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

DRAGON

Dragon Project Report

COATED PARTICLE FUEL FOR THE DRAGON REACTOR EXPERIMENT

by

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ABSTRACT

A brief description of the core of the Dragon Reactor is presented with emphasis on the major objectives concerning fuel element development.

Reference is made to the proposed specification for the initial charge in describing the methods chosen for production of the coated particle fuel assemblies. An experimental fluidised bed employed for all coating studies is described and the development of the prototype production apparatus traced through its various stages.

Methods used for making composite coatings of pyrolytic carbon/graphite and silicon carbide are discussed and initial results of the evaluation studies presented.

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1. INTRODUCTION

Early in 1956 a small team was formed at the Atomic Energy Research Establishment, Harwell, to investigate the possibilities of the high temperature gas cooled reactor system. As part of this work, a design study of a relatively small (10-20 MW(t)) reactor experiment was carried out: in addition a considerable amount of research and development work associated with such a reactor was initiated. In April 1959 the responsibility for this work was taken over by the O.E.C.D. High Temperature Gas Cooled Reactor Project (the DRAGON Project) at the Atomic Energy Establishment, Winfrith, the major objective being to build and operate a reactor experiment.

The main purpose of this reactor experiment is to demonstrate the principles on which any high temperature gas cooled reactor must be based. Its principle features are the use of helium as coolant, with fuel elements of low permeability graphite, containing fuel cartridges in which the dispersed fissile and fertile material is in the carbide, oxide, or other ceramic form. Provision is made for the removal of fission products which escape from the fuel cartridge by passing a fraction of the total coolant (the purge flow) directly over the cartridges and into a fission product clean-up system. Even with such a fission product clean-up system, it has been accepted from the outset that the primary coolant circuit would be active.

A diagrammatic arrangement of the reactor is shown in Figure 1. The development of the design has been described in a previous paper [1] whilst details of progress are given in the Project Annual Reports [2]. In this paper the major steps in the development of the fuel cartridge are described with particular reference to coated particle fuel.

2. THE FUEL ELEMENTS

In the design of the core, efforts have been made to avoid those problems which were considered to restrict the development of conventional gas cooled reactors. To this end, all parasitic material has, where possible been avoided and the fuel elements have been designed so that the whole core, including the graphite moderator is replaceable on each fuel change. The core (Figs. 2 and 3) consists of 37 fuel elements each of which comprises 7 fuel tubes of low permeability graphite, joined at the top by a metal reinforced graphite block and at the bottom by a stainless steel assembly which serves to route the fission product purge flow to the fission product clean-up system (Fig. 4). Each tube has a bore $1\frac{3}{4}$" in diameter, 5' in length into which the fuel cartridges are inserted. This design, which will be used for the initial charge, is appropriate for fuel which is expected to release a significant proportion of its fission products. With the satisfactory accomplishment of the development of fission product retaining fuel, such a fuel element would be inappropriate and it is inevitable that major changes will be incorporated when such fuels have been proven.

From the outset, it was appreciated that the problem of retaining fission products within the fuel element required major technical developments, and the whole philosophy of the design of the reactor experiment has been based on a fission product emitting system involving an active primary circuit coupled with a fission product delay system.

Although this principle has been adhered to, the advantages of having a retaining fuel element were obvious, and soon after the initiation of the Design Study thoughts were directed towards the methods which seemed likely to produce satisfactory fission product retention. Of the various methods considered the coated particle seemed the most appropriate method of approach and some experimental work was carried out on pyrolytic carbon coatings at A.E.R.E., Harwell.

As the detailed design developed the necessity for effecting some fission product control within the fuel element itself became apparent, and a cartridge comprising annular fuel inserts of uranium and thorium dicarbides dispersed in graphite, and sealed in a fuel box of ultra low permeability graphite, was recommended for the initial charge of the reactor: in addition, a delay trap of active charcoal was incorporated into the bottom of each fuel rod. This system has been developed to the production stage.

Earlier proposals concerning the fuel loading of the core have assumed a homogeneous loading. However, recent physics calculations have indicated the necessity of using a two zone core in which the thorium is concentrated in the centre zone. In the case of coated particle fuel it seems unlikely that an unalloyed fully enriched fissile particle could withstand a burn-up (fissions per initial fissile atom - F.I.F.A.) of the order of 30-50%, and it is therefore necessary to employ a diluent for the fuel in the outer zone; for this, zirconium has been chosen. At the present time an atomic ratio of Th/U-235 of 15/1 is recommended for the inner zone, whilst for the outer zone the Zr/U-235 ratio is 8/1.

3. COATED PARTICLE FUEL

During 1960 experimental information concerning the fission product control circuit emphasised the desirability of providing fuel with the maximum degree of retention possible for the first charge. In any case, in such a novel system it seemed the right philosophy to start off with the primary circuit having as low an activity as possible, so as to reduce the load on the fission product plant, and to minimise maintenance problems of the primary circuit which will inevitably arise during the initial stages of operation of the reactor experiment. It was therefore decided to mount a major research and development programme to ascertain the possibility of employing coated particle fuel for the initial charges. The object of this work was:

(a) To develop the optimum process for producing a fission product retaining insert.

(b) The development of "Pilot Plant" production apparatus.

(c) The testing of the resultant products for their fission product retention characteristics.

At that time facilities available within the Project were fully occupied with the development of the "Fuel Box" cartridge and all work associated with this programme was carried out in signatory countries under research and development contracts. The work on particles has been concentrated in Austria at Metallwerk-Plansee (Reutte, Tyrol) and S.G.A.E., (Seibersdorf, Vienna) and also at the C.E.N., Mol, in Belgium; work on coating has been carried out at the Royal Aircraft Establishment, Farnborough, England. Since the commissioning early this year of the Dragon Fuel Element laboratories development work has been carried out by Project staff at Winfrith.

3.1 The Fuel Particle

In Austria the work was directed initially to solving the problems associated with the fabrication of uranium dicarbide and thorium/uranium dicarbide. However, during 1961 it became apparent that the method under development (involving fabrication of the massive dicarbide followed by comminution and sizing) was running into serious difficulties in that it was not possible to obtain adequate yields bearing in mind the nature of the materials involved. It was decided therefore, following an overall assessment of the situation, that the powder metallurgy agglomeration process as developed at C.E.N., Mol, for oxide fuels [3] should be studied as an alternative.

Initially, experiments were carried out with uranium dicarbide to see what general modifications were required to the methods previously employed for oxide fuel. Experiments showed that some modifications were in fact necessary and the appropriate techniques to fabricate spherical particles in the "green" state were defined: these particles can be sintered to provide a range of porosity. Because of the encouraging results obtained, this process has been chosen for the development of production equipment. It is capable of giving very high efficiencies without complicated recycling: furthermore, its inherent flexibility to produce any composition of fuel is a most important factor in its favour. Preliminary experiments employing this method for the fabrication of the Zr/UO have been successful.

Early work on the fission product retention of carbon coated fuel particles had shown that one of the essentials for good retention was that the fuel particles should be spherical. It was not known, however, if this improved retention was due to the better geometry of a sphere (from the point of view of the coating as a pressure vessel) or if it was associated with the fact that the spherical particles tested had been melted. It is still not clear whether the high burn-up retention characteristics will favour the porous or the high density particle. The powder metallurgy agglomeration process enables both types to be fabricated side by side.

Work on the equilibrium of the thorium-uranium-carbon system has shown that the dicarbide is not stable at temperatures below 1550°C it does, in fact, break down into the monocarbide (or possibly the sesquicarbide) and carbon.

This reaction is accompanied by an increase in volume and it is therefore possible that the coating of fuel particles made by melting (and therefore in the dicarbide form), could be ruptured as sufficient decomposition takes place at the operating temperature - accelerated by the irradiation - to provide the necessary expansion. Although this mechanism is not necessarily responsible for the poor retention characteristics of certain batches of fuel, it is certainly a possible explanation of the observed effects, and suggests experiments on fuel made from the truly stable components. Such experiments are in hand.

Two methods of melting such agglomerates have been studied:

(a) A three-phase arc system employing hydrogen in the feed to give an extended plasma and

(b) a specially-developed plasma torch.

The work on the three-phase arc system has been carried out at S.G.A.E., Seibersdorf, whilst the plasma arc method has been developed within the Project at Winfrith.

Work within the Project has been directed towards evaluating the various processes as well as producing specimens for irradiation tests. Having considered the alternatives, the following steps are proposed for the development of prototype production apparatus:

(a) Thorium/Uranium fuel

(i) A mixture of uranium metal powder and carbon is reacted at 1500°C to form the dicarbide.

(ii) After grinding to -37 microns the uranium dicarbide powder, together with the appropriate quantities of thorium metal powder and carbon powder is mixed with a binder (e.g. camphor) and a solvent (e.g. isopropyl-alcohol) to form a cake.

(iii) Agglomerates of the required size are prepared from this cake by granulation through a sieve.

(iv) If porous particles are required, these green agglomerates can be spheroidised by tumbling in a rotating cylinder, the inside of which is covered with a fine abrasive.

(v) The resultant spheroids are sintered to form the equilibrium phase having the desired porosity.

(vi) If melted spheres are required.

(vii) The particles are melted either by passing through a plasma jet or through a 3-phase arc.

(b) Zirconium/Uranium fuel

(i) Zirconium metal powder, uranium metal powder and carbon powder (to form the monocarbide) are mixed in the atomic ratio, Zr/U:3/1. After compacting, the mixture is reacted at 1200°C to form a solid solution monocarbide master alloy.

(ii) After grinding, the zirconium/uranium monocarbide is mixed with additional zirconium metal powder and carbon powder to give the desired composition.

(iii) This mixture is treated in the same way as the thorium/uranium dicarbide agglomerates to produce spherical particles. Precise details of the sintering procedure are presently being evaluated.

Whilst the precise particle size is still to be determined, present work is based on a diameter of 300 ± 50 microns.

3.2 Coating

The work on coating has been divided as follows:

(a) Laboratory scale work, for investigating the major parameters involved in the coating process and for the preparation of irradiation specimens, and

(b) Production equipment for working on the kilogramme scale.

Laboratory Scale Work

Considerable experience existed at the R.A.E. Farnborough on the deposition of pyrolytic carbon and other refractory coatings, and following the successful application of fluidising techniques for coating fuel particles by J. H. Oxley and his co-workers at the Batelle Memorial Institute, Columbus, Ohio, a fluidising system capable of operating continuously at temperatures up to 2250°C was developed at the R.A.E. by R. L. Bickerdike and R. H. Ranson.

Exploratory work was carried out using perspex models to determine the optimum conditions for fluidisation. Particular attention was paid to the design of the nozzle assembly to enable satisfactory coatings to be laid down at the higher temperatures without carbon deposition at the orifice. For working with thorium dicarbide as well as with fully enriched uranium, it was considered desirable to build the whole equipment to normal laboratory vacuum standards since this greatly facilitated problems associated with the handling of thorium dicarbide.

Furthermore, such a system offers significant advantages in relation to the problems of "accounting and safety."

The graphite resistance furnace is water-cooled and can be evacuated to a pressure of 10^{-4} torr. A design has been standardised and is shown in Figs 5, 6 and 7. A number of such units have been constructed and are operating satisfactorily at Winfrith and at other contractors' laboratories. The important characteristics of this equipment are given below:

Fluidising vessel	1" dia. x 15" long
Total gas throughput	2 l/min.
Capacity	20 cc. particles
Pressure drop through nozzle and bed	1 psi.
Furnace	Graphite resistance - single phase 30 KVA.
Maximum temperature	2250°C
Length of hot zone	18"

The coating furnace is evacuated and flushed with purified argon before each run to ensure freedom from atmospheric contamination. Particles are charged into the hot furnace after the flow of carrier gas and hydro-carbon has been established. When the fluidising operation is complete, discharge is effected through the nozzle system, it being unnecessary to dismantle the bed in any way. In the case of silicon carbide coatings, the hydro-carbon is replaced by hydrogen, saturated (at room temperature) with methyltrichlorosilane.

A programme of research and development has been carried out at the R.A.E. Farnborough and within the Project laboratories on the deposition of pyrolytic carbon coatings from propane, methane and hexane at different concentrations and at different temperatures. This work [4] has shown that it is possible to obtain particles with coatings of different density and having different structures. At high concentrations (i.e. high rates of deposition) the coatings have an onion skin appearance, whilst at low concentrations (i.e. low rates of deposition) a columnar structure is observed. With intermediate conditions the coatings are generally referred to as "structureless" since no obvious structure can be seen on metallographic examination of the unetched section. The relationship between the density, temperature of deposition, flow rate and deposition rate, using methane as a source of carbon, is shown in Table I.

TABLE I

Densities of Carbon Deposits on Uranium Dicarbide Particles

Bed Temperature °C	Methane Flow Rate cc/min.	Mean Deposition Rate cm/sec.	Density g/cc
1450	375	5.5×10^{-7}	1.83
1600	100	5.5×10^{-7}	1.46
"	200	1.2×10^{-6}	1.37
"	375	2.2×10^{-6}	1.36
1800	375	2.2×10^{-6}	1.61
2000	100	5.9×10^{-7}	2.14
"	200	1.1×10^{-6}	2.07
"	400	2.9×10^{-6}	1.90

Preliminary results on the evaluation of these particles, involving neutron activation followed by out of pile heating to determine the release of fission products, by J. S. Stubbs at A.E.R.E., Harwell showed that some factor not directly associated with a diffusion phenomenon, was influencing the results. An investigation of this phenomenon showed that there was a significant uranium contamination at the surface of the coating. Following the introduction of an alpha counting technique, it was observed that such contamination was always present when the coating temperature was in excess of 1500°C and it was concluded that a complex mechanism resulting in uranium migration was operative above this temperature.

Since the fuel will operate at temperatures in excess of 1500°C, it is essential that the coating should be produced at a higher temperature in order to avoid failure due to the difference of expansion between fuel and coating. The above fact, together with the experimental results on diffusion of barium through carbon coatings, directed attention towards alternative diffusion barriers such as silicon carbide and zirconium carbide, and work on these composite coatings is now in progress. Exploratory results on the evaluation of pyro-carbon/silicon carbide/pyro-carbon composite coatings are now becoming available and it appears that such coatings offer significant resistance to fuel migration and fission product diffusion.

However, it will not be until the results of "purged capsule" irradiation experiments are available that the effectiveness of this type of coating will be proven.

According to our present knowledge, the following procedure is recommended:-

Stage	Thickness	Deposition Temp.	Coating Agent
1	10-15 microns	1350°C	Hexane
2	30 "	1800°C	Methyltrichloro-silane in hydrogen
3	30 "	1800°C	Hexane
	Total 70		

Representative micrographs of such duplex coatings are shown in Figs.8, 9 and 10.

Prototype Production Apparatus

Following work at Metallwerk Plansee, a prototype fluidising apparatus has been developed in the Project laboratories employing the general principles of the laboratory model. Safety considerations, in particular criticality, restrict the capacity of each unit to 1 kg of fuel particles. With such a system, three units, each capable of independent operation would be required to maintain the rate of production necessary for fabricating two fuel elements per week.

A perspective view of the prototype, which has recently been commissioned is shown in Fig. 11 . The fluidising reactor, having a capacity of about 750 cc, is constructed of graphite, with an internal diameter of 2" and an angle of the conical base of 60°. This fluidising reactor is fitted directly to a water cooled nozzle system as shown in Fig. 12. The centre nozzle, made of molybdenum, reaches into the cone base of the fluidising tube. It carries the hydro-carbon or silicon containing gas: the carrier gas enters through an annular gap surrounding the centre nozzle. Such a design has made it possible to prevent carbon deposition (in the case of carbon coatings) at the entry zone of the fluidising reactor, which would lead to serious blockage resulting in loss of fluidisation. The entry velocity of the carrier gas can be varied by moving the centre nozzle axially, relative to the fluidising reactor, by means of a micrometer adjustment. Heating is accomplished by a specially developed 3-phase resistance furnace, the heater tube being split from the bottom into three segments; the current is fed into the bottom of each segment by means of a water cooled clamping device the top end of the heater acting as the neutral starpoint.

The effective hot zone of the furnace is 20"; it has an almost uniform temperature distribution within ± 50°C. Carbonised cotton wool is used for thermal insulation. This prototype furnace which consumes about 25 kW has been operated up to 2250°C.

The particle charging apparatus and the gas exhaust system are situated on top of the furnace. The particles are fed through a molybdenum tube into the pre-heated furnace and can be discharged at an elevated temperature through the water cooled nozzle system. The exhaust gases are passed through a filter system consisting of eight exchangeable filter units packed with silica fibre. By this means it is possible to retain active dust and excess carbon within the furnace. Furthermore, they can be easily checked for uranium contamination after each run.

The whole apparatus is made to vacuum standards and the top and bottom assemblies will be enclosed in glove boxes, purged with nitrogen. This is not only a safety requirement necessary for fissile material accounting, but it avoids exposing the furnace to atmospheric contamination during charge and discharge.

The particle movement of this system was investigated (at room temperature) using transparent perspex models. By appropriate adjustment of the entry velocity of the carrier gas, either a boiling bed or a spouting bed can be produced when using 300 micron diameter particles. The adjustment for boiling conditions is somewhat critical since a slight change of gas throughput induces a tendency to slugging when the bed is charged to its full capacity. However, spouting conditions can be achieved easily with a charge of 1 kg. together with good vertical mixing of the particles. It is important to appreciate that it is difficult to predict the operating conditions of such a system since the precise temperature conditions within the fluidising vessel are difficult to assess. Final operating conditions must therefore await operational experience with the prototype. The total gas throughput is expected to be of the order of 10-20 litres per minute.

The operation of this apparatus involves, apart from charge and discharge, a complex procedure of flow and temperature control, particularly when working on composite coatings. To this end, development of such an automatic system has proceeded at Metallwerk-Plansee and it is intended to employ such automatic control on the production apparatus.

4. CONSOLIDATION

Because of the desirability of avoiding excessive fuel temperatures attention has been given to reducing the maximum temperature at which the coated particle fuel will operate.

To this end, the fuel cartridge has been designed to give maximum heat flow to the inner wall of the fuel tube, and the fuel has been concentrated in as narrow an annulus as possible to reduce the centre temperature. A photograph of the current conception of fuel cartidge is shown in Fig. 13. Each cartridge of nominal length 2", diameter $1\frac{3}{4}$" has a central hole of approximately 1" in diameter. The six longitudinal channels at the outer circumference carry the fission product purge flow between the cartridge and the inner surface of the fuel tube. The chamfer at one end obviates the need to align the grooves during assembly. Because of the required high concentration of fuel particles, a consolidation process developed at R.A.E. Farnborough, has been adopted for the initial production fuel elements.

In this process reactor grade petroleum coke, previously micronised to less than 50 microns and graphitised, is coated with 12-14% by weight of phenolic resin; it is then crushed and sized. Micronised and graphitised coke was found to have a higher bulk density than a range of other graphite powders: furthermore, graphitised material is desirable from the point of view of stability under irradiation. The prepared powder is mixed with coated particles in the required proportion, with a small addition of paraffin. The mixture is pressed at low pressure (10-250 psi.) to avoid possible damage to the particle, the resin being polymerised at a low temperature (180°C) whilst the pressure is maintained. A typical die for this application is shown in Fig. 14.

After removing the compact from the die, it is heated to 900°C in a stream of nitrogen carrier gas, saturated with benzene vapour at 50°C or with hexane, at room temperature. In this operation the resin is carbonised and pyrocarbon deposited into the pores of the matrix. As the pores become smaller, the temperature, and hence the rate of deposition, are successively reduced. Finally the fuel cartridge is heat treated to remove occluded hydrogen.

Carbonisation of the resin has been found to cause a uniform and consistent shrinkage of 0.5%; this must be allowed for in the dimensions of the die. The gas cracking operation using benzene vapour in a nitrogen carrier gas increases the matrix density from 1.4 g/cc "as pressed", to between 1.6 and 1.8 g/cc, depending on the time and temperature of treatment. The surface finish of the cartridge is good and no machining operation is necessary. Final heat treatment results in a very small contraction of about 0.005%.

Fig. 15 shows radiographs of a fuel cartridge containing 93% enriched uranium dicarbide fuel particles coated with pyrolytic carbon. The coated particles can be seen to be uniformly dispersed.

No results are yet available on the integrity, under operational conditions, of the full size cartridges, however, specimens consolidated by this process and irradiated at temperatures between 1000°C and 1750°C have remained intact and shown only the contractions expected of such a material.

5. ACKNOWLEDGMENTS

Acknowledgment is made to the Chief Executive, Dragon Project (Mr. C. A. Rennie) for permission to publish this paper. In addition, the authors wish to thank all those people associated with the Dragon Project, who have contributed towards this programme.

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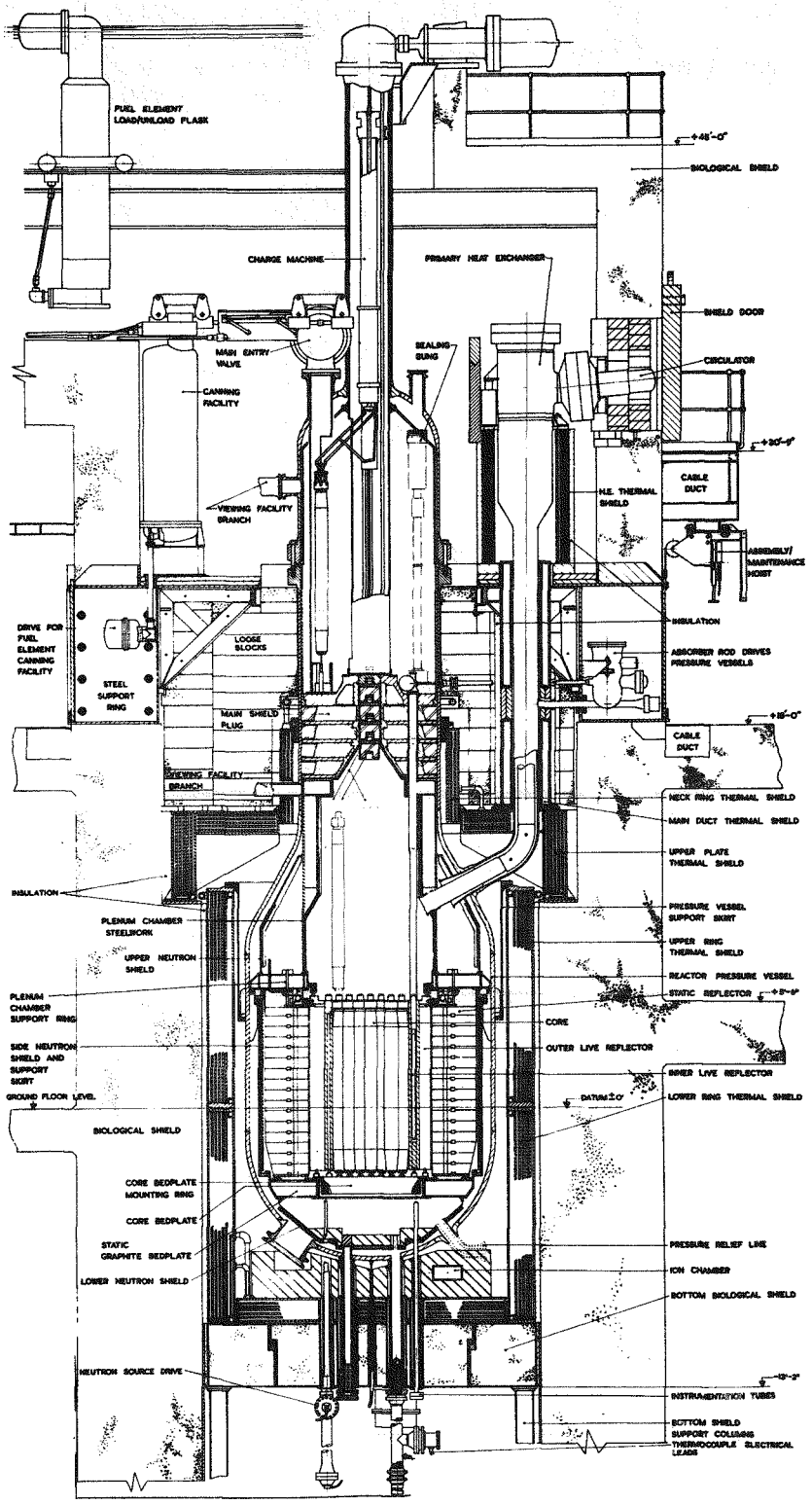


Fig. 1. DRAGON REACTOR EXPERIMENT DIAGRAMMATIC ARRANGEMENT OF REACTOR

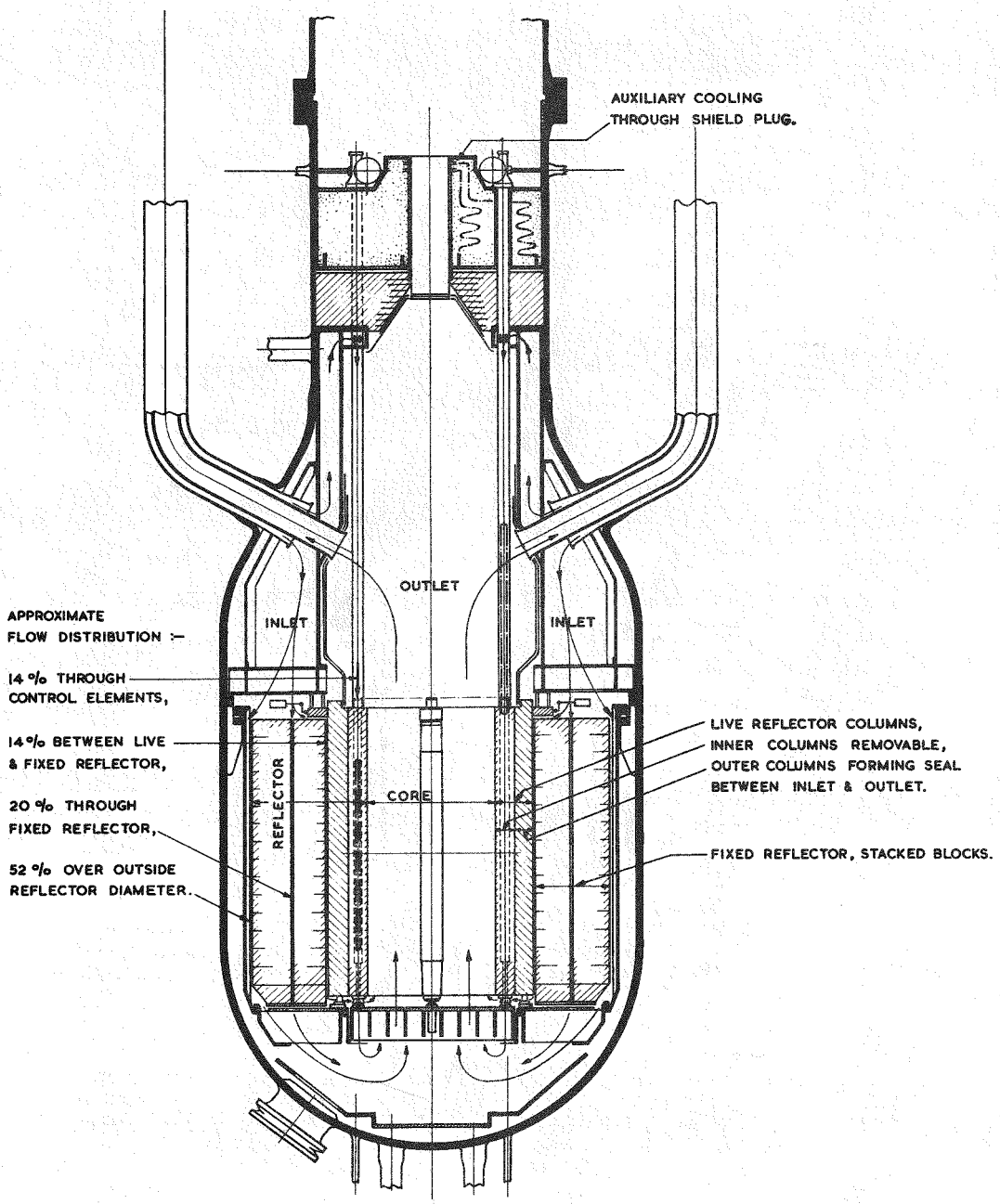


FIG. 2 SECTIONAL DIAGRAM OF REACTOR

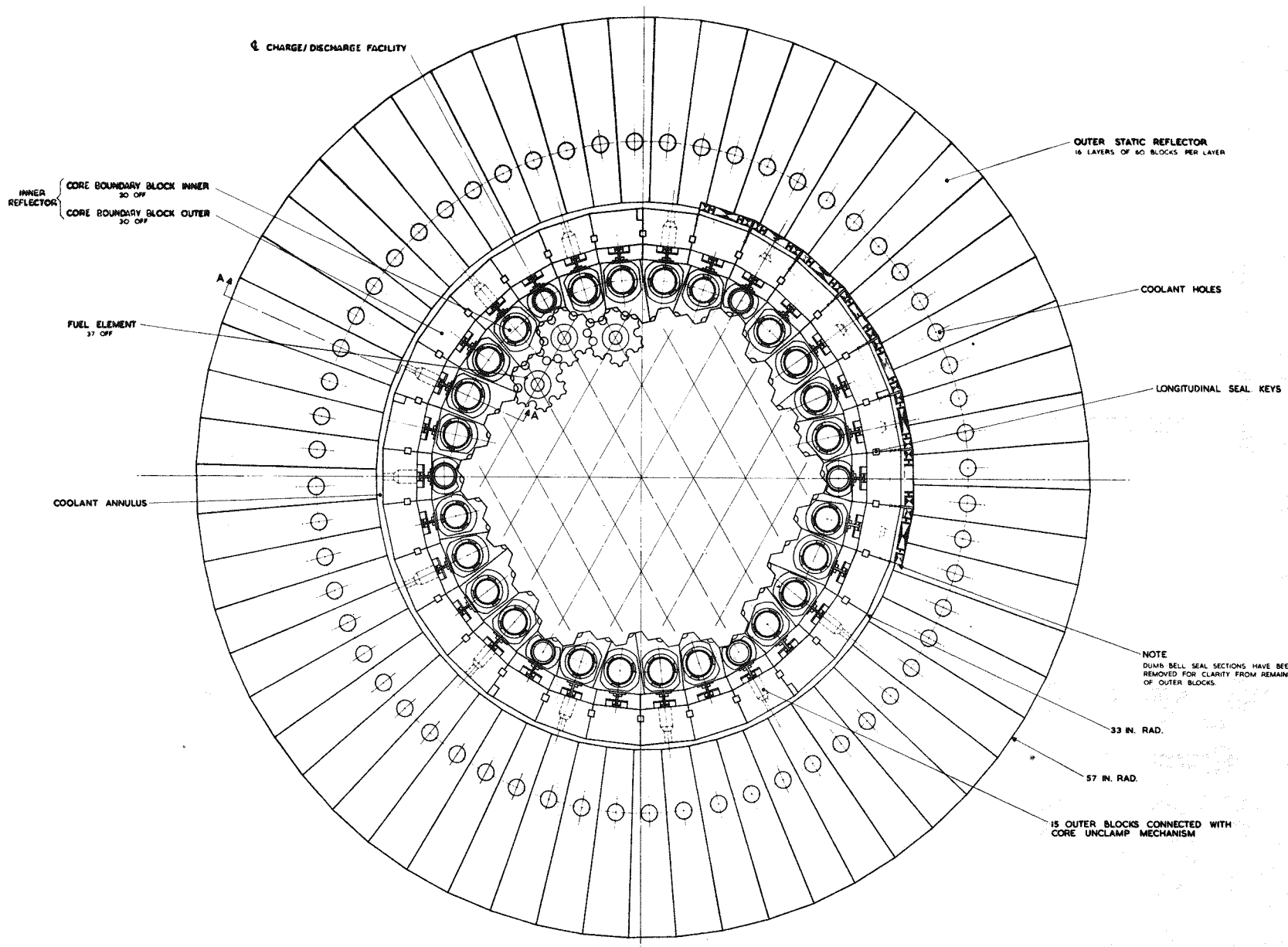


Fig. 3. PLAN VIEW OF CORE AND REFLECTOR

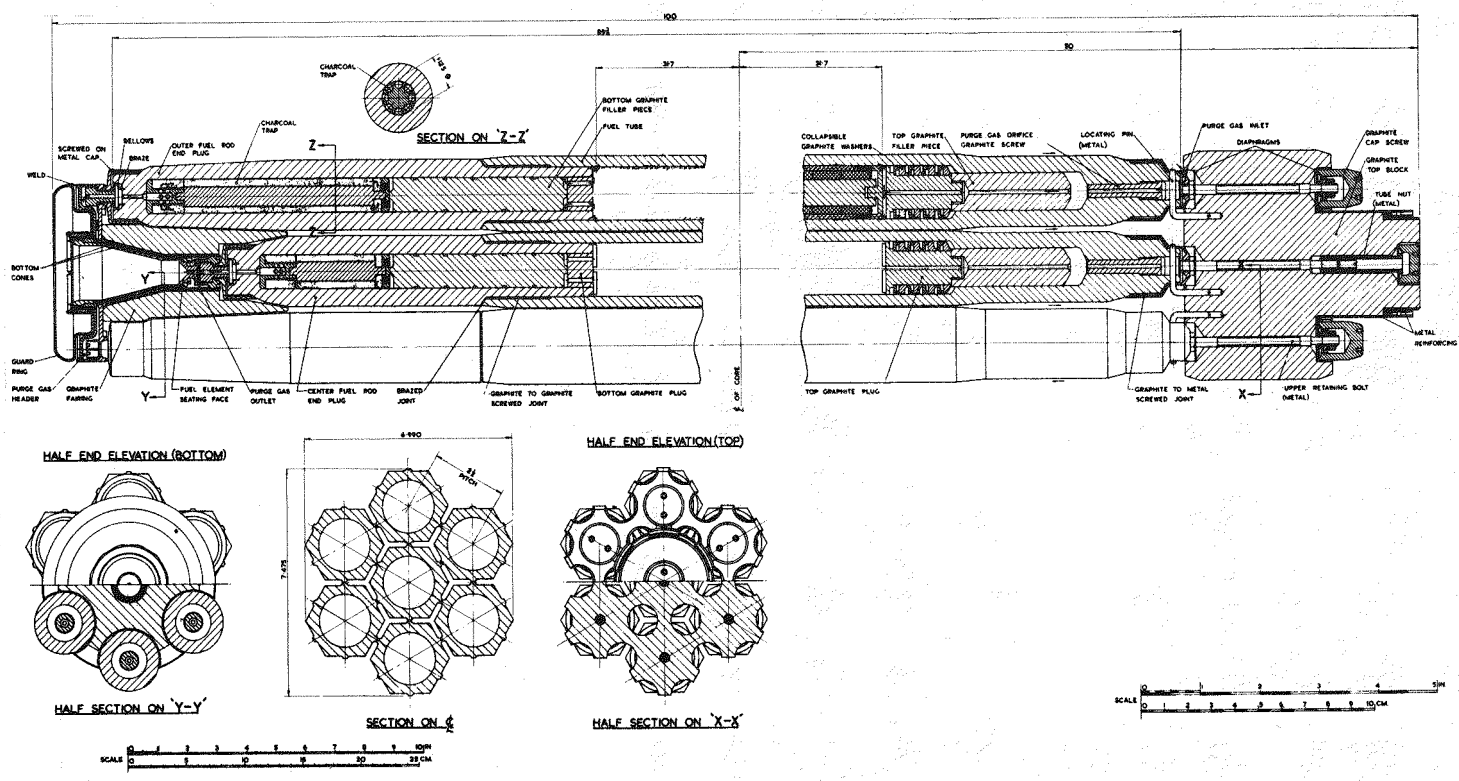


Fig. 4. DRAGON FUEL ELEMENT ASSEMBLY MARK IX

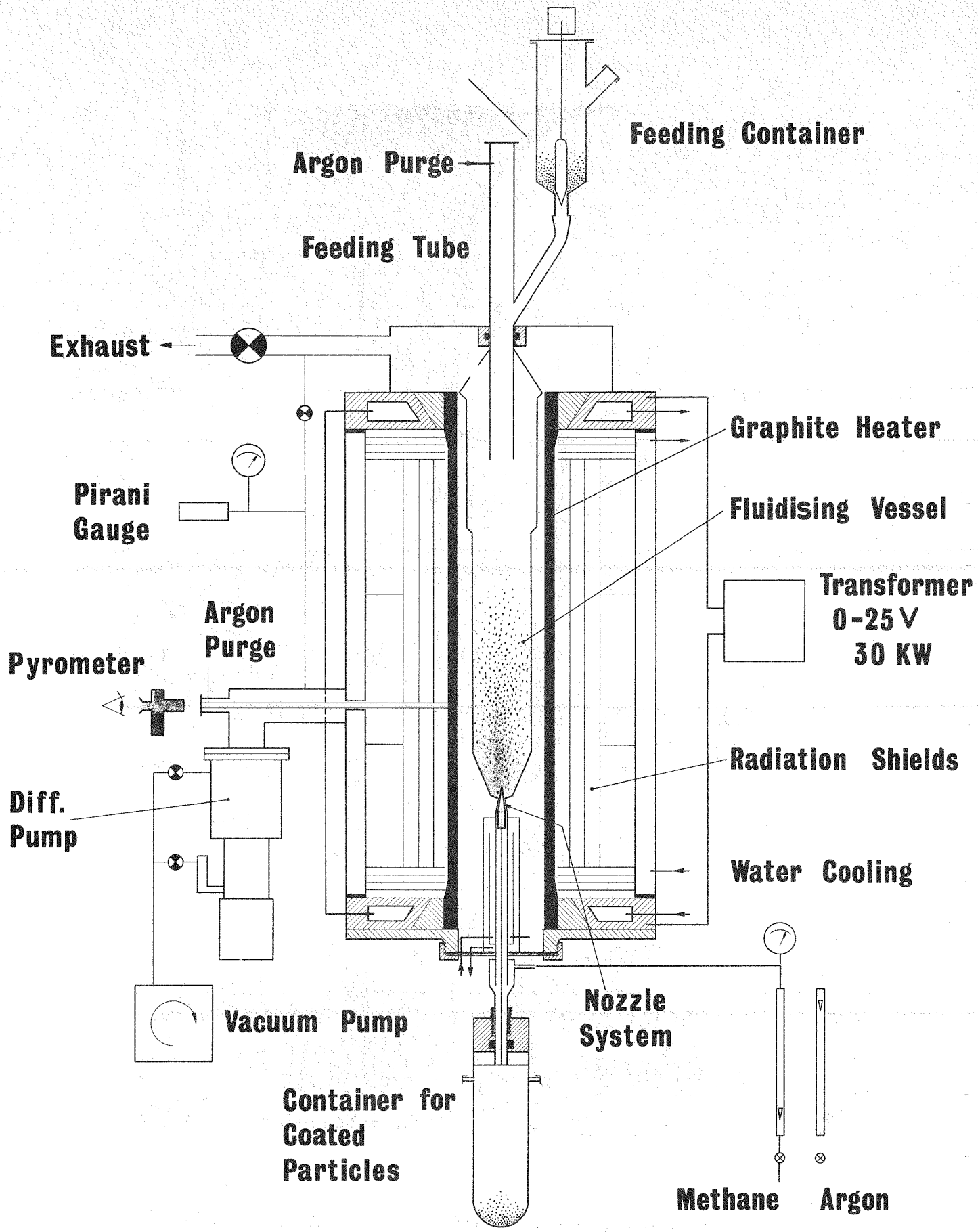


FIG. 5 SCHEMATIC DIAGRAM OF LABORATORY SCALE FLUIDISING FURNACE.

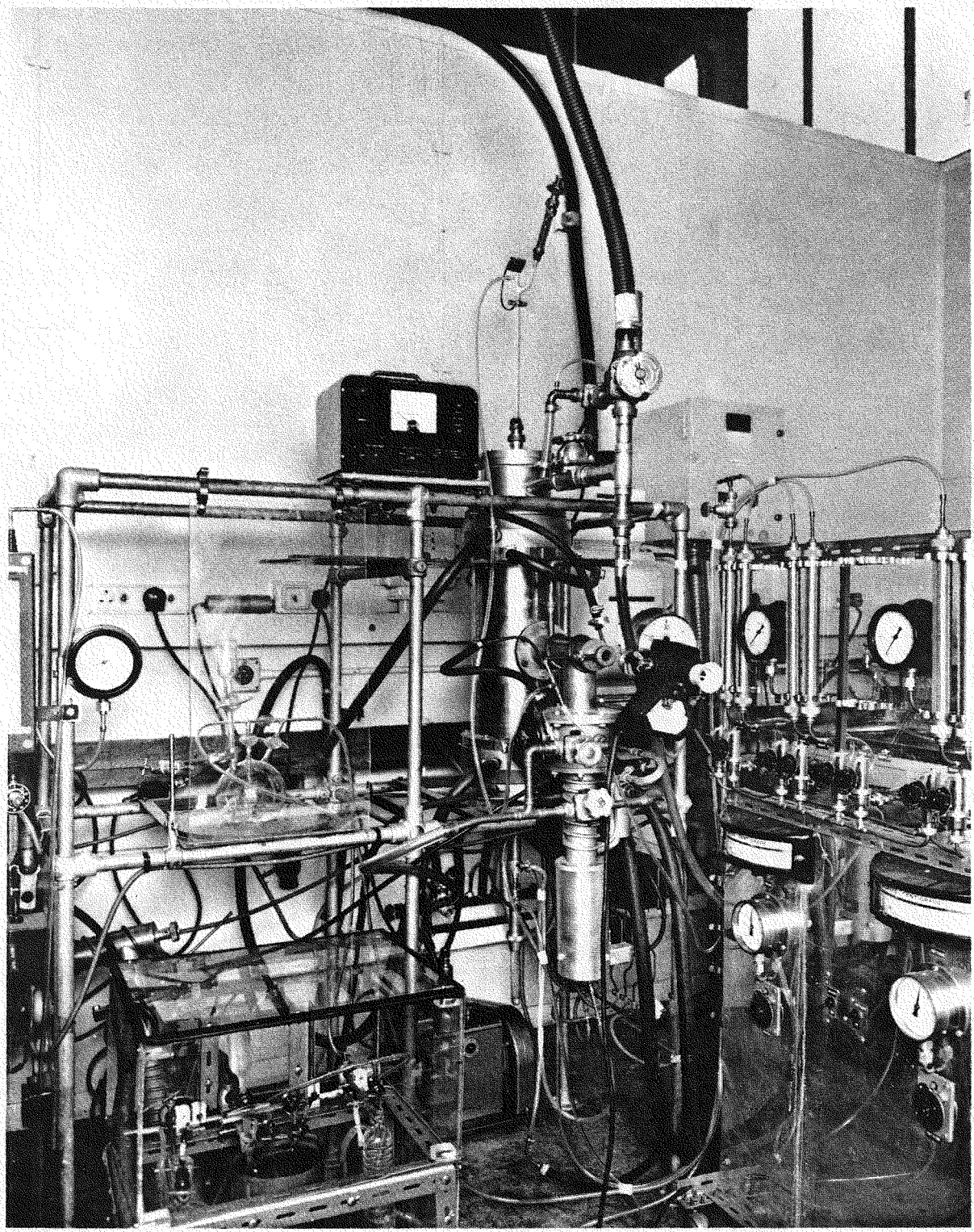


Fig. 6. LABORATORY SCALE FLUIDISING EQUIPMENT SHOWING FURNACE ASSEMBLY AND GAS PURIFICATION AND CONTROL PANEL

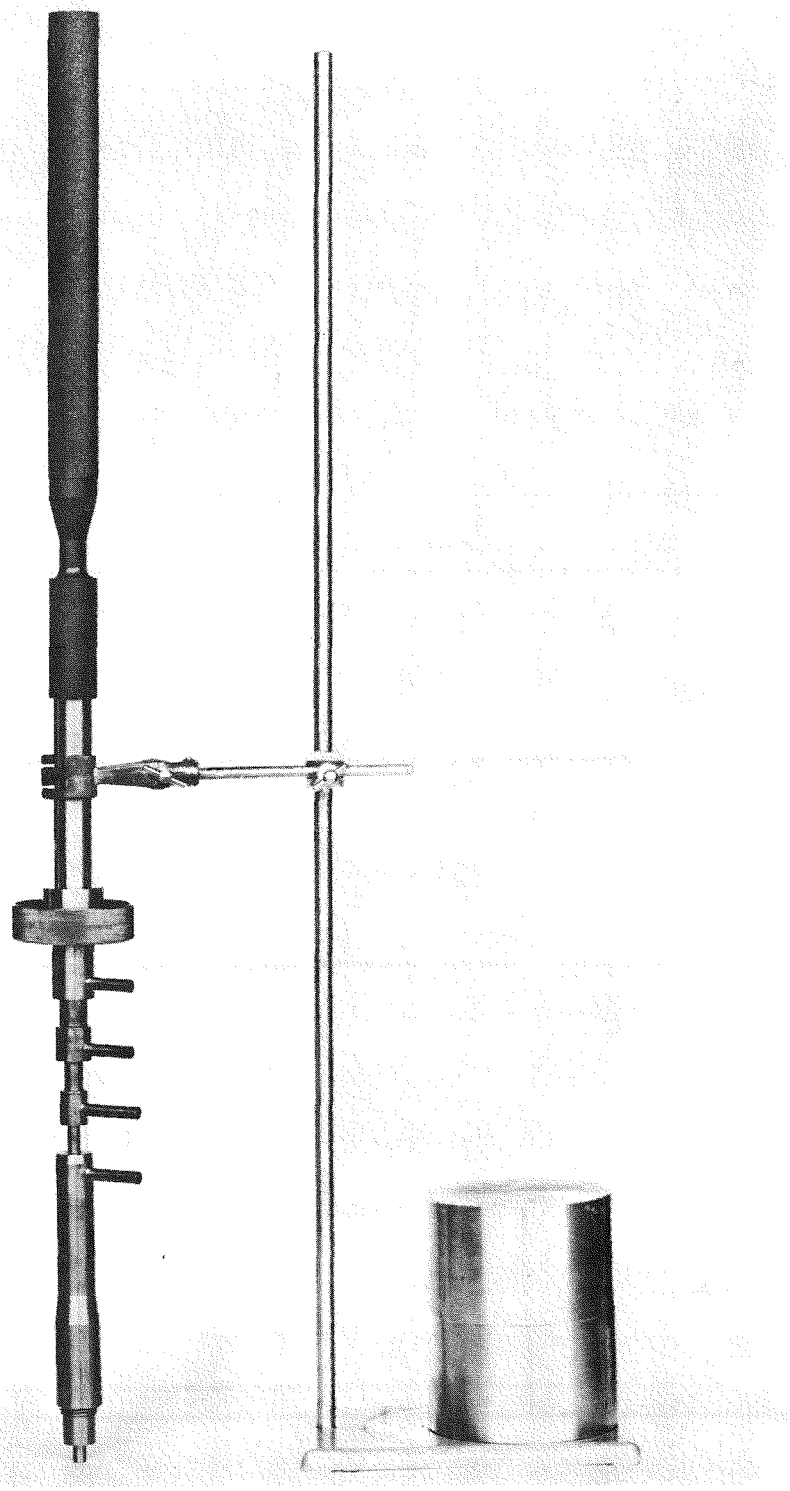


Fig. 7. WATER COOLED NOZZLE AND 1 INCH FLUIDISING REACTOR

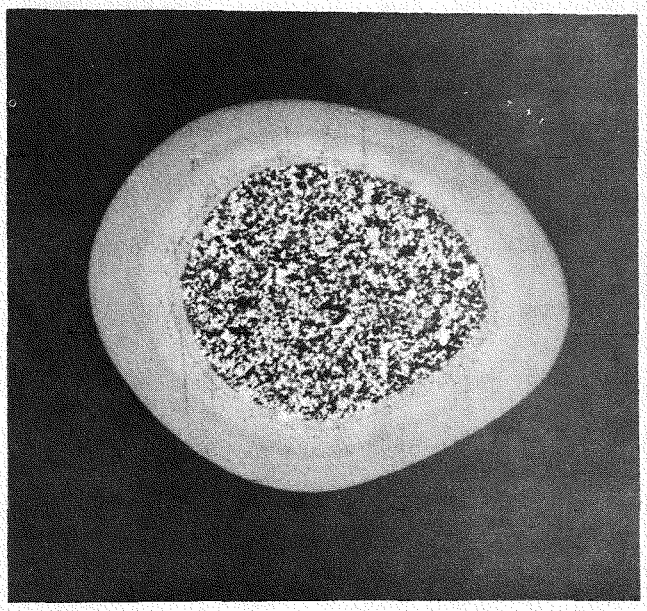


Fig. 8. SECTION OF 93% ENRICHED URANIUM DICARBIDE SINTERED PARTICLE 200 x 175μ DIAMETER COATED WITH TWO LAYERS OF PYROLYTIC CARBON

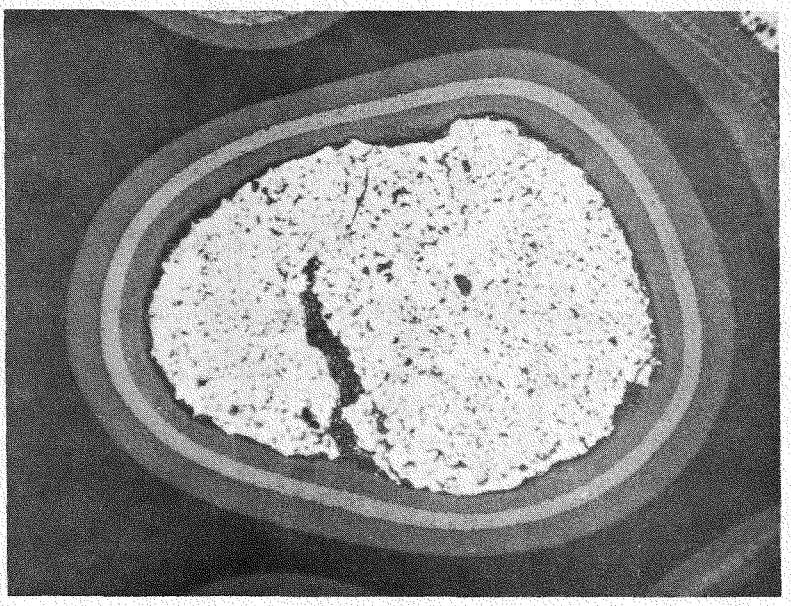


Fig. 9. SECTION OF URANIUM - THORIUM DICARBIDE SINTERED PARTICLE, COATED WITH PYROLYTIC CARBON, SILICON CARBIDE AND PYROLYTIC CARBON

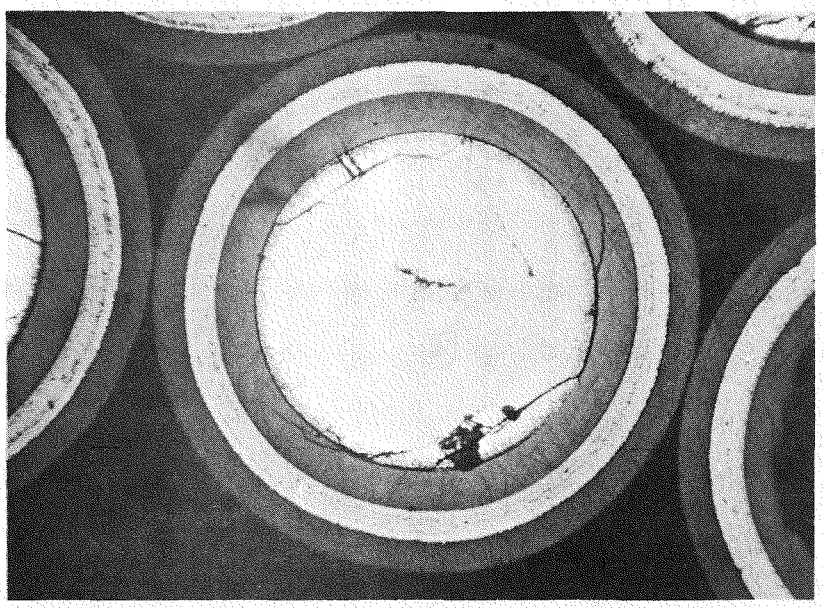


Fig. 10. SECTION OF URANIUM - THORIUM DICARBIDE MELTED PARTICLE, COATED WITH PYROLYTIC CARBON, SILICON CARBIDE AND PYROLYTIC CARBON. THERMALLY CYCLED.

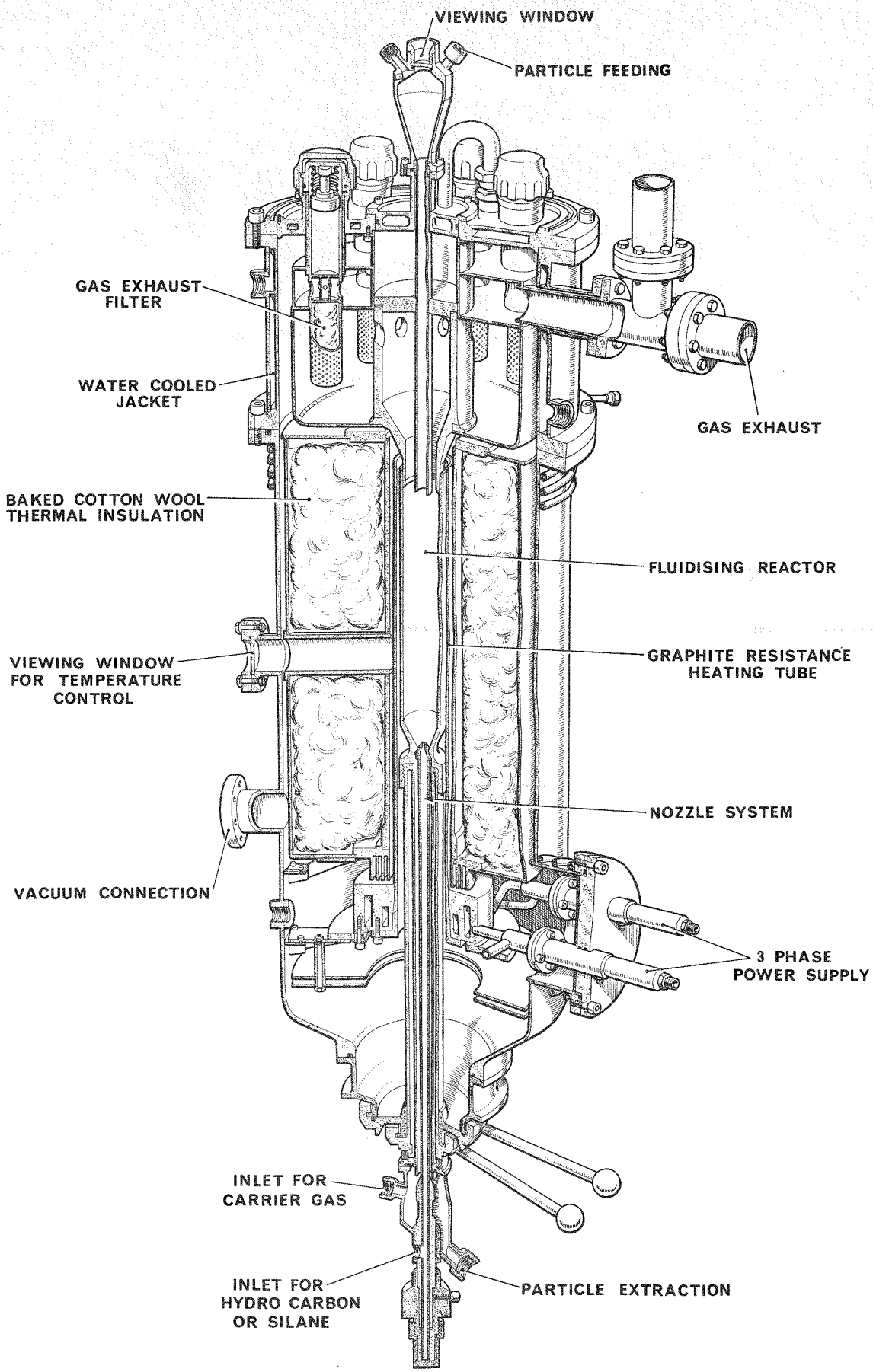


FIGURE 11 PROTOTYPE PRODUCTION SCALE FLUIDISED BED

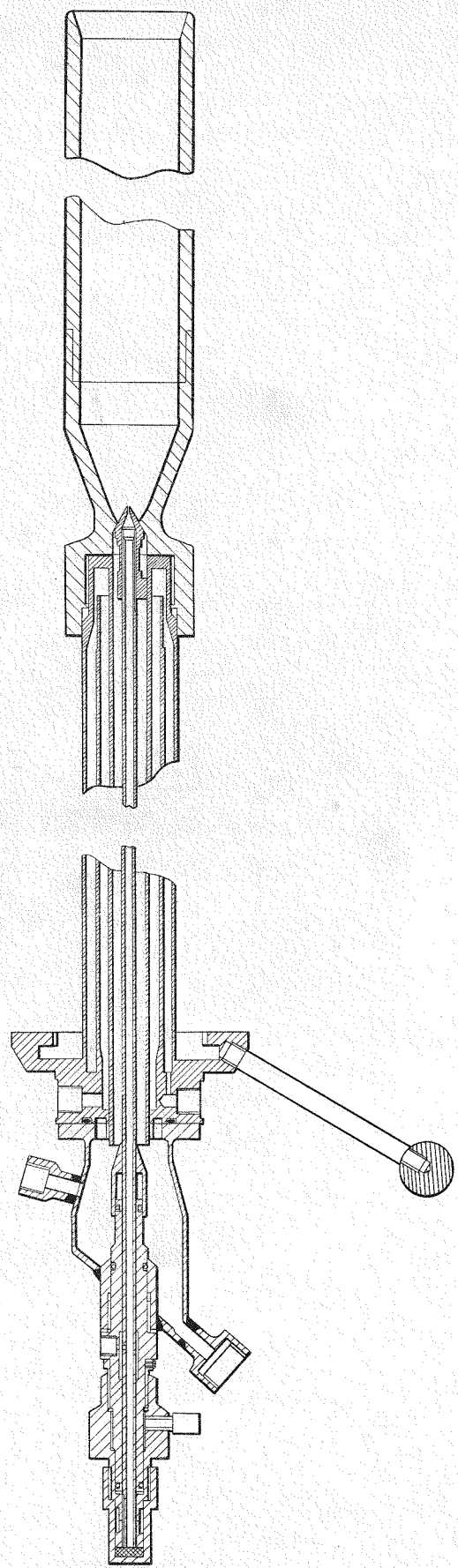


FIGURE 12 SECTION OF NOZZLE SYSTEM AND FLUIDISING REACTOR FOR PROTOTYPE PRODUCTION SCALE FLUIDISED BED

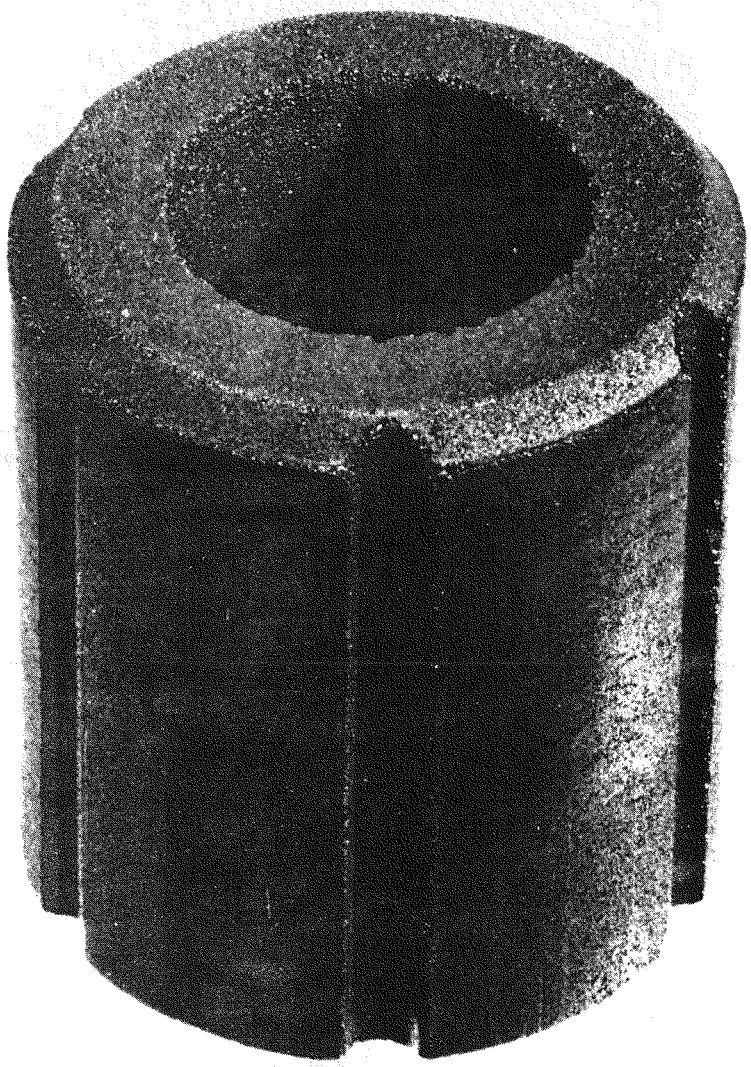


Fig. 13. CURRENT CONCEPTION OF FUEL CARTRIDGE

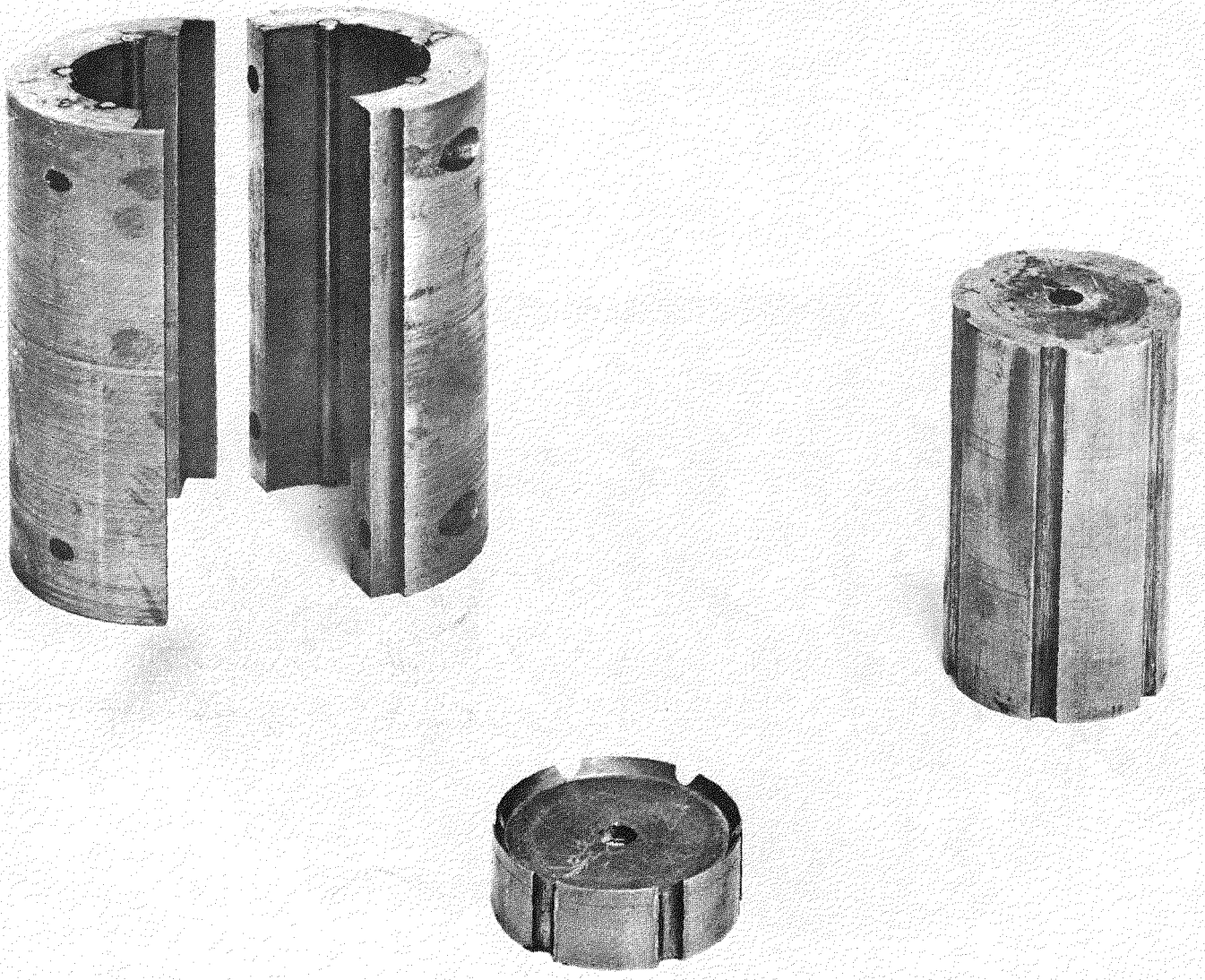
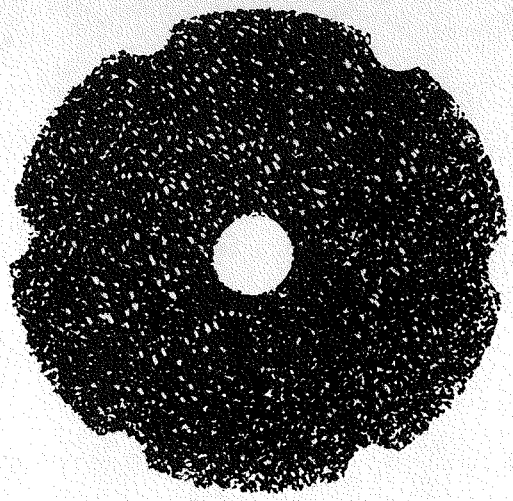


Fig. 14. TYPICAL DIE FOR WARM PRESSING OF FUEL CARTRIDGES



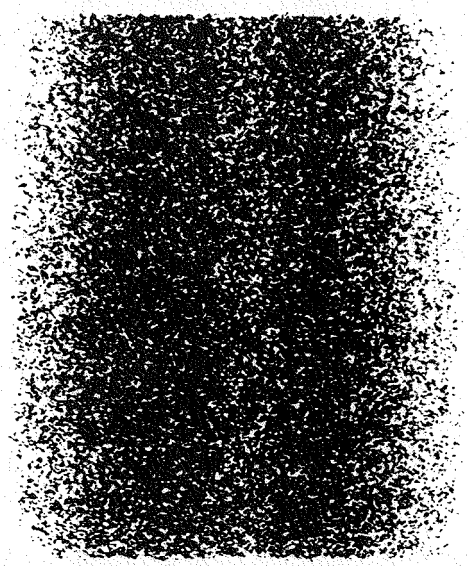


Fig. 15. RADIOGRAPHS OF FUEL CARTRIDGE SHOWING UNIFORM DISPERSION OF FUEL PARTICLES