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RESEARCH ESTABLISHMENT
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OXIDATION OF 1% Cr, 0.5% Mo STEEL IN CARBON DIOXIDE

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ABSTRACT

Carbon steels do not suffice as structural materials in carbon–dioxide cooled reactors at gas temperatures above 410°C , because of insufficient creep resistance. Low alloy steels of the "Croloy" variety appear to be the first alternatives as the small additions of chromium and molybdenum provide increased creep resistance.

The corrosion of a 1% Cr, 0.5% Mo steel in carbon dioxide has been measured over the range 450 to 525°C under varying conditions of surface preparation, pressure, velocity, and impurity content of the gas. Weight changes were measured as a function of time of exposure in tests of up to 4,000 hours.

It has been found that surface preparation of the specimens and pressure of the gas have little effect on the rate of oxidation of this steel in CO_2. Also presence of moisture up to 20,000 p.p.m. does not materially alter the rate of attack. Weight–gains of specimens in pure oxygen were always found to be less than weight–gains obtained in carbon dioxide under identical conditions of temperature, pressure, and moisture content. Scaling of the oxide layer was never encountered under static or semi–static conditions. However, scaling occurred on many specimens exposed in flowing gas; the extent depended on the temperature and gas velocity.

Metallographic examination verified that a protective Cr_2O_3 film was never likely to be formed on this steel under the conditions of the tests. The major products of the reaction were Fe_3O_4 and another unidentified spinel.

This study has shown that it is not safe to recommend this steel for use in carbon dioxide cooled reactors at temperatures above 450°C.

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1. INTRODUCTION

Various forms of carbon steel satisfy all requirements for the major components of the gas circuit in the Calder Hall family of reactors where carbon dioxide temperatures do not exceed 410°C. Above this temperature the creep properties are inadequate although the oxidation resistance may be satisfactory up to 450°C. Thus other steels must be considered for the gas circuit in the Australian High Temperature Gas Cooled Reactor where gas outlet temperatures of at least 500°C have to be achieved. The selection of the best steel for each part of the circuit will depend on cost considerations together with corrosion resistance and mechanical strength at the working temperature. It is probable that the circuit will consist of a variety of steels provided some welding and fabrication difficulties can be overcome. The corrosion characteristics of possible materials in carbon dioxide are therefore being studied while the Metallurgy Section is investigating the welding characteristics of the same materials.

One of the cheaper low-alloy steels which has been used for many years in conventional high temperature steam plant, mainly because of its enhanced creep strength in the 400–450°C range, is the nominal 1% chromium, 0.5% molybdenum steel. This report presents the results of tests on the compatibility of this steel with carbon dioxide.

2. EXPERIMENTAL METHODS

The steel was supplied by Babcock and Wilcox (Aust.) Pty. Ltd., from a batch being used in their latest high temperature boilers. It was of German origin and had the following analysis:

Cr	0.75%
Si	0.2%
Mo	0.35%
Cu	0.1%
Ni	0.1%
Mn	0.5%
C	0.22%

The carbon dioxide was supplied from a six ton storage vessel and was of high commercial purity, the main contaminants being water (maximum 20 p.p.m.) and air (maximum 100 p.p.m.). The effects of the following variables were determined:

temperature: 430° – 550°C

pressure: 0 – 225 p.s.i.g.

surface preparation: six different surface finishes

water content: 10 – 20,000 p.p.m.

velocity: 0 – 190 f.p.s.

The six surface finishes tested were:

(a) surface-ground,
(b) surface-ground and polished,
(c) surface-ground and etched,
(d) surface-ground and vapour blasted,
(e) as received, and
(f) as received and etched by treatment with 50 per cent. hot hydrochloric acid solution for 40 minutes.

Some tests were also made to examine the reactions of this steel with oxygen and to compare these with the reactions in carbon dioxide under identical conditions.

The autoclaves previously described by Draycott and Smith (1960) were used for all the experiments at pressures above atmospheric. Specimens were removed at defined intervals of time, weighed, and replaced. The normal duration of an experiment was 1,000 hours although some tests of 4,000 hours were completed. The longer tests were made to determine whether scaling of the oxide film occurred over extended periods of time. The temperature and pressure variables were fully studied by exposing at least 6 identical specimens under each set of conditions and taking mean values.

The velocity variable was studied in the small loop used by Draycott and Smith (1960), using rod specimens 4 inches long and of 0.3 inch diameter. The loop operated on standard commercial gas of purity specified above, and at a pressure slightly above atmospheric.

Stanton recording thermobalances were used to study the effect of water impurity in the carbon dioxide and also to differentiate between the reactions of the steel with carbon dioxide and oxygen. On this apparatus continuous weight changes were recorded as a function of time at a particular temperature in a controlled atmosphere. The tests were all of 100 hours duration. In some cases water was removed from the carbon dioxide by passing it through a bed of molecular sieves, while in other cases water was introduced by bubbling the flow of gas through water at a fixed temperature. Water contents were measured by means of an electrolytic moisture monitor.

The information obtained from the weight gain data was supplemented by x-ray diffraction and metallographic examination of selected specimens.

3. EXPERIMENTAL RESULTS

3.1 General

Macroscopically the oxide films obtained were of two types. The usual film was brown with a velvety or powdery appearance but in some cases at pressures of 150 p.s.i.g. or more an adherent dull grey scale was first formed; this grey scale continued for up to 500 hours before changing to the brown type.

X-ray diffraction studies on representative samples indicated the presence of two types of structure in the oxide, one being Fe_2O_3 and the other a spinel phase with a parameter close to that of Fe_3O_4. However, metallographic examination of the oxides revealed three distinct layers in most cases. Figure 22 is a typical example of this effect. The outer layer was identified as Fe_2O_3 by its anisotropic response to polarised light and thus the remaining two layers are considered to be spinel structures. The middle layer is presumably the inverse spinel structure Fe_3O_4 while the inner layer is presumably a normal spinel with a parameter close to that of Fe_3O_4. In both cases some of the Fe atoms may be replaced by atoms of alloying elements (Cr, Mn, etc.). The middle layer was characterised by considerable porosity while the layer beneath it showed a dotted appearance possibly due to fine porosity or a precipitate of another oxide. There was some evidence to suggest that the interface between the spinel phases was close to the original surface of the metal. On some samples the Fe_2O_3 layer was too thin to be detected by metallographic examination but it was revealed by electron diffraction.

3.2 Effect of Surface Preparation

The weight-gain data of the various test specimens are given in Table 1 and Figures 1 to 4, which show that the effect of surface preparation of 1% Cr, 0.5% Mo steel is much less pronounced than that obtained in the study of stainless steel corrosion (Draycott and Smith, 1960). It was so insignificant that it was not investigated fully at all temperatures and pressures. At 490° C and 150 p.s.i.g. (Figure 2) the scatter of weight-gain data due to different surface preparations represented only approximately 38 per cent. of total weight gain, while at 525° C and 150 p.s.i.g. (Figure 3) the scatter after 1000 hours exposure was even less and represented only 10 per cent. of total weight-gain.

Usually specimens tested in the "as received" condition yielded the smallest weight-gains, presumably because of the protective effect of the existing oxide film. Otherwise no definite order of weight-gain with different surface treatments was noticed, although slight trends could be observed. In both experiments in which surface preparation was studied, specimens with surfaces work-hardened by grinding or by vapour-blasting tended to gain more weight than specimens with other surface treatments. However, this effect was small in all cases and any variations in rate of attack could possibly be attributed to differences in surface area caused by the different treatments.

X-ray and metallographic examination of some of these specimens did not reveal any striking differences between scales on specimens having different surface treatments. Minor differences were observed in some cases but, again, these did not follow a regular pattern.

The following table summarises the results of the work on surface treatment of samples exposed to carbon dioxide at 510 - 540°C and 150 p.s.i.g. for 125 hours; the metallographic records are shown in Figures 14 to 18.

Sample No.	Figure No.	Surface Treatment	Appearance	Oxide Thickness (microns)	Remarks
3	14	surface ground	deep rich velvet brown	17	4 micron Fe_2O_3 layer
11	15	surface ground and polished	grey-brown	19	2 micron Fe_2O_3 layer
65	16	vapour-blasted	uniform dull grey	14	very thin Fe_2O_3 layer not apparent in micrograph
45	17	as received	uniform dull grey	10	very thin Fe_2O_3 layer not apparent in micrograph
53	18	as received and etched	uniform dull grey	12	very thin Fe_2O_3 layer, oxide intrusions into metal

After periods of 750 to 1000 hours both macroscopic and microscopic differences between these samples became less. All were brown in colour after this period and showed similar three-layered scales on metallographic examination.

Therefore, it can be concluded that while in the initial stages of reaction some variation in appearance of scale form is observed on specimens with different surface treatments, this variation disappears on prolonged exposure. The effect of surface preparation on the oxidation of this steel in carbon dioxide is slight in all cases, and need not be considered further as a major variable.

3.3 Effect of Temperature and Pressure

Weight-gain data for all specimens at different temperatures and pressures are reproduced in Table 1, and, in Figures 1, 2, and 5 weight-gain versus time curves are shown for experiments carried out under 150 p.s.i.g. pressure at 490, 525, and 450° C respectively. Each of the points on these figures represents a mean of six results. Little scatter was encountered. Tests were made on specimens with different surface finishes at the former two temperatures, but in view of the slight effect of this variable, only surface ground specimens were exposed in the experiments at 450°C and in all subsequent work at different pressures. Most of the experiments were of 1,000 hours duration, but extended tests were made on individual specimens at 490°C and 525° C (nominal temperatures only) and the results are shown in Figures 3 and 4. Generally the curves approached linearity after times varying from 400 to 1,000 hours; this is particularly true of the 525° C curves.

In all cases rate of attack increased with increase in temperature.

The rate followed the equation

$$\Delta W = kt^n$$

where ΔW = weight–gain in mg/cm^2,

k = rate constant,

t = time in hours.

The weight–gain data over 1,000 hour periods are plotted logarithmically for all experiments at 75 p.s.i.g. in Figure 7 and for the runs at 150 p.s.i.g. and 225 p.s.i.g. in Figures 8 and 9 respectively. From these graphs values of n and k were obtained as listed in Table 2. Some variation in the values of n was noted although it was not as great as that encountered in the experiments on 18/8/1 stainless steel (Draycott and Smith, 1960). Generally, values of n decreased with increase in temperature and values of k increased with temperature. At the lower temperatures the values of n suggest a parabolic rate law but at 525° C a cubic law is more closely approached.

Some attempt has been made to fit the results into an Arrhenius type expression

$$k = Ae^{\frac{E}{RT}}$$

where A is the frequency factor,

and E is the activation energy.

From the graphs of the rate constant against the reciprocal of the absolute temperature, as shown in Figure 10, values of A and E can be obtained. (Table 2). The values of E are considerably higher than values of E for the iron – carbon dioxide reaction as reported by Darras et al. (1958) and approach those for the iron – carbon monoxide reaction. The activation energies obtained in this study are also considerably greater than the ones obtained in the stainless steel study. However, better experimental reproducibility was obtained with the 1% Cr, 0.5% Mo steel. (No explanation is offered for the low value of E obtained at 150 p.s.i.g.) .

The effect of temperature on the reaction of this steel with carbon dioxide is clearly demonstrated by the isochronal curves for 225 p.s.i.g. shown in Figure 11. Curves are given for weight–gain data obtained after 100, 250, 500, 750, and 1,000 hours respectively. The rate of weight–gain is clearly seen to increase with increase in temperature.

A summary of all results from the study of the temperature and pressure variables is given in Figure 6. The effect of pressure variation is not large and no clearly defined trends were observed. The weight–gains appeared to vary randomly with pressure at all temperatures and so a detailed study of this variable was not attempted.

To study more closely the effect of temperature on the oxidation process, metallographic and x–ray examinations were made of two series of specimens isochronally exposed at different temperatures. Photomicrographs of the scales produced under a pressure of 150 p.s.i.g. at 450°, 490° , and 525°C after 1,000 hours exposure are reproduced in Figures 19, 20 and 21 respectively.

At 450°C (Figure 19) a dark chocolate–brown scale 15 microns thick was produced. The scale was somewhat flaky in appearance, some Fe_2O_3 layer being present. At 490°C (Figure 20) the scale was again dark brown with the velvet or suede type appearance. The thickness was about 19 microns and possessed two distinct layers. Only a very thin spasmodic Fe_2O_3 layer was detected. At 525° C (Figure 21) the scale formed was grey–brown and was approximately 36 microns thick. Microscopic study revealed three layers, an Fe_2O_3 layer being irregular in thickness and enclosing some pores near the surface. Some flaking had occurred at the metal oxide interface as well as between layers 2 and 3. These pictures show that the thickness of Fe_2O_3 relative to the Fe_3O_4 layer increased steadily with increasing temperature.

In these tests no actual flaking of the scale occurred even at 525°C after 4,000 hours exposure when, in some cases, weight gains of approximately 10 mg/cm^2 were obtained. A photomicrograph of one of these thick scales is shown in Figure 22. Macroscopically, this scale had the usual velvet brown appearance and appeared quite adherent. However, microscopic examination showed a 63 micron thick three–layered scale with an Fe_2O_3 layer about 10 microns thick. All three layers grew as time proceeded but the most significant growth occurred in the Fe_3O_4 layer. Some cracks in the scale normal to the metal surface were observed. Accelerated attack could take place through these cracks while general flaking was possible anywhere in this scale. Etching of some of the specimens with thick scales in 5 per cent. nitric acid revealed no signs of decarburisation; some areas of pearlite were noted right on the scale–metal interface.

Estimated metal penetration depths have been calculated from the weight–gain data obtained in these experiments and are presented in Table 3. Mean weight–gain values for surface ground specimens have been used in these calculations. However, these values are based on the reaction rates existing over the first 1,000 hours of exposure. Figure 3 shows this to be a justifiable extrapolation at least to 3,000 hours in the case of experiments carried out at 490°C . However, at 525 to 550°C (Figure 4) the reaction rate becomes linear between 1,000 and 1,500 hours and extrapolation of this relationship to 10,000 hours gives a weight–gain of 16.27 mg/cm^2 and a penetration depth of 0.0153 mm for surface ground specimens at 550°C. These figures are much higher than those based on 1,000 hour exposures. The penetrations are not excessive, even at the higher temperatures and at pressures up to 225 p.s.i.g., and suggest that this material may be satisfactory in CO_2 at these conditions provided scaling does not occur. However, even though scaling was not encountered in these semi–static experiments, metallographic examination of the scales suggests that these may not be completely adherent.

3.4 Effect of Velocity

The velocity variable was studied on the atmospheric pressure loop referred to in Section 2. Experiments were carried out at the three reference temperatures 450, 490, and 525°C; four different values of velocity in the range 50 – 200 ft/sec. being studied at each temperature. All experiments were of 100 hours duration.

The results obtained are presented in Table 4 and Figure 12. At 450°C, velocity had little effect up to 150 ft/sec but in the experiment at 177 ft/sec a smaller weight gain was obtained. Closer examination of the specimen revealed an area approximately ¾ inch from the leading edge where the scale had a rougher appearance and where some minute flaking may have occurred.

At 490°C increase in velocity up to 150 ft/sec yielded increased weight gains but at 187 ft/sec definite scaling occurred in the same relative position. This area was greater than in the specimen exposed at 450°C and 200 ft/sec.

At 525°C weight–gain increased with velocity up to 75 ft/sec but at 100 ft/sec scaling occurred, the extent of scaling becoming worse at a velocity of 184 ft/sec.

In Figure 12 the dotted lines indicate the conditions where flaking could be expected to occur within 100 hours. Thus at 525°C it is expected that, at velocities greater than 80 ft/sec, flaking would occur while at 450° C this limiting velocity would increase to 150 ft/sec. Tests at longer periods may show that flaking occurs at lower velocities. Little reference is made in the literature to the effect of velocity on steel corrosion. Upthegrove and Murphy (1933) report scaling of mild steel at velocities as low as 15 cm/min. (0.01 ft/sec).

All the specimens exposed in these tests were examined by metallographic and x-ray techniques. Two representative photomicrographs are reproduced in Figures 23 and 24. Figure 23 shows a section of a specimen exposed at 490°C with a gas velocity of 75 ft/sec. Scaling did not occur on this specimen. The scale which was bronze-brown appeared quite adherent. It was 7 microns thick and consisted of two layers, the outer layer of Fe_2O_3 being quite appreciable. The specimen shown in Figure 24 had been exposed at 525°C with a velocity of 75 ft/sec. The scale was dark velvet brown similar in appearance to the scales obtained in the semi-static tests and was an average of 13 microns thick. It was two-layered and possessed an appreciable outer Fe_2O_3 layer. However, this scale was only loosely adherent, some cracks normal to the metal being noted. In both cases the overall scale thickness is comparable to that experienced under semi-static conditions. However, the Fe_2O_3 layer is much more pronounced in these velocity specimens showing an increase from less than 1 micron in semi-static tests after 100 hours to about 3 microns in flowing gas. No indications of any second spinel phase were observed in any of the specimens tested in the study of the velocity variable.

3.5 Effect of Impurities in the Gas

The effect of the presence of moisture in carbon dioxide was studied on Stanton thermo-balances over 100 hour periods. The gas tested in the dry state was prepared by passing through a bed of molecular sieves, the moisture content of the product being always less than 5 p.p.m. and generally was of the order of 1 p.p.m. The wet gas was prepared by bubbling through water and a moisture content of about 20,000 p.p.m. was obtained. Some tests were also made in pure oxygen to determine the effect small amounts of oxygen as an impurity in CO_2 would have on the corrosion rate.

The results obtained are given in Tables 4 and 5 and Figure 13. At temperatures up to 525°C specimens exhibited lower weight-gains in the dry gas, the differences between the weight-gains in the wet and dry environments decreasing as the temperature was increased from 450°C to 525°C. At 525°C some weight-gains were approximately the same while at 575°C lower weight-gains were always obtained in the wet gas.

Appreciable differences were observed between weight-gains in oxygen and carbon dioxide. In all cases specimens exposed to oxygen gave lower weight increases than those exposed to carbon dioxide. These tests show that the presence of either oxygen or moisture in carbon dioxide does not greatly affect the compatibility of 1%Cr, 0.5% Mo steel in this medium.

3.6 Mechanism of Attack

To elucidate the mechanism of attack, numerous specimens with ground surface finish were exposed to commercially pure CO_2 at 490°C and 150 p.s.i.g. Specimens were removed at intervals and after weighing were subjected to x-ray and metallographic examination to reveal the state of the attack.

Photomicrographs of some of the specimens are reproduced in Figures 25 to 30. They clearly illustrate the progress of the attack which is summarised below:

Exposure Time (hr.)	Figure	Weight Gain (mg/cm^2)	Remarks
115	25	1.26	A porous outer Fe_3O_4 layer covers another spinel layer. No Fe_2O_3 can be observed.
194	26	1.93	Scale consists mainly of Fe_3O_4 which has appreciable porosity. A very thin discontinuous Fe_2O_3 layer appears on the top of the scale, and a spinel is present between the Fe_3O_4 layer and the body of the metal.
306	27	2.20	Both the spinel and Fe_3O_4 layers have increased in thickness but the outer Fe_2O_3 is still very thin and discontinuous. The porosity of the Fe_3O_4 layer has increased.
513	28	2.69	The Fe_2O_3 layer has thickened and now covers the whole surface of the scale. Both the Fe_3O_4 and spinel layers have thickened, with appreciable porosity persisting in the former and a few spots appearing in the spinel phase.
744	29	3.46	All three layers have thickened and the spinel phase has a dotted appearance. Some of the pores in the Fe_3O_4 layer have enlarged and are quite appreciable in size.
3000	30	5.26	The development has continued of three distinct layers of: (1) continuous Fe_2O_3 (2) porous Fe_3O_4 (3) spotted spinel

This experiment indicated that the formation of Fe_3O_4 may nucleate the attack which eventually proceeds by the simultaneous growth of all three constituent layers.

4. DISCUSSION

The superior mechanical and creep properties of low alloy steels account for their use in normal boilers at higher temperatures than those possible with carbon steels. In such applications the oxidation resistance is usually not a limiting factor; however, in a carbon dioxide cooled nuclear reactor the rate and mode of oxidation are important. Unless the scaling of any structural material is almost negligible, particles of oxide will eventually be carried into the core. As well as possibly causing disturbances in coolant flow these particles will certainly yield radioactive isotopes such as Fe^{59}. If the scale particles containing these isotopes are later carried out of the core into the gas ducting, heat exchangers, or circulators, embarrassing shielding problems may arise. Therefore, the use of any material must be avoided at any temperature where it is shown to be susceptible to scaling.

This study has shown that the 1% Cr, 0.5% Mo steel exhibits scaling even at 450° C in flowing gas. The scaling was not excessive at this temperature but nevertheless over the surface areas being considered for a heat exchanger the total amounts removed would be considerable. Therefore it does not appear feasible to use this steel in a carbon dioxide circuit at temperatures of 450°C or above.

Generally the corrosion resistance of the 1% Cr, 0.5% Mo steel in carbon dioxide is worse than that of the normal carbon steel. For instance values of weight-gain given by Watkins (1959) for carbon steel at 500° C are approximately 60 per cent. of the weight-gains obtained by the low alloy steel at 490°C.

It was mentioned in the introduction to Watkins' paper that few results for low alloy steels in carbon dioxide have been reported. In an initial survey published by the General Nuclear Engineering Corporation of the U.S.A., (1960), some figures are given for a T-11 alloy steel. This steel has approximately the same composition as that studied here. Weight-gains over a 1,000 hour period reported by this firm vary from 0.8 mg/cm^2 at 400°C in static gas (this is double the weight-gain reported by Watkins (1959) for carbon steel) to 18 mg/cm^2 at 500°C in flowing gas.

Similarly Leclercq et al. (1960) have completed a survey, under static conditions, of carbon steels, low alloy steels, and stainless steels in carbon dioxide. Absolute figures for the weight-gains of the low alloy steels are similar to the ones reported here. However, Leclercq et al. claim that small amounts of chromium, nickel, or aluminium do enhance the oxidation resistance. Their results do not completely substantiate this claim particularly at low levels of chromium additions. Also they have not made tests under dynamic conditions and so have not encountered any scaling.

Thus, it appears that the oxidation resistance of this 1% Cr, 0.5% Mo steel to carbon dioxide is not better and is probably worse than the resistance of a carbon steel for the same conditions. This statement particularly applies to the temperature range 400 - 500°C.

Thus if carbon steel is limited to 400°C on strength and creep considerations it may be possible to use this low alloy steel in parts of the circuit operating between 400 and 440°C (provided further experiments show that scaling is not encountered at 440°C). Figure 31 shows the gas temperatures through the heat exchanger in one possible reactor (Lawther and Draycott, 1961). If this steel were only used in the proposed range it would only constitute approximately one quarter of the material for the evaporator section. There is no point in using this steel at temperatures below 400°C where carbon steel will suffice because whereas carbon steel costs £60 per ton the low alloy steel would cost about £150 - £170 per ton. (Both prices quoted in £A with steel unfabricated). Therefore, the steel would only be used in a very small section of the heat exchanger. In addition the steel is not easy to fabricate, welding being a rather difficult process. Also, if we consider different steels for each 40°C range in the heat exchanger and hot gas ducting a multi-variety unit results which could present many problems. Therefore it does not appear feasible or advantageous to use this steel in the present design. A material which would be used throughout the complete range 400 - 500°C would be much more satisfactory and even though the cost of the material may be higher, fabrication problems would be less.

Some further evidence of the lack of oxidation resistance enhancement is provided from the metallographic examinations. Some porosity was always observed in the Fe_3O_4 layer although never uniform. From the general appearance and location of this porosity it seems possible that the Fe_3O_4 layer grows away from the metal surface while the spinel is growing into the body of the metal. After long periods of exposure the spinel exhibits a dotted appearance which has not been explained. It could be fine porosity or a fine precipitate of another phase.

If flaking occurs in the early stages of oxidation metallographic examinations indicate this would occur at the interface of the Fe_3O_4 with the spinel, cracks usually appearing at this interface due to contraction on cooling the mounted specimen. In the later stages of oxidation the spalling of the film appears more likely to take place at the spinel-metal interface.

5. CONCLUSIONS

(1) From these experiments it is concluded that 1% Cr, 0.5% Mo steels should not be used in reactor circuits containing carbon dioxide at temperatures at or above 450°C. The rate of oxidation is more or less independent of surface preparation and gas pressure but increases rapidly with temperature over the range 450 - 525°C.

(2) No spalling of the scale was noted in static or semi-static conditions but at the gas velocities likely in a reactor circuit, scaling occurred even in a 100 hour period. However, metallographic examination of the specimens exposed under semi-static conditions after extended periods of time shows that the scale is not really adherent; many cracks normal to the surface are noted.

(3) Oxygen and water vapour as impurities in the gas are not likely to affect the oxidation rate greatly.

(4) The mechanism of oxidation is similar to that of carbon steel although weight-gains are generally greater than those reported for carbon steel under the same conditions. Fe_3O_4 is the predominant constituent of the scale; this is usually porous and may be the product of the initial nucleation process. An unidentified spinel was also observed. An outer Fe_2O_3 layer became more prominent after long periods of exposure.

(5) The small amount of chromium which has been added to the steel to enhance creep resistance has not essentially changed the oxidation characteristics. It appears that much larger amounts will be required to give greater resistance to attack by CO_2.

6. ACKNOWLEDGMENTS

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TABLE 1

WEIGHT-GAIN DATA FROM SEMI-STATIC COMPATIBILITY TESTS

Specimen No.	Temp. °C	Wt.-gain (mg/cm^2)				
		125 hr.	250 hr.	500 hr.	750 hr.	1000 hr.
150 p.s.i.g. Surface Ground						
1	543	2.83	3.73	4.52	5.30	5.82
2	543	2.23	3.16	3.85	4.48	4.90
4	540	2.50	3.34	4.04	4.65	5.19
5	523	2.02	2.74	3.37	3.94	4.37
6	523	2.23	2.98	3.61	4.20	4.59
7	530	2.28	3.04	3.78	4.29	–
8	530	2.46	3.27	3.92	4.50	4.99
150 p.s.i.g. Ground and Polished						
9	550	2.45	3.22	4.08	4.91	5.47
10	550	2.41	2.76	3.52	4.28	4.73
12	541	2.07	2.36	3.59	4.36	4.83
13	522	1.78	2.44	3.16	3.87	4.28
14	522	1.51	2.07	2.71	3.37	3.76
15	531	2.06	2.69	3.46	4.21	–
16	531	1.96	2.70	3.49	4.25	4.72
150 p.s.i.g. Ground and Etched						
17	547	1.97	2.66	3.51	4.26	5.01
18	547	1.73	2.27	2.96	3.57	4.16
19	540	1.99	2.58	–	–	–
20	540	1.92	2.56	3.42	4.16	4.90
21	505	1.67	2.21	2.92	3.55	4.14
22	505	1.58	2.10	2.78	3.37	3.97
23	525	1.91	2.55	3.37	4.11	–
24	525	1.93	2.58	3.43	4.19	4.92
150 p.s.i.g. Ground and Vapour Blasted						
58	535	1.88	3.33	4.20	4.71	5.08
59	535	1.41	2.64	3.43	3.90	4.29
66	536	1.77	3.15	4.02	4.53	4.92
67	524	1.43	2.56	3.24	3.68	4.20
68	524	1.34	2.42	3.06	3.49	–
69	532	1.65	2.94	3.72	4.19	4.55
72	532	1.79	3.14	3.91	4.39	4.75
150 p.s.i.g. As Received and Etched						
46	530	1.74	2.29	3.12	3.70	4.21
51	530	1.43	1.88	2.64	3.17	3.66
52	534	2.18	2.83	3.89	4.58	5.26
54	500	1.38	1.85	2.63	3.17	3.58
55	500	1.37	1.83	2.55	3.06	3.42
56	520	1.59	2.18	3.11	3.75	4.27
57	520	1.82	2.44	3.47	4.16	4.72
150 p.s.i.g. As Received						
39	526	1.77	3.52	4.33	4.67	5.16
44	526	1.36	2.77	3.41	3.72	4.11
75	534	1.27	2.42	2.98	3.27	3.61
76	513	1.64	3.08	3.75	4.08	4.50
77	513	1.54	2.95	3.70	4.04	4.49
78	527	1.48	2.85	3.58	3.96	4.39
79	527	1.62	2.99	3.74	4.12	4.55

(continued)

TABLE 1 (continued)

Specimen No.	Temp.°C	Wt.-gain (mg/cm^2)				
		100 hr.	250 hr.	500 hr.	750 hr.	1000hr.
150 p.s.i.g. Surface Ground						
159	507	1.44	1.96	2.66	3.19	3.48
177	507	1.35	1.85	2.52	3.09	3.41
186	502	1.46	1.96	2.69	3.23	3.54
188	479	1.31	1.77	2.45	3.00	3.31
196	479	1.32	1.79	2.47	3.02	3.32
199	492	1.30	1.78	2.49	3.04	3.36
200	492	1.42	1.93	2.70	3.23	3.55
150 p.s.i.g. Ground and Etched						
1	503	1.25	1.83	2.40	2.77	3.03
156	503	0.94	1.46	1.90	2.20	2.40
170	499	1.26	1.87	2.46	2.89	3.19
183	499	1.15	1.73	2.31	2.73	3.03
190	462	0.95	1.44	1.92	2.22	2.44
191	462	0.90	1.36	1.81	2.10	2.30
194	487	1.15	1.73	2.30	2.69	2.95
198	487	1.21	1.80	2.41	2.78	3.06
150 p.s.i.g. Ground and Polished						
169	497	0.98	1.48	2.15	2.52	2.82
172	497	0.75	1.20	1.75	2.09	2.33
181	501	1.01	1.54	2.25	2.67	2.99
184	458	0.72	1.11	1.67	2.03	2.29
185	458	0.66	1.00	1.52	1.85	2.09
195	481	0.96	1.47	2.14	2.55	2.86
197	481	1.07	1.63	2.34	2.77	3.10
150 p.s.i.g. Ground and Vapour Blasted						
160	496	1.87	2.38	2.88	3.40	3.67
174	501	2.07	2.64	3.15	3.70	4.02
175	501	1.88	2.38	2.91	3.44	3.75
176	461	1.60	2.02	2.55	3.07	3.36
178	461	1.32	1.67	2.14	2.62	2.78
179	486	1.78	2.26	2.78	3.33	3.56
180	486	1.77	2.28	2.84	3.43	3.47
150 p.s.i.g. As Received						
86	507	0.97	1.46	1.94	2.60	2.93
87	500	0.95	1.42	1.87	2.39	2.65
88	500	1.01	1.43	1.88	2.47	2.77
89	482	1.03	1.49	1.98	2.54	2.83
90	482	1.04	1.51	1.99	2.54	2.84
91	495	1.01	1.43	1.88	2.43	2.73
92	495	1.14	1.66	2.18	2.72	3.01
150 p.s.i.g. Surface Ground						
260	457	1.02	1.36	1.65	1.96	2.18
261	457	0.84	1.09	1.28	1.51	1.67
262	458	0.85	1.10	1.32	1.57	1.75
263	458	0.85	1.13	1.36	1.60	1.79
264	439	0.76	1.00	1.18	1.39	1.53
265	439	0.76	1.00	1.16	1.36	1.52
266	454	0.82	1.10	1.34	1.58	1.77
267	454	0.87	1.17	1.42	1.68	1.87

(continued)

TABLE 1 (continued)

		Wt.-gain (mg/cm^2)				
Specimen No.	Temp.°C	100 hr.	250 hr.	500 hr.	750 hr.	1000 hr.
225 p.s.i.g. Surface Ground						
158	535	2.02	2.91	3.52	3.88	4.11
161	535	1.71	2.57	3.10	3.41	3.83
162	537	1.94	2.87	3.54	3.96	4.50
163	537	1.97	2.88	3.52	3.94	4.43
164	494	1.64	2.39	2.90	3.27	3.73
165	494	1.48	2.28	2.80	3.18	3.63
168	517	1.86	2.67	3.24	3.62	4.12
201	460	0.87	1.47	2.07	2.44	2.79
202	460	0.75	1.27	1.83	2.17	2.51
203	455	0.69	1.18	1.70	2.00	2.28
204	455	0.70	1.21	1.74	2.03	2.32
205	432	0.72	1.18	1.72	2.01	2.31
206	432	0.65	1.13	1.67	1.94	2.22
208	459	0.76	1.30	1.86	2.16	2.46
209	514	1.37	2.00	2.60	3.11	3.59
210	514	1.11	1.65	2.14	2.54	2.89
211	500	1.19	1.81	2.40	2.88	3.34
212	500	1.15	1.70	2.25	2.69	3.10
213	467	1.04	1.55	2.04	2.41	2.76
214	467	1.02	1.53	2.01	2.36	2.70
216	481	1.16	1.71	2.25	2.70	3.11
75 p.s.i.g. Surface Ground						
217	525	1.81	2.66	3.39	3.88	4.35
218	525	1.30	1.88	2.44	2.77	3.25
219	533	2.15	3.15	3.98	4.53	5.09
220	533	2.04	2.91	3.71	4.25	4.78
221	483	1.38	1.94	2.56	2.93	3.33
222	483	1.23	1.73	2.27	2.66	3.04
224	516	2.04	2.80	3.60	4.14	4.67
225	510	1.39	2.08	2.73	3.13	3.56
226	510	1.15	1.73	2.21	2.54	2.86
227	503	1.42	2.12	2.75	3.17	3.58
228	503	1.36	2.03	2.63	3.01	3.40
229	477	1.09	1.64	2.09	2.40	2.71
230	477	1.92	1.38	1.88	2.21	2.55
232	487	1.28	1.93	2.56	2.93	3.31
233	458	0.68	1.20	1.66	1.93	2.16
234	458	0.51	0.85	1.20	1.42	1.70
235	461	0.87	1.37	1.85	2.14	2.42
236	461	0.80	1.24	1.71	1.98	2.12
237	430	0.52	0.84	1.19	1.40	1.59
238	430	0.50	0.79	1.13	1.32	1.49
240	451	0.74	1.19	1.63	1.90	2.15

TABLE 2

REACTION KINETIC DATA FOR 1% Cr, 0.5% Mo STEEL IN CO_2

Pressure p.s.i.g.	Temp. °C	Slope n	Rate Constant k mg/cm^2 hr^n	Activation Energy E cal/mole metal	Frequency Factor A mg/cm^2 hr^n
75	450	0.469	0.077	23,000	0.72×10^6
	490	0.404	0.189		
	525	0.368	0.344		
150	450	0.313	0.194	11,500	5.22×10^2
	490	0.436	0.176		
	525	0.342	0.429		
225	450	0.519	0.070	25,800	4.13×10^6
	490	0.423	0.163		
	525	0.343	0.388		

TABLE 3

ESTIMATED PENETRATION DEPTHS BASED ON
1000 HOUR SEMI-STATIC COMPATIBILITY TESTS

Temp. °C	Pressure p.s.i.g.	Wt-gain in 10,000 hr. mg/cm^2	Penetration depth in 10,000 hr. mm
450	75	5.85	0.0055
	150	4.28	0.0033
	225	8.24	0.0077
490	75	7.77	0.0073
	150	8.95	0.0084
	225	8.00	0.0075
525	75	10.17	0.0096
	150	10.00	0.0094
	225	9.12	0.0086

TABLE 4

RESULTS OF DYNAMIC COMPATIBILITY TESTS (100 HOUR EXPOSURES)

Temp. °C	Velocity ft/sec	Wt.-Gain mg/cm^2	Wt.-Gain (Static 75 p.s.i.g.) mg/cm^2
525	184	1.73	1.82
525	100	2.27	
525	75	2.23	
525	50	1.61	
490	187	1.56	1.17
490	100	1.39	
490	75	1.07	
490	50	0.84	
450	177	0.64	0.67
450	150	0.80	
450	100	0.73	
450	50	0.73	

TABLE 5

WEIGHT-GAIN DATA FOR SPECIMENS EXPOSED TO DRY OXYGEN AND WET AND DRY CO_2 ON STANTON THERMOBALANCES

Conditions of Exposure	Wt.-Gains in mg/cm^2 after exposure of									
	10 hr.	20 hr.	30 hr.	40 hr.	50 hr.	60 hr.	70 hr.	80 hr.	90 hr.	100 hr.
450°C wet CO_2	0.39	0.54	0.67	0.73	0.87	0.90	1.04	1.06	1.13	1.23
450°C dry CO_2	0.14	0.22	0.33	0.34	0.40	0.40	0.46	0.50	0.46	0.49
490°C wet CO_2	0.40	0.67	0.78	0.83	0.86	0.96	0.99	1.07	1.14	1.22
490°C dry CO_2	0.26	0.42	0.50	0.58	0.68	0.72	0.80	0.83	0.86	0.93
525°C wet CO_2	0.99	1.32	1.61	1.60	1.65	1.78	1.82	1.81	1.74	1.84
525°C dry CO_2	1.03	1.20	1.41	1.57	1.71	1.80	1.84	1.87	1.90	1.96
575°C wet CO_2	1.07	1.37	1.62	1.79	1.95	2.05	2.22	2.26	2.35	2.38
575°C dry CO_2	1.31	1.63	1.91	2.06	2.25	2.40	2.57	2.63	2.72	2.79
525°C dry O_2	0.41	0.68	0.85	0.91	1.15	1.17	1.31	1.46	1.53	1.72
575°C dry O_2	0.59	0.93	1.21	1.36	1.57	1.70	1.85	1.97	2.08	2.35

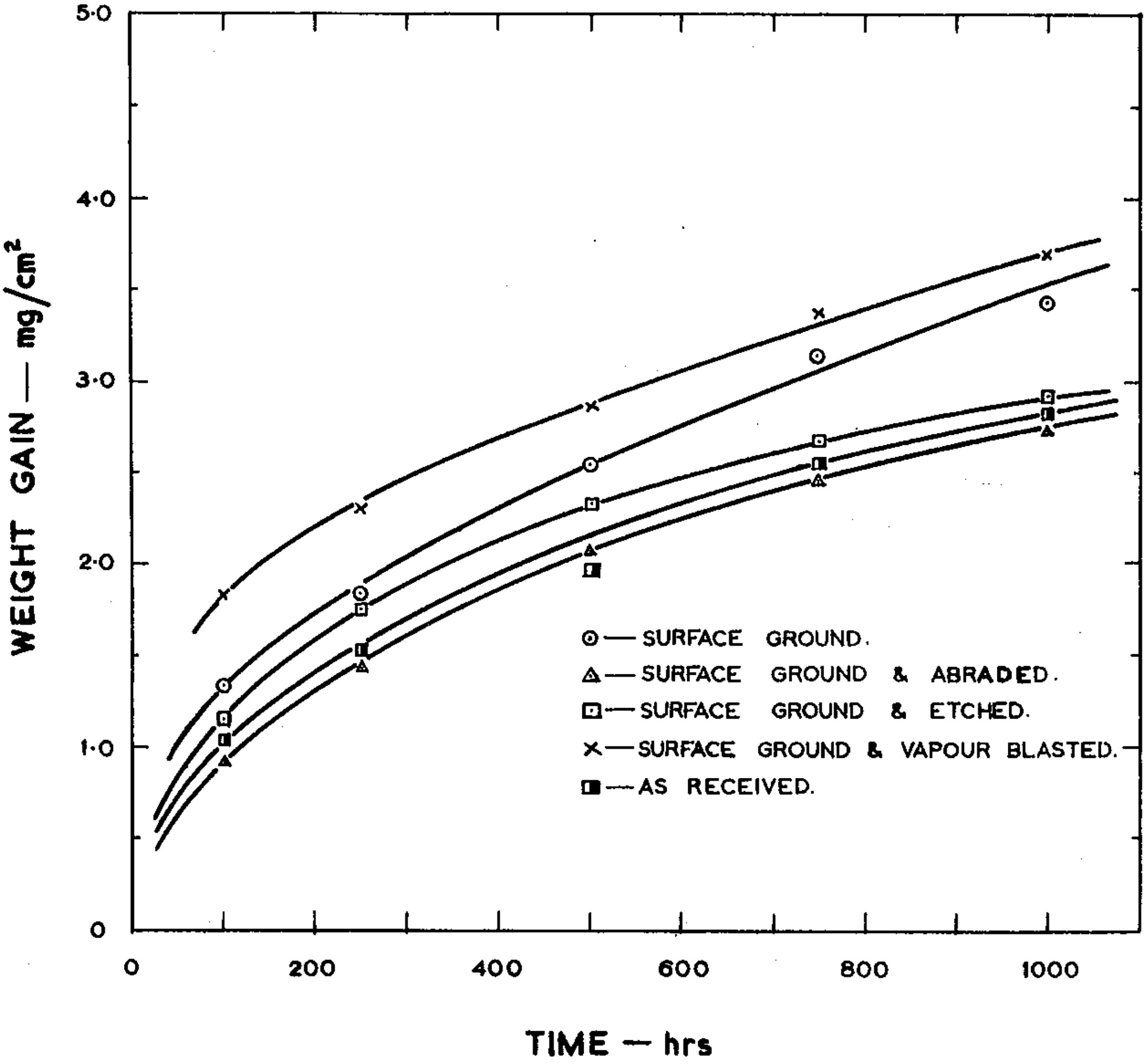


Fig. I. EFFECT OF SURFACE TREATMENT ON WEIGHT GAINS OF 1% Cr 0·5% Mo STEEL IN CO_2 AT 490°C & 150 psig.

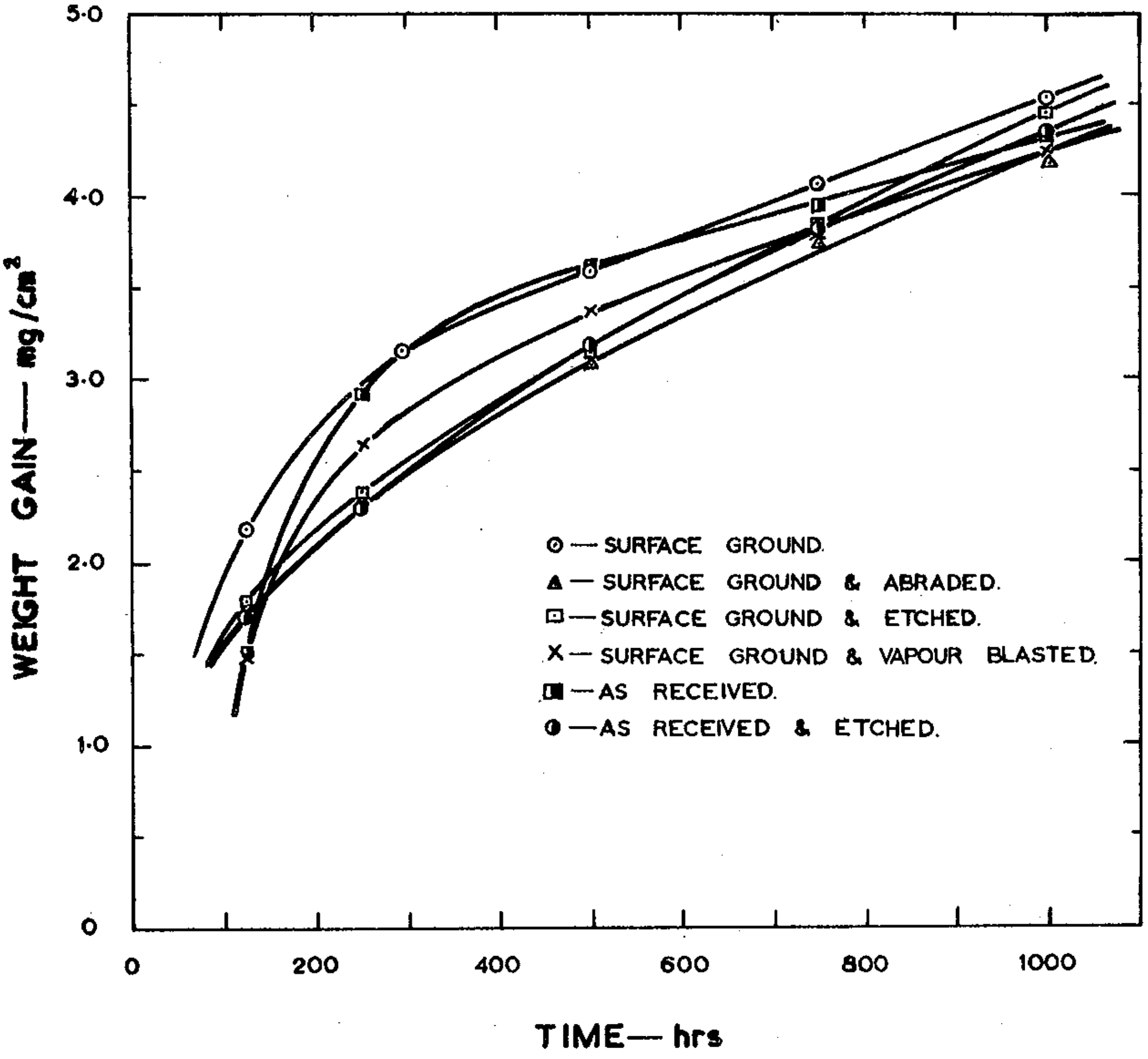


Fig. 2. EFFECT OF SURFACE TREATMENT ON WEIGHT GAINS OF 1%Cr 0.5%Mo STEEL IN CO_2 AT 525°C & 150psig.

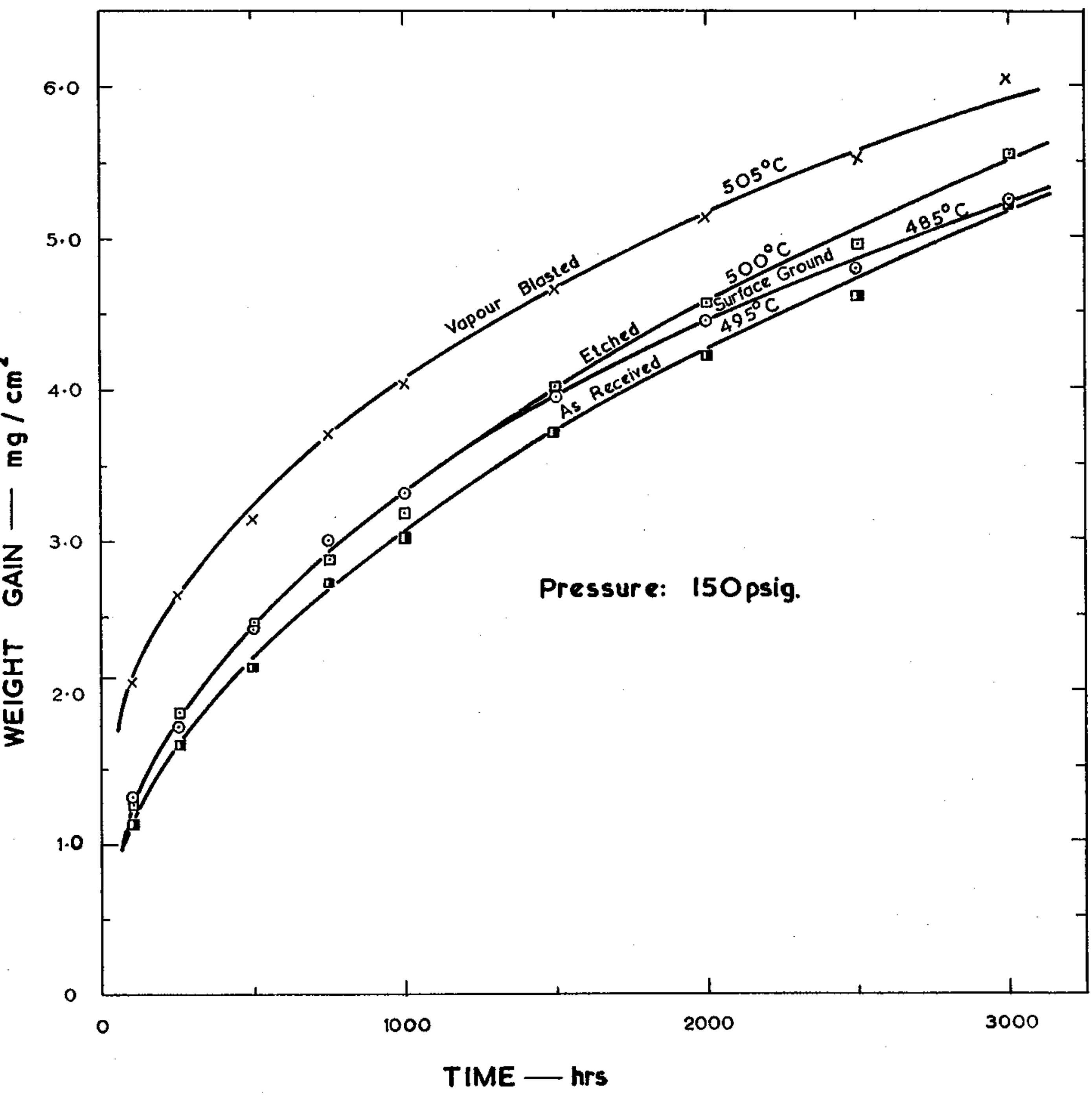


Fig. 3. WEIGHT GAIN DATA OVER 3000 HOURS.

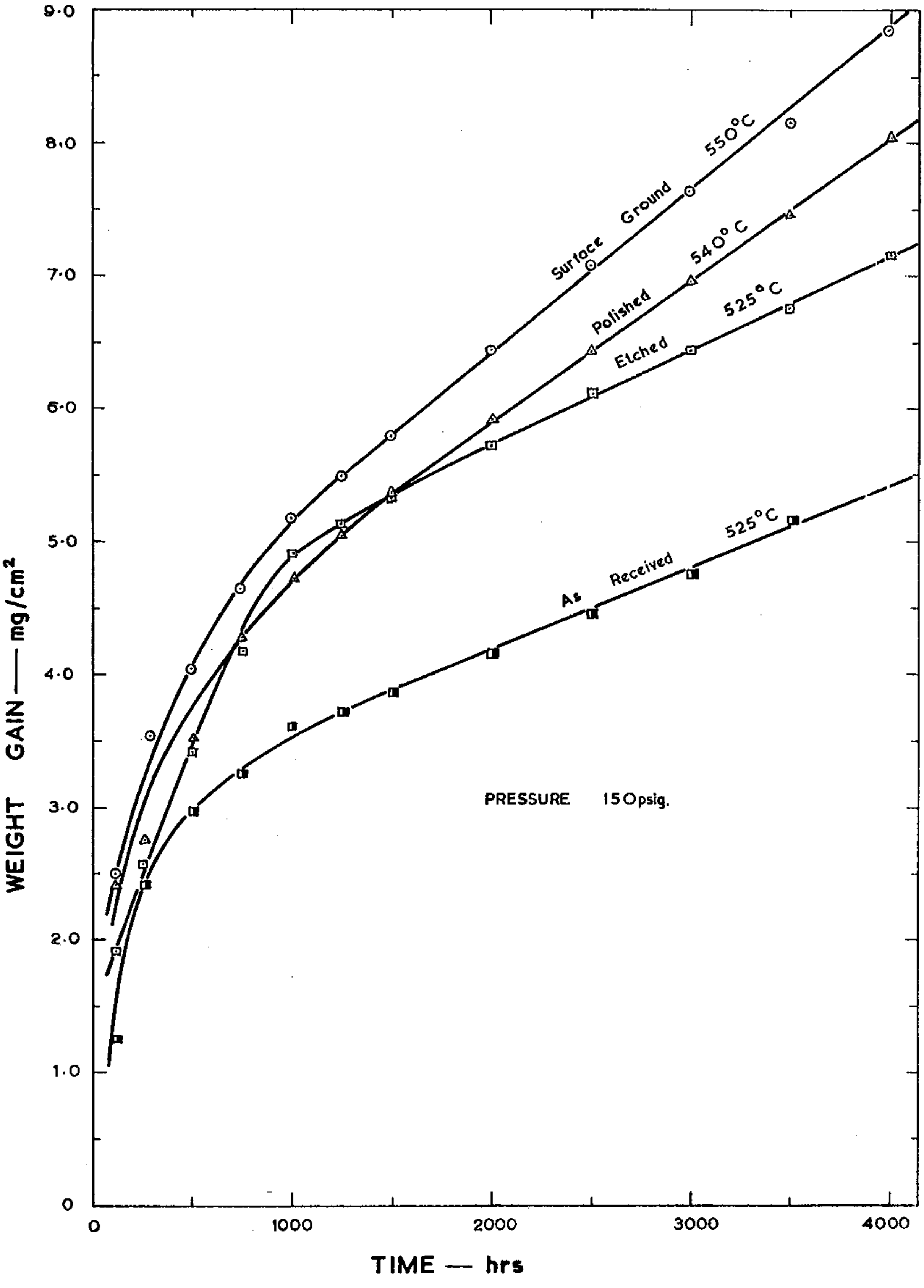


Fig. 4. WEIGHT GAIN DATA OVER 4000 HOURS.

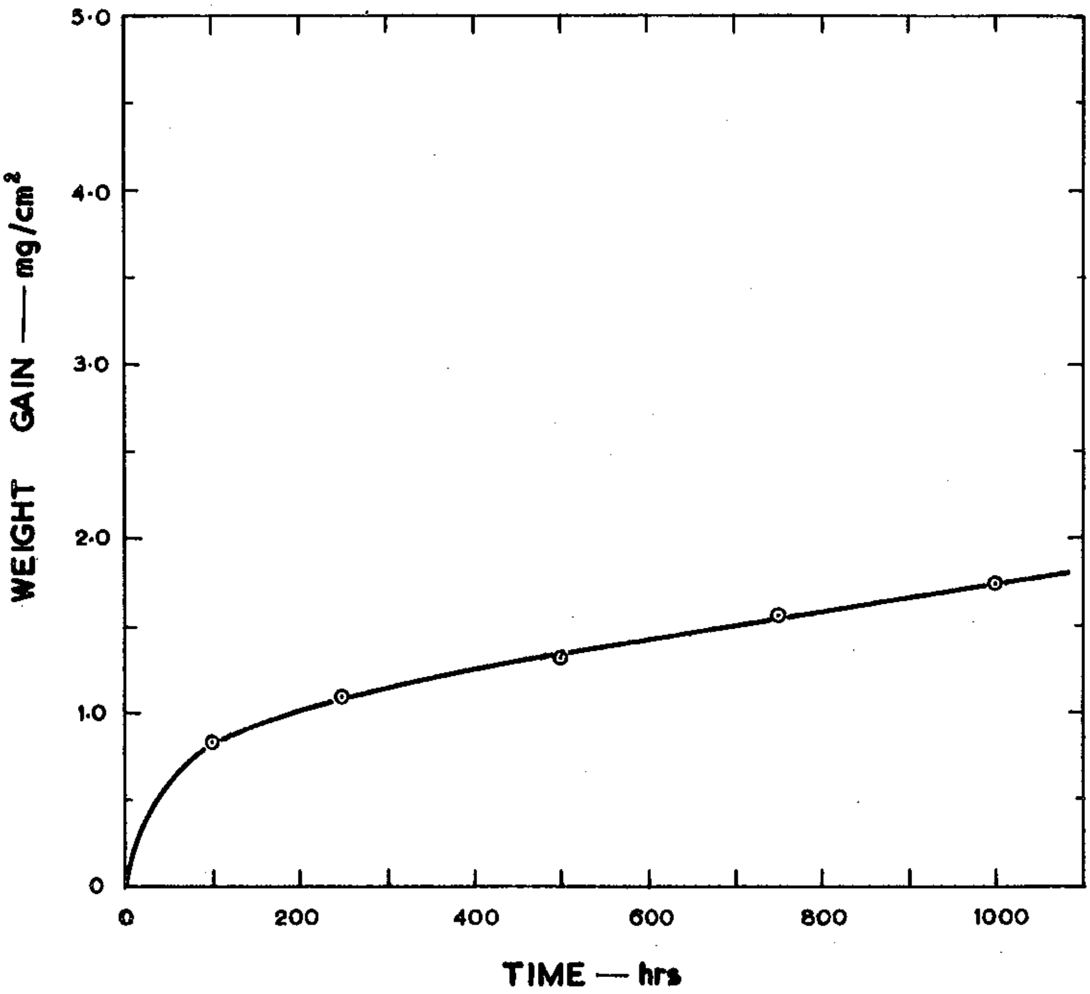


Fig.5. WEIGHT GAIN DATA AT 450°C AND 150psig.

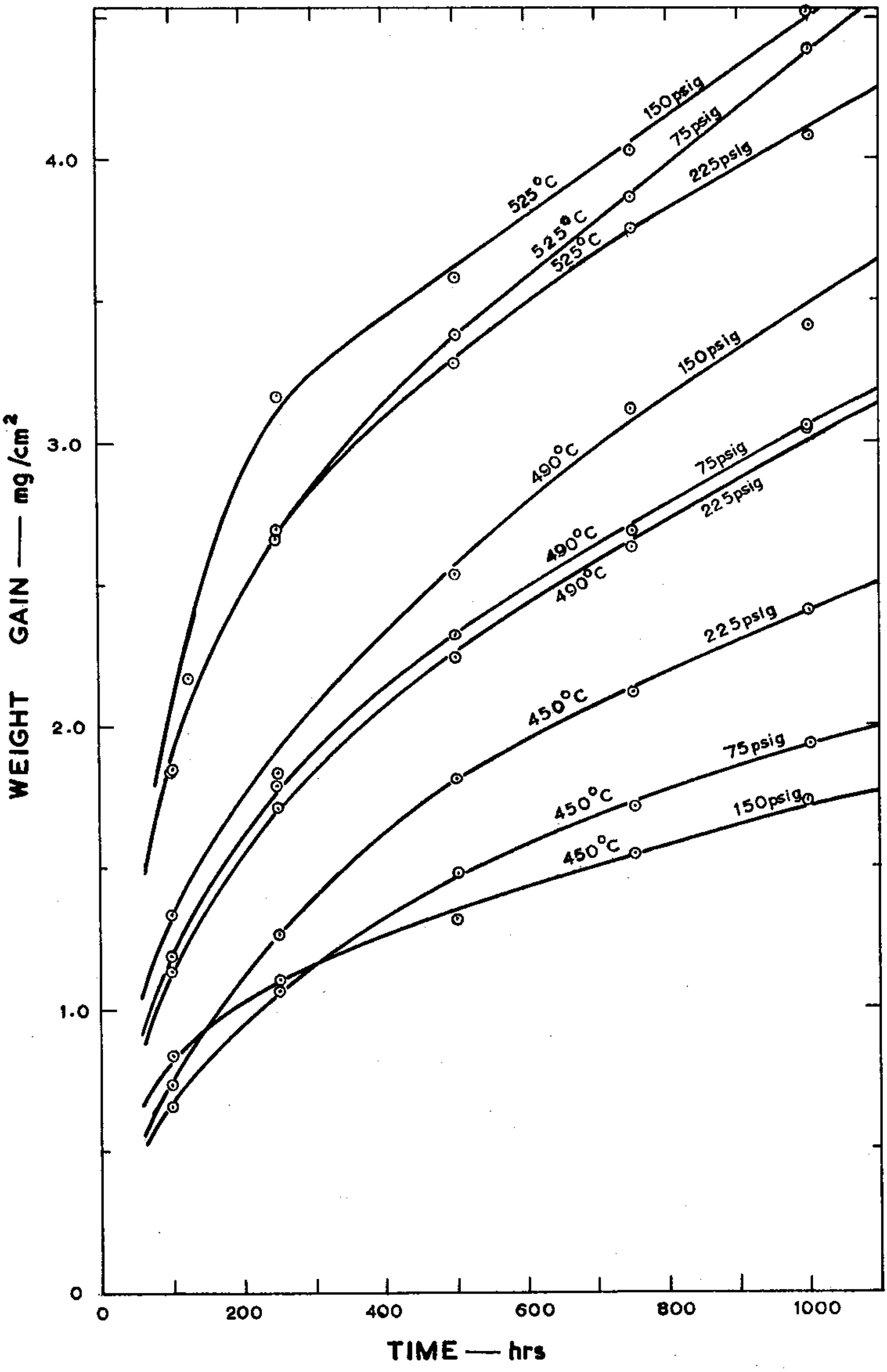


Fig. 6. SUMMARY OF WEIGHT GAIN DATA FOR SURFACE GROUND SPECIMENS AT ALL TEMPERATURES AND PRESSURES OVER 1000 hr PERIODS.

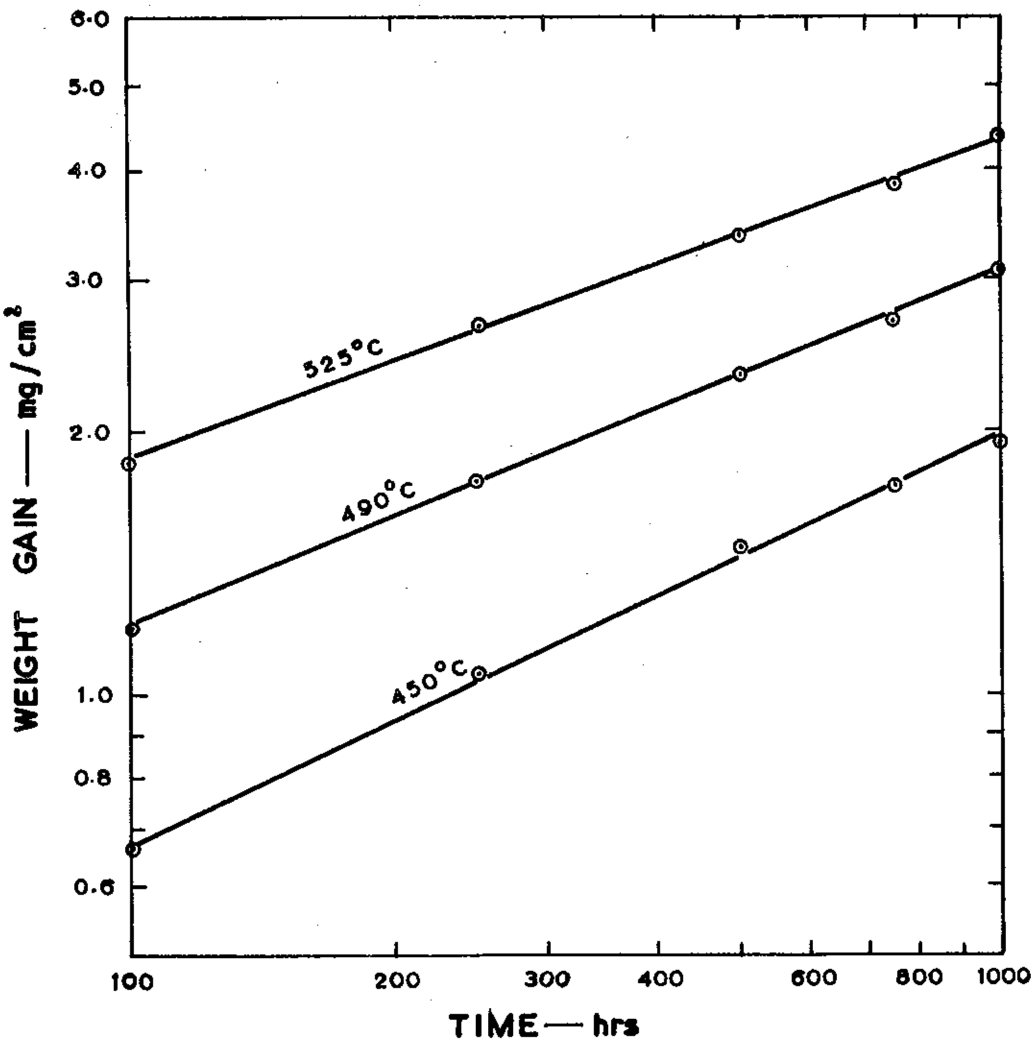


Fig. 7. LOGARITHMIC PLOT OF WEIGHT GAIN DATA AT 75psig.

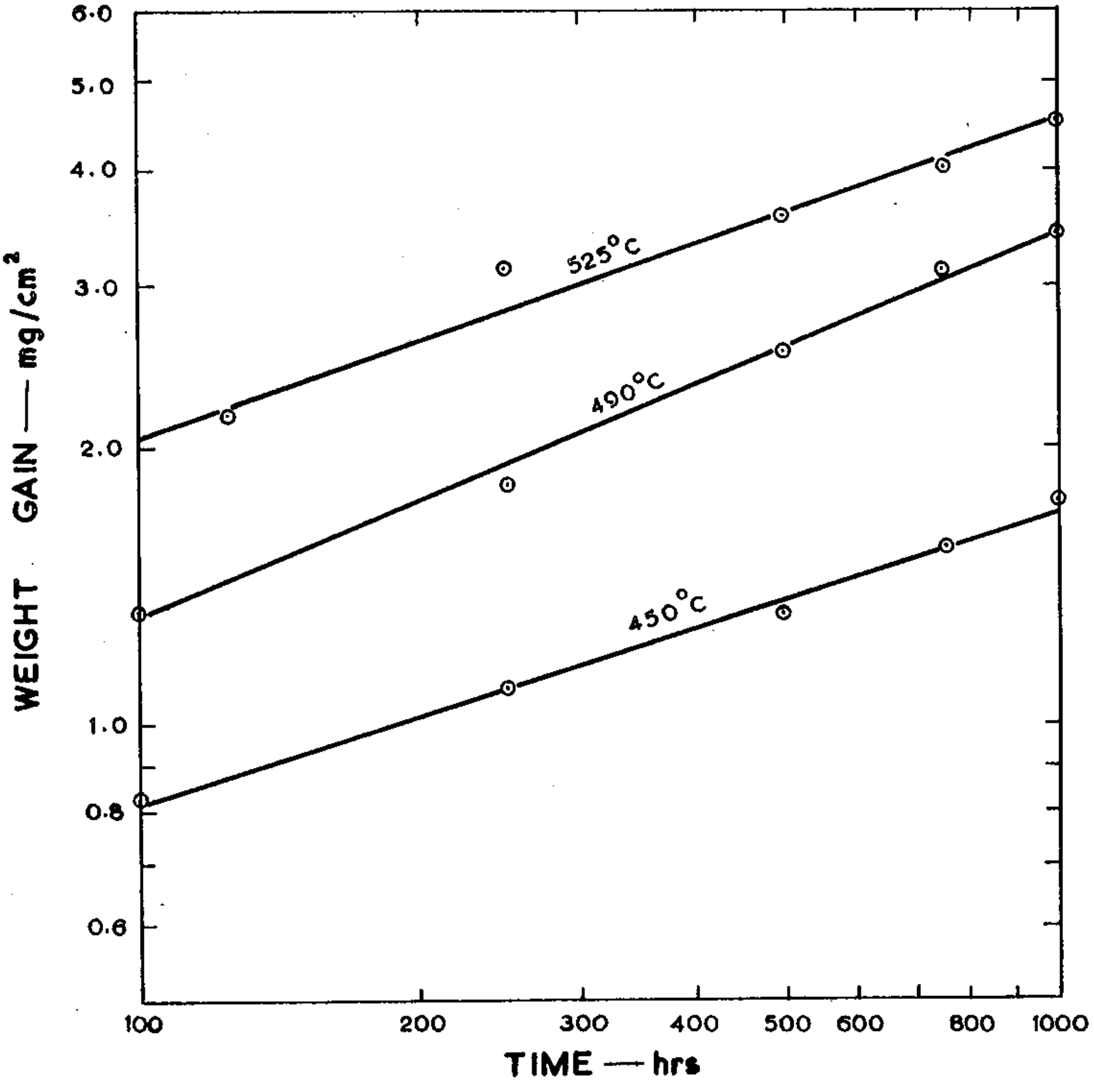


Fig. 8. LOGARITHMIC PLOT OF WEIGHT GAIN DATA AT 150 psig.

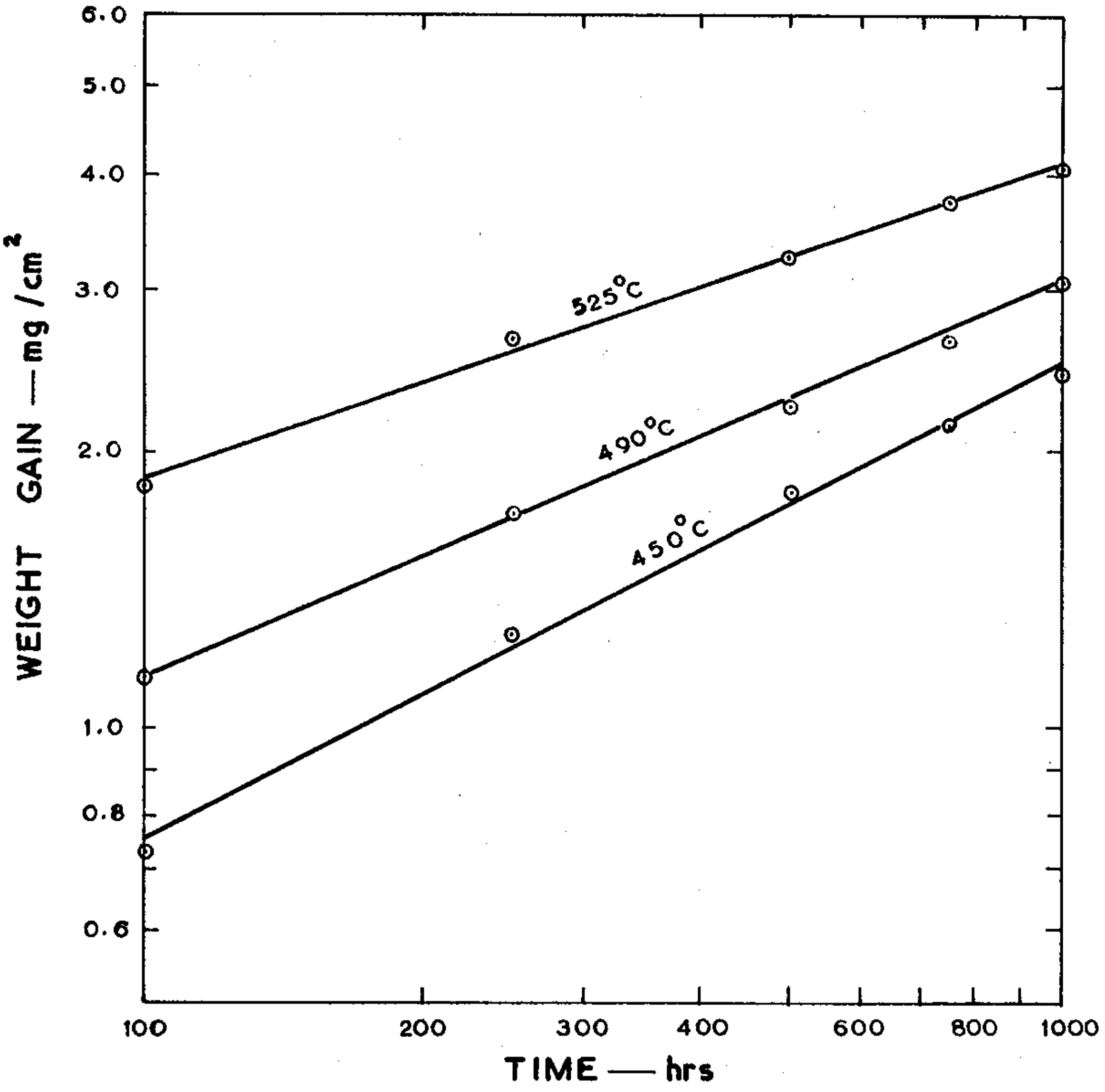


Fig. 9. LOGARITHMIC PLOT OF WEIGHT GAIN DATA AT 225psig.

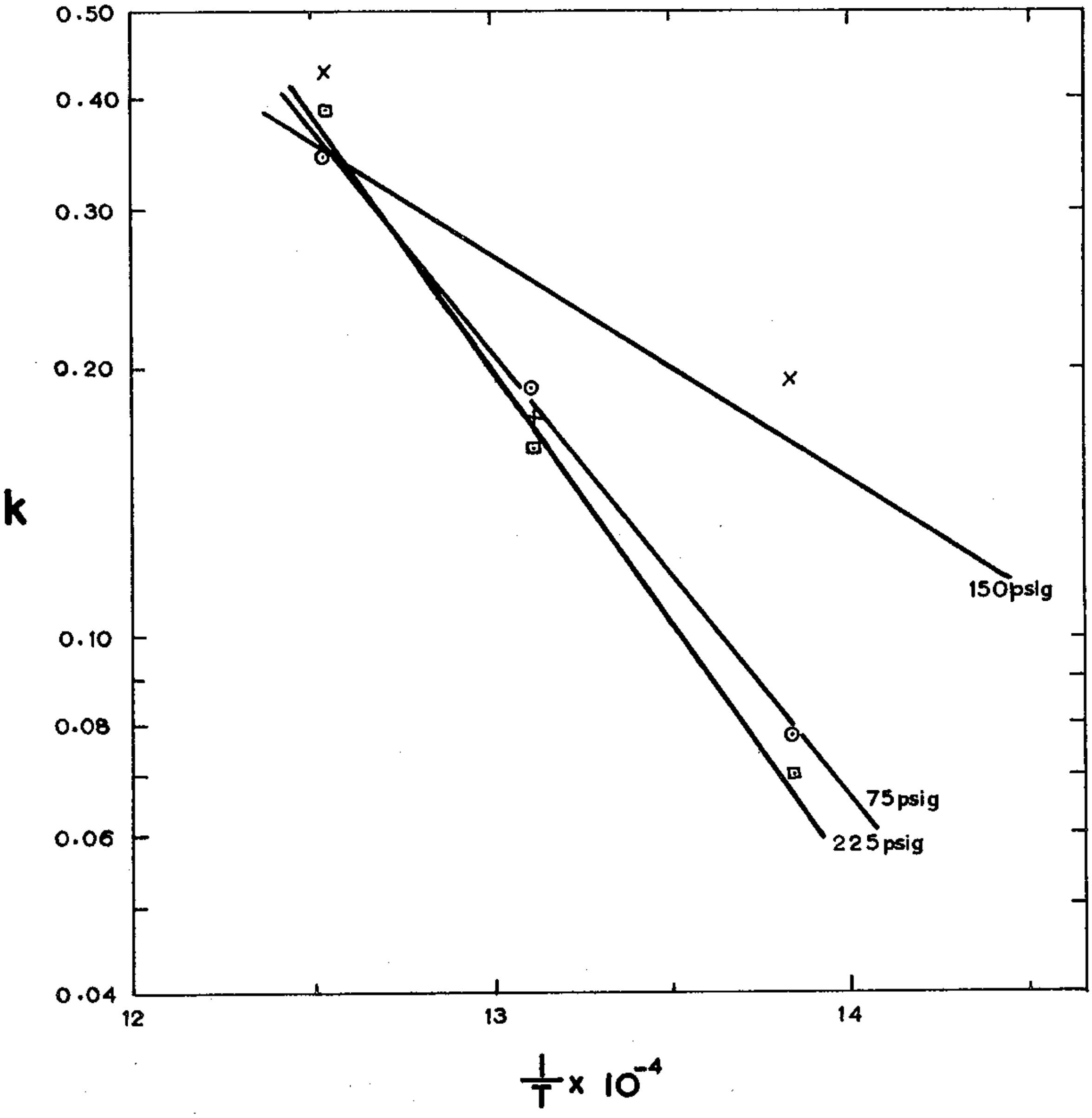


Fig. 10. ARRHENIUS PLOT OF WEIGHT GAIN DATA.

$$\left[\ k = A\,e^{-\frac{E}{RT}}\right]$$

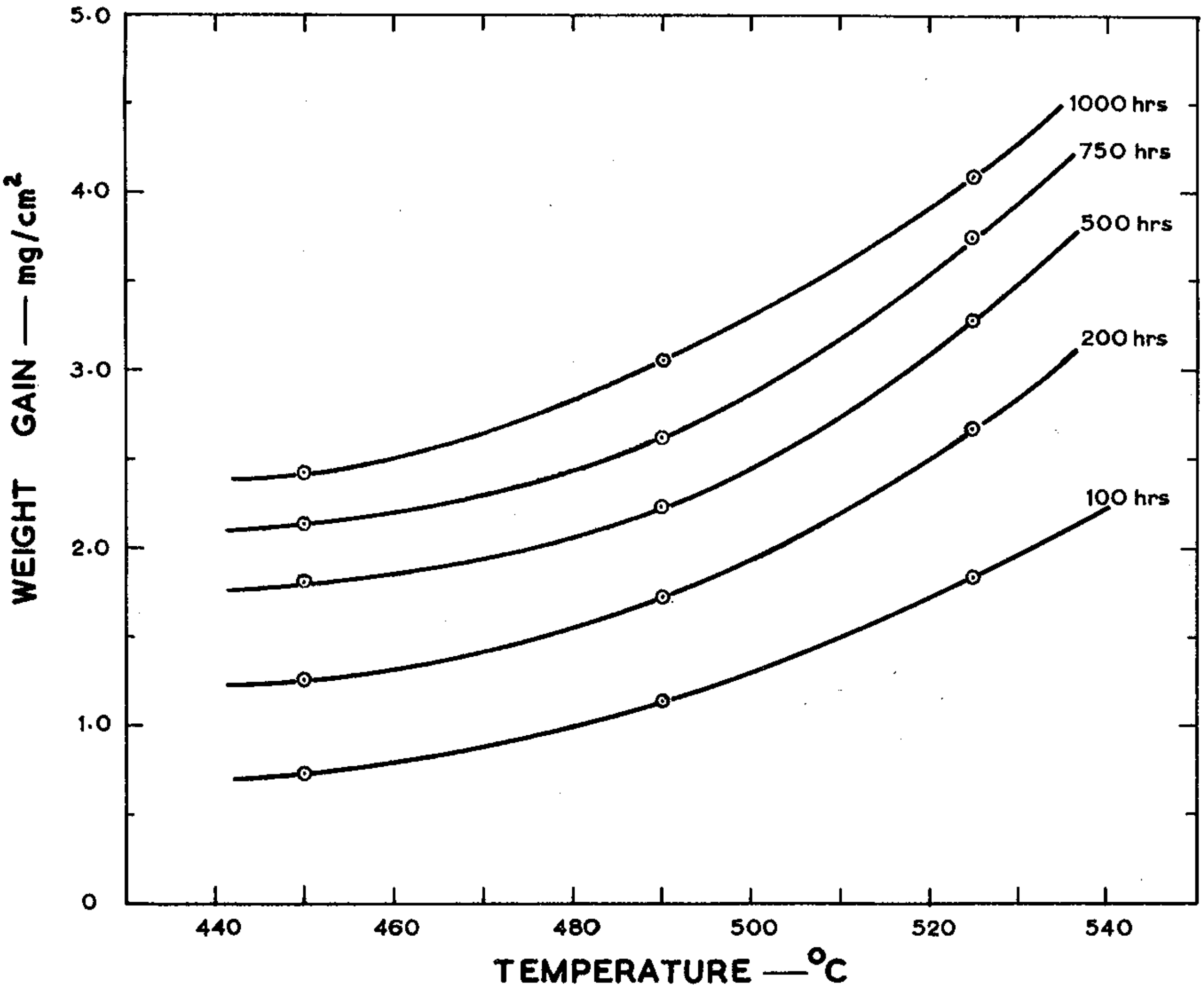


Fig. 11. ISOCHRONAL CURVES AT 225psig.

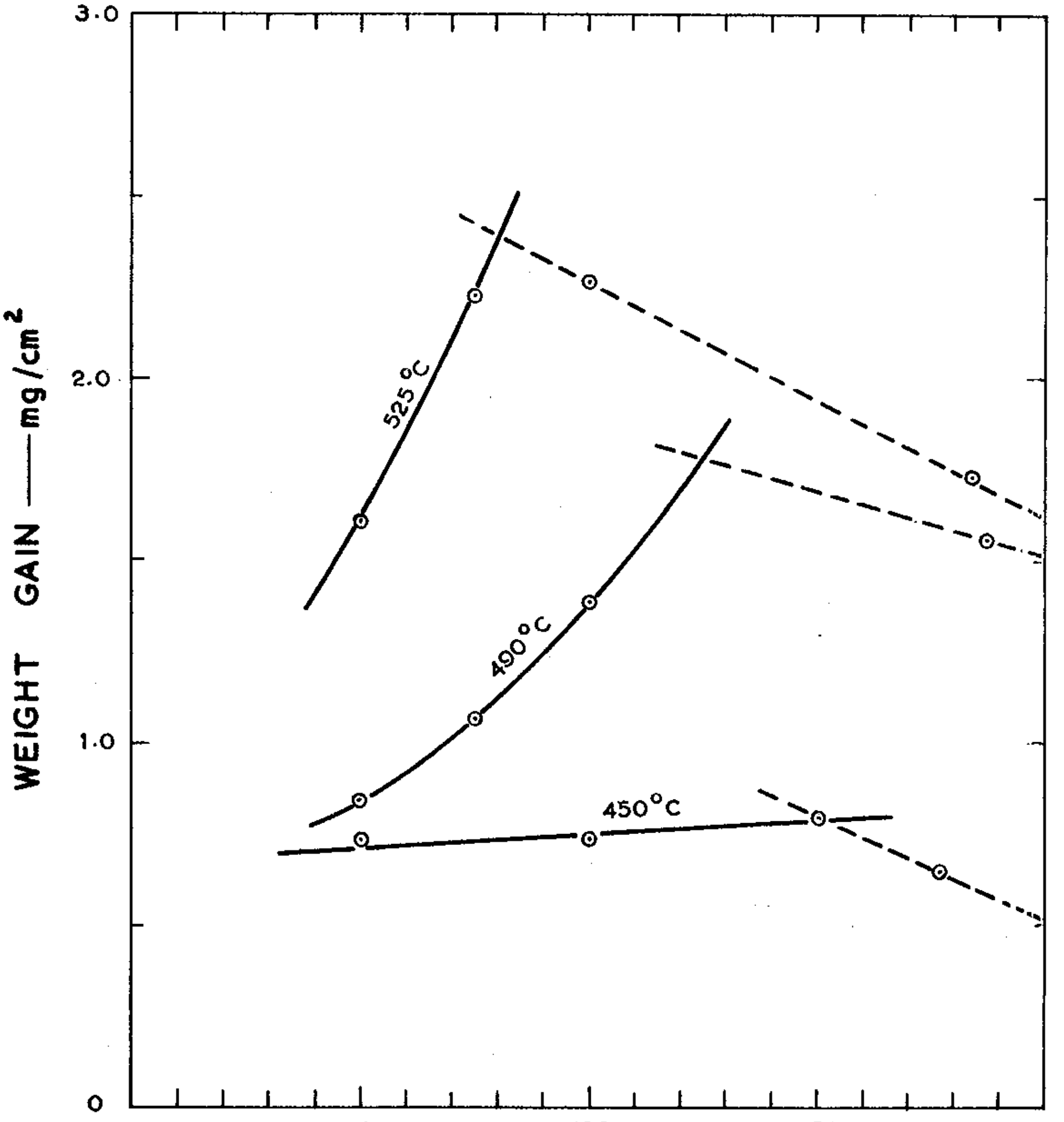


Fig. 12. EFFECT OF VELOCITY ON SCALING POINT.

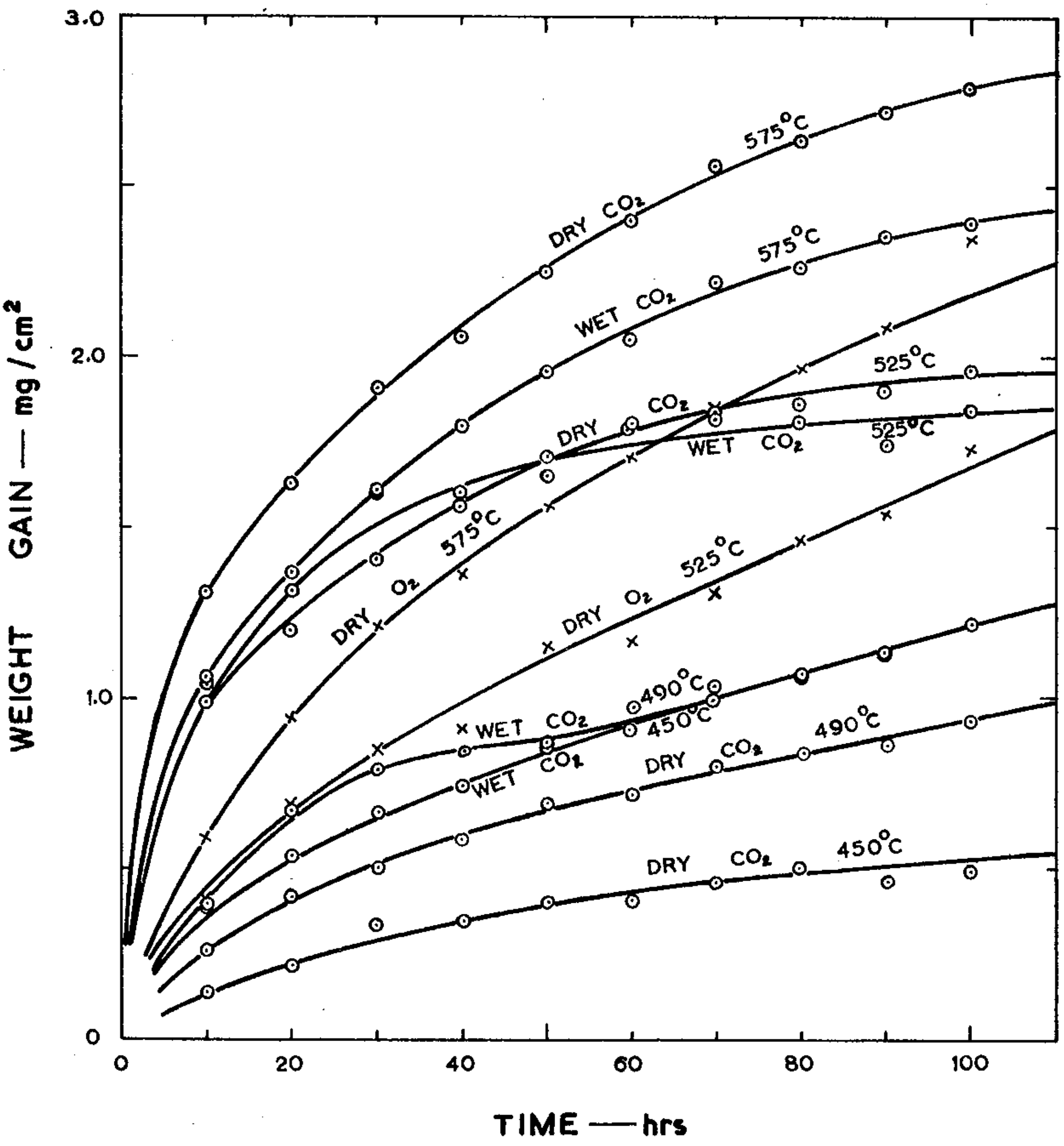


Fig. 13. WEIGHT GAIN DATA FOR 1%Cr 0·5%Mo STEEL IN DIFFERENT ATMOSPHERES.

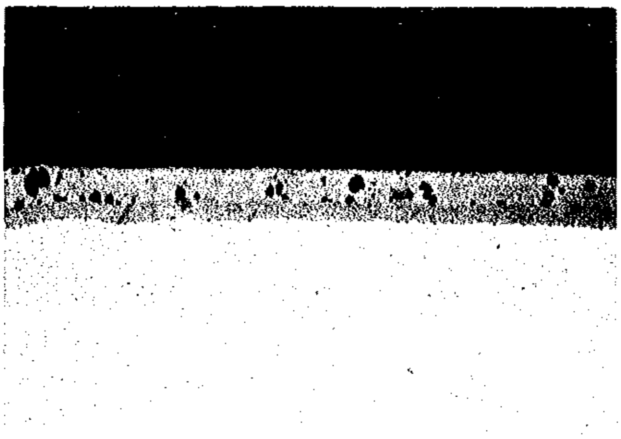
EFFECT OF SURFACE TREATMENT

x500

Fig. 14 – Oxide scale on surface ground specimen heated in CO_2 for 125 hours at 510°C, 150 p.s.i.g. Unetched.

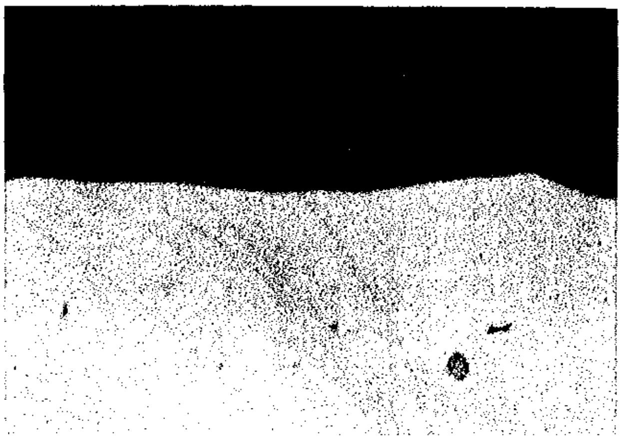
x500

Fig. 15 – Oxide scale on surface ground and polished specimen heated in CO_2 for 125 hours at 540°C, 150 p.s.i.g. Unetched.



x500

Fig. 16 – Oxide scale on vapour–blasted specimen heated in CO_2 for 125 hours at 540°C, 150 p.s.i.g. Unetched.



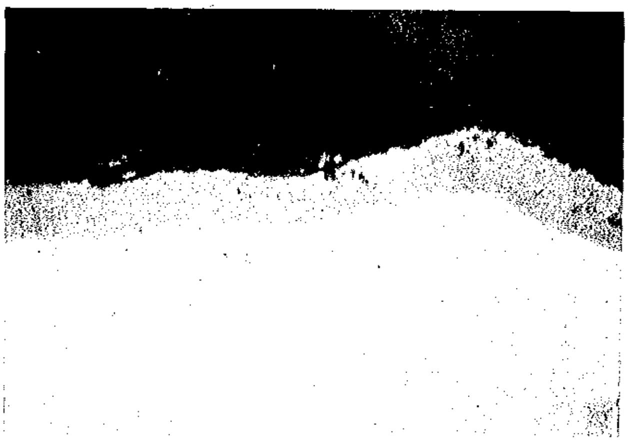
x500

Fig. 17 – Oxide scale on "as received" specimen heated in CO_2 for 125 hours at 534°C, 150 p.s.i.g. Unetched.

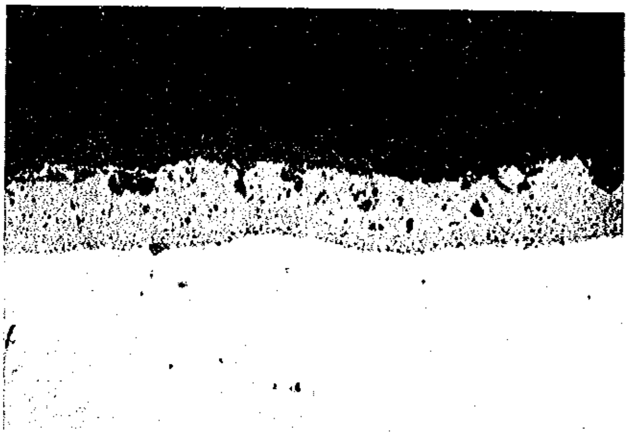
x500

Fig. 18 – Oxide scale on "as received" and etched specimen heated in CO_2 for 125 hours at 534°C, 150 p.s.i.g. Unetched.

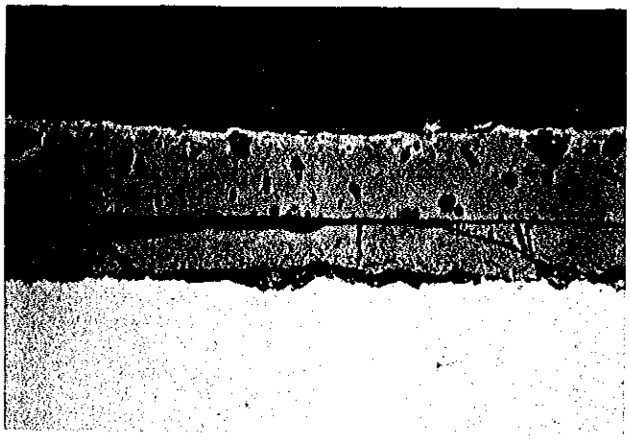
EFFECT OF TEMPERATURE



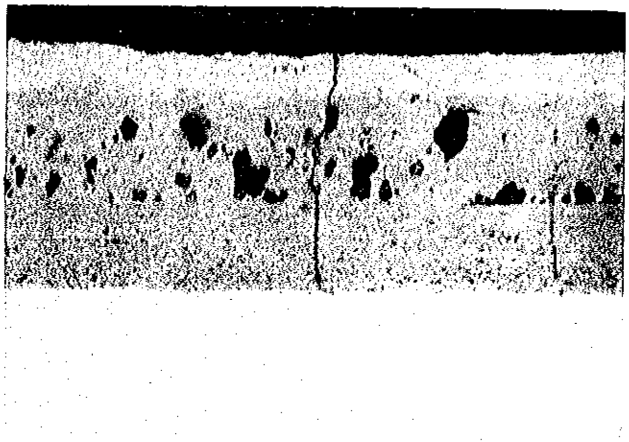
x500
Fig. 19 – Oxide scale on surface ground specimen heated in CO_2 for 1,000 hours at 450°C and 150 p.s.i.g. Unetched.



x500
Fig. 20 – Oxide scale on surface ground and etched specimen heated in CO_2 for 1,000 hours at 490°C and 150 p.s.i.g. Unetched.

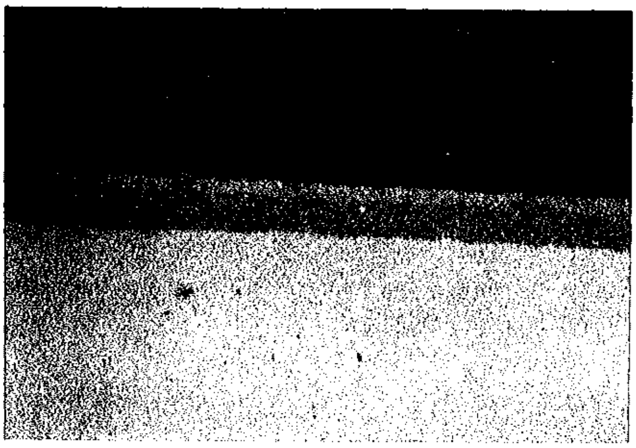


x500
Fig. 21 – Oxide scale on surface ground and polished specimen heated in CO_2 for 1,500 hours at 525°C and 150 p.s.i.g. Unetched.



x500
Fig. 22 – Oxide scale on surface ground and polished specimen heated in CO_2 for 4,000 hours at 541°C and 150 p.s.i.g. Unetched.

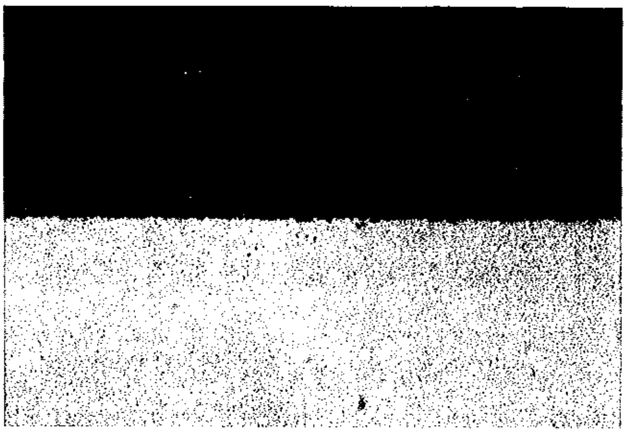
EFFECT OF VELOCITY



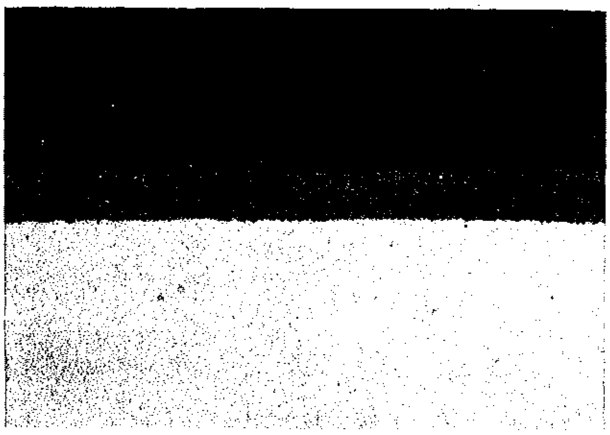
x1000
Fig. 23 – Oxide scale on rough polished specimen heated in CO_2 flowing at 75 ft/sec. for 100 hours. Temperature 490°C atmospheric pressure. Unetched.

x1000
Fig. 24 – Oxide scale on rough polished specimen heated in CO_2 flowing at 75 ft/sec. for 100 hours. Temperature 525°C atmospheric pressure. Unetched.

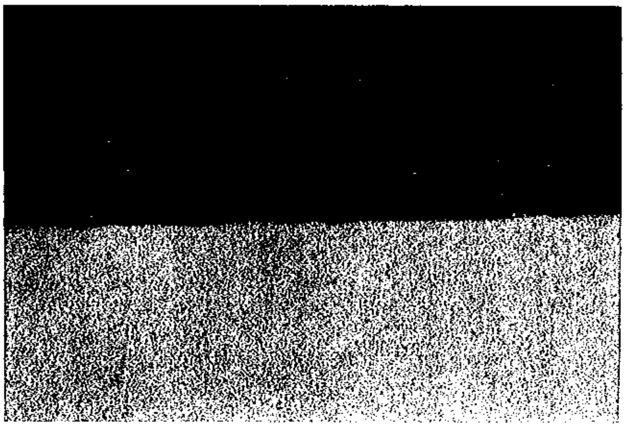
EFFECT OF EXPOSURE TIME



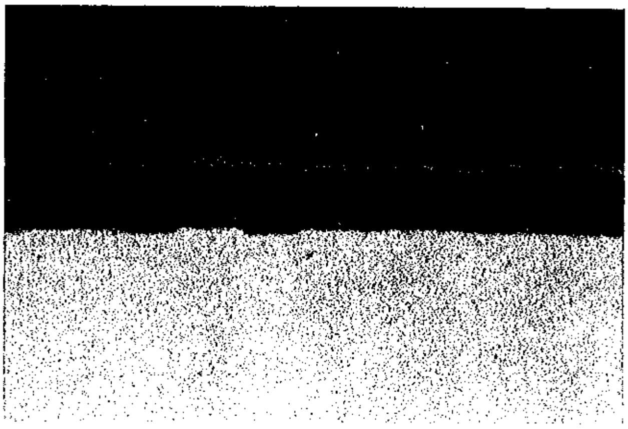
x500
Fig. 25 – Oxide scale on surface ground specimen heated in CO_2 for 115 hours at 490°C and 150 p.s.i.g. Unetched.



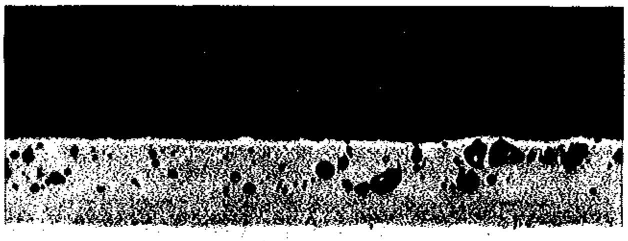
x500
Fig. 26 – Oxide scale on surface ground specimen heated in CO_2 for 194 hours at 490°C and 150 p.s.i.g. Unetched.



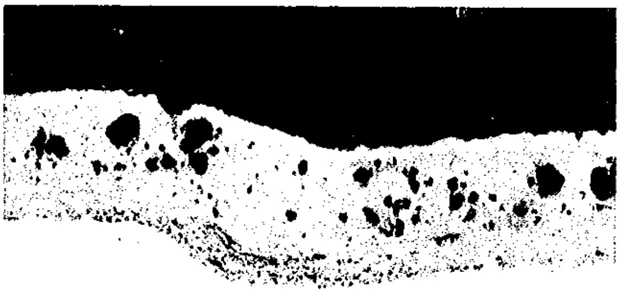
x500
Fig. 27 – Oxide scale on surface ground specimen heated in CO_2 for 306 hours at 490°C, 150 p.s.i.g. Unetched.



x500
Fig. 28 – Oxide scale on surface ground specimen heated in CO_2 for 513 hours at 490°C, 150 p.s.i.g. Unetched.



x500
Fig. 29 – Oxide scale on surface ground specimen heated in CO_2 for 744 hours at 490°C, 150 p.s.i.g. Unetched.



x500
Fig. 30 – Oxide scale on surface ground specimen heated in CO_2 for 3,000 hours at 490° C, 150 p.s.i. Unetched.

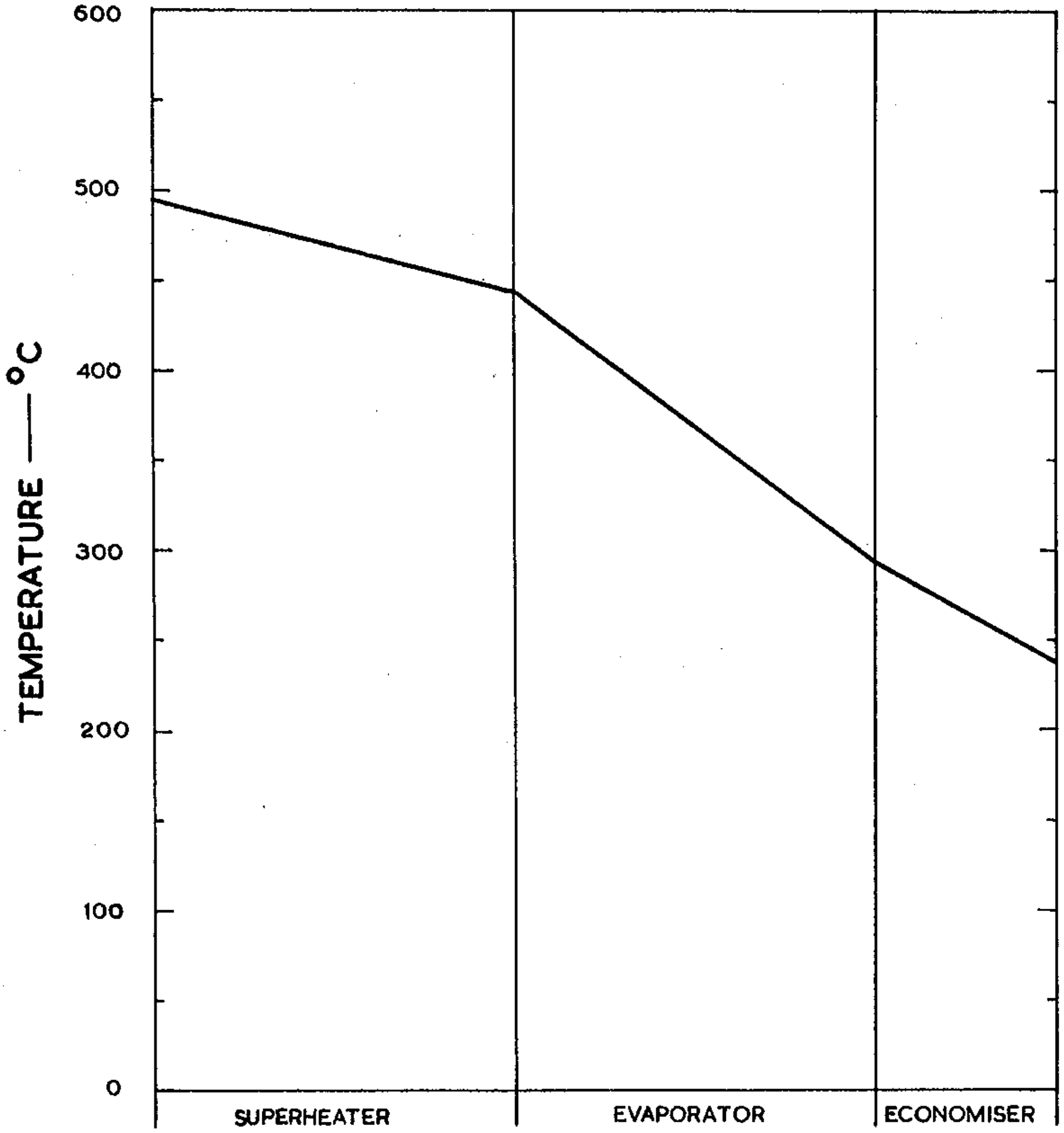


Fig. 31. GAS TEMPERATURES THROUGH HEAT EXCHANGERS