

EUR 2762 e

ANNEX

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

INFLUENCE OF IRRADIATION ON
ADMISSIBLE WATER IN LEAKAGE IN H.T.G.C.R.

by

L.J. VALETTE

1967



Work performed at the
Dragon Project, Winfrith - England

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(This report has been presented as "These Annex" of the Report EUR 2762 e)

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In a high temperature gas cooled reactor of the DRAGON type, the temperature dependence of the radiolytically induced graphite oxidation is such that for one specified admissible local attack the water leakage can be increased.

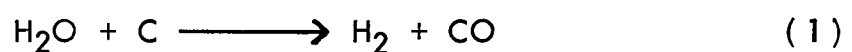
1. Introduction

In a high temperature gas cooled reactor, with prismatic fuel element, the graphite will be operating at temperature ranging between 500°C and 1.100°C. The maximum admissible concentration of oxidising impurities, is for one specified maximum local attack of the graphite dictated by the hottest point of the fuel element surface, on the other hand the steady state concentration of the oxidising impurities and their reaction products with graphite in a degassed primary circuit depends on the leakage rate of impurities, the rate of gas purification, the rate of reaction of the oxidising impurities in the core and the rate of regeneration of these impurities by carbon deposition in the heat exchangers. It can be shown that for one maximum temperature of the fuel element, the admissible water leakage can be increased, all other parameters being kept constant, if the temperature dependence (activation energy) of the oxidation rate is reduced. [1] Finally it will be shown that the radiation in the core influences the graphite reaction rate in a way as to decrease its temperature dependence. [2]

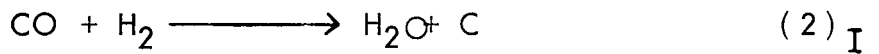
2. Steady state concentration of impurities in the primary circuit

The following simplifying hypotheses are used for establishment of the equations of the steady state equilibrium concentration:

- a) in a thoroughly degassed circuit the only possible inleaking impurity is water from a failed heat exchanger
- b) a steady flow passes through the purification plant and the purification process is 100 % efficient
- c) the reactions which take place are the following ones and they are first order;
in the core



in the heat exchangers



We assume, in fact, that the carbon deposition occurs as the reverse of the water gas reaction and that the primary reaction products of H_2O and C are CO and H_2 , and they are present in equal concentration in the core. Experimental evidence show that the reaction (2) is proportional to the C_{CO} and C_{H_2} concentrations [3] and we will then use the concentration of H_2 as being representative of both the concentration of CO and H_2 . It is worth noting here that if, in fact, the carbon deposition occurs by the reverse of the Boudouard reaction a similar discussion with similar conclusion can be used at the expense of a more equations.

For the assessment of the impurity level in the circuit more quantitative informations are required on the sources and sinks of impurities in the circuit.

2.1 The water leakage acts as a source of the oxidising impurity. Although it is technologically possible to build perfectly leaktight heat exchangers, nobody can at this stage guarantee that they will operate without failure for 20 years. The reactor operation should be acceptable with small steam leakage which would be cured at the normal reactor shut-down. We assume then that a leak of W mole / s H_2O is established in the heat exchangers

2.2 The purification plant acts as a sink for all the impurities H_2O , H_2 and CO . The rate of purification although not theoretically limited should be kept as small as possible for economical reasons.

Let us assume a steady purification flow of q cm³ / s.

2.3 The integrated corrosion in the core acts as a sink for the oxidising impurity H_2O and as a source for the CO and H_2 .

The integrated corrosion in the core depends on the water concentration, the local graphite reactivity, the temperature distribution in the core and the available surface for reaction.

The integrated reaction along one coolant channel of perimeter Pe (cm) and length L (cm) is given by

$$Pe \cdot \int_0^L k \cdot dx \cdot C_{\text{H}_2\text{O}} \quad (3)$$

Assuming N similar channels in a reactor one can define the term Z_c as the integrated reaction per unit C_{H_2O} expressed in cm^3/s

$$Z_c = \sum_0^N Pe \cdot \int_0^L k \cdot dx \quad (4)$$

We know that the thermal reaction rate is an exponential function of the type

$$k = k_o \cdot e^{-\frac{E}{RT}} \quad (5)$$

where k_o is the frequency factor E is the activation energy and R the universal gas constant.

Expression (4) can be rewritten

$$Z_c = Pe \cdot \sum_0^N \int_0^L k_o \cdot e^{-\frac{E}{RT}} \cdot dx \quad (6)$$

Fig. 1 gives a typical temperature, curve (1) and reaction rate curve (2) distribution as function of the core height in a H.T.G.C. Power Reactor. The curve (3) gives the integrated reaction rate Z_c .

2.4 The integrated carbon deposition in the heat exchangers following equations (2)

acts as a source for H_2O and a sink for CO_2 and H_2

A term Z_R : integrated reaction in the heat exchanger per unit $C_{(H_2)}$ and

unit $C_{(CO)}$ can be defined in a similar manner as Z_c . The temperature de-

pendence of this reaction is not yet known. Experiments which are in hand

[4] [5] have shown that by the selection of a suitable purification flow and the use of suitable material this term can be eliminated. We will however keep this term for the establishment of the general equations and further on in the discussion we can delete it.

With these elements the following equation gives the differential evolution of the H_2O concentration for a clean circuit of volume $V(cm^3)$ where a leak of W mole/s of water has developed.

$$\frac{d C_{H_2O}}{dt} = \frac{W}{V} - \frac{Z_c \cdot C_{H_2O}}{V} + \frac{Z_R \cdot C_{H_2}}{V} - \frac{q \cdot C_{H_2O}}{V} \quad (7)$$

Similarly, the following equation can be given for the differential evolution of the H₂ and CO reaction product.

$$\frac{d C_{H_2}}{dt} = \frac{Z_c \cdot C_{H_2O}}{V} - \frac{Z_R \cdot C_{H_2}}{V} - \frac{q \cdot C_{H_2}}{V} \quad (8)$$

By solving these equations with $C_{H_2O} = 0$ and $C_{H_2} = 0$ as boundary condition at the

time $t = 0$ one obtains for t sufficiently great

$$C_{H_2} = \frac{Z_c \cdot C_{H_2O}}{Z_R + q} \quad (9)$$

$$C_{H_2O} = \frac{W}{Z_c \left(1 - \frac{1}{1 + \frac{q}{Z_R}}\right) + q} \quad (10)$$

which for Z_R negligible can be rewritten

$$C_{H_2} = \frac{Z_c \cdot C_{H_2O}}{q} \quad (11)$$

$$C_{H_2O} = \frac{W}{Z_c + q} \quad (12)$$

More refined and elaborate equations taking into account the variables, which for sake of simplification were here omitted, such as the exact order of reaction, catalysis of the oxidation reaction by fission products and iron, radial temperature distribution in the core etc. can be established. But for the purpose of these discussion equations (11) and (12) are sufficient and give a good insight into the phenomena discussed.

3. Admissible water concentration in the core

The admissible water concentration in the core is defined by the maximum corrosion at the hottest point of the graphite coolant channels. If we assume that the specification for the maximum admissible corrosion is expressed as the maximum depth of penetration in the graphite during the fuel lifetime we can write the following equation

$$C_{H_2O} = \frac{K \cdot x_{\max}}{k_{\max}} = \frac{K \cdot x_{\max}}{k_0 \cdot e^{-\frac{E}{RT_{\max}}}} \quad (13)$$

$$K = \frac{\delta}{12 \cdot K'} = \text{constant} \quad \text{mole-year} / \text{cm}^3 \cdot \text{s}$$

$$\delta = \text{density of graphite} \quad \text{g} / \text{cm}^3$$

$$K' = \text{number of s} / \text{year} \quad \text{s} / \text{year}$$

$$x_{\max} = \text{maximum admissible corrosion per year} \quad \text{cm} / \text{year}$$

$$k_{\max} = \text{maximum superficial rate of attack of the graphite fuel sleeves at the hottest point} \quad \text{cm} / \text{s}$$

$$12 = \text{molecular weight of graphite}$$

4. Admissible water leakage

The admissible water leakage in the primary circuit can be obtained by combining equations (12) and (13)

$$W = \frac{K \cdot x_{\max}}{k_{\max}} \left[Z_c + q \right] \quad (14)$$

which can be rewritten

$$W = K \cdot x_{\max} \left[\frac{Pe \cdot \sum_0^N \int_0^L e^{-\frac{E}{RT}} \cdot dx}{e^{-\frac{E}{RT_{\max}}}} + \frac{q}{k_{\max}} \right] \quad (15)$$

From this equation it can be seen that for a given x_{\max} , q and k_{\max} the water

inleakage W can be increased by increasing the ratio $\frac{\int_0^L e^{-\frac{E}{RT}} \cdot dx}{e^{-\frac{E}{RT_{\max}}}}$.

One way of increasing this term is to reduce E the activation energy of the reaction.

5. Irradiation effect on the graphite oxidation

Tests on graphite corrosion by traces of oxidising impurities CO_2 and H_2O in 10 atm helium under irradiation have been performed in a loop in the BR 2 reactor at C.E.N., Mol, Belgium.

The loop consists mainly of two furnances (thimbles) one out-of-pile and one in-pile (Fig. 2) . These two furnances working in parallel under exactly the same conditions give a clear indication of the influence of irradiation on the reaction rates. The use of C^{14} labelled samples allowed the measurement of the corrosion rate by measuring C^{14} activity in the gases. The experiments covered the temperature range $250^\circ C - 900^\circ C$ in fast neutron fluxes up to $5 \cdot 10^{14} \text{ n / cm}^2 \cdot \text{s}$ and γ fluxes up to 15 W / g .

Although most of the tests were carried out with CO_2 the same behaviour with H_2O has been observed. It was established that the observed radiolytic effects are largely due to energy transfer from the helium to the reacting impurities and consequently are proportional to the radiation level (power density) and to the pressure of helium. The observed corrosion rates are almost independent of the temperature as indicated in (Fig. 3) which gives the rate of oxidation expressed in activity of C^{14} measured in the effluent gas as function of temperature.

In the (Fig. 4) we compare in an Arrhenius plot the rate of thermal reaction to the radiolytically induced rates.

The results presented in this figure are only qualitative because the radiolytic oxidation rates are

- 1) not proportional to the concentration of oxidising impurities for partial pressures greater than $100 \mu \text{ atm}$
- 2) dependent on the radiation level and helium pressure.

But the figure clearly show that the influence of irradiation is to increase the reaction rate with graphite at the lower temperatures, while at higher temperatures the thermal reaction is the leading one.

This effect results in an apparent decrease of the activation energy of graphite oxidation reaction occurring in pile.

6. Conclusion

In paragraph 4 we have shown that under certain circumstances which would occur in a High Temperature Gas Cooled Reactor the maximum admissible water leakage could be increased if the integrated corrosion rate over the core Z_c is increased. One way of achieving this increase in Z_c is to decrease the temperature dependence of the reaction. On the other hand experimental evidence have shown that the influence of irradiation on the oxidation reaction is to decrease the apparent activation energy of the reaction. It can then be concluded that:

"In a high temperature gas cooled reactor of the DRAGON type, the temperature dependence of the radiolytically induced graphite oxidation is such that for one specified admissible local attack the water leakage can be increased."

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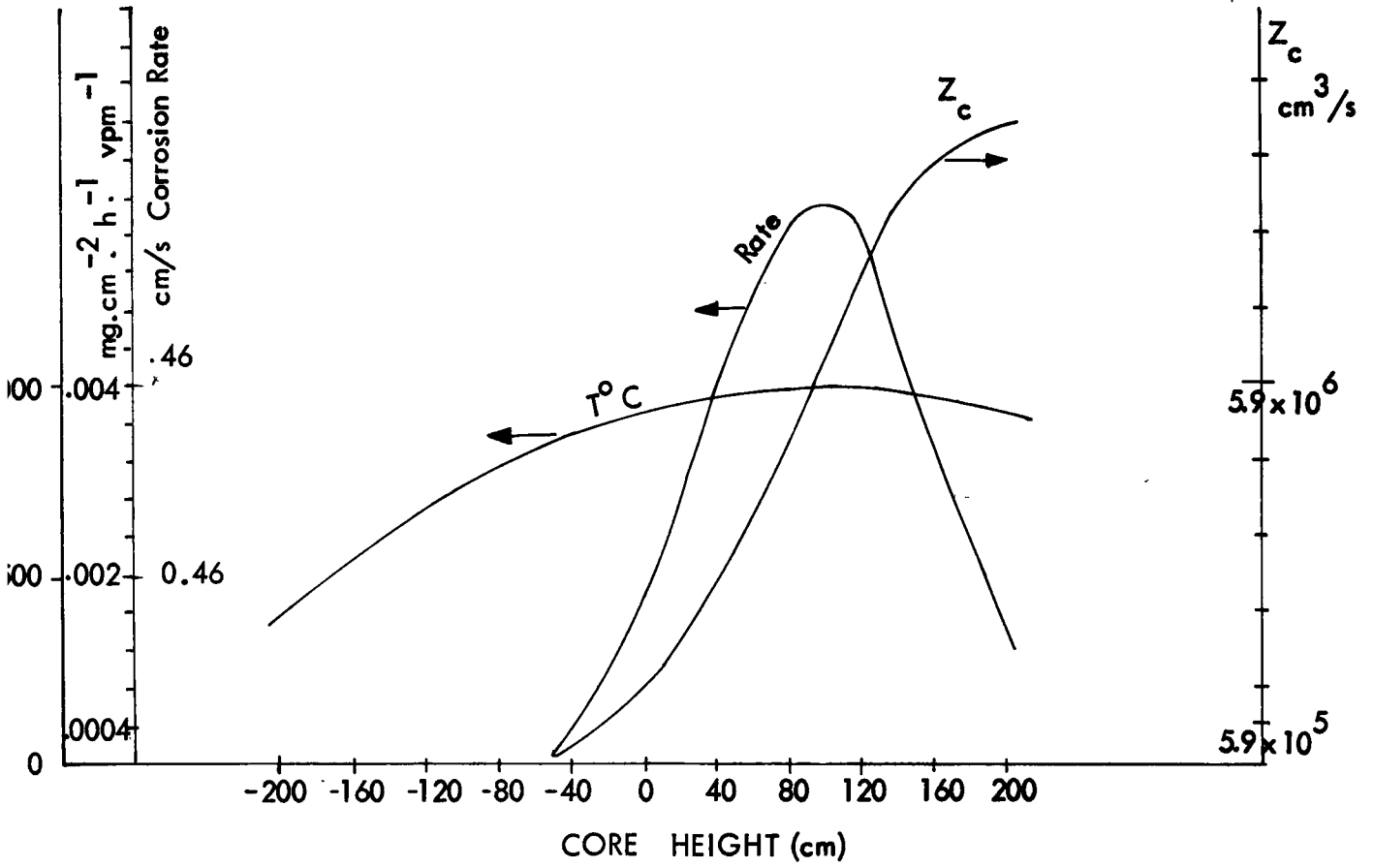
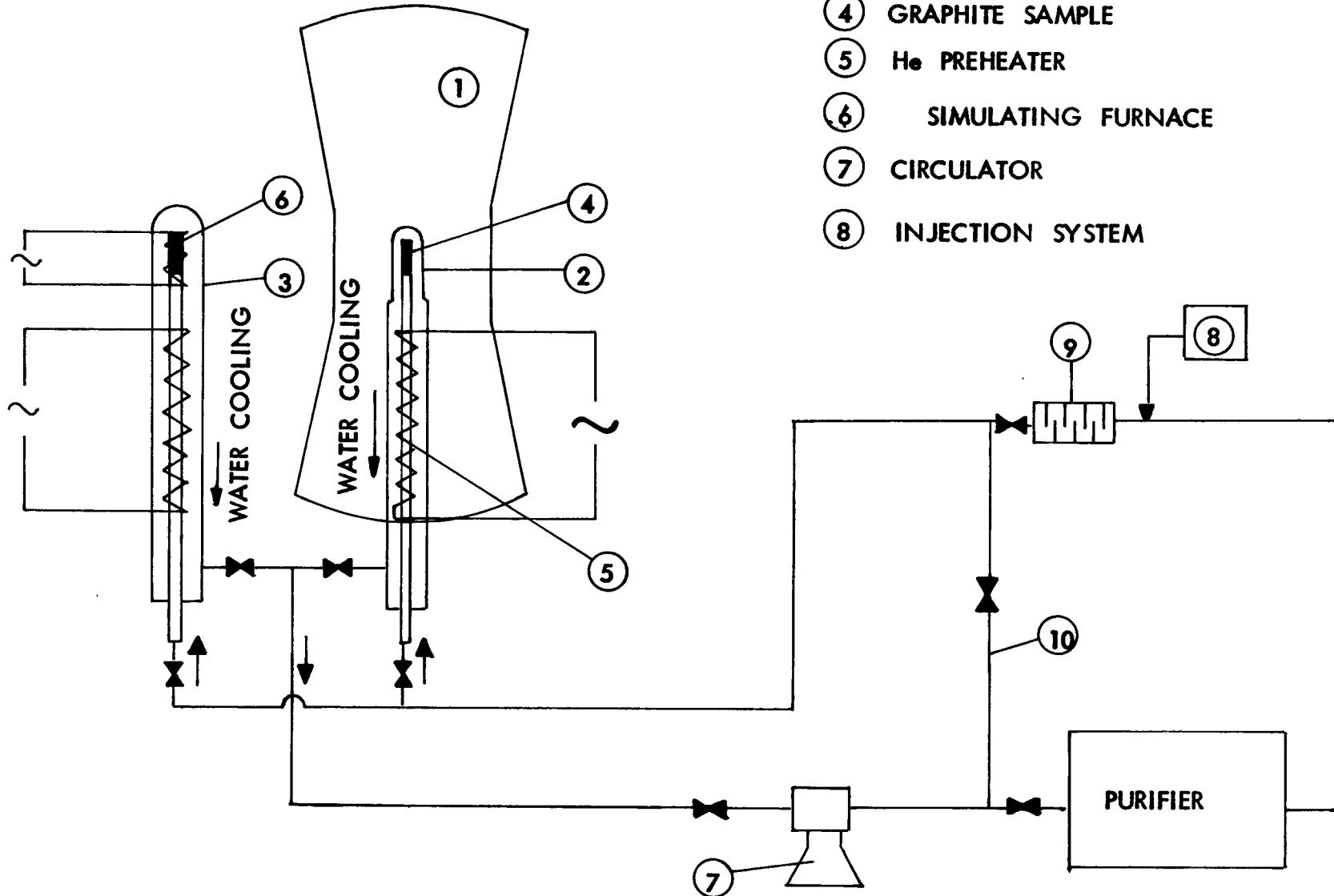


FIG. 1 H.T.G.C. POWER REACTOR
TEMPERATURE, CORROSION RATE, AND Z_c DISTRIBUTION
 $E = 75 \text{ k cal/mole}$

- ① REACTOR
- ② I.P. THIMBLE
- ③ O.P. THIMBLE
- ④ GRAPHITE SAMPLE
- ⑤ He PREHEATER
- ⑥ SIMULATING FURNACE
- ⑦ CIRCULATOR
- ⑧ INJECTION SYSTEM
- ⑨ MIXING CHAMBER
- ⑩ PURIFIER BY-PASS



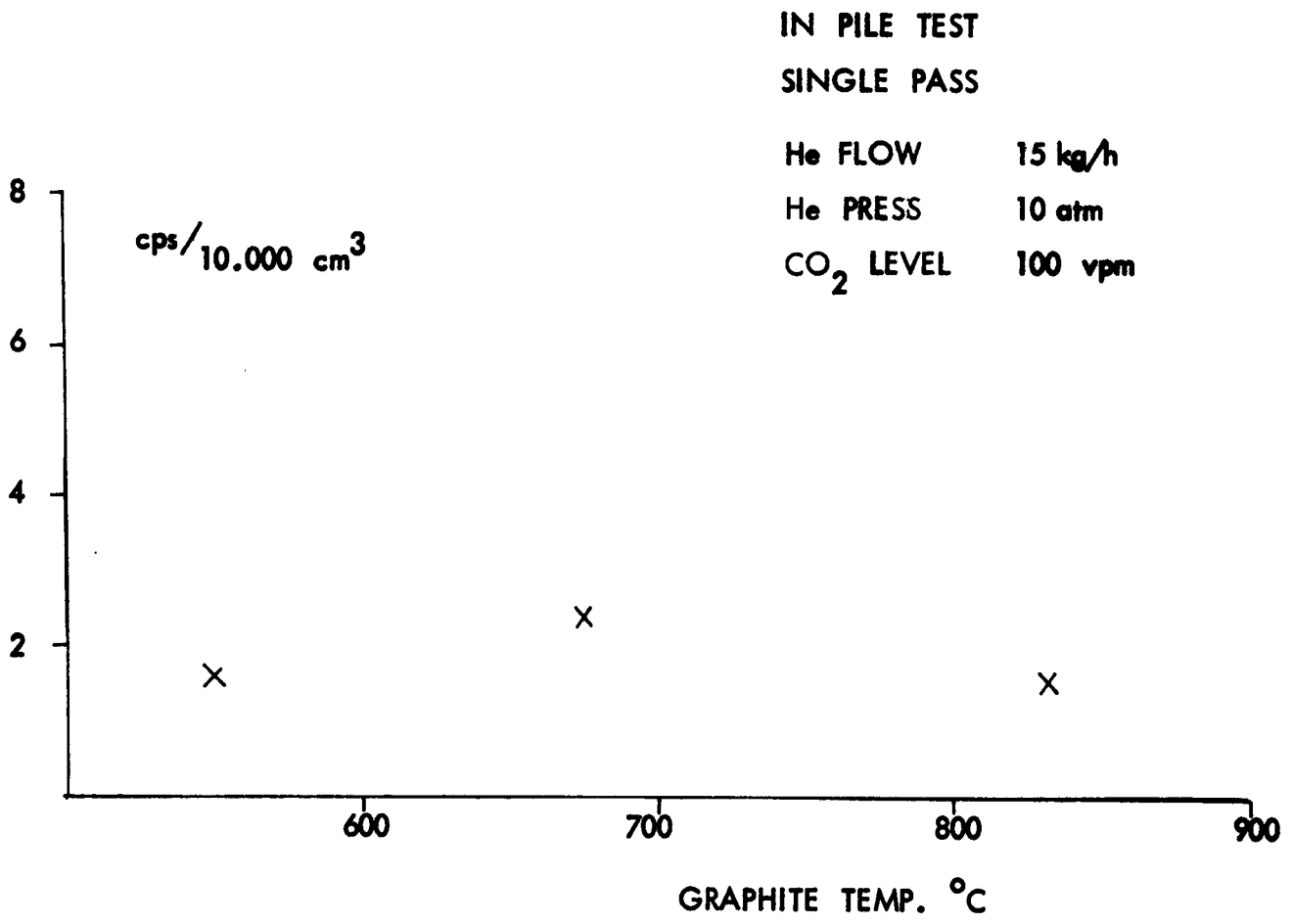


FIG. 3 OXIDATION RATE EXPRESSED IN C.P.S. OF C¹⁴
IN 10.000 cm³ OF GAS AS FUNCTION OF T°C

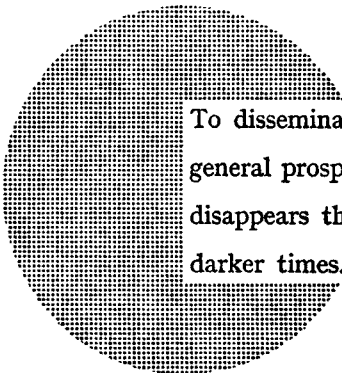
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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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