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PROGRAM OF CHEMICAL RESEARCH ON ORGANIC MODERATORS AND COOLANTS IN REGARD WITH THE PROJECT OF THE SPANISH DON-REACTOR

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I N D E X

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1. INTRODUCTION

Within the project of the 30 MW electrical power (102 MW thermal power) Reactor, moderated by heavy water and organic cooled, which is being developed by the Junta de Energia Nuclear (Spain), the Chemistry Division undertakes the study of the chemical problems in connection with these coolants. The selection of the most convenient mixtures among those commercially available is included. The number of titulated personnel connected with the program is sixteen, with the adecuated number of technicians, corresponding to the Sections of Chemical Research, Analytical Chemistry and Radiochemistry of the Division of Chemistry.

Although the supply of these organic coolants by the national industry should be the ideal, there is no limitations regarding the use of mixtures of foreign origin, like those already known in the markets of U. S. A. and Europe.

In any case the use of organic coolants has to be based on data of radiation and thermal stability and of certain physical constants, which determination can be a part of this program.

A rigorous analytical control of the organic coolants including the organic composition, the inorganic impurities from the initial contamination or from corrosion, the evolution gases and the polymer fraction is specially considered within this program.

División de Química

The necessity to keep the contents of polymers under a certain value to be able to operate in the pile justifies the studies on polymerization inhibitors and some technological aspects of the purification.

The experiences of thermal and radiolytic stability and of putification, the analytical control, the determination of physical constants and the selection of mixtures able to be used as organic coolants are the points included in the present program, which are described in detail in the following chapters.

2. PYROLYTIC TESTS

2.1 Static tests

Static experiences of pyrolytic stability of commercial and synthetic mixtures of polyphenyls are being developed in order to check or to obtain the following points :

a) Upper temperature limit for thermal stability.

b) Gaseous evolution and polymerization velocity at a fixed temperature as a function of the heating time, with the analytical characterization of the derivatives.

c) Study of some interesting technological aspects, such as the influence of water, considered as an impurity of the polyphenyls, in the pyrolysis, the catalytic action of metal surfaces, etc.

The following experimental technique is being used : samples of polyphenyl mixtures (5-10 gm) are sealed into Pyrex breakseal ampoules under vacuum (about 10^{-5} mm Hg). These ampoules are enclosed in steel containers which are standing in an aluminium block (fig. 1), the whole assembly being heated in a furnace (fig. 2 at temperatures between 350 °C - - 480 °C controlled within $\pm$ 3 °C, and at variable time intervals. After the pyrolytic treatment, the ampoules are welded to a vacuum line equiped with a Toepler pump (fig. 3). Then the septum of every ampoule is broken by means of an iron breaker, and the evolved gases are determined on the conventional gas-line by measurement of the pressure of a known gas volume; the gases, previously fractionated at -196 °C, - 80 °C and 0 °C are analized by mass-spectrometry. The liquid fraction, containing benzene, toluene and other volatile derivatives, is separated by distillation, and the high boiling residue is determined by vacuum sublimation methods.

2.2 Dynamic tests

We are designing an "out of pile tests loop" in order to perform the following experiences :

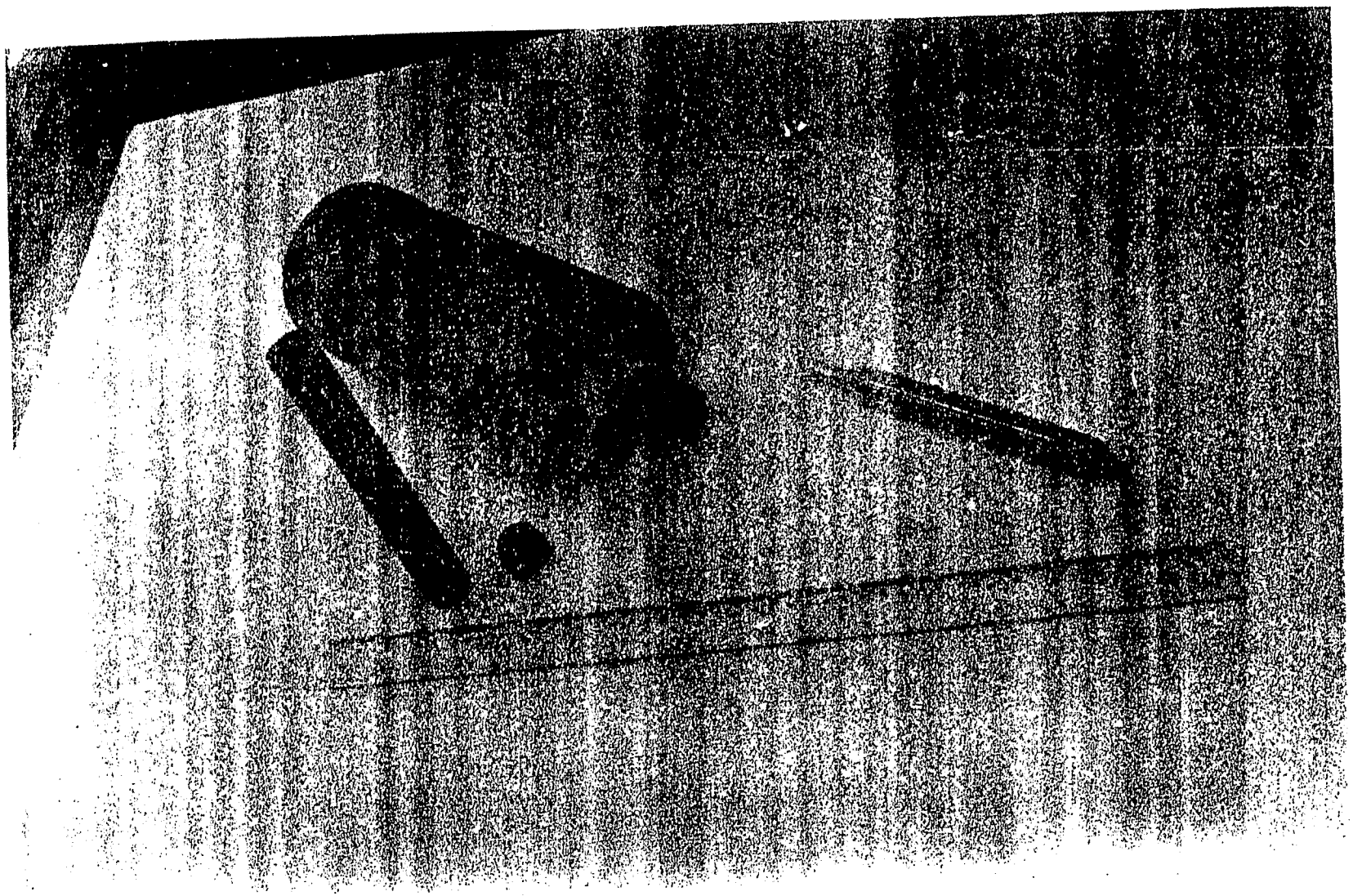

Fig. 2. - Furnace for pyrolysis experiments

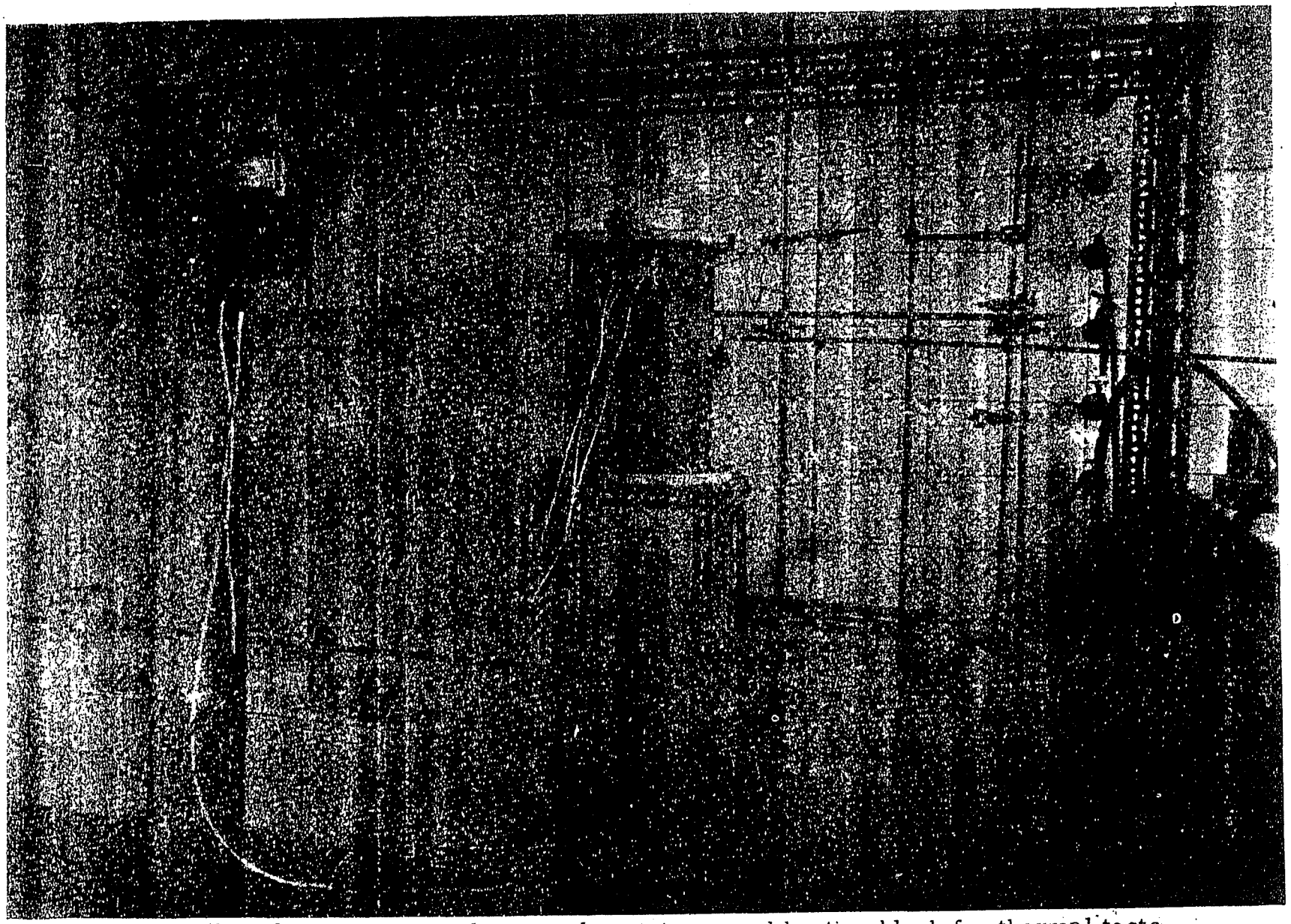

Fig. 1. - Pyrex capsules, steel containers and heating block for thermal tests.

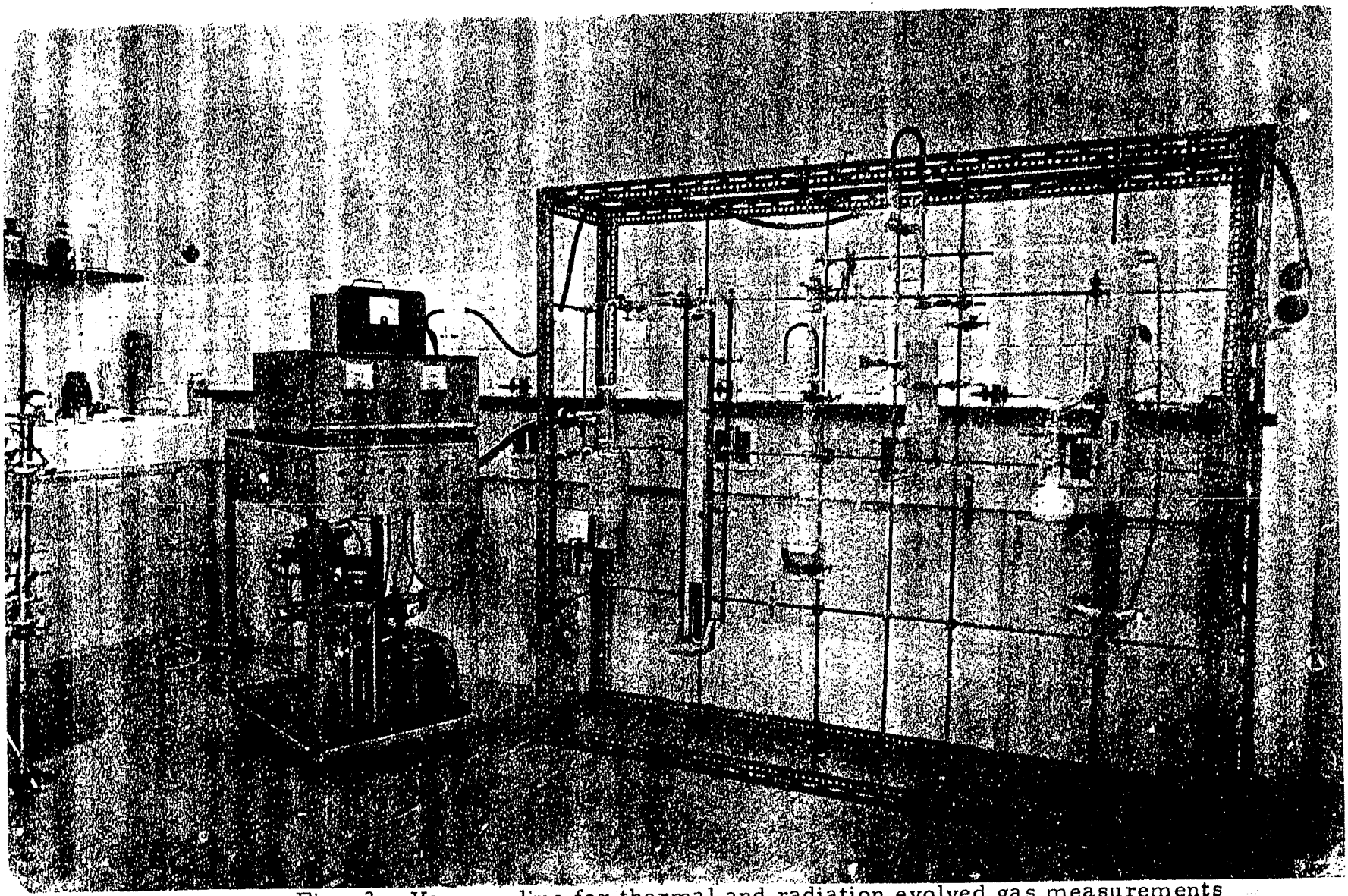

Fig. 3. - Vacuum-line for thermal and radiation evolved gas measurements

a) Pyrolytic stability of organic coolants under tests.

b) The study of the components of the mechanic assembly, such as circulating pump, valves, connecting gaskets, control equipment, etc.

c) Study of the deposits of polymerization residues on the hot metallic surfaces, under work conditions estimated in the reactor project.

d) Optionally groups of the Metallurgical Division as well as the Engineering Division will assume the study of the correspondent problems related with corrosion and heat transfer.

The aforementioned loop is schematically represented in fig. 4

3. RADIOLYTIC TESTS

3.1 Static tests

Static irradiation tests are being accomplished in the JEN-1 Reactor (3 MW thermal power and 3×10^{13} maximum thermal neutron flux) in order to develop a general program on the action of inhibitors in the thermal and radiation polymerization of polyphenyls. The material being irradiated consists on synthetic or commercially available samples of Santowax-R with organic additives to be assayed as possible inhibitors. The samples are sealed in quartz tubes under vacuum, these ampoules being enclosed into aluminium cans containing pure cobalt samples to evaluate the integrated thermal neutron dose. An aluminium furnace is used to heat the material under irradiation up to 400 ^{o}C, the entire unit being placed near the reactor core by means of an aluminium tube anchored in the pool of the reactor. However, we are considering the possibilities of carrying out the irradiations in the reactor core self, in order to accumulate in the shortest time an integrated thermal neutron dose of about 10^{18} neutrons/cm^2; this is the minimum suitable dose to attain comparative results concerning the stability of polyphenyls with or without inhibitors.

On the irradiated samples, after stored to allow the short-lived activity to decay, measurements of gaseous evolution, and liquid and polymer separation will be effected, in accordance with the same technique, already described, for the static pyrolytic tests.

3.2 Dynamic tests

We consider the installation of a test-loop in the JEN-1 Reactor depending on the development of the pyrolytic experimental program in the out-of-pile loop as well as on the static radiolytic tests. The training and results to be attained in these experiments will help us to evaluate the feasibility, convenience and economical factors related to such an in-pile loop for organic coolant tests.

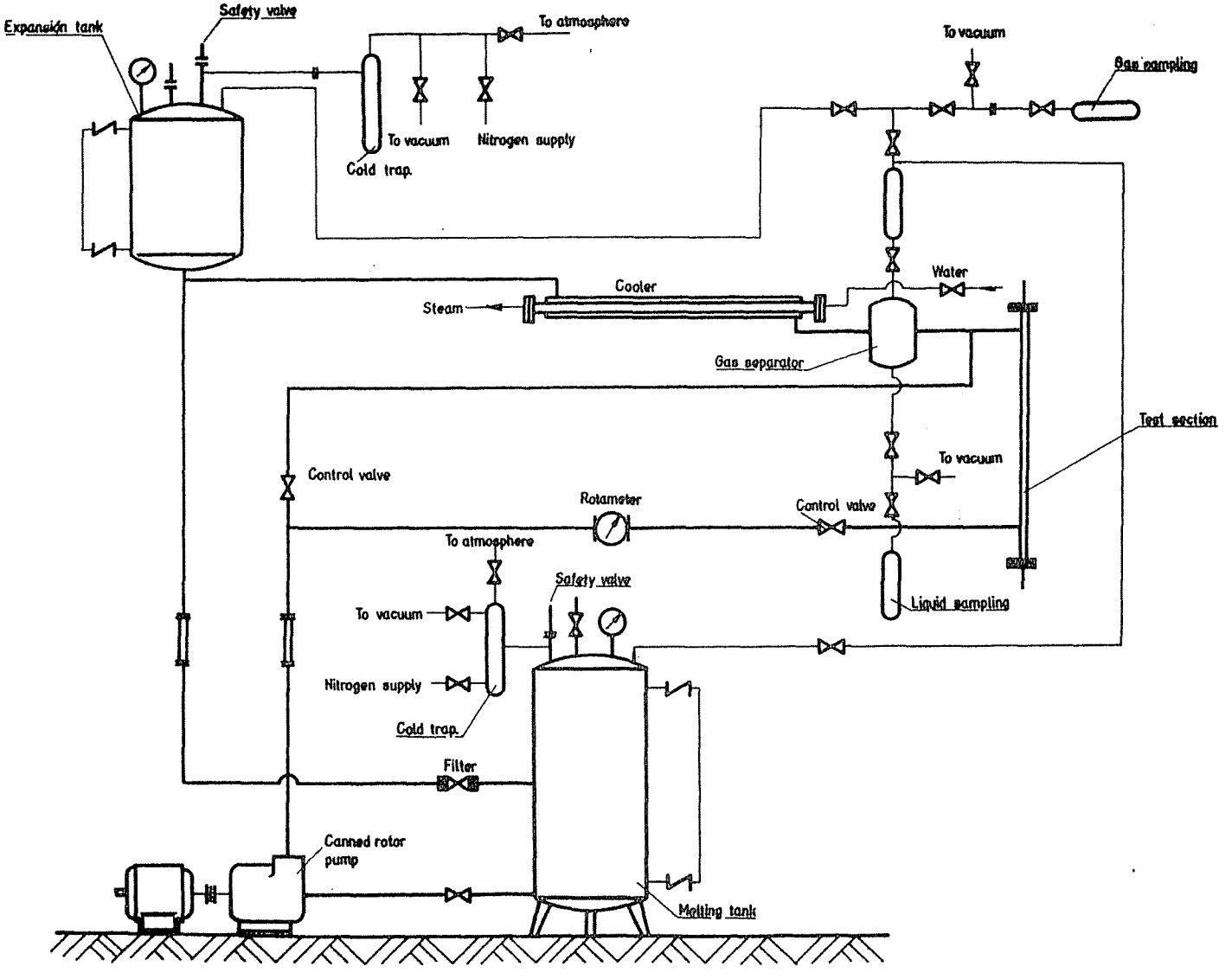

FIG.4.—OUT-OF-PILE TEST LOOP DIAGRAM.

4. ORGANIC COOLANT PURIFICATION

Up to the present moment, experiences of vacuum distillation of synthetic mixtures of polyphenyls have been carried out with an exclusive analytical characterization purpose.

On this basis a program of purification by vacuum distillation of any therphenyl coolant with a certain contents of polymers and degradation products has been initiated.

Fig. 5 shows a scheme of the glass distillation apparatus used. The still pot has a capacity of 10 liters and can be used up to 8 kg of polyphenyl mixtures. It has connected a tubular circuit to one of its sides, where the heating of the products is carried out. A capillary entrance for air keeps the movement of the materials in the circuit. This circuit is attached tangentially to the still pot, which produces a whirly movement of the material to be distillated when the fluid is circulating through the tubular circuit. These experiences of distillation, carried out by batch at a pressure of 20 mm Hg and at a rate of 2 kg/hour, have given satisfactory results.

Based on these experiments a new unit of vacuum distillation to keep a concentration of polymers constant in the dynamic experiences circuit is being designed.

The project of the final distillation unit for the DON Reactor of 30 MW will be based on the information gathered from these experiences.

5. RESEARCH ON POLYMER WASTES

The considerable amount of high boiling wastes, which periodically will have to be taken out from the DON Reactor (a total of about 200 Ton/year), has encouraged us to start studies on possible profits of such polymers. These studies will be carried out by the Research Section according to the following ways :

a) High boiling wastes combustion experiments and their application to the steam production necessary for auxiliar services of the reactor.

b) Organic coolant reclamation tests, applying catalytic hidrogenation cracking techniques to the polymer chains.

This second point will be obviously complemented by a vaste research program on the nature of the polymer mixtures, highly complex because of the variable number of phenyl rings and the isomeric arrangements of their components. The separation and identification of such high boiling compounds

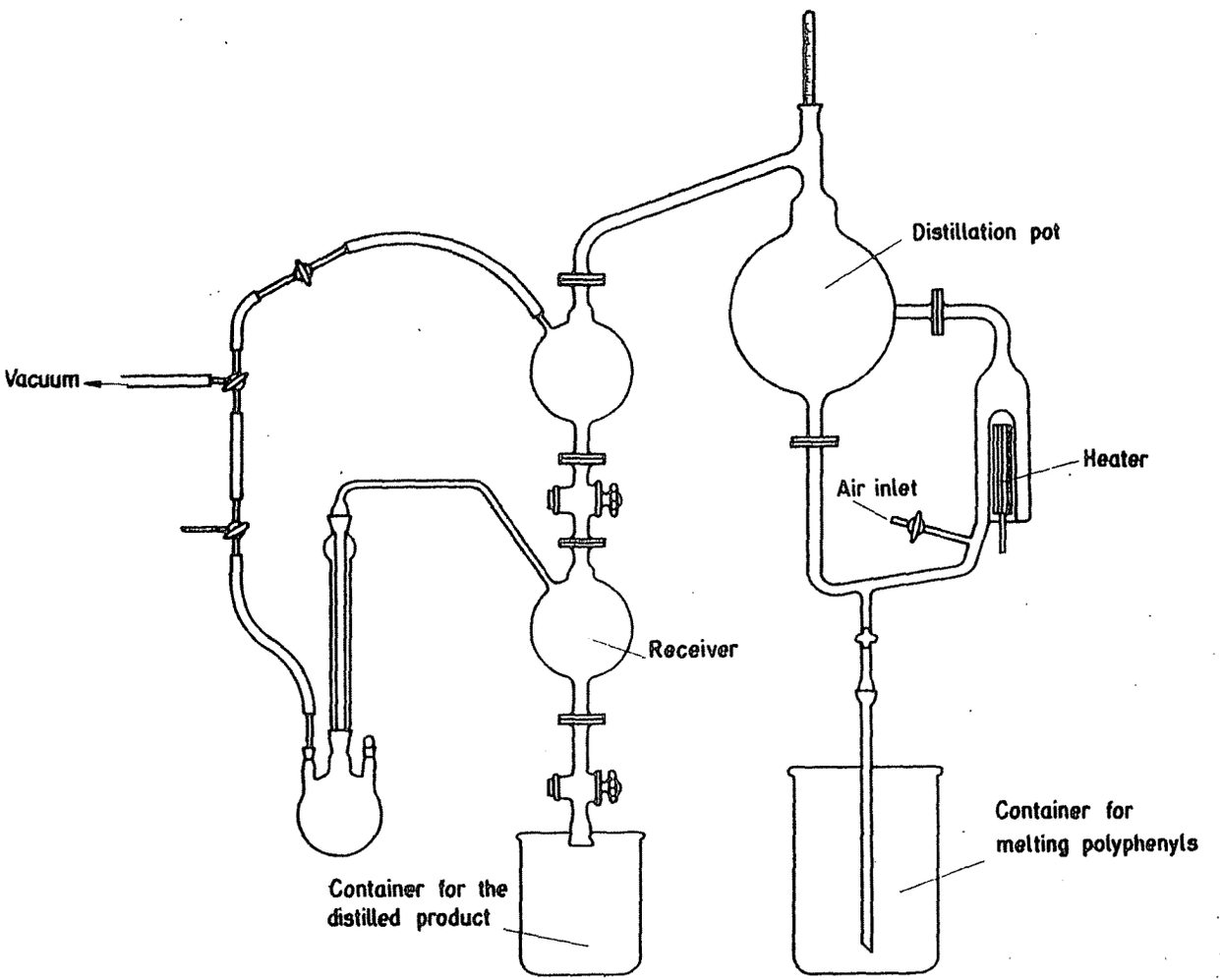

FIG. 5. – DISTILLATION APPARATUS

becomes a previous condition for the knowledge of the thermal and radiation polimerization mechanisms, to which the possible progress on the use of polimerization inhibitors and on the catalytic organic coolant reclamation are related.

6. PHYSICAL AND CHEMICAL CONTROL

6.1 Physical Properties Determination

On the mixtures to be studied the following physical properties will be measured, if possible in the most extreme conditions (i.e. up to 400 °C and 20 kg/cm^2) : those depending on the composition as melting, boiling and fire points and combustion heat; those depending on the polimerization percentage as well as on the temperature : specific gravity, hydrogen density, viscosity, specific heat, average molecular weights, etc.

This program has been partially initiated with the determination of viscosities, densities, melting characteristics and molecular weights.

A furnace is being built for the use of viscosimeters and dilatometers in the temperature range between 100 and 400 °C. It has been designed to have a good stabilization of the temperature, and has two automatically regulated heating circuits on the sides and a third circuit at the bottom, which can be regulated by means of a variac. Two quartz windows in the stainless steel body let observe the instruments placed inside. Fig. 6 shows a scheme of the vertical section of this furnace.

A capillary type viscosimeter and a two arms type dilatometer have been chosen. Both apparatus are connected to a nitrogen pressure system in order to reproduce the future working conditions. Besides, dilatometers with only an arm under an arm under an inert atmosphere, already described in the literature, have been reproduced.

6.2 Chemical control

The analytical control of the polyphenyl mixtures will be directed to check the purity of the commercial materials and the composition of the thermal and radiation damaged samples.

6.21 Organic composition : Organic analysis of polyphenyl mixtures have been carried out by us following several techniques such as vacuum fractionating distillation, vacuum sublimation, chromatography on alumina colums, paper chromatography, ultraviolet and visible spectrophotometry, and polarography. A description of the results obtained in our research is done in other paper presented at this meeting.

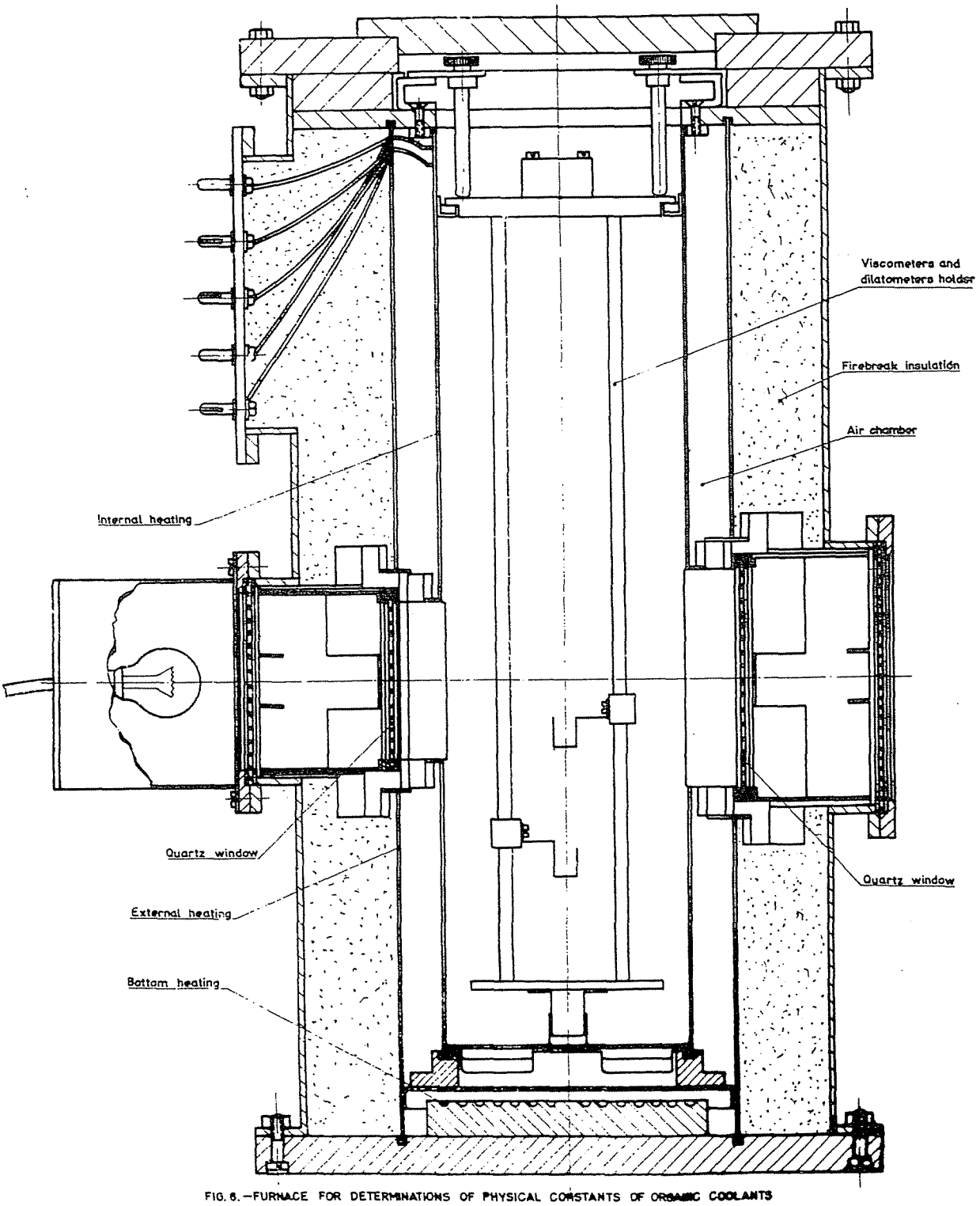

FIG. 6.—FURNACE FOR DETERMINATIONS OF PHYSICAL CONSTANTS OF ORGANIC COOLANTS

This work will be completed with the use of gas chromatography and infrared spectrophotometry techniques.

6.22 Inorganic impurities determination : Water contents is determined by the well-known Fisher method, being modified to render it suitable to the present problem. The other inorganic impurities in the polyphenyl coolants are being determined by spectrographic and activation methods.

A) Spectrographic method

Samples are prepared by eliminating the organic material previously, either by reduced pressure distillation or by mineralization techniques. Then the inorganic residue is dissolved in an acid medium, preferently HCl. A spark technique with copper electrodes is being used for the determination of the following elements : Al, As, B, Ca, Cd, Cr, Fe, La, Mg, Mn, Ni, Pb, Si, Sn and Te.

Apparatus : An automatic, Littrow Type, Hilger Large Quartz Spectrograph, equiped with a JACC-Varisource. Spec-pure copper electrodes from "Johnson Matthey". A special chamber for evaporating the standard and problem solution on the electrodes.

The comparision between both the standard and the sample plates is done visually by means of a double field spectrum comparator. Molibdenum is used as an internal standard for quantitative analysis.

The sensitivity reached for several elements is shown in the following Table :

Element	Sensitivity	Element	Sensitivity
Al	0.1 µg/ml	Mg	0.1 µg/ml
As	0 "	Mn	0.1 "
B	0.3 "	Ni	0.3 "
Ca	0.1 "	Pb	0.3 "
Cd	0.1 "	Si	0.1 "
Cr	0.1 "	Sn	0.3 "
Fe	0.1 "	Te	3 "
La	0.3 "		

B) Activation analysis

In a first stage, which is now under development, we are studying and working out procedures for the activation determination of impurities in polyphenyl samples. Taking into account the present irradiation possibilities offered by the JEN-1 Reactor and the theoretical sensitivity values of the activation method, the following elements have been selected : sodium, phosphorus, sulphur, chlorine, manganese, copper and zinc; all of them have been already qualitatively characterized by activation on samples of polyphenyls. Other interesting elements will not be assayed by activation because the sensitivity for them is equal or less than the sensitivity offered by other analytical techniques employed in the Chemistry Division.

The polyphenyl samples and standards are irradiated in polyethylene capsules which are grouped in water tight irradiation cans made of polyethylene or aluminium tubing.

In some cases (chlorine, phosphorus and sulphur) a destruction of organic matter is made on the irradiated samples; the destruction is carried out by alcaline and oxidyzing techniques with a Parr bomb. In the remaining cases most of the organic matter is eliminated by vacuum sublimation. The non-sublimable residue is fire-ashed; use is thus made of the fact that metallic elements do not occur in polyphenyls as a part of the molecule.

After elimination of the organic matter, a separation and purification of the radioactive isotope is done; for this purpose, the common techniques of radiochemical analysis are used. Finally, the activity of the radiochemically pure isotope thus separated is compared with the activity of a suitable standard simultaneously irradiated; if the chemical separation yield is taken into account, a quantitative determination of the element in the polyphenyl sample can be made.