AAEC/E143

UNCLASSIFIED

AAEC/E143

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

LABORATORY DEVELOPMENT OF THE GRIND – LEACH PROCESS FOR THE H.T.G.C.R. FUEL CYCLE

PART 1. DISSOLUTION OF URANIA – THORIA FUEL PARTICLES IN NITRIC ACID SOLUTIONS

by

M.S. FARRELL

S. R. ISAACS

Issued Sydney, September 1965

UNCLASSIFIED

PREFACE

This report is Part I of a series of reports on the laboratory development of the grind – leach process for the High Temperature Gas–cooled Reactor fuel cycle.

Companion series deal with :

Development of Solvent Extraction Processes for the H.T.G.C.R. Fuel Cycle.

Part I, Design of a Flowsheet for the Recovery of Actinides, has been issued as AAEC/E139.

and

Economics of the H.T.G.C.R. Fuel Cycle.

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

LABORATORY DEVELOPMENT OF THE GRIND – LEACH PROCESS FOR THE H.T.G.C.R. FUEL CYCLE

PART 1. DISSOLUTION OF URANIA – THORIA FUEL PARTICLES IN NITRIC ACID SOLUTIONS

by

M.S. FARRELL

S.R. ISAACS

ABSTRACT

The dissolution of 5 w/o UO_2 in ThO_2 fuel particles in nitric acid – fluoride solutions is a function of the ThO_2 dissolution rate. The ThO_2 dissolution rate has an apparent first order dependency on nitric acid concentration and a fractional order dependency on fluoride ion concentration.

The apparent activation energy of the dissolution of the ThO_2 in 13M nitric acid – 0·05M fluoride is 19 kcal/mole.

The presence of metal ions such as zirconium, aluminium, and beryllium inhibits the dissolution of the thoria. The order of inhibiting power is ZrIV > AlIII > BeII and this order is the same as the stability of their simplest fluoro – complexes.

The addition of small quantities of sulphate also seriously inhibits the dissolution, precipitating thorium as $Th(SO_4)_2 \cdot 4H_2O$ and quantitatively removing the fluoride.

CONTENTS

1. INTRODUCTION

A dispersion–type fuel with a beryllia matrix as described by Smith (1964) has been chosen for the Australian high temperature gas–cooled reactor (H.T.G.C.R) feasibility study.

Cairns (1964) indicated the need to examine the fuel cycle of such a reactor and suggested the possibility of using a grind – leach process to bring the actinide components of the fuel into solution by leaching the comminuted fuel in nitric acid solution, leaving the bulk of the beryllia as a nitric – acid – insoluble residue.

The chemical feasibility of such a grind – leach head–end process is being examined. The grind – leach process consists of three sub–processes :

(i) comminution of the fuelled beryllia,

(ii) nitric acid leaching of the comminuted material to dissolve selectively the actinide components, and

(iii) dissolution of the beryllia residue in sulphuric acid solution.

Figure 1 illustrates the relationship between the sub–processes in the grind – leach process, and the relationship of the grind – leach process as a whole to the proposed fuel cycle.

The leaching process to be effective must dissolve the maximum quantity of fuel with the minimum quantity of beryllia. The major factor in the leaching process is therefore the relative dissolution rates of the thoria and the beryllia.

In an attempt to limit the number of leaching trials required to optimize the process, separate studies of the dissolution of the urania – thoria fuel particles and of the comminuted beryllia were made.

This is the first report of a series on the laboratory development of the grind–leach process, and describes results obtained from the dissolution of urania – thoria fuel particles in nitric acid solutions. The next report will discuss dissolution of the beryllia, to be followed by reports on the comminution and leaching of beryllia matrix fuels, and the dissolution of beryllia in sulphuric acid.

This report considers the effects of solution variables on the dissolution of the fuel particles, no attempt being made to examine the effect of fuel particle properties such as grain size, available surface area, and density. It is known that density is important; a very low rate of attack is obtained with high density thoria (Farrell 1959). However the fuel particles used have been well characterized, and all major properties measured.

The effects of irradiation and burnup on the dissolution rates of the fuel particles have not been considered in the present study. However, Ferris and Ullmann (1964) have examined the dissolution of irradiated urania – thoria fuel particles of different origins. All material irrespective of origin was more readily dissolved after neutron irradiation. Sol–gel material was the most refractory.

2. EXPERIMENTAL

2.1 Materials and Reagents

The fuel particles consisted of a solid solution of 5 w/o UO_2 in ThO_2. These fuel particles were prepared in the following manner.

Weighed quantities of ThO_2 powder nominally –100 BSS size, calcined at 900°C for 12 hours, were wet ball–milled with natural UO_2 for 40 hours. (The UO_2 was –300 BSS Mallinckrodt ceramic grade; the ThO_2 was obtained from the U.K.A.E.A.) The mixed powder was compacted into pellets

4 inches in diameter and 1/2 inch in height at 20 tons per square inch using a 1000 - ton press. The pellets were crushed to -1/4 inch in a mortar and pestle and then fed to a Glen Creston micro-hammer mill for further size reduction to give a maximum size fraction of 20 per cent. greater than that finally required, that is, -60 +85 BSS size for a fully sintered -72 +100 BSS size material. The crushed particles were sintered at 1700 °C for 2 hours in hydrogen, and re-sieved after sintering to give the required size fraction.

Microphotographs of the fuel particles are given in Figure 2. It was difficult to bring out the grains by etching in the dissolvent 13M HNO_3 + 0.05M F'. However another phase was found to be present and this enabled the grain boundaries to be seen. The estimated approximate grain size range was 5μ to 50μ. The second phase contained Al_2O_3 and SiO_2, identified by electron probe analysis. The Al_2O_3 was probably introduced into UO_2 - ThO_2 during the ball-milling operation.

Densities and specific surface areas of each batch of fuel particles used were measured. The average density was measured with a specific gravity bottle using xylene as the immersion liquid, and the surface areas were measured by the B.E.T. Kr^{85} gas adsorption method (Harding 1962). The values obtained are as follows :

Batch No.	B.E.T. Surface Area cm^2/g	Average Density g/cm^3
282	240	9.76
310	375	9.76

The reagents used in the dissolution experiments were of analytical grade quality except for the aluminium and zirconium nitrates which were laboratory grade reagents. The beryllium nitrate was prepared as an acid-deficient solution from Minox AAA beryllia by dissolution in A.R. nitric acid. The excess nitric acid was removed by distillation.

2.2 Apparatus

Dissolution experiments were performed in a Teflon dissolver, a cylinder of inside diameter 1½ inches and height 4½ inches, which was heated by a mantle controlled by a trip-amplifier unit. The chromel-alumel thermocouples were inserted into a Teflon pocket fitted through the lid of the dissolver. A Teflon air-condenser was used; however most of the experiments were conducted at temperatures below the boiling point of the dissolvent. The temperature control was ± 2 °C. The contents were agitated using a magnetic stirrer, the soft iron spinner being enclosed in a Teflon jacket. Samples of solution were withdrawn from the dissolver through a Teflon tube inserted through the lid of the dissolver.

2.3 Procedure

A known mass (approximately 1 g) of the dry urania - thoria fuel particles was added to the dissolver containing the preheated nitric acid solution plus additives at the required temperature (normally 115 °C). The contents were stirred and samples of the solution were withdrawn at fixed intervals during the dissolution. The volume of reagent in the dissolver was kept constant by adding fresh dissolvent after each sampling.

The solution sample was analysed for thorium and uranium and the mass dissolved was calculated, after correcting for sampling losses.

2.4 Analyses

The solution samples were analysed spectrophotometrically for thorium and uranium content using Thoronol (Thomason et al. 1949) and P.A.R. (Florence and Farrar 1963) reagents respectively. Beryllium, aluminium, and zirconium nitrate solutions were analysed spectrophotometrically using chrome azurol S (Cerrai and Testa 1962; Pakalns 1964, 1965)

Total nitrate analysis was obtained gravimetrically using nitron reagent (Vogel 1939). Total nitrate analyses were required as a check on free acid concentration when making up nitric acid – beryllium nitrate solutions.

3. RESULTS

The effect of varying initial nitric acid and fluoride ion concentrations is shown in Figures 4 and 5, and Figure 6 illustrates the effect of temperature. The effect of the addition of other metal ions, namely beryllium, aluminium, and zirconium, on the initial dissolution rate of the thoria is shown in Figures 7, 8, and 9 respectively. Figure 10 compares the relative effects of the three metals examined. A tabulated summary of the relevant results is included with each figure.

4. DISCUSSION

The mass (M) of oxide dissolved was plotted against time (T) to give the M–T curve as illustrated in Figure 3. Not all M–T curves passed through the origin and, since this "induction period" was different for each experiment, the origin was ignored in plotting the curves. A considerable part of nearly all the curves was linear and the slope of this part gives the initial dissolution rate. This is a specific rate expressed as mass dissolved, mg ThO_2 or UO_2, per initial unit mass of urania – thoria fuel particles per minute, that is, mg/g. min. The unit chosen here is convenient and conventional for powder dissolution studies (Levenspiel 1962).

It was decided to base all conclusions on the study of the dissolution rate of thoria and assume that the urania rate is related proportionally. That thoria was controlling the dissolution rate of the fuel particles is evident from Figure 3 where the U : Th atomic ratio is constant at 1 : 20, the initial composition. As well, the usual dissolution rate of urania in nitric acid solution is appreciably higher (Taylor et al. 1963), which likewise indicates that the thoria controls the overall dissolution rate.

Similarly Ferris and Kibbey (1961) found that the overall dissolution rate of urania – thoria compacts in nitric acid – fluoride solutions was independent of the urania content up to ten per cent.

4.1 Effect of Nitric Acid Concentration

With a fixed initial fluoride ion concentration 0.05M and a fixed temperature of 115 °C, the effect of varying the initial nitric acid concentration was examined. The results obtained (Figure 4) indicate that in the range 8 to 13M HNO_3 the initial dissolution rate is first order with respect to nitric acid concentration. At 15M the dissolution rate was lower than at 13.4M. Bond (1958) obtained similar results for the dissolution of ThO_2 using 4 w/o UO_2 in ThO_2 pellets.

4.2 The Effect of Fluoride Concentration

Nitric acid will dissolve the thoria at an extremely low rate (less than 0.1 mg/g.min) in the absence of fluoride. With the addition of 0.001M F′ the rate increases some 100 times; further increases in initial fluoride ion concentration increase the rate but not in such a spectacular fashion. The apparent order of reaction with respect to fluoride is about half, whereas Bond (1958) found that the amount of thoria dissolving under similar conditions, but at the boiling point, was independent of fluoride ion concentration in the range 0.01 to 0.5M. Workers at C.E.N. – Belgo – Nucleaire (1962) studying the dissolution of PuO_2 in nitric acid, which also requires fluoride to catalyse the reaction, found that the dissolution rate was first order with respect to fluoride concentration. They suggested a mechanism in the dissolution of the PuO_2 (where the first step is rate determining), which may be applicable to ThO_2:

$$HNO_3 + HF + PuO_2 \xrightarrow{slow} PuF_y \xrightarrow{fast} H_{z-4}\ Pu(NO_3)_x \longrightarrow Pu(NO_3)_6{}''$$

A relatively high nitric acid concentration is necessary to ensure that there is nearly complete conversion of the plutonium fluoro–complex to the nitrate–complex. As this intermediate fluoro–complex of the plutonium is not detectable by spectrophotometry the concentration of intermediate is very small.

The fractional order obtained in the present work infers that the reaction taking place involves an adsorption step onto a non–uniform surface (Frank–Kamentskii 1955). It is not possible to elucidate the mechanism of this fluoride – catalysed reaction further from the present data.

4.3 Effect of Temperature

The effect of temperature on the dissolution rate of the ThO_2 in 13M HNO_3 + 0.05M F' was investigated over the range 70 to 115 °C. An Arrhenius plot (Figure 6) was linear, the slope giving a value of 19 kcal/mole for the apparent activation energy. There was no concavity or convexity in the curve, indicating that no change in the reaction mechanism occurred with increase in temperature (Hulett 1964). The value of 19 for the apparent activation energy indicates a kinetically–controlled reaction (Frank–Kamentskii 1955), and this value is close to the value of 15 kcal/mole obtained by C.E.N – Belgo Nucleaire (1962) for the fluoride–catalysed dissolution of PuO_2 in nitric acid solutions. In their case the activation energy was independent of nitric acid and/or fluoride ion concentration.

4.4 Effect of Cation Additives

Previous workers have shown that as thorium metal or thoria is dissolved, the increasing thorium concentration in the aqueous solution inhibits further dissolution (of this fluoride – catalysed reaction) by forming relatively strong thorium complexes which do not take part in the dissolution process (Moore et al. 1957; Bond 1958). The latter's results show a 50 per cent. decrease in dissolution rate for an addition of thorium (Th^{4+}) to 0.3M.

In the grind – leach process, selected for investigation as a possible head–end step for BeO–based dispersion–type fuels, beryllium will be the main cation present, as a typical atomic ratio for the fuel will be of the order 1:20:2000 for fissile (U): fertile (Th): moderator–matrix (Be). Uranium and thorium quantities present in solution at any time will be relatively low. The dissolution rate of the ThO_2 is therefore unlikely to be inhibited by the dissolved ThO_2, but dissolved BeO may inhibit the rate of dissolution of the ThO_2, the Be^{2+} ion in solution complexing the F' ion. Similarly the ions of aluminium, which is commonly used as an additive to HNO_3 – HF dissolvents to decrease stainless steel corrosion, and zirconium, which is a proposed construction material for the leacher–dissolver to be used in the grind – leach process, may also inhibit the dissolution of the ThO_2 by complexing with the fluoride ion.

The effect of the three metal ions beryllium, aluminium, and zirconium, on thoria dissolution was examined separately. The urania – thoria fuel particles were dissolved in 13M HNO_3 + 0.05M F' at 115 °C with the addition of various initial concentrations, of beryllium, aluminium, and zirconium ions.

Plots of initial dissolution rate of the thoria versus initial metal ion concentration are given in Figures 7, 8, and 9. The comparative effects of the three metal ions investigated are illustrated in Figure 10. The semi–log plot is used for convenience in Figure 10 because of the wide range of additive metal ion concentrations investigated.

From these results it is evident that the three metal ions all inhibit the dissolution of the thoria in the chosen medium. The degree of inhibition is quite severe and is in the order ZrIV > AlIII > BeII. Although the effect of the ThIV, FeIII, and BIII as BO_2^- was not examined in the present study, the results obtained by others (Blanco 1960; Ferris and Kibbey 1961) indicate that the order of inhibiting power is :

ZrIV > ThIV > AlIII > BeII > FeIII > BO_2^-

This order is the same as that obtained by Babko and Shimadina (1959) (using the metal–indicator systems FeIII – SCN^- and TiIV – H_2O_2) for the stabilities of the simplest fluoro-complexes of the type MF^{n+}, that is :

ZrIV > ThIV > CaIII > NbV > TaV > AlIII > SnIV > BeII

> GaIII > TiIII > SiO_2, InIII, GeIV.

One other effect of the metal ion additives has been to prevent precipitation of ThF_4. Other evidence (Moore et al. 1957; Bond 1958; Farrell 1959) confirms that precipitation of ThF_4 occurs if the fluoride ion concentration is raised above 0.04M in the presence of Th^{4+} in 13M HNO_3 acid. Precipitation of ThF_4 tends to inhibit the dissolution by "passivating" the oxide surface and so decreasing the dissolution rate. We have noticed that the addition of BeII and AlIII has prevented precipitation of ThF_4 when using 0.05M F' in 13M HNO_3 acid. The addition of small quantities of beryllium ion also appears to increase the rate of dissolution but, as can be seen from Figure 7, there was considerable scatter of results and the evidence is not conclusive. Even so, Blanco et al. (1960) have reported that FeIII up to 0.5M increased the rate of ThO_2 dissolution in nitric acid – fluoride solution. It appears that the use of a small quantity of additive metal ion, providing it does not form too strong a fluoro-complex, may assist in dissolution. The additive ion prevents the formation of a ThF_4 film on the oxide surface, and permits the use of a higher initial fluoride concentration, which is normally limited by the solubility product of ThF_4.

4.5 Effect of Sulphate Concentration

In the grind – leach process (Figure 1) it is proposed to dissolve the bulk of the beryllia residue in sulphuric acid, any residual heel being added to the next batch for nitric acid leaching. As residual sulphate may carry over with the heel it is important to know the effect of this sulphate "addition" on the fluoride-ion-catalysed nitric acid dissolution of the urania – thoria fuel particles. The results in the table below show that the effect of sulphate addition is deleterious. There was also a precipitate formed which coated the fuel particles.

EFFECT OF SULPHATE ADDITION ON THORIA DISSOLUTION

IN 13M HNO_3 + 0.05M F' AT 115°C

Run No.	Initial Sulphate Concentration (M)	Initial Dissolution Rate (mg/g.min)
33	nil	51.
38	0.02	9.0
37	0.20	1.5

Blanco et al. (1960) have reported that the addition of 0.1M SO_4'' decreased the rate of attack of 13.0M HNO_3 + 0.04M F' on urania – thoria pellets by 60 per cent. for a 1 hour dissolution period. They also reported the presence of an impervious coating of a precipitate suggested to be thorium sulphate.

To confirm the nature of the precipitate found in the present work a small quantity of sulphuric acid was added to a solution of 13M HNO_3 + 0.2M Th^{4+} at 25°C with and without 0.05M F'. In both cases a water-soluble white precipitate formed which was analysed and found to be $Th(SO_4)_2 \cdot 4H_2O$. In the case where fluoride was present, analyses showed that the fluoride had been quantitatively removed from solution by the precipitation of $Th(SO_4)_2 \cdot 4H_2O$. X-ray diffraction measurements confirmed that the water-soluble precipitate was $Th(SO_4)_2 \cdot 4H_2O$.

A small quantity of crystalline water–insoluble precipitate arising from dissolution runs Nos. 38 and 37 was examined by X-ray diffraction and found to be $ThF_4 \cdot x\, H_2O$ where x is approximately unity.

The inhibition of the dissolution of the thoria by addition of sulphate may therefore be due to the removal of fluoride ion from solution rather than to any passivation effect by the thorium sulphate coating the oxide surface.

5. CONCLUSIONS

(1) With 5 w/o UO_2 in ThO_2 fuel particles the ThO_2 controls the overall dissolution rate when dissolving in nitric acid–fluoride solutions.

(2) The initial dissolution rate of the thoria has an apparent first order relationship with initial nitric acid concentration in the range 8 to 14M, and an apparent fractional order relationship of about 1/2 with initial fluoride ion concentration, that is,

$$-\frac{d(ThO_2)}{dT} \propto [HNO_3]\;[HF]^{1/2}\;.$$

(3) The apparent activation energy is about 19 kcal/mole, indicating a kinetically-controlled reaction.

(4) The presence of metal ions which form strong fluoro-complexes inhibits thoria dissolution in nitric acid – fluoride solution. The present study has shown that the metal ions examined inhibit thoria dissolution in the order ZrIV > AlIII > BeII and this order is related to the strength of their fluoro – complexes as measured by Babko and Shimadina (1959).

(5) The presence of sulphate seriously inhibits thoria dissolution by precipitating thorium sulphate from concentrated nitric acid solution and quantitatively removing the fluoride ion from that solution.

6. RECOMMENDATIONS FOR THE GRIND–LEACH PROCESS

This study indicates the optimum conditions for obtaining maximum rate of dissolution of the urania –thoria fuel particles from the beryllia matrix in the chosen dissolvent. These conditions probably apply irrespective of the nature of the process for manufacture of the fuel–particles and resultant properties of the fuel–particles, even though a higher density fine–grained urania – thoria may dissolve much more slowly (Ferris and Ullmann 1964). Plutonia – thoria fuel particles could be expected to behave in a similar manner.

The optimum conditions are 12.5 to 13.5M HNO_3; 0.04M F′; and 115 °C or higher temperature. The presence of ZrIV and to a lesser extent AlIII cannot be tolerated. The presence of BeII can be tolerated up to 0.3M and in fact may enhance the dissolution rate up to that concentration. Sulphate cannot be tolerated, and heel from the beryllia–sulphuric acid dissolution step must be thoroughly washed free of sulphate before recycle to the nitric acid leaching.

7. ACKNOWLEDGEMENTS

The assistance of the following are gratefully acknowledged:

Mr. P.G. Alfredson for preparation of the fuel particles, Mr. P.J. Davis for the metallographic examination of the fuel particles, Mr. K.G. Watson for the X–ray diffraction analyses of the sulphate precipitates, Mr. A. Berzins for the surface area determinations, and the Analytical Chemistry Section under Dr. L.E. Smythe for the many analyses which they performed.

8. REFERENCES

Babko, A.K., and Shimadina, L.G. (1959). – Russian J. of Inorganic Chemistry 4 (1195): 482.

Blanco, R.E., Ferris, L.M., Flanary, J.R., Kitts, F.G., Rainey, R.H., and Roberts, J.J. (1960). – Proc. A.E.C. Symposium for Chem. Process of Irrad. Fuels from Power Test and Research Reactors, Richland, U.S.A. 1959. TID–7583, p.234.

Bond, W.D. (1958). – ORNL–2519.

Cairns, R.C. (1964). – J. Nuclear Materials 14 : 55–68.

C.E.N. – Belgo Nucleaire (1962). – EURAEC–708.

Cerrai, E., and Testa, C. (1962). – Anal. Chim. Acta 26 : 204.

Farrell, M.S. (1959). – AAEC/E42.

Ferris, L.M., and Kibbey, A.H. (1961). – ORNL–3143.

Ferris, L.M., and Ullman, J.W. (1964). – ORNL–TM–867.

Florence, T.M., and Farrar Y.J. (1963). – Anal. Chem. 35 : 1613.

Frank–Kamentskii (1955). – Diffusion and Heat Exchange in Chemical Kinetics (Princeton University).

Harding, B.C. (1962). – AAEC/TM142.

Hulett, J.R. (1964). – Quarterly Review 18 (3) : 227.

Levenspiel, O. (1962). – Chemical Reaction Engineering (John Wiley and Son).

Moore, R.L., Goodall, C.A., Hepworth J.L., and Watts, R.A. (1957). – Ind. and Eng. Chem. 49 : 885.

Pakalns, P. (1964). – Anal. Chim. Acta 31 : 576.

Pakalns, P. (1965). – Anal. Chim. Acta 32 : 57.

Smith, R. (1964). – Third Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva 1964. Paper 543.

Taylor, R.F., Sharratt, E.N., de Chazal, L.E.M., Logsdail, D.H. (1963). – J. Applied Chemistry 13 : 32–40.

Thomason, P.F., Perry, M.A., and Byerly, W.M. (1949). – Anal. Chem. 21 : 1239.

Vogel, A.I. (1939). – A Textbook of Quantitative Inorganic Analysis (Longmans).

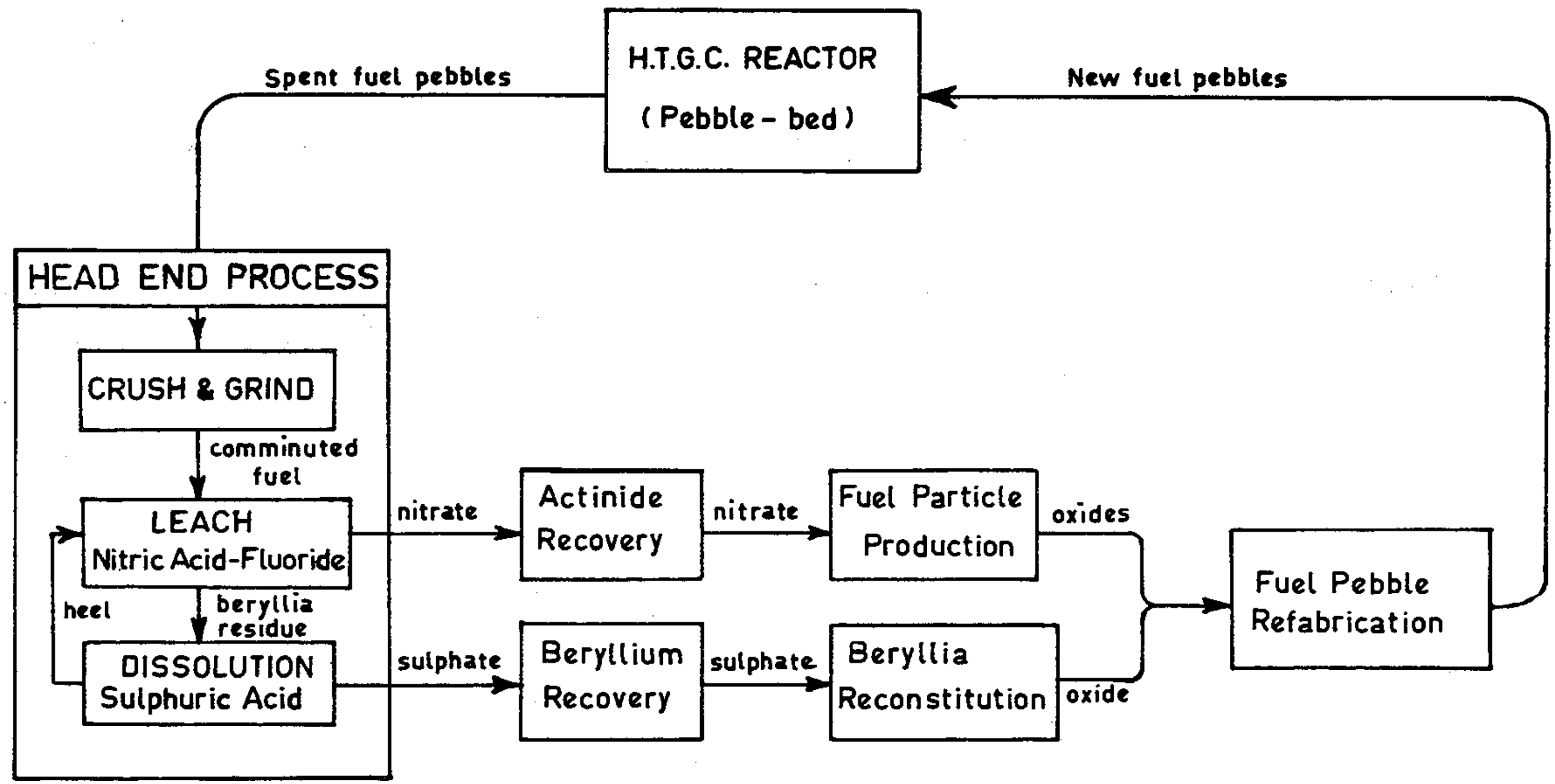
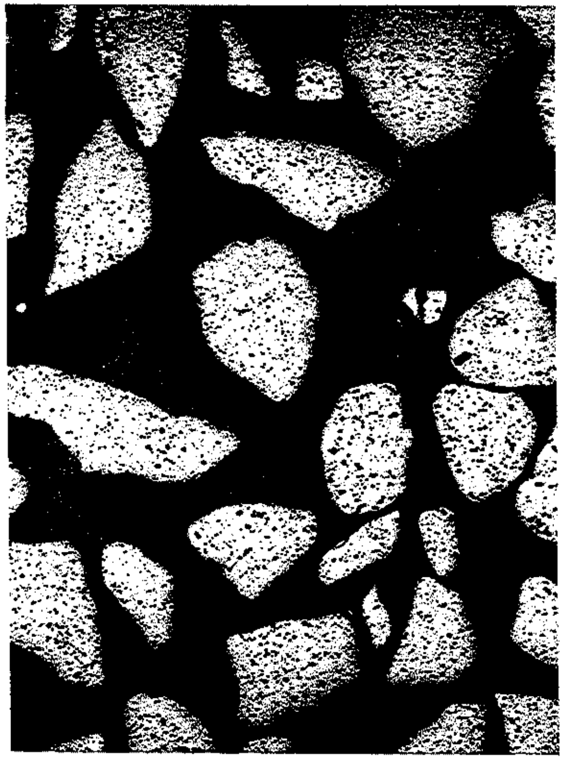


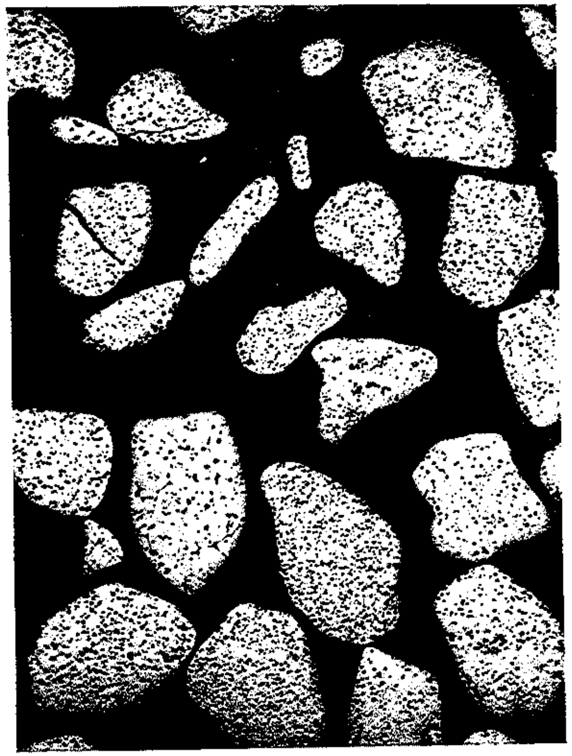
FIGURE 1. FUEL CYCLE FOR H.T.G.C. REACTOR USING A BERYLLIA-BASED DISPERSION TYPE FUEL

P836



X 100

BATCH 310 – FIELD SHOWING SHAPE OF PARTICLES



X 100

BATCH 282 – FIELD SHOWING SHAPE OF PARTICLES

X 350

BATCH 282 – UNETCHED PARTICLE SHOWING GRAIN MORPHOLOGY. GRAIN SIZE FROM ~5μ TO 50μ

FIGURE 2. MICROPHOTOGRAPHS OF THE URANIA–THORIA FUEL PARTICLES

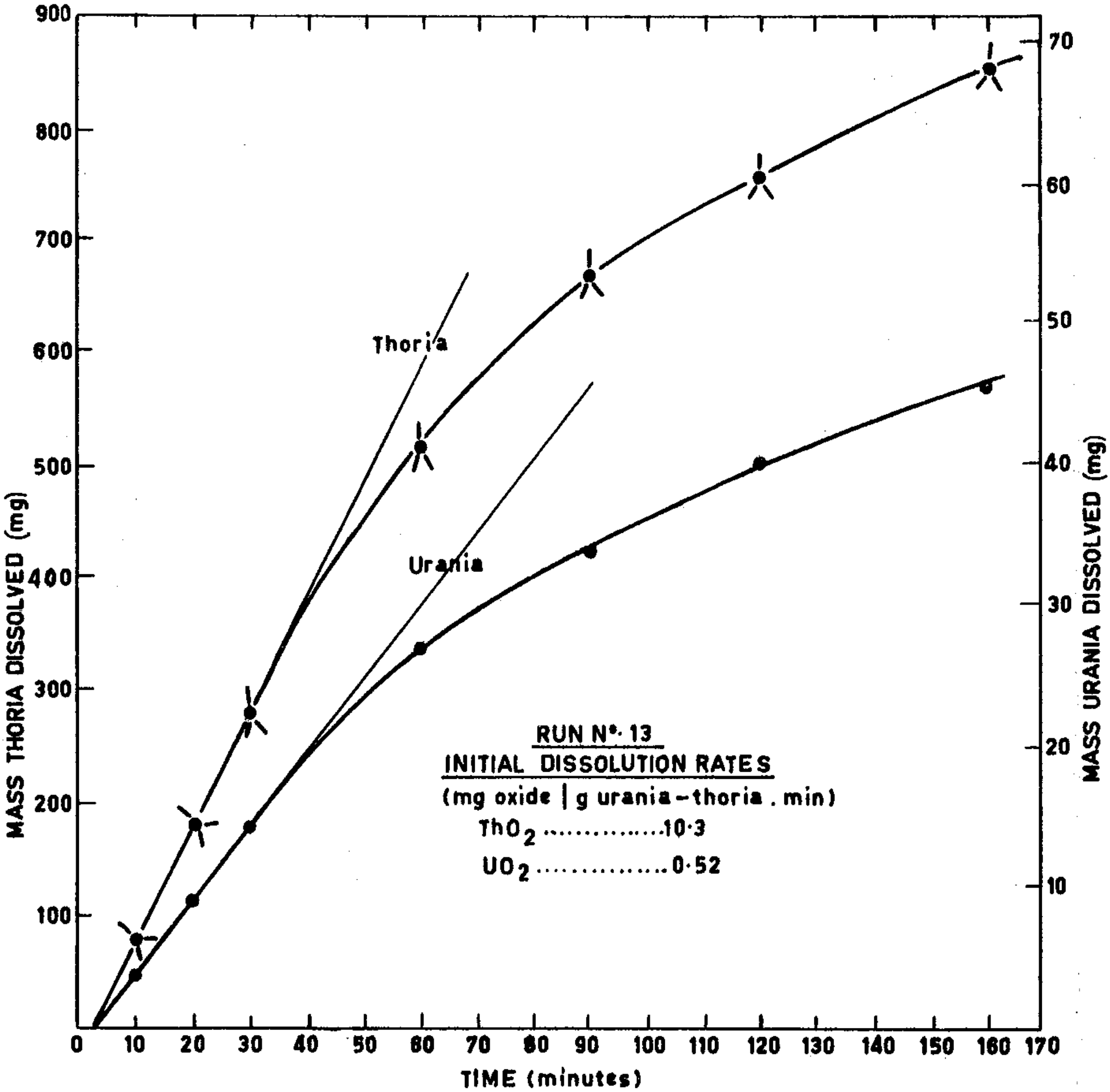
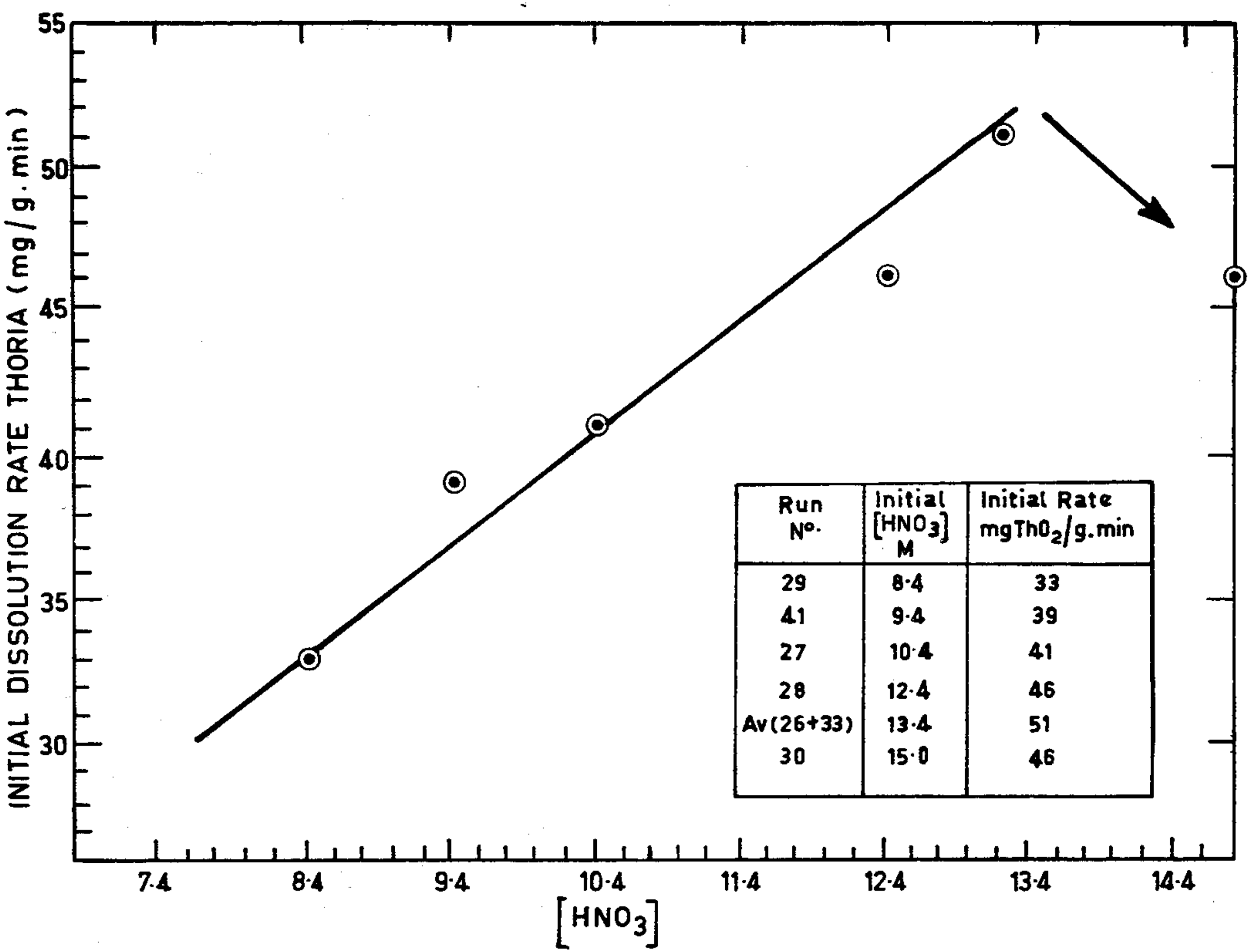


FIGURE 3. A MASS–TIME PLOT (1 g urania – thoria fuel particles in 13 M HNO_3 + 0·001 M F′ at 115°C)

P836

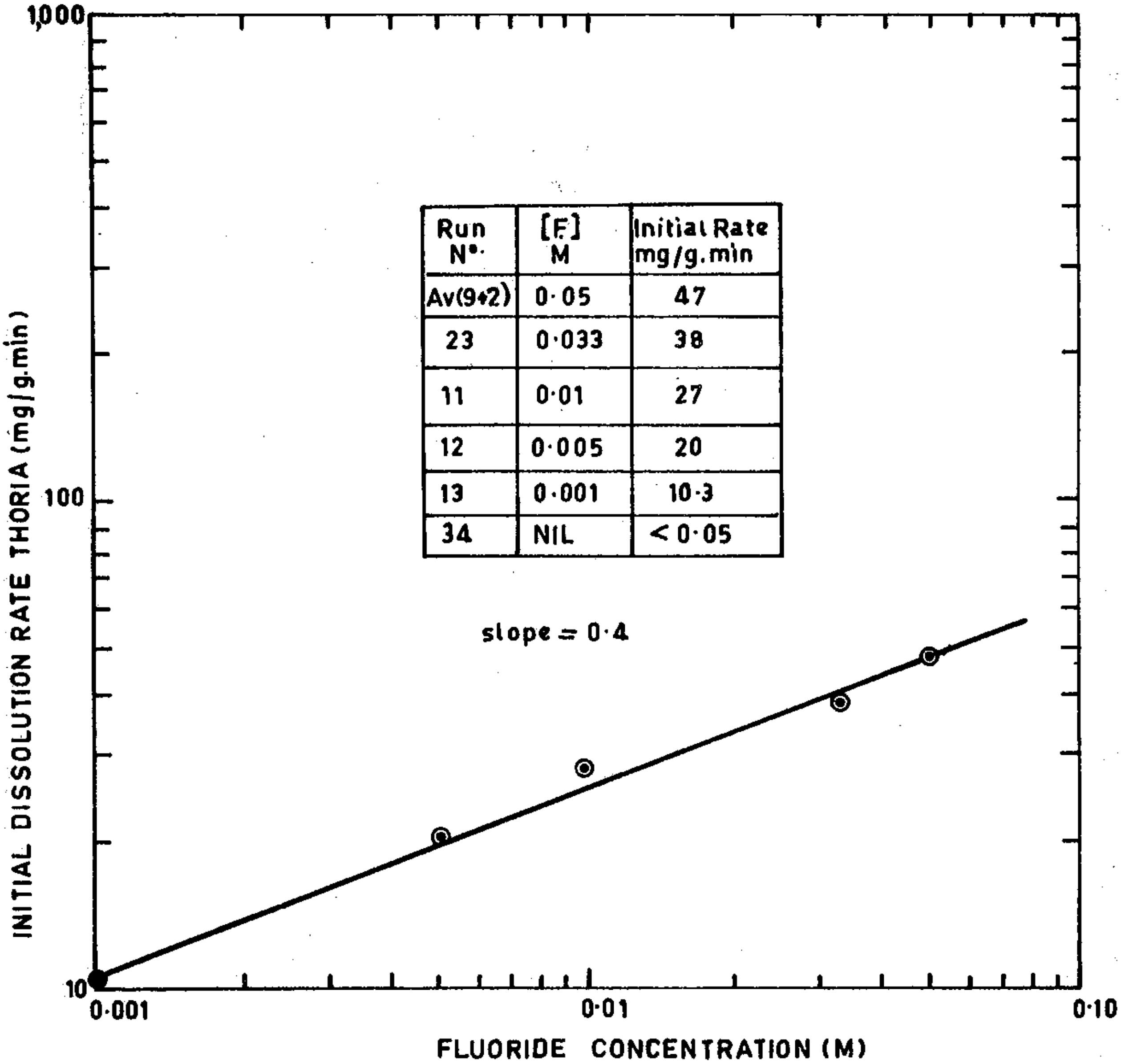


Run N°.	Initial [HNO_3] M	Initial Rate $mgThO_2/g.min$
29	8·4	33
41	9·4	39
27	10·4	41
28	12·4	46
Av(26+33)	13·4	51
30	15·0	46

FIGURE 4. EFFECT OF NITRIC ACID CONCENTRATION

(using 0·05 MF′ at 115°C)

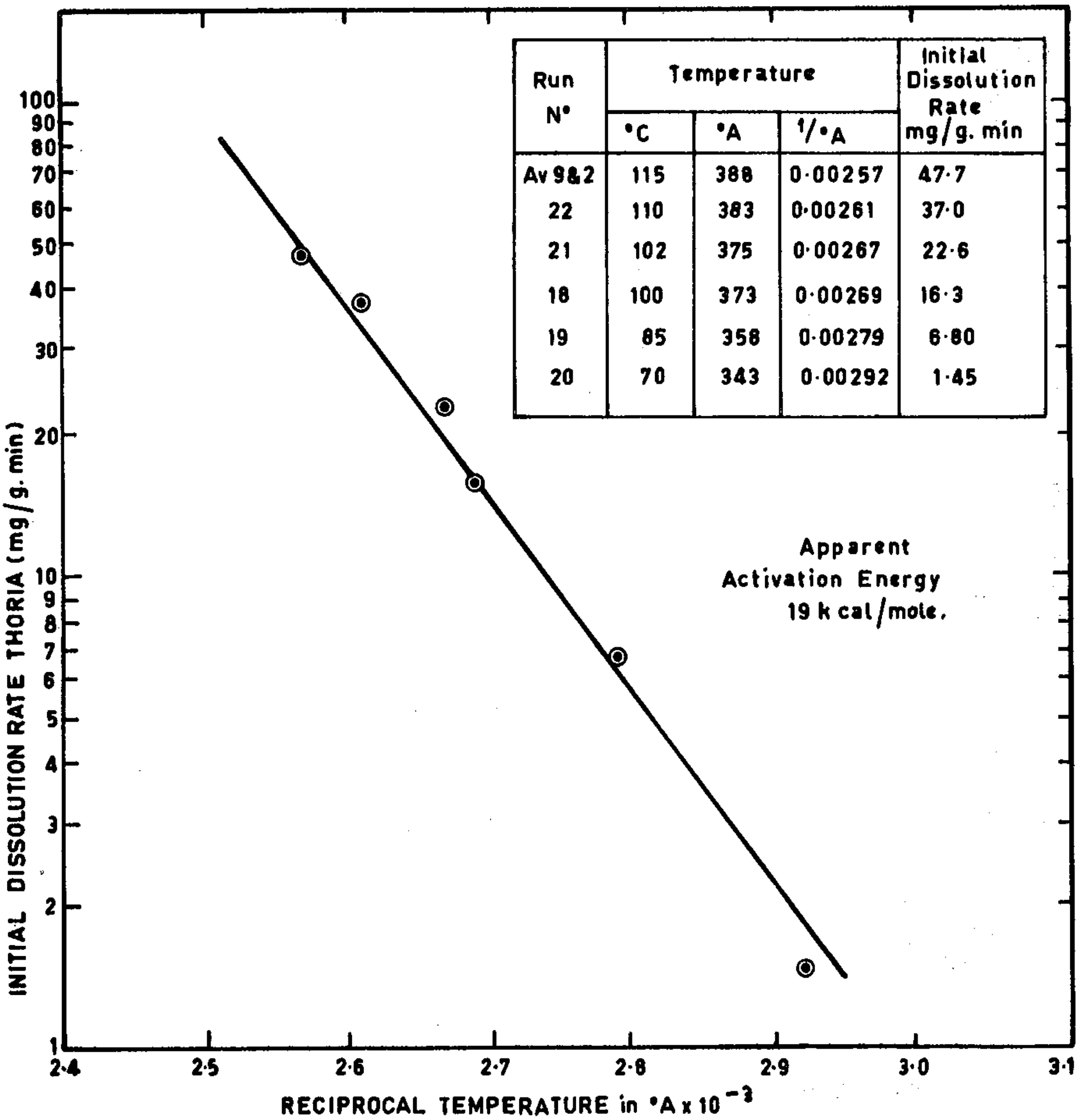
P836



Run N°.	[F] M	Initial Rate mg/g.min
Av(9+2)	0·05	47
23	0·033	38
11	0·01	27
12	0·005	20
13	0·001	10·3
34	NIL	< 0·05

FIGURE 5. EFFECT OF FLUORIDE CONCENTRATION ($13 \cdot 0M\ HNO_3$ at 115 °C)

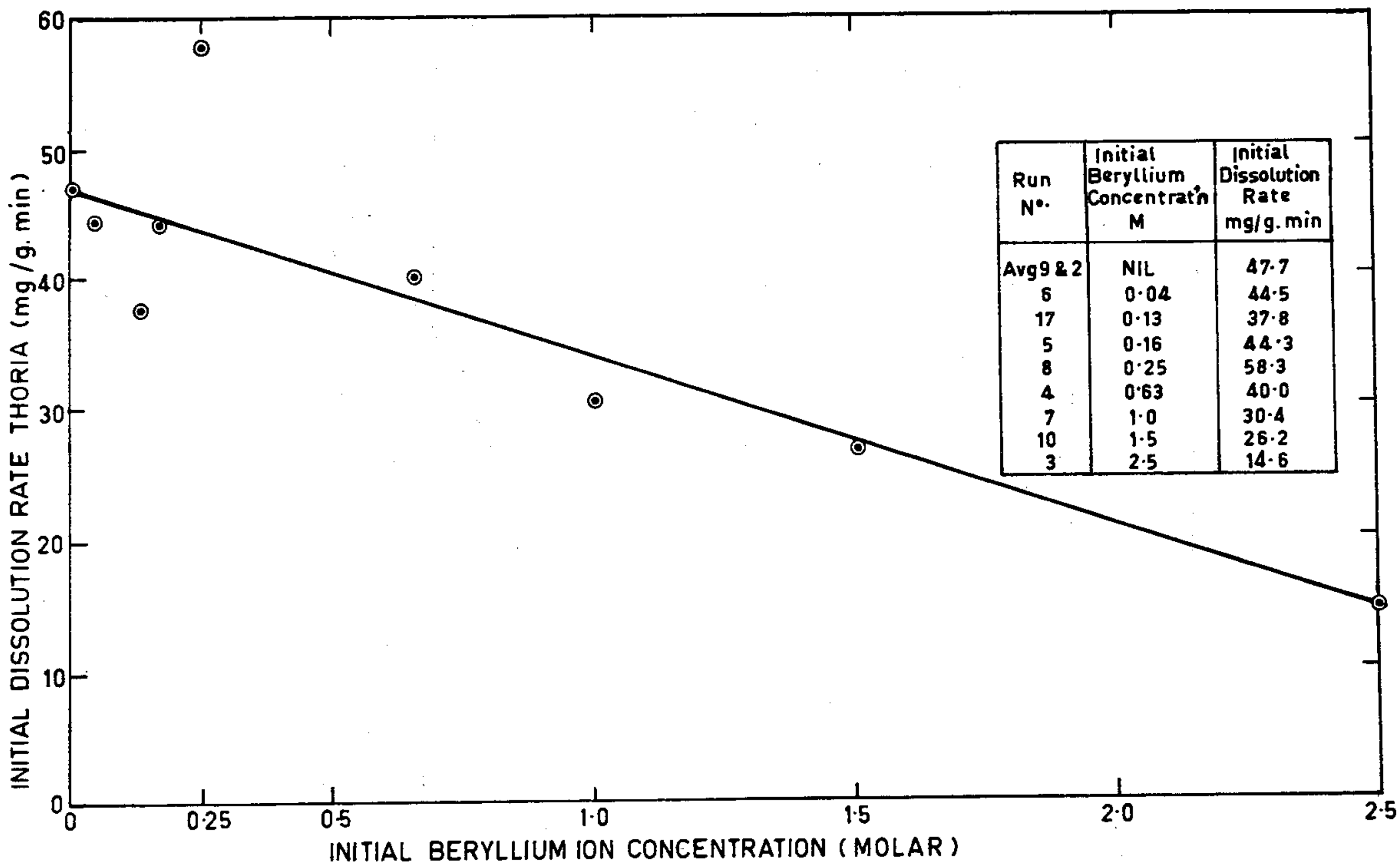
P836



Run N°	Temperature °C	Temperature °A	Temperature 1/°A	Initial Dissolution Rate mg/g. min
Av 9&2	115	388	0·00257	47·7
22	110	383	0·00261	37·0
21	102	375	0·00267	22·6
18	100	373	0·00269	16·3
19	85	358	0·00279	6·80
20	70	343	0·00292	1·45

FIGURE 6. EFFECT OF TEMPERATURE (13M HNO_3 + 0·05 MF')

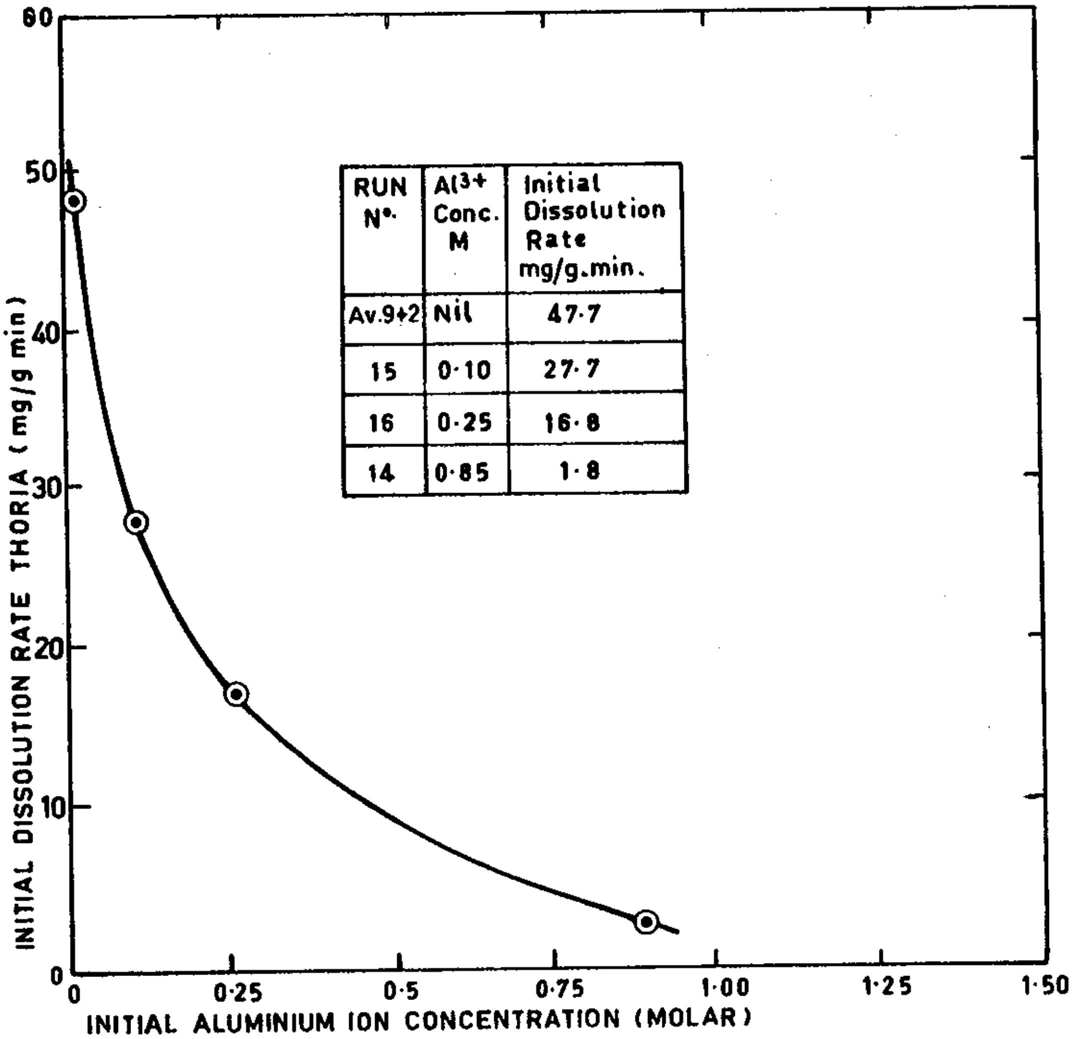
P836



Run N°.	Initial Beryllium Concentrat'n M	Initial Dissolution Rate mg/g. min
Avg 9 & 2	NIL	47·7
6	0·04	44·5
17	0·13	37·8
5	0·16	44·3
8	0·25	58·3
4	0·63	40·0
7	1·0	30·4
10	1·5	26·2
3	2·5	14·6

FIGURE 7. EFFECT OF BERYLLIUM ION CONCENTRATION
(13·0M HNO_3 + 0·05 MF$'$ at 115°C)

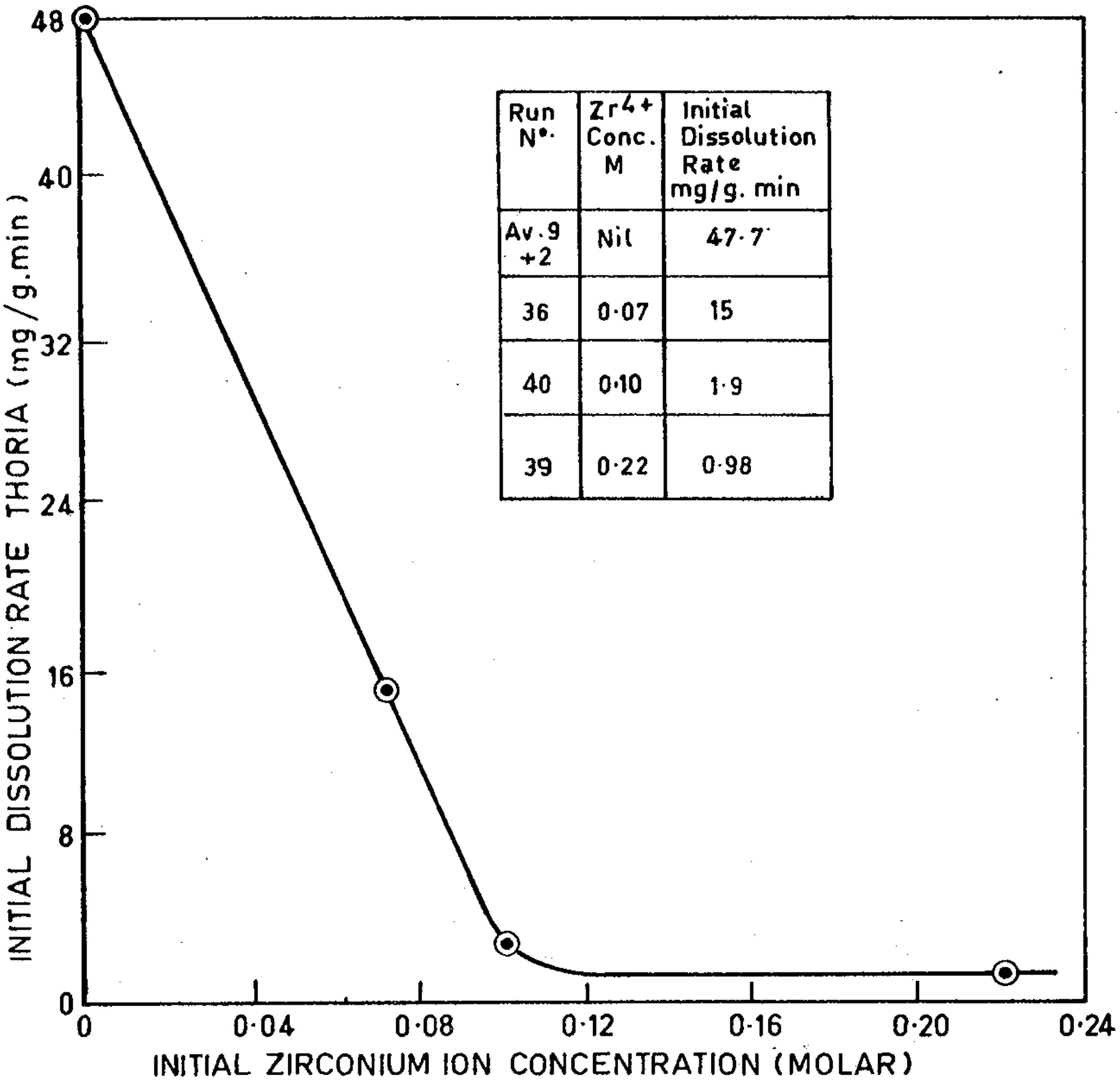
P836



RUN N°.	Al^{3+} Conc. M	Initial Dissolution Rate mg/g.min.
Av.9+2	Nil	47·7
15	0·10	27·7
16	0·25	16·8
14	0·85	1·8

Figure 8. EFFECT OF ALUMINIUM ION CONCENTRATION
($13{\cdot}0$ M HNO_3 + $0{\cdot}05$ MF′ at 115 °C)

P836



Run N°.	Zr^{4+} Conc. M	Initial Dissolution Rate mg/g. min
Av. 9 +2	Nil	47·7
36	0·07	15
40	0·10	1·9
39	0·22	0·98

FIGURE 9. EFFECT OF ZIRCONIUM ION CONCENTRATION
($13{\cdot}0M\ HNO_3 + 0{\cdot}05\ MF'$ at 115 °C)

P836

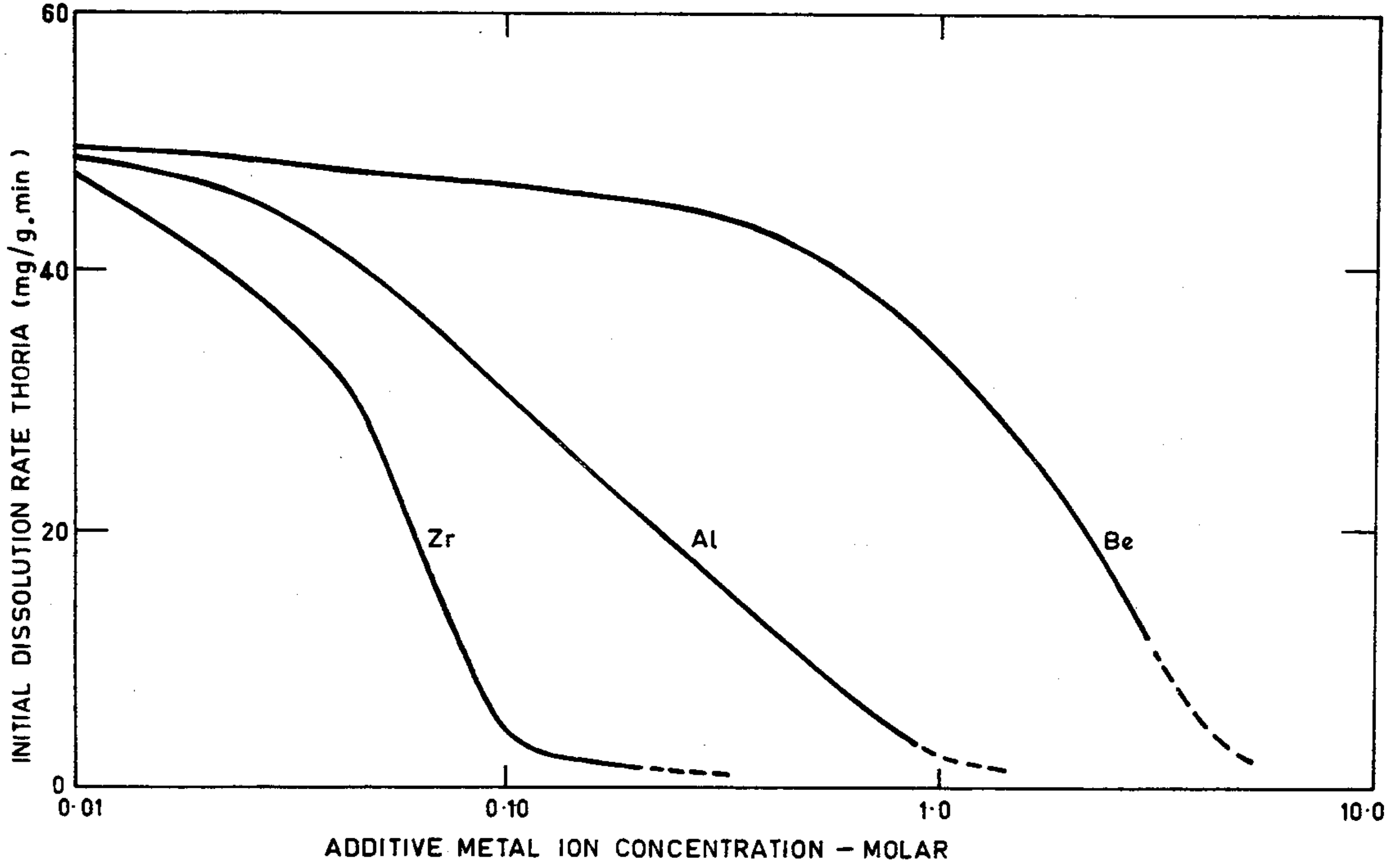


FIGURE 10. COMPARATIVE EFFECT OF Be, Al, and Zr ON INITIAL DISSOLUTION RATE OF THORIA
(taken from Figures 7, 8, and 9)

P836