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O.E.E.C. HIGH TEMPERATURE REACTOR PROJECT

DRAGON

Dragon Project Report

THE DEVELOPMENT OF LOW PERMEABILITY GRAPHITE FOR THE DRAGON REACTOR EXPERIMENT

by

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A.E.E. Winfrith, Dorchester, Dorset, England.

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(Paper to be presented at the Fifth Conference on Carbon, Pennsylvania State University, 19-23 June, 1961)

ABSTRACT

A brief description is given of the graphite core components of the O.E.E.C., High Temperature Gas-Cooled Reactor Experiment (DRAGON) now being constructed and the required gas permeability characteristics outlined. Development research carried out in an endeavour to produce these components through the impregnation of a commercially available graphite using a furfuryl alcohol impregnation process is reported. In addition to giving detailed results concerning the operation of the process on a large scale, the results of experiments in which the properties of the impregnated material have been evaluated are presented.

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1. INTRODUCTION

During 1959 an Agreement was signed by thirteen European countries to co-operate in research and development in the field of high temperature gas-cooled nuclear reactors. One of the objectives of the newly formed O.E.E.C. Dragon Project was to design, construct and operate an H.T.G.C.R. at Winfrith Heath, Dorset, England(1).

The type of reactor chosen for construction was a helium cooled carbon moderated system in which outlet gas temperatures of the order of 750°C are expected. Descriptions of the reactor design have been published (2,3); the purpose of this paper is to describe the work which is being undertaken to prepare impregnated graphite core components for the reactor and to determine the properties of the material so produced.

The two main components required for the core are the fuel box and the fuel rod, the current designs of which are shown in Figures 1 and 2. The purpose of the fuel box is to contain ceramic nuclear fuel. Each fuel rod contains ten sealed fuel boxes and seven fuel rods stacked in a hexagonal array make up a fuel element. The reactor core is composed of 37 such fuel elements.

It is anticipated that the fuel operating temperature will be 900-1600°C when most of the fission products will be gaseous. Then the temperatures of the fuel rods and the fuel boxes will be 500-1000°C and 850-1350°C respectively.

The function of the fuel box is four-fold:-

(i) to delay the emission of gaseous and volatile fission products into the purge stream;

(ii) to maintain the annular purge stream gap inside the fuel tube in the face of changes in fuel dimensions under irradiation;

(iii) to act together with the helium purge stream gap as a barrier to those fission products which move by surface diffusion(4);

(iv) to protect the fuel tube from physical damage to its inside surface by recoil of fission products.

The problem of sealing the fuel boxes after loading with fuel is not considered here.

Existing design requirements demand that a fuel box must not be so impermeable as to allow fission product gas pressures to build up to such a level that bursting occurs. Equally, to reduce the load on the fission product traps, sufficient hold-up must be provided for the decay of short-lived species. A practical compromise is a box with a relative permeability to air of 1.5×10^{-5} to 5×10^{-6} cm^2/sec, when measured with nitrogen at a mean pressure of 0.5 atmosphere.

The fuel tube is a main structural member in the reactor. One of its functions is to separate the main coolant circuit from the active helium purge. Although the main coolant pressure is above that operating in the purge stream and thus it might be expected that fission products escaping through the fuel tube wall would be swept back, this cannot be relied upon because of back diffusion against the sweeping flow. This back diffusion into the main coolant stream has to be such therefore that problems associated with leaks in the pressure vessel and with fission product deposition in the heat exchangers are minimised. The objective of the present work was to produce material with overall permeabilities better than 10^{-6} cm^2/sec again measured with nitrogen at 0.5 atmosphere mean pressure. Completely impermeable fuel tubes would be an advantage. The reactor could, in fact, be operated with fuel tube materials having a range of viscous and molecular flow permeabilities but this point will not be examined here.

Before the work reported in this paper commenced, two processes were examined for the treatment of commercial graphites, using carbon itself as the pore-blocking material:-

(i) Low temperature hydrocarbon pyrolysis (pyrolytic deposition of carbon within the pores).

(ii) Furfuryl alcohol impregnation with subsequent heat treatment.

Another approach was to examine the possibility of surface coating graphite using high temperature pyrolysis of gaseous hydrocarbons. These processes were initially evaluated at the Royal Aircraft Establishment and furfuryl alcohol impregnation was eventually chosen for development by the Hawker Siddeley Nuclear Power Company.

The initial furfuryl alcohol impregnation work indicated that the process was only practicable with graphite materials having a restricted range of accessible porosity. It was decided that, for the first phase, effort should be concentrated on a commercially available material. The graphite used in the work reported was The Morgan Crucible Company's EY 9 type.

2. IMPREGNATION PROCEDURE

The accessible porosity in EY 9 type graphite commences at about 1 micron and the total porosity is between 15 and 20%. Mercury porosimeter curves obtained on examining this type of material are shown in Figs. 3 and 4.

Furfuryl alcohol of commercial quality was used as the impregnant in all the work reported. Of a number of polymerisation catalysts examined, a 2% by volume addition of phosphoric acid was preferred due to the relative stability of large volumes of the resulting resin and the ability to alter the viscosity as desired by pre-ageing.

All impregnations were carried out on fully machined fuel rods and boxes. In the case of the fuel boxes in which the wall thickness is approximately 0.150" it was anticipated that, since the escape path is relatively short, spalling resulting from the release of pyrolysis gases would be minimised. Accordingly, the fuel boxes were impregnated by filling the impregnation vessel with the catalysed alcohol after evacuation at room temperature. Resin penetration of the charge was allowed to proceed for sixteen hours after opening the impregnation vessel to the atmosphere. Serious spalling difficulties were met with when the fuel rods were impregnated in this manner.

To minimise spalling it was found necessary to impregnate through one face of the tube in each impregnation cycle. Ideally, it would appear that the impregnation should be forced through opposite faces of the tube in alternate impregnation cycles, only half the wall being penetrated each time. This is impracticable because of the complex geometry of the fuel tube and textural inhomogeneity in the basic graphite. The results reported are for fuel tubes impregnated by applying a pressure of 100 p.s.i.g. to the impregnant and forcing it through the tube from the inside face only. The first impregnation was terminated when the outer surface of the fuel tube was observed to be penetrated, while the second was of seven hours duration. Pre-ageing of the impregnant to about 120 cp. was found to be desirable for the initial impregnation.

After impregnation components were stored in air-tight containers until the desired furnace charge was built up. During this period, curing of the alcohol proceeds slowly without excessive evaporation.

Both boxes and rods were heated according to the schedule indicated in Table 1, the curing and pyrolysis being telescoped into one operation. The bulk of the gas permeability measurements made during the work were determined by pressure decay and vacuum leak methods, air being the test medium. Permeabilities are quoted in terms of the permeability coefficient K in cm^2/sec units.

3. IMPREGNATION RESULTS

3.1 Properties of the Resin

To provide background information, simple experiments were carried out to investigate the curing of furfuryl alcohol and the pyrolysis of the resulting resin. During curing, evaporation and resinification compete. Even so, by heating samples of the catalysed liquid through different heating cycles, it was found that the resin could be solidified at temperatures approaching 100°C with virtually no loss in weight provided the range up to 60°C is passed quickly. Further heating to 200°C was found to cause a loss in weight of approximately 20% primarily due to the elimination of water. Gas evolution and weight loss studies were made during the heating of fully cured specimens up to 1000°C. Gas evolution peaks were observed (Fig. 5) at approximately 470°C and 750°C. Table 2 indicates that virtually 80% of the total weight loss and almost two thirds of the total volumetric shrinkage had already occured at 550°C.

After pyrolysis to 1000°C carbon yields approaching 49% were obtained. Although this corresponds with the idealised breakdown of each molecule of furfuryl alcohol to one molecule each of water and carbon monoxide, and two molecules of hydrogen, leaving a residue of four carbon atoms, it is to be noted that the 1000°C char is not more than 98% carbon. Some properties of the char produced from furfuryl alcohol are given in Table 3.

3.2 Impregnation of Fuel Boxes

Impregnation, curing and carbonization studies carried out on thin sections of graphite indicated that the polymerisation and breakdown characteristics established for the free resin were essentially unchanged. It was found, however, that rapid heating in the range 300 - 600°C resulted in the disruption of the graphite due to excessive gas pressure build-up in the pore network. This spalling was minimised by reducing the rate of heating, the schedule indicated in Table 1 being finally adopted.

Table 4 gives the results of a typical batch of fuel boxes impregnated and heat treated in the standard manner.

The results from a different batch of specimens are presented in Table 5. In this case a third impregnation was carried out. However, for this third impregnation vacuum impregnation followed by the standard heating cycle invariably leads to the reappearance of the spalling difficulties mentioned above. These were avoided in this case by limiting the resin uptake, allowing penetration of the pore system to proceed by capillary attraction on immersing the boxes in the impregnant without prior evacuation.

3.3 Impregnation of Fuel Rods

The avoidance of spalling becomes increasingly difficult with increasing thickness of component.

First, observations of the weight changes during curing indicate that it becomes more difficult to effect a complete cure of the impregnant contained in the pore system. Fig. 6 which illustrates this effect, shows the weight changes occurring on holding vacuum impregnated bars of different thicknesses at 200°C for periods of up to 140 hours. The failure to achieve the theoretical weight loss attributable to the elimination of the water of polymerisation may be interpreted in two ways:

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(i) Complete polymerisation of the resin has in fact occurred but the elimination of the polymerisation products becomes increasingly difficult with increasing thickness.

(ii) Polymerisation has only occurred at the outer skin of the components while the resin contained within the body remains liquid.

Recent results, obtained on the residual liquid vacuum - distilled from the centre of nominally 200°C cured bars, suggest that (i) is operative and that the polymerisation products, mainly water, are retained. On heating to temperatures above 200°C, high internal stress will be set up as a result of both gas pressure build-up and liquid expansion. In fact on heating the thicker components at rates as low as 0.5°C/hr. above 200°C spalling invariably occurs before a temperature of 300°C is attained.

Secondly, even if this first spalling hazard is overcome the material must still be heated at such a rate as to strike a balance between the rates of evolution and elimination of gases produced by the pyrolysis of the resin. It has been indicated previously that in the case of the vacuum impregnated fuel boxes, a pyrolysis heating rate of 5°C/hr. was sufficient to suppress spalling to a reasonable level. If the assumption is made that pyrolysis gases escape via a Knudsen flow mechanism primarily, then an inverse square law is operative in relating maximum heating rate to thickness of component. Calculation, assuming such a flow mechanism for gas escape, indicates that the heating rate must be reduced forty-fold to 0.13°C/hr. to eliminate the spalling of vacuum impregnated fuel rods.

In the present work the heating rate during the carbonisation of the impregnated fuel rods was maintained at 5°C/hr and spalling minimised by impregnating from one face of the tube only. It is thought that this is successful for two reasons. First, the degree of pore filling is less than that given by a vacuum impregnation. Thus approximately 85% of the accessible pore volume is filled during the first impregnation of the fuel rods compared to about 96% in the case of the boxes. Secondly, it is likely that the degree of pore filling is less with increasing distance from the tube face in contact with the impregnant and this produces a situation in which the outer face of the tube is relatively open, allowing gases to escape more readily.

Fuel rods have been impregnated on a large scale: Table 6 presents results obtained on a batch of 20 rods.

3.4 Degassing of Impregnated Components and Dimensional Changes

Results are quoted in Table 7 for the gas content of as-pyrolysed material both before and after various heat treatments. The gas content of as-pyrolysed material is high and is principally hydrogen not wholly eliminated from the char. The presence of this hydrogen rich char markedly increases the nuclear cross-section and is associated with high rates of oxidation (See Section 4). Heat treatment, to temperatures above the final pyrolysis temperature, is necessary, therefore, to clean up the material chemically. In the present work it was decided in the first instance to standardise on vacuum degassing at a temperature of 1500°C. At temperatures above the final pyrolysis temperature cracking and spalling are again encountered unless the heating rate is closely controlled. It was established empirically that rates of heating below 100°C/hr. were acceptable. As indicated in Tables 4 and 5, the gas permeability of vacuum degassed material is noticeably higher than that of the as-pyrolysed material.

Dimensional changes occur as a result of impregnation and subsequent heat treatment. An indication of the order of magnitude is given in Table 8. The contraction produced by impregnation and pyrolysis to 1000°C is probably caused by constraint put on the graphite by polymer contraction occurring during pyrolysis. Photomicrographs showing resin contraction within the pore system of a coarse-grained graphite, British Acheson CS quality, are shown in Figures 7 to 9. The resin apparently shrinks away from the walls leaving an annular gap. The longitudinal contraction in a pore tends to sent the resin on a pore neck and so restrict gas flow. This may account for the marked reduction in permeability produced by furfuryl alcohol impregnation. A crack produced by the longitudinal contraction of a resin thread connecting the pore necks is shown in Figure 7.

Vacuum degassing results in an expansion which can be attributed to partial stress relief through the formation of more cracks. Further heat treatment to about 2200°C causes an additional expansion. Table 8 indicates that heat treatment to 2400°C and 2600°C has the effect of causing marked contractions. This effect may be due to structural changes occurring in the char but can also be related to the thermal history of the base graphite, as this has been found to contract noticeably on heating to 2600°C.

4. PROPERTIES

4.1 Permeability Studies

Some studies have been made to assess the uniformity of the components produced by the furfuryl alcohol process. In addition, some measurements have been made to determine the nature of the gas flow involved.

The manner in which the permeability varies through the wall is of particular interest in the fuel rod since the impregnation technique used may not produce a uniform carbon deposition pattern through the wall. Two different methods have been used to determine the manner in which the permeability varies. The first is a non-destructive method which involves performing a standard vacuum leak permeability test, during which leak rate determinations are made at known intervals from the commencement. Using non-steady state diffusion theory, it can be shown that, with appropriate boundary conditions:-

$$\frac{dp}{dt} = 0.59 \frac{AN \bar{c}^2}{V} \left(\frac{He}{t}\right)^{\frac{1}{2}}$$

where

$\frac{dp}{dt}$ = rate of pressure rise (dynes/cm^2/sec)

A = area of cross-flow (cm^2)

N = density of test gas at outer boundary (g/cm^3).

V = enclosed volume undergoing pressure rise (cm^3).

H = permeability (cm^2/sec).

e = pore volume of material/unit apparent volume.

t = time from start of test (sec)

$\bar{c}^2$ = mean square molecular velocity $(cm/sec)^2$

The H value obtained in this case is the average permeability for the depth of material penetrated at the time of measurement. The thickness of material penetrated is determined by assuming that the full pressure difference acts across the penetrated layer and by using the steady state equation:-

$$H = \frac{xV}{Ah} \frac{dp}{dt}$$

where x is the thickness and h the pressure difference, the other symbols having the meanings previously given.

The above treatment is valid for conditions of molecular flow.

A second method for examining the permeability distribution involves the measurement of K after machining successive layers of material from the tube wall. Figure 10 shows the results of a series of tests on a fuel tube test section in which both the non-destructive and destructive methods were employed. Both methods indicated the presence of very low permeability regions close to the inside face of the tube. The presence of this type of distribution was also shown by mercury porosimetry tests in which the variation in the accessibility of pores to mercury across a similarly impregnated tube was determined. (Fig. 11).

Simple high pressure leak tests have been done by pressurising tubes to 200 p.s.i.g. with nitrogen and immersing them in water. Invariably the gas flow was confined to small patches or isolated holes. This suggests inhomogeneity in the starting material which is difficult to measure with a mercury porosimeter due to the small sample size used.

4.2 Physical and Mechanical Properties

Information on the physical and mechanical properties of the impregnated material is required to provide design data for the Reactor Experiment. The property requirements for the current design are not stringent but with increases in the rating of H.T.G.C. reactors, improvements in properties, particularly those affecting thermal stress and dimensional stability under irradiation, will become a pressing requirement. The test programme is still proceeding and being extended to the determination of properties at temperatures up to 1500°C. Some currently available results are presented in Tables 9 and 10. The changes in the properties as a result of impregnation are much as would be expected on laying down a hard carbon in the pore network. In general the values quoted for properties in these tables are mean results after performing at least ten experiments.

4.3 Oxidation

Impurities in the helium coolant will react with the graphite and may result in transfer of carbon from the core to the primary heat exchangers. To give some indication as to the effect of impregnation on the chemical activity with oxidising gases, experiments were carried out in which the rate of oxidation in air was measured. A more realistic picture of the oxidation which can be expected to occur in the reactor is being obtained by carrying out in pile experiments under reactor operating conditions, though no results are as yet available from this work.

Two types of test were carried out at 550°C. In the first, bars of material were placed in a muffle furnace for eighteen hours and the total weight loss determined. In a second series of experiments, thin specimens were oxidised under a slow flow of preheated air. The weight changes in this case were observed continuously with specimens suspended from a previously calibrated glass spring. The results obtained from these two series of experiments are given in Tables 11 and 12; the usual handling precautions were taken to avoid possible catalytic oxidation effects.

The results were similar in both sets of experiments. The presence of furfuryl alcohol char in the graphite markedly increases the oxidation rate but this can be minimised by heating to high temperatures. Some improvement is also gained in the as-pyrolysed material if the polymerisation of the alcohol is catalysed by phosphoric acid and very low oxidation rates are observed on vacuum heat treating this material (specimens 13 to 17). It is considered that this is due to the adsorption of an oxy-phosphorous radicle at active sites. The increase in oxidation rate on prolonging the vacuum treatment (specimen 17) may be due to the removal of this protective adsorbed species. Thus a specimen containing 0.15% by weight of phosphorus after carbonising to 1000°C gave 0.11% and 0.05% P after vacuum heating for two hours at 1300° and 1800°C respectively. The reduction in the rate of reaction with oxygen as a result of high temperature degassing even in the absence of oxy-phosphorous complexes is thought to be related to the removal of hydrogen(5) and the ability of carbon to move to less reactive sites during the degassing treatment.

4.4 Water Adsorption

The gas content of this graphite has been found to be very high for use in a pure helium cooled reactor. Most of this is due to water vapour adsorption. The water content may amount to 500 p.p.m. both for unimpregnated and impregnated graphite but can be decreased to 30 p.p.m. by several successive treatments in vacuo up to 2000°C(6). Other work, in progress, suggests that the adsorption follows the Elovitch equation(7):-

$$q = a \log \left(\frac{t + t_o}{t_o}\right)$$

where q is the amount in p.p.m. of adsorbed water at time t, a and t_o are constants.

For this graphite a is of the order of 100 p.p.m. after the standard vacuum heat treatment. Moreover, at any stage of the adsorption, it is possible to remove in vacuo at room temperature, a quantity of water which is constant for a given graphite exposed to air of constant relative humidity. It is thought that the water removable in vacuo is physically adsorbed. Figure 12 indicates the typical adsorption/desorption history of a doubly impregnated fuel box. This was initially degassed in vacuo for two hours at 1500°C, subsequently exposed to ordinary air for 50 days and eventually degassed in vacuo at room temperature for two days.

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6. ACKNOWLEDGMENTS

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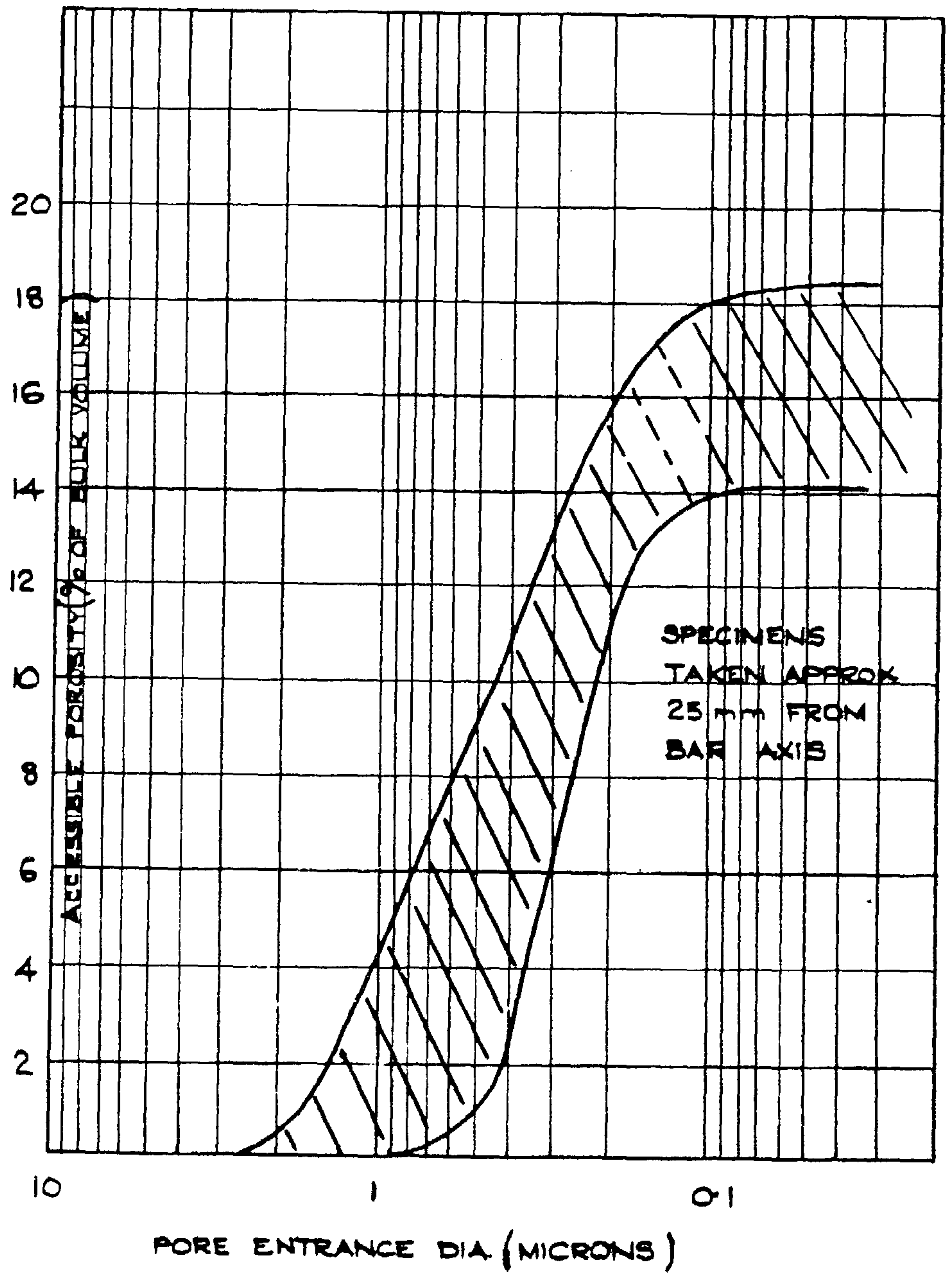


FIGURE 3 SHOWING RANGE OF ACCESSIBLE POROSITY ENCOUNTERED IN THE BASE GRAPHITE DURING IMPREGNATION WORK

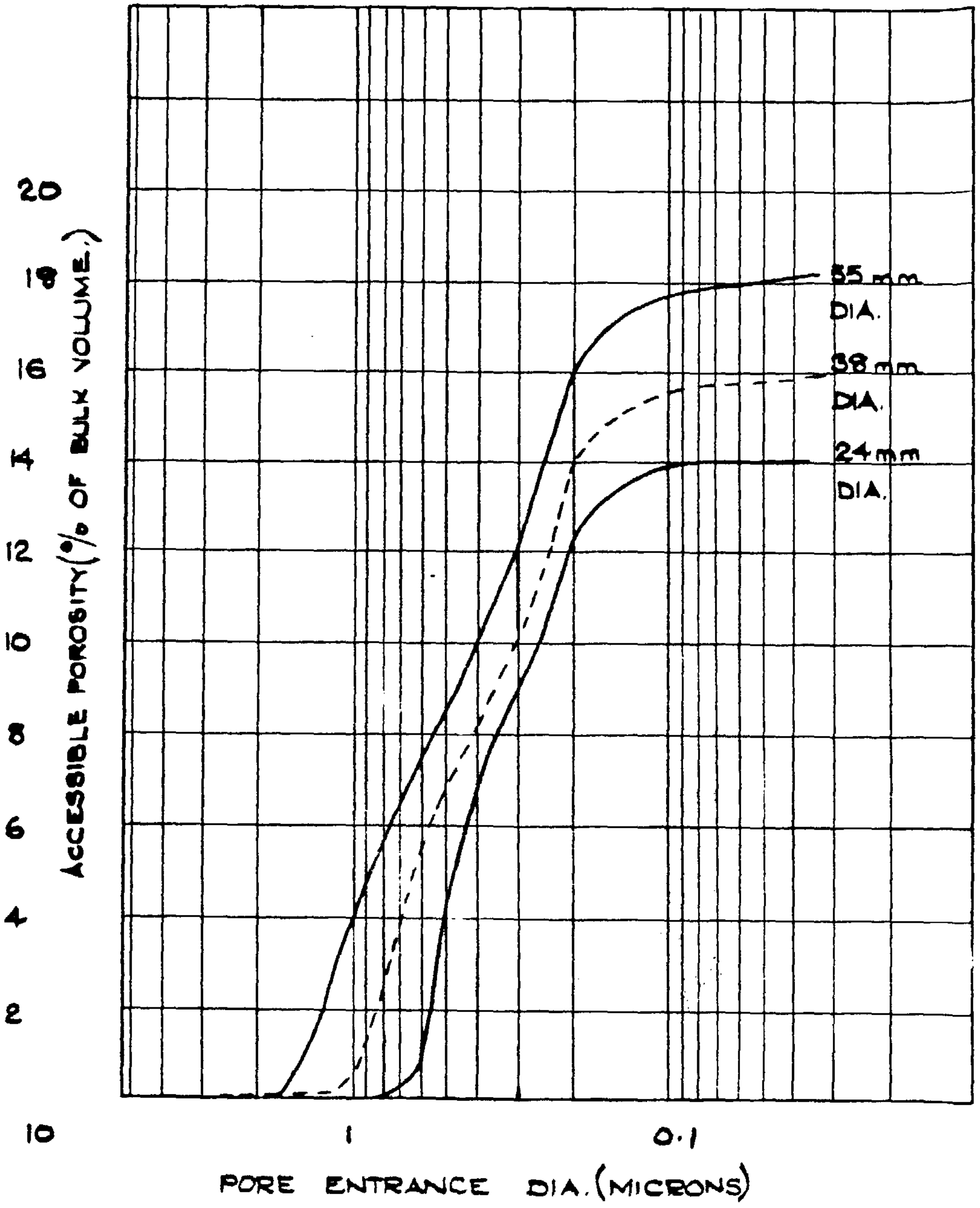


FIGURE 4. VARIATION OF PORE DISTRIBUTION ACROSS EXTRUDED BAR.

(NOTE: POROSIMETER SAMPLES WERE CUT AT

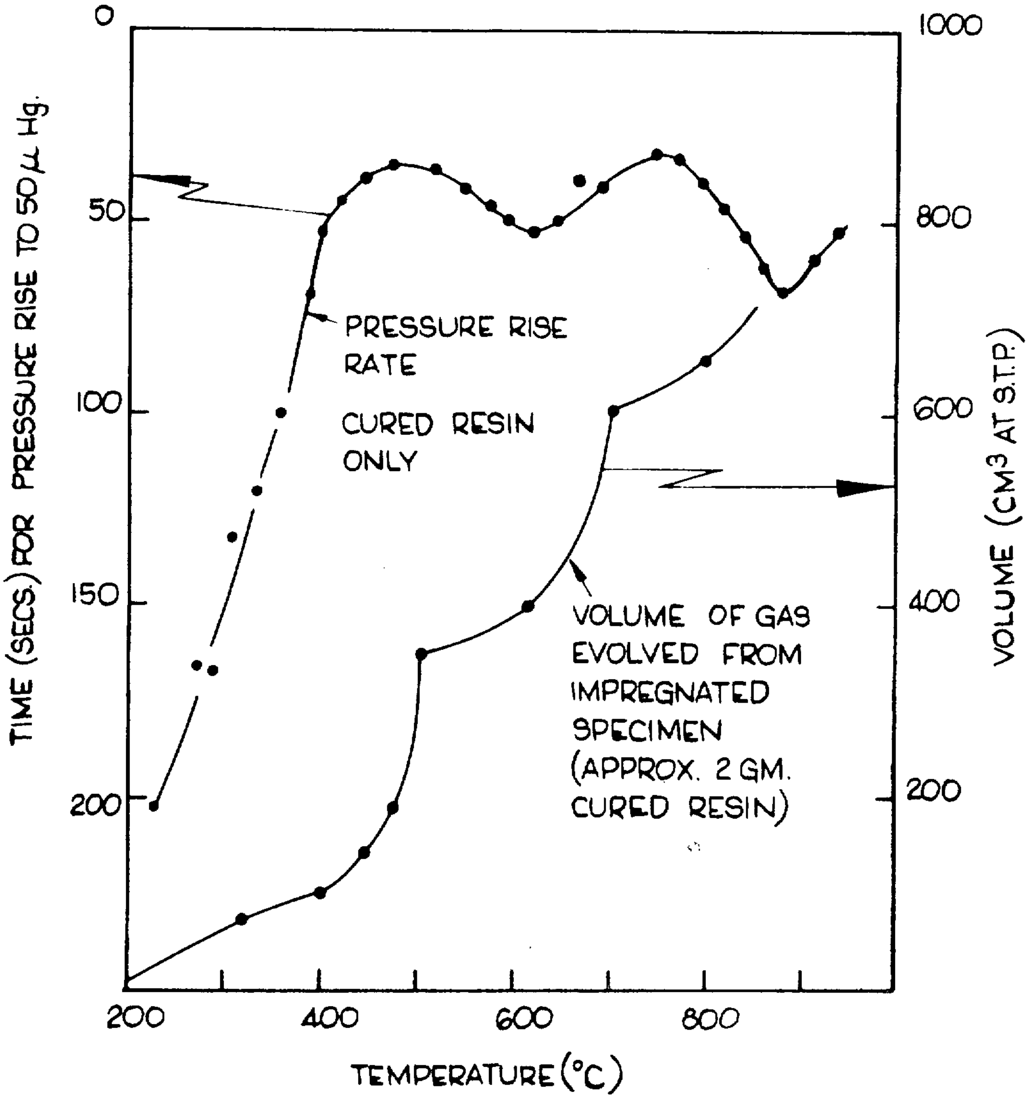


FIG. 5. DECOMPOSITION OF FURFURYL ALCOHOL POLYMER DURING PYROLYSIS

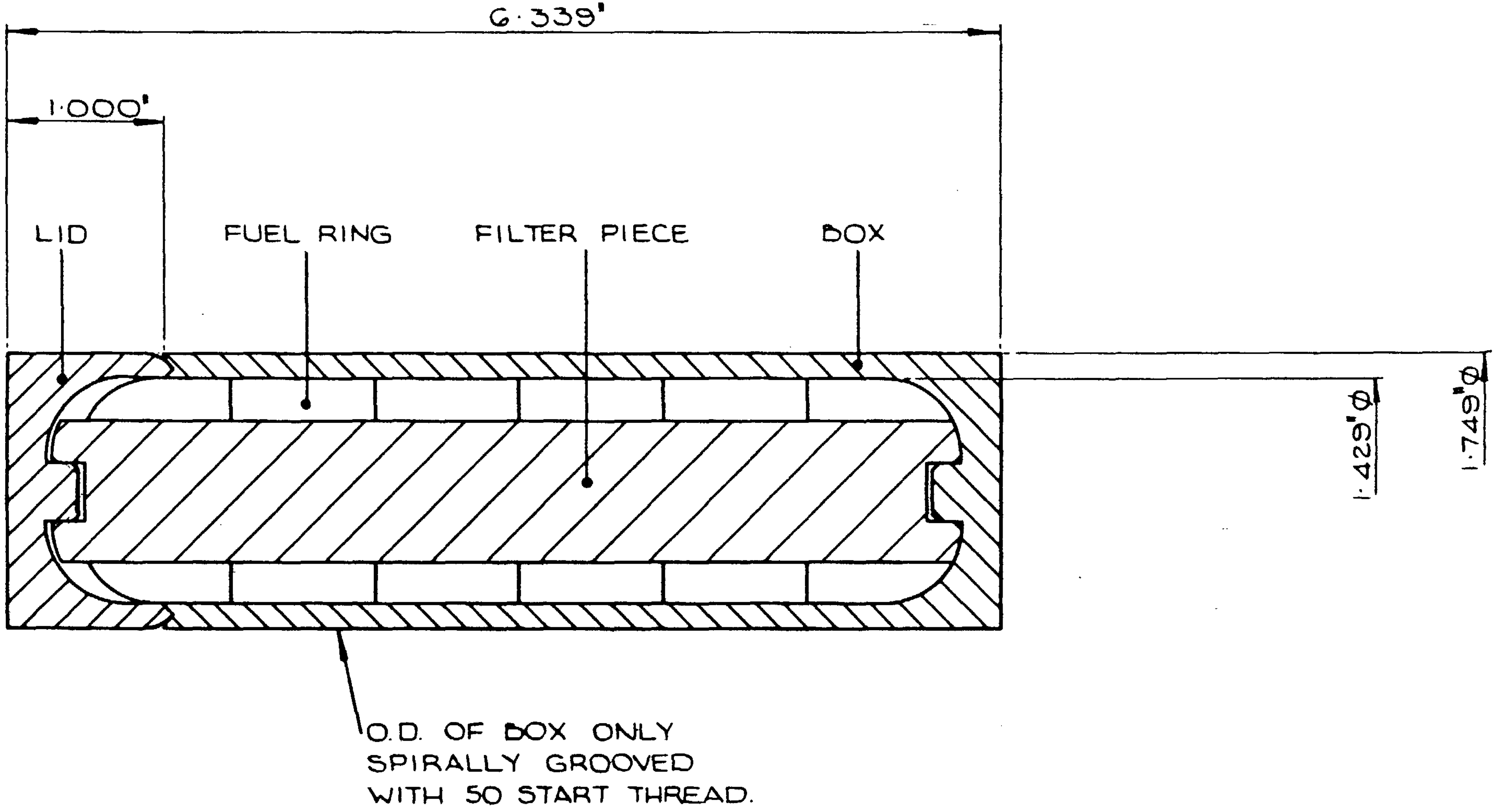
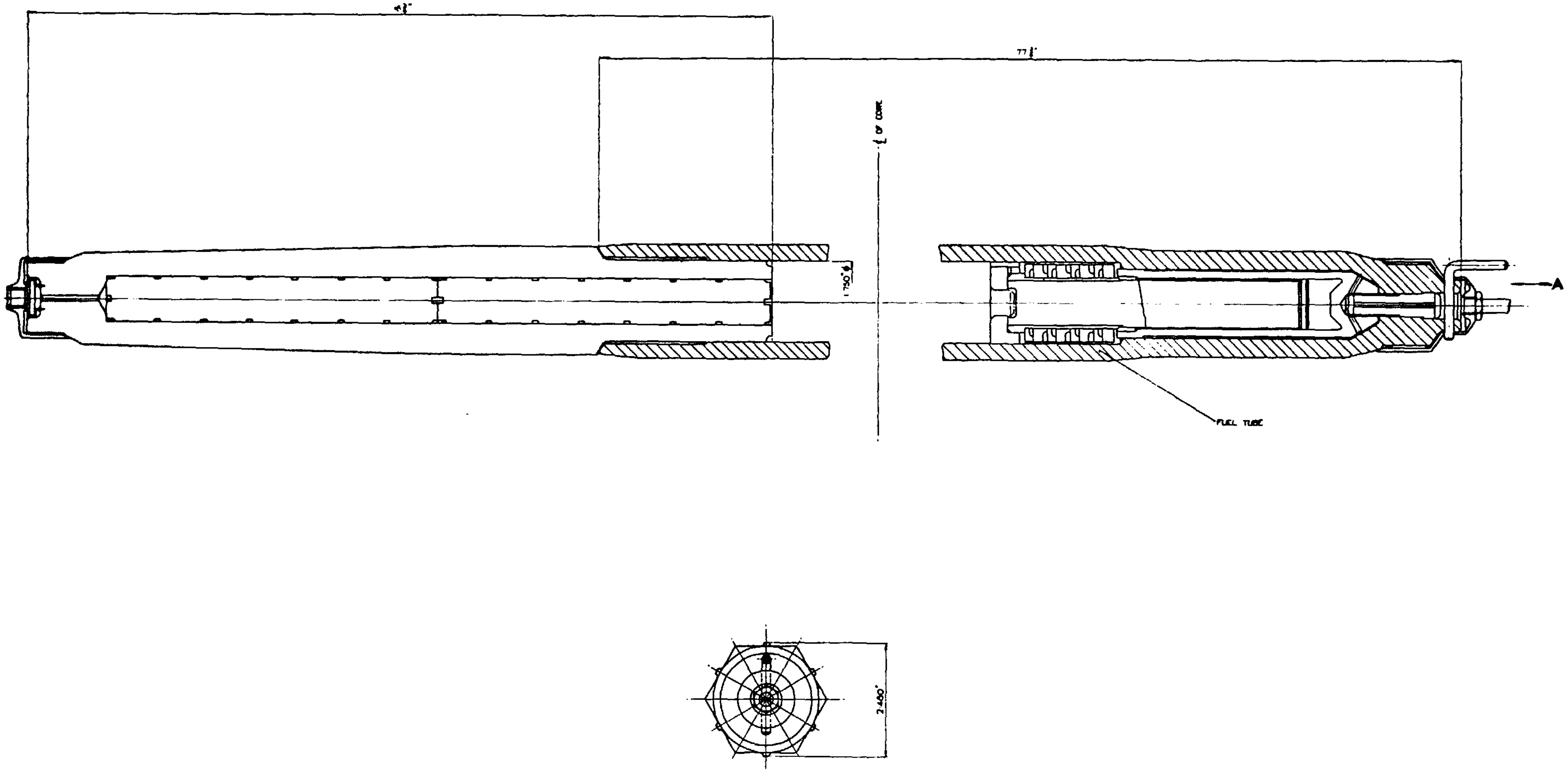


FIG. 1 PROPOSED DRAGON FUEL BOX



END VIEW ON ARROW 'A'

FIG. 2 DRAGON FUEL ELEMENT
OUTER FUEL ROD ASSEMBLY

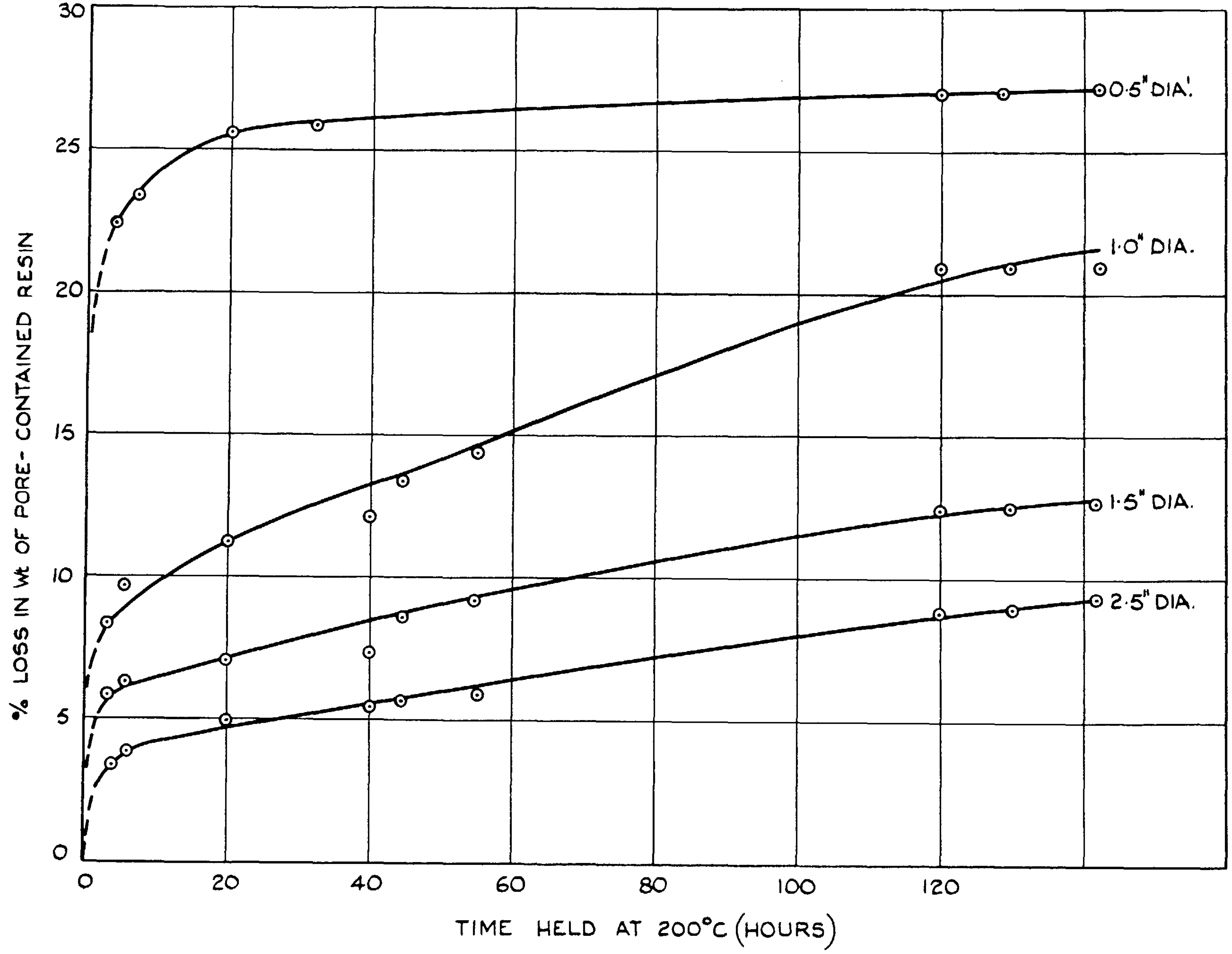


FIG. 6. WEIGHT LOSS ON CURING IMPREGNATED BARS OF DIFFERENT DIAMETERS.

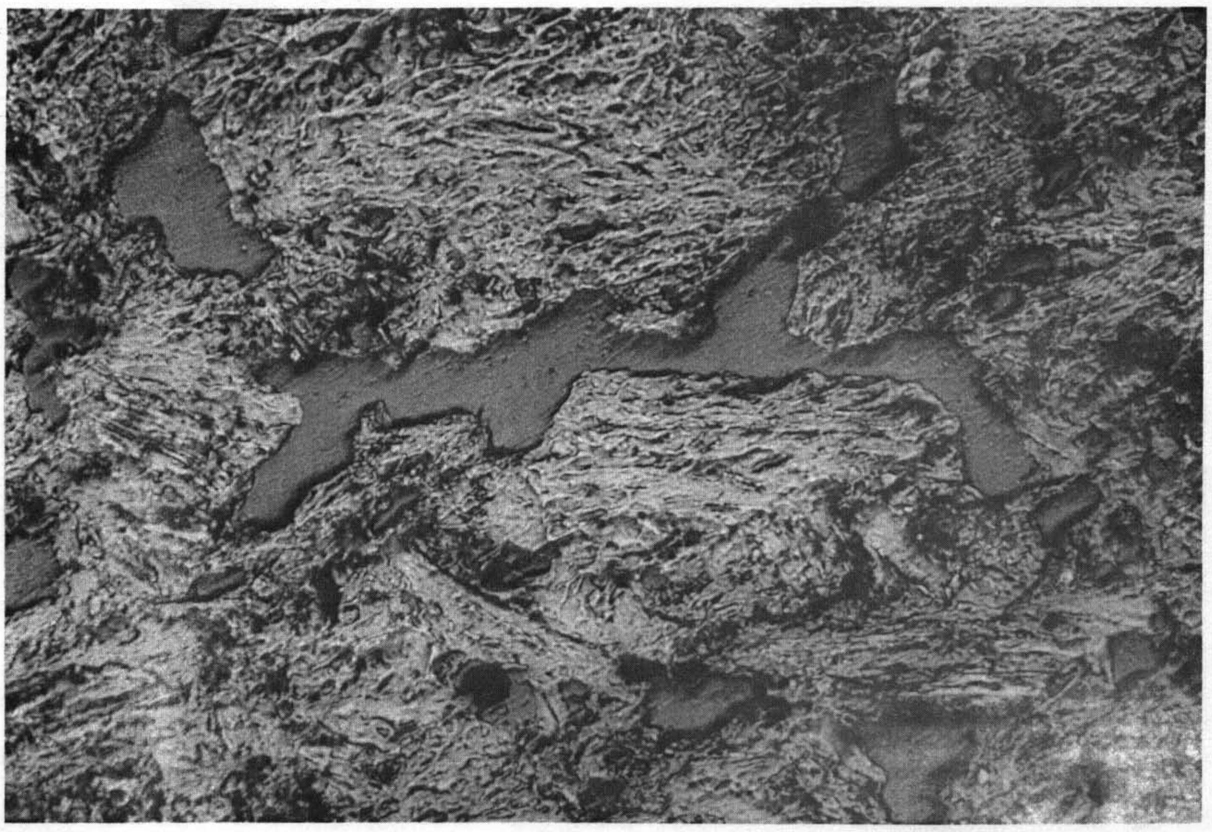


Figure 7(a)
RESIN IN PORE OF
CS GRAPHITE AFTER
CURING TO 120°C
(Mag. X 200)

Figure 7(b)
SAME FIELD AS
FIG. 7(a) AFTER
HEATING TO 450°C
(Mag. X 200)

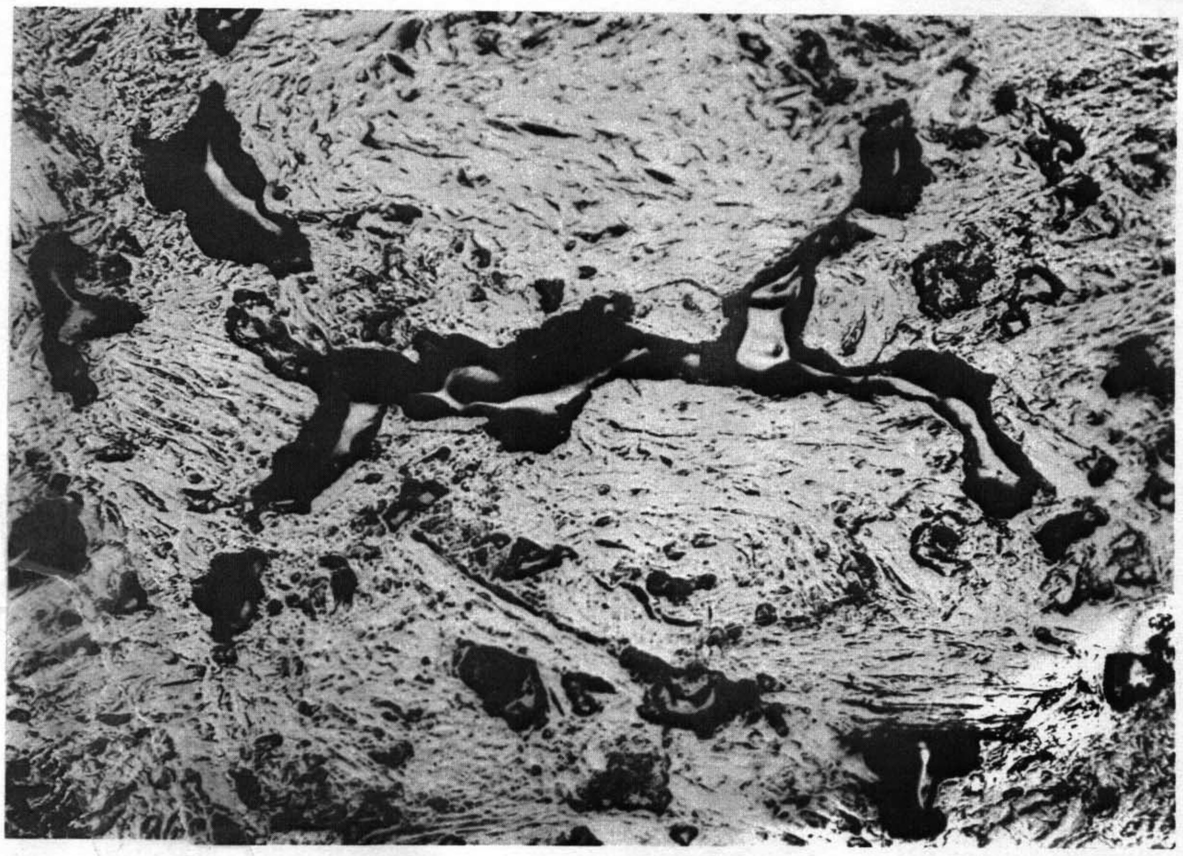


Figure 7(c)
SAME FIELD AS
FIG. 7(a) AFTER
HEATING TO 1000°C
(Mag. X 200)

FIGURE 7

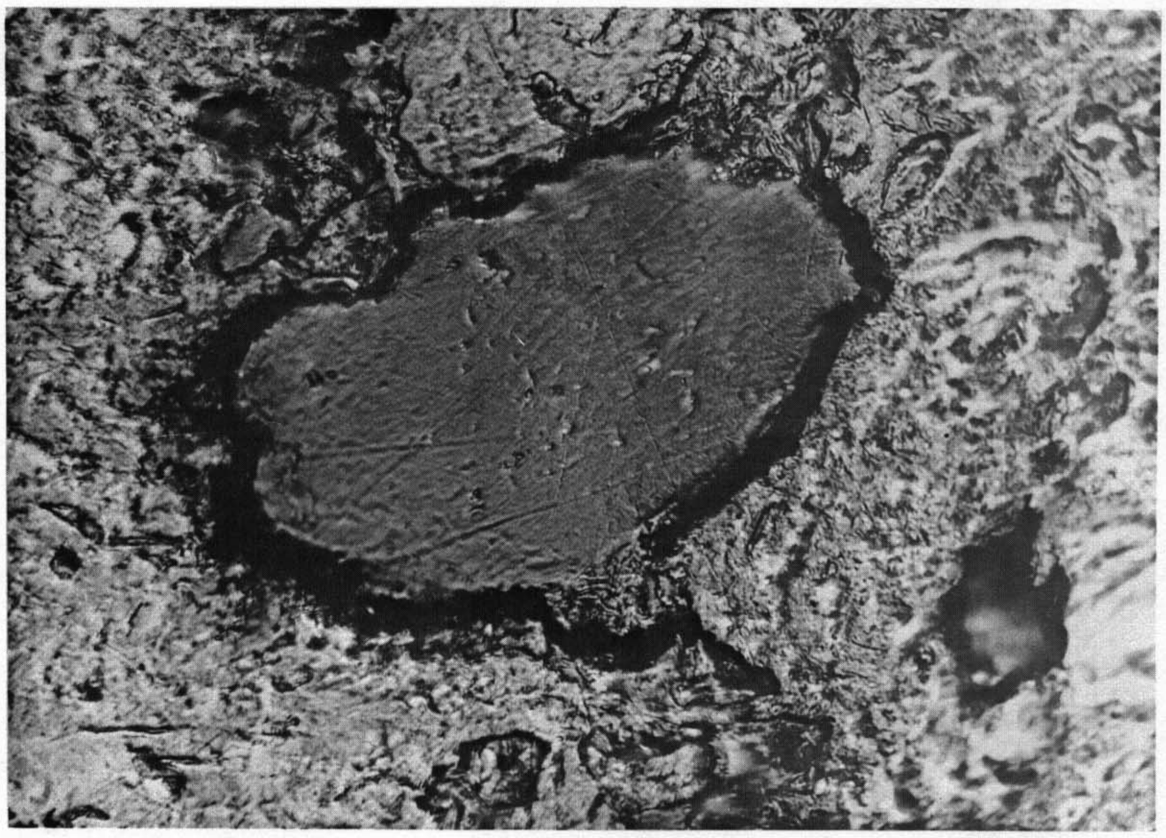


Figure 8(a)
RESIN FILLED PORE
AFTER HEATING TO
450°C (Mag. X 750)

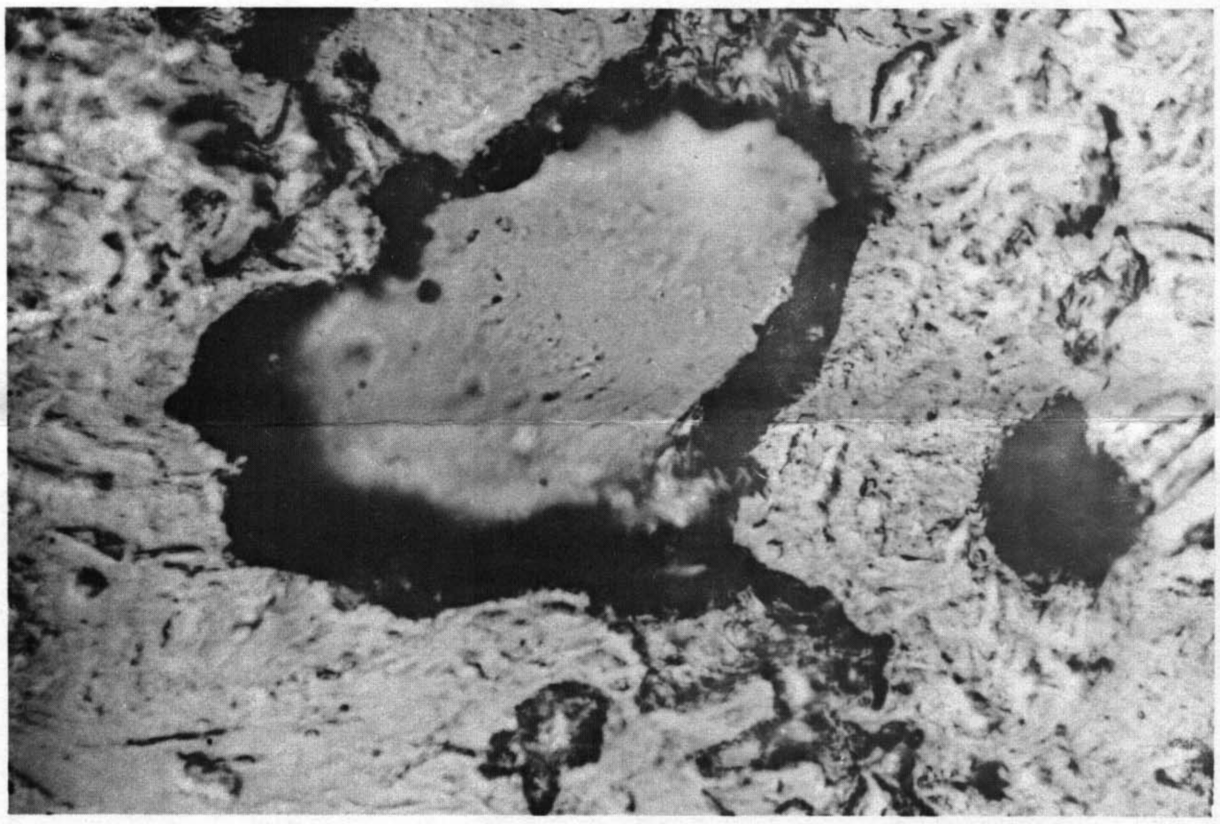


Figure 8(b)
SAME FIELD AS FIG. 8(a)
AFTER HEATING TO 710°C
(with resin carbon
shrinking out of focus)
(Mag. X 750)

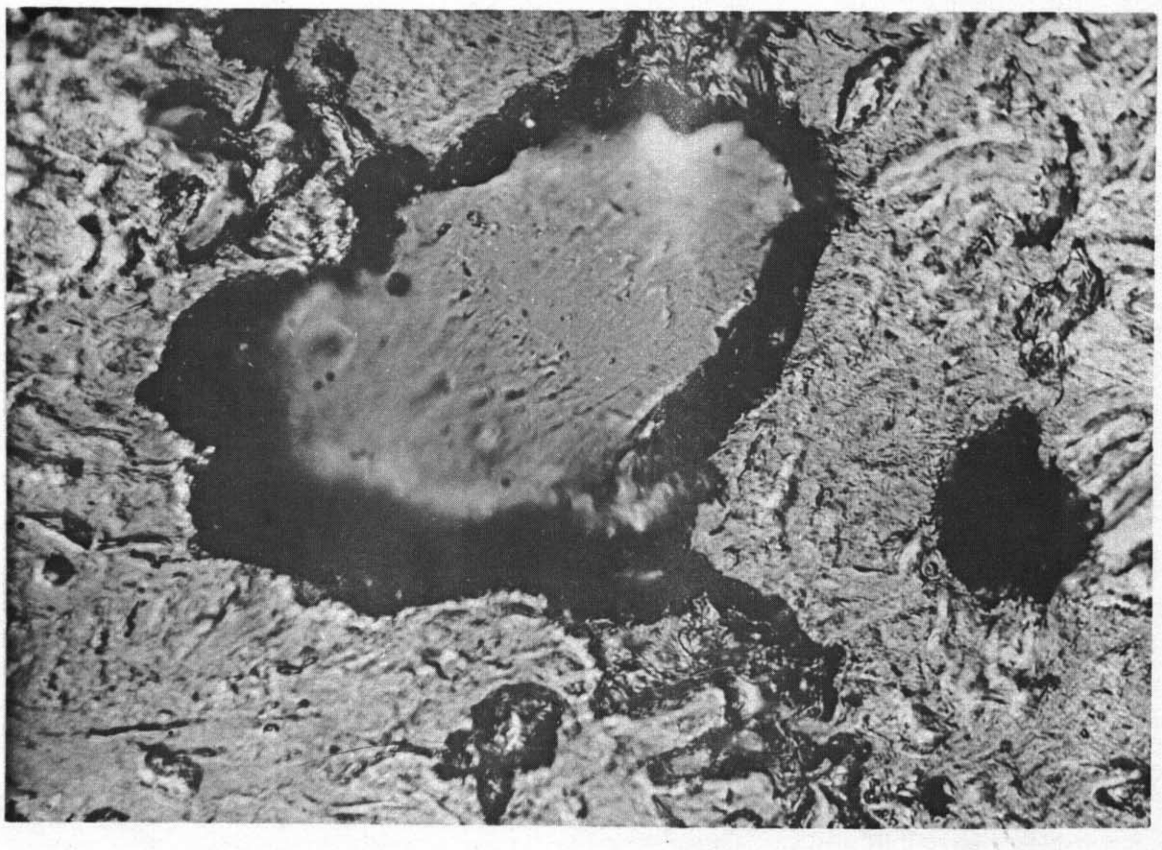
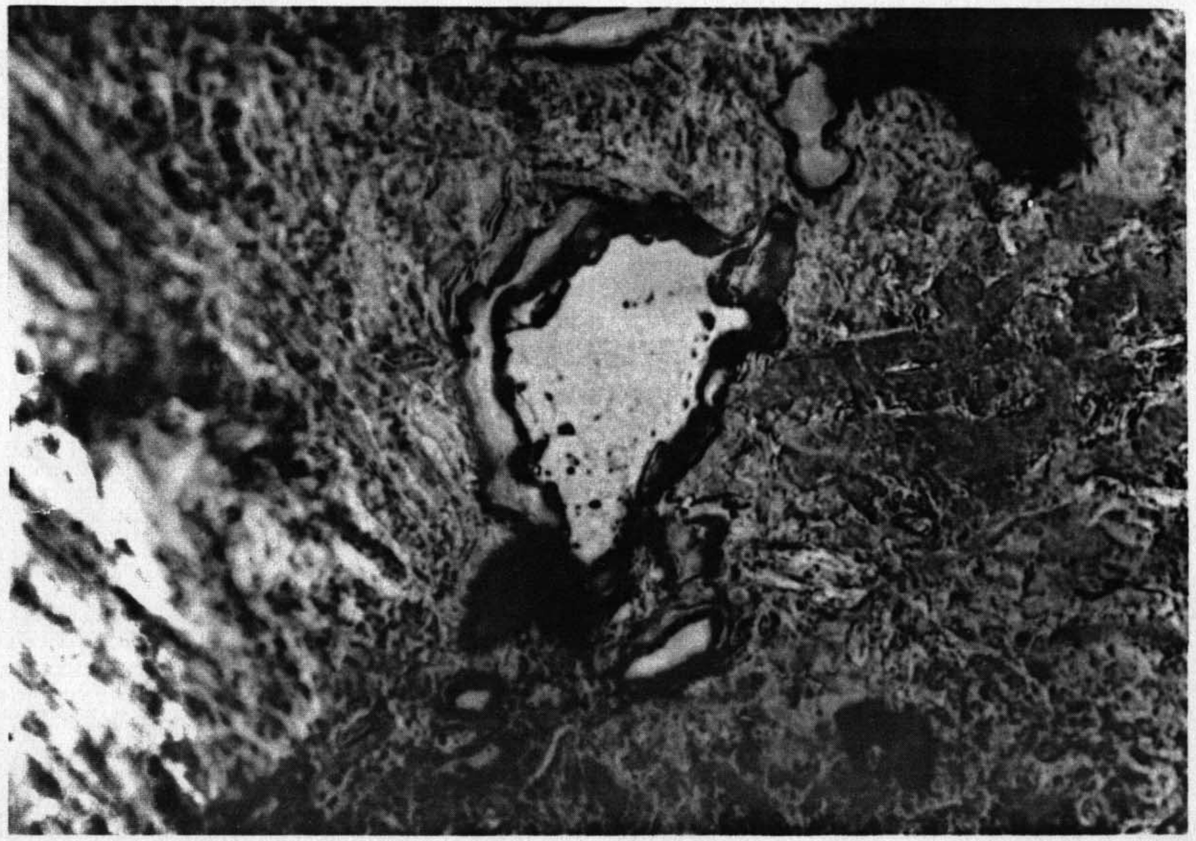


Figure 8(c)
SAME FIELD AS FIG. 8(a)
AFTER HEATING TO 1000°C
(Mag. X 750)

FIGURE 8

Figure 9(a) RESIN IN PORE OF CS GRAPHITE AFTER SECOND IMPREGNATION AND CURING TO 120°C (with resin surrounding carbon core remaining from first impregnation) (Mag. X 750)



SAME FIELD AS Fig. 9(a) AFTER HEATING TO 450°C (Mag. X 750)

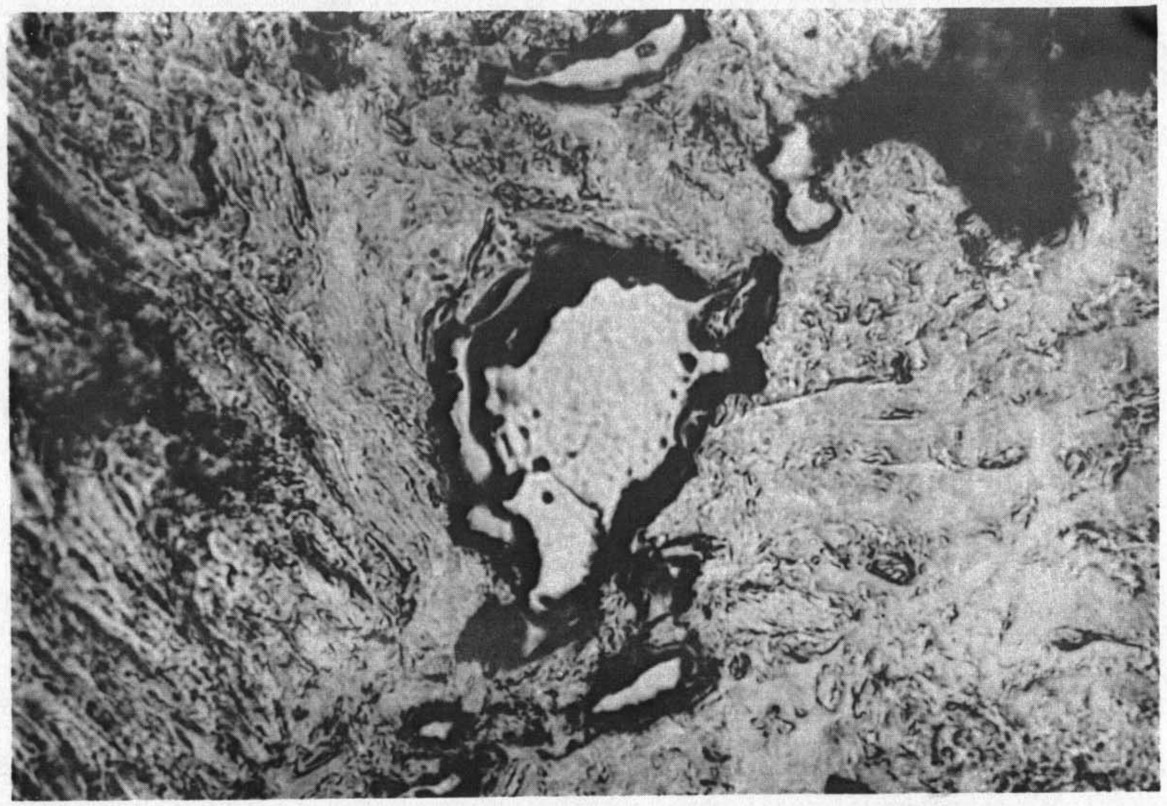
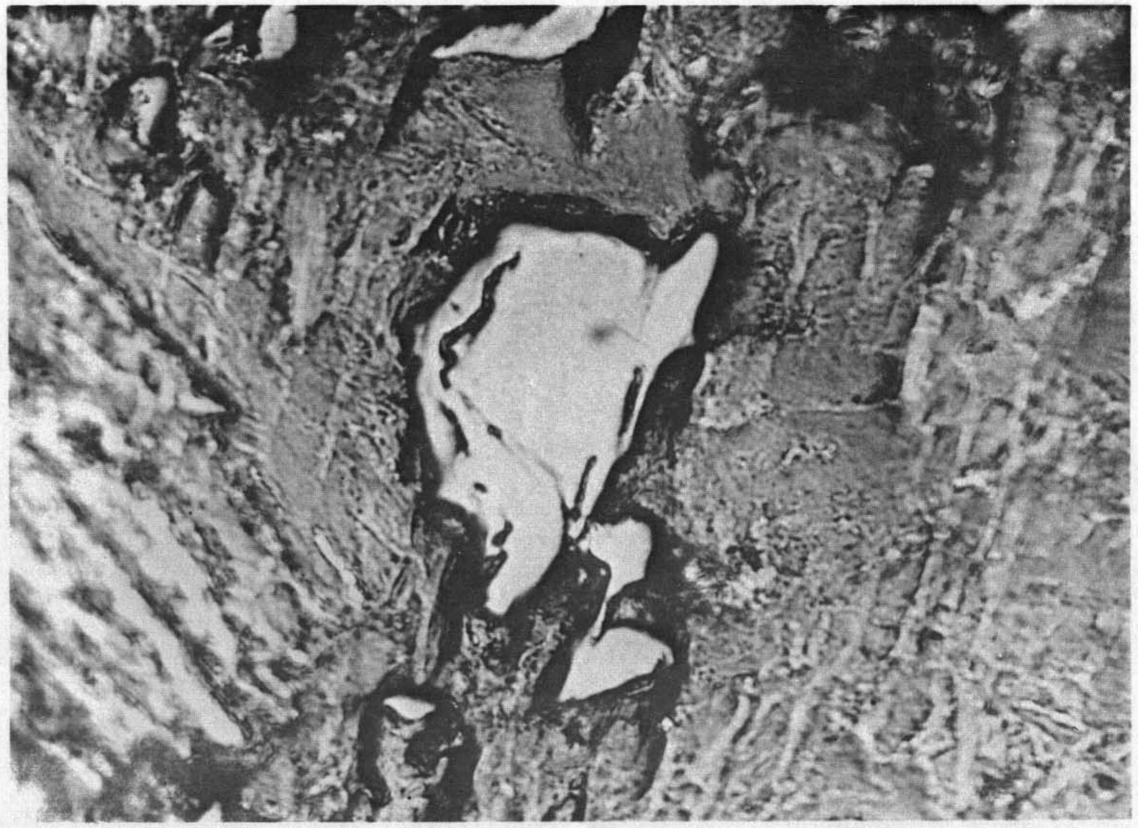


Figure 9(c) SAME FIELD AS Fig. 9(a) AFTER HEATING TO 1000°C (Mag. X 750)



SAME FIELD AS Fig. 9(c) AFTER REPOLISHING (Mag. X 750)

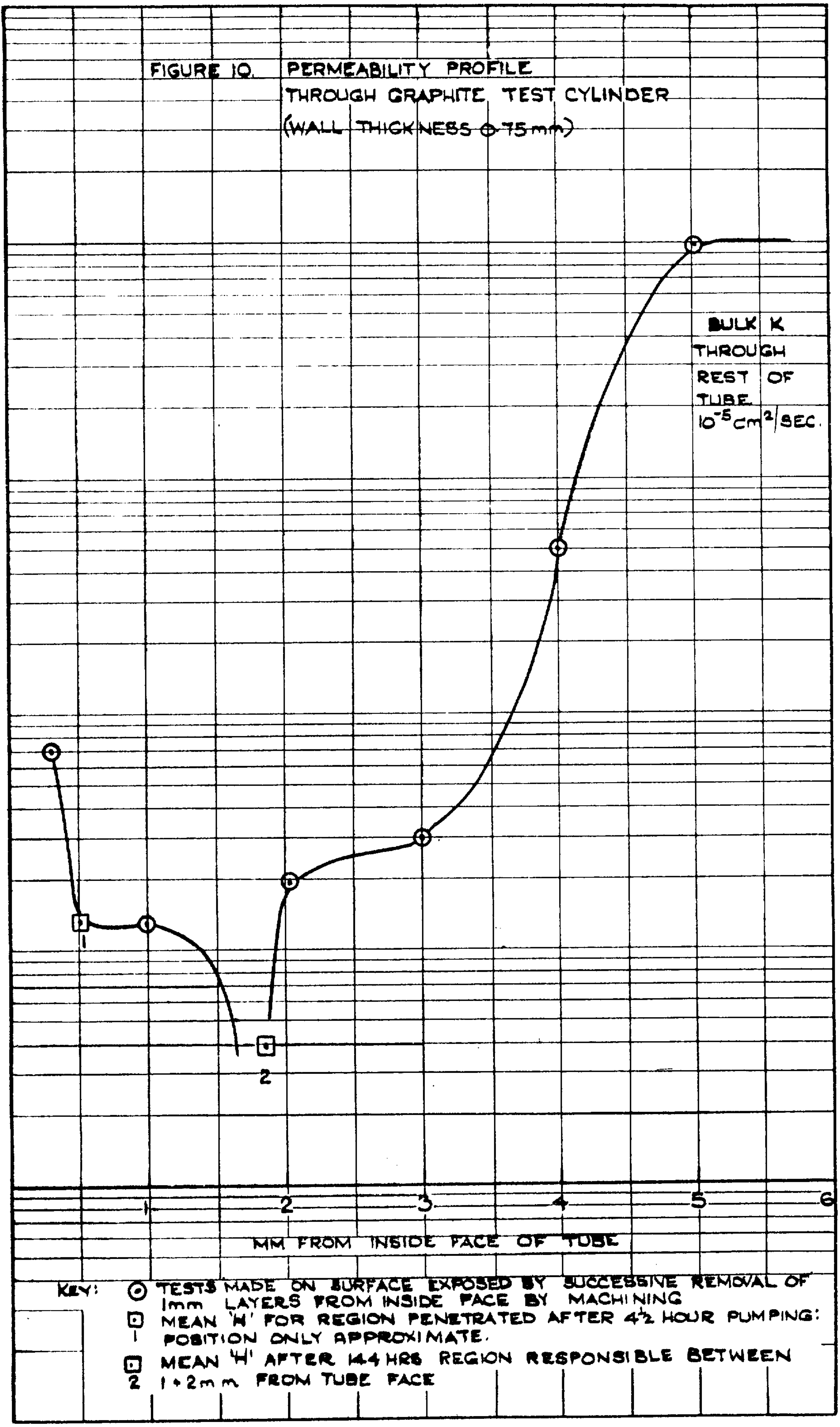


FIGURE 10. PERMEABILITY PROFILE THROUGH GRAPHITE TEST CYLINDER (WALL THICKNESS 6·75mm)

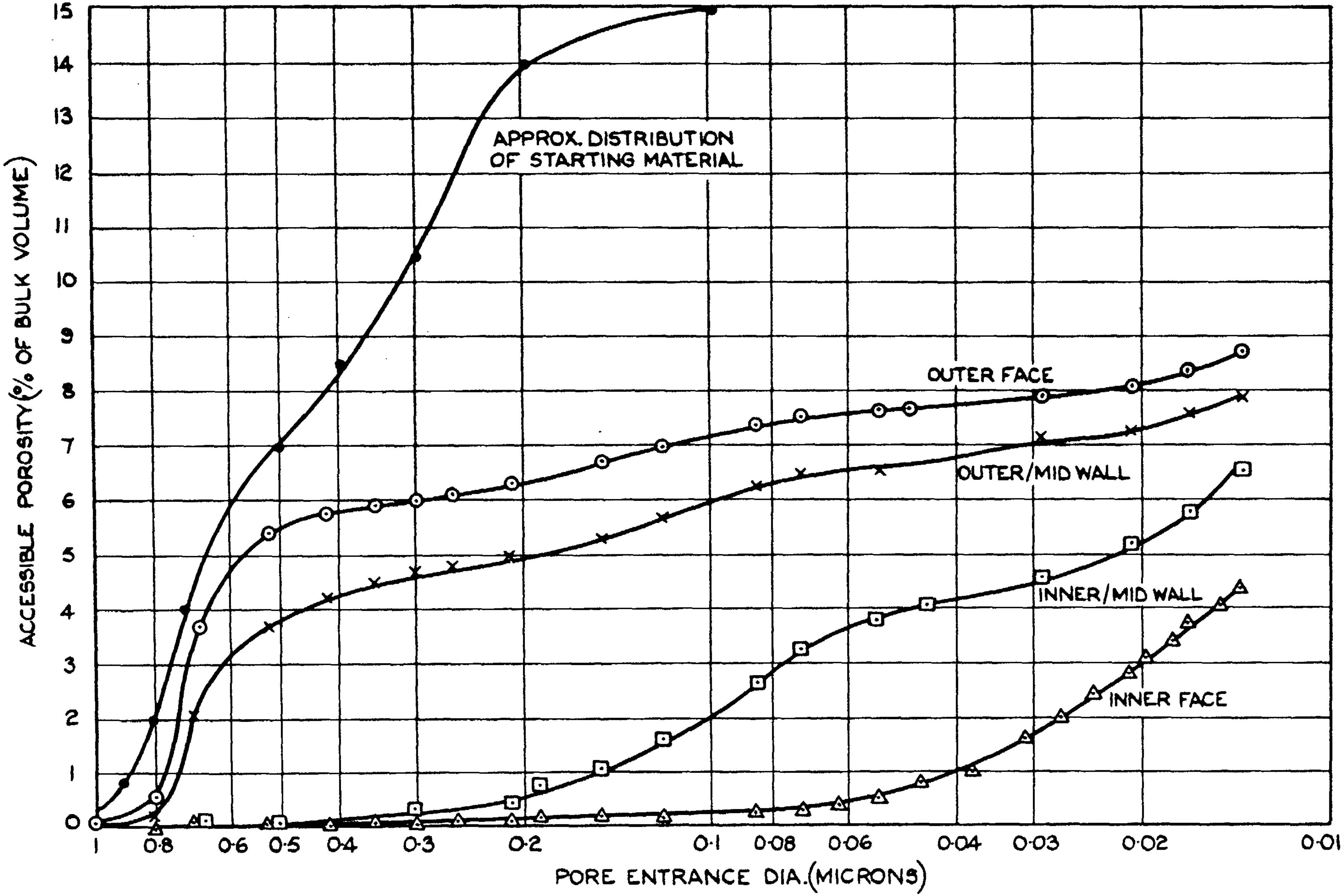


FIG.11. PORE SIZE CURVES OBTAINED ON SPECIMEN IMPREGNATED USING FUEL ROD PROCESS.

SPECIMENS USED WERE APPROXIMATELY ¼ OF THE WALL THICKNESS.
MEASUREMENTS MADE BY T.R. JENKINS, A.E.R.E. HARWELL.

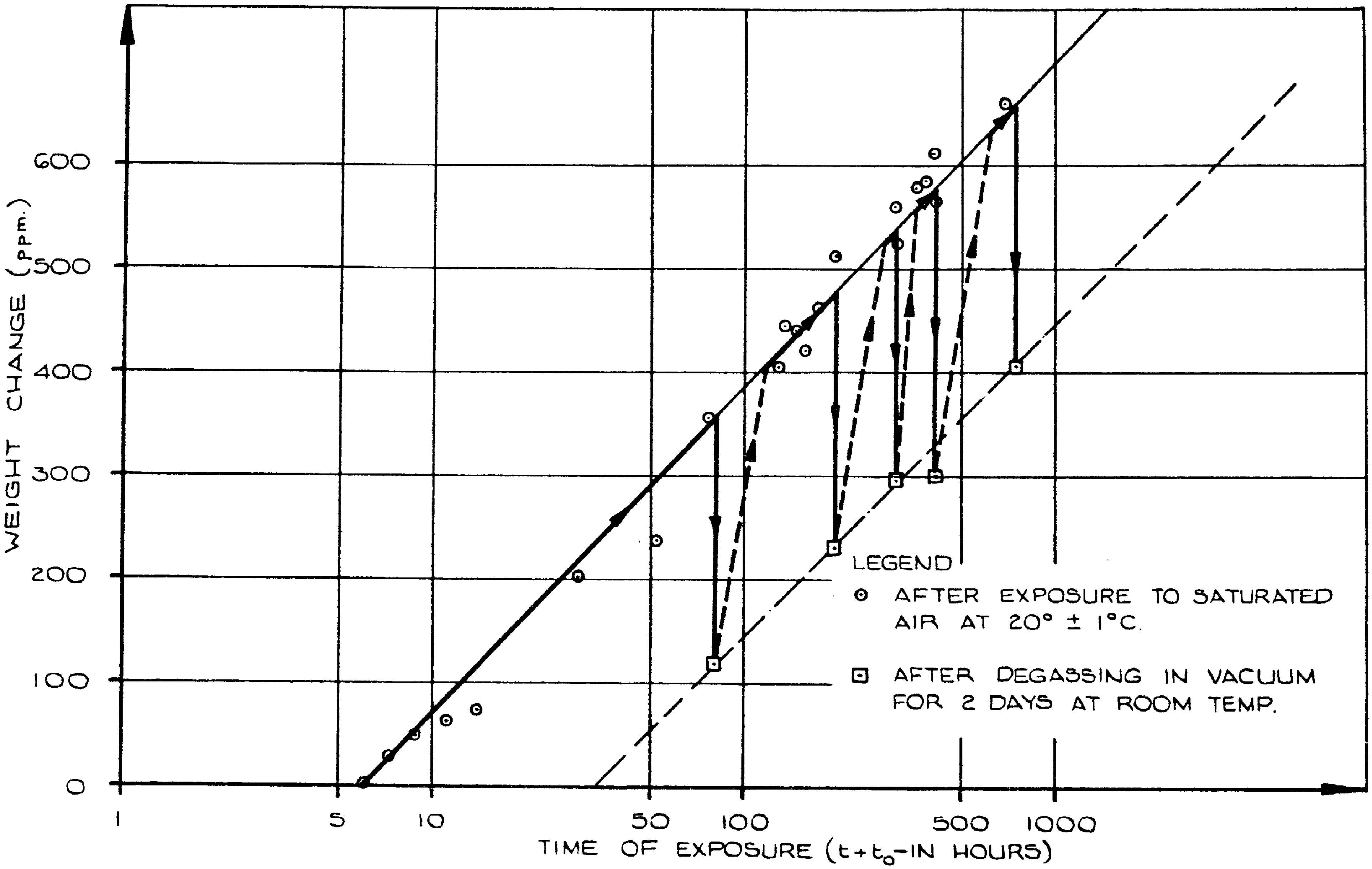


FIG. 12 CHANGE IN WEIGHT OF FUEL BOX DURING ADSORPTION—DESORPTION CYCLES.

TABLE I. HEATING SCHEDULE FOR IMPREGNATED MATERIAL

TEMPERATURE (°C)	TIME (HR)
60	2
80	2
100	2
120	16
150	1·5
180	1·5
200	1·5
200-600	5°/HR
600-1000	RISING TO 50°C/HR

TABLE 2. CARBONISATION DATA FOR FURFURYL ALCOHOL RESIN

Temperature Range (°C)	Cumulative Weight Loss* (% original uncured weight	Apparent Density* (g/cm^3)	Volume of gas evolved at temp. (cm^3/g of cured resin)	Gas Composition (% by wt.)				
				H_2O	CO_2	CO	H_2	Organics (mean mol. wt = 18)
up to 200	20	1.42	-	-	-	-	-	-
200-500	48	1.07	100	9	22	18	1.0	50
500-1000	56	1.26	200	3	50	37	6.0	4

* after heat treatment to the max. temperature of the appropriate temperature range

TABLE 3. PROPERTIES OF FURFURYL ALCOHOL CHAR.

PROPERTY	TREATMENT	
	AFTER CARBONISATION IN LAMPBLACK TO 1000°C.	AFTER VACUUM HEAT TREATMENT FOR 2HRS. AT 1300°C.
APPARENT DENSITY (g / cm^3)	1·31	1·27
ELECTRICAL RESISTIVITY (ohm - cm. x 10^{-3})	13·4	5·79
THERMAL CONDUCTIVITY (c.g.s. units)	—	0·0058
GAS CONTENT * (% by wt.)	2 – 4	0·19 (degassed for 2hrs at 1100°C)

* THE GAS CONTENT IS MAINLY HYDROGEN IN MOLE. PER CENT.

TABLE 4. IMPREGNATION RESULTS FOR EXPERIMENTAL AND STANDARD FUEL BOXES AND LIDS

INITIAL DATA			1ST TREATMENT RESULTS			2ND TREATMENT RESULTS			K (cm^2/sec) @ p_m = 0.5 x 10^6 dynes/cm^2	
Type	Batch and Specimen Number	Weight (gm)	% Weight Increase (resin)	% Weight Increase (carbon)	% Carbon Yield of Resin	% Weight Increase (resin)	Total % Carbon Gain	% Carbon Yield of Resin	After Second Treatment	After Vacuum Degassing
Experimental Non Purified Stock	42.24	154.8	9.92	4.07	40.9	6.40	7.05	45.2	1.5×10^{-6}	1.3×10^{-5}
	43.11	153.0	10.20	4.12	40.1	7.34	7.92	49.9	2.9×10^{-7}	0.9×10^{-5}
	44.11	155.2	9.48	3.86	40.8	6.32	6.77	44.5	1.0×10^{-6}	0.9×10^{-5}
	113.2	153.2	8.98	3.32	36.9	6.25	6.19	44.9	7.7×10^{-6}	1.4×10^{-5}
Standard Purified Stock	AE.1	132.5	9.61	3.93	41.3	6.03	6.71	45.2	1.6×10^{-6}	-
	AE.2	131.0	10.40	4.35	41.6	6.67	7.47	45.6	2.6×10^{-6}	-
	AE.3	132.5	9.20	3.93	42.6	5.74	6.57	45.5	1.12×10^{-3}	-
	AE.4	133.0	9.18	3.91	42.6	5.63	6.47	44.8	3.3×10^{-7}	-
	AE.5	133.0	9.37	3.99	42.4	5.78	6.68	45.7	8.5×10^{-7}	-
	AE.6	132.0	9.23	4.01	43.4	5.75	6.66	45.5	2.5×10^{-7}	-
Standard Box Lids Purified Stock	AG.1	31.036	9.24	3.80	41.2	5.09	6.07	43.4	3.9×10^{-7}	-
	AG.2	30.663	10.2	4.95	48.4	5.56	7.49	44.3	2.2×10^{-7}	-
	AG.3	30.796	9.70	4.02	41.4	5.79	6.72	44.5	3.8×10^{-7}	-
	AG.4	30.845	9.12	4.06	44.6	5.01	6.28	44.0	4.8×10^{-8}	-
	AG.5	30.907	9.55	4.20	43.9	5.38	6.50	41.7	4.4×10^{-6}	-
	AG.6	31.096	9.37	4.17	44.5	5.39	6.61	43.8	2.7×10^{-7}	-

Notes (i) For each Impregnation Samples were evacuated prior to a 16 hour total immersion in fresh F.A. + 2% H_3PO_4 of Viscosity 10 cp.

(ii) Vacuum Degassed Specimens were maintained at 1500°C for 2 hours.

TABLE 5. IMPREGNATION RESULTS FOR EXPERIMENTAL FUEL BOXES

	INITIAL DATA		1 ST TREATMENT RESULTS			2ND TREATMENT RESULTS			3RD TREATMENT RESULTS			K(cm^2/sec) @ p_m = 0.5 x 10^6 dynes/cm^2	
BATCH AND SPECIMEN NO.	Weight (gm)	K(10^{-2} cm^2/sec) @ p_m = 1.5 x 10^6 dynes/cm^2	% Weight Increase (Resin)	% Weight Increase (Carbon)	% Carbon Yield of Resin	% Weight Increase (Resin)	Total % Carbon Gain	% Carbon Yield of Resin	% Weight Increase (Resin)	Total % Carbon Gain	% Carbon Yield of Resin	After 3rd Treatment	After Vacuum Degassing
42.20	155.1	1.16	9.28	4.44	48.8	4.07	6.37	47.0	0.42	6.37	Nil	1.2 x 10^{-7}	5.6 x 10^{-7}
42.21	155.3	1.19	9.34	4.50	49.3	4.06	6.37	45.4	0.48	6.43	14.3	5.6 x 10^{-8}	6.8 x 10^{-7}
42.22	155.5	1.12	9.34	4.56	49.6	3.57	Surface Crack	-	-	-	-	5.8 x 10^{-8}	4.4 x 10^{-7}
43.7	157.3	1.51	9.52	4.70	49.7	4.14	6.62	45.4	0.42	6.67	16.7	4.0 x 10^{-8}	5.9 x 10^{-7}
43.8	152.6	1.56	9.58	4.65	49.3	4.45	6.76	45.8	0.37	6.82	20.0	2.5 x 10^{-7}	1.7 x 10^{-6}
43.9	156.2	1.41	9.46	4.67	49.6	4.31	6.40	45.0	0.42	6.58	60.0	6.6 x 10^{-8}	9.2 x 10^{-7}
44.7	154.2	1.58	9.60	4.73	49.2	4.15	6.68	46.2	0.30	6.81	50.0	5.8 x 10^{-8}	9.3 x 10^{-7}
44.8	154.7	1.56	9.53	4.53	49.3	4.33	6.52	45.6	0.49	6.67	33.3	6.0 x 10^{-7}	6.5 x 10^{-6}
44.9	154.9	1.56	9.58	4.65	49.2	4.25	6.67	46.3	0.36	6.73	20.0	5.0 x 10^{-8}	8.3 x 10^{-7}
53.4	152.5	1.13	9.30	4.47	48.6	3.70	6.23	47.4	0.43	6.36	33.3	3.7 x 10^{-9}	1.1 x 10^{-6}
53.5	155.1	1.10	9.42	4.50	48.6	3.51	6.18	48.2	0.43	6.30	40.0	3.7 x 10^{-9}	9.2 x 10^{-7}
53.6	155.4	1.12	9.40	4.63	50.0	3.69	6.45	49.2	0.30	6.45	Nil	1.9 x 10^{-9}	8.1 x 10^{-7}
65.1	150.5	1.54	9.57	4.65	49.0	4.00	6.51	46.7	0.44	6.64	40.0	4.8 x 10^{-9}	1.1 x 10^{-6}
65.2	150.7	1.20	9.23	4.50	49.3	4.00	6.36	46.6	0.44	6.50	40.0	3.6 x 10^{-9}	7.4 x 10^{-7}
65.3	153.5	1.21	9.40	4.50	48.6	4.12	6.45	46.2	0.55	6.51	14.3	Spalled	-

Notes (i) Treatments: 1st) 2nd) Evacuation Prior to a 16 hour total immersion in fresh F.A. + H_3PO_4 of viscosity ~ 10 cp.

3rd 16 hour total immersion in fresh F.A. + 2% H_3PO_4 of viscosity ~ 10 cp.

(ii) Vacuum degassed specimen 65.1 Developed slight cracks on 2nd treatment pyrolysis.

TABLE 6 FUEL ROD IMPREGNATION RESULTS

	INITIAL DATA		1st. IMPREGNATION			2nd IMPREGNATION		
SPECIMEN NUMBER	WEIGHT GM.	K* CM^{2}x10^{-2}/SEC.	RESIN UPTAKE WT.%	CARBON GAIN WT %	K* CM^{2}x10^{-3}/SEC.	RESIN UPTAKE WT%	CARBON GAIN WT.% (TOTAL)	K+ CM^{2}x10^{-6}/SEC.
20	4944	1·5	7·7	3·7	0·16	0·61	3·95	0·46
21	4912	1·9	8·8	3·7	0·11	0·41	3·95	1·1
22	4839	4·6	9·7	4·6	1·7	2·50	5·85	3·2
23	4899	2·8	8·5	4·0	0·012	0·41	4·25	0·50
24	4919	4·6	9·3	4·3	0·51	0·82	4·80	1·0
25	4846	7·0	10·0	4·6	1·7	2·00	5·70	3·9
26	4858	7·0	9·8	4·6	2·1	2·30	5·80	2·6
27	4841	4·6	9·0	4·1	—	1·70	5·15	1·6
28	4878	7·0	9·7	4·5	4·3	3·30	6·20	<40
29	4932	1·9	7·7	3·7	0·13	0·51	3·95	1·2
30	4927	2·8	8·3	3·9	0·25	0·59	4·15	1·2
31	4842	7·0	9·8	4·6	3·1	3·90	6·45	3·3
32	4881	3·5	9·7	4·7	0·49	1·20	5·15	2·6
33	4895	3·5	9·3	4·5	0·35	0·84	4·90	0·90
34	4899	4·6	9·0	4·3	1·8	1·90	5·20	4·4
35	4815	7·0	10·5	5·3	0·93	2·24	7·15	1·8
36	4838	7·0	9·7	4·7	0·18	2·32	5·80	1·5
37	4874	4·8	8·5	3·9	1·8	3·26	5·50	<70
39	4880	2·8	8·8	4·3	0·28	0·73	4·75	0·79
40	4948	2·0	7·7	3·7	0·25	0·62	4·00	2·2

* AT 3·6 x 10^6 DYNES/CM^2 MEAN PRESSURE

\+ AT 0·5 x 10^6 DYNES/CM^2 MEAN PRESSURE

TABLE 7. GAS CONTENT OF IMPREGNATED MATERIALS

MATERIALS	GAS CONTENT CM ^{3}/GM (100 - 1000°C)	COMPOSITION %				
		CO_2	CO	H_2O	CH_4	H_2
PYROLYSED TO 1,000°C	2·04	0	22	0	0	72
PYROLYSED TO 1,000°C 1 HR. VAC. TREATMENT AT 1100°C	0·260	0	17	0	-	-
PYROLYSED TO 1,000°C 1 HR. VAC. TREATMENT AT 1800°C	0·056	3	38	0	2	48
PYROLYSED TO 1000°C 1 HR. VAC. TREATMENT AT 1800°C	0·025	0	50	0	-	-
FURFURYL ALCOHOL CHAR PYROLYSED TO 1000°C AND VACUUM TREATED AT 1100°	7·8	0	8·4	0	0	87

NOTE :- MEASUREMENTS WERE MADE BY R.C. ASHER, A.E.R.E., HARWELL

TABLE 8. DIMENSIONAL CHANGES PRODUCED BY IMPREGNATION AND SUBSEQUENT HEAT TREATMENT.

CONDITIONS	RELATIVE DIAMETER CHANGE (MEASURED AT ROOM TEMPERATURE)				
	PER TREATMENT			CUMULATIVE	
	SAMPLE 1	SAMPLE 2	UNIMPREGNAT^{D} CONTROL.	SAMPLE 1	SAMPLE 2
AS RECEIVED	ORIGIN	ORIGIN	ORIGIN	ORIGIN	ORIGIN
TRIPLY IMPREGNATED & BAKED TO 1000 °C.	$-1\cdot6 \times 10^{-3}$	$-2\cdot0 \times 10^{-3}$	—	$-1\cdot6 \times 10^{-3}$	$-2\cdot0 \times 10^{-3}$
AFTER VACUUM DEGASSING AT 1500°C.	$+0\cdot40 \times 10^{-3}$	$+0\cdot45 \times 10^{-3}$	0·0	$-1\cdot2 \times 10^{-3}$	$-1\cdot55 \times 10^{-3}$
AFTER HEAT TREATMENT TO 2200 °C.	$+0\cdot60 \times 10^{-3}$	$+0\cdot70 \times 10^{-3}$	0·0	$-0\cdot60 \times 10^{-3}$	$-0\cdot85 \times 10^{-3}$
AFTER HEAT TREATMENT TO 2400 °C.	$-2\cdot6 \times 10^{-3}$	$-3\cdot5 \times 10^{-3}$	—	$-2\cdot0 \times 10^{-3}$	$-4\cdot35 \times 10^{-3}$
AFTER HEAT TREATMENT TO 2600 °C.	$-0\cdot40 \times 10^{-3}$	$-0\cdot35 \times 10^{-3}$	$-2\cdot3 \times 10^{-3}$	$-2\cdot4 \times 10^{-3}$	$-4\cdot7 \times 10^{-3}$

NOTE :- + AND – INDICATE EXPANSION AND CONTRACTION RESPECTIVELY.

TABLE 9. THERMAL PROPERTIES

TEMPERATURES °C	330	370	485	545	745
Thermal Conductivity cal/cms °C (Parallel) (Untreated)	0.147	0.122	0.105	0.093	0.087

TEMPERATURE RANGES	20-400°C	20-600°C	20-800°C	20-1000°C
Thermal Expansion Coefficient x 10^6				
Parallel (Untreated)	1.89	2.13	2.34	2.49
Perpendicular (Untreated)	3.8	4.5	4.8	5.5
Parallel (2 Impregnations)	1.81	2.05	2.20	2.31

T

TABLE 10. MECHANICAL PROPERTIES	PARALLEL			PERPENDICULAR
	20°C	600°C	1,000°C	20°C
1. Transverse Rupture Test				
Elastic Modulus - Untreated	1.76 + 12% - 8%	1.79 + 14% - 9%	1.83 + 12% - 4%	0.71
x 10^{-6} (p.s.i.) 2 Impregnations	2.65 + 8% - 9%	2.57 + 7% - 12%	2.44 + 10% - 8%	-
Flexural Strength - Untreated	3,600 + 8% - 14%	4,000 + 20% - 13%	4,400 + 11% - 39%	3,000
(p.s.i.) 2 Impregnations	5,800 + 5% - 9%	6,600 + 8% - 11%	7,200 + 11% - 20%	-
% Strain at Fracture - Untreated	0.18 + 11% - 28%	0.20 + 20% - 20%	0.22 + 18% - 41%	0.13
(4 Point Loading) 2 Impregnations	0.20 + 15% - 15%	0.24 + 8% - 13%	0.28 + 7% - 14%	-
2. Compression Test				
Elastic Modulus - Untreated	0.81	-	-	0.42
x 10^{-6} (p.s.i.) 2 Impregnations	1.32	-	-	0.64
Ultimate Compressive - Untreated	11,000	-	-	9,100
Strength (p.s.i.) 2 Impregnations	17,400	-	-	12,300

TABLE 11. Bar oxidation tests.

(on samples ½" x ½" x 4")

No.	DETAILS	% Wt loss after 18 hrs in Air at 550°C
1	Untreated	3.97
2	"	3.22
3	Doubly impregnated, heated to 1000°C	28.5
4	" " " " "	23.7
5	Double impregnation, heated to 2800°C	0.17
6	Furfuryl alcohol char heated to 1000°C	100.0
7	Furfuryl alcohol char heated to 2800°C	0.20
8	Single impregnation, re-impregnated with H_3PO_4 and re-heated to 1000°C.	2.7

TABLE 12. <u>Slab Oxidation Tests</u>

(on samples 2 cm. x 4 cm. x 0.2 cm.)

Spec^n. No.	No. of Impregnation Treatments	Catalyst	Degassing or Inert Atmosphere Treatment	Oxidation Rate mg/cm^2/hr.
1	None	-	-	2.5
2	"	-	-	1.9
3	"	-	-	2.1
4	1	HCl	Carbonized to 1000°C in carbon chips	30.0
5	"	"	" " " " " "	33.4
6	"	"	" " " " " "	35.0
7	2	HCl	Carbonized to 1000°C in carbon chips	53.0
8	"	"	" " " " " "	56.0
9	"	"	" " " " " "	59.1
10	1	HCl	1000°C bake followed by 2 hr. 1100°C vac.	10.8
11	"	"	1000°C bake followed by 2 hr. 1400°C vac.	2.0
12	"	"	1000°C bake followed by 2600°C graphitization	0.1
13	2	H_3PO_4	1000°C bake, held @ 1000°C 4 hrs.	4.6
14	"	"	1000°C bake, held @ 1000°C 72 hrs.	0.83
15	"	"	1000°C bake followed by 2 hr. 1800°C vac.	0.016
16	"	"	1000°C bake followed by 4 hr. 1800°C vac.	0.016
17	"	"	1000°C bake followed by 8 hr. 1800°C vac.	0.239
18	None	-	1400°C vac. 2 hrs.	0.53
19	"	-	1400°C vac. 4 hrs.	2.9
20	"	-	1400°C vac. 8 hrs.	1.0
21	"	-	1800°C vac. 2 hrs.	0.22
22	"	-	1800°C vac. 4 hrs.	1.7