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DISSOLUTION OF SINTERED THORIA

by

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Summary

Thoria, prepared by calcining thorium oxalate, and compacted and sintered, became increasingly more difficult to dissolve in HNO_3 – HF mixtures as the sintering temperature was increased.

The temperature of calcination of the oxalate is an important factor. Low calcination temperatures produced a more reactive thoria with a greater surface area. This thoria sintered more readily, producing denser compacts which had a smaller B.E.T. surface area and were more difficult to dissolve.

Thoria produced by calcination at 600°C. showed "mottling" when sintered at 1700°C. These dark-coloured mottles dissolved much more slowly than the white matrix in which they were embedded. No material other than thoria was detected in an X-ray analysis of the mottled material. No extra lines or deformations were visible, and although interstitial carbon was suspected, no evidence for this was obtained.

CONTENTS

1. INTRODUCTION

1.1 General

The present work was done to elucidate further the factors that affect the dissolution of compacted thoria, particularly the degree of sintering and sintering temperature. If dense thoria is required for irradiation, presintering of the thoria is necessary. If, on the other hand, low density thoria is used in the reactor, the low thermal conductivity may cause sintering, as the centre heats up due to fissioning of the accumulating U233.

In particular, there is a lack of precise information on the factors affecting the dissolving rate of thoria in concentrated nitric acid, using a fluoride catalyst. This is the most desirable method of dissolution since a considerable body of information is available on solvent extraction in nitrate systems. Clarification of the problem should allow a better assessment of the role that thoria could play as a blanket material. If dissolution of sintered thoria proves too slow, it may be necessary to employ thorium in some other form, but for economic reasons the use of the oxide is preferable.

1.2 Available Information

The usual dissolving medium for thoria has been concentrated nitric acid, with fluoride–ion as catalyst. Moore and Goodall found that the optimum conditions for dissolving thoria were 13M. HNO_3 and at least 0.02 M. fluoride–ion at 110°C. (1), (2). They dissolved cold pressed (20,000 p.s.i.) and sintered (1800° C) thoria containing 1% CaO (96.9% theoretical density.) The dissolving rate was approximately 10 mg/cm^2/min. This is about 15 times slower than for the thorium metal. Moore and Goodall also showed that the presence of Th^{4+} and Al^{3+} ions in solution seriously inhibited dissolution, probably owing to the removal of F^- by complexing.

Schuler, Steahly and Stoughton found that finely divided thoria dissolved in concentrated nitric acid with 0.05M fluoride–ion at 75°C. at a practically useful rate (3).

Curtis and Johnson (4) dissolved small cylinders of thoria fabricated at 700°C., 1200°C. and 1630°C. The time required for 100% dissolution was 1.5 hr., 2.6 hr., and 5 to 5.5 hr; i.e., the higher the temperature of fabrication, the more difficult the thoria compact was to dissolve.

Bond (5) dissolved cylinders of thoria containing 3.6% UO_2, and 0.4% CaF as binder, sintered at 1700° C., in various concentrations of HNO_3. In boiling 13M HNO_3 – 0.04M NaF a 98% dissolution of unirradiated 1/4 inch diameter pellets was obtained in 5.3 hrs., producing a final product solution of 8.6M HNO_3 – 1M $Th(NO_3)_4$ – 0.041M $UO_2(NO_3)_2$ at an overall dissolution rate of 3.4 mg/cm^2/min.

2. EXPERIMENTAL

2.1 Production of Thoria

The A.R. grade thorium nitrate was dissolved in hot demineralised water. Thorium oxalate was precipitated with a slight excess of hot oxalic acid solution. The precipitate was allowed to settle overnight and the cold solution was decanted off the precipitate. The precipitate was filtered and washed with hot 2.5% oxalic acid and several times with hot demineralised water. The precipitate was dried in an oven at 100° C. The final cake was then broken up and calcined in a muffle furnace. The calcination temperature was varied. Two batches were calcined, one at 1000°C., and the other at 600° C., respectively, for four hours.

2.2 Hot–pressing

The Ceramics Section of C.S.I.R.O. Chemical Research Laboratories, Melbourne, prepared the compacts by hot pressing, using the thoria prepared at Lucas Heights.

Annuli are the best shape for dissolving when it is required to rotate the thoria shape in the dissolving media. A fairly thin annulus also has the advantage that the area remains sensibly constant as the dissolving proceeds. The compacts were therefore made in the form of a disc with a centre hole drilled out.

The details of the hot pressing of the thoria compacts are as follows, the technique being similar to that of Murray, Rodgers and Williams (17).

The thoria powder was loosely packed into dies of standard electrode grade graphite (3 inches O.D., 1 inch I.D., sealed with 1 inch dia. plunger and plug), and heated by R.F. to 1000°C., in 10 minutes with 1/2 ton/sq.in. pressure applied to the plunger. At 1000°C. the pressure was increased to 1 ton/sq.in. and heating times varied from 5 minutes to 1200°C. to 15 – 20 minutes to 1700°C. The thoria was allowed a 15 minutes "soak" at the maximum temperature.

A silica sleeve was placed over the graphite die leaving a 4 inch annular space which was filled with a mixture of fairly coarse graphite and alumina powders. This powder mixture also covers the top of the die, and the die sat on a graphite disc. The compact was thus fairly well protected from penetration of air during heating.

Compacts pressed at 1800° C. were found to be broken on extraction from the die, due to crystallization of the thoria to give a large grain size. Compacts pressed at 1700°C. and lower temperatures remained intact. The specimens were ground and a central hole drilled in each compact. The specimens were then reheated slowly to 950°C. in air.

The volume was calculated from measurements of diameter and thickness. The bulk density was calculated as gm/cc. The percent theoretical density (T.D.) was calculated using an X–ray density of 10.15 gm/cc (6).

The surface area was determined by the B.E.T. method using nitrogen gas at liquid nitrogen temperatures after heating and out–gassing of each compact.

2.3 Dissolution

Figure 7 shows the design of a small dissolver constructed of 18/8/1 stainless steel. After measuring and weighing the thoria annulus was fitted to the threaded agitator shaft with teflon and stainless steel washers and a nut. The teflon expands sufficiently on heating to seal off the centre of the annulus from acid attack. About 350 ml. of 11.5M nitric acid was added to the dissolver and heated to about 105°C. The thoria on the agitator shaft was then placed in the dissolver, the seal screwed down, and the shaft connected to the output shaft of the motor. The agitator was kept at approximately 50 r.p.m.

Ammonium fluoride sufficient for the required concentration (0.05, 0.03 or 0.01M) was dissolved in about 20 ml. of 11.5M nitric acid and added to the dissolver through the reflux condenser tube. A further quantity of nitric acid was added down the reflux condenser tube to flush all fluoride into the dissolver. This final quantity brought the total volume to 400 ml. This large volume of acid was used to avoid the effects of decreasing acid concentration and high thorium nitrate concentration on dissolving rate. The temperature was adjusted to 95°C.

Samples were taken by withdrawing the solution from the dissolver through the stainless steel capillary tube into a calibrated centrifuge tube. The sample was centrifuged hot to remove any undissolved thoria eroded from the annulus and the supernatant liquor analysed for thorium using a colorimetric method (7). On cooling, a precipitate formed in the bottom of the centrifuge tube but re–dissolved on reheating the sample. As the solution was nowhere near saturation with respect to thorium nitrate, it is assumed that this precipitate may have been ThF4 (1) (5), the precipitate was not positively identified. It was also noticed that when the F^{1} ion concentration was lowered from 0.05M to 0.03M, this precipitate did not form so readily.

Dissolving rate curves were plotted ~~for~~ each annulus; the average dissolving rate was calculated from the average gradient. A constant figure of 9 cm^2 was used for the exposed area to calculate dissolving rate as mg/cm^2/minute. Photographs (Figures 8 and 9) show that the diameter of the disc did not decrease greatly as the thickness of the disc diminishes.

3. RESULTS

The results with other relevant data are given in Table I. Graphs (fig. 1, 2, 3 and 4) illustrate the relationship between sintering temperature, density, surface area and dissolving rate. Figs. 5 and 6 give the individual dissolving rate curves for the thoria calcined at 1000°C. and 600° C. respectively.

4. DISCUSSION OF THE RESULTS

4.1 General

The variable whose effect on dissolving rate has the greatest interest is the "degree of sintering". The degree of sintering is indicated by expressing the density as a percent of the "theoretical density".

The experimental work shows that:

(i) As sintering temperature is increased, the density increases at a roughly linear rate, although there is a change of gradient at about 1500°C. corresponding to 70% of theoretical density (T.D.) (See figure 1). Table II shows that the dissolving rates obtained in this work are roughly of the same order as obtained by the other workers. It is obvious that the previous treatment of the thoria has an appreciable effect on the dissolving rate.

(ii) B.E.T. surface area decreases as the density increases, with a sharp change of gradient at 65–70% T.D. (Fig. 2).

(iii) Dissolving rate decreases rapidly as density increases but tends to level out at about 70% T.D. (fig. 3).

(iv) The curves of density versus dissolving–rate, B.E.T. surface area, and sintering–temperature (figs. 1, 2 and 3) have a similar shape for the thoria calcined at 600°C. and at 1000° C. but are not identical. The thoria with the lower calcination temperature densifies more rapidly in the latter stages of sintering. The B.E.T. surface area and the dissolving rate also decrease more rapidly with this material.

(v) The most obvious relationship that one is tempted to examine is that between "available" surface area and dissolving rate. As in the case of all porous materials, the available surface is difficult to define, and even more difficult to determine with any certainty. It is probably true to say, however, that the B.E.T. surface area is a better measure of it than the area calculated from overall physical dimensions.

Although the rate of dissolution in mgm/M^2 can be calculated using the B.E.T. areas, the data are too few for the results to be very reliable. When this is done and the results plotted against sintering temperature, there appears to be very little variation for the material calcined at 1000°C. In other words, the effect of sintering on dissolving rate appears to be merely a reduction in the available surface area. On the other hand, the results for the material calcined at 600°C. appear to show a pronounced maximum at about 1400° C. With the scanty data that are available it is not possible to do more than to record this without further comment. A possible explanation for the effect of the temperature of calcination is given by Gregg, who, with others, has found a similar effect with other oxides, (8) (9) (10) (11) (12) (13) (14). Gregg explains the decrease in "activity" of the oxide, with higher calcination temperatures, as being due to the two main factors, viz:

(a) A decrease in internal surface area

(b) A decrease in lattice strain

The lattice strain is thought to be due mainly to the product of calcination taking up the pseudo–lattice of its parent. This lattice strain is decreased by heating to a higher temperature. Whilst in a state of strain, the oxide will have a higher free energy and will be more chemically reactive. The reactivity of the oxide is also decreased by decreasing the internal surface area, which does decrease on heating to a higher temperature due to early sintering and the welding together of particles. Thus, in the present case, the thoria calcined at the lower temperature, with its higher surface area* and probably higher lattice strain, is more reactive and therefore it sinters more readily on being compacted and heated, producing a denser compact with a lower surface area that is more difficult to dissolve. (See figure 4, noting that the dissolving rate versus sintering temperature curve for the thoria calcined at 600°C. is below the 1000°C. curve.)

The change is gradient shown in figures 1, 2 and 3 is no doubt related, and is thought to coincide with the replacement of the open pore stage by the closed pore stage (15) (16) in the sintering process. Porosity measurements were not made, however.

It may be possible to produce a thoria compact from material that has been calcined at high temperature (e.g. 1400° C.), which will sinter less readily, but would be more readily soluble after sintering as a result. A compact of this type could be expected to have a lower density and therefore a lower thermal conductivity. In practice, however, a thoria fuel–element with a lower thermal conductivity may heat up more due to U233 fission, thus cancelling out any advantage gained by using the thoria calcined at high temperature. Thermal conductivity measurements on sintered thoria are required before this can be solved.

4.2 The Effect of Fluoride–ion Concentration of the Dissolving–Rate

Moore et al. indicate that 0.01 – .02M is the optimum concentration (1). Whilst Bond (5) indicates that 0.04M F' is sufficient, and a greater concentration of fluoride–ion caused precipitation of thorium fluoride. In the study reported here a concentration of 0.05M was used except for a few runs where 0.03M and 0.01M were used to study the effect of F' concentration. The few results obtained indicate that the dissolving–rate is higher with 0.05 MF' (Table III). The effects are not large, however, and with the small number of runs made are probably not significant. A precipitate did not form in the dissolver solution when 0.03 and 0.01M fluoride was used, whereas a fairly large precipitate formed when 0.05M was used; 0.05M F' may therefore be excessive. Agitation of the specimen may have prevented a gelatinous precipitate of ThF_4 coating the specimen and slowing down the dissolution.

* B.E.T. surface areas of the uncompacted thoria powder were measured, and are as follows:–

Thoria calcined at 600°C. for 4 hrs. 27.0 M^2/g.

Thoria calcined at 1000°C. for 4 hrs. 3.0 M^2/g.

4.3 Mottling

The dissolving rate of the compact, sintered at 1700°C. from the batch of ThO_2 prepared by calcination at 600° C, may be higher than is actually shown (fig. 6). This would be due to a decrease in the available surface area due to the presence of dark coloured mottles which dissolve much more slowly than the white thoria matrix. (See photograph Fig. 10).

These mottles are not purely surface phenomena but occur inside the compact as shown in the photographs (figures 11 and 12). Figure 12 shows the undissolved mottles sitting on stalks of white thoria which they protect from attack. It is noticed that the mottles stand at different heights above the present surface indicating their depth in from the original surface. It is also evident that the mottles are all normal to the direction of pressure. An X-ray examination of the mottles failed to show that their composition was other than pure thoria. No interstitial carbon was detected. A spectrographic analysis of the thoria powder used is given in Table IV. The most probable explanation is that the mottles are examples of anisotropic grain growth aided by the hot pressing.

5. CONCLUSIONS

5.1

All other things being equal, the higher the sintering temperature, the denser and more sintered is the thoria compact, and the more difficult it is to dissolve. Thoria that has been sintered above a temperature of about 1600° C. under the conditions used above is difficult to dissolve, but there appears to be no real problem below that temperature if 5mg/cm^2/min. is acceptable as an economic dissolving rate.

5.2

The temperature of calcination of the thorium oxalate to the oxide has an appreciable effect on the sintering rate. The thoria calcined at the lower temperature has a much higher B.E.T. surface area before sintering, and is much more reactive, so that compacts made from this thoria are much denser (i.e. more sintered) and dissolve much more slowly than those made from thoria calcined at 1000°C.

6. ACKNOWLEDGMENTS

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7. REFERENCES

1. Moore et al., I and E.C., 49, 5 May, 1957, p. 885.

2. Goodall et al., H.W., 40250, 1955.

3. Schuler et al., T.I.D.-5223, 30.1.57.

4. Curtis and Johnson, J. Am. Ceram. Soc., 40, 2, Feb., 1957.

5. Bond, W.D. ORNL–2519, November, 1958.

6. Reeve, K.D., "Some oxide ceramics as reactor materials" – Symposium on Peaceful uses of Atomic Energy in Australia, June, 1958.

7. Palmer, A.R., A.A.E.C. –E25, Feb., 1958.

8. Gregg, S.J., J. Chem. Soc., 1953, p.3940.

9. Gregg, S.J. and Hill, J. Chem. Soc., 1953, p. 3945.

10. Gregg, S.J. et al, J. Chem. Soc., 1955, p. 46

11. Gregg, S.J. and Packer, J. Chem. Soc., 1955, p. 51.

12. Glasson, D.R., J. Chem. Soc., 1956, p. 1506.

13. Glasson, D.R., J. Appl. Chem., 8, Dec., 1958, p. 793.

14. Livey and Murray, Nature, 182, p. 1362, 15th Nov., 1958.

15. Allison and Murray, A.E.R.E., M/R 1099, Jan., 1953.

16. Belle and Lustman, T.I.D.–7546, Nov., 1957.

17. Murray, Rodgers and Williams, A.E.R.E. M/R 893, 30.7.52.

TABLE I

Calcination Temperature °C.	Sintering Temperature °C.	Bulk Density g/cm^3	Theoretical Density Attained % (T.D.–10.15 gm/cc).	Dissolving Rate		B.E.T. Surface Area M^2/g.
				per nominal area mg/min/cm^2	per B.E.T. area mg/min/M^2	
600	1200	5.42	53.4	27	--	--
600	1200	5.61	55.7	25	16	1.66
600	1400	6.61	65.3	21	73	0.26
600	1400	6.57	59.7	45.5	--	--
600	1500	7.17	69.5	8.5 *	--	--
600	1500	6.98	68.9	10.5	44	0.20 **
600	1600	8.18	81.0	5.0 *	--	--
600	1600	8.23	81.4	7.0	42	0.12 **
600	1700	9.23	91.2	1.7	19	0.58
1000	1200	5.65	55.7	30.0	10	3.16
1000	1400	6.43	63.3	24.0	21	1.01
1000	1500	6.90	68.0	12.0	15	0.72
1000	1600	7.27	71.6	8.0	11	0.55
1000	1700	8.06	79.7	7.5	14	0.38

* Used 0.01M F' ** interpolated

TABLE II

COMPARISON OF DISSOLVING RATES OF THORIA OBTAINED BY OTHERS

Reference	Thoria Properties	Dissolution Conditions	Dissolving Rate mg/cm^2/min.
Moore et al. (1)	Cold pressed and sintered at 1800° C. 97% T.D.	13M HNO_3 0.02 MF' 110°C.	10.0
Bond (6)	Sintered at 1700°C. containing UO_2 + 0.4%CaF.	13M HNO_3 0.04 MF' B.Pt.	3.4
This report.	(a) Hot pressed at 1700°C. and 1 ton/sq. inch pressure – Thoria calcined from oxalate at 600° C.	11.5M HNO_3 0.05 MF' 95°C.	1.7
	(b) As for (a) except thoria calcined from oxalate at 1000° C.	As for (a)	7.5

TABLE III

EFFECT OF FLUORIDE–ION CONCENTRATION ON DISSOLVING RATE OF THORIA

Fluoride Concentration Molarity	Sintering Temp. °C.	Dissolving Rate mg/cm^2/min.
0.01	1600	5
0.03	1600	5½
0.05	1600	7
0.01	1500	8½
0.05	1500	10½

TABLE IV

SPECTROGRAPHIC ANALYSES OF THE UNCOMPACTED (600°C. CALCINED) THORIA.

Element	Quantity
Mg	Trace
Ca	Faint Trace
Sr	Nil
Ba	Faint Trace
Fe	Faint Trace
Ti	Very Faint Trace
Cr	Nil
Ni	Nil

Nominal order: Trace 0.05%
Faint Trace 0.01%
Very Faint Trace 0.002%

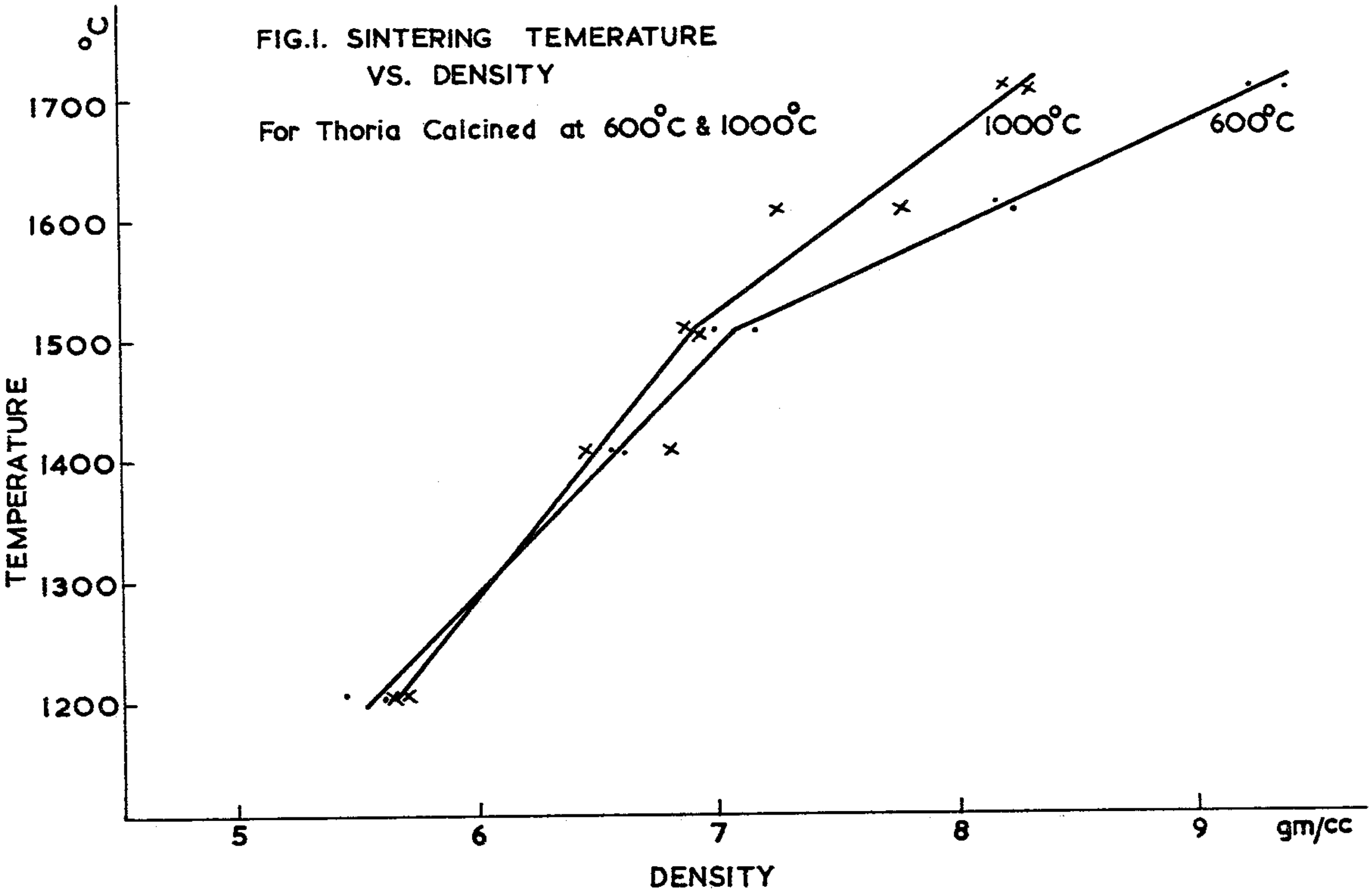


FIG.I. SINTERING TEMERATURE
VS. DENSITY

For Thoria Calcined at 600°C & 1000°C

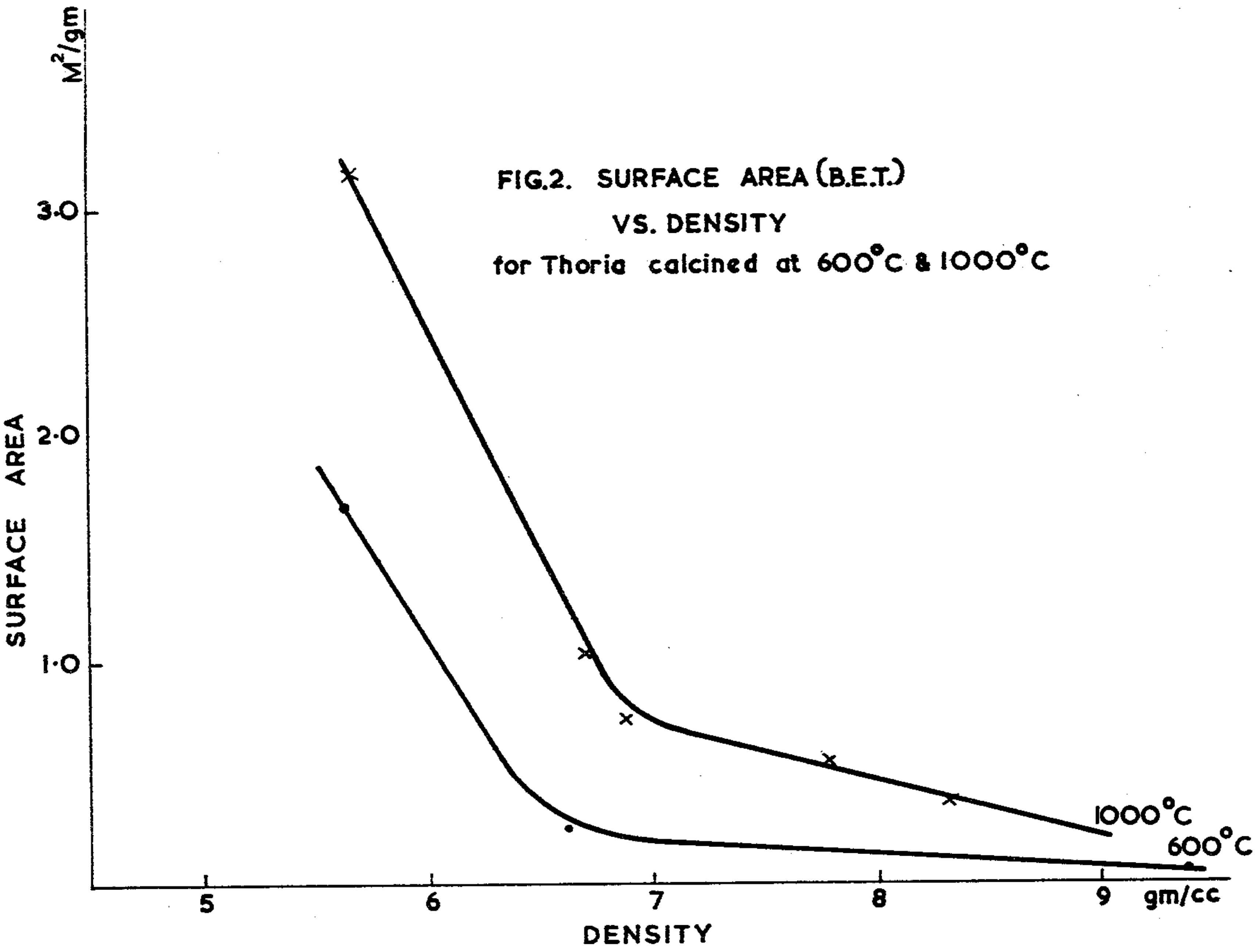


FIG.2. SURFACE AREA (B.E.T.) VS. DENSITY for Thoria calcined at 600°C & 1000°C

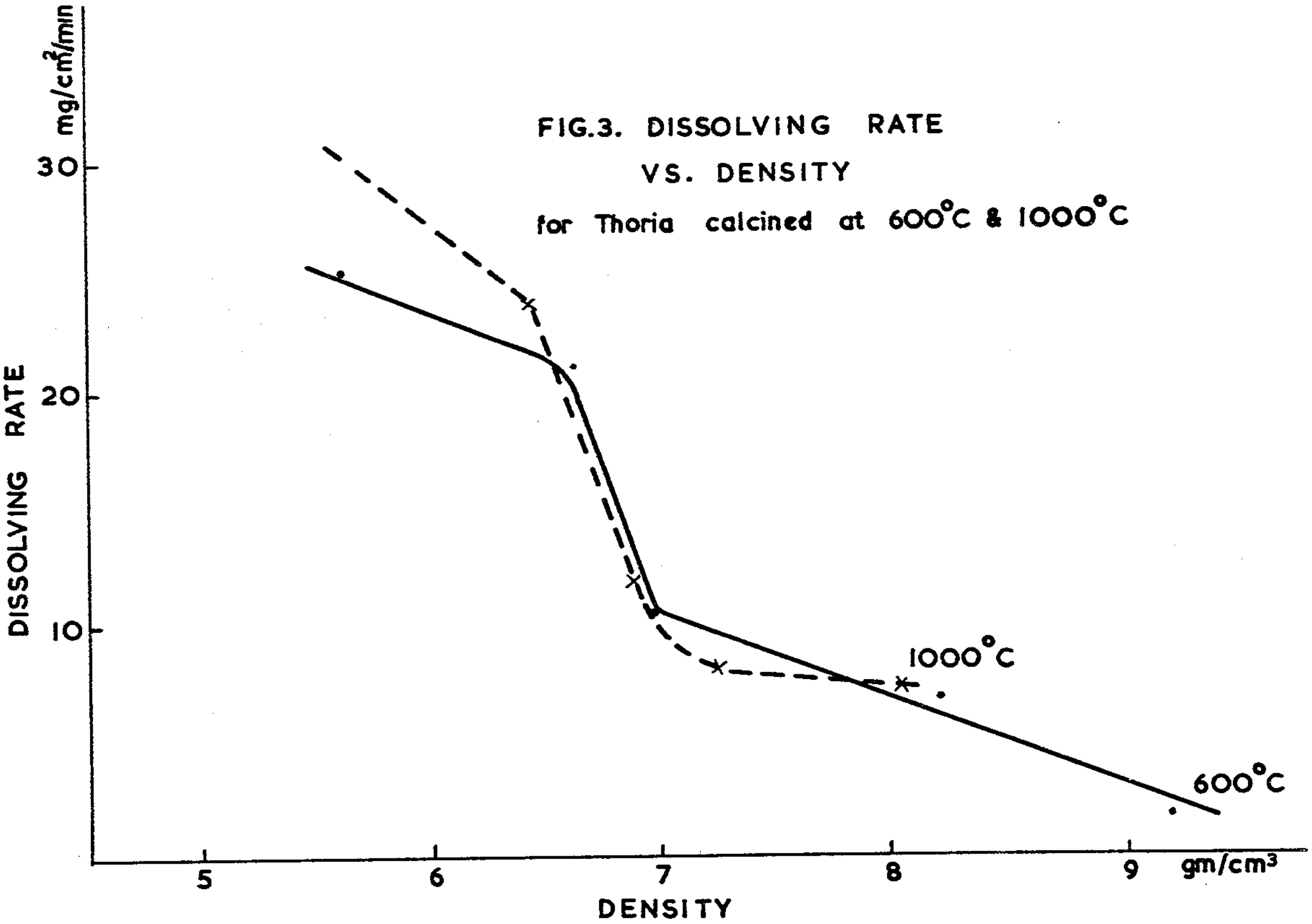


FIG.3. DISSOLVING RATE
VS. DENSITY
for Thoria calcined at 600°C & 1000°C

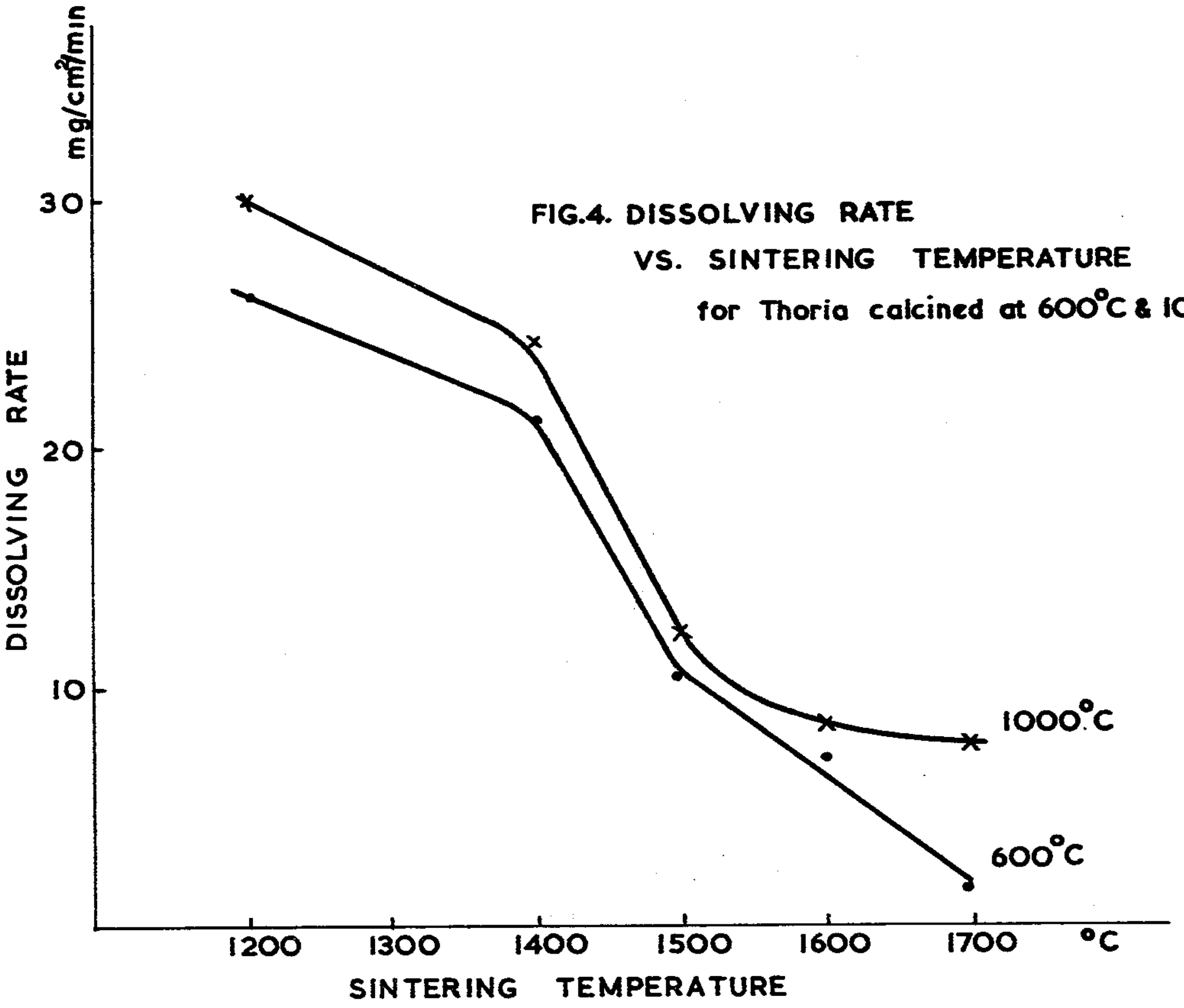
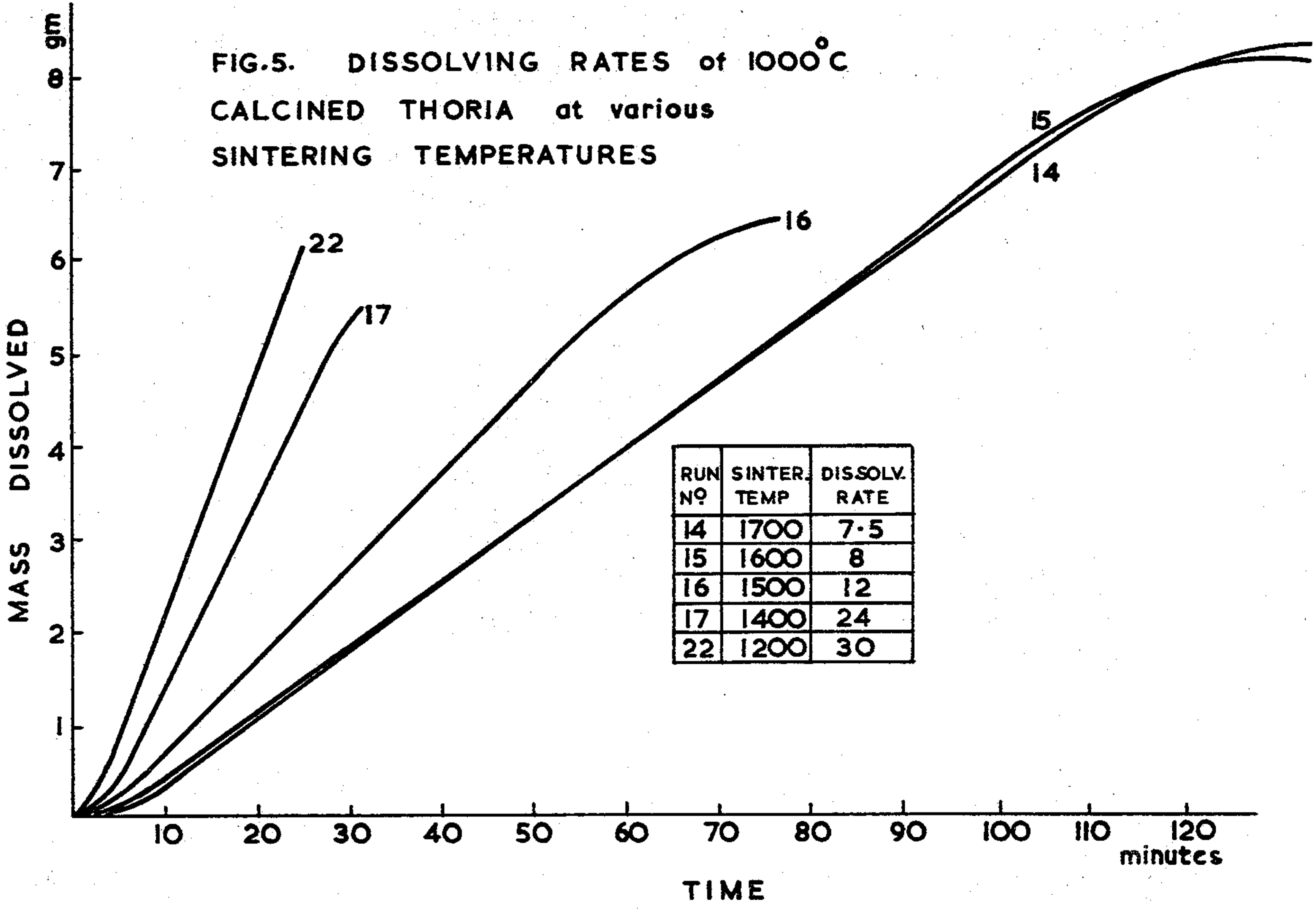


FIG.4. DISSOLVING RATE VS. SINTERING TEMPERATURE for Thoria calcined at 600°C & 1000°C

FIG. 5. DISSOLVING RATES of 1000°C CALCINED THORIA at various SINTERING TEMPERATURES



RUN Nº	SINTER. TEMP	DISSOLV. RATE
14	1700	7·5
15	1600	8
16	1500	12
17	1400	24
22	1200	30

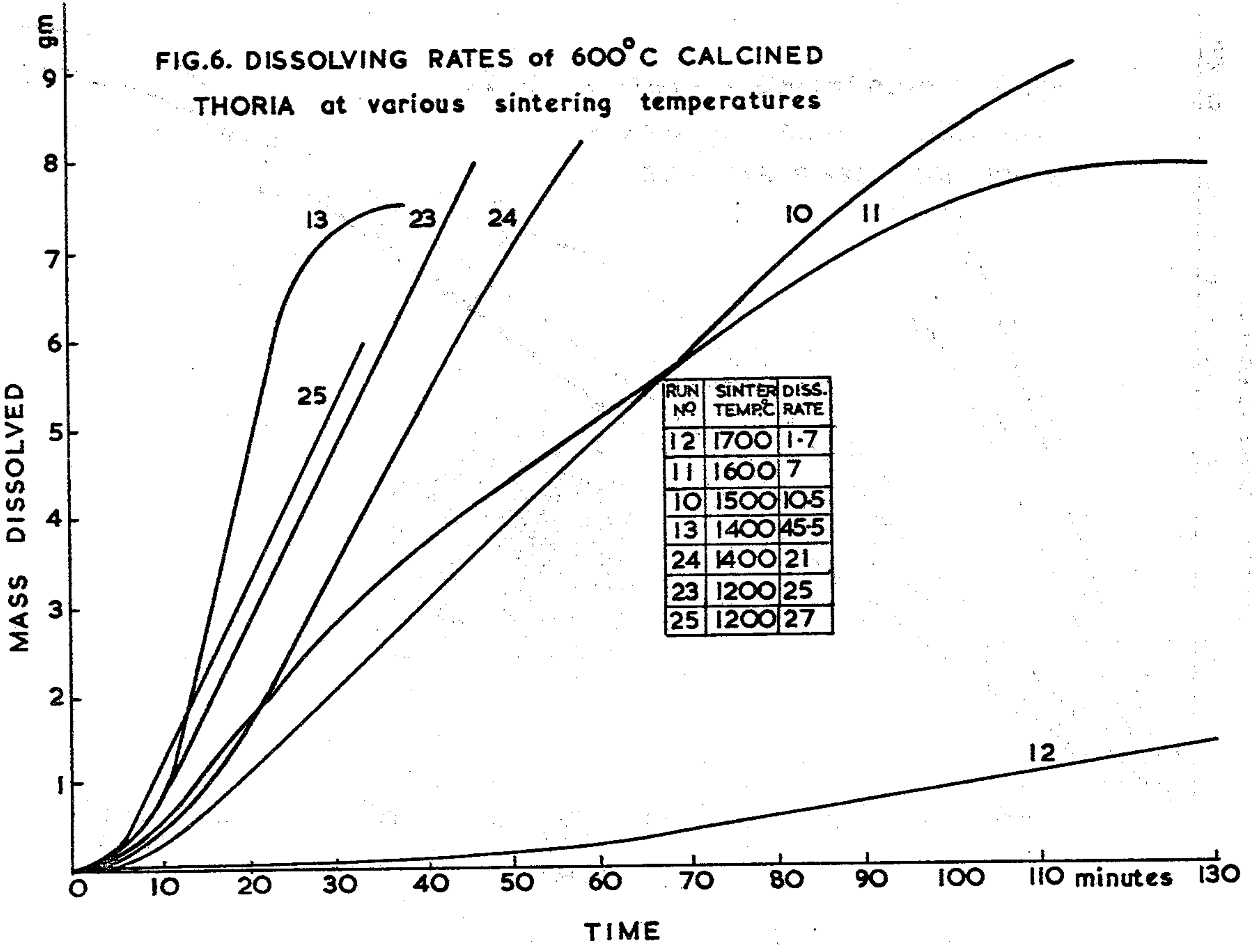


FIG.6. DISSOLVING RATES of 600°C CALCINED THORIA at various sintering temperatures

RUN No	SINTER TEMP.°C	DISS. RATE
12	1700	1·7
11	1600	7
10	1500	10·5
13	1400	45·5
24	1400	21
23	1200	25
25	1200	27

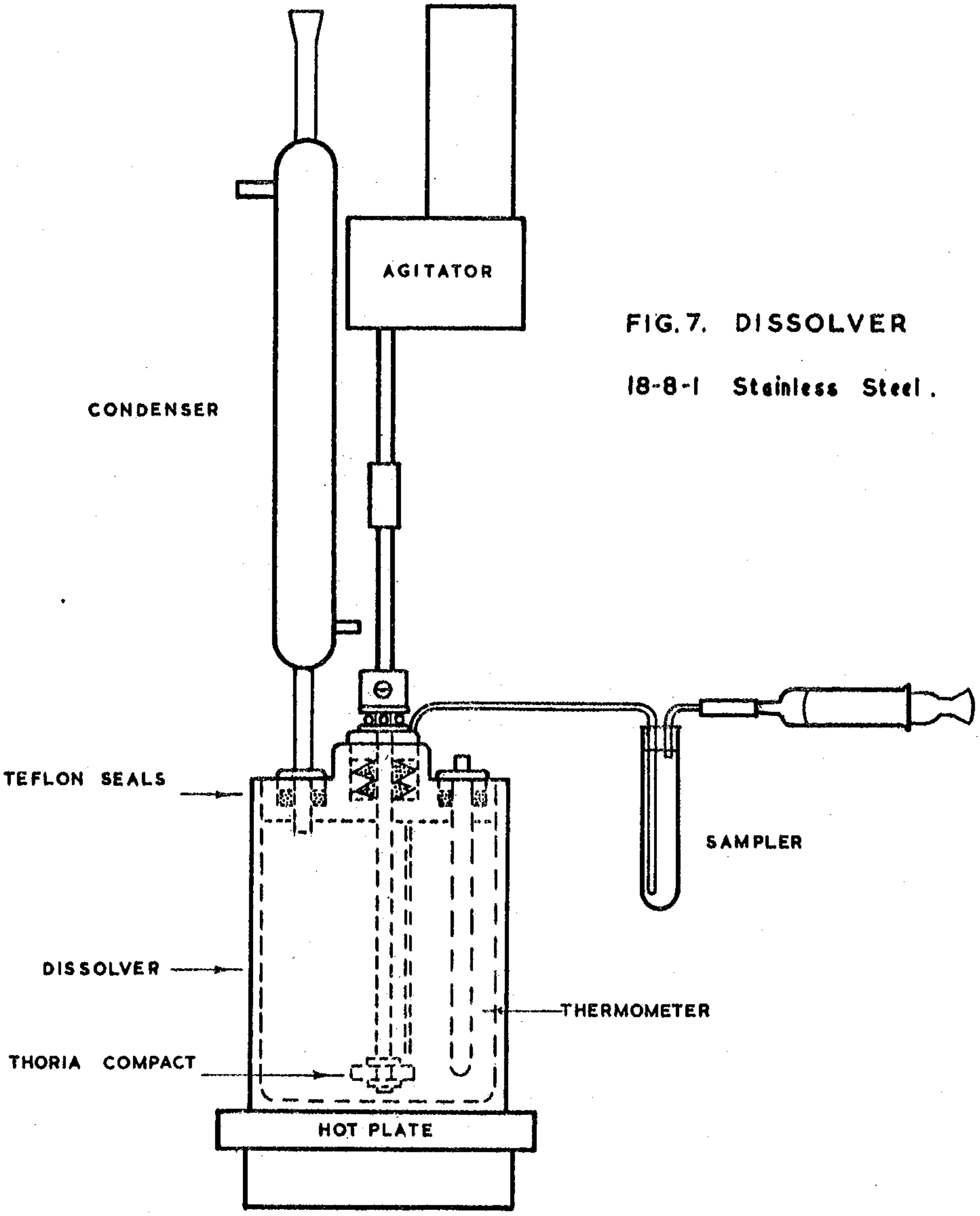


FIG. 7. DISSOLVER

18-8-1 Stainless Steel.

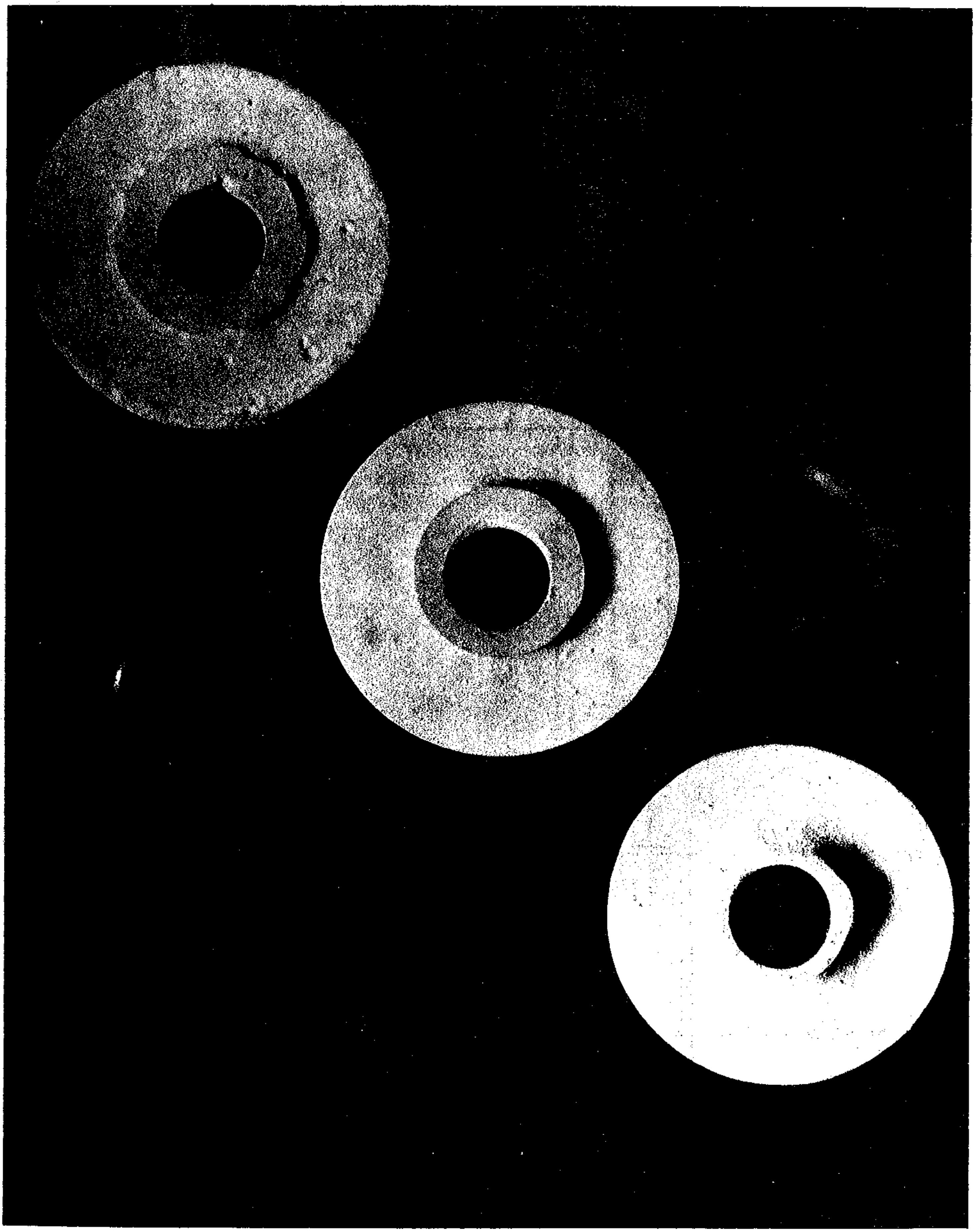


FIGURE 8: Three partially dissolved annular compacts of thoria.
PLAIN VIEW.

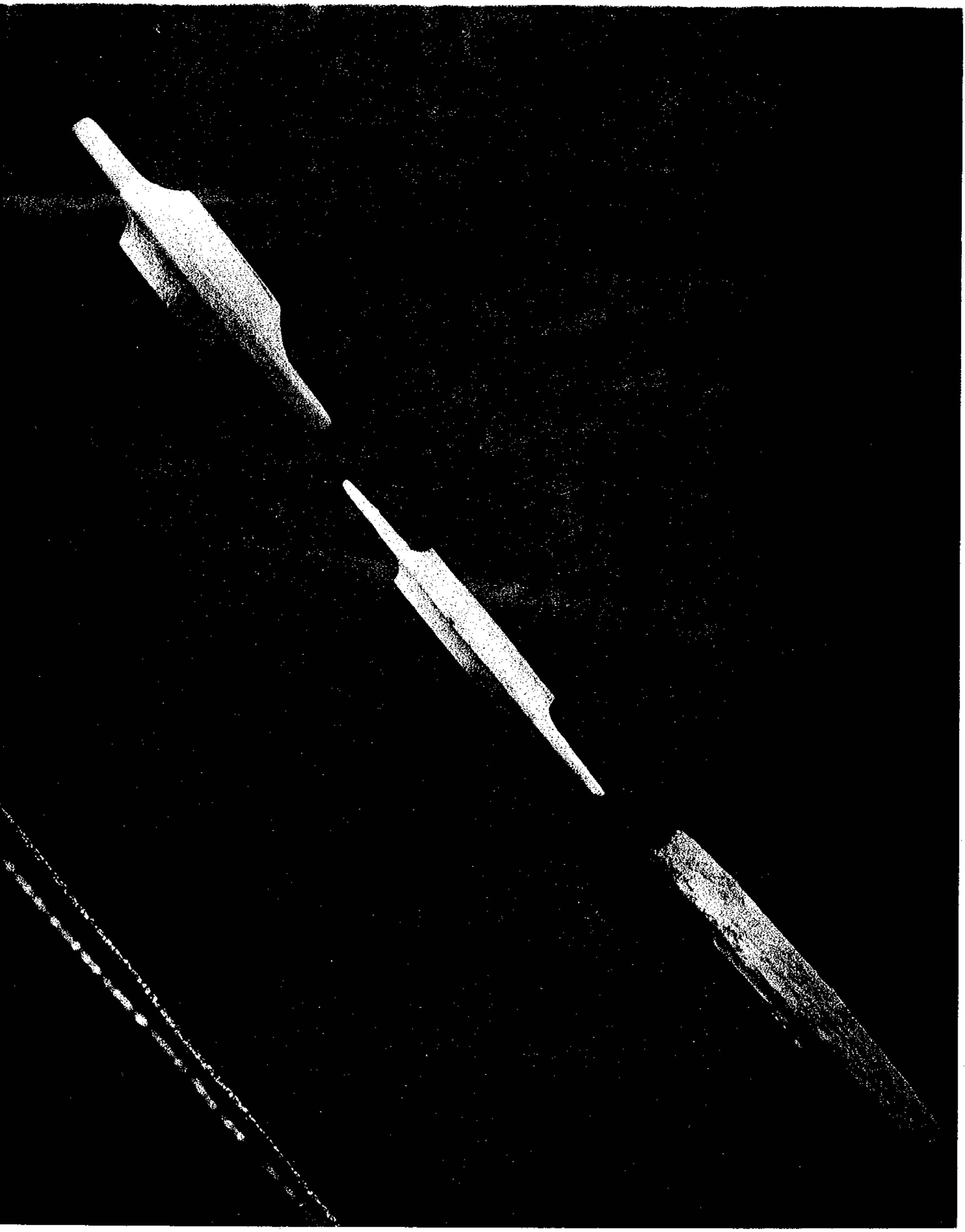


FIGURE 9: Three partially dissolved annular compacts of thoria. SIDE VIEW.

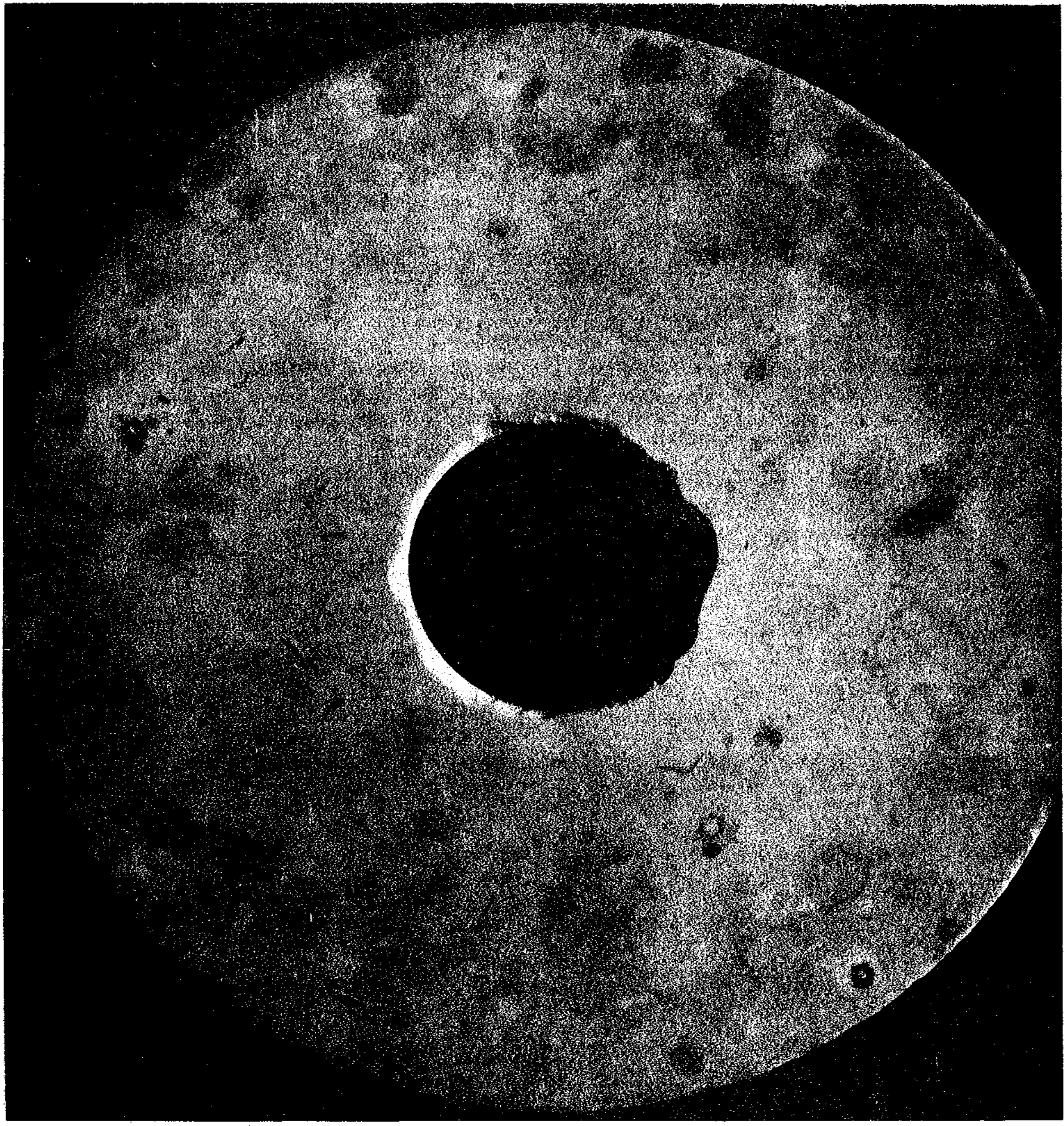


FIGURE 10 : Mottled Annulus before dissolution.

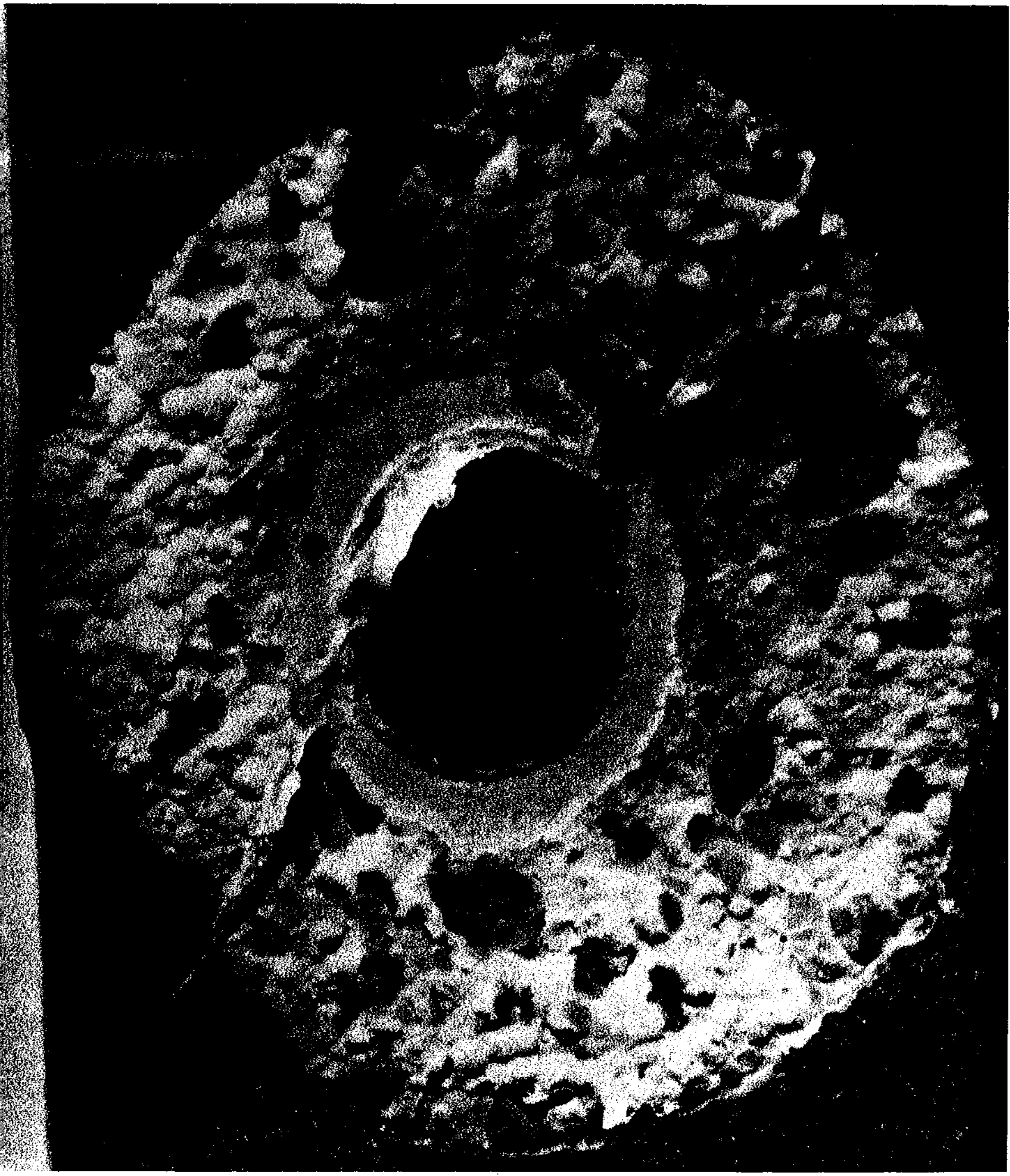


Figure 11: Mottled Annulus after partial dissolution showing differential dissolution of the normal white areas and the dark mottled areas.

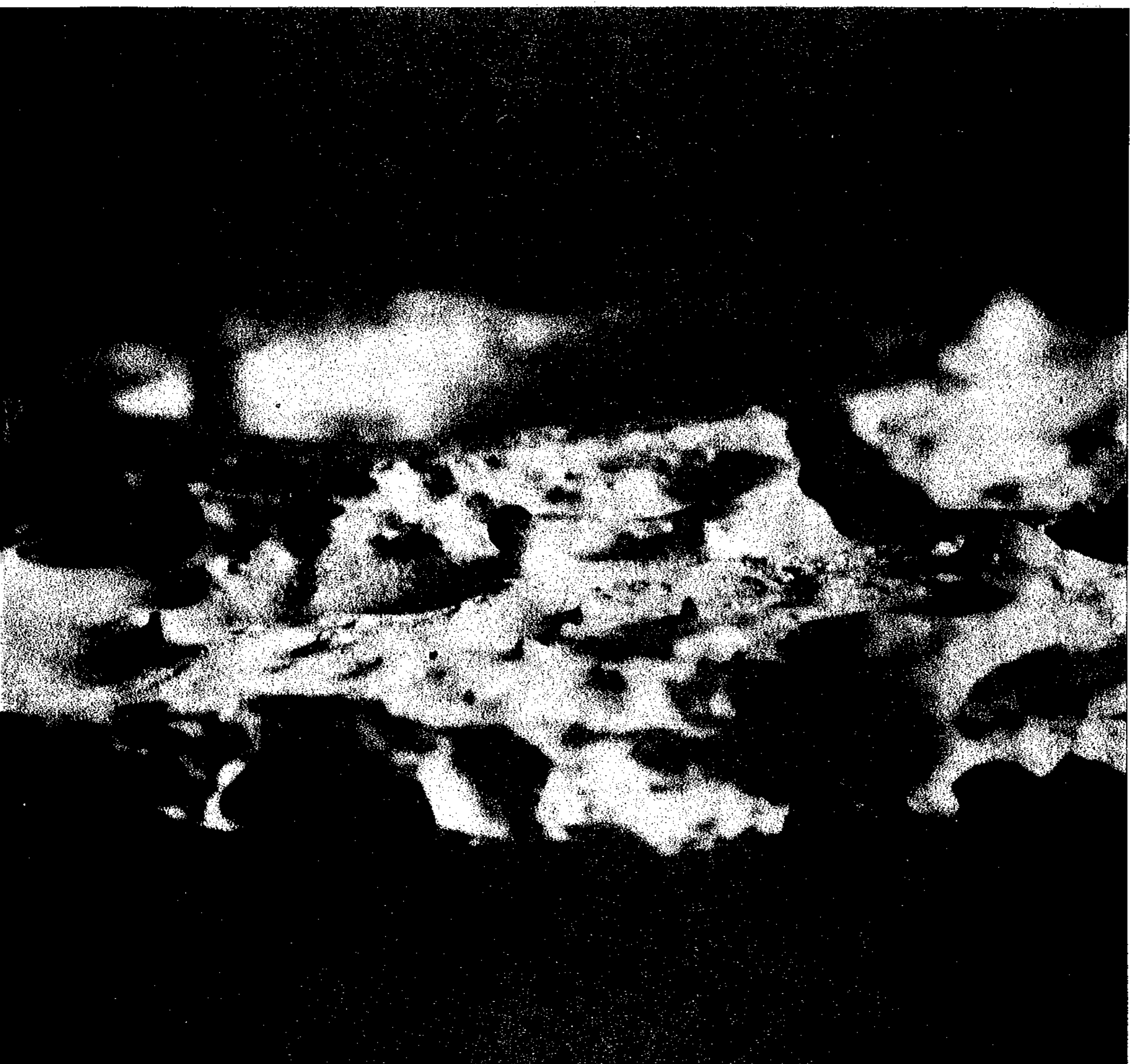


FIGURE 12: Close-up of same annulus shown in figure 11 showing the "mushroom" effect of the much more slowly dissolved mottles sitting on "stalks" of white thoria.