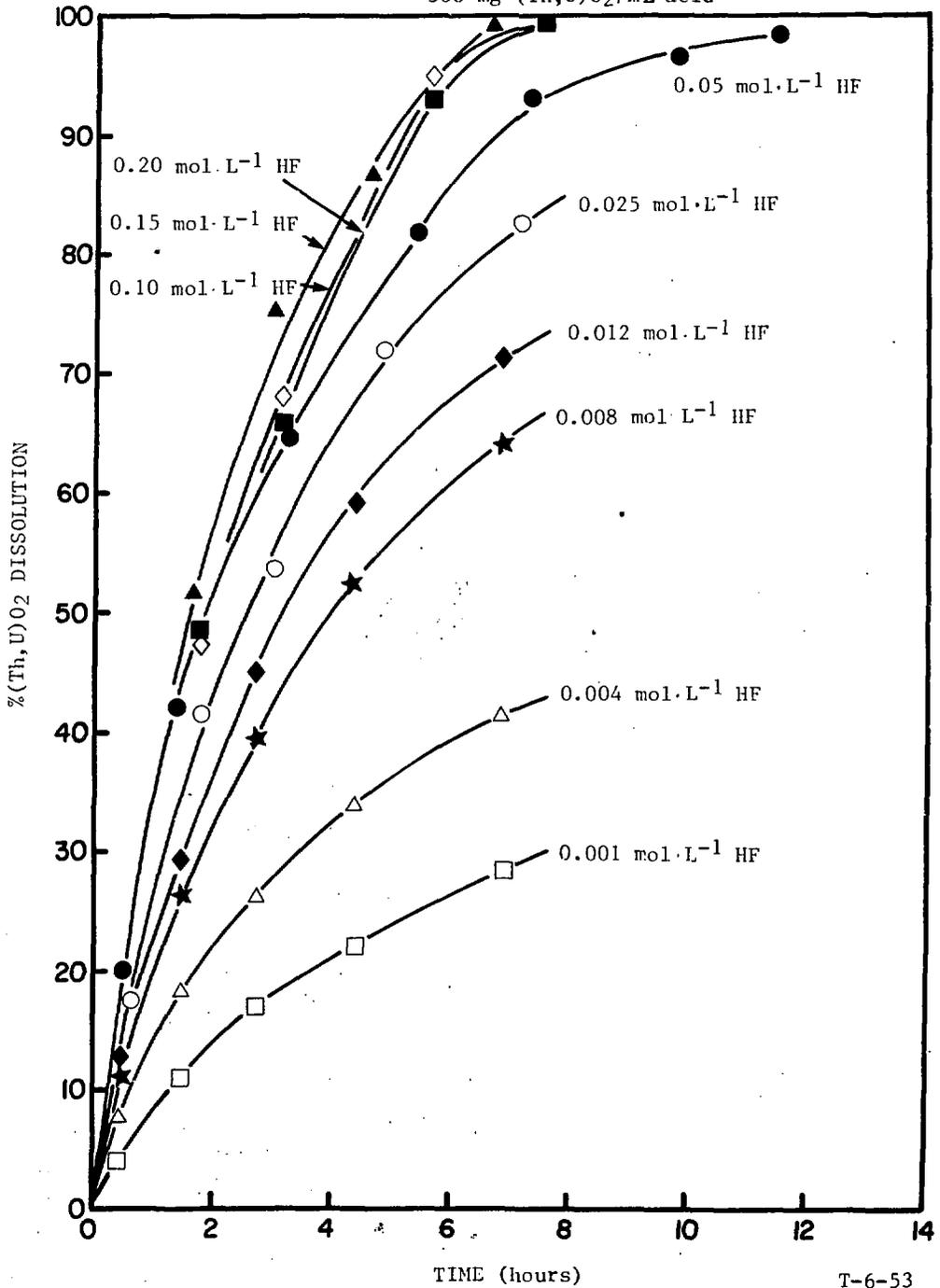
FIGURE 3. EFFECT OF HF CONCENTRATION ON THE DISSOLUTION
OF (Th,U)O$_2$

CONDITIONS: DP-14 half discs
13 mol·L^{-1} HNO_3/various HF
Boiling Point
300 mg(Th,U)O_2/mL acid
Rates calculated at 10% reaction
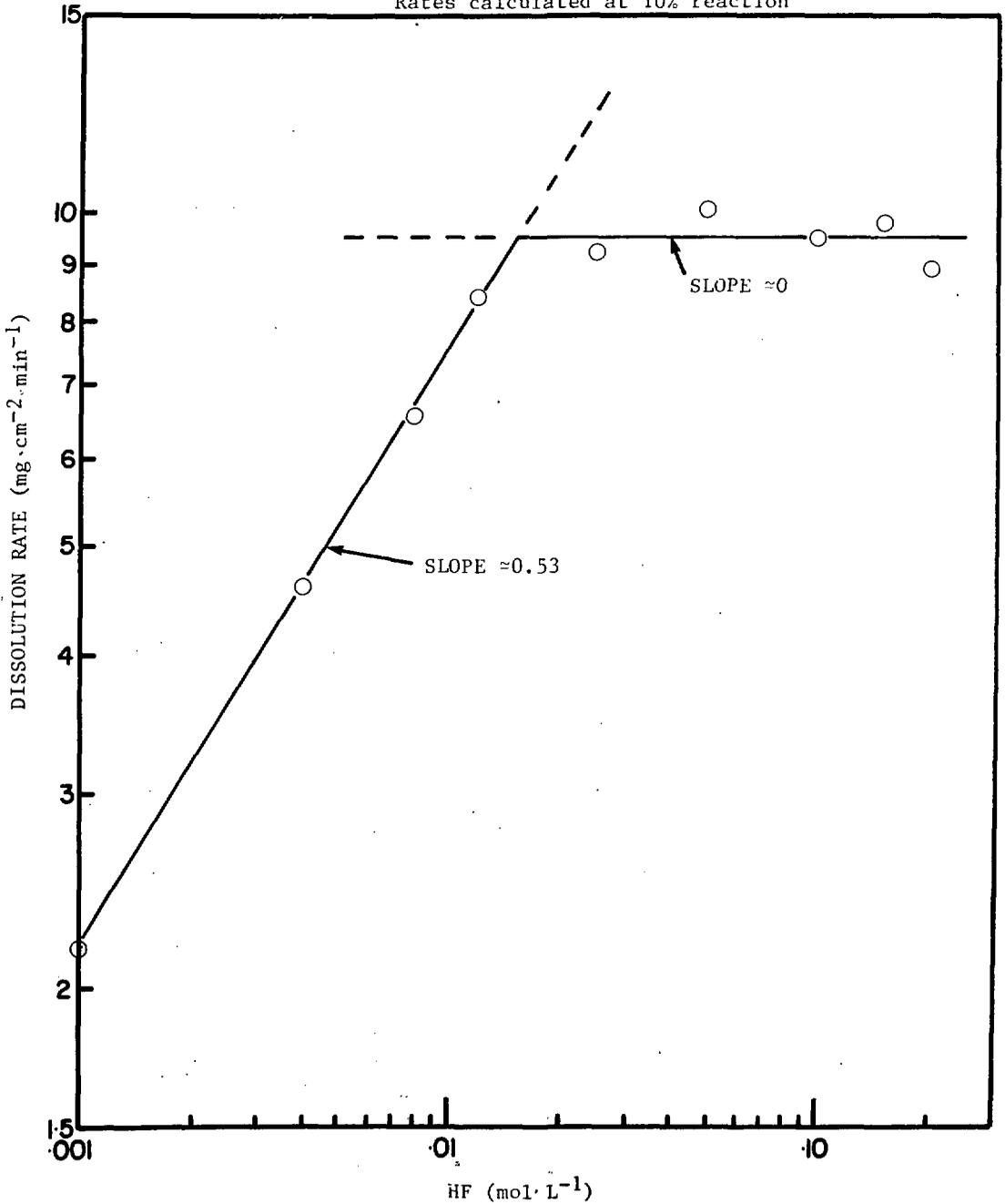
FIGURE 4.   DETERMINATION OF THE APPARENT ORDER OF REACTION
WITH RESPECT TO HF CONCENTRATION

T-6-54

CONDITIONS: DP-14   various geometries
              13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
              Boiling Point
              300 mg (Th,U)O$_2$/mL acid

%(Th,U)O$_2$ DISSOLUTION

TIME (min)

◆ – 38 μm powder

○ – 75 + 38 μm powder

△ – 150 + 75 μm powder

□ – 300 + 150 μm powder

◇ – 850 + 300 μm powder

Half discs

Single pellets and multiple pellets
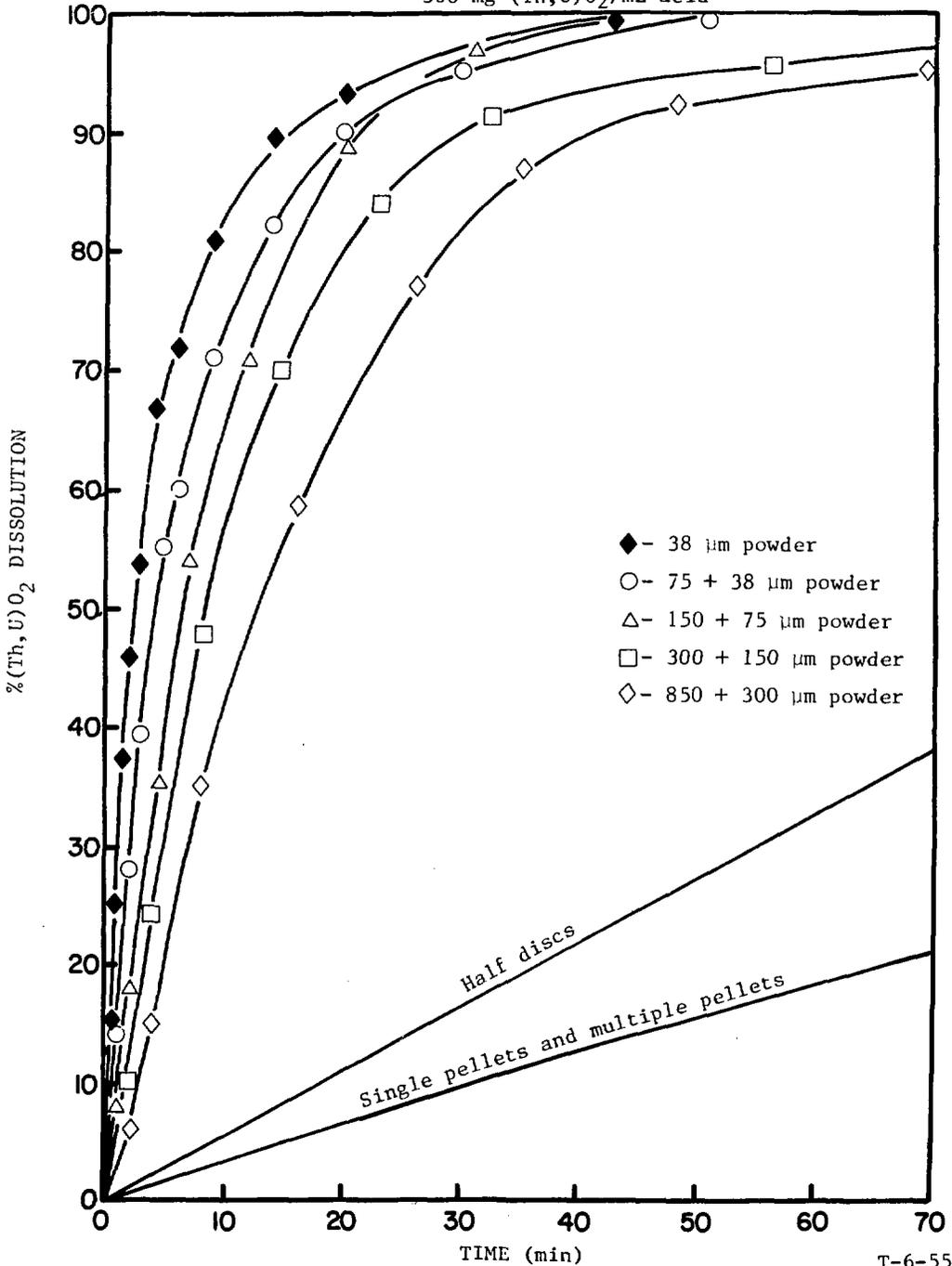
T-6-55

FIGURE 5.   EFFECT OF PARTICLE SIZE ON THE DISSOLUTION OF (Th,U)O$_2$

CONDITIONS: DP-14   single pellets
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
Various temperatures
300 mg(Th,U)O$_2$/mL acid
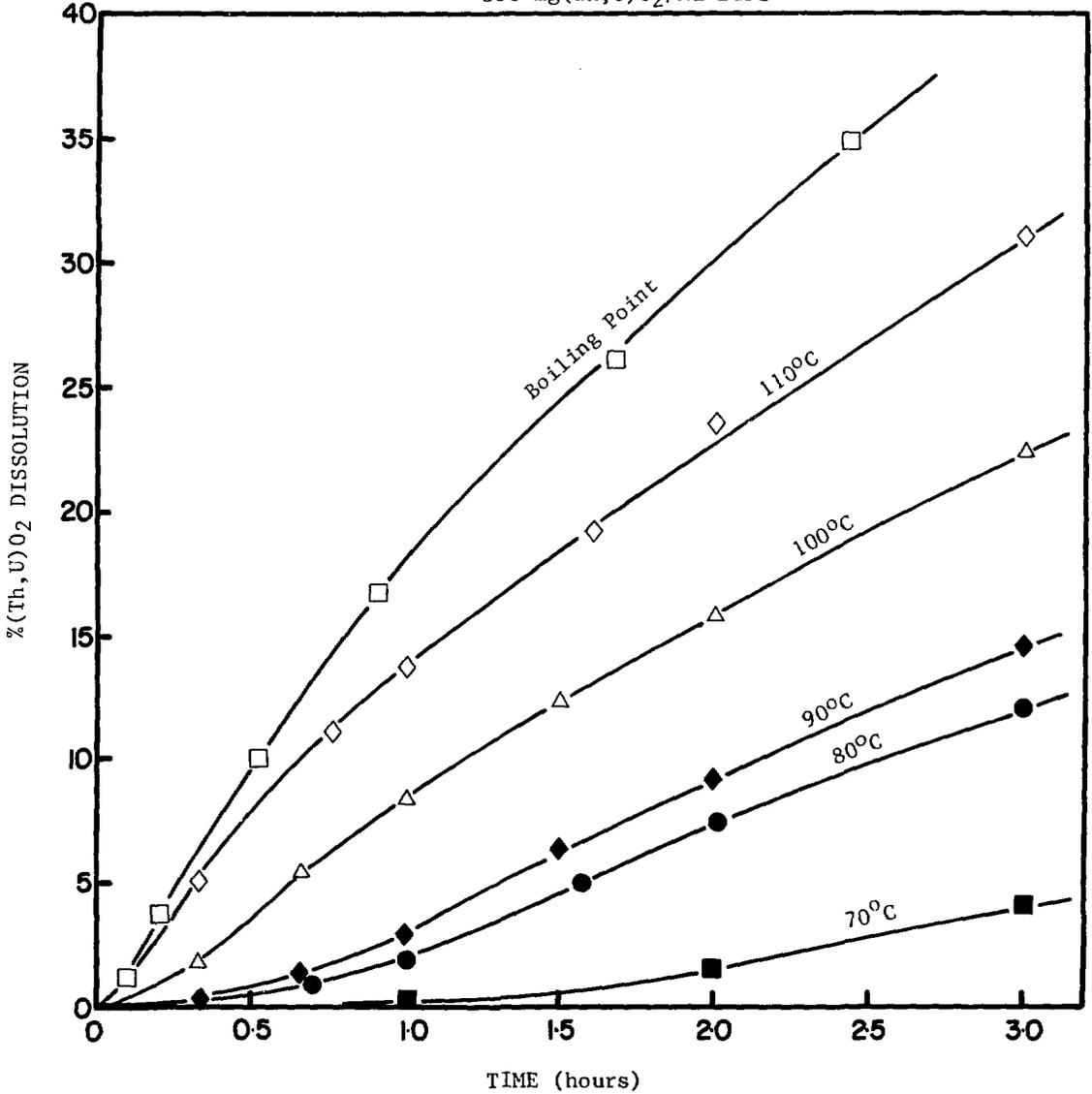
FIGURE 6.   EFFECT OF TEMPERATURE ON THE DISSOLUTION OF (Th,U)O$_2$

CONDITIONS: DP-14   single pellets
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
300 mg(Th,U)O$_2$/mL acid
Rates calculated at 10% reaction

Apparent activation

energy ≈ 54.4 kJ/mol
(13.0 kcal/mol)

DISSOLUTION RATE (mg·cm^{-2}·min^{-1})

$\frac{1}{T}$ × 10^3
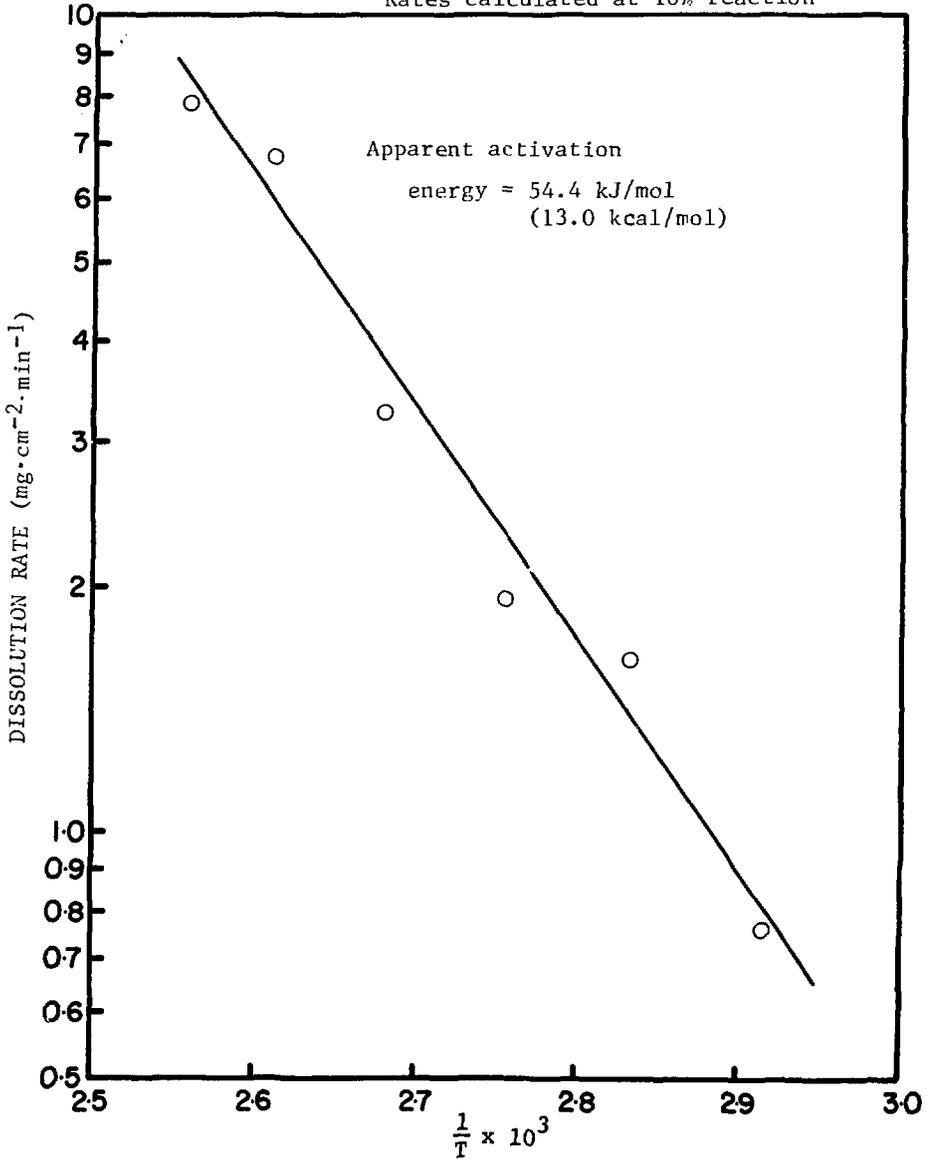
FIGURE 7.   ARRHENIUS PLOT OF (Th,U)O$_2$ DISSOLUTION RATE

FIGURE 8.   EFFECT OF Al(NO₃)₃ ON THE DISSOLUTION OF (Th,U)O₂

CONDITIONS: As shown
300 mg oxide/mL acid

% DISSOLUTION

TIME (hours)

◆UO$_2$ irregular fragments
8 mol·L^{-1} HNO$_3$
80°C

△(Th,U)O$_2$ WR1-947 irregular fragments
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
Boiling Point

□(Th,U)O$_2$ WR1-947 irregular fragments
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
80°C

O(Th,U)O$_2$ WR1-947 irregular fragments
8 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
80°C

T-6-59
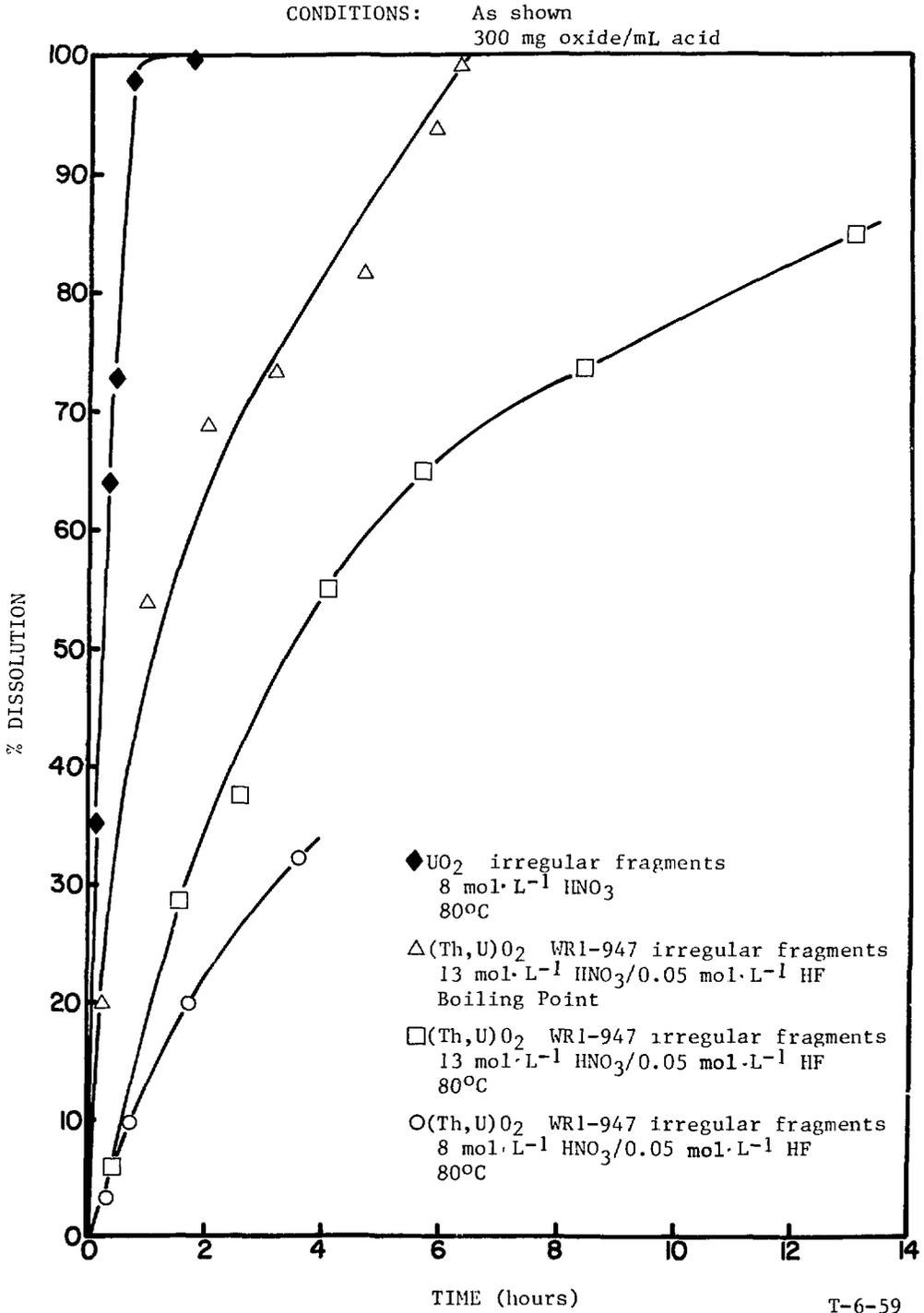
FIGURE 9.   COMPARISON OF THE DISSOLUTION OF (Th,U)O$_2$ AND UO$_2$

CONDITIONS: DP-14 single pellets
13 mol· L^{-1} HNO$_3$/0.05 mol· L^{-1} HF
Boiling Point
300 mg(Th,U)O$_2$/mL acid
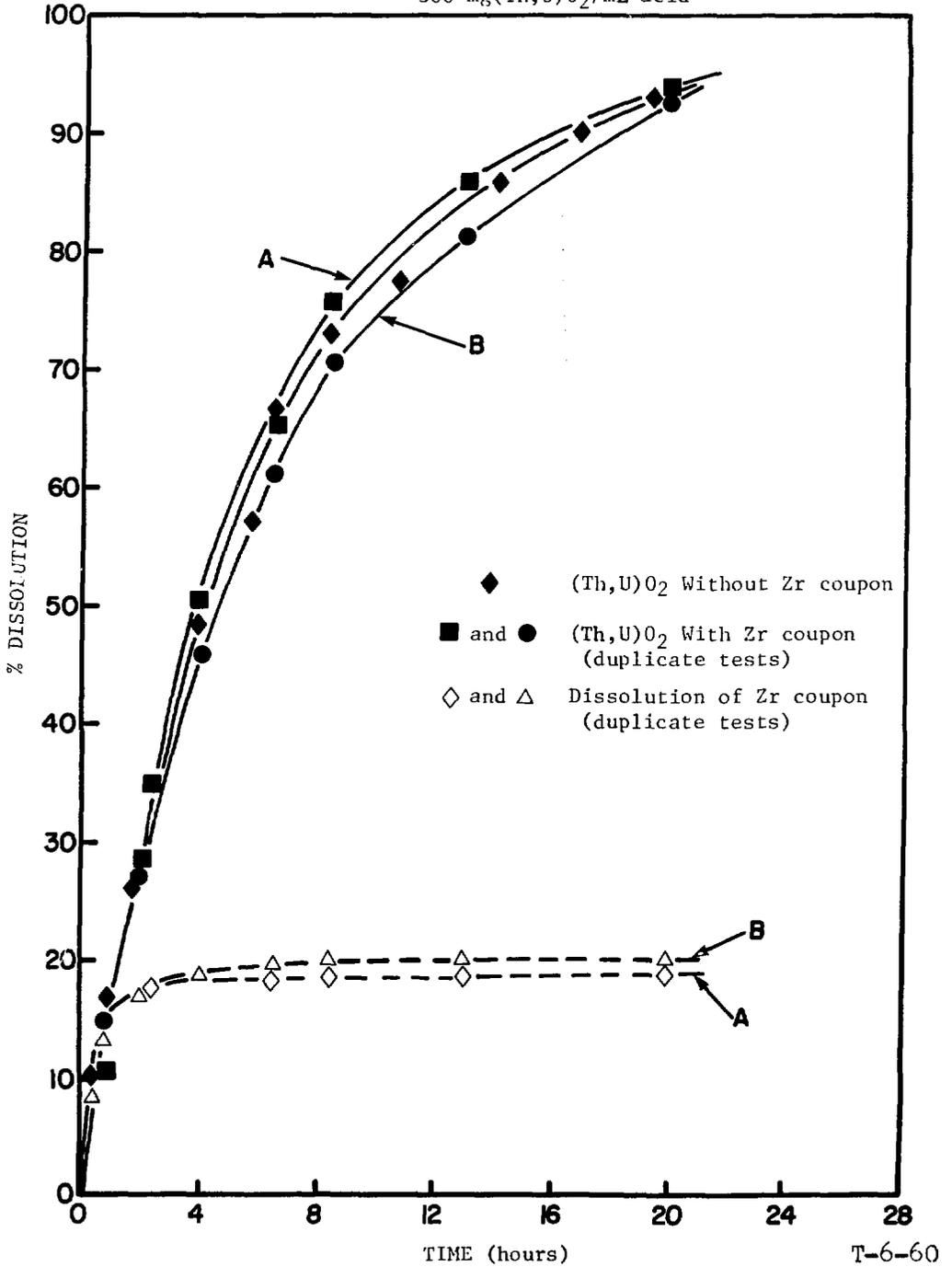
FIGURE 10.   EFFECT Zr SHEATH COUPON ON THE DISSOLUTION OF
(Th,U)O$_2$ PELLETS

CONDITIONS: DP-14 -850 + 300 μm powder
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
Boiling Point
300 mg (Th,U)O$_2$ mL acid

(Th,U)O$_2$
With Zr coupon

(Th,U)O$_2$
Without Zr

(Th,U)O$_2$
With Zr Turnings

DISSOLUTION OF Zr TURNINGS

DISSOLUTION OF Zr COUPON

% DISSOLUTION

TIME (min)
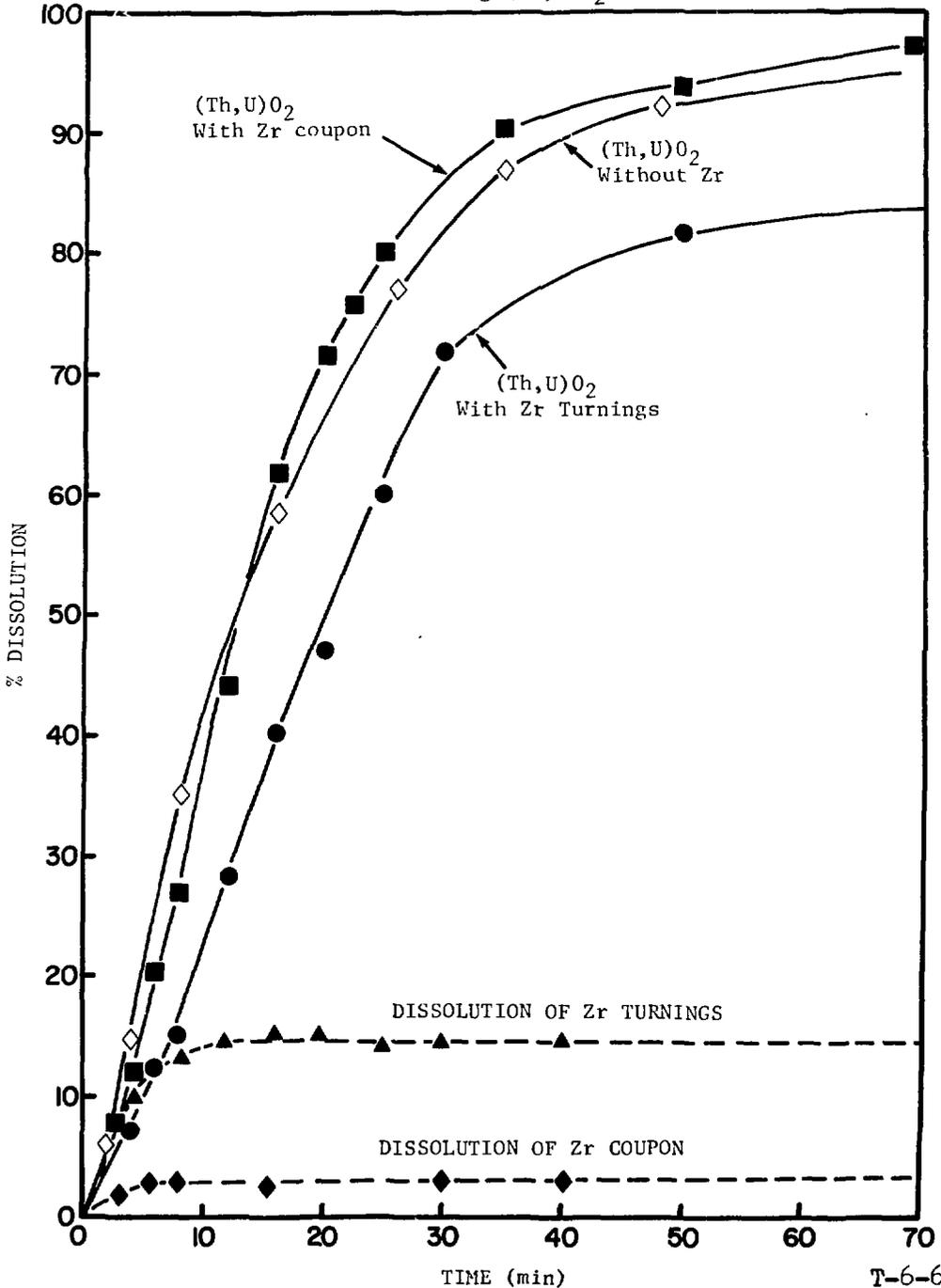
T-6-61

FIGURE 11.   EFFECT OF Zr ON THE DISSOLUTION OF (Th,U)O$_2$ POWDER

CONDITIONS: DP-14   half discs
13 mol·L^{-1} HNO$_3$ 0.05 mol·L^{-1} HF
Boiling Point
300 mg (Th,U)O$_2$/mL acid
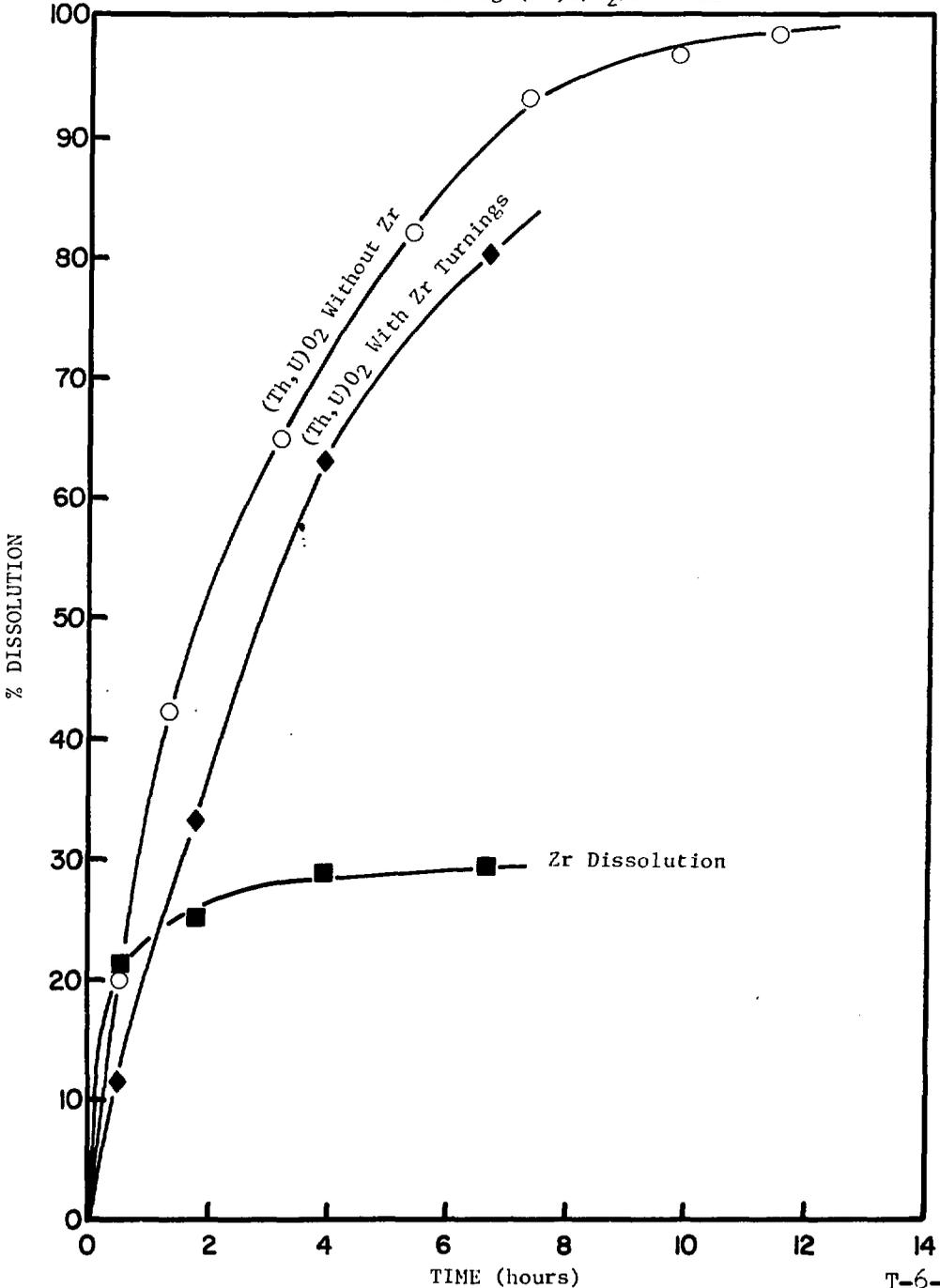
FIGURE 12.   EFFECT OF Zr TURNINGS ON THE DISSOLUTION OF
(Th,U)O$_2$ HALF DISCS

T-6-62

CONDITIONS: DP-14 half discs
13 mol·L^{-1} HNO$_3$/various HF
Boiling Point
300 mg(Th,U)O$_2$/mL acid
Rates calculated at 10% reaction

Without Zr

With Zr Turnings

No HF

DISSOLUTION RATE (mg·cm^{-2} min^{-1})

HF(mol·L^{-1}) x 10^2
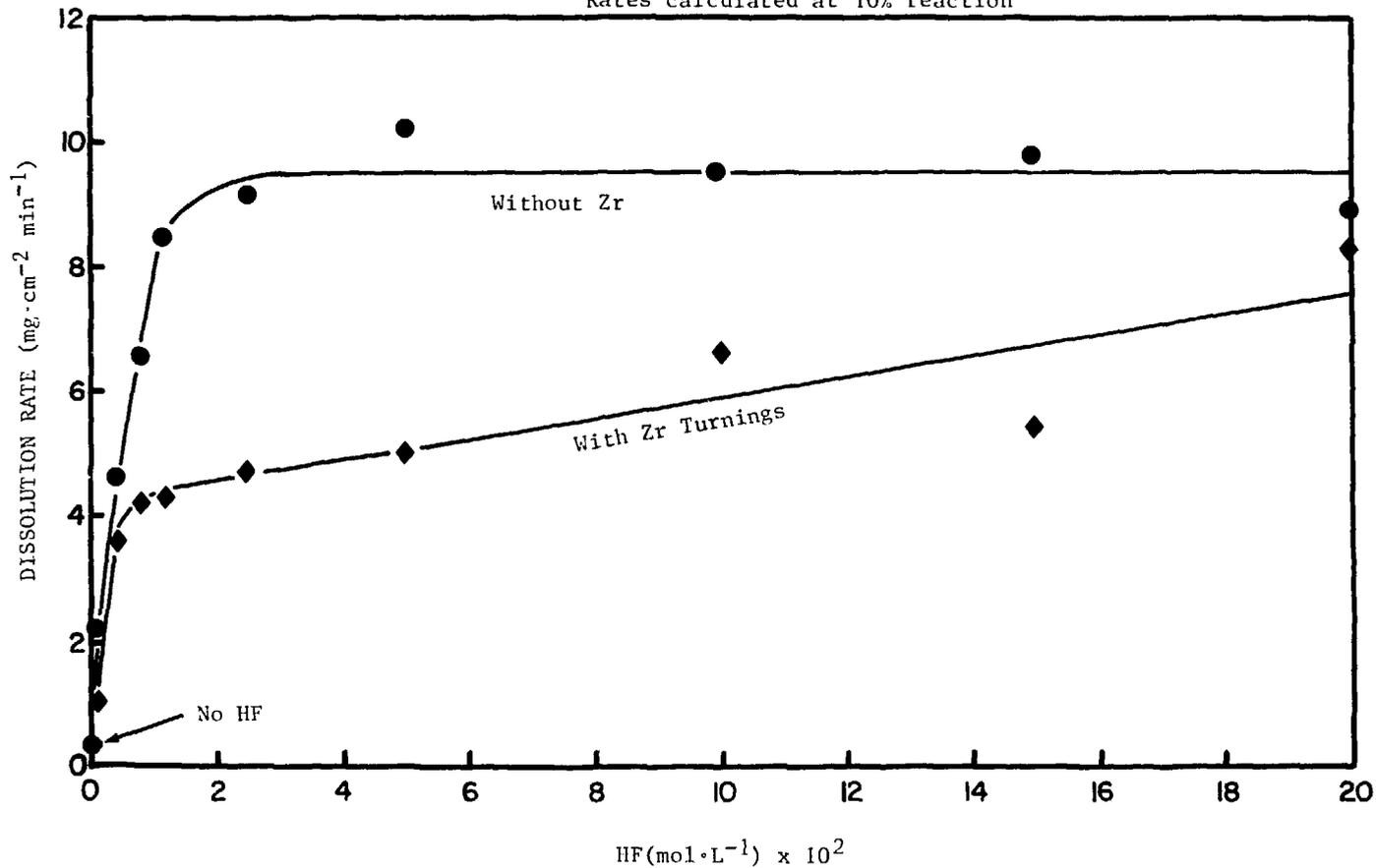
T-6-63

FIGURE 13. EFFECT OF HF CONCENTRATION AND Zr ON THE
DISSOLUTION OF (Th,U)O$_2$

CONDITIONS: Zr turnings
13 mol·L^{-1} HNO$_3$/various HF
Boiling Point
(Th,U)O$_2$ present (10:1 Th to Zr ratio)
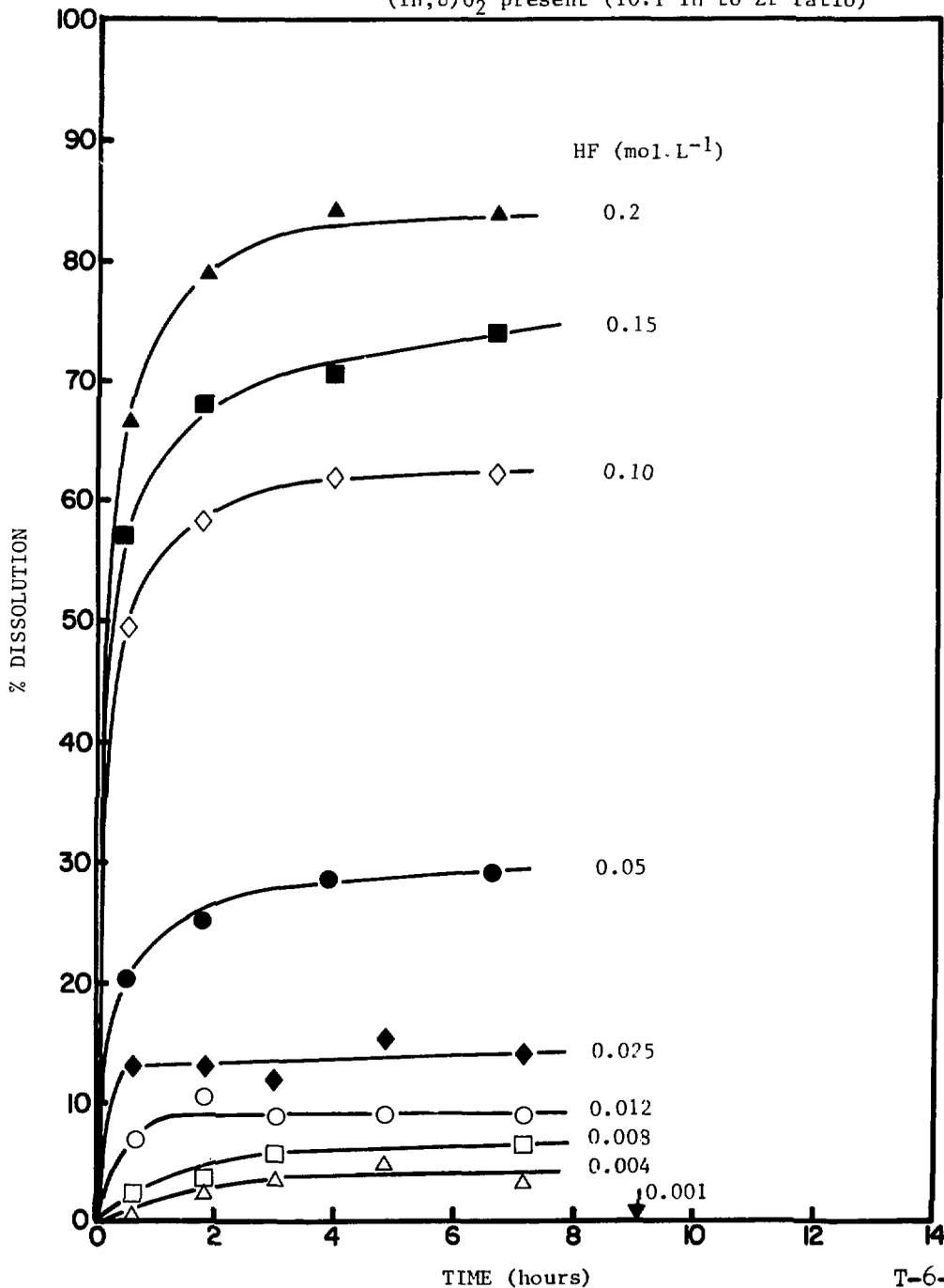
FIGURE 14.   EFFECT OF HF CONCENTRATION ON THE DISSOLUTION OF Zr

T-6-64

CONDITIONS: Various fuels   half **discs**
13 mol·L^{-1} HF 0·05 mol·L^{-1} HF
Boiling point
300 mg(Th,U)O$_2$/mL acid

△ WR1-947
◆ FDO-680
○ DP-14
□ DME-166
◇ H1
● H2 (single pellet)
■ H1 (single pellet)
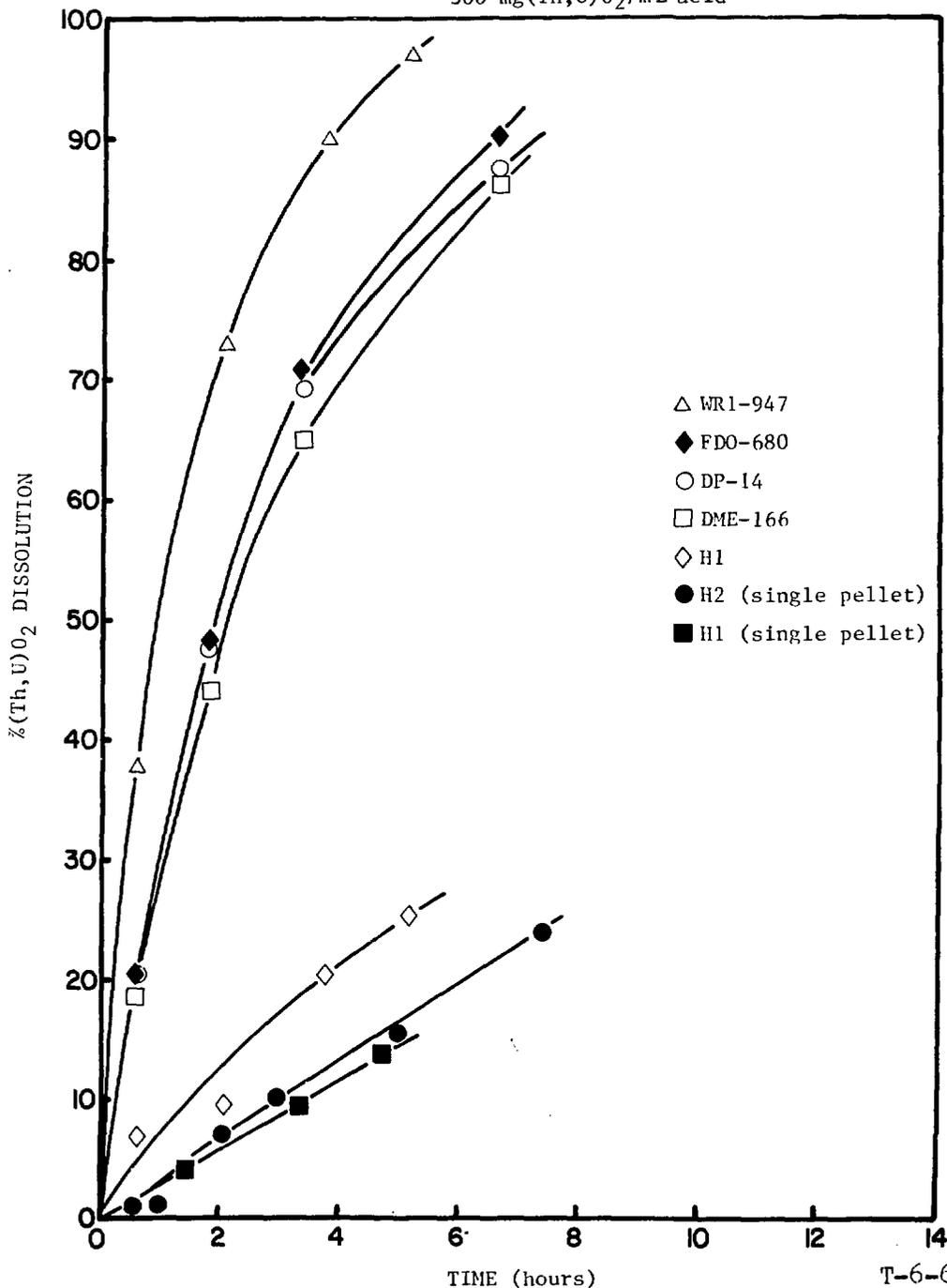
T-6-65

FIGURE 15.   COMPARISON OF THE DISSOLUTION OF VARIOUS
(Th,U)O$_2$ FABRICATION LOTS

CONDITIONS: DME-166 and H1 fuel   half discs
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
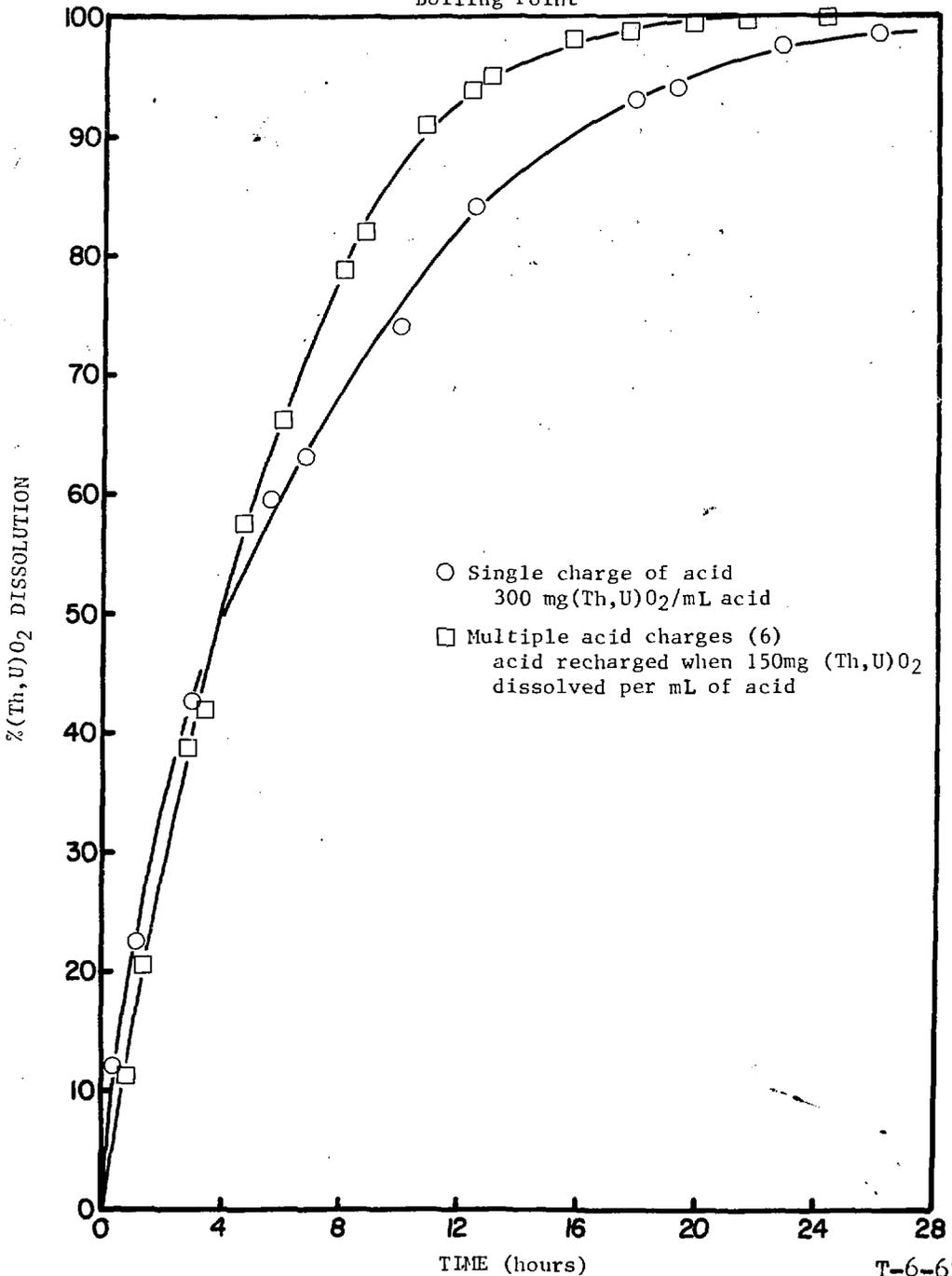Boiling point
300 mg(Th,U)O$_2$/mL acid

○ DME-166
    no treatment

△ DME-166
    heated to 900°C for 16 hours

□ DME-166
    heated to 1000°C
    quenched in water

■ H1
    no treatment

● H1
    heated to 1000°C
    quenched in water

TIME (hours)
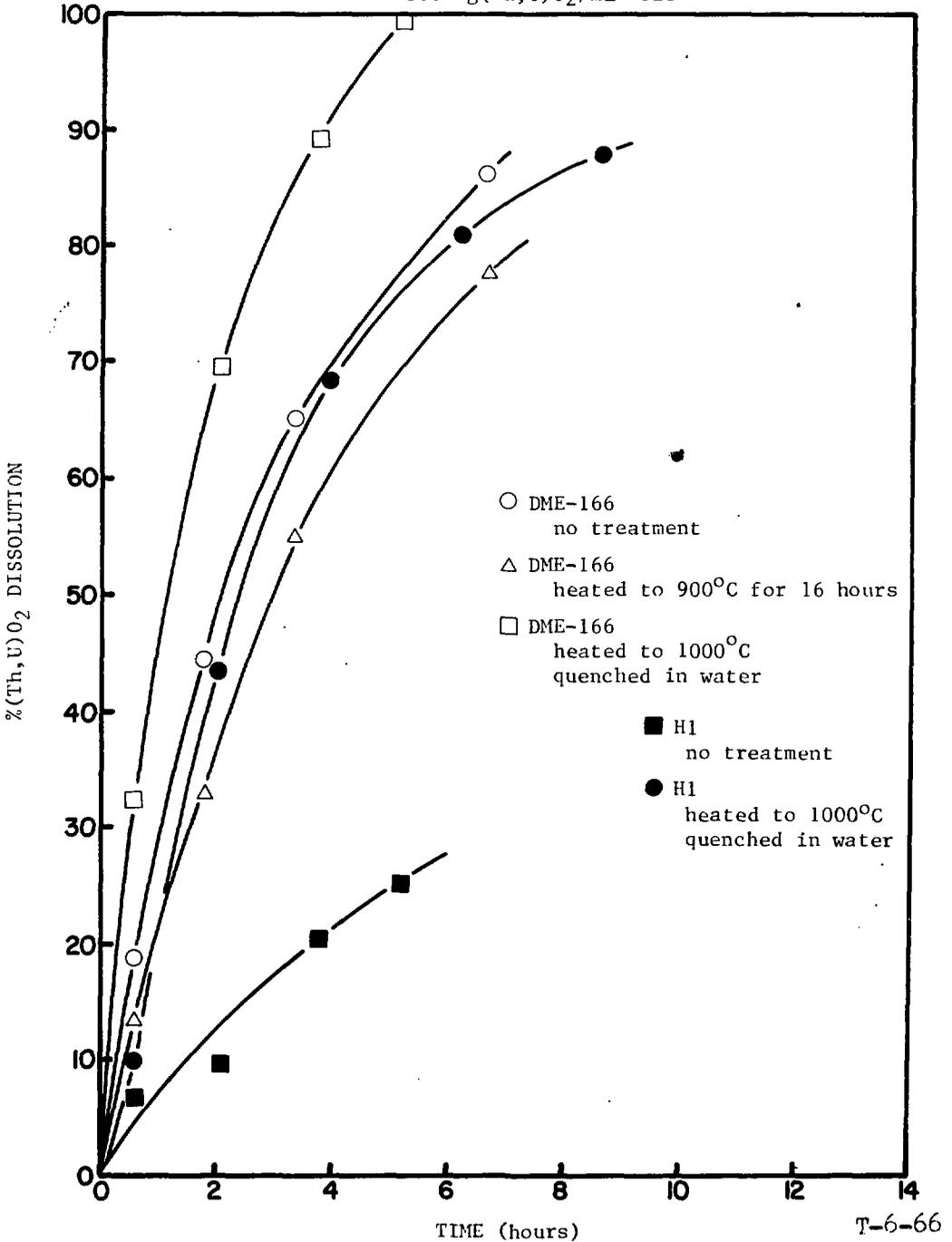
T-6-66

FIGURE 16.   EFFECT OF HEATING AND COOLING ON THE DISSOLUTION
              OF (Th,U)O$_2$

FIGURE 17.   EFFECT OF ACID REPLENISHMENT ON THE DISSOLUTION OF $(Th,U)O_2$
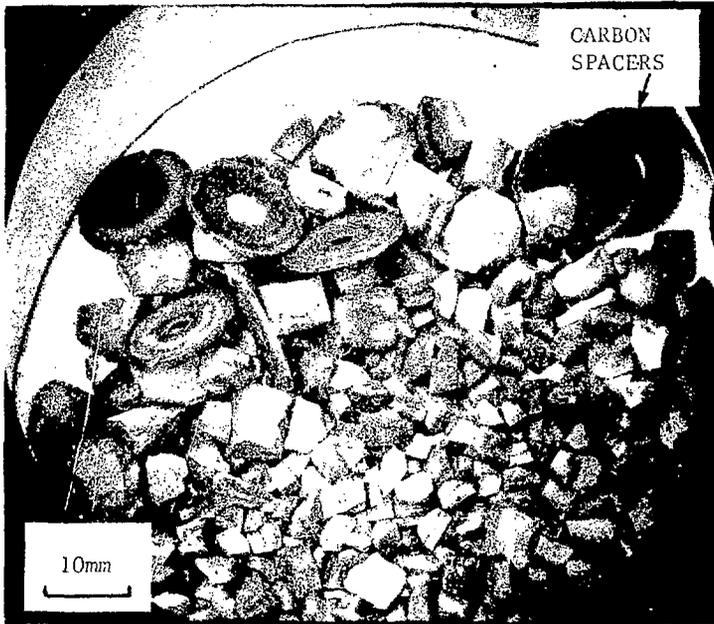
FIGURE 18. PHOTOGRAPH OF IRRADIATED WR1-947 (Th,U)O_2 FUEL (2.16 GJ/g)
AFTER SHEATH REMOVAL
(13.8mm DIAMETER CARBON SPACERS WITH CENTER HOLES ALSO SHOWN)

T-6-68

CONDITIONS: WR1-947   irregular fragments
13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
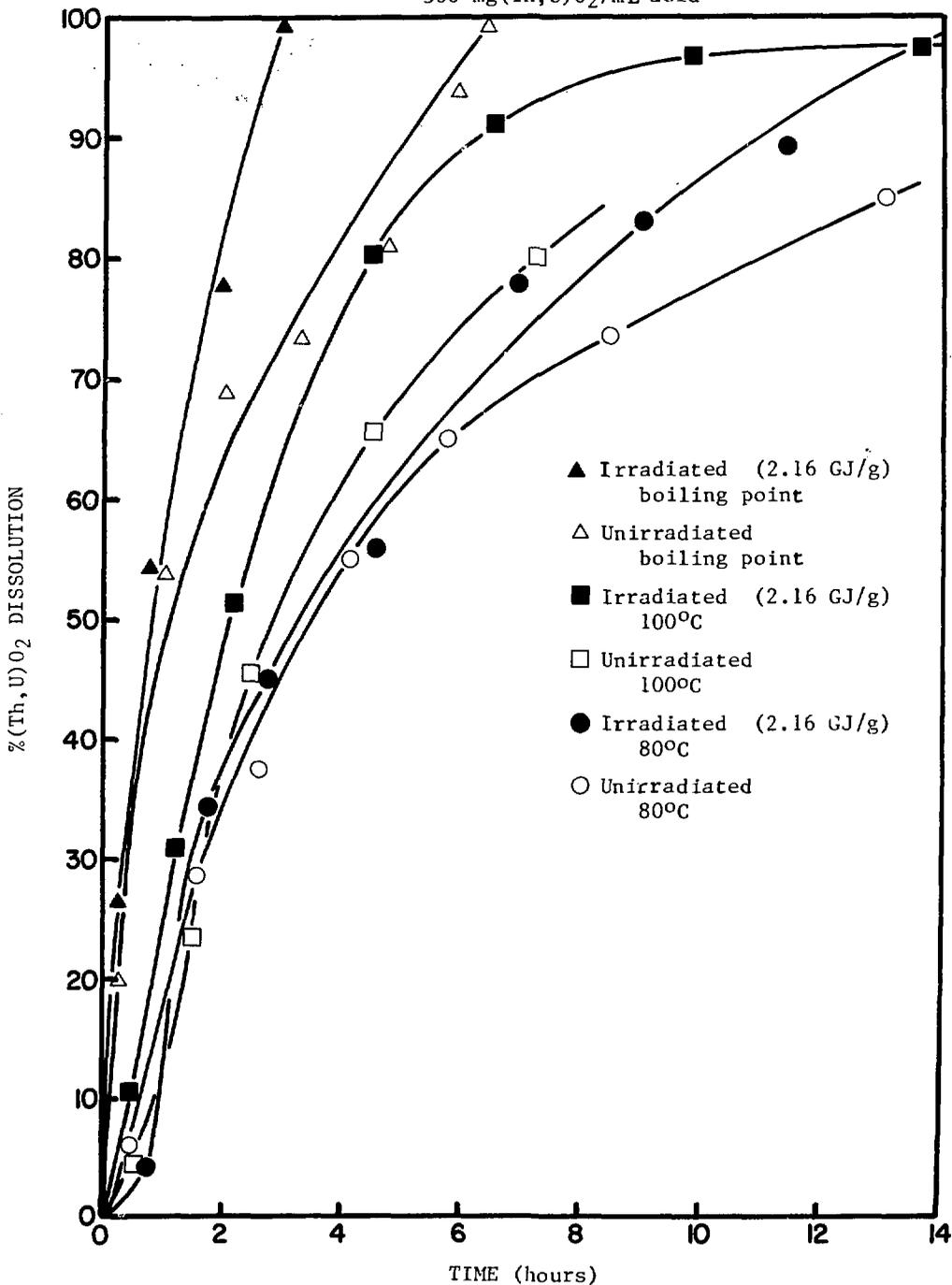Various temperatures
300 mg(Th,U)O$_2$/mL acid

▲ Irradiated   (2.16 GJ/g)
     boiling point

△ Unirradiated
     boiling point

■ Irradiated   (2.16 GJ/g)
     100°C

□ Unirradiated
     100°C

● Irradiated   (2.16 GJ/g)
     80°C

○ Unirradiated
     80°C

%(Th,U)O$_2$ DISSOLUTION

TIME (hours)

FIGURE 19.   COMPARISON OF THE DISSOLUTION OF IRRADIATED AND
UNIRRADIATED (Th,U)O$_2$

CONDITIONS: WR1-947 Irradiated fuel (2.16 GJ/g), irregular fragments
             13 mol·L^{-1} HNO$_3$/0.05 mol·L^{-1} HF
             100°C
             300 mg(Th,U)O$_2$/mL acid
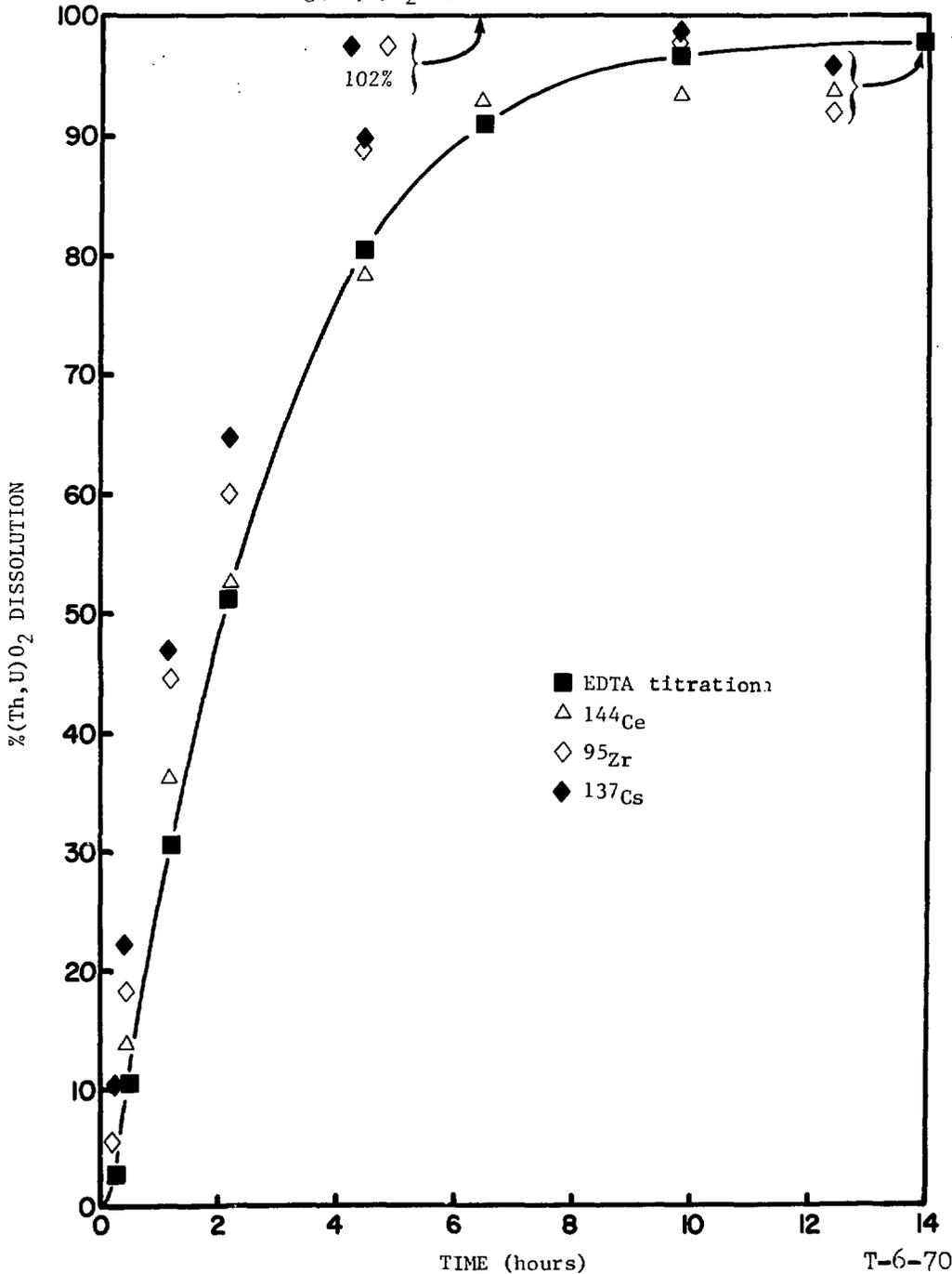

FIGURE 20.   MONITORING OF IRRADIATED (Th,U)O$_2$ DISSOLUTION BY
              FISSION PRODUCT ACTIVITY

T-6-70

CONDITIONS: WR1-947 irradiated fuel (2.16 GJ/g), irregular fragments
13 $mol \cdot L^{-1}$ HNO_3/0.05 $mol \cdot L^{-1}$ HF
300 mg(Th,U)O_2/mL acid
Zr sheath segments
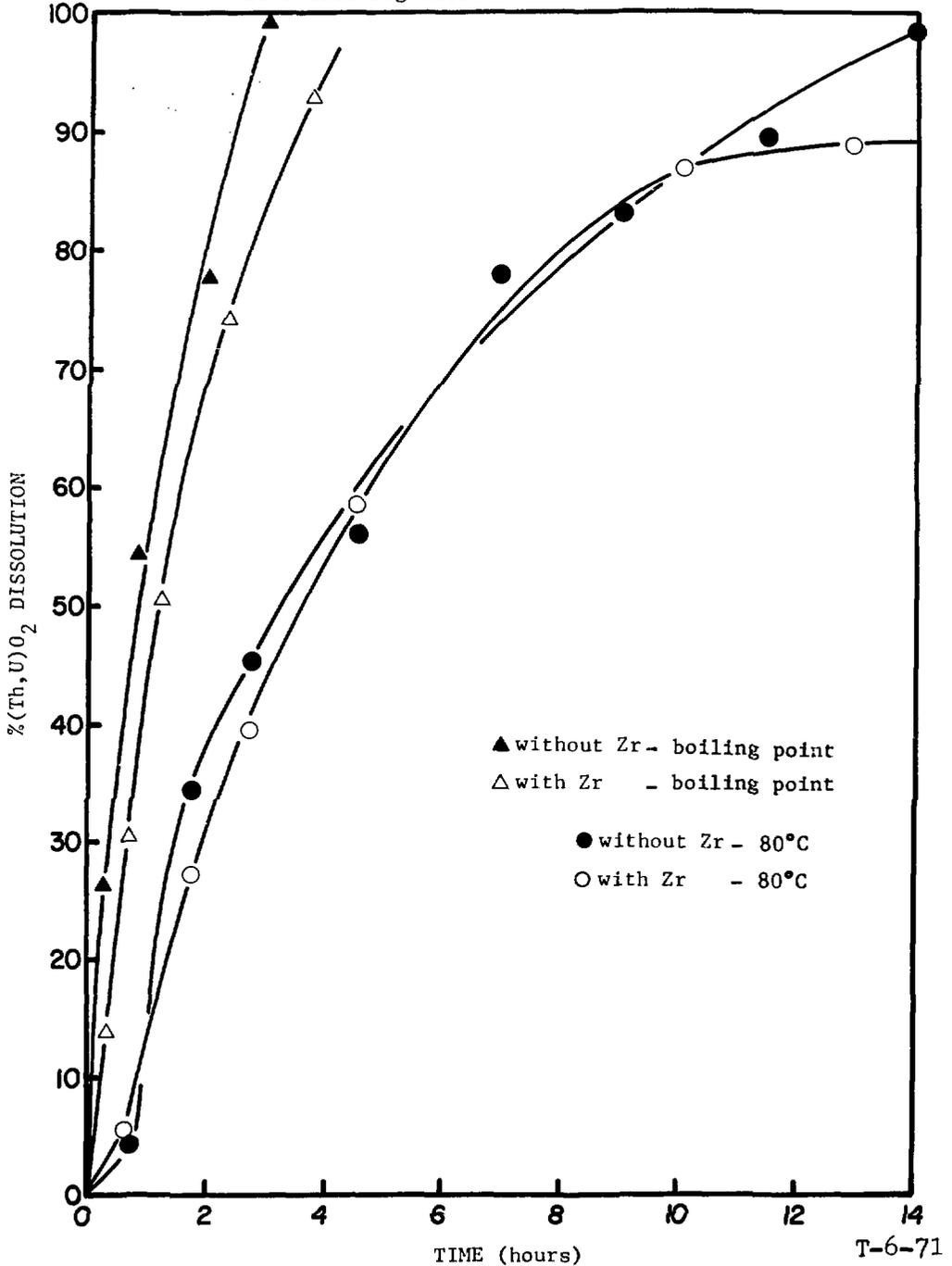
FIGURE 21.   EFFECT OF Zr ON THE DISSOLUTION OF IRRADIATED (Th,U)O_2

T-6-71

2379-77