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DRAGON



Dragon Project Report

**CATALYTIC INFLUENCE OF DIFFERENT METALS
ON CORROSION RATE OF GRAPHITE**

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ABSTRACT

This report is intended to give a summary of the work carried out within Dragon, at Winfrith and under contract at CIIR, (Oslo), on the catalysis by different metals of the corrosion of graphite in presence of water vapour, carbon dioxide or oxygen.

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1. INTRODUCTION

From the first experiments on the different grades of graphite proposed for the Reactor, some severe localised pitting had been noticed. Similar observations have been reported by different authors [1, 2, 3, 4, 5, 6 and 7] who established a relationship between the location of corrosion pits and the location of metallic impurities. This relationship has been confirmed for the grades of graphite studied at Winfrith and the influence of the impurities on the rates and the activation energies of the reactions in water vapour and carbon dioxide has been investigated.

The second step has been to deliberately contaminate some graphite with different metals in order to assess the part played by each of them and to get a proper understanding of the phenomenon. The different catalysts studied have been chosen, either because

- (1) they are present in the reactor graphite in high concentrations (iron, vanadium, nickel)
- (2) they can come into contact with graphite during operation of the Reactor (fission products like barium, strontium, and iron, and nickel dust blown away from metallic parts of the Reactor or from sites where carbon deposition may occur) or
- (3) they may be placed in contact with graphite (platinum and molybdenum, likely to be used as thermocouple sheath material).

2. EXPERIMENTAL

2.1 Materials

Different grades of graphite have been investigated which can be divided into two groups: the reactor grade graphites, and the pure graphites used for more basic research on catalysis after contamination with different metals.

2.1.1 Reactor Grade Graphites

A number of nuclear graphites have been studied for their catalytic behaviour during thermal oxidation. These graphites include Pile Grade 'A' (UKAEA) and Dragon Grades, 1, 3, 9 and G5.

Pile Grade 'A' is the well known coarse grained nuclear grade graphite used in the "Magnox" reactors.

Dragon Grade graphites Nos. 1, 3 and 9 are fine grained graphites made from the following mix:

Granulated Nuclear Graphite (0.1 to 0.5 mm mesh size)	30%
Carbon Black	30%
Pitch	40%

These fine grained graphites were developed specifically for impregnation with furfuryl alcohol resin. Unfortunately the presence of large amounts of carbon black results in severe shrinkage of the graphite when subjected to fast neutron bombardment.

In order to overcome this problem Grade G5 graphite was developed containing graphite powder only, plus enough coal tar pitch to suit the extrusion conditions. The mix is approximately 67% graphite powder (60 mesh) and 33% micronised graphite powder.

Spectrographic analysis, carried out by the UKAEA at Capenhurst, have shown that all these graphites contain similar impurities although the actual concentrations vary widely. Table 1 shows typical values for a number of graphite bars analysed and it can be seen that the main impurities are iron, aluminium, calcium, nickel, silicon, titanium and vanadium. Most of the other common metals are present in amounts less than 1 ppm.

The B.E.T. surface areas are approximately:

Pile Grade A	0.25 m ² /g
Grade 1	0.7 m ² /g
Grades 3 and 9	1.2 m ² /g
G5	0.5 m ² /g.

2.1.2 Pure Graphites

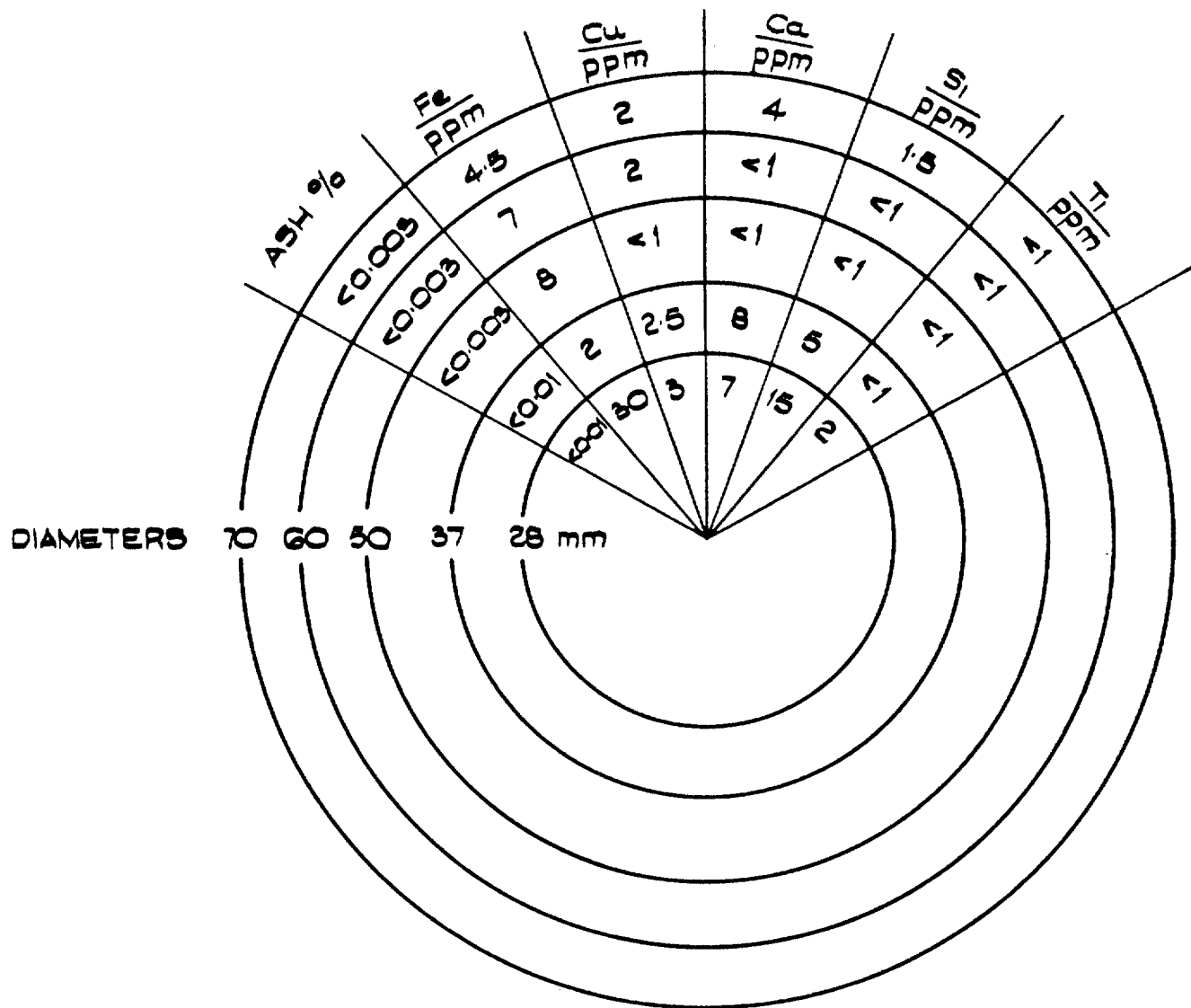
At CIIR the investigation has been mostly carried out with a spectroscopic pure powder called SP.1, from National Carbon Co. (maximum impurity level 6 ppm). The density of this powder is 2.2 g/cm³ and the B.E.T. surface area is 3 m²/g.

At Winfrith, most of the tests have been performed with G5 graphite purified in the laboratory at Pechiney. The analysis after purification is given in Table 2. Some qualitative tests have also been done on Grade 1 purified at 3000°C in argon.

Table 1 Typical Levels of Impurities Present in the Nuclear Grade Graphite Investigated (in parts per million by weight)						
	Grade 0 P.G.A.	Grade 1	Grade 3	Grade 9	Grade 9 (I)	Grade G5
Ash	200-320	100-400	190-390	100-270	300	50-750
Fe	3-7	15-70	5-34	1-43	8-30	2-20
Al	2-4	6-30	<1	<2	5-100	1-10
Ca	40-80	30-80	2-30	1-15	25-50	15-200
Ni	<1	<2	5-10	<1	3	<3
Si	20-70	5-50	30-60	2-60	2-15	50-150
Ti	<2	<7	6-40	1-40	3-5	4-70
V	15-40	8-20	40-60	30-60	20-25	4-60

The following common metals are present in very low concentration (usually less than 1 ppm)

Cu, Ba, Be, Bi, Cr, Co, In, Pb, Li, Mg, Mn, Mo, Na, Sr, Sn, W, Zn.



NOTE 1 B, Al, Ba, Bl, Cr, Co, In, Pb, Mg, Mn, Mo, Ni, Sn, Sn, W, V & Zn, WERE PRESENT IN AMOUNTS LESS THAN 1 ppm

TABLE 2 ANALYSIS OF IMPURITIES IN BAR No. 0286 G5 GRAPHITE AFTER PURIFICATION.

2.1.3 Contamination of Pure Graphite with Catalyst

The catalyst was added by three different processes:

- (1) Impregnation in vacuum with a solution of the salt of the metal in question.
- (2) Simple contact by deposition of catalyst powder on the surface of a solid sample or by mixing of graphite and catalyst powders.
- (3) Coating by evaporation of pure metal in vacuum.

2.2 Experimental Techniques

Two types of experiments have been performed, one technological, concerning mainly the reactor grade graphites and one more basic on contaminated pure graphites.

2.2.1 Apparatus and Procedure - Basic Research

Silica spring technique was used to follow the reaction rate. The weight loss of graphite was recorded as a function of time, by means of a travelling microscope. The samples of SP.1 powder weighed approximately 750 mg and were supported in a platinum container. They were usually given a pretreatment in vacuum for 30 min at temperatures between 900 and 1000°C.

The samples of reactor graphites, purified or not, were 40 x 15 mm slabs. Their thickness was usually 2 mm and in some cases 1 or 4 mm. They weighed approximately 2 g, 1 g, or 4 g respectively. A hole was drilled at the top of the samples which were suspended on silica hooks. They were all degassed in vacuum before the corrosion tests. The temperature was raised by steps to 1000°C. This treatment lasted about 2 days. The corrosion by H₂O and CO₂ was studied in two different types of apparatus.

2.2.1.1 Corrosion by H₂O

No carrier gas was used. The water vapour flowed over the graphite at a pressure and a flow rate controlled by two capillaries, one at the inlet and the other at the outlet of the reactor tube. When investigating the effect of hydrogen, it was added through another capillary before the reaction tube. Fig. 1 shows the arrangement used at CIIR. The apparatus used at Winfrith was similar except that five furnaces in parallel were fed with the same flow of water vapour.

By changing the inlet or outlet capillaries, it was possible to change the pressure and the flow rate, or the pressure alone.

At CIIR the experiments were carried out over a large range of pressures [8].

From 0.06 to 2.7 Torr the flow rate was 8.9×10^{-2} mole/h, at 0.03 Torr it was 2.2×10^{-2} mole/h, and at 0.02 Torr it was 1×10^{-2} mole/h.

The range of temperatures depended on the catalyst used. At Winfrith, the pressure was generally 3.4 Torr with a flow rate of 8×10^{-3} mole/h in each furnace. The temperature was varied between 800 and 1050°C.

2.2.1.2 Corrosion by CO₂

A scheme of the apparatus is given in Fig. 2. Nitrogen was used as a carrier gas and CO₂ was added to it in a pressurised mixing unit. The mixture was then purified in the apparatus before reaching the six silica spring thermo balances in parallel. The flow rate was approximately 150 cm³/m. Most of the experiments were carried out in 3,000 vpm \pm 300 vpm CO₂ and at temperatures between 850 and 1250°C.

2.2.2 Apparatus and Procedure - Engineering Loop

Graphite specimens in the form of cylinders (40 mm long, 12 mm o. diam. and 6 mm i. diam.) were heated to between 1000 and 1300°C in the presence of helium gas containing a regulated and known amount of oxidising gas.

The furnace was based on the design described in D.P. Report 37 in which the heat is generated in the graphite itself by passing a heavy current through the specimens. (Fig. 3.) The seven specimens needed to form the heater were held together by means of a strong compression spring, and good electrical connections ensured by the use of cone and socket joints between specimens.

A 3 inch diameter quartz tube acted as an envelope for the helium gas and also enabled the graphite temperature to be measured directly with the aid of an optical pyrometer. The helium flowed over the graphite at a linear velocity of approximately 10 cm per s. (Reynolds' No. 100.) The gas was then circulated at approximately 5 psig in a closed loop consisting of heat exchanger, diaphragm pump and furnace. (Fig. 4.)

A simple purifier containing a bed of Molecular Sieve 5A granules, maintained at the temperature of liquid nitrogen, was installed in a by-pass line. This purifier could be connected to the circuit whenever it was necessary to reduce the amount of excess oxidising impurities in the loop.

The oxidising gases used were carbon dioxide (10-200 vpm range) and water vapour (200-300 vpm range). In all the

experiments the following additional impurities were present:

H ₂	>1,000 vpm
CC	3,000-6,000 vpm
O ₂	<1 vpm

2.2.3 Surface Area Measurements

The internal surface areas were measured with the B.E.T. method, by adsorption of methane, or krypton, at liquid nitrogen temperature.

3. OXIDATION OF REACTOR GRAPHITE

The influence of impurities can be studied as follows:

- (1) qualitatively by visual and micrographic examination of the samples, and by radiography,
- (2) quantitatively, by measurement of the reaction rates.

3.1 Presence of Pitting

The experiments done on an engineering scale concerning the surface pitting and those done on a laboratory scale concerning the internal attack are now considered.

3.1.1 Surface Pitting - Engineering Aspect

Oxidation experiments on fine grained Dragon Reactor graphites, heated to temperatures in excess of 1100°C in mildly oxidising atmospheres, (100-200 vpm CO₂) have shown that corrosion of the graphite surface does not proceed at a uniform rate at all points [5]. This non-uniform rate of attack results in severe localised corrosion of the graphite with the formation of well defined pits, or craters, randomly spread over the surface of the specimen. (Figs. 5 and 6.)

A full description of this phenomena has been given in D.P. Report 294 [9].

In the case of Dragon grade graphites the principal metal catalytic impurity appears to be vanadium. This has been confirmed by probing inside individual craters with a micro-electrode and analysing the discharge with a mass-spectrometer [10]. However, other metals, e.g., nickel and iron, which may be present in the graphite in appreciable amounts, may have a secondary catalytic effect on the oxidation.

In Fig. 7 are three radiographs showing clearly the size and distribution of the metallic impurities in thin discs of

Grade 3, 9 and G5 graphite respectively.

The experimental results have shown that surface pitting does not occur below approximately 1000°C (even for "burn-off" as high as 14.6 mg/cm²) but does occur above approximately 1050°C. These results refer to Grade 9 graphite only, but from observations made during other experiments, it is believed that a similar "threshold" temperature applies to Grade 3 graphite.

Prevention of Pitting

Suppression of corrosion pitting can be achieved by lowering the concentration level of the metallic impurities in the graphite to a few parts per million.

Two methods of purification have been investigated:

(1) Chlorination

Heating the graphite specimen to 1000°C for 1 h in a stream of chlorine gas (Horsley [11]) resulted in the removal of sufficient of the main catalytic impurities, in the untreated graphites investigated, to prevent pitting on subsequent oxidation. This method was not successful when applied to furfuryl alcohol impregnated graphites.

(2) Heat Treatment

Straightforward heat treatment under vacuum to temperatures in excess of 2000°C was found to be very effective in lowering the impurity level to an acceptable figure, provided that the equipment was clean and free from other graphite components. An all silica apparatus with an external R/F heating coil was found to be best. Heat treatment usually lasted 1 h and was equally effective with furfuryl alcohol impregnated samples.

The efficiency of the two processes is shown in Table 3 where impurity levels are quoted after purification, for Grades 3 and 9 (impregnated) respectively.

3.1.2 Internal Attack - Basic Research

Apart from the surface pitting a localised preferential attack occurs throughout the samples in CO₂ as well as in H₂O as shown in the cross sections Fig. 8. This preferential attack takes place even at temperatures as low as 950°C in 3.4 Torr H₂O and after small burn-off (Fig. 9). The relationship between the holes and the impurities is demonstrated by X-ray radiography (Fig. 10).

Table 3 Impurity Levels in Grade 9 Graphite after Purification (in parts per million by weight)						
Impurity	Chlorination, 1 h at 1000°C				Heat Treatment 1 h at 2000°C	
	Grade 9		Grade 9 (I)		Grade 9 (I)	
	Before	After	Before	After	Before	After
Ash	-	-	300	300	-	50
Cl	-	100	-	-	-	-
Fe	7	1	30	8	10	2
Al	1.5	1	5	1.5	100	6
Cu	1	1	1	1	1	1
Ca	3	1.5	30	25	1.5	1
Si	30	30	10	10	15	15
V	50	1	20	20	25	1.5

Remaining common metals less than 1 ppm

3.1.2.1 Effect of Heat Treatment

Purification of Grade 9 graphite was tried by heating in vacuum at temperatures between 1800 and 2950°C. Unfortunately in the method used the samples were in contact with a graphite heater of doubtful purity. This could explain why the results differ from those obtained in Section 3.1.1, purification could only be achieved above 2400°C, as shown in Figs. 11 and 12.

3.2 Reaction Rates - Basic Research

The reactivities of Grade 3 and Grade 9 graphite were found to be quite identical. The reaction rate of Grade 9 with H₂O and CO₂ is shown in an Arrhenius plot, Fig. 13. It can be noticed that the activation energies of the reactions are approximately the ones usually reported for pure graphite in the chemical and in-pore diffusion controlled zones [12 and 13]. The order of reaction is fractional in CO₂ in the range of pressures investigated. Some short runs in H₂O seemed to indicate a half-order reaction.

3.2.1 Influence of Heat Treatment

The decrease of reactivity after purification by heat treatment in vacuum is shown in Fig. 14. The corrosion rate per unit of geometrical surface area is reduced by a factor 1.5 to 1.8, depending on the temperature of heat treatment. A heat treatment at 2000°C is efficient even though it does not remove all impurities (Fig. 11). The internal surface area after 5% burn-off was 1.3 less than that of the untreated specimen.

3.2.2 Influence of Hydrogen Added to Water Vapour

It is well known that hydrogen inhibits the reaction between pure carbon and water vapour [12, 14, 15 and 16]. However, several experiments carried out with Grade 9 graphite in atmospheres of 3.4 Torr H₂O plus 3.4 Torr H₂, gave conflicting results.

These results have been presented in Fig. 15 as Arrhenius curves. It will be seen that whilst one sample showed the normal behaviour expected of pure graphite, the remaining samples gave points lying on a different curve. This latter curve, which cuts the Arrhenius plot for the Grade 9/water reaction at approximately 925°C, gives a value of only 25 kcal/mole for the activation energy of the reaction. The activation energy of the uninhibited reaction is approximately 76 kcal/mole.

Apparently, the addition of hydrogen to the water vapour, at these partial pressures, has the effect of increasing the reactivity of Grade 9 graphite below approximately 900°C, whilst decreasing its reactivity above this temperature.

3.3 Discussion

It can be concluded in agreement with other workers [2, 17] that

the reactivity varies as a function of the concentration of impurities, and pitting as a function of the size of the impurities which are unevenly distributed in the graphite.

The chemical nature of the impurities can also be important. Vanadium and iron have already been reported as being responsible for severe pitting and corrosion rates [1, 2 and 3]. Moreover, Lang [1] reported that the joint presence of several metallic impurities can result in an accelerated corrosion due to non-additive effect of catalysts. At CIIR an important promoting effect on the catalysis of iron by traces of potassium has also been observed [8].

Several authors have reported a change in the activation energy of carbon with different oxidising gases in presence of impurities [5, 17 and 18]. In this work, it seems that such an effect occurs only in the reaction with water vapour in presence of 50% hydrogen. Long and Sykes [17] mention that the well known retarding effect of hydrogen should be stronger in absence of impurities because the adsorption of water vapour on carbon is affected much more than the adsorption of hydrogen by the presence of these impurities. It appears here that above 1000°C, the reaction rate of Grade 9 graphite with water vapour is reduced by hydrogen in approximately the same ratio as it would be for a pure graphite, and that the presence of impurities has an effect only at lower temperatures. The slightly higher reaction rate at 900°C in presence of hydrogen could also suggest a change of chemical state of the impurities in presence of hydrogen which would bring about an increase of catalytic effect. It seems logical to assume a reduction of oxide to metal. However, most of the impurities contained in graphite cannot be reduced by hydrogen, at the partial pressures of hydrogen and water vapour used for these experiments. On the other hand they can be reduced by carbon and in some cases be present as carbides. It is possible there is competition between carbon and water vapour and that in presence of hydrogen, the reduction rate by carbon prevails over the oxidation rate by water vapour.

4. CATALYSIS OF GRAPHITE OXIDATION BY METALS

Much work has been done at CIIR, (Oslo) during the last two years on the catalysis by different metals and has already been reported in annual reports [16, 8 and 19]. The metals investigated were barium, strontium and the transition metals: iron, vanadium, nickel, cobalt, molybdenum, platinum. More recently their efforts have been concentrated on iron impregnated SP.1 powder. We will report here only the main results.

At Winfrith most of the research has concerned the catalysis by iron and the effect of the method of contamination. Solid samples of purified G5 have been used for this investigation.

4.1 Catalysis by Barium and Strontium

Barium and strontium were usually introduced in SP.1 powder as hydroxides. In some experiments, Ba was introduced from a barium acetate solution. The range of temperatures investigated was 700-850°C for Ba-contaminated SP.1 and 800-915°C for Sr-contaminated SP.1.

The experiments were carried out in water vapour at pressures between 1.2 and 4 Torr.

Much difficulty arose from uptake of silica during the oxidation tests. When using a silica container, this uptake could reach 0.01-0.2% silica [16]. This resulted in reaction rates decreasing with time in the case of Ba-samples. Sr-impregnated samples were less sensitive to silica. Even when using a platinum container, the samples underwent an uptake of silica from the mullite tube, which could falsify the real catalytic effect.

4.1.1 Activation Energy and Order of the Reaction

In 2.7 Torr H₂O the activation energies in the range of temperature studied was 75 kcal/mole for 0.05% Sr-graphite and 59 kcal/mole for 0.05% Ba-graphite sample. (See Fig. 16)

At 800°C a zero order reaction was obtained for Ba-impregnated sample between 1.2 and 4 Torr H₂O. At 850°C the catalytic factor of 0.05% Ba was 1,000 and the catalytic factor of 0.05% Sr was 130.

These results can be compared with the ones of R. D. Burnette and L. R. Zumwalt [20]. Between 700 and 1000°C, they obtained an activation energy of 51 kcal/mole for Ba-graphite H₂O reaction and 25 kcal/mole for Sr-graphite H₂O reaction to be compared with an activation energy of 48 kcal/mole for non-catalysed graphite, which would indicate that the reactions were in-pore diffusion controlled.

At 1000°C, and between 2.5 and 39% H₂O in helium, the order of the reaction varied from 0.5 to 1 depending on the flow rate of helium.

At 800°C, the catalytic factor of 0.057% Ba was 200 and the catalytic factor of 0.036% Sr was 10.

4.1.2 Effect of Pretreatment and Catalyst Concentration

Pretreatment above 1000°C reduced the reaction rates. This effect is probably due to loss of catalyst and uptake of silica.

The effect of the catalyst concentration is shown in Figs. 17 and 18. The rates increase with the concentrations. At 912°C and 2.7 Torr H₂O the reaction rates of Sr-graphite increase with burn-off in the range of concentrations investigated (80-1200 ppm) while at 850°C and 2.7 Torr, the reaction rates of Ba-graphite increase with burn-off for concentrations higher than 0.04% and decrease at lower concentrations.

R. D. Burnette and L. R. Zumwalt [20] have found rates increasing linearly with Ba or Sr concentrations from 0 to 14×10^{-4} mole fractions. The rates were always increasing with time. It must be noted that their specimen was inserted

in a graphite holder which was supposed to preclude any poisoning by the mullite furnace tube.

It is thought that the decrease of reaction at low concentration of barium can be due to uptake of silica.

4.1.3 Inhibitors of the Ba and Sr-Catalysis

As it was noticed that silica decreases the catalytic effect of barium, some quantitative tests were performed with silica, alumina and zirconia. The results are shown in Table 4. The three oxides seem inhibitors, at least if they are added at the same concentrations as barium and strontium. A heat treatment at 1000°C for 1 h is also effective for reducing the reaction rate. No loss of barium was revealed after this heat treatment, but there is still the possibility of uptake of silica.

4.1.4 Effect of Hydrogen Added to Water Vapour

The effect was very small. Twenty-seven mole % reduced the rate by 15%, whereas the same amount reduces the reaction rate of pure graphite by a factor of 3.

4.1.5 Reaction Rate with CO₂

Preliminary tests indicated approximately the same catalytic factor in 4 Torr CO₂ as in 2.7 Torr H₂O.

Some tests carried out at Winfrith on cylinders of Grade 9 impregnated with Ba (NO₃)₂ or Sr (NO₃)₂, oxidised in 50 vpm CO₂ in helium at 1000° during 40 h, gave the following results:

	Concentration ppm	Catalytic factor
Ba	70	42
Sr	40	20

4.2 Catalysis by Iron

From the numerous experiments carried out in Oslo as well as in Winfrith, it appears with certainty that the experimental conditions can change completely the picture of the catalysis.

The results obtained at CIIR and at Dragon will therefore be reported separately. The standard experimental conditions were reported in Section 2. When some change has been introduced it will be mentioned in this Section.

4.2.1 Oslo Results

The SP.1 graphite powder samples were usually contaminated

Table 4
Effects of Inhibitors on
Catalytic Factor of Barium (0.05% Ba)

$$\left\{ \text{Catalytic Factor} = \frac{k_{\text{graphite + catalyst}}}{k_{\text{graphite}}} \right\}$$

Inhibitor	Before HT	After HT
	350°C	1060°C
None	1200	12
0.02 % Al ₂ O ₃	50	3.8
0.05 %		4.2
0.02 % ZrO ₂	80	2.6
0.05 %	50	2.3
0.005% SiO ₂	1300	
0.02 %	50	3.3
0.05 %	10	1.1

Effect of Inhibitors on
Catalytic Factor of Strontium (0.05% Sr)

Inhibitor	Before HT	After HT	
	912°C	1060°C	912°C
None	100	(high)	60
0.02 % Al ₂ O ₃	50	3.5	4
0.05 %	30	13	12
0.02 % ZrO ₂	130	(22)	28
0.05 %	100	5.5	6
0.005% SiO ₂	120	(17)	16
0.02 %	45	3.3	4
0.05 %	40	2.1	

by impregnation with iron nitrate.

4.2.1.1 Effect of Pretreatment

Several temperatures of pretreatment in vacuum for 30 min, were tried before corrosion at 850°C in 0.3 Torr H₂O. The results are shown in Fig. 19. It seems that a pretreatment at 900°C is necessary to get constant reaction rates from the beginning of the experiment. At lower temperatures, the rates increase until they reach approximately the same value. In consideration of this result, the samples have always been pretreated at 900°C for 30 min, except when mentioned differently in the Sections below.

4.2.1.2 The Effect of Concentration of Catalyst

The increase of reaction rate with the concentration of iron at 850°C in 0.3 Torr H₂O is shown in Fig. 20. The reaction rates decrease slightly with time at the lower concentrations.

4.2.1.3 The Effect of Temperature

The variation of the reaction rates as a function of temperature has been studied between 750 and 1000°C at 0.1 and 0.3 Torr water vapour pressure.

The results obtained at 0.3 Torr are given in Fig. 21. They were quite similar at 0.1 Torr. A maximum of reactivity occurs at 825-850°C. At 1000°C the reaction is low.

However, it must be pointed out that this temperature effect is dependent on the pressure. For instance in 1 Torr H₂O, the reaction started like an explosion at 1000°C with sputtering of graphite and the rate could not be measured.

4.2.1.4 The Effect of H₂O Pressure

Likewise, the effect of the pressure depends on the temperature. Several experiments have been carried out at 800, 825, 850 and 1000°C. Typical results are shown in Fig. 22. The initial reactivity increases with the pressure. The rates of reaction decrease with time, the decrease being most pronounced at the highest pressures. However, it seems there is a threshold pressure above which the reaction becomes very violent at the start. This threshold seems to be 1 Torr at 1000°C. Some similar explosion-like reactions have been obtained in 2.7 Torr at 850-900°C [8].

4.2.1.5 Reactivation of the Catalyst

When a decrease of reactivity has occurred, a heat treatment in vacuum or hydrogen can reactivate the catalyst. The rates measured after heat treatment are even higher than they were at any time before. It is not clear whether this is due to insufficient previous pretreatment or to iron becoming more active.

4.2.1.6 Effect of Hydrogen Added to Water Vapour

Reactivation of the catalyst can also occur when hydrogen is added during the oxidation. Fig. 23 shows the effect of adding 0.7 Torr H_2 to 0.6 Torr H_2O at $780^\circ C$ in the presence of SP.1 powder containing 600 ppm iron. A similar effect has been observed at $1000^\circ C$.

4.2.1.7 Inhibition of the Catalysis

Some experiments have been done to try to reduce the iron catalysis by adding silica or alumina. Until now the results are not reproducible. It can just be mentioned that the rates are more or less decreased and alumina has a somewhat greater effect.

4.2.1.8 Catalytic Effect on Purified G5 Cylinders

Cylinders, 1 mm thick, were impregnated with 500 and 800 ppm Fe. It can be noticed (Fig. 24) that the rates are increasing with time at $850^\circ C$ in 0.3 Torr H_2O .

4.2.1.9 Contamination by Mixture of Powders

One per cent Fe was added to SP.1 powder, as pure metal and as oxide. The reaction rates are considerably less in the latter case. (Fig. 25.) A pretreatment at $1000^\circ C$ for 15 h improves the catalytic effect of the oxide.

At $800^\circ C$ the rates are increasing with H_2O pressure between 0.3 and 0.8 Torr. In this range they are also increasing with time.

4.2.2 Winfrith Results

Several methods of contamination were used as reported in Section 2.1.3. All the tests were done on 40 x 15 x 2 mm slabs of purified G5. When the method by impregnation was chosen the samples, after having been degassed at $300^\circ C$, were soaked for 30 min in vacuum in a solution of $NH_4Fe(SO_4)_2$ $\frac{11}{40}$, $\frac{11}{80}$ or $\frac{11}{100}$, kept slightly acid in order to prevent formation of colloidal Fe_2O_3 aq which could block the pores.

By several tests, it was demonstrated that after 15 min the samples do not absorb any more liquid. The weight gain was about 100 mg after a quick drying of the surface, done in order to avoid a higher concentration of impurity on the surface. Even so it is possible that a concentration gradient of iron is established through the thickness of the sample. The samples still wet, were exposed in an atmosphere of ammonia in order to convert the sulphate to the oxide hydrate, afterwards they were dried in vacuum.

The concentration of iron in each sample was determined after the corrosion test by a spectrophotometric method.

The results are shown in Figs. 26 and 27. They are given in an Arrhenius plot in weight loss per unit of geometrical surface area, per h. For comparison with CIIIR results, the conversion factor is: $1 \text{ mg/h cm}^2 = 2 \times 10^{-3} \text{ m/g s}$.

The reactivity of G5 is increasing with burn-off until a high burn-off (more than 10%). It seems to follow a similar increase in the internal surface area. The same applies to iron-contaminated samples. The results in the Arrhenius plots have been given after 7% burn-off. It can be mentioned that the catalytic effect as a function of time would be much greater.

The difference in behaviour of the samples as a function of the method of contamination used, is shown in Fig. 28.

4.2.2.1 Catalysis by Impregnation

The samples contaminated by impregnation showed a very high reactivity in CO_2 as well as in H_2O or $\text{H}_2\text{O} + \text{H}_2$, with iron concentrations as low as 20 ppm Fe.

(i) CO_2 Reaction

It seems (Fig. 26) that the catalytic effect increases with the concentration of iron. It can be noticed that the results are a little scattered. Due to this dispersion the decrease of activation energy noted in Fig. 26 with increase of iron concentration is perhaps not significant. However, it can be established that the activation energy is very low (around 10 kcal/mole), in the range of temperature investigated. The effect of decrease of activation energy in the presence of iron results in a catalytic factor of about 50 at 1000°C and only 3 at 1150°C . At 850°C this catalytic factor would be about 5,000.

The internal surface area after burn-off is greater in presence of iron, by a factor 2 at 12% burn-off with 21 ppm Fe and by a factor 3 at 15% burn-off with 70 ppm Fe.

(ii) H₂O Reaction

The reaction with water vapour proceeds very rapidly (3 mg/h cm²) above 700°C, and appears to be independent of temperature between 700 and 1000°C. (Fig. 27.)

Below 700°C there is a rapid fall in the reaction rate and at 600°C the reaction is too slow to be measured by weight loss techniques.

(iii) H₂O - H₂ Reaction

The hydrogen added to water vapour in a ratio of 70% has no effect or a very small inhibiting one. It must be pointed out that at these high reaction rates which reach 3 mg/cm² h the conversion of water into products can reach 50%.

A variation of iron concentration between 10 and 30 ppm does not seem to change the catalytic effect.

The internal surface area after burn-off is the same as for pure G5 graphite. Microscopic examination shows a very high corrosion on the surface.

4.2.2.2 Catalysis by Iron Powder

Thirteen ppm of powder were dispersed on the surface of samples which were tested in H₂O and H₂O + H₂. The story of the samples can be followed in Fig. 28. During a short time a catalysed reaction took place in

H₂O + H₂ in a ratio $\frac{p_{H_2}}{p_{H_2O}} = 1$. Afterwards the reaction stopped at 900°C. It could be started again by increasing the temperature at 1000°C. The catalytic factor was about 13. (Fig. 27.) Stopping the supply of hydrogen reduced the rate down to approximately the rate measured on pure G5 graphite. The effect was the same at 950°C. It can be noticed that probably the reactivation of the catalyst at 1000°C is only partial, as the reaction rate at 950°C after 3% burn-off is the same as at 900°C during the first hours.

4.2.2.3 Coated Samples

The behaviour of the samples contaminated by evaporation of iron in vacuum was more surprising.

(i) CO₂ Reaction

No catalysed reaction was observed at any

moment between 1000 and 1200°C with samples containing about 30 ppm Fe. The rates measured during the test were exactly the same as for pure G5 graphite.

(ii) H₂O and H₂O + H₂ Reaction

In the same way as for the samples contaminated with powder, a catalytic effect appears during the first hours of the test and then stops completely in H₂O as well as in a ratio $\frac{p_{H_2}}{p_{H_2O}} = 1.5$ at 1000°C.

It was thought after consideration of the results obtained in Oslo and on powder contaminated samples that the interruption of catalysis could be due to an oxidation of iron. However, after treatment in pure hydrogen and subsequent oxidation at 1050°C, with a mixture of hydrogen and water vapour in a ratio $\frac{p_{H_2}}{p_{H_2O}} = 2.3$ high enough to prevent any oxidation of iron the reactivity was about the same as the one of pure G5 graphite. Repeated efforts to reactivate the catalyst have been ineffectual.

The internal surface areas before and after corrosion tests of the samples were not affected by coating.

4.3 Catalysis by Other Transition Metals

The influence of some other transition metals has also been briefly investigated at CIIR [8]. It is interesting to see whether some correlation can be established between their behaviour and the one of iron.

4.3.1 Catalysis by Vanadium

Vanadium was added to SP.1 from a solution of vanadyl sulphate or ammonium vanadate. No difference between these impregnations was observed in the reaction with H₂O.

A pretreatment in vacuum at 1100°C for 30 min increased the initial reactivity. After a certain time, which depended on the temperature and the concentration of catalyst, the rates were decreasing with burn-off in the range of temperatures and pressure investigated (0.1% V from 1010 to 1097°C in 0.06 Torr and from 0.02 to 2.7 Torr at 1060°C). However some tests with an impregnated rod of graphite gave rates increasing with time.

As with iron catalysis, the effect of temperature is probably

highly pressure dependent. At 1060°C, a decrease in pressure results in greatly increased reactivity, at least down to 0.3 Torr (Fig. 29). In 0.06 Torr, the rates increased with increasing temperature.

Like iron, the catalyst could be reactivated by heat treatment at 1100° in vacuum.

Some experiments in CO₂ showed the same effect of increased rates by decreasing pressure between 4 and 0.1 Torr.

4.3.2 Catalysis by Nickel

Nickel was introduced from Ni(NO₃)₂ solutions at concentrations of 0.05%. It is a very strong catalyst at temperatures as low as 600°C. Fig. 30 shows the effect of burn-off at different pressures of water vapour at 640°C. It appears that there is almost no effect by changing the pressure from 0.3 to 2.7 Torr.

The catalyst can be reactivated by heat treatment in vacuum.

Comparative experiments with impregnated rods gave rate curves decreasing with time but much less sharply than with powder.

The same catalytic factor was obtained in 4 Torr CO₂ as in 2.7 Torr H₂O, at 700°C.

However, some experiments carried out at Winfrith on Grade 9 graphite impregnated with Ni(NO₃)₂ and reacted in 50 vpm in CO₂ in helium at 1000°C for 40 h revealed a small catalytic factor of 5, for a concentration of 200 ppm nickel. This apparent disagreement could quite easily come from the different experimental conditions.

4.3.3 Catalysis by Cobalt

0.05% cobalt was introduced from a cobalt nitrate solution.

At 760°C, the rate increase with time at the lower pressures (<0.3 Torr) and decrease with time at higher pressures. However, as with the other transition metals, it seems that the effect of pressure is temperature dependent. For instance, at 810°C, the rate increases with time even in 2.7 Torr H₂O.

4.3.4 Catalysis by Molybdenum

Some experiments carried out on SP.1 impregnated with 0.05% Mo, from a dilute NH₃ - solution of MoO₃, have showed a great drop of reactivity when the temperature was decreased from 912 to 870°C in 2.7 Torr H₂O, corresponding to an activation energy higher than 75 kcal/mole. At 912°C, the rate was increasing with time.

4.3.5 Catalysis by Platinum

Samples impregnated with PtCl_4 showed a great reactivity, comparable to the one of strontium impregnated samples at 912°C and in 2.7 Torr H_2O . However the catalysis was very small when the graphite was in contact with platinum metal (wire or crucible).

Some experiments were carried out at Winfrith on Grade 3 graphite slabs in contact with platinum wires in 2,000 vpm CO_2 , or on crushed Grade 3 in a platinum container 3.4 Torr H_2O . With the platinum wire, the results did not have good reproducibility. However, some catalytic effect appeared when the temperature was below 1050°C .

In the case of crushed graphite, a catalytic factor of 2.5 was obtained at 900°C , whereas at 1000°C no effect could be detected.

It is obvious that the degree of contact is the limiting factor.

4.3.6 Catalysis in Oxygen

It may be of interest to mention here the results obtained at Winfrith for some tests carried out in oxygen. Discs of Grade 9 graphite, approximately 2 mm thick and 25 mm in diameter, were soaked in concentrated solutions of vanadyl, nickel and silver nitrate salts respectively. After drying and decomposing the salts at 1000°C the discs were oxidised in an atmosphere of 5% oxygen in argon at various temperatures. Their Arrhenius plots are given in Fig. 31.

It would appear from the slope of the curves that their activation energies differ greatly. After making allowances for the fact that the impurity levels were not equal (approximately V = 600 ppm, Ni = 1,000 ppm and Ag = 2,000 ppm) the relative strength of the catalyst appears to be V, Ag, Ni in descending order of magnitude at temperatures below 700°C and Ni, V, Ag at temperatures above 800°C .

4.4 Discussion

It is likely that the mechanism of catalysis for barium and strontium, and for the transition metals is different. All the effects noticed with iron, which have been confirmed to a certain extent with other transition metals investigated, do not appear with barium and strontium.

Catalysis by Barium and Strontium

From the work carried out at CIIR, Oslo it appears that the barium and strontium oxides are strong catalysts. The only result of pretreatment is to reduce the reactivity by loss of catalyst and uptake of silica which is proved to inhibit the catalysis. The decrease of activation energy (more pronounced for barium which is a stronger

catalyst than strontium) is in agreement with the findings of different authors [18]. An interpretation of the smaller inhibitive effect of hydrogen on the reaction with water vapour has been given by Long and Sykes (Section 3.3). R. D. Burnette and L. R. Zumwalt [20] have proposed an attractive theory based on the fact that caesium is not a catalyst of the reaction which seems to preclude the electronic theory of Long and Sykes [17] and on the observation that the reactivity varies approximately linearly with the catalyst concentration which suggests a direct involvement of Ba and Sr. These metals would be able to modify the reaction steps which involve first the chemisorption of OH and H groups. The formation of groups having Ba or Sr attached as HOMO-C \leftarrow would bring about a different scheme in the further steps of the reaction.

Catalysis by Iron and Other Transitions Metals

The consequence of the way of contamination on the catalytic effect has already been pointed out by different authors. For instance J. R. Arthur and J. R. Bowring [21] obtained increased reactivities by impregnating graphite with alkali salts at concentrations which were small in relation to the original impurity content of the graphite used.

Sykes and Thomas [22] and J. F. Rakszawski, et al. [23] found a much greater catalysis by iron with impregnated samples than with a powder mixture. The catalytic effect decreased as the particle size of iron was increased.

The very low activation energies found at Winfrith for the reaction with CO₂ are in agreement with the data published by Sykes and Thomas [22] Rakszawski, et al. [23]. Sykes and Thomas obtained an activation energy of 25 kcal/mole with impregnated graphite (0.8% Fe) in 10⁻² mm CO₂ between 750 and 900°C. Rakszawski, et al. found an activation energy of zero for impregnated samples (0.05% Fe) in 1 atm CO₂ between 1050 and 1100°C.

The work done at CLIR and the experiments with powder contaminated G5 graphite seems to prove that iron in the reduced form is the strong catalyst whereas the oxide is a very weak one.

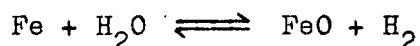
This is demonstrated by the effect of pretreatment, of regeneration of catalysis by heat treatment in vacuum or in hydrogen, by increase of reactivity when hydrogen is added to water vapour and by the decrease of the reaction rates as a function of time which is more pronounced at the higher pressures of water vapour.

Some of these effects had previously been pointed out by other investigators. Sykes and Thomas [22] mention that powdered ferric oxide is a catalyst provided the mixture has been degassed for at least 24 h at 1000°C. Gulbransen and Andrew [24] report a catalytic factor of 530 for graphite containing 0.079% Fe introduced by impregnation with ferrous nitrate solution provided a pretreatment in vacuum at 850°C for 1 h. A pretreatment at 700°C for 15 h had no effect.

If, therefore, one assumes that the metal is the strong catalyst and that the different shapes of curves obtained can be explained by a

transformation from metal to oxide or vice versa, some points still remain to be clarified.

For instance, reduction of the iron oxide by hydrogen will not occur unless the ratio of $\frac{H_2}{H_2O}$ is favourable. This is shown so in the reversible equation:



In cases where the $\frac{H_2}{H_2O}$ ratio is too low for the above reaction to move to the left and yet high catalytic effects have been observed (i.e., impregnated SP.1 powder and powder contaminated G5 graphite) other factors must be responsible.

It seems that the reduction of the iron oxide is due to carbon and the only effect of hydrogen is to inhibit the oxidation of iron by water vapour when it is present in a high enough percentage. In the experiments carried out at Winfrith, hydrogen produced by the reaction of graphite with water vapour is always present in a rather high ratio because the flow rate is ten times lower than at CIIR. This could explain why the addition of hydrogen has no effect and that the reaction rates are always increasing with time. However, experiments done in Oslo with impregnated rods also gave increasing rate curves, whereas in the same conditions, powder gave decreasing rate curves. This could be due to an unhomogeneous distribution of the catalyst through the rod with a higher concentration on the surface, as rate curves increasing with time were also observed with samples containing higher concentration of iron. It is also possible that because the surface energies of impregnated powder and solid are different the total changes of energies of the various reactions which can take place in the system C-Fe-H₂O-H₂ are different for powder and solid. This would lead to one reaction or another occurring preferentially.

When hydrogen is present at a very low concentration, it seems there is competition between the rates of the three different reactions:



and the catalysed reaction



Depending on the temperature and pressure, one reaction or another will be faster at the start of the experiment. So, in 0.3 Torr H₂O it seems that the oxidation of iron is very fast at 1000°C, while in 1 Torr H₂O the catalysed reaction (3) of oxidation of the graphite is so violent at the start that the oxidation of iron has no time to take place. The rates of the three reactions should increase with temperature and the rates of the reaction (1) and (3) should increase with H₂O pressure but with different coefficients.

Some contradiction to this theory appears when we consider the case of nickel or cobalt, although these elements also gave decreasing rate curves with respect to time it does not seem thermodynamically possible to form NiO and CoO in the system studied.

This leads one to think that the stoichiometric oxide may not be needed to poison the catalysis by the metal. The transition metals can form non-stoichiometric oxides which have lower free energies of formation [25]. However, more information on the catalysis by nickel is needed to confirm this.

Finally, the case of the coated samples has been examined carefully and has not received any very satisfactory explanation. A bad contact between graphite and the evaporated iron film could be the cause of the lack of catalysis. However, according to L. Holland [26] the deposits are usually in an aggregated structure. Therefore it seems that many points of contact should be available between graphite and iron. Presland and Hedley [7], who have studied the catalytic effect of platinum introduced by evaporation as a thin film, on the corrosion of graphite by air at low pressure, also report a coagulation of the film during the oxidation tests and they were able to follow the catalysis with an electron microscope.

It is worth noting that when a catalytic reaction took place at the start of a test and stopped, the atmosphere was oxidising for iron. Inactive iron oxide could be formed. However, one concludes that it should have been reduced by further heat treatments. More tests will have to be done in order to elucidate the phenomenon.

5. CONCLUSIONS

From the numerous studies on the catalytic properties of iron, and the more limited studies on barium, strontium and the transitional metals, the following tentative conclusions have been reached.

1. In the case of iron, and possibly in the case of other transitional metals, the free metal is the active catalyst. The oxides appear to be relatively weak catalysts.
2. The more finely divided the metal, the more active it is as a catalyst.
3. SiO_2 , Al_2O_3 and ZrO_2 have the property of strongly inhibiting the catalytic activity of barium, and to a lesser degree that of strontium. From the limited evidence available Al_2O_3 appear to have a slightly inhibiting effect on iron.
4. Most of the catalytic oxidation experiments have been performed using low partial pressures of water vapour. However, some work has been carried out using carbon dioxide and oxygen, and it would appear that no significant difference in behaviour occurs with these oxidants apart from the obvious change in activation energy.

5. The addition of hydrogen to the H_2O/C reaction strongly inhibits the reaction when the carbon is pure and free of catalytic impurities. However, when the system contains traces of Fe, Ni or Co as impurities, conflicting secondary reactions completely alter the picture. Certain conditions will favour the oxidation of the metal to an inactive oxide whilst another set of conditions will favour reduction of the oxide to the catalytic free metal.

It is obvious, therefore, that the overall reaction rate will be influenced by gas pressure, ratio $\frac{H_2}{H_2O}$ and temperature, making it impossible to predict the behaviour² of a particular contaminated graphite, unless these conditions are known with a fair degree of accuracy.

6. The presence of discrete particles of catalytic metals within the graphite causes severe localised corrosion in the vicinity of these particles, resulting in the characteristic pitting corrosion observed in many Dragon grade graphites. Removal of these impurities either by heat treatment or chlorination completely suppresses the pitting.

6. ACKNOWLEDGMENTS

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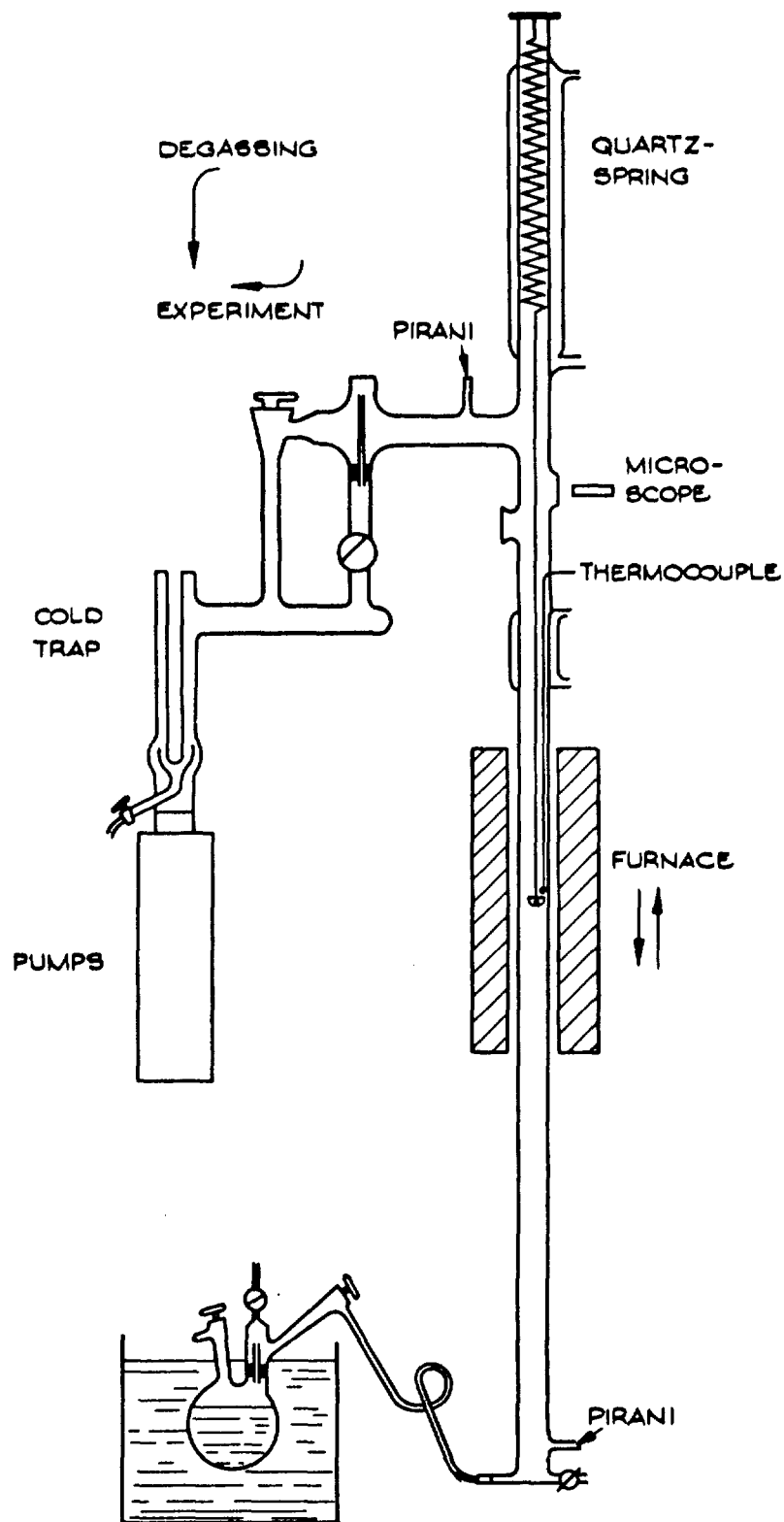


FIG. 1 THE QUARTZ SPRING OXIDATION APPARATUS

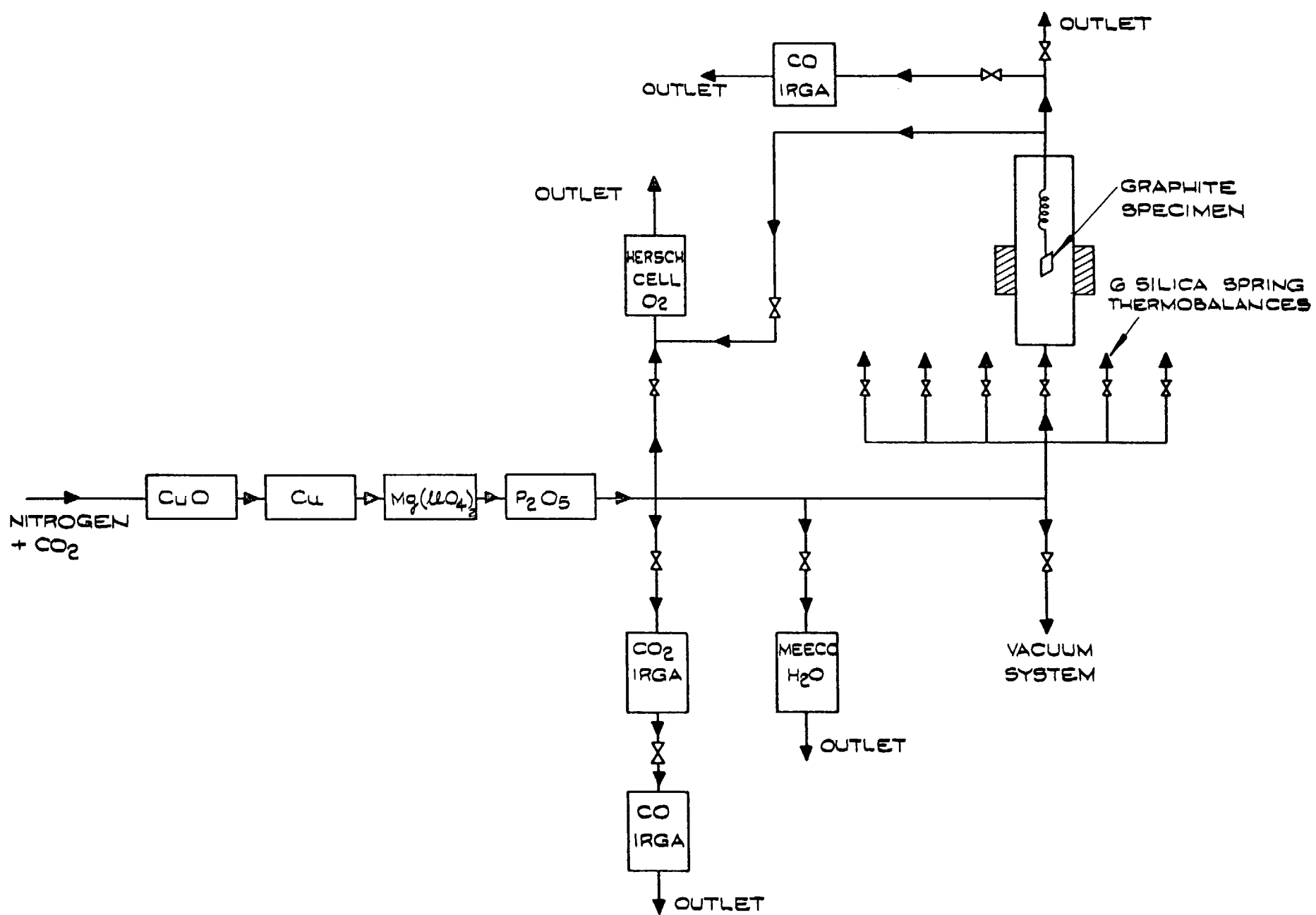


FIG. 2 SCHEME OF THE APPARATUS FOR THE STUDY OF GRAPHITE CORROSION BY CARBON DIOXIDE.

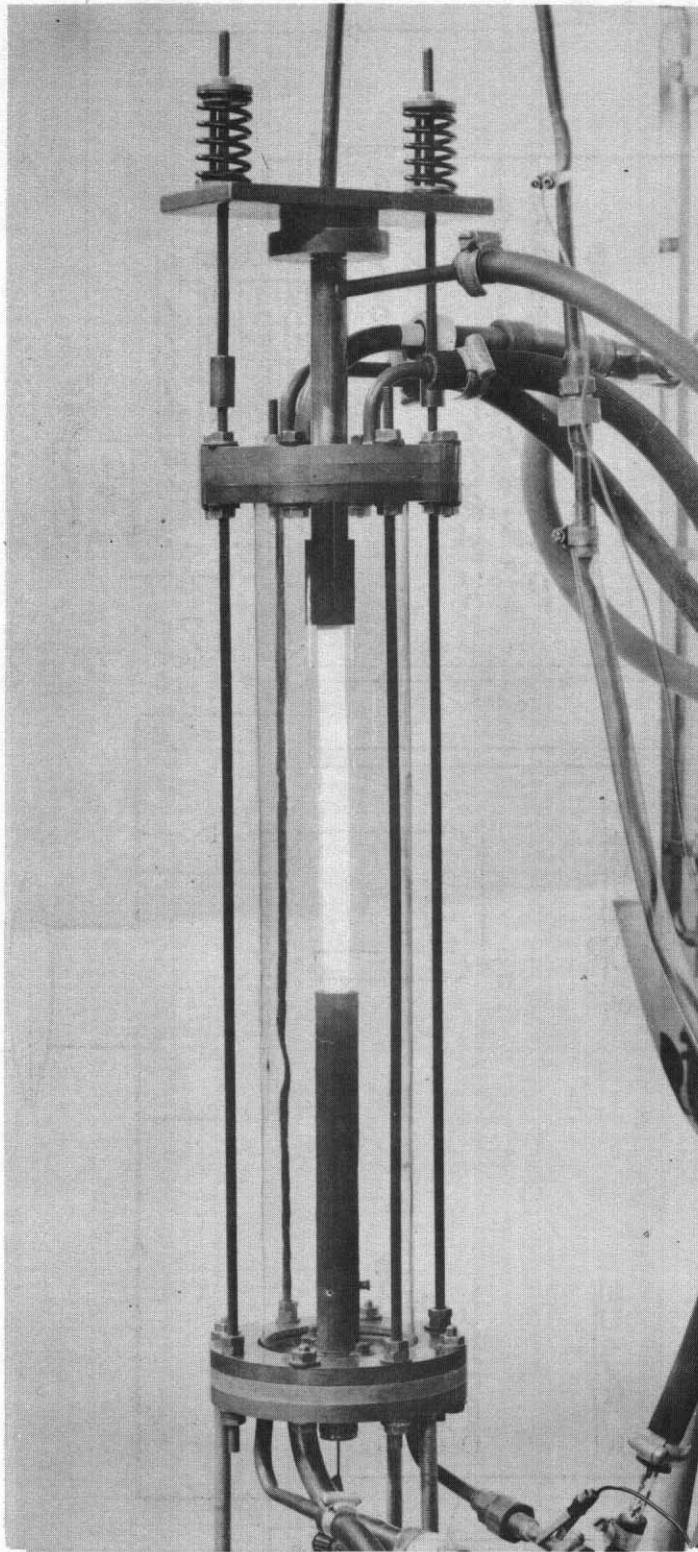


FIG. 3. CORROSION LOOP FURNACE

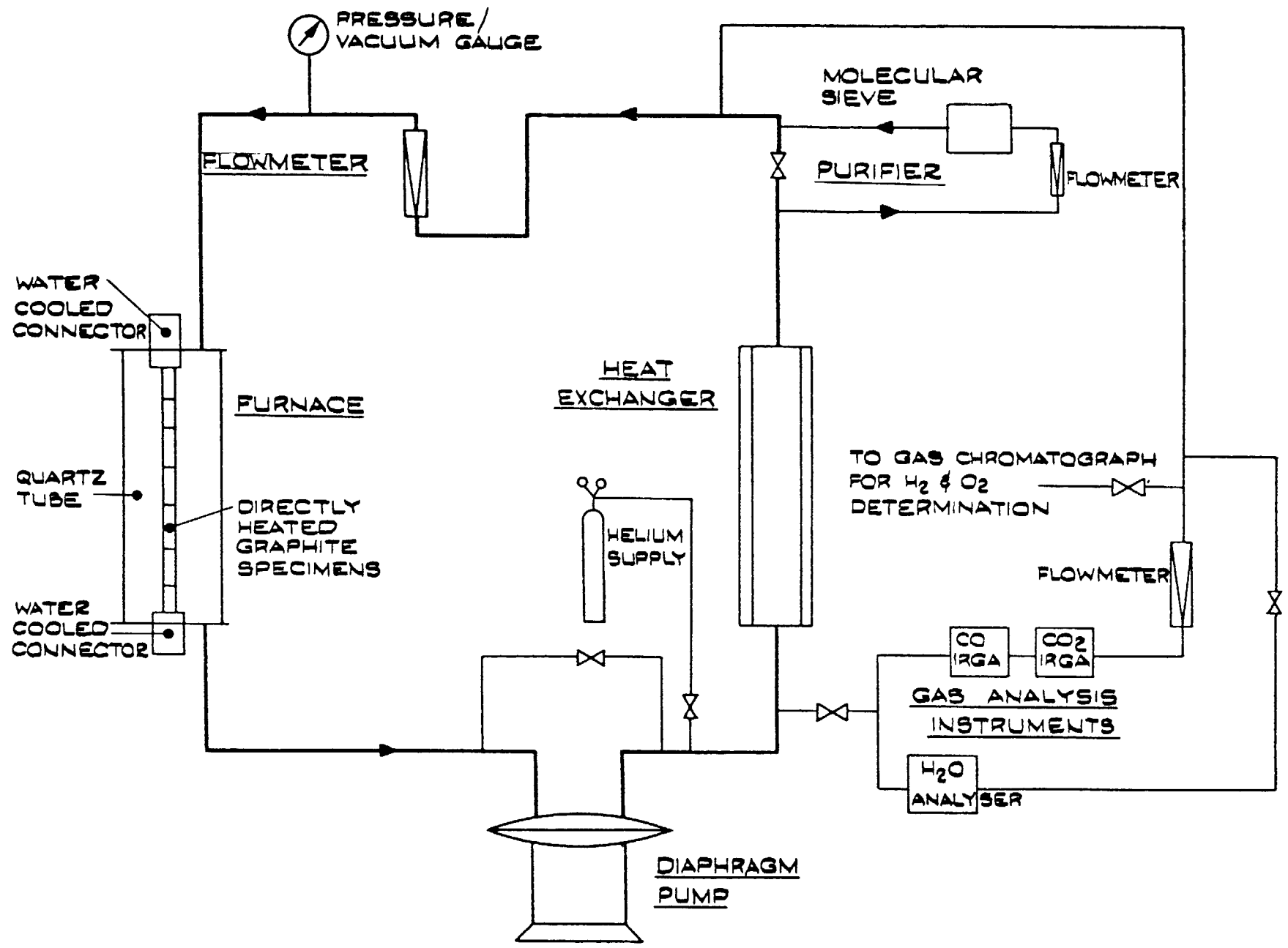
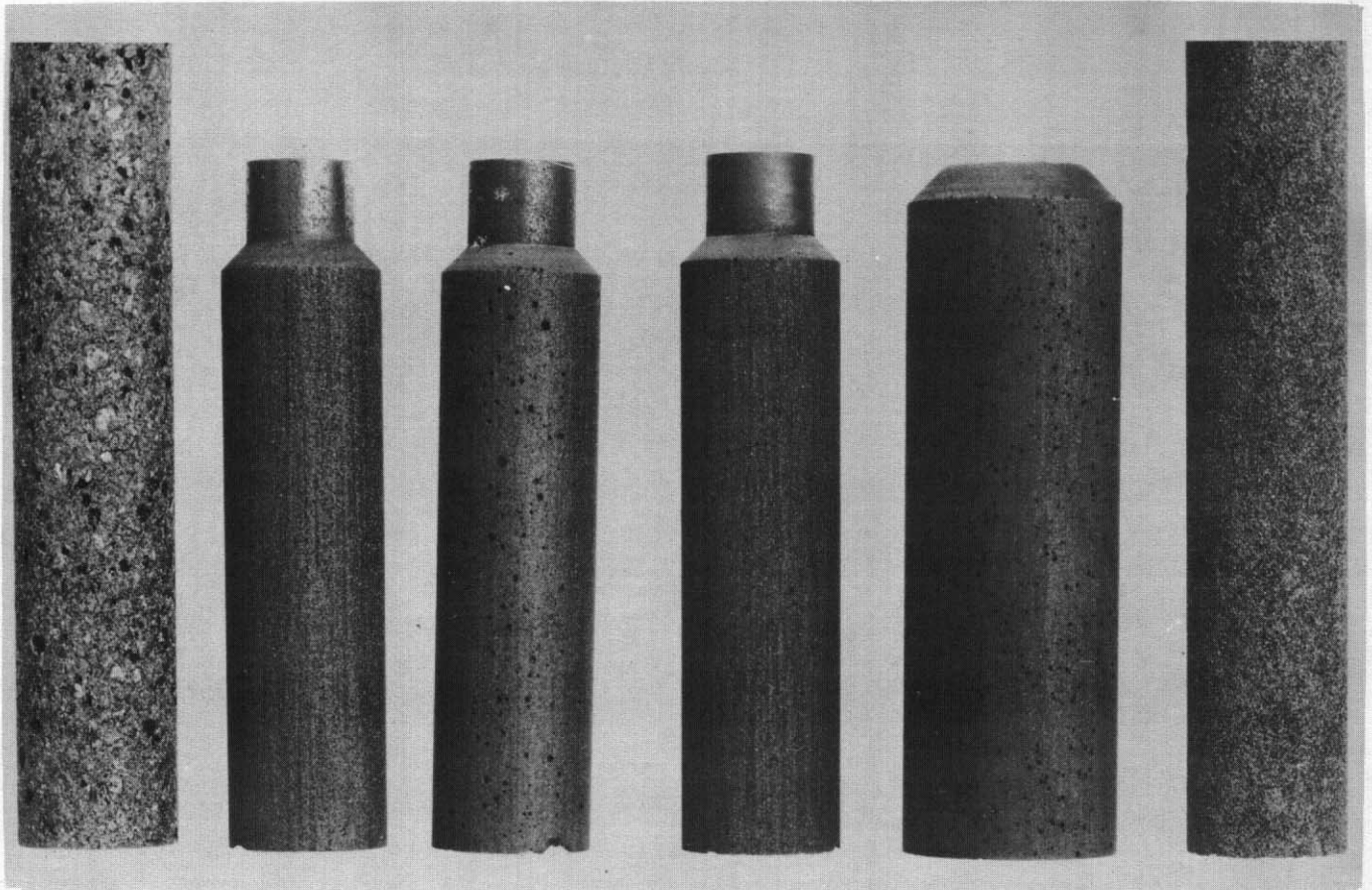


FIG. 4 SIMPLIFIED FLOW SHEET FOR GRAPHITE CORROSION LOOP.



GRADE
0

1

3

3 SPECIAL

9

SPECTRO

FIG. 5. EXAMPLES OF PITTING CORROSION IN VARIOUS GRADES OF GRAPHITE
(MAGNIFICATION APPROX. 2X)

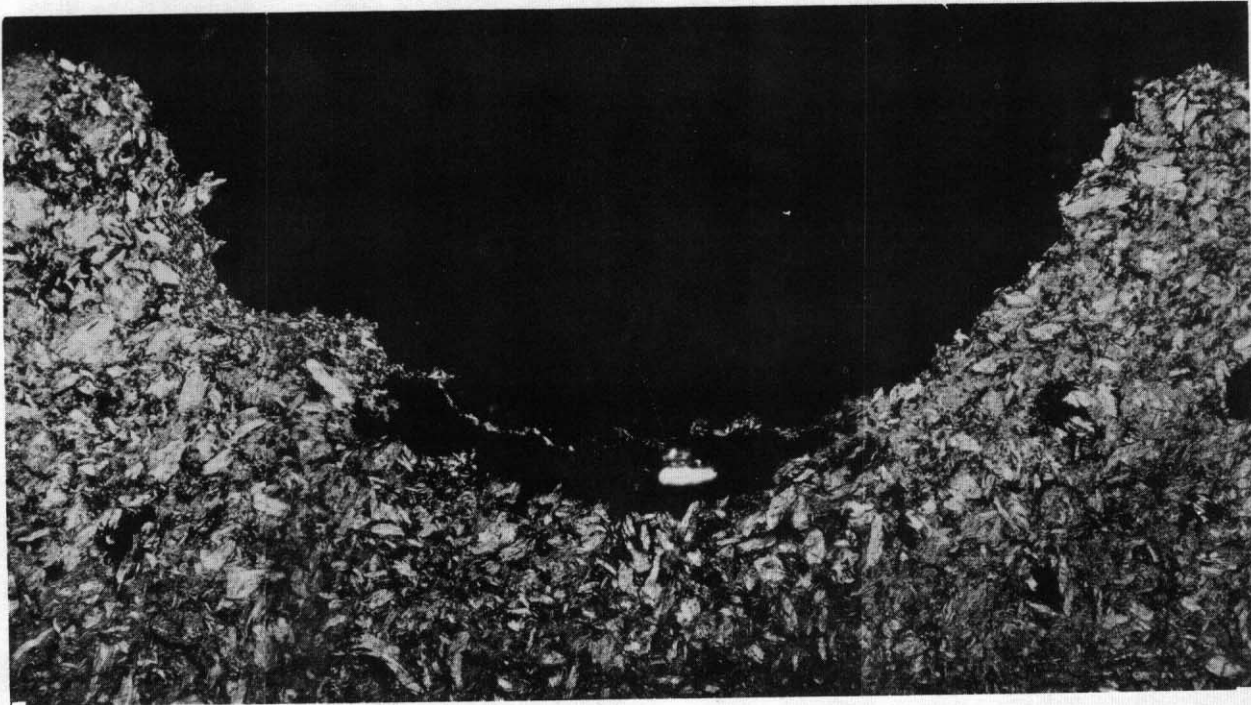
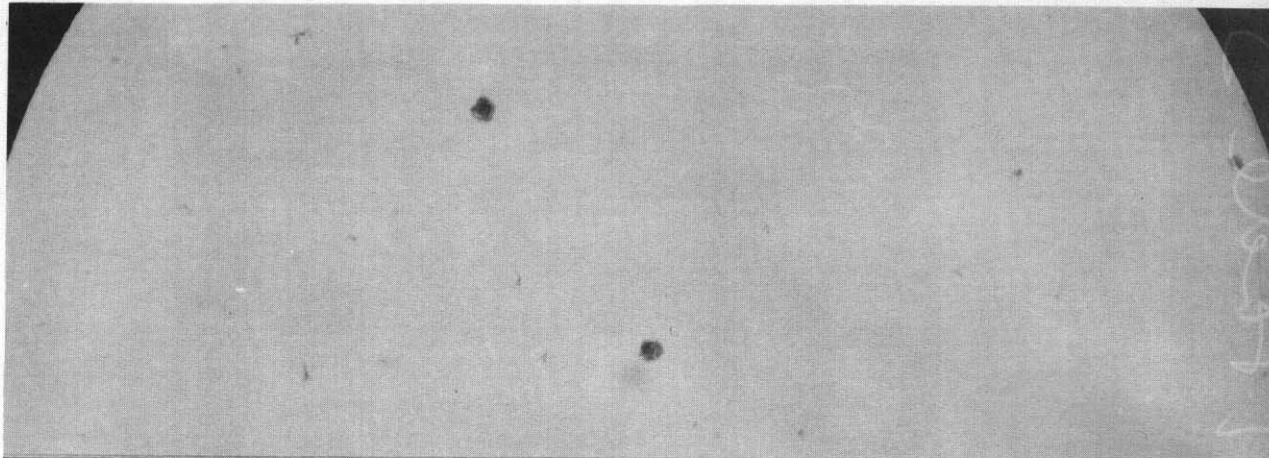
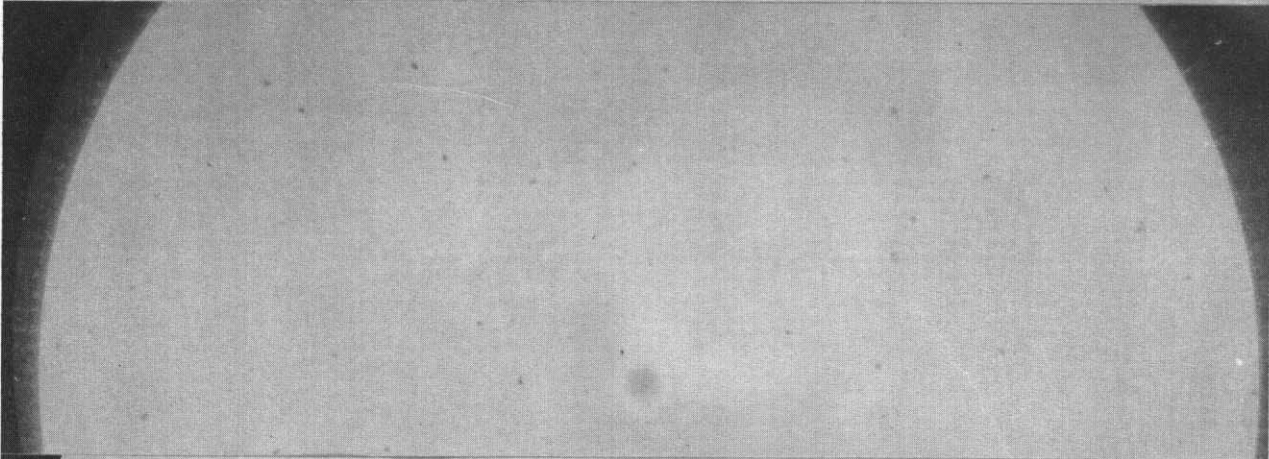


FIG. 6. SECTION THROUGH A CORROSION PIT, GRADE 9 GRAPHITE.
MAGNIFICATION APPROX. 125X.

GRADE 3



GRADE 9



GRADE G.5

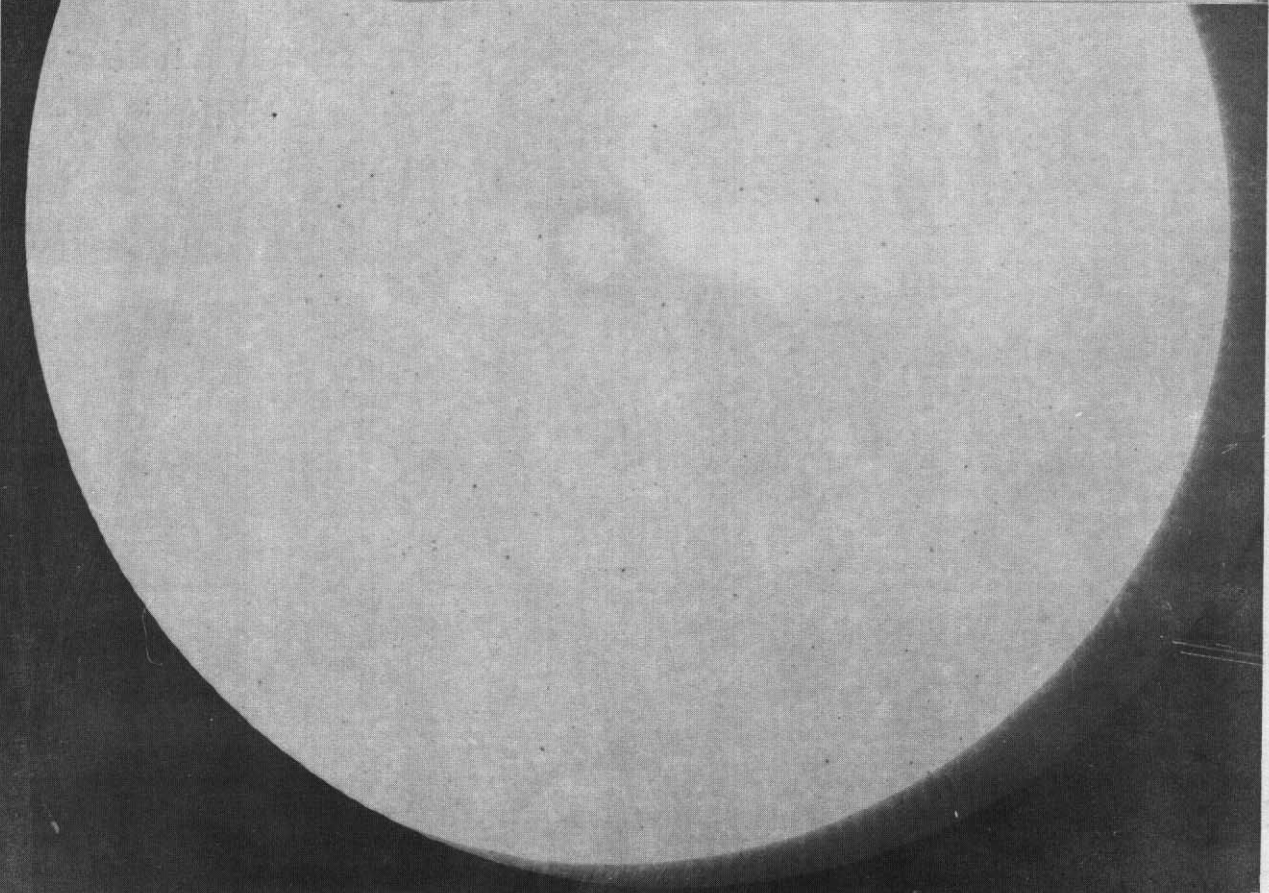


FIG. 7. MICRORADIOGRAPHS OF DRAGON GRADE GRAPHITES.
MAGNIFICATION APPROX. 8X.

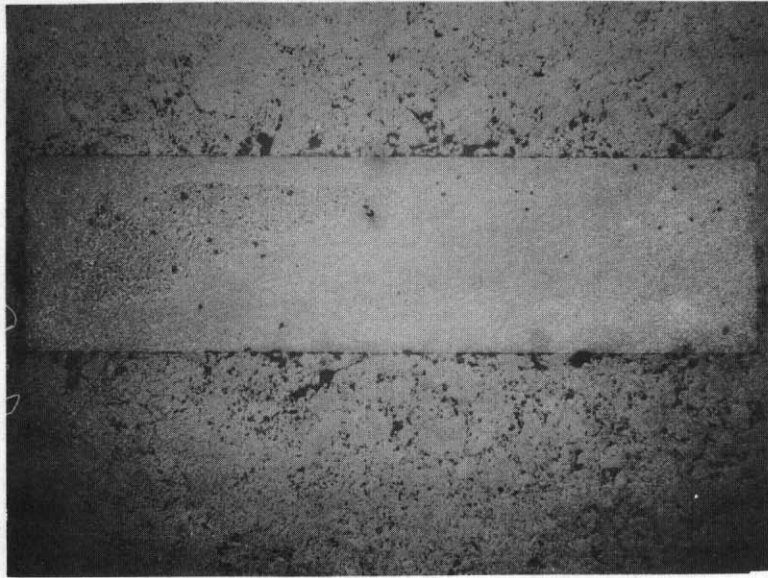


FIG. 8. SECTION OF GRADE 9 GRAPHITE AFTER 4% BURN-OFF IN CO_2
MAGNIFICATION 6.4X

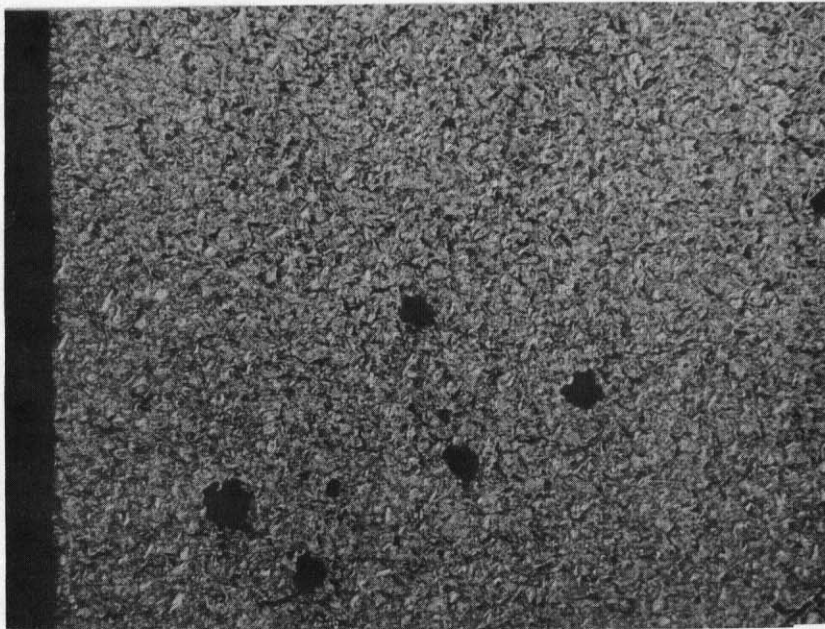


FIG. 9. SECTION OF GRADE 9 GRAPHITE AFTER 2% BURN-OFF IN H_2O
MAGNIFICATION 35X

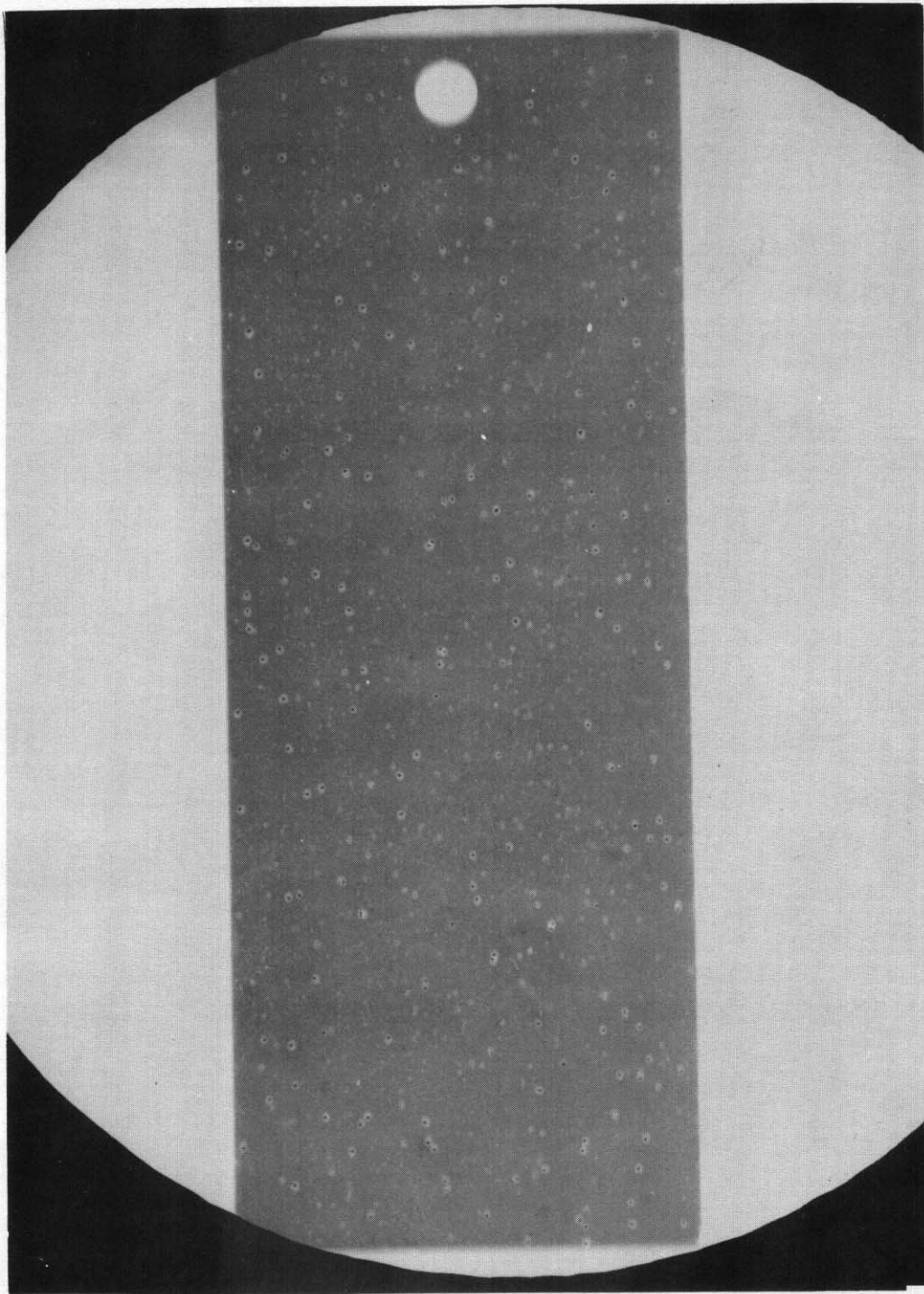


FIG. 10. MICRORADIOGRAPH OF GRADE 9 GRAPHITE AFTER 9% BURN-OFF IN H_2O
MAGNIFICATION 4.4X

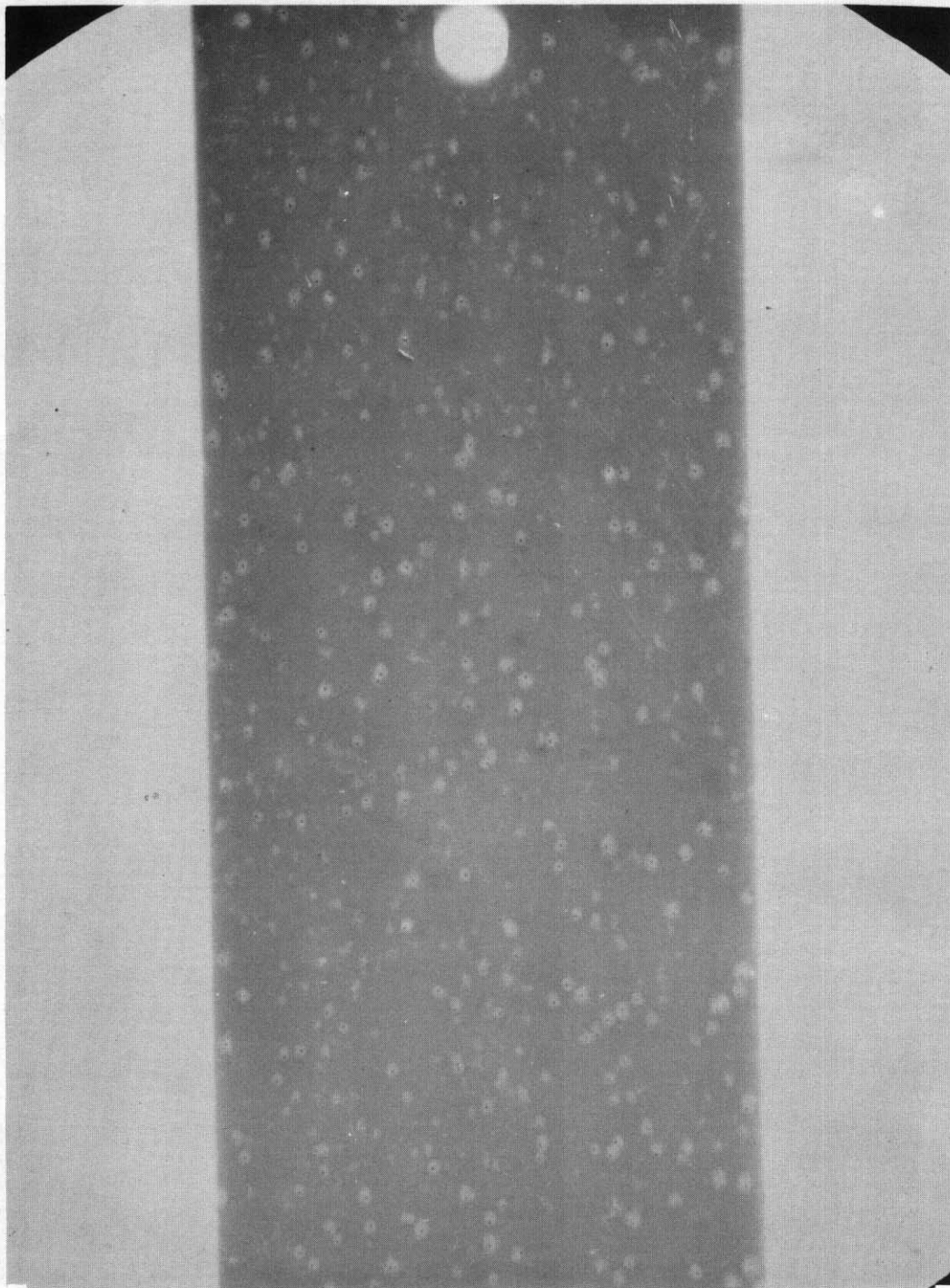


FIG. 11. MICRORADIOGRAPH OF GRADE 9 GRAPHITE (HEAT TREATED AT 2000°C)
AFTER 7.6% BURN-OFF MAGNIFICATION 5X

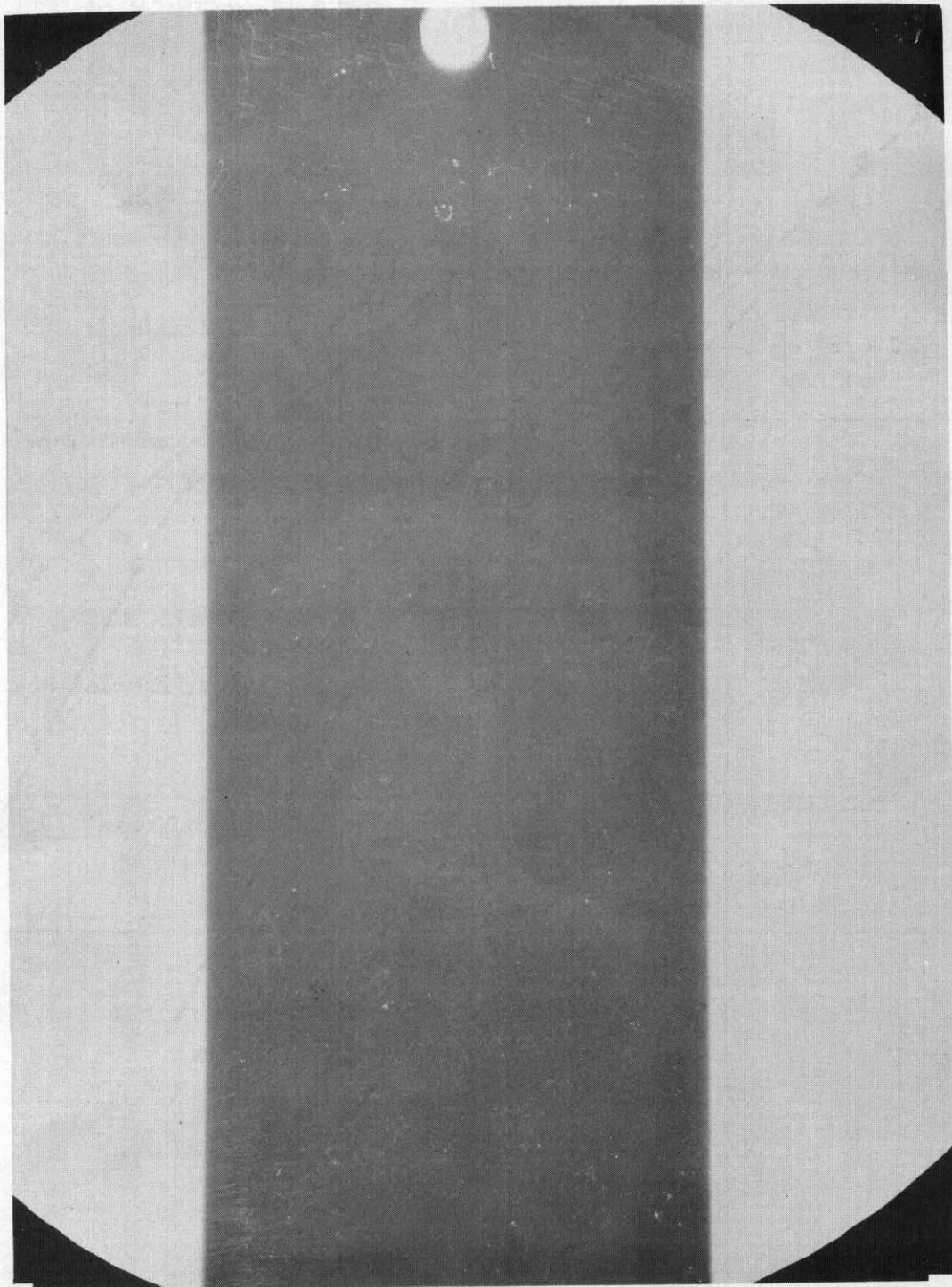


FIG. 12. MICRORADIOGRAPH OF GRADE 9 GRAPHITE (HEAT TREATED AT 2950°C)
AFTER 6.5% BURN-OFF MAGNIFICATION 5X

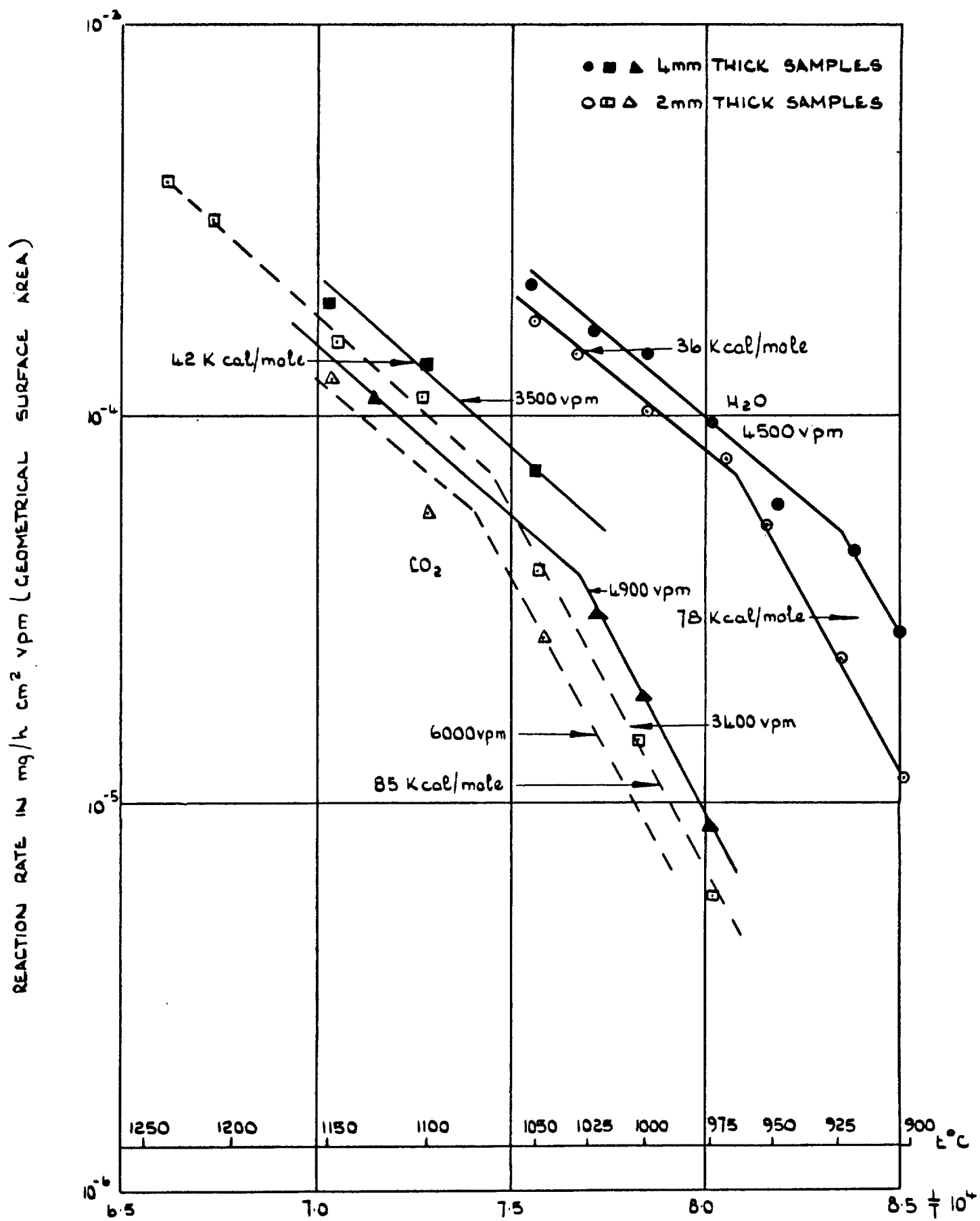


FIG. 13 REACTION RATE OF GRADE 9 GRAPHITE WITH H₂O AND CO₂

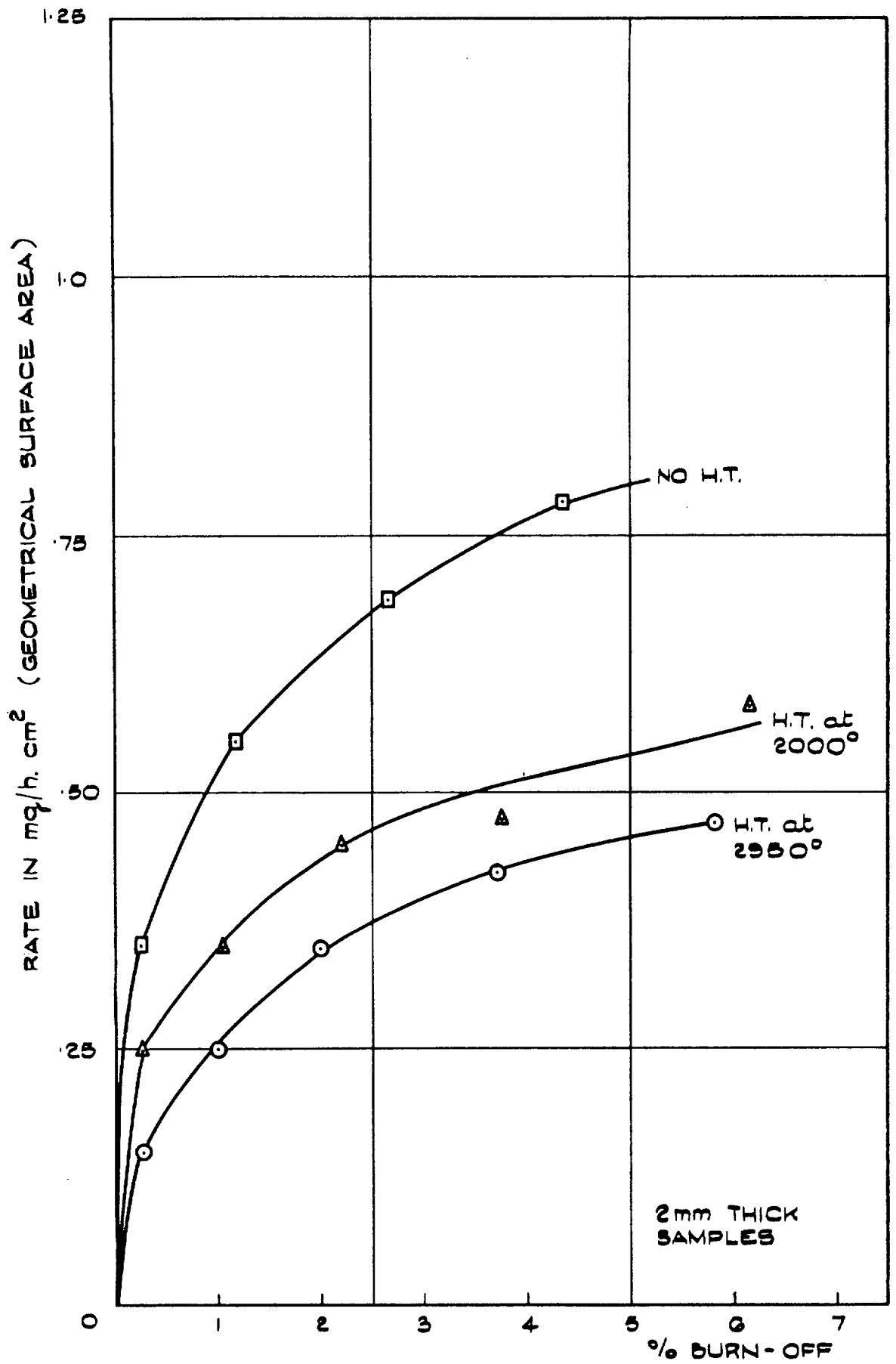


FIG.14 REACTION RATE OF HEAT TREATED GRADE 9 IN 3.4 TORR H₂O AT 1050°C

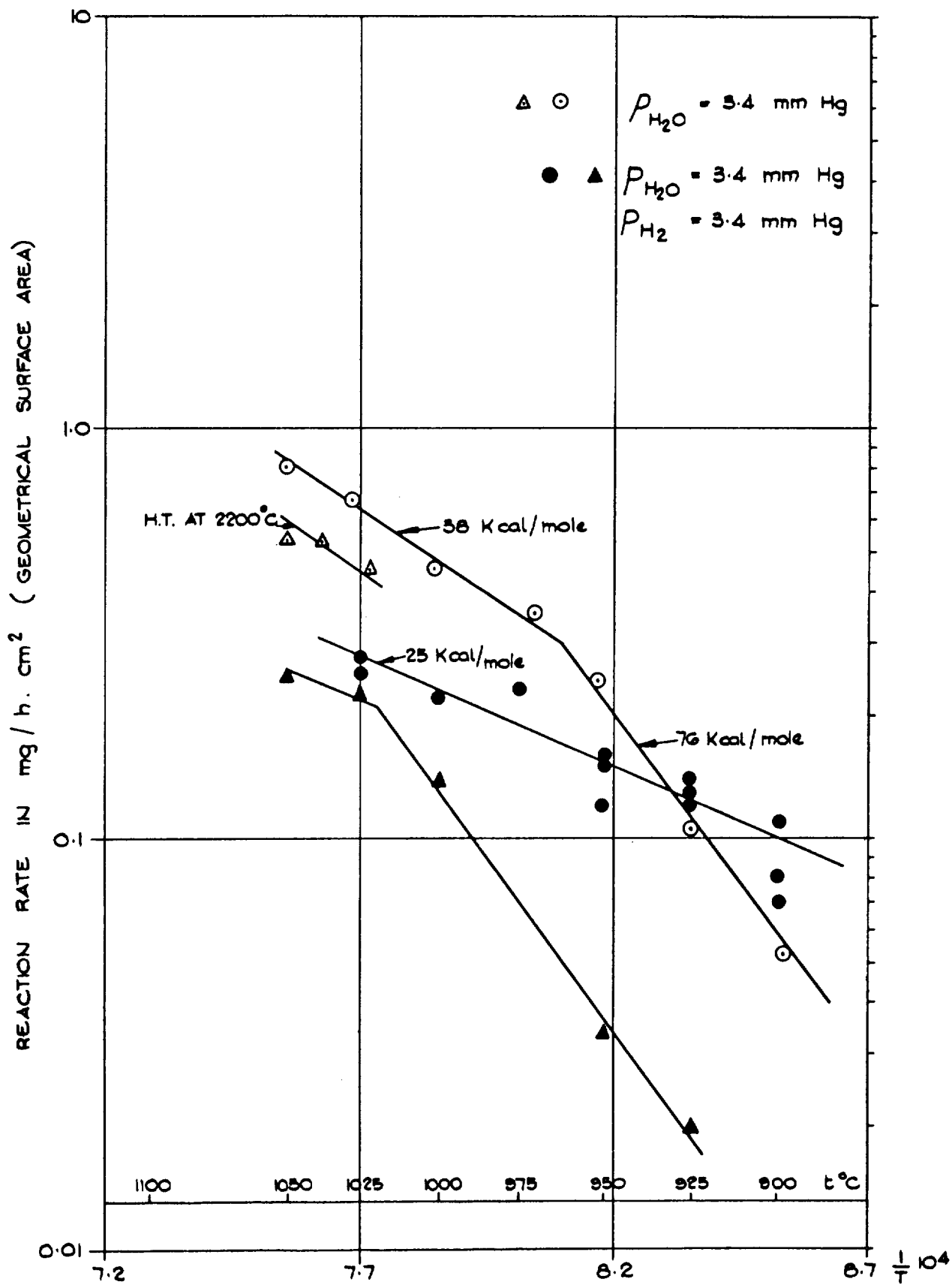


FIG.15 REACTION RATE OF GRADE 9 GRAPHITE WITH H₂O
 AND 50% H₂O - 50% H₂ MIXTURE.
 (2mm. THICK SAMPLES - 5% BURN-OFF)

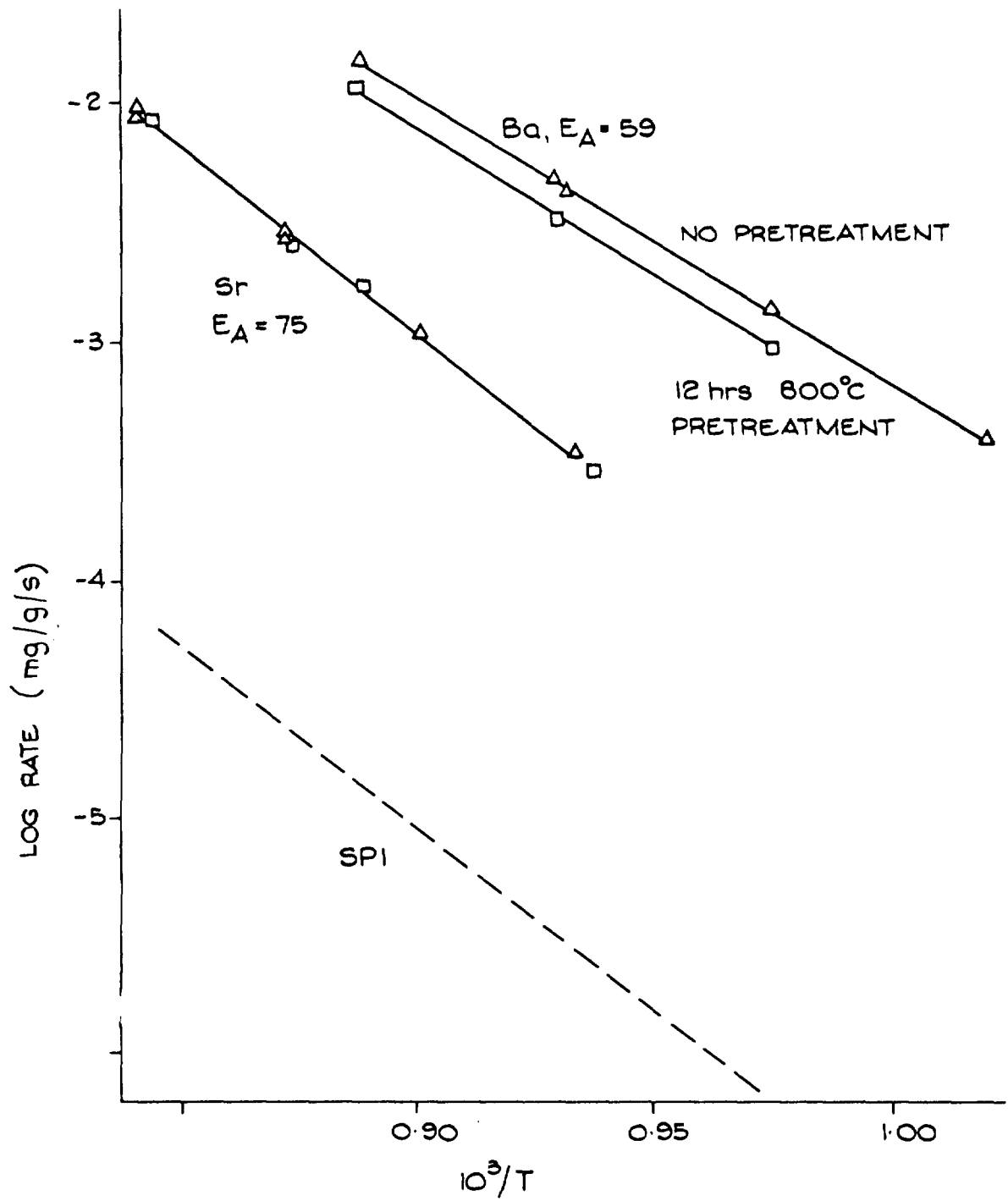


FIG. 16 ACTIVATION ENERGY OF Ba AND Sr IMPREGNATED SP-1, GRAPHITE 0.05% Ba OR Sr

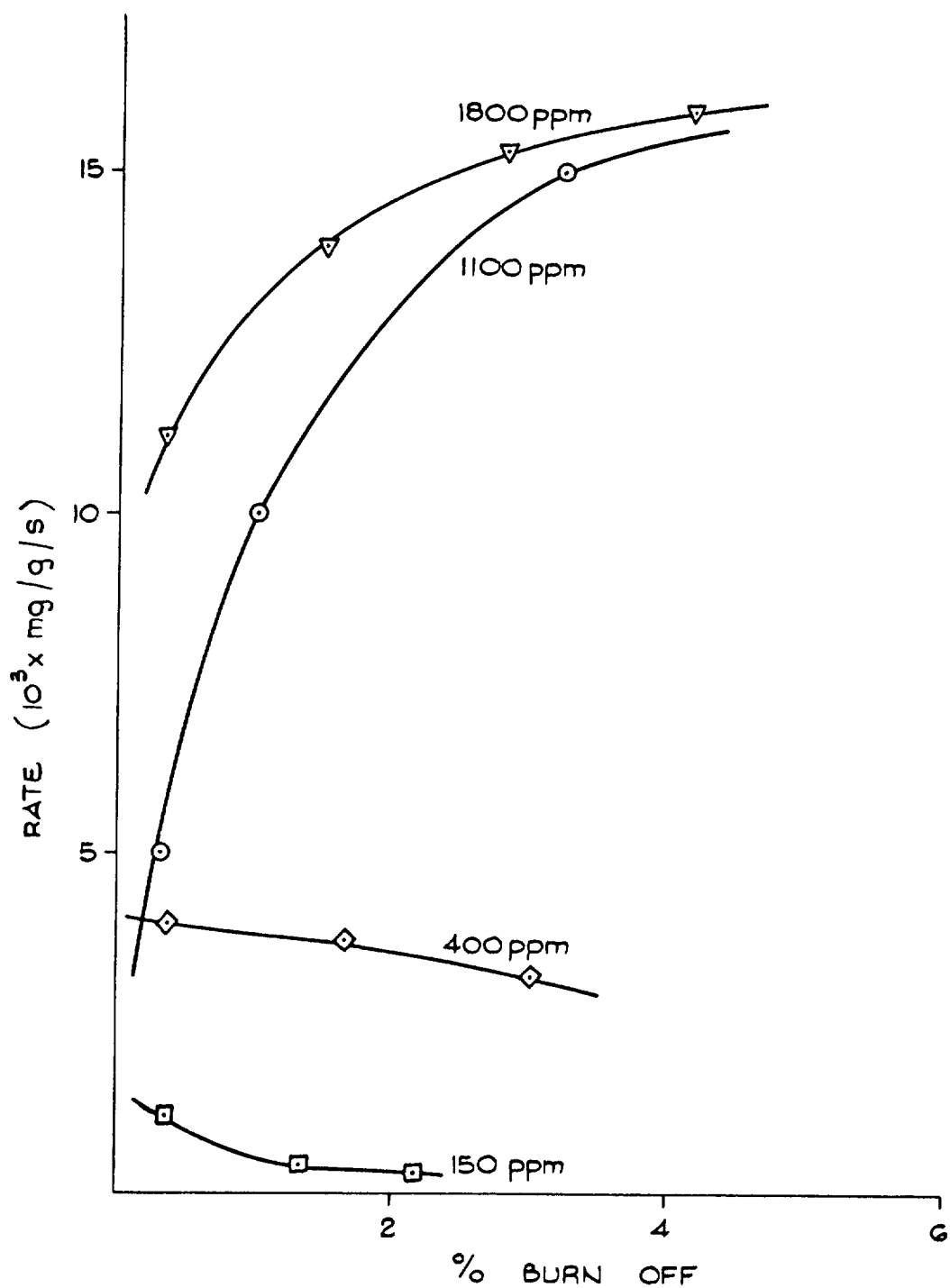


FIG. 17 EFFECT OF BARIUM CONCENTRATION ON CATALYSIS OF SP-1 GRAPHITE. OXIDATION AT 850 °C IN 2.7 Torr H₂O NO PRETREATMENT.

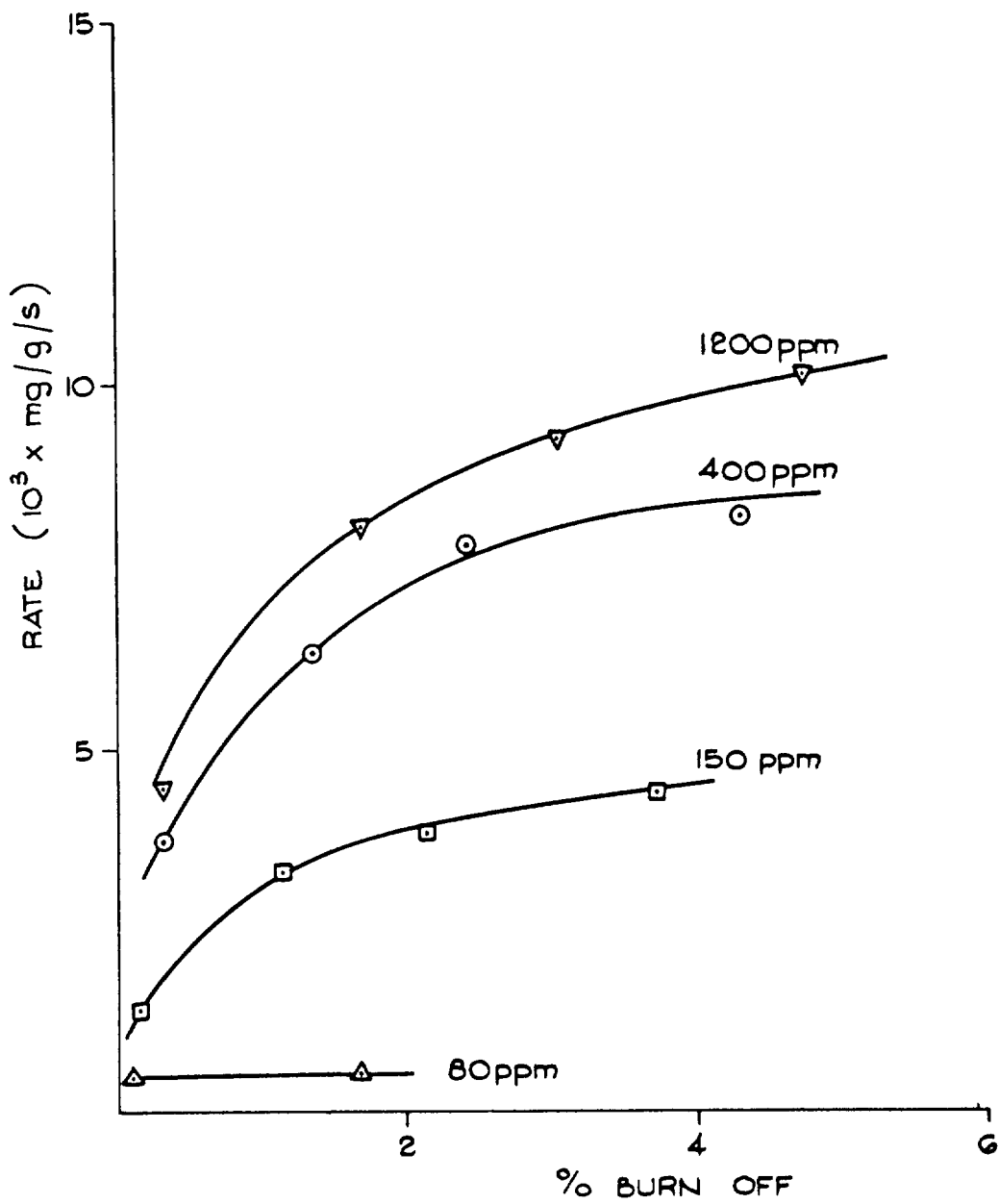


FIG. 18 EFFECT OF STRONTIUM CONCENTRATION ON CATALYSIS OF SP-1 GRAPHITE. OXIDATION AT 912 °C IN 2.7 Torr H₂O, NO PRETREATMENT.

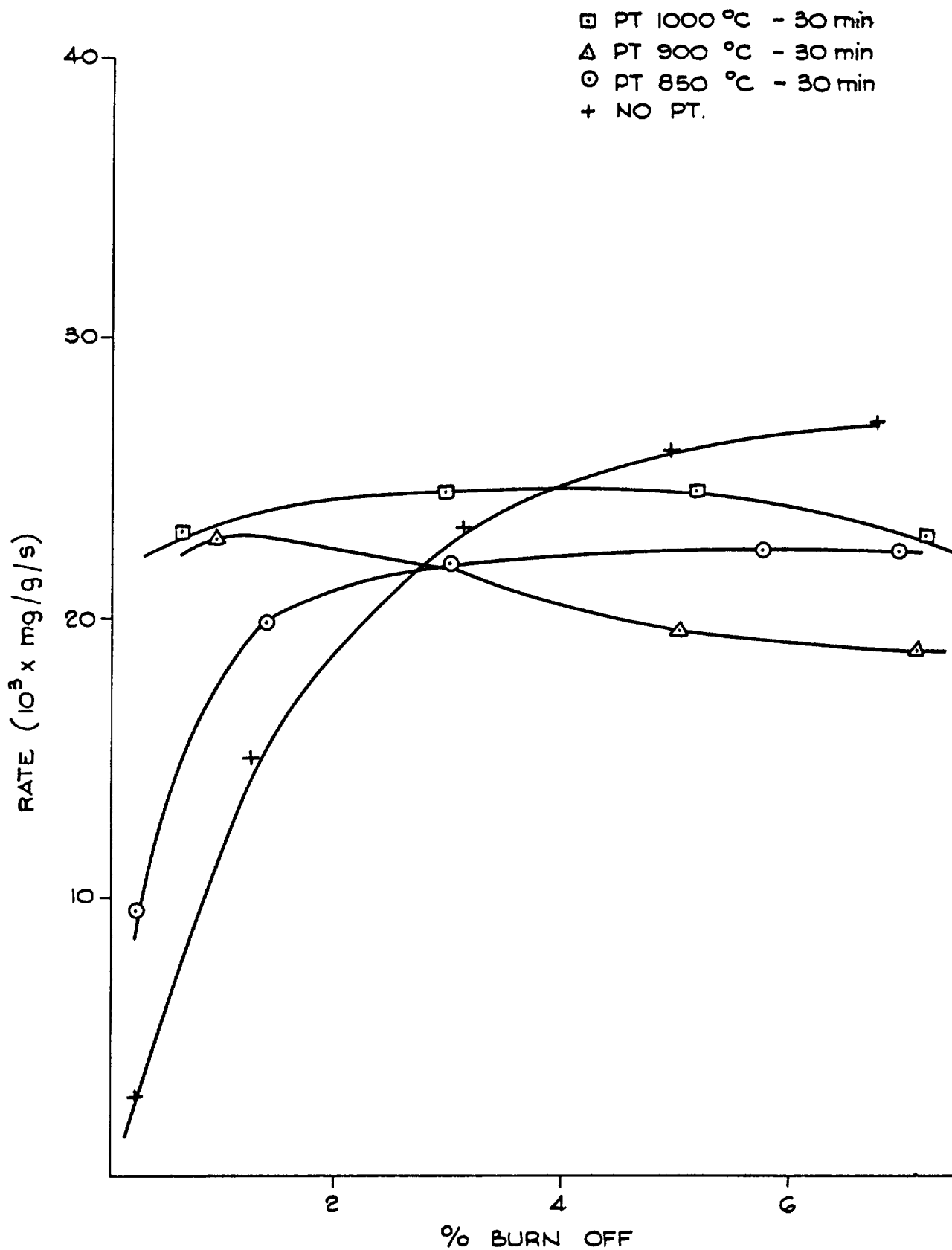


FIG. 19 EFFECT OF PRETREATMENT
 ON Fe CATALYSIS OF SPI
 OX. 850 °C, 0.3 Torr, 600 ppm Fe

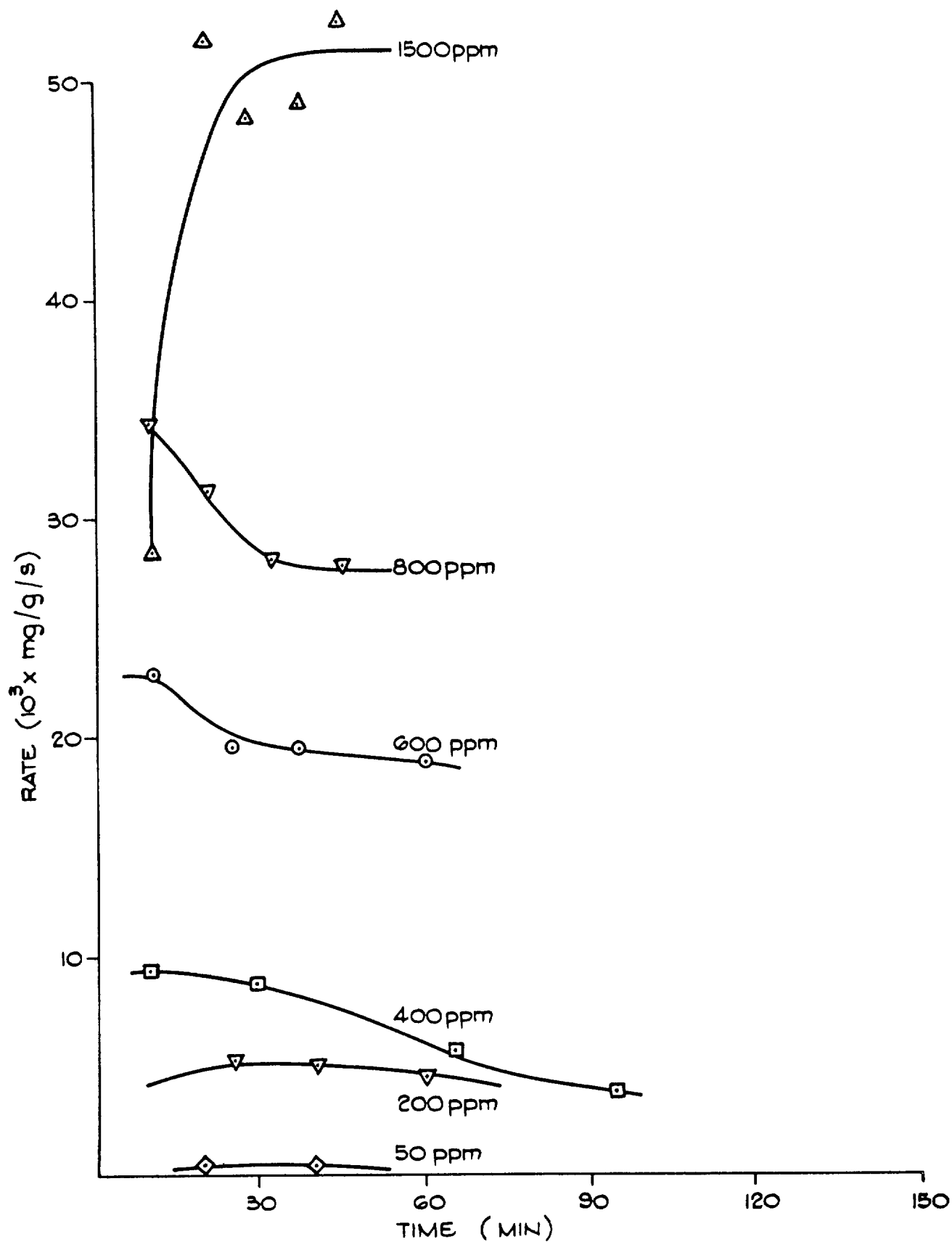


FIG. 20 EFFECT OF Fe - CONCENTRATION ON Fe - CATALYSIS OF SPI.
 PT 900 °C 1/2 h, ox. 850 °C p = 0.3 Torr

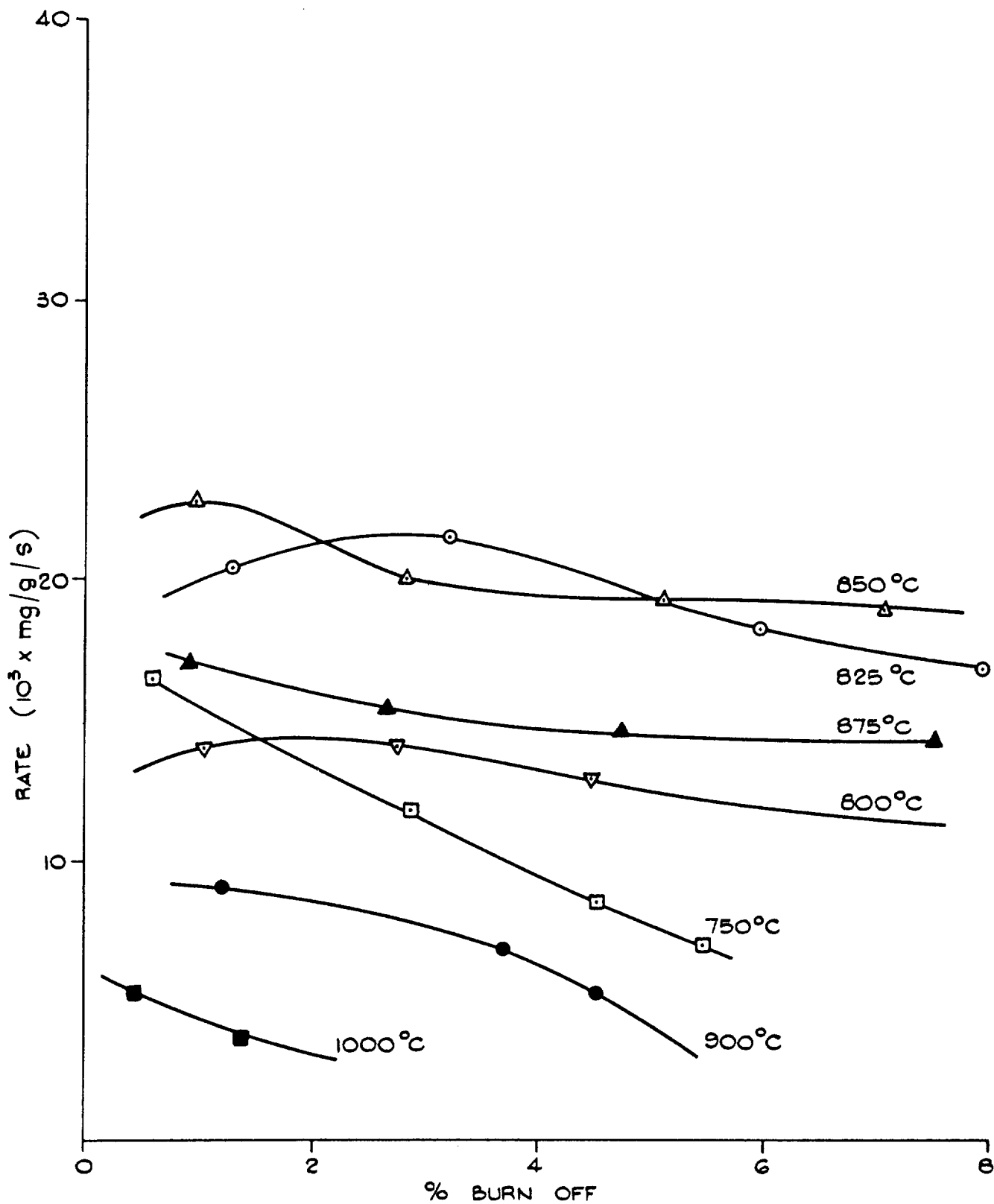


FIG. 21 EFFECT OF OXIDATION TEMPERATURE ON
 Fe CATALYSIS OF SPI .
 p = 0.3 Torr , 600 ppm Fe ■ : PT 1000°C , 1/2 h
 THE REST : PT 900°C , 1/2 h

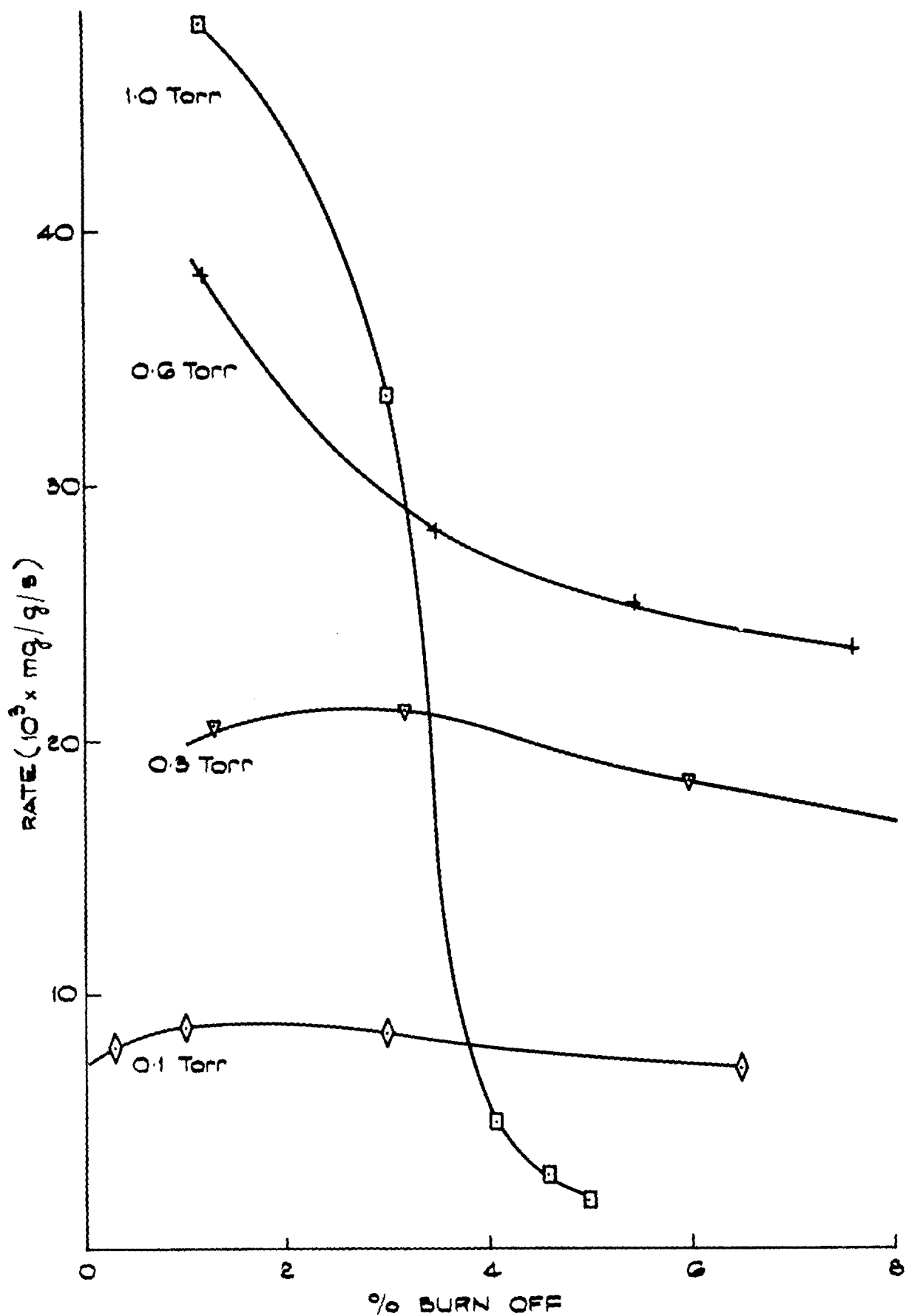


FIG. 22 EFFECT OF WATER VAPOUR PRESSURE ON Fe-CATALYSIS OF SP-1. PT 900 1/2 hr, 600 ppm Fe OX. 825°C

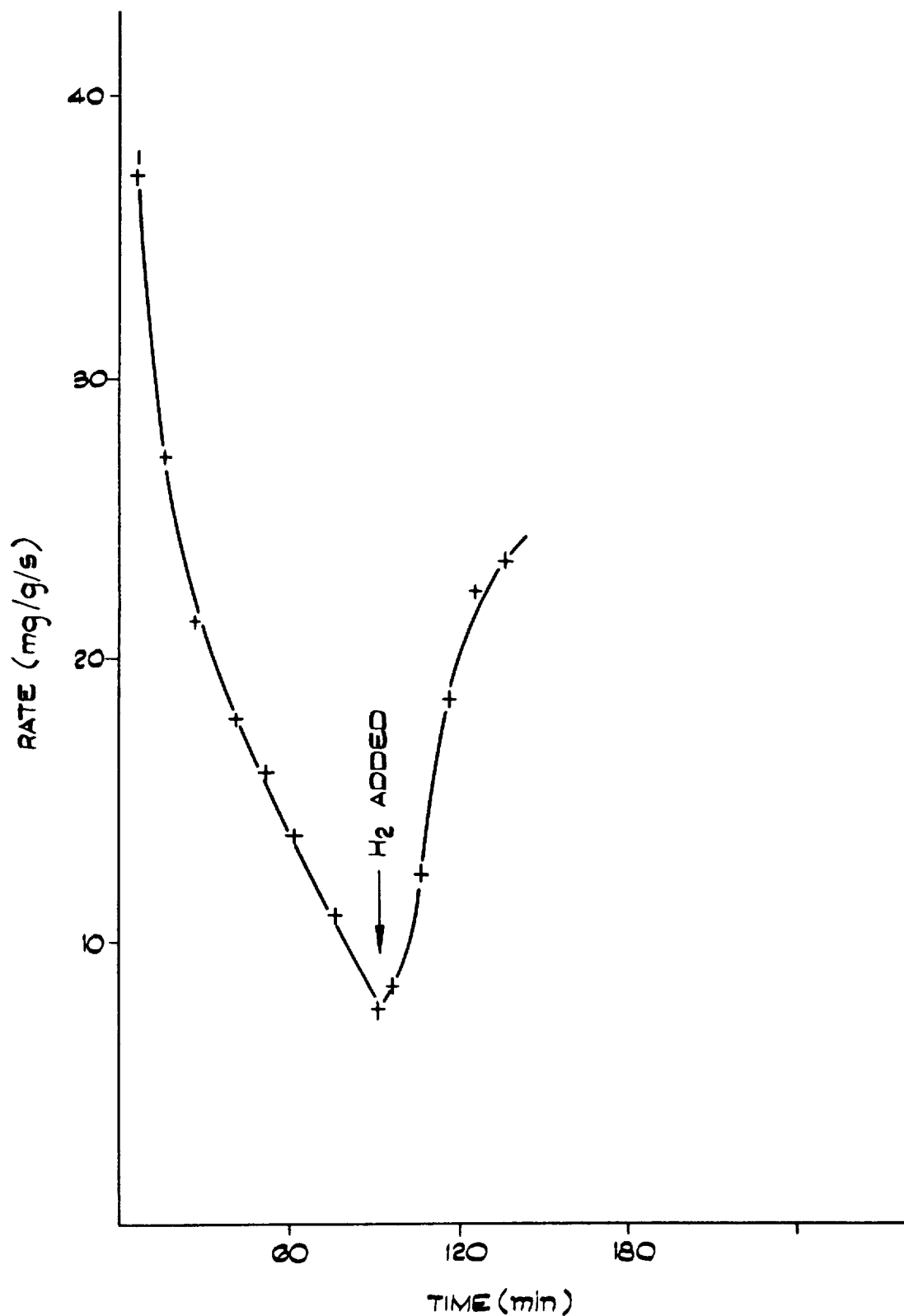


FIG. 23 EFFECT OF ADDING H_2 IN $Fe/H_2O/c$
 REACTION $PT900^\circ C$ $\frac{1}{2}$ hr OXIDATION TEMP. $780^\circ C$
 $P_{H_2O} = 0.6$ Torr, $P_{H_2} = 0.7$ Torr 600 ppm Fe (impr)
 SP-1 GRAPHITE POWDER

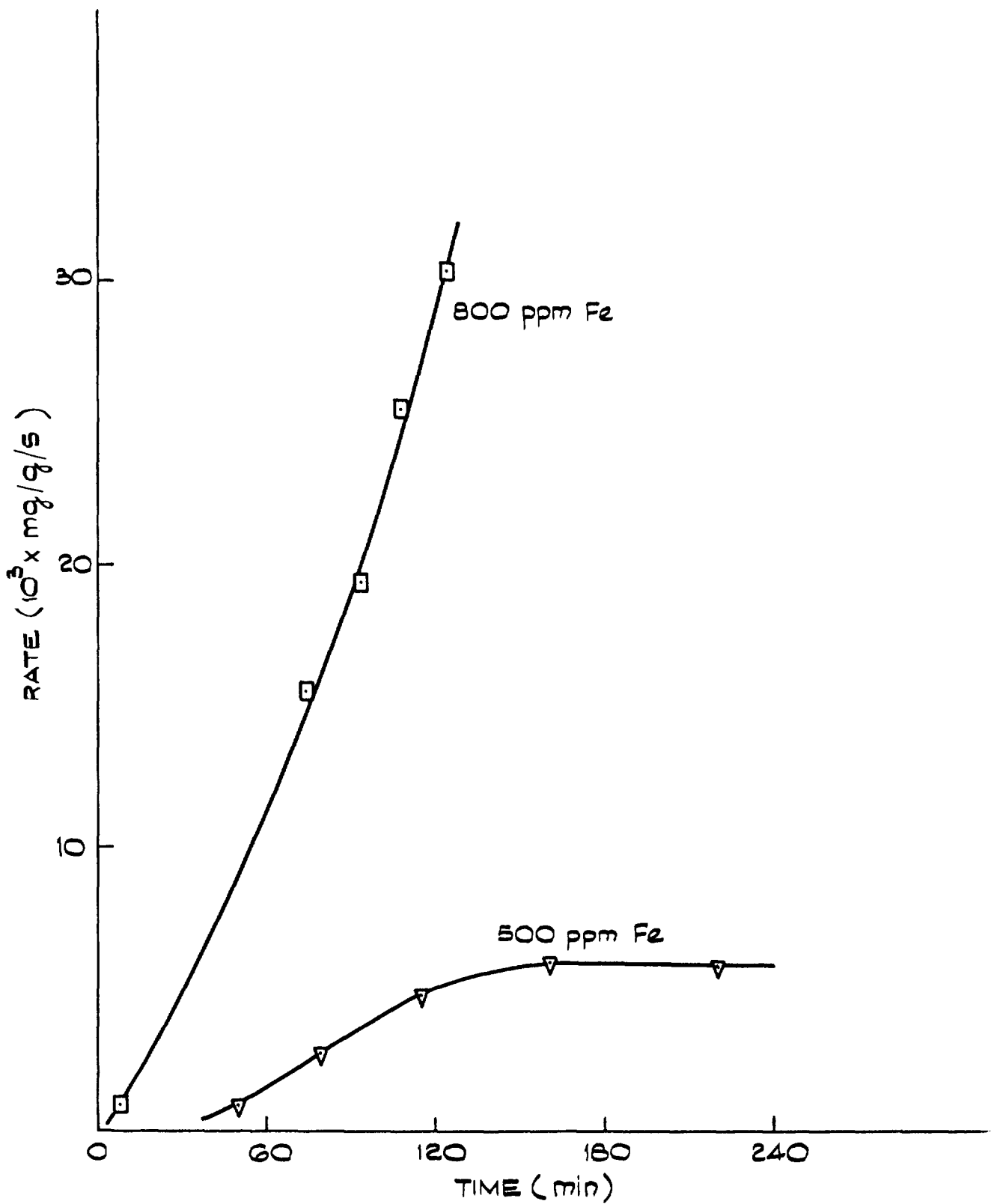


FIG. 24 EFFECT OF IRON CONCENTRATION ON CATALYSIS OF G5 GRAPHITE CYLINDERS. PT 900°C
 15 hrs, OX 850°C P = 0.3 Torr

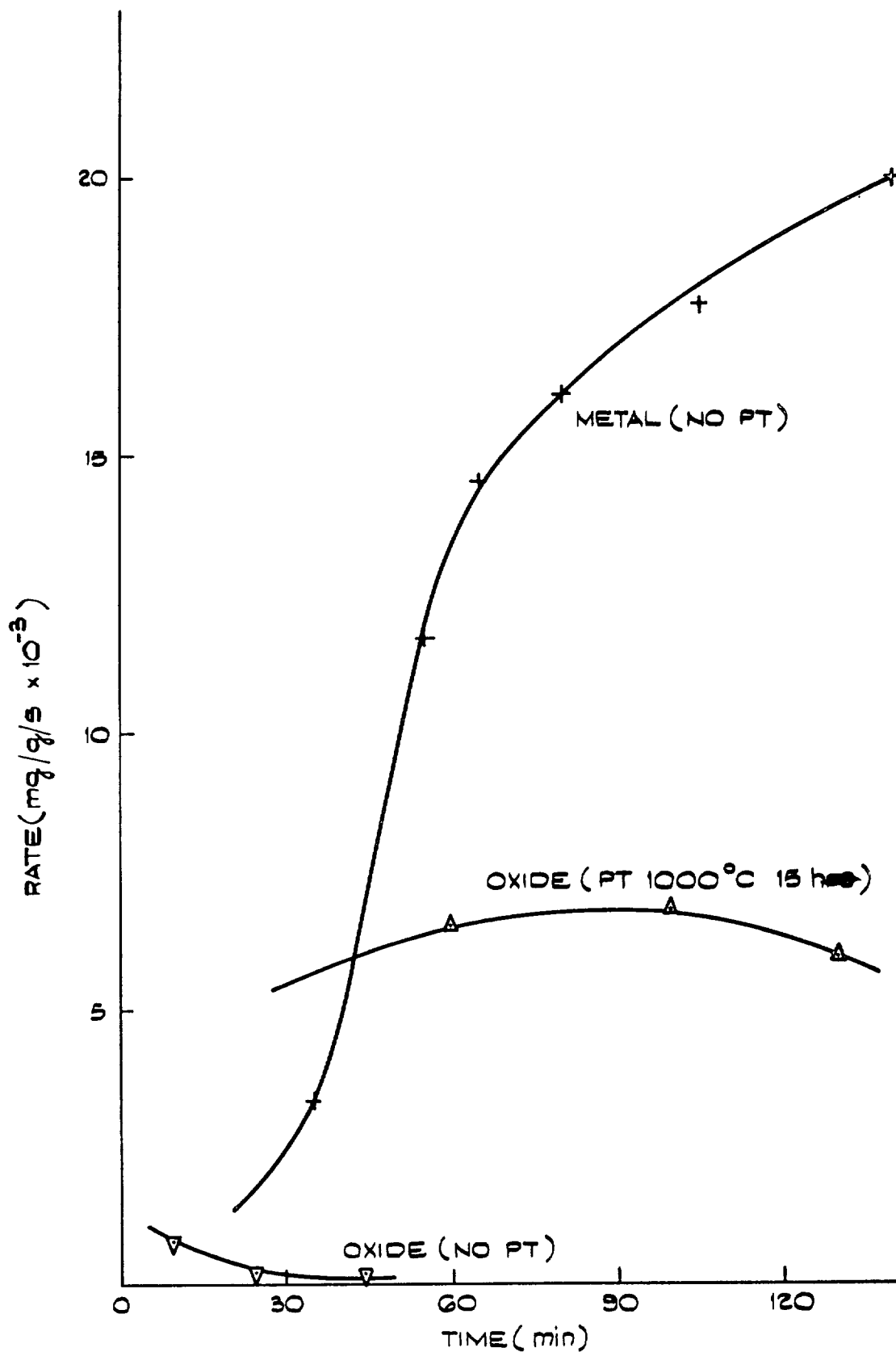


FIG. 25 COMPARISON BETWEEN METALLIC IRON & IRON OXIDE. ON CATALYSIS OF SPI. OX TEMP 850°C P_{H₂O} : 0.3 Torr 1% Fe (ADDED AS POWDER)

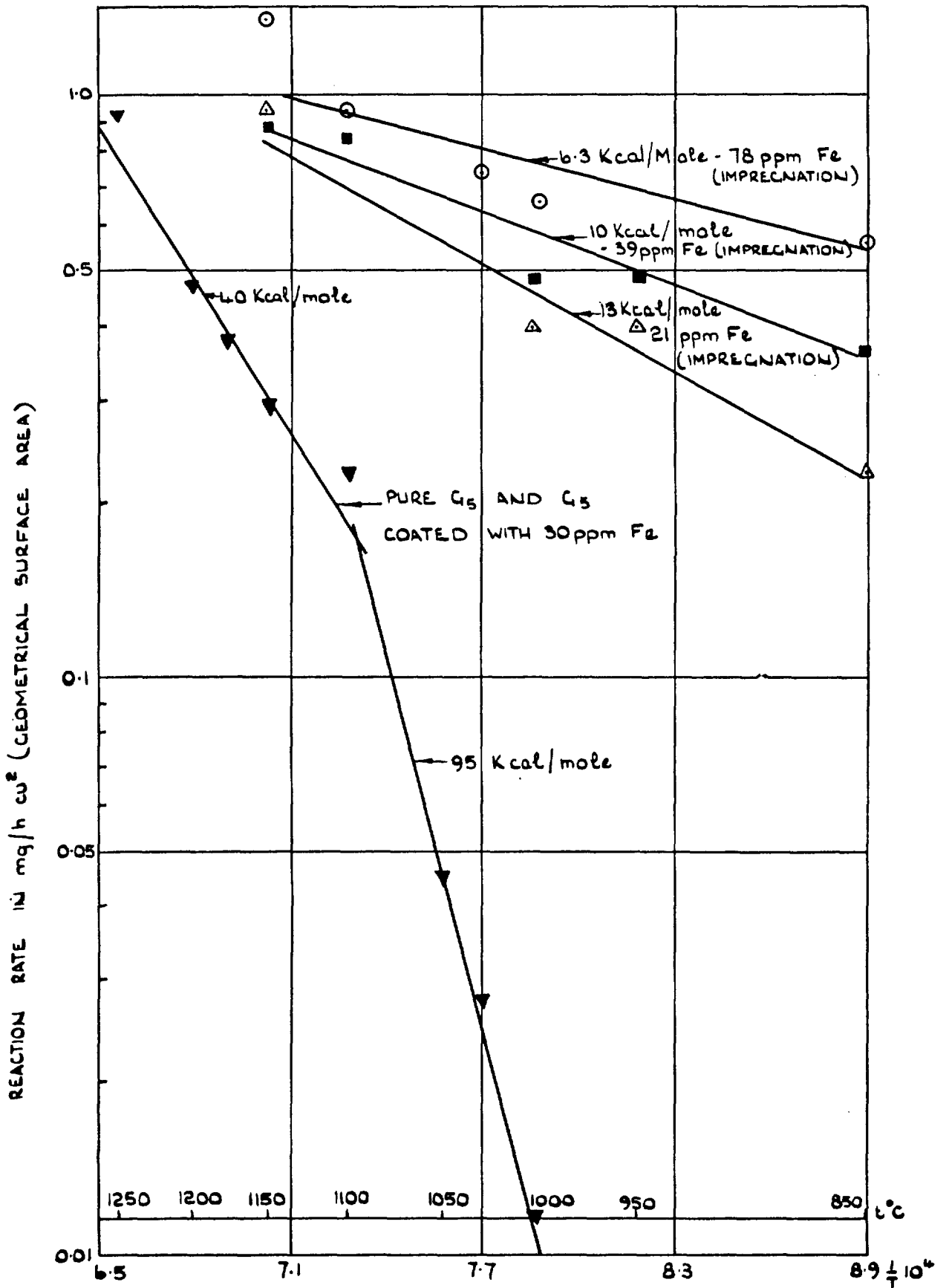


FIG. 26 REACTION RATE OF PURIFIED AND Fe IMPREGNATED G5 GRAPHITE IN 3000 vpm CO₂ AFTER 7% BURN-OFF.

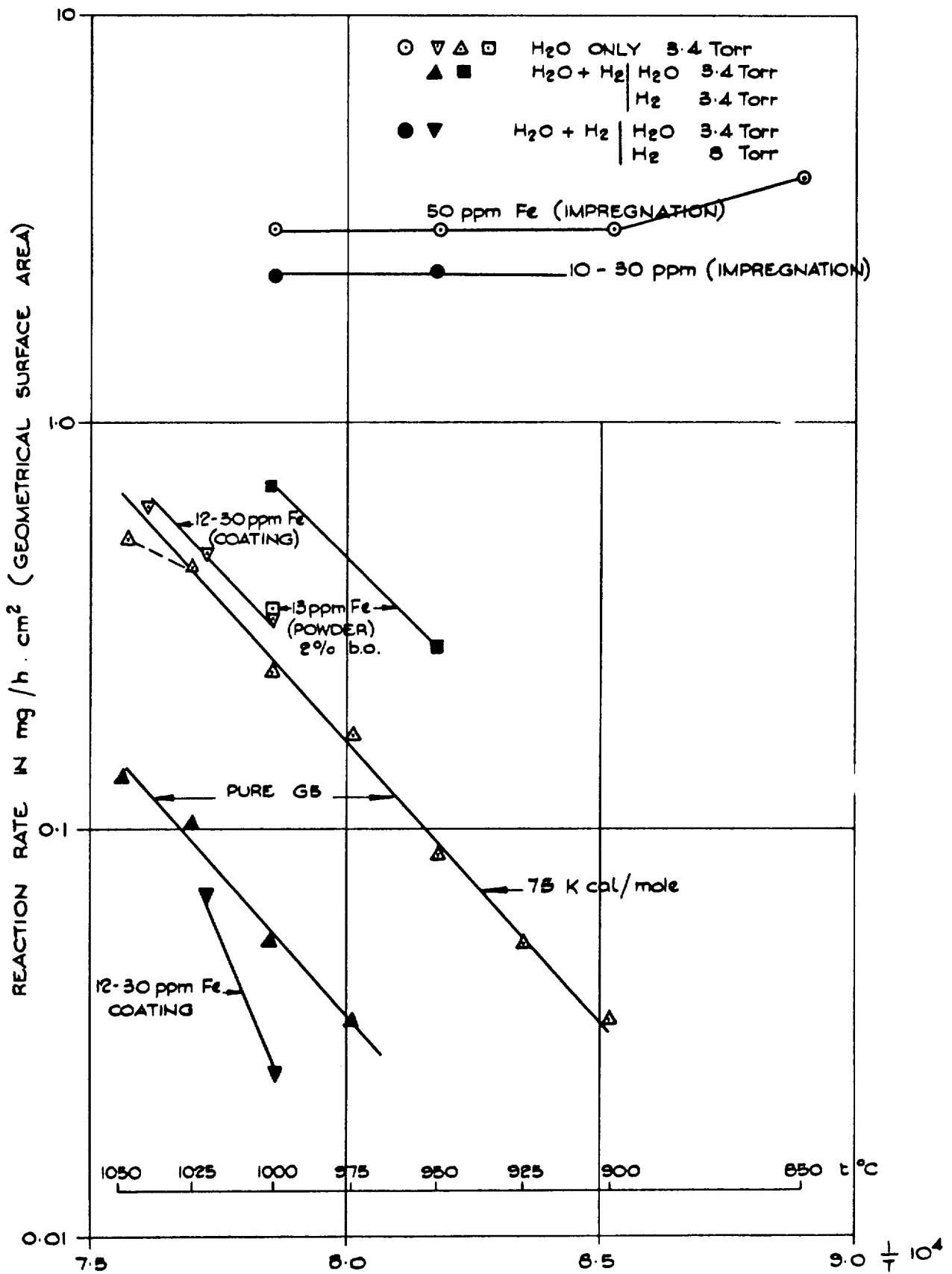


FIG. 27 REACTION RATE OF PURIFIED AND Fe IMPREGNATED G5 GRAPHITE IN H₂O AND H₂O + H₂ - AFTER 7% BURN-OFF.

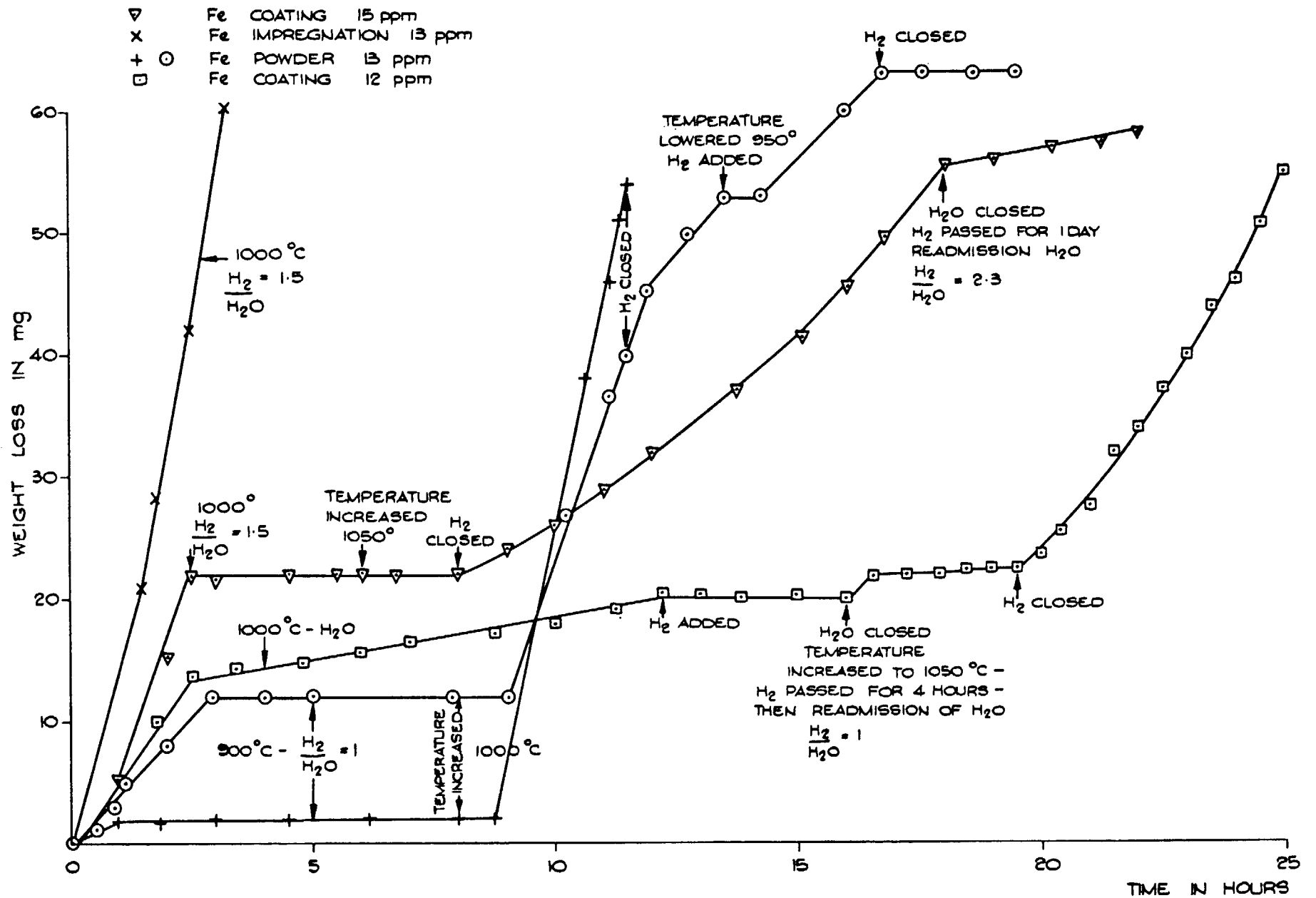


FIG. 28 COMPARISON OF BEHAVIOUR OF DIFFERENT Fe - GRAPHITE SAMPLES ACCORDING TO THE WAY OF CONTAMINATING.

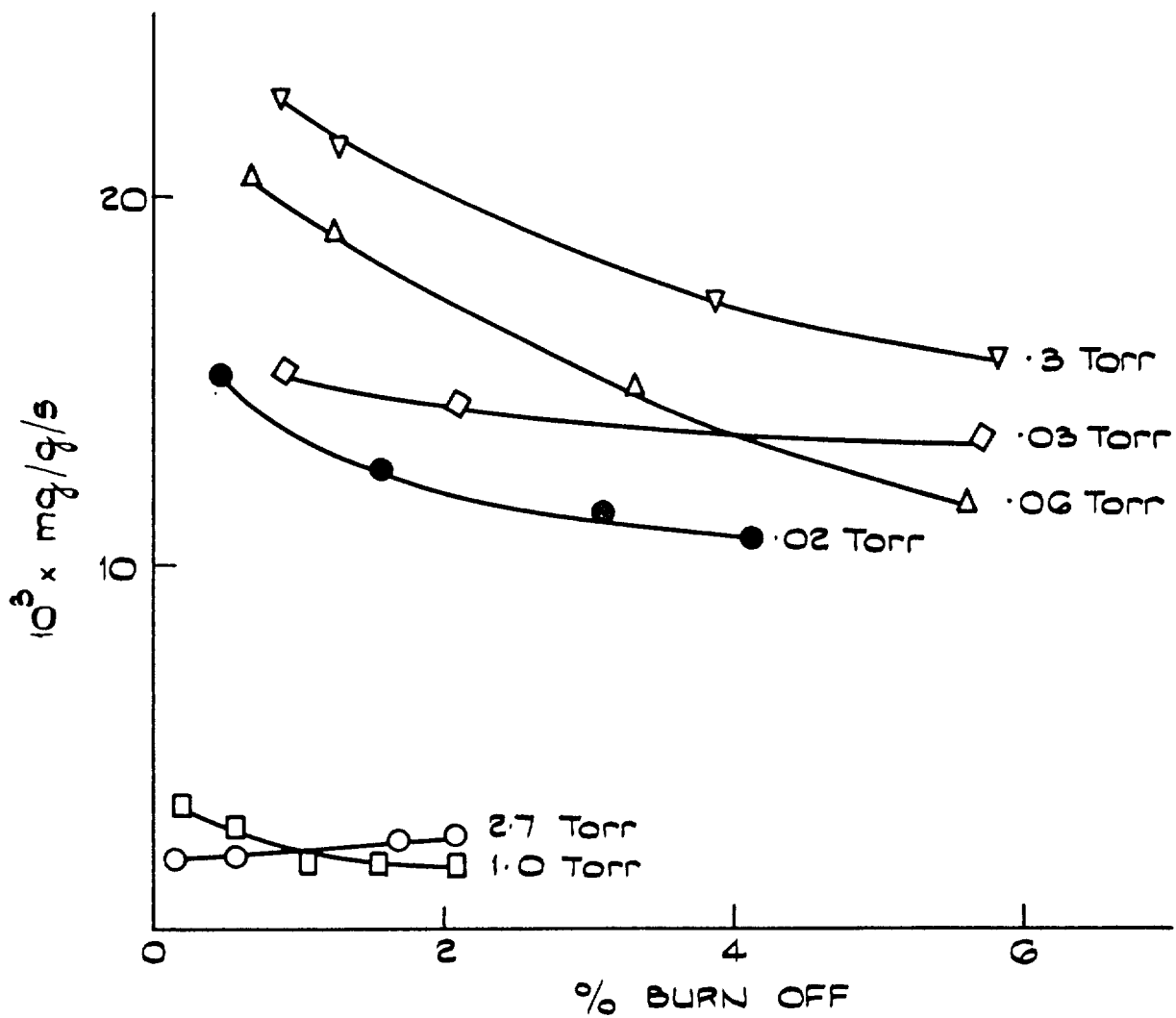


FIG. 29 EFFECT OF PRESSURE OF H₂O ON OXIDATION OF V-GRAPHITE

OX AT 1060°C
0.1 % V

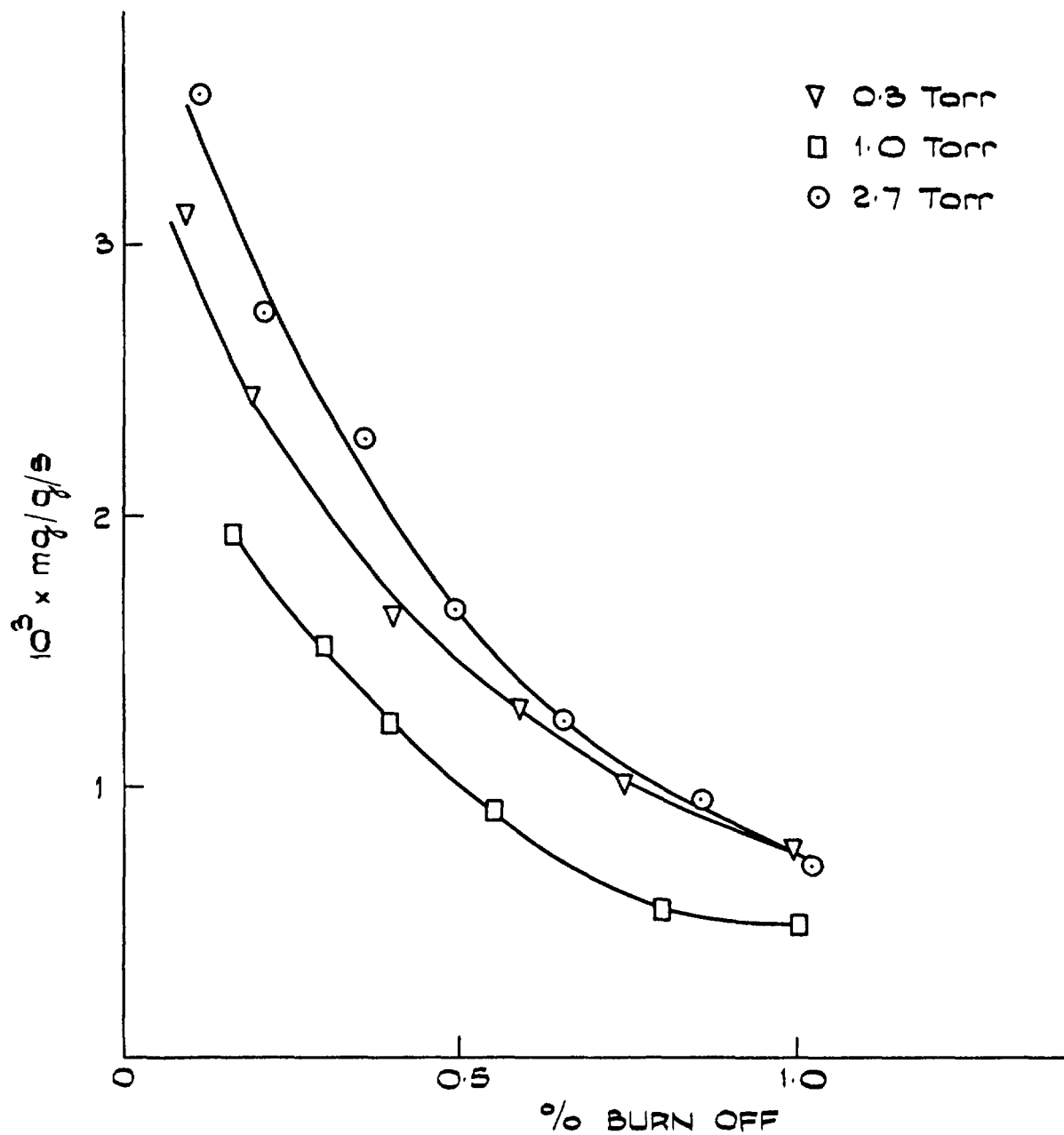


FIG. 30 EFFECT OF PRESSURE OF H₂O ON OXIDATION OF Ni-GRAPHITE.

OX AT 640°C
0.05% Ni

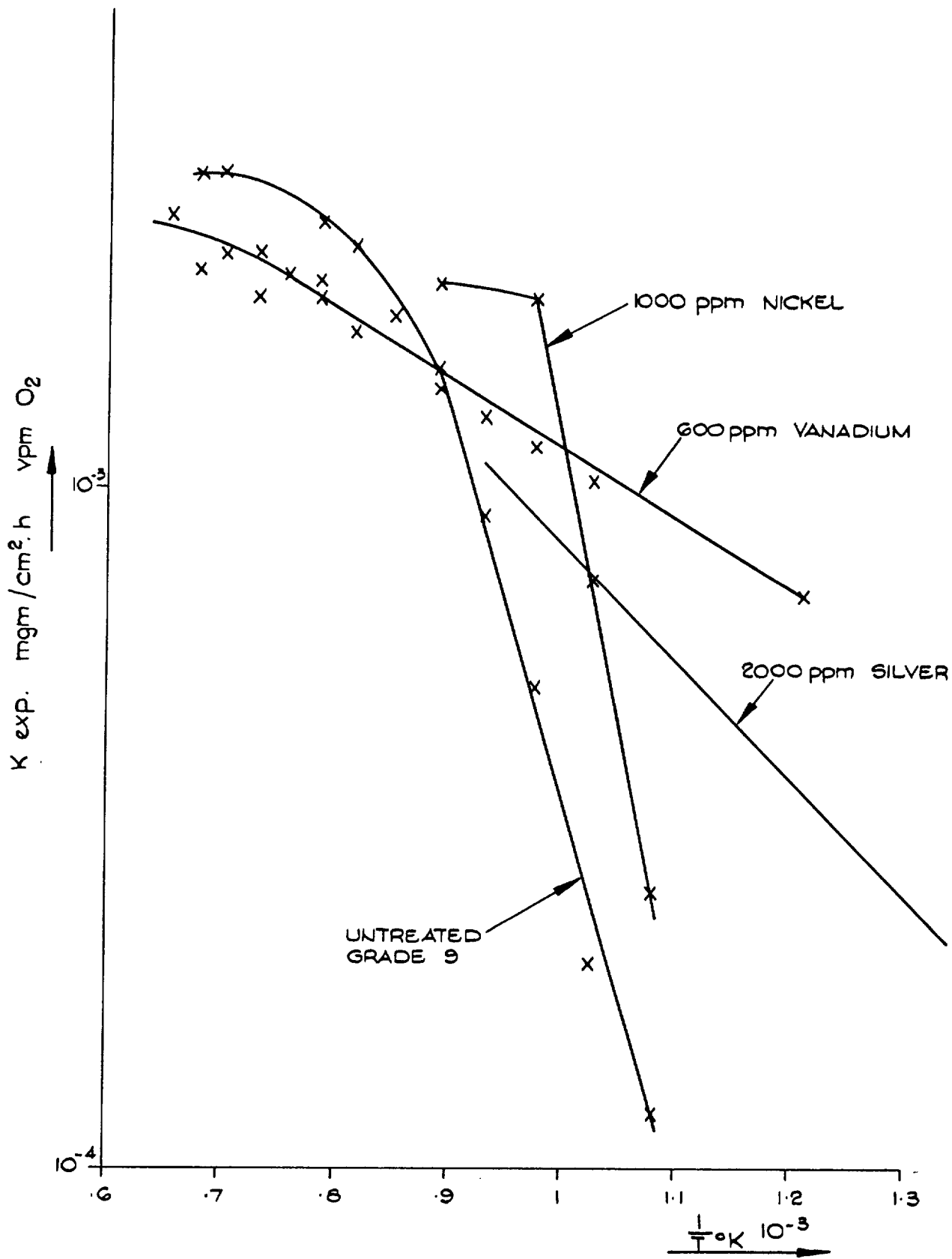


FIG. 31 EFFECT OF DIFFERENT METAL CATALYSTS ON OXIDATION OF GRADE 9 GRAPHITE.