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THE MECHANISM OF FUME FORMATION
IN OXYGEN STEELMAKING

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SUMMARY

Iron oxide fume, characteristic of oxygen steelmaking processes, has been measured when produced from approximately 12 g. iron/carbon alloys contained in an alumina boat in a transparent silica reaction tube. Various oxygen/argon mixtures have been passed over the molten alloys and while a sufficiently high carbon content was present in the metal, surface decarburization occurred accompanied by vaporization of iron. The rate of decarburization was measured by means of an infra-red analyser which indicated that during this period, the rate was proportional to the oxygen partial pressure. When the carbon content was insufficient to prevent oxide formation occurring on the metal surface, a carbon monoxide boil was nucleated.

This boil has been photographed at 5000 frames/second, showing the ejection of droplets out of the bath, some of which exploded into fume.

From the difference in the nature and quantity of fume produced in the "bubbling" and "vaporization" stages, it is concluded that bubble bursting and the subsequent oxidation of iron droplets in an exothermic atmosphere is the major cause of fume formation in oxygen steelmaking.

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1. Introduction

An important stage in the production of steel is the refining process in which blast furnace iron has its constituents oxidised to a varying degree to meet a required specification. A major problem of this process has always been the production of iron oxide fume.

Present day demands for greater speed of production has entailed the use of tonnage oxygen to a rapidly increasing degree and the fume problem has escalated correspondingly.

The elimination of fume as far as legislation is concerned (Section 1 (ii)) can be achieved by two different methods. It can either be filtered off from the gases leaving the converter or it can be eliminated at source.

Some degree of success has been achieved in the latter case by blowing the bath with oxygen and various hydrocarbons, either in the form of gas or oil (Appendix 2), but clearly the most constructive means of attempting to eliminate fume is to determine the means by which it is formed initially and then to alter or remove a key stage in the process.

Thus, the aim of the research was to investigate fume and determine the mechanism of its formation.

1(1) The Fume Problem

The production of steelmaking fume is a nuisance in three different ways.

(a) Loss of Metal Yield

¹
Sargent has given approximate fume yields for various steel-making processes as follows:-

Table I

	Fume Yield %
Open Hearth	0.4
Electric Arc	0.4
Bessemer	1.0
L. D	1.0(ref 27)
Kaldo	0.5

Figure.1

The Emission of Fume from an Oxygen Blown Furnace



V.L.N. Plant,
Port Talbot.

Thus for an annual steel production of 25,8 million tons, as in 1968, an approximate fume yield would be 0.2 million tons.

(b) Cost of Fume Cleaning Plant 1, 18, 115.

The need to separate fume from its exhaust gases is a costly item, both in terms of capital expenditure, and in its operation and maintenance. Between 1957 and 1967, the use of high purity oxygen in steelmaking increased twelvefold and necessitated known capital expenditure of about £17 million on cleaning installations to comply with clean-air requirements. Sargent quotes fume cleaning as costing about 5s. per ton of steel or about £6 million per annum.

The high cost of fume separation is illustrated by the fact that about 10 percent of the capital cost of the new L.D plant at B.S.C. Port Talbot, which incorporates the O.G. system, is required for waste gas cleaning.

(c) Refractory Attack

Iron oxide, either in the form of fume or oxidised ejections is well known to have a devastating effect on steel plant refractories.^{1,74}

Silica bricks react with iron oxide to form fayalite $2\text{FeO} \cdot \text{SiO}_2$ with a consequent lowering in melting-point to about 1200°C . Chesters⁶⁵ has shown that the rate of wear of a silica open hearth roof is linearly related to the deposition of iron oxide.

For alumino-silicate refractories or clays, the silicate part forms fayalite with iron oxide as before while the alumina part forms hercynite $\text{FeO} \cdot \text{Al}_2\text{O}_3$, a spinel having a melting point of 1850°C . This, however, enters into solid solution with other spinels (e.g. $\text{FeO} \cdot \text{Fe}_2\text{O}_3$) with a resulting drop in melting point.

Magnesia refractories absorb iron oxide and form magnesio-wustite $\text{MgO} \cdot \text{FeO}$ in a reducing atmosphere and magnesio-ferrite $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ in oxidising atmospheres, both having lower melting points.

In addition, changes in refractory atmosphere,

i.e. oxidising - reducing - oxidising, cause expansions and contractions in the refractory and cracking occurs.

Finally, chrome-magnesite refractories absorb iron oxide which results in a rapid expansion and bursting.

The cost of this refractory attack is difficult to assess without having detailed figures available.

Sargent ¹ quotes refractory costs at between 5/- to 18/- per ton of steel. Present day refractory costs for the open hearth are somewhat higher than the figures given - in the order of 25/- per ton but the cost is drastically reduced to about 3/- per ton for L.D. furnaces.

1 (ii) Legislation Controlling Fume Emission From Iron and Steel Works in the U. K.

The main relevant legislation forming the basis for present day control of fume pollution from iron and steel works is the Alkali, etc. Works Regulation Act 1906 and its subsequent Orders, for which the controlling authority is the Alkali Inspectorate of the Ministry of Housing and Local Authority. Steelmaking furnaces come within the Act and the requirement is that "the best practicable means" must be used to prevent offensive emissions. The Alkali Inspectorate has defined "presumptive limits" for these emissions which must not be exceeded at any stage. The limit imposed for brown fume emission is 0.05 grains per cu. ft. (115 mg. /m³) at 15°C and 760 m.m. which applies to steelmaking processes in which oxygen is used for refining; in practice the criterion is that the stack exhaust to atmosphere should be near to the invisibility limit.

Literature Survey

2 (i) (a) Introduction

In the last ten years, the increasing use of oxygen in steelmaking with its corresponding fume problem has caused many papers to appear in the literature on fume formation.

They have either centred around the four main theories which have at sometime, been used to explain the quantities evolved, or have, given laboratory or plant observations in the hope that it would shed some light on the mechanism of fume formation. The majority of information has been qualitative and the different techniques used in producing and sampling fume have made the comparison of quantitative data unreliable.

(b) Composition

The usual concept of fume is the orange-brown haematite, Fe_2O_3 , which occurs when there is ample air entrainment into the waste gases leaving the furnace. The other extreme is the O.G. process in which no air entrainment takes place. In this case the fume is black and contains predominantly metallic iron and wustite (FeO). Thus it can be seen that the composition of fume will depend on the point of sampling and the method of collection.

The proportion of iron oxides in the total solids contained in the fume is usually within the range 85 - 95% when oxygen is being blown ¹, the remainder being made up of the oxides of other metalloids in the metal, or slag constituents.

2(c) Particle Size

Nearly every report on fume measurements has included particle size observations but these are known to be dependent on the position and particularly the method of sampling. In addition, the primary particles readily agglomerate into clusters of several microns size, whereas the initial particle diameter is usually in the range 0.01μ to 1μ .⁷⁸ The electron microscope is the only satisfactory method of particle size measurement and then only after the agglomerates have been broken down by means of ultrasonics ^{1,68}.

There has been no accepted definition of fume with reference to its particle size.

For the purposes of this investigation, fume is considered to be that proportion of material leaving the bath which is less than 5μ in diameter. Anything greater than this size would in practice present no difficulty in gas cleaning ¹⁸ providing no other objectionable factors were present.

2(d) Fume Content of Waste Gases

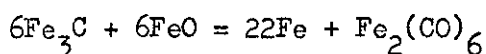
Measurements of the fume content of waste gases have produced as wide a variation of figures as have particle size measurements. This has probably been due to different sampling points and also to the difficulty in sampling isokinetically, i.e. at the same velocity as that existing at the point of sampling, in order to get a representative result. Belton ⁴⁷ quotes values ranging from 1g. /m^3 for open hearths using oxide for refining to 90 g. /m^3 for L.D. converters. Other workers quote similar results ^{42,80,81,116}.

2(ii) Current Theories on Fume Formation

(a) Volatile Compound Formation

Initial studies were carried out by Schaller and Kohlmeyer in 1939⁴⁴. They introduced into a carbon crucible containing molten iron/carbon alloy, ferric oxide pellets which were reduced to iron, absorbing carbon from the crucible. There then followed a reaction between the iron-carbon melt and a layer of molten ferrous oxide floating on the surface. Brown smoke was evolved in the burning gases, the emission of which continued until no oxide remained on the surface. They found that iron losses amounted to 45% which was reduced to 4% if the experiment was stopped before the reaction took place. Simple vaporization was discounted because of the high boiling point of iron and so the authors concluded that a volatile compound had been formed. Losses due to spraying were eliminated by using a lid to the crucible. They then investigated the factors which influenced fuming when using ferric oxide pellets and when blowing with oxygen, and found that if carbon was absent from the reaction, no fuming occurred.

Also, if there was an oxygen-free atmosphere above the melt, there were no iron losses. To determine which volatile compound was formed, they took material balances on the carbon and iron present before and after the experiment, and concluded that $\text{Fe}_2(\text{CO})_6$ was produced by the reaction:-

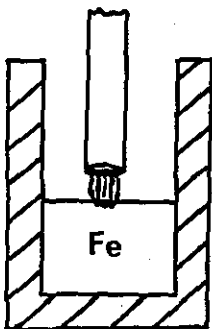


The work was continued by Kohlmeyer and Spandau⁴⁵ in 1944,

They reproduced the material balances carried out when air was blown onto a molten iron bath, held in a carbon crucible, taking a further precaution to ensure that the whole

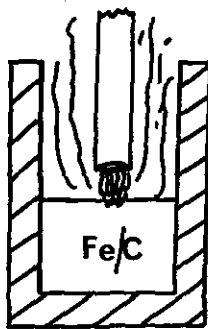
FIGURE 2

EARLY INVESTIGATIONS INTO FUME FORMATION (refs 44,45)



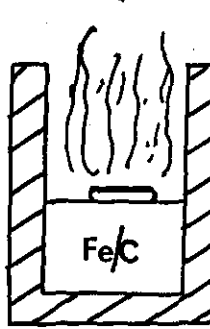
Air blown on
pure iron.

NO FUME.



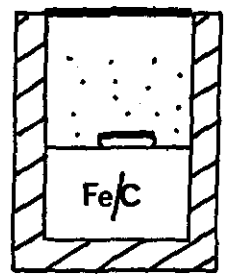
Air blown on
iron/carbon alloy.

COPIOUS FUME.



Ferric oxide pellets
on molten
iron/carbon
surface.

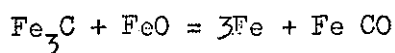
COPIOUS FUME
which continued
while oxide
remained on the
surface.



Ferric oxide pellets
on molten
iron/carbon
surface.

Inert atmosphere
over bath.
Ejections but
NO FUME.

carbon surface was covered with iron during the experiment, since they considered that the carbon loss in the early experiments could be due to direct reaction with oxygen. They found that the weight ratio of iron/carbon losses varied from 1/1 to 1/1.65, and deduced that ferrous oxide was formed when the air hit the iron surface, which reacted as follows:-



This carbonyl would immediately decompose above the bath and react with oxidising gases present to give iron oxide fume and carbon dioxide.

Characteristics of carbonyls have been given by Anderson⁴⁶ and Pearson⁹⁸. Iron pentacarbonyl is a yellow liquid with a boiling point of 103°C. Above this temperature it decomposes to iron and carbon monoxide. $\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ are unstable and $\text{Fe}_2(\text{CO})_6$ is said to be produced as a radical during the decomposition of $\text{Fe}(\text{CO})_5$.

Turkdogan and Leake⁵² examined fume formation on two different scales using 1 g. melts held in reaction boats in a horizontal furnace and 900 g. samples melted in a high frequency furnace. They investigated various alloys of iron and found that for fume formation to take place, carbon must be present. On the larger scale, they obtained a linear correlation between carbon content and fume formation rate until approximately 2% carbon was reached when there was a sharp cut-off with little fume formation occurring at lower carbon contents. Their maximum fume rates were 0.4 mg./cm²sec of Fe at 3.5% carbon which reduced to 0.016 mg./cm²sec at 2% carbon irrespective of whether air or oxygen was being blown.

When carbon monoxide was bubbled through iron-carbon melts, no fumes were observed which they considered would make the carbonyl theory even more unlikely. They favoured the theory of a sub-oxide formation by considering the data of known sub-oxides, SiO , Al_2O and Zr_2O . From their results of quantity of fume for known carbon reduction, and assuming that all gases evolved were carbon monoxide, the apparent vapour pressure of iron was about one tenth of an atmosphere although Sargent ¹ considers that the fume measurements may have been high due to the entrainment of large particles from the bath. In the small-scale experiments on a series of iron-carbon alloys, there appeared to be a definite correlation between the iron collected and the volume of carbon monoxide generated. Bates ⁵¹ carried out some experiments investigating volatile compound formation using a small carbon crucible and ferrous oxide. The fume was collected under argon on a copper condenser, and provision was made to avoid splashes being collected. This fume was examined by X-ray diffraction and a compound was found which did not appear in the ASTM index. Nevertheless, he concludes that volatile compound formation probably plays only a minor part in fume formation.

The most detailed study on volatile compound formation was reported by Belton ^{47,66}. He studied the volatilization of solid iron in atmospheres of $\text{H}_2\text{O} - \text{H}_2$ and $\text{CO} - \text{CO}_2$. The gases were not sufficiently oxidising for free FeO to form on the metal surface. The iron loss in weight was greater than that expected from normal vapour pressure effects. An enhanced volatility was observed in every case, the volatility increasing with increasing partial pressure of steam or carbon dioxide.

He obtained apparent vapour pressures of iron in the volatile species as approximately 10^{-5} atmospheres depending on the temperature and gas composition, considerably less than the 10^{-2} atmospheres that a volatile iron compound would need to exhibit to explain commercial fume quantities.

Belton deduced that the volatile species in $H_2O - H_2$ atmospheres was $Fe(OH)_2$. With $CO - CO_2$ atmospheres, the formation of FeO_2 and $FeCO_3$ was suggested but not confirmed. He considered that if a volatile compound existed, it would have been observed in his work and that the enhanced volatilities measured could not account for the quantities of fume obtained in industrial steelmaking.

(b) The "Hot Spot" Theory

When oxygen or air reacts with any of the elements contained in a steel bath, the result is usually a liberation of heat and an observation of the impact zone in a steel converter clearly shows that it is at a much higher temperature than that of the bulk of the bath. Because of the considerable increase in vapour pressure of iron for increasing temperatures above about 1700°C (fig. 3), a theory has been postulated which suggests that the fume is a consequence of the enhanced vapour pressure of the impact zone.

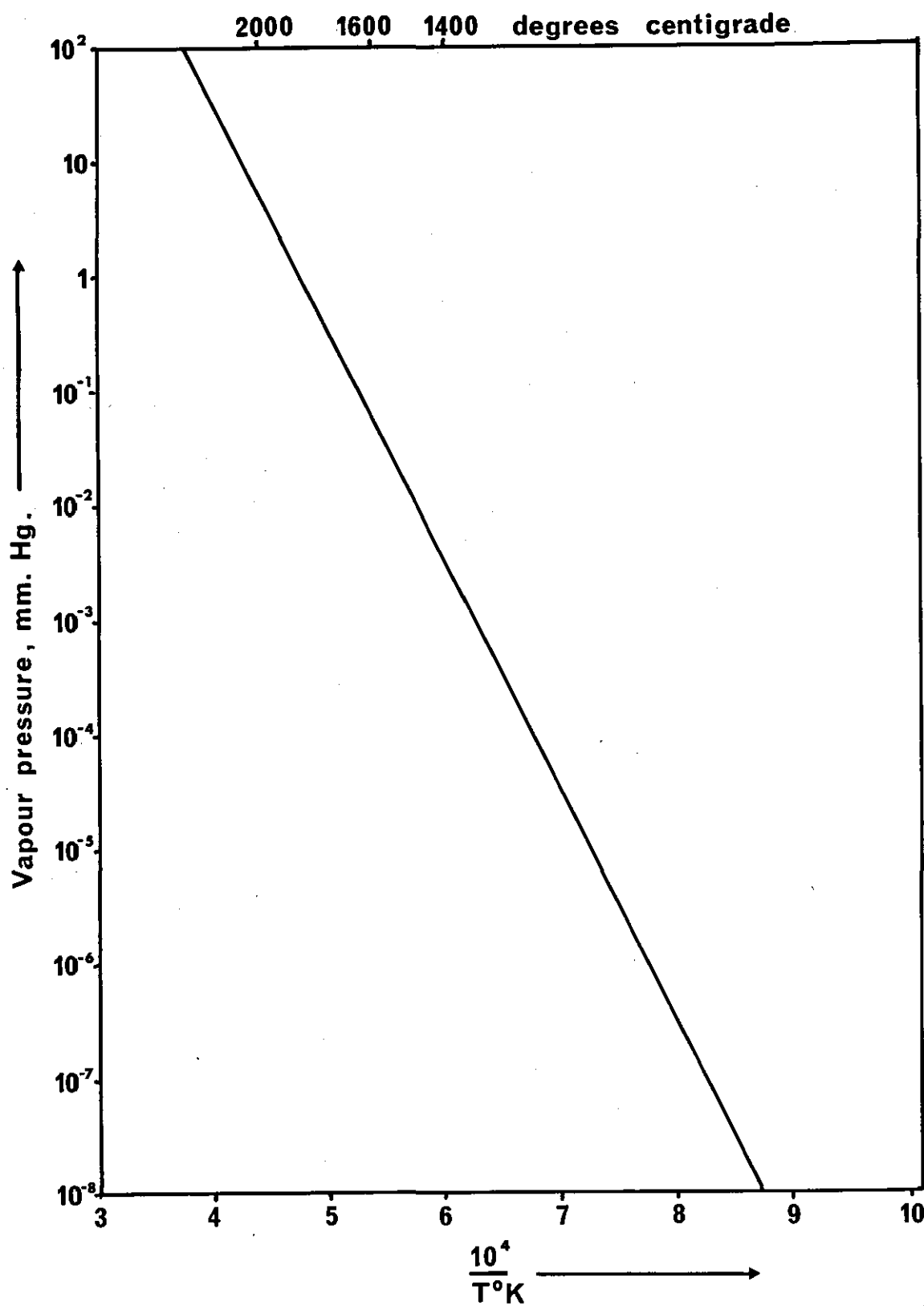
Workers who have investigated this theory have obtained results either by measurement of the temperature contours around the hot-spot or by calculation of the temperature which should exist if assumptions which have to be made, are valid.

Kosmider, Neuhas and Kratzenstein⁷⁷ calculated the temperatures occurring at the tuyere in a bottom-blown converter. They considered that the heat generated would not be conducted away from the rising bubbles. When blowing air, temperatures of $2,300^{\circ}\text{C}$. were calculated; with 35% oxygen, this rose to 2650°C . Richardson^{3(g)} considered that the heat transfer assumptions were not valid leading to large errors in the calculations. Pearson⁹⁸ modified the calculations of Kosmider so that the temperature of the gases passing through the melt were at the same temperature as the iron oxide skin round the bubble. He was able to show that the fume concentrations produced in the diluted gas (0.8g./m^3) were similar to those reported by Kosmider ($0.4 - 0.9\text{ g./m}^3$). Rengstorff⁵⁴ repeated Kosmider's calculations and investigated the effect of various additions into the inlet gas. Adding 10% hydrogen into the air reduced the temperature by 90°C and he concluded that temperature considerations alone could not explain why hydrogen additions suppress fume.

FIGURE 3

THE VAPOUR PRESSURE OF IRON

from Hultgren(ref. 21)



Bogdandy and Pantke¹⁴, also considering bottom-blown converters, calculated the impact temperatures from known dust concentrations and depending on oxygen concentrations, they obtained figures of $200^{\circ}\text{C} - 500^{\circ}\text{C}$ above the bulk bath temperature. They considered that as the bubbles cooled, the iron atoms would agglomerate into droplets so reducing their mobility in the nitrogen carrier gas, and making the likelihood of their coming into contact with the wall of the bubble very remote. The virtual absence of fume at high carbon levels was explained in that additional bath convection was produced during carbon monoxide formation which would increase the probability of the iron droplets coming into contact with the bubble walls.

Engh and Widmark^{30,32} have derived a computer programme to simulate the operation of an oxygen blown open-hearth. They assumed a temperature of 2400°C at the gas metal interface and showed theoretically that when a bubble of CO + iron vapour breaks off from the main gas jet only one quarter of the iron gas escapes with the bubble, the remainder diffusing through the CO and striking the bubble walls.

In order that the hot-spot temperature can be measured, some form of optical pyrometer is used. Unfortunately, this mode of measuring temperature provides a source of considerable error in as much as with all non-black bodies, the temperature observed is always below the true temperature. Hence the need for emissivity corrections arises. The emissivity of pure iron varies from 0.42 to 0.5 over the temperature range $1540^{\circ} - 1900^{\circ}\text{C}$ ⁶⁴ while that of oxidised iron lies within the range 0.5 - 0.7¹⁰⁰. The results of Dastur⁶⁴ have been extended by Rist and Chipman¹⁰¹ to include iron/carbon alloys. Thus with emissivity corrections being temperature dependent and possible doubts arising from the composition of metal being observed, published temperature figures have to be interpreted with caution.

Urbain ² studied the effect of bath composition on the temperature of the hot-spot. He assumed an emissivity figure of 0.4 and obtained excess temperatures of 600°C with iron/carbon alloys in a 2lb furnace, which dropped as the silicon content in the initial charge was increased, giving an excess temperature of 330°C at 2.4% silicon. The silicon/oxygen reaction is considerably more exothermic than the equivalent carbon/oxygen reaction, and so Urbain's results would not appear to fit in with the thermodynamic data. Sargent ¹ considers that in the case of silicon/iron alloys, a silica film will be formed over the metal, limiting the rate of reaction.

This effect is mentioned by Distin ⁸⁴ who refers to experiments using levitated copper spheres in oxidising atmospheres in which very small traces of silicon in the metal gave rise to a silica film on the metal surface. He considered that the same effect was occurring in his work on iron/carbon levitated spheres which impeded the transfer of oxygen into the bulk metal from the gas phase. Naeser ¹⁰² measured hot-spot temperatures in excess of 2200°C when using an oxygen enriched blast. This figure is typical of many (eg) ¹².

It appears that the best means of overcoming emissivity errors at present is to use the two colour pyrometer. ¹⁰³ This instrument is based on the assumption that the ratio of the emissivities in two wavelength bands can be more accurately known than the absolute value of either emissivity. Results obtained by Beitelman (reported in ref. 86) using this special optical technique show hot-spot temperatures 630°C higher than the bulk bath temperature.

The effect of bath temperature on fuming is somewhat confusing in the literature. Rengstorff ⁵⁵ showed a significant drop in fuming for increase in temperature, the fume at 1620°C (.044mg/cm²sec) being one-fifth of that at 1320°C.

A graphite crucible was used and it was assumed that the iron was always saturated with carbon. These results are contrary to other results published ^{1,50,97}. Turkdogan ⁴⁸ whose theory is reported in the next section, considered that temperature would have little effect. Munro ⁸⁶ considered that at different temperatures, there were different conditions existing in Rengstorff's experiments. The carbon monoxide produced by blowing oxygen onto the bath would be oxidised to carbon dioxide. At low temperatures this will oxidise the vaporized iron giving an enhanced vaporization effect. At higher temperatures, the endothermic reaction between carbon and carbon dioxide will be favoured, which might produce reducing conditions within the boundary layer, so preventing enhanced vaporization.

In conclusion, it is difficult, particularly in top-blowing, to explain fume formation as saturation of carbon monoxide at the hot-spot temperature, since much of the gas will emerge at the bulk bath temperature rather than in the impact zone. Results ^{1,52,58} show that a temperature of 2300°C is required if simple saturation of gas is the only mechanism to exist.

(c) Vaporization Enhancement

Vaporization - Oxidation Theory

The most precise explanation of fume formation has come from Turkdogan, Grievson and Darken 13,48,49.

The following is an outline of their theory:-

When a stream of oxygen and argon flows over a molten metal surface, there is a counterflux of oxygen and metal vapour. In the case of molten iron for example, iron vapour and oxygen react close to the metal surface and form wustite, which for the sake of simplicity is written as FeO. This is in a state of fine sub-division and provides a sink for the vaporized iron and oxygen. Thus concentration profiles will be set up as shown in figure 4.

Under laminar flow conditions in the steady state, the counterflux of iron vapour and oxygen is given by Fick's law.

$$J_{Fe} = \frac{D_{Fe}}{\delta RT} (P_{Fe} - P_{Fe}^1) \text{ moles/cm}^2 \text{ sec.}$$

$$J_{O_2} = - \frac{D_o}{(\Delta - \delta) RT} (P_{O_2} - P_{O_2}^1) \text{ moles/cm}^2 \text{ sec.}$$

Where D_{Fe} = interdiffusivity of Ar + Fe vapour

D_o = interdiffusivity of Ar + O_2

R = gas content

T = temperature

x = distance measured from metal surface.

Δ = thickness of boundary layer.

P_{Fe} = vapour pressure of iron at $x = 0$

P_{Fe}^1 = vapour pressure of iron at $x = \delta$

δ = distance from metal surface where iron oxide

fog is formed.

P_{O_2} = partial pressure of oxygen at $x = \Delta$

$P_{O_2}^1$ = partial pressure of oxygen at $x = \delta$

FIGURE 4

VAPORIZATION-OXIDATION THEORY

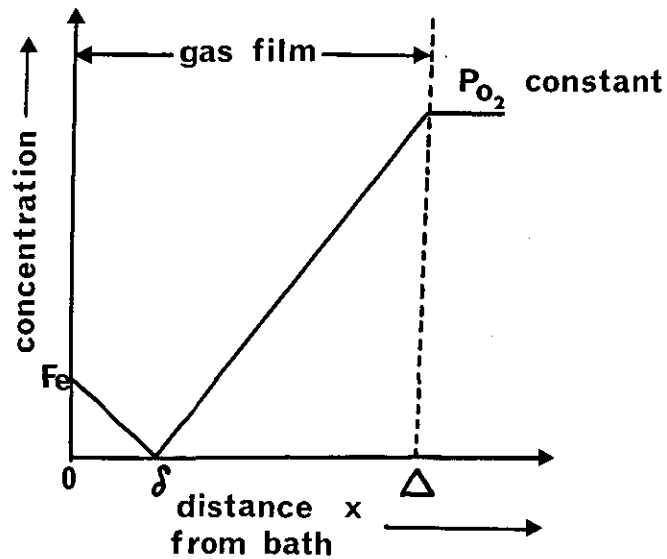


Diagram showing the concentration of iron vapour and oxygen in argon under isothermal conditions

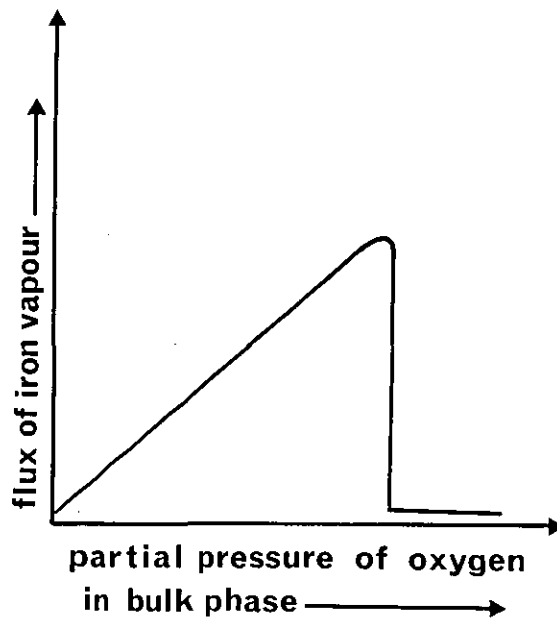
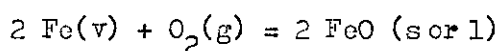


Diagram showing the variation of flux of iron vapour with oxygen partial pressure

At a distance δ , the reaction



is assumed, and since P_{Fe}' and $P_{\text{O}_2}' \ll P_{\text{Fe}}$ and P_{O_2}

$$J_{\text{Fe}} = 2 J_{\text{O}_2} = 2 \frac{D_{\text{O}_2}}{\Delta} \frac{P_{\text{O}_2}}{RT} \text{ moles / cm}^2 \text{ sec.}$$

$$\therefore J_{\text{Fe}} = 2h \frac{P_{\text{O}_2}}{RT}$$

Where $h = \frac{D_{\text{O}_2}}{\Delta}$ the average film mass transfer coefficient for the transport of oxygen through the diffusion boundary layer.

The mass transfer coefficient can be calculated for known flow conditions and hence it can be seen that for a given temperature and constant flow conditions, the rate of vaporization of iron should increase linearly with the partial pressure of oxygen.

However, the rate of evaporation at any temperature cannot exceed that which would occur in vacuo. The maximum rate of evaporation in vacuo is given by the Langmuir equation

$$J_{\text{max}} = \frac{P_i}{\sqrt{2 \pi R T M_i}}$$

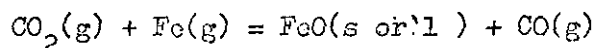
where P_i and M_i are the vapour pressure of metal i and the molecular weight of the metal vapour respectively. As the limiting value for the flux of vapour is approached, δ approaches the value of the mean free path at which Fick's law does not apply, and the vapour in contact with the metal surface is no longer saturated. On further increase in the oxygen partial pressure at Δ , i.e. decrease in δ , the flux of oxygen towards the metal surface is greater than the equivalent counter-flux of metal vapour, resulting in oxidation of the metal surface. Turkdogan refers to the work of Darken and Gurry¹⁵ who found that the vapour pressure of Fe at 1600°C decreases by a factor of 10^5 at the oxide/oxygen interface compared to the metal/oxide layer.

Thus a cut-off of fume will occur, as shown in figure 4, when the oxygen partial pressure in the gas stream exceeds a critical value.

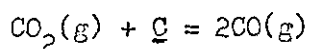
Using equipment similar to that described later, they obtained results which completely agreed with their theory. The calculated values for interdiffusivities which they used agreed within $\pm 10\%$ of experimental results which they obtained elsewhere ¹⁶.

Turkdogan found that this theory was valid for any metal and that the flux of vapour was independent of the vapour pressure of the metal.

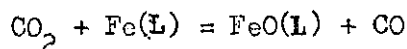
In the case of iron/carbon, however, he extended his theory but did not provide the results to substantiate it. He considered that within the boundary layer, oxygen and carbon monoxide would counterdiffuse and react to form carbon dioxide. For simplicity this reaction was assumed to go to completion. Near the surface CO_2 reacts with iron vapour thus:-



If the flux of CO_2 is greater than that required to obtain maximum vaporization, the remainder of CO_2 diffuses to the surface where the following reaction takes place:-



If this reaction is slow compared to the flux of CO_2 , then:-



causing a fume cut-off.

Sargent¹ has considered the extension to Turkdogan's theory and concluded that it did not explain the finite slope of the graph of fume against carbon content above the cut-off^{52,58}. Turkdogan referred back to an earlier paper when top blowing oxygen onto an iron/carbon bath, where at the highest carbon contents (3.5%) his fume quantities (.024g. Fe/cm²min) were close to those predicted on the grounds of maximum vaporization (.026g. Fe/cm²min) at 1600°C. Table 2 gives

figures for the maximum evaporation rates of iron at different temperatures and also a calculated total loss from a 20 minute blow with an arbitrary reaction area of 1000 cm^2 . The rates for iron/carbon melts will be lower due to carbon having a substantial influence on the activity of iron. A 4% carbon content for example would reduce the vaporization by about 30% and a 1% carbon content by 5%.

TABLE 2

Calculated Maximum Evaporation Rates (in Vacuo)

Temperature °C	1600	1800	2000	2200	2400	2600
J_{Fe} moles/cm ² sec	1.2×10^{-5}	1.1×10^{-4}	7.2×10^{-4}	3.2×10^{-3}	1.2×10^{-2}	3.8×10^{-2}
Batch loss, Kg. Fe	0.8	7	48	215	810	2540

Now that the concept of slag-metal emulsions has been recognised as perhaps the major contributory factor to the bath reactions, the idea of a hot-spot reaction zone or even a hot crater zone providing the chief area for decarburization is almost certainly erroneous. Meyer⁹⁰ talks in terms of a reaction area of $150,000 \text{ ft}^2$ for a 200 ton B.O.F. One can only speculate on how much of this area reacts with oxygen and how much with the slag.

If maximum evaporation produced all of the 1% fume loss for a 20 minute blow at 1600°C , the reaction area would be about $2,700 \text{ ft}^2$. At 1800°C the area would be about a tenth of this.

Enhancement of Vaporization by a Convection - Condensation Process

A bath of molten steel at 1600°C will vaporize according to its vapour pressure into the atmosphere above the bath. If this atmosphere is at a reduced temperature compared with that of the bath, condensation may occur close to the metal surface.

Thus a steeper concentration gradient will be produced with a correspondingly higher flux of iron than that predicted on mass-transfer considerations alone. This has been the subject of a number of recent papers ^{28,29,57,60}.

An enhancement of tenfold was predicted by Hills and Szekely⁵⁷ who considered that condensation occurred as soon as the vapour pressure at the cooler temperature was exceeded. Turkdogan and Mills^{28,29} predicted an increase of 2 to 4 times might be expected for an iron droplet at 2000°C held in static helium at an ambient temperature of 77°C . Their predictions were verified by experimental results and differed from the predictions of Hills in that they allowed for a degree of ~~super~~-saturation in the gas phase before condensation occurred. An enhancement of 3 to 5 times was obtained by Distin⁸⁴ for levitated spheres and is in good agreement with the measurements of Toop²⁰. This effect will be magnified if the convection process is occurring from a droplet thrown up from the bath. The vapour pressure over a droplet is greater than that over a plane surface according to the expression:-

$$\log_e \frac{c_p}{c_p} = \frac{2\gamma V_m}{RT_r}$$

where c_p & c_p are the vapour pressures over the plane and curved surfaces respectively, γ is the surface tension and V_m is the molar volume.

Sargent¹ has shown that an enhanced vaporization of approximately 10 would only be obtained from a droplet having a radius of $10^{-4} \mu$ and as such this enhancement would be unlikely to contribute significantly to fume formation.

(d) Ejection of Droplets

In this mechanism, particles are ejected into the atmosphere above the bath, where they either explode or evaporate into fume. The method of getting these particles out of the bath is assumed to be either a consequence of carbon monoxide bubbles bursting or splash caused by the high oxygen lance velocities used in modern furnaces. It has been shown^{50,67} that although this latter case may well be a contributory factor, it is certainly not a necessary cause of ejections. This was verified in the large scale experiments (Appendix I) where "soft" blows which produced no splashing with argon, produced copious ejections with oxygen.

Mechanism of Bubble Bursting

Szekely⁶⁷ and Sargent¹ have reviewed the topic. They found that bubbles can burst according to two mechanisms (figure 5).

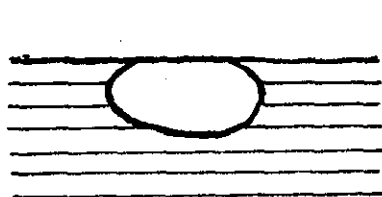
When a small bubble arrives at the gas/liquid interface, a gas dome protrudes from the surface which then explodes into minute fragments.

If a large gas bubble arrives at the surface, the inertia of liquid flow in the tail of the rising bubble ejects a liquid jet. This jet breaks up into droplets. Newitt et al¹⁰⁴ observed both effects occurring for air bubbles in water. Richardson¹⁰⁵ and Distin⁸⁴ have shown high speed photographs illustrating the latter effect taking place in molten iron/carbon alloys.

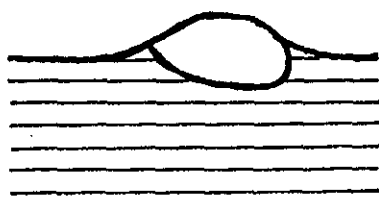
Newitt gave typical sizes for the droplets ejected. The small droplets produced by the disintegration of the dome were a few microns in diameter in his experiments, whereas the large droplets produced by the break-up of the jet were in the order of 1mm.

FIGURE 5

MECHANISM OF BUBBLE BURSTING .



1



2



3



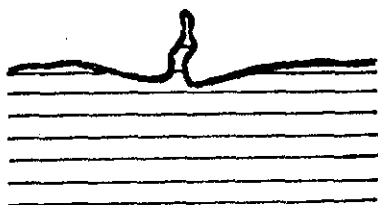
4



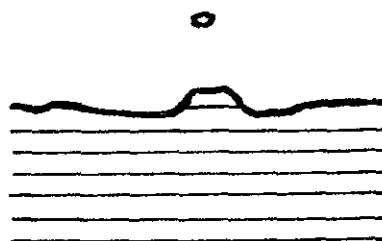
5



6



7



8

Experimental Work

Turkdogan⁴⁹ has reported that in laboratory experiments using 2lb melts, it was noted that below 2% carbon, carbon monoxide bubbles came from within the melt, while at higher carbon contents, the reaction appeared to be occurring at the gas-metal interface, judging from the size of the bubbles and the way in which they burst. Rengstorff⁵⁵ noted the exact opposite effect with a deep seated boil at high carbon contents and surface decarburization at below 1% carbon. Using a system of concentric graphite baffles around the impact zone in an experimental top-blown furnace, Morris⁵⁰ studied the origin of ejections when blowing oxygen at different carbon levels. There was no splashing from the jet. At the highest carbon levels (3.8%), all ejections came from the impact zone and were small in size consistent with bubble generation near the surface of the bath. As the carbon content fell, the ejections spread over the whole of the bath and both the weight and particle size increased apparently as a result of an increase in bubble size (figure 6).

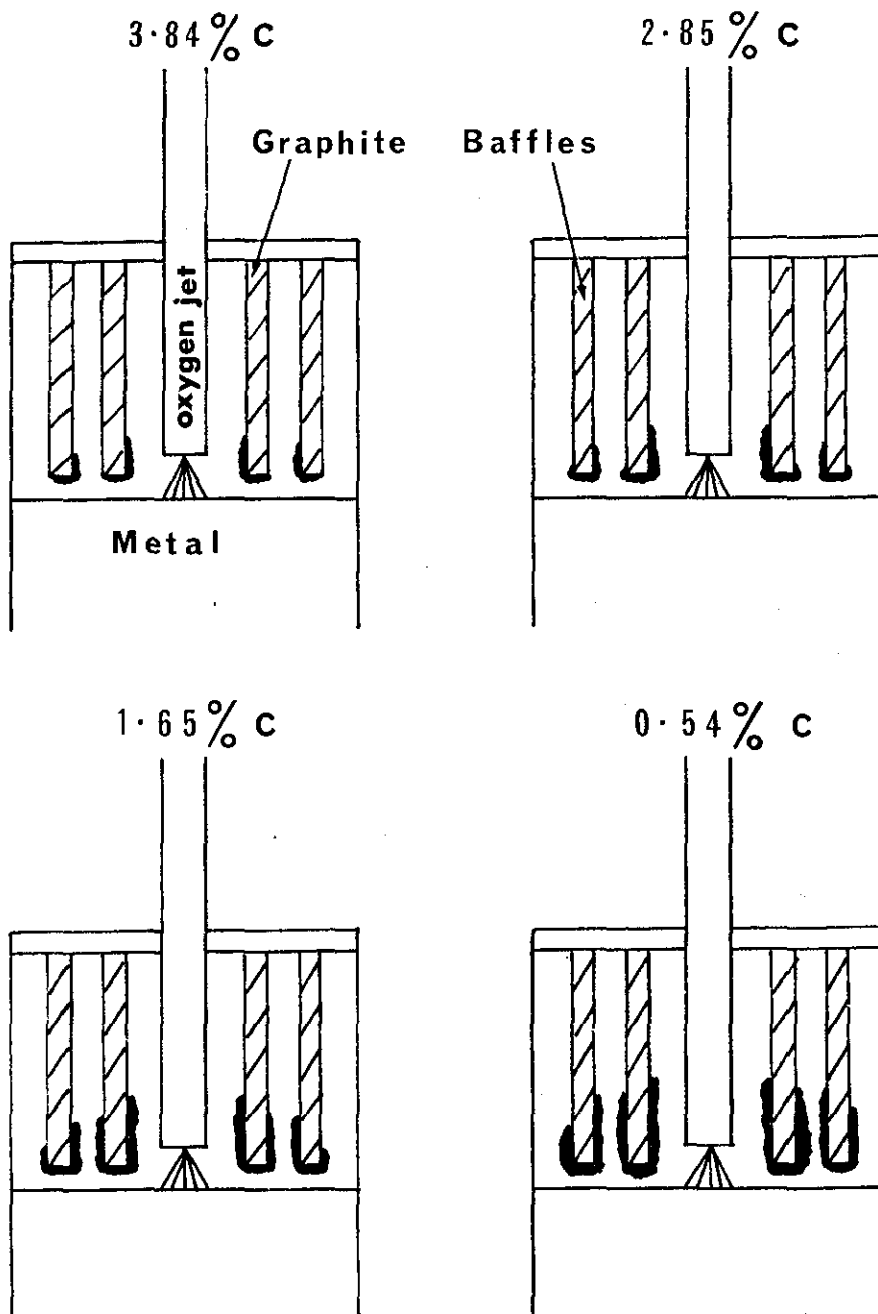
This may give a clue to the dependence of fuming on carbon content, in conjunction with the observations of Baker⁸ who found that small droplets falling through oxygen decarburized at a faster rate than larger ones. At a particular carbon content the droplets exploded into fume so that the smaller particles would disintegrate more quickly. Thus at high carbon contents, there are small particles ejected into the region of the jet which is highly oxidising, giving large quantities of fume. Now it has been widely reported that there is a zone above a steel furnace which has a reducing atmosphere when the furnace is being blown with oxygen eg. ¹⁰⁶. At low carbon contents, therefore, ejections will pass into this region and remain unoxidised.

Kootz²⁶ reported that fuming during top-blowing was coincident with the conditions for spraying of metal droplets. Rote and Flinn⁷⁵ using a 300lb furnace investigated the quantity of spray thrown up from

FIGURE 6

EFFECT OF CARBON CONTENT ON SPRAY PATTERNS .

from Morris (Ref. 50)



As carbon content decreases :

- a) weight of spray increases
- b) particle size of spray increases

the furnace under normal conditions and found that for a $5\frac{1}{2}$ minute run, the weight of droplets ejected was about equal to the bath weight when top-blowing oxygen at 30 p.s.i.g.

(iii) General Investigations on Fume Formation

An examination of the effects influencing fume formation was carried out by Miqawi^{68,70} using a 1.5 k.g. induction furnace. He found with oxygen blowing that up to a carbon content of 0.5%, practically no brown smoke was formed. Up to 2% resulted in a slight, but continuous, increase (up to 0.8g./m.³sec) but with higher carbon contents there was a marked increase in fuming rates, (up to 16g./m.³sec at 4% C). He examined the composition of the fume produced when blowing various gases onto the melt. The fume was drawn off the surface of the metal and cooled in a copper container placed in a Dewar flask of liquid nitrogen. He found that the dust particles were Fe_3O_4 irrespective of the composition of the gas phase with a particle size of 0.01 μ , compared with 0.5 μ when slower cooling took place. He discounted the bubble bursting theory on the grounds of small particle size and considered that fuming was a result of the vaporisation of Fe_3O_4 . He obtained vapour pressure figures for Fe_3O_4 using a platinum boat containing Fe_3O_4 connected to a weighing system and placed inside a sealed quartz ampoule. The vapour pressure was determined from the loss in weight of the boat and contents when the ampoule was placed in a muffle furnace at various temperatures. He also obtained approximate vapour pressure figures for wustite which were in agreement with Darken and Gurry¹⁵ and showed that the vapour pressure of Fe_3O_4 is considerably greater than those of FeO and Fe and less temperature dependent.

Holden⁵³ reported investigations by B.C.I.R.A. on the effect of metalloids on fuming which were extended to include results at different temperatures. Iron with 1% phosphorus produced white fume for a few seconds but apart from this, no fume was produced from alloys not containing carbon. Increasing the temperature had no visual effect.

Knaggs and Slater ⁵⁸ investigated fuming from a 350lb furnace. They found that for a fixed mean carbon level, the rate of fume evolution increased as the oxygen flow rate increased, and thus the rate of fume evolution also increased with the rate of carbon removal. For a mean carbon content of 0.8% (i.e. average of the initial and final contents for a 30 second blow), 7.5 litres/sec oxygen produced 2.7 mg. fume/sec, 12.2 litres/sec. produced 4.3 mg./sec. and 15.5 litres/sec produced 6.7 mg./sec. They sampled the fume 3 inches above the slag surface and some 15 inches higher and found it to consist mainly of elemental iron and ferrous oxide while samples taken from the duct leaving the furnace consisted of Fe_3O_4 .

(iv) Decarburization of Iron/Carbon Alloys

The mechanism of carbon oxidation in steelmaking processes has attracted considerable attention in recent years. The classical model considers that the carbon/oxygen reaction takes place at the surface of carbon monoxide bubbles which have originated either in crevices in the refractory surface or other suitable nucleation sites and subsequently rise through the metal bath.

Studies in this subject have considered the molten iron/carbon system in three different ways.

(a) Top blowing a molten steel bath with oxygen

In a series of papers, Fujii⁵⁹ has made a comprehensive study of decarburization. His findings which have been confirmed by several workers, show that at high carbon contents, the reaction rate is determined by the mass transfer of oxygen through the gas film and hence with a constant oxygen input, a corresponding constant rate of decarburization is obtained. At a certain low carbon content, there is a change of control and the decarburization rate decreases, being no longer a function of the oxygen input, but dependent on the carbon content of the bath. This change of control occurred at 0.15% C for 20% oxygen, decreasing with decreasing oxygen partial pressure to 0.03% C for 5% oxygen. He found that the decarburization rate was proportional to the area of metal surface.

Li⁷ working with a 500lb induction furnace found that the change of control took place at about 0.5% C, but showed that there can be a considerable variation in the path of decarburization for experimental heats blown under nearly identical conditions. Szekely⁷² postulated a model in which the principal mechanism of decarburization was the reaction between carbon monoxide bubbles and an emulsion consisting of molten iron and molten iron oxide particles in the vicinity of the slag-metal interface. He considered that the diffusion path of oxygen would be much shorter than that of carbon which would explain the carbon-control model.

The importance of slag-metal emulsions has been reported recently by Meyer^{88,90}. He has given the sizes of metal droplets within the slag as $1\frac{1}{2}$ mm. down to 150μ having a carbon content lower than that of the bath, sometimes by as much as 1.5%. Electron microprobe studies identified iron oxide particles within some of the droplets. He stated that at least 30% of the metal bath can be in the slag-metal emulsion layer and as much as 65% of decarburization over the entire blowing period can take place in this region.

Several workers eg. Breuer¹⁰⁷ and Kosaka⁷¹ have noted that at high carbon contents, bubble formation is only noticeable in the vicinity of the jet crater and at low carbon contents, the melts exhibit particularly powerful bubble movements from the lower layers of the bath. This agreed with the observations of Morris⁵⁰ mentioned in an earlier section who studied the origin of ejections using graphite baffles.

(b) Falling droplets

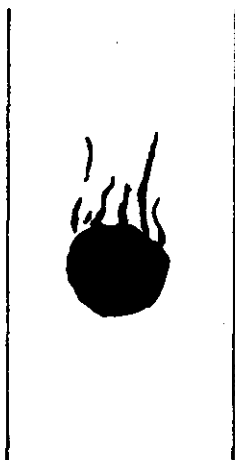
Baker, L. A. and Ward⁴ have examined the reaction of an iron-carbon droplet during free fall through oxygen, in view of the potential of spray-steelmaking. The drops were photographed at 4000 frames/second (fig. 7). They found that at a carbon content of about 4.2% the drops fell with a tail of burning carbon monoxide. At about 1.6% carbon, ejections of small particles of liquid iron-carbon were produced and considerable fume formation took place. About 25% of the total mass was lost during a 3 feet fall. With a carbon content of about 0.5% however, the boil and fume formation were very intense and the droplets exploded into fume before reaching the bottom. The high speed film indicated that fume formation occurred at a maximum rate at this stage. R. Baker⁸ extended the study to a series of alloys of iron. He found that carbon removal was very dependent on drop size, being six times as great for 2-3 mm spheres as for 5-6 mm spheres.

FIGURE 7

REACTION OF AN IRON-CARBON DROPLET
DURING FREE FALL THROUGH OXYGEN

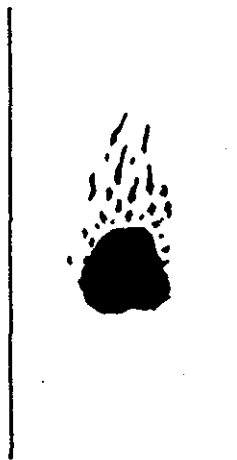
From Baker et al. (Ref.4)

4.2% C



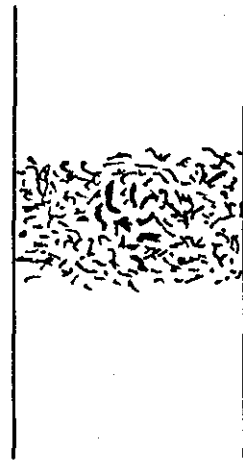
Trail of
burning carbon
monoxide

1.6% C



Small ejections
but total mass
loss is only 25%

0.5% C



Droplet explodes

As carbon content decreases, fume production (i.e. mass per time) increases.

He considered that true gaseous diffusion control of the decarburization rate did not occur in the free fall which was seriously questioned by Hamielec⁸⁷ who found that using suitable experimental correlations gave close agreement between a diffusion model and observed rate data. His model showed that the decarburization rate should vary linearly with droplet diameter to the $-3/2$ power which is verified by Baker's⁸ results. Some pilot plant data was given⁹³⁻⁹⁵ in the literature when pre-treatment of molten iron with oxygen was causing interest. It was, however, mostly of a qualitative nature and the process received little implementation.

(c) Levitation Studies

Baker et al⁶ studied decarburization of liquid iron-carbon alloys using carbon dioxide and showed that gaseous diffusion controlled the reaction down to a carbon content of 0.5%. Swisher et al⁹ extended the study using CO_2/CO mixtures and also found that a change of control took place at 0.5% carbon. They considered that carbon dioxide was absorbed onto the metal surface and that its dissociation was the rate limiting step. Baker et al⁵ made a further study using oxygen in the gas phase. They found that graphite spheres oxidised at the same rate as iron-carbon droplets under identical experimental conditions showing that gaseous diffusion control existed. They observed the presence of oxide on the surface of the metal spheres just prior to the decreasing rate period. This oxide layer was also noticed by Distin⁸⁴. He found that the drops did not start to boil before the oxide phase had been produced and it appeared from visual observations that fume was evolved much faster after the formation of surface oxide and the start of boiling, than before these events. The falling rate period did not occur immediately at oxide formation since the boil provided a new means of gas escape, but commenced some seconds later.

3. Small Scale Research Programme.

(1) Introduction.

The basic aim of the small scale work was to extend the research of Turkdogan⁴⁸ to include the interaction of iron/carbon melts with controlled partial pressures of oxygen. Boundary conditions would be more accurately known and there would be fewer variables than with large scale work. The chief disadvantage would be the uncertainty in scaling up from 12g. samples to industrial size quantities.

In addition, by using transparent silica to enclose the reaction zone, the programme lent itself to high speed photographic examination.

Description of Apparatus.

Commercial oxygen and argon were used as supplied in cylinders. The oxygen was stated to be 99.5% pure, having as its chief impurities argon (less than 0.5%), moisture (0.15g./m^3), and hydrogen (50 volumes per million). Argon had a quoted purity of 99.95% and contained as impurities nitrogen (less than 500 volumes per million) and oxygen (less than 10 volumes per million).

The oxygen was purified by passing it initially through a rough drier containing calcium chloride and through soda asbestos to remove carbon dioxide. It was then passed through an Engelhard Catalytic Purifier heated to 120°C to remove hydrogen and finally through magnesium perchlorate as a final drier.

The argon was also initially purified by passing it through calcium chloride and soda asbestos. It was then passed through a furnace packed with titanium granules and heated to about 800°C , to remove oxygen, and then through magnesium perchlorate as a final drier.

The gas flowrates were measured using variable - area flowmeters and after being mixed, the gas was passed into the reaction tube. This was made of high purity transparent silica, supplied by Thermal Syndicate and having the same dimensions as the tube used by Turkdogan⁴⁸, namely 18 inches by $1\frac{1}{2}$ inches bore and 12 inches by 2 inches bore. The gas was preheated by passing it over a recrystallised alumina sheath $\frac{5}{8}$ th inch O.D having a winding of platinum 20% rhodium wire, .020 inches diameter with an

FIGURE 8

SMALL - SCALE EQUIPMENT

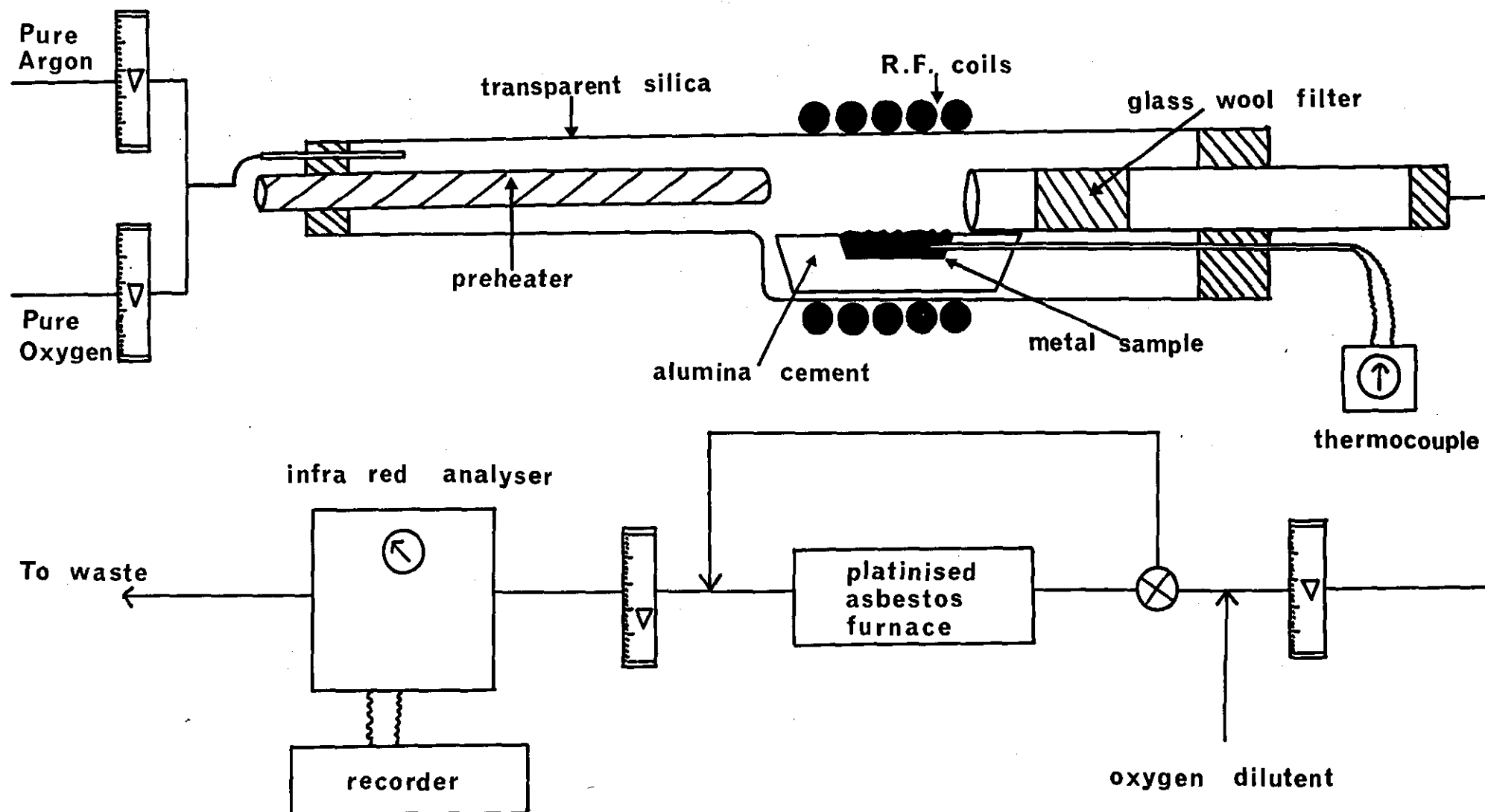
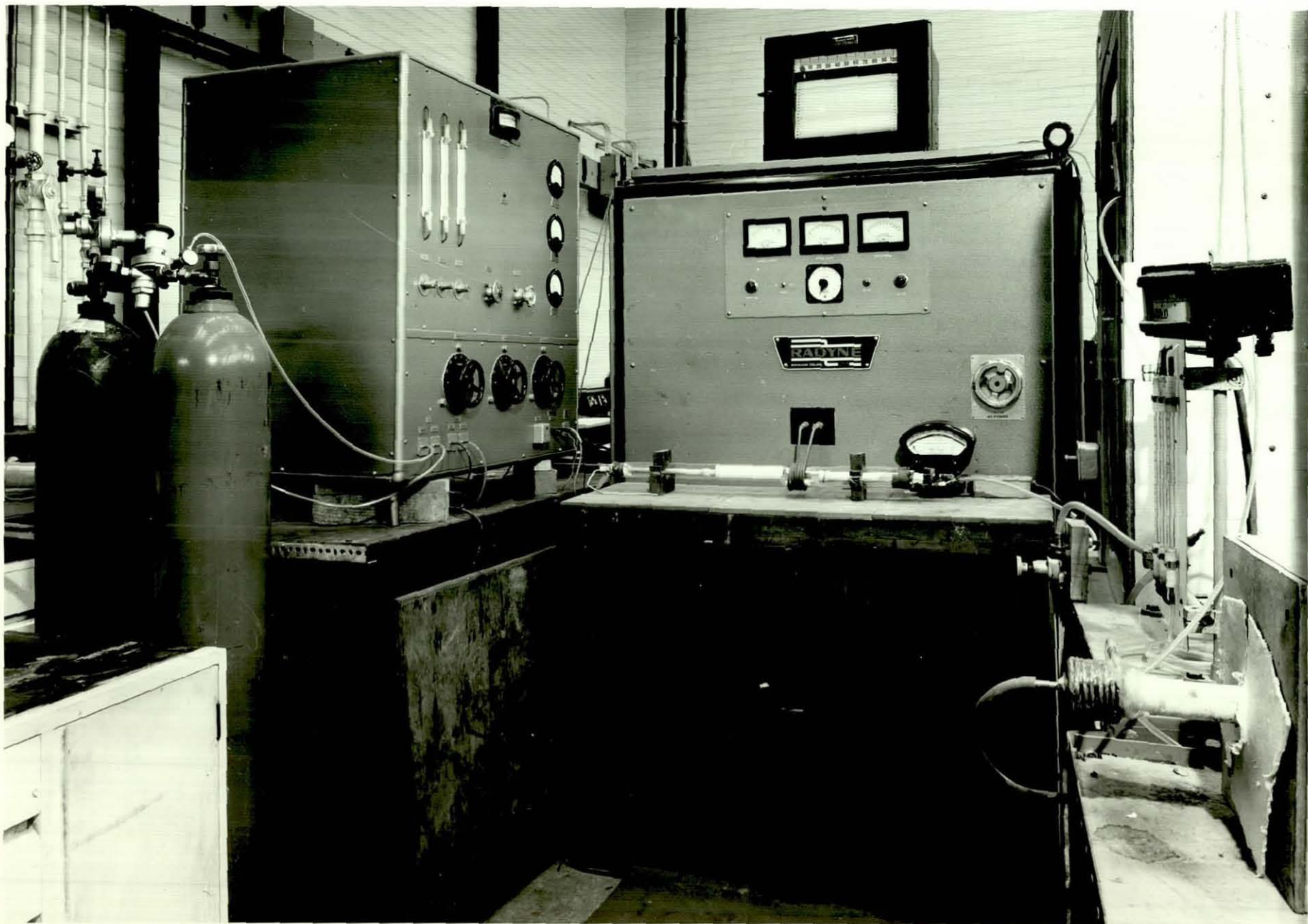


Figure 9

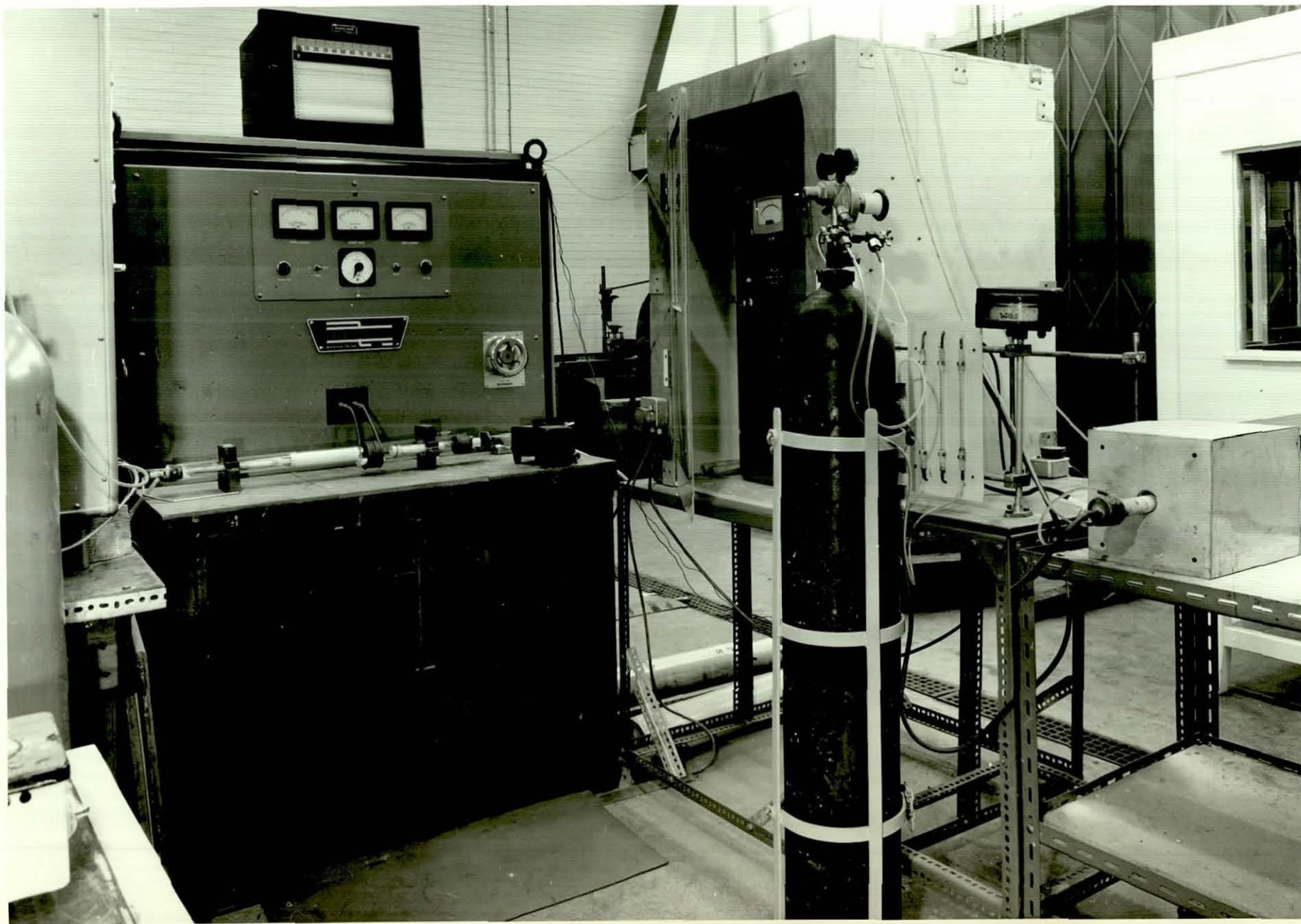
Small Scale Equipment

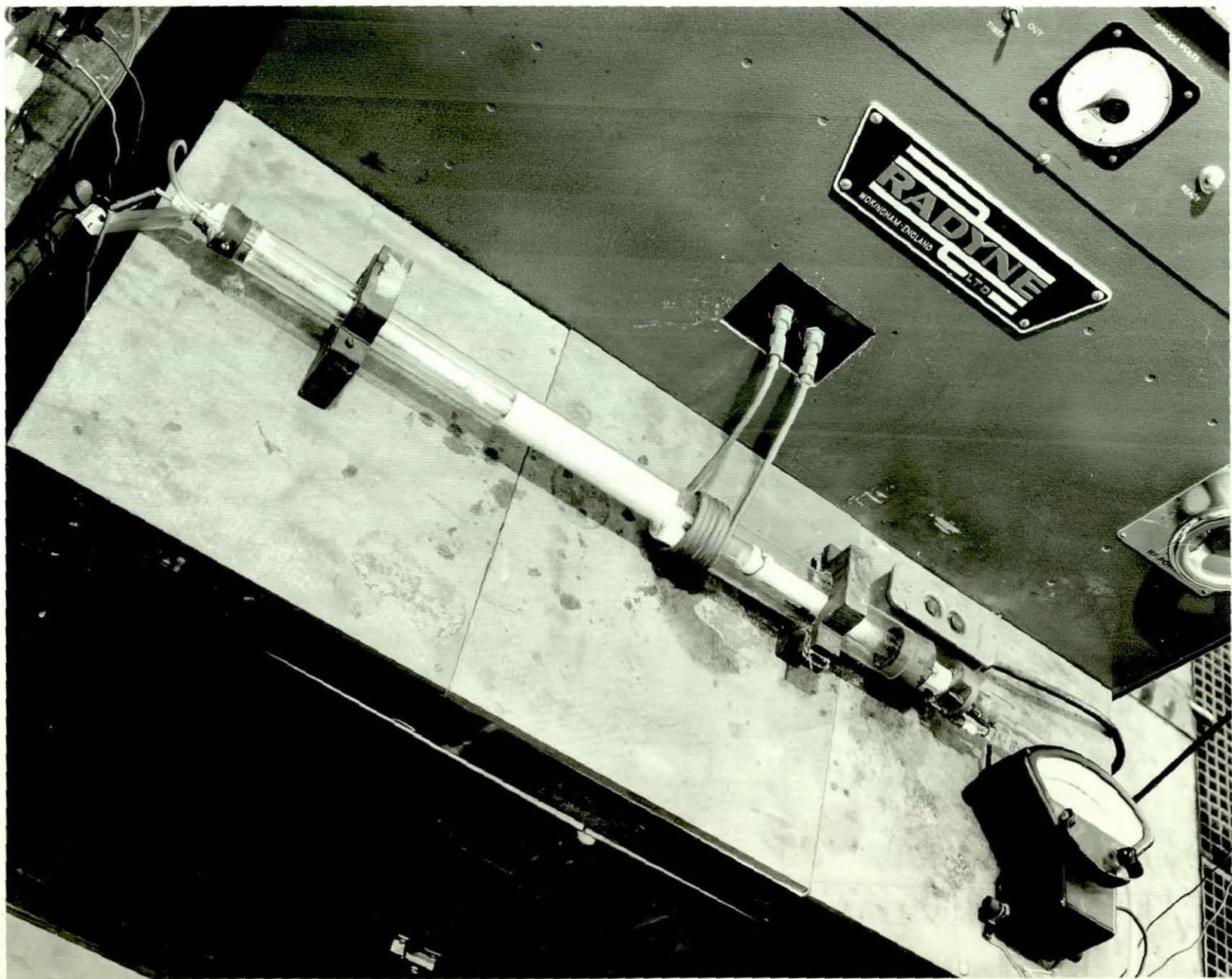
- A. General Arrangement
- B. General Arrangement
- C. Transparent Silica Reaction Tube.
- D. Gas Purification System.

A

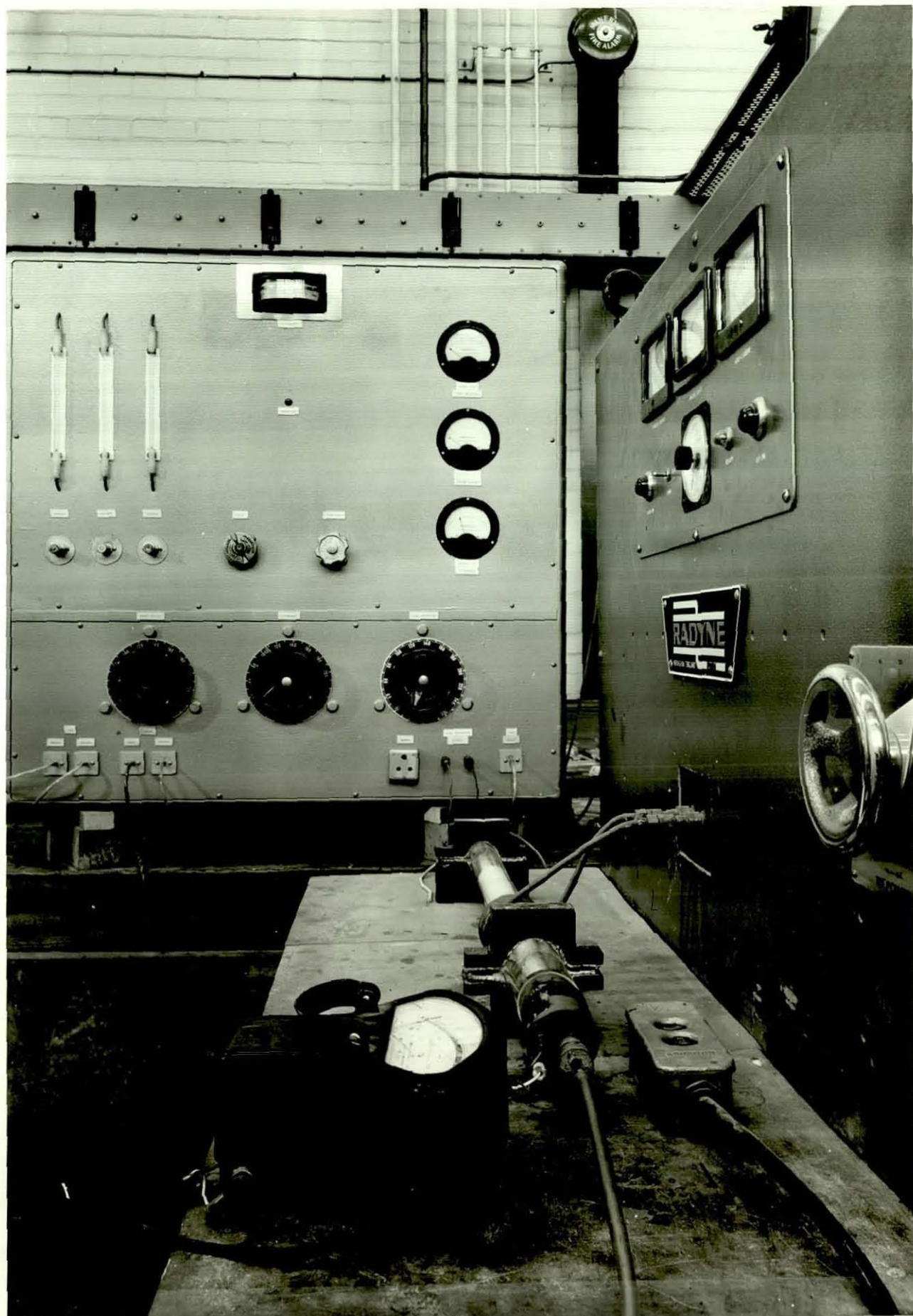


B





C



D

approximate spacing of $1/25$ th inch. The power supply to the preheater was from an 8 amp variac.

A recrystallised alumina tube fitted inside the reaction tube $1\frac{1}{2}$ inch bore section to protect it from the preheater.

Molten metal was contained in recrystallised alumina boats 40mm long, 10mm wide by 8mm deep. These were seated in alumina cement to cut down heat losses from the boat and reduce the temperature gradient within the melt.

The metal samples were heated by means of a Radyne 15 k.w. R.F. generator using an induction coil wrapped round the tube.

Temperature measurement was achieved using a platinum/ platinum 13% rhodium thermocouple together with recrystallised alumina sheaths 3 mm O.D. by 1.6mm bore produced by Degussa of Frankfurt. A notch was cut in one end of the boats to take the sheaths which were cemented in position.

The gases and fume produced passed into a filter which was a pyrex tube $\frac{3}{4}$ inch diameter packed with glass wool. After leaving the reaction tube, the majority of the gas was bled off to atmosphere. The remainder was diluted with oxygen and passed through a furnace at approximately 800°C packed with platinised asbestos. The purpose of the oxygen was twofold - to convert any remaining carbon monoxide to dioxide in the furnace and to dilute the carbon dioxide content of the gas stream to within the range of the gas analyser. A Grubb Parsons infra-red analyser was used having three concentration ranges (0 - .01%, 0 - .1%, 0 - 1.0% CO₂).

The output from the analyser was registered on a Honeywell high speed recorder, having a chart speed of 1 inch per minute. This method of gas analysis has been used on the industrial scale ⁸⁹.

(iii) Further Equipment Details.a) Preheater.

The preheater proved to be a source of considerable difficulty. Turkdogan⁴⁸ claimed that the temperature of the gas reaching the melt was 1600°C which was checked by placing a thermocouple in the zone above the melt. Clearly the source of heat must have been in excess of this temperature and so the initial aim was to get the alumina sheath to a temperature above 1600°C . Platinum 20% rhodium was chosen for its relatively high melting point (compared with Pt 10% Rh used by Turkdogan) and tests took place at various spacings to determine the feasibility of such an objective. The relative temperatures obtained were estimated by means of a thermocouple placed inside the sheath. The most concentrated practicable spacing was found to be $1/25$ th inch but even at this spacing, a temperature of 1100°C inside the former meant that the wire was close to fusing. A higher temperature could be obtained by covering the wires with cement but the higher temperature represented heat that was passing inwards rather than out to the gas. It was not possible to measure the outside surface of the former directly using a radiation pyrometer because of the alumina tube protecting the glass, but a reading of about 1250°C was obtained by focussing the pyrometer from the end of the preheater at the annulus between the tube and former. At this preheater temperature, an estimate of the gas temperature was obtained with the R.F. power off. Using a flowrate of 4 litres/minute (N.T.P.), the maximum gas temperature obtained was 730°C . The problem was referred to both Johnson Matthey and Engelhards, neither of whom considered that such a preheater could be built to give the required gas temperature and also possess a reasonable working life.

A series of tests then took place to determine the value of the preheater in its present form. The results given in table 2 show that the preheater temperature did not have any effect on the rate of vaporization.

The effect of gas flowrate on the surface temperature of the bath with the preheater off was then investigated using both a disappearing

filament pyrometer and a Lands radiation pyrometer. The difference in metal surface temperature when there was a static atmosphere of argon over the melt, as compared with that when passing argon at 4 litres/min over the melt was indistinguishable (i.e. less than 5°C) using either pyrometer, and was approximately 20°C below the temperature of the bulk of the metal.

The relative radiation and convection losses from the bath were calculated (Appendix 6) and the results showed that only about 9% of the total heat loss was due to convection. Thus, gas preheating would only reduce the heat loss from the bath by about one tenth.

In view of these considerations, it was decided that a preheater would no longer be used, the former remaining in position to keep the gas velocity consistent with previous tests.

Table 2.

Effect of Preheater Temperature on Fume Production.

Gas Flowrate: 4 litres/minute of Argon/Oxygen.

Melting Stock: Pure Iron.

Test Number	Gas Composition (% O_2)	Preheater Temperature ($^{\circ}\text{C}$) *	Fume Produced (mg.)
86	6	off	8.5
87	6	off	8.0
88	6	off	7.5
89	6	600	7.5
90	6	600	7.0
65	6	1000	7.0
66	6	1000	4.5

* temperature measured from inside of preheater.

b) Cement Boat-Holders

During early trials it was discovered that the total carbon represented by the print-out from the infra-red analyser was greater than the loss of carbon occurring in the metal. The source of carbon was eventually found to be the alumina cement. An analysis of a sample showed it to contain 0.22%C.

Leading manufacturers were contacted for samples of "carbon-free" cement but none were found to be suitable either on the grounds of carbon content or ability to stand the extreme conditions occurring.

The most satisfactory arrangement was to use an alumina cement C 40 produced by Thermal Syndicate and heat it to 1000°C in an atmosphere of oxygen. The boat-holders were also cooled in an oxygen atmosphere and stored in a desiccator. This reduced the carbon level to 0.015%, a level which did not interfere with the infra-red print-out

c) Metal Samples.

It was first thought that the most convenient means of producing samples particularly at a low carbon level was by obtaining drillings from a series of small ingots of varying carbon content. It was soon found however, that although a 12g. piece of metal melted without difficulty 12g. of drillings would only glow red and could not be melted irrespective of the time of heating on maximum output from the generator.

This was because for samples of small cross-section, the efficiency of the coupling coil was markedly lower than for larger samples, and in addition there was a greater heat loss by radiation from the drillings at the same temperature.

A range of iron/carbon alloys was prepared in a 20lb air induction furnace. Electrolytic iron was used together with high purity carbon powder supplied by Cabot Carbon Company, the carbon contents ranging from 4.60% to 0.014%. Each sample was analysed both at Aylesbury and Port Talbot (Section 3 (iv)). The samples were cylindrical, 1 inch in diameter and slices approximately 3/16" inch thick were sawn off, a special refractory saw being required for the high carbon samples. The slices were then either sawn or broken up to give the required 12g.

samples for each test, which were pickled in concentrated hydrochloric acid to remove any oxide scale.

For tests on pure iron, vacuum refined electrolytic iron was used, having a carbon content of 0.003%.

d) Fume Separation

For the purpose of the investigation, fume was considered to be that proportion of material leaving the bath as ejections which was less than 5/16 in diameter.

A glass-wool filter was found to be entirely satisfactory in separating out the quantities of fume produced in any of the tests. A separation was judged to be efficient when the end of the filter furthest from the bath was clear of fume. The glass-wool plugs were finally analysed for their iron contents (Section 3(iv)). A blank test on the glass wool when free of fume and also when containing a known weight of Fe_2O_3 showed it to have a negligible iron content. Any fume which coated the inside of the reaction tube and was free from ejections was removed with a small plug of cotton-wool soaked in acetone. Blank analytical determinations were also carried out on these plugs and showed them to be a suitable means of collecting fume for analysis.

e) Impactors.

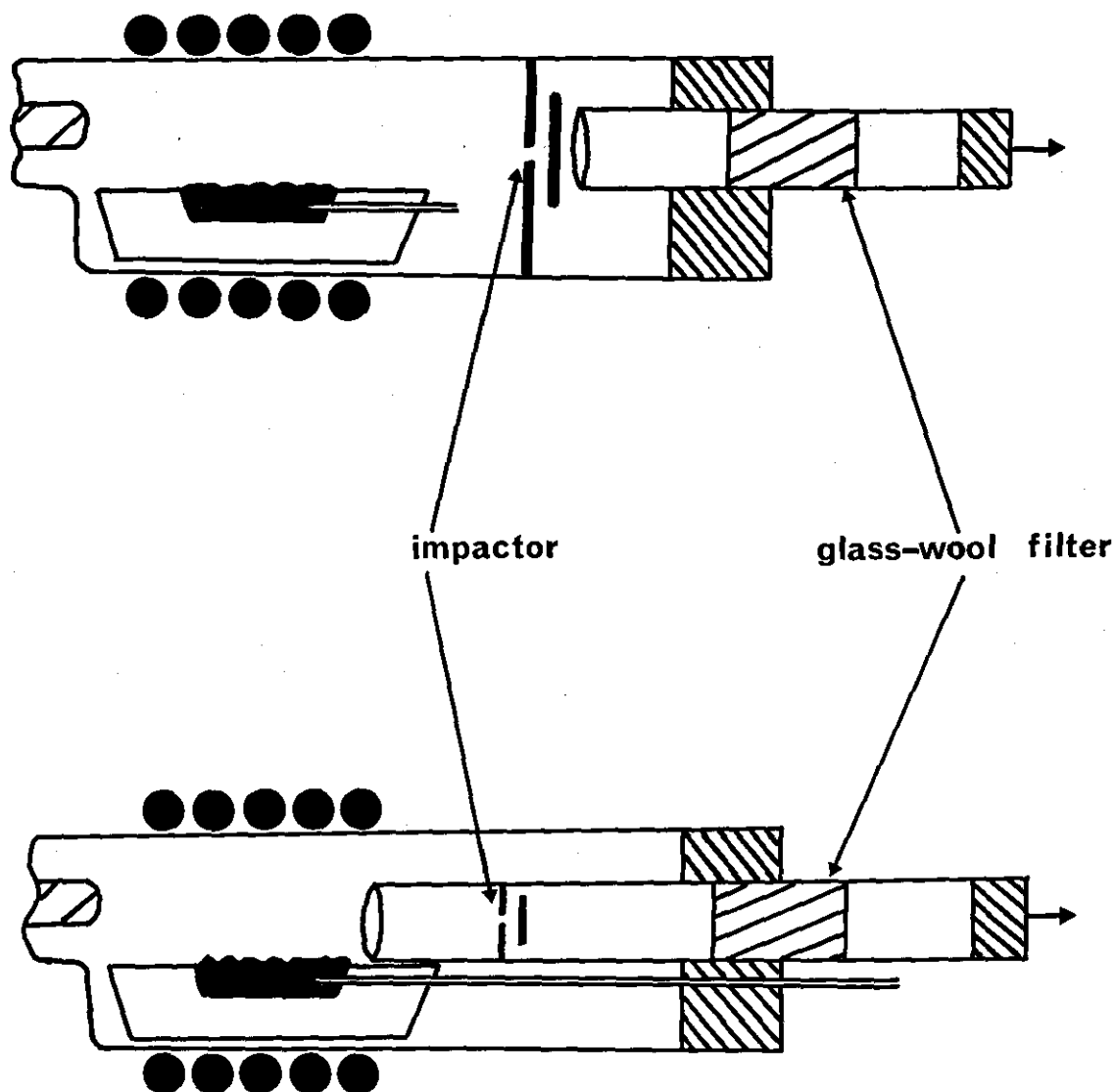
In the tests using iron/carbon alloys, any bubbling of the melt caused ejections to be thrown into the atmosphere above the bath, where they either stuck to the roof of the tube, or were swept into the filter.

Clearly their presence tended to mask any fume results because of their relatively large particle size.

In order to separate the ejections from the fume, an impactor was used. The gas and contents were made to accelerate through a small orifice and be deflected at 90° by a baffle plate onto which the ejections impinged. The two systems used are shown in Figure 10. The dimensions of the impactor were obtained experimentally and the filter contents checked with a microscope to see that the required separation was taking place. The most suitable orifice diameter was found to be 6mm and the distance between the orifice plate and impactor plate was 7mm.

ALTERNATIVE FUME SEPARATION SYSTEM

For experiments using manganese alloys



For experiments using iron-carbon alloys

FIGURE 10

f) Temperature Control.

Initially, a proportional control system was fitted to the output from the thermocouple reading bath temperature. It was found more satisfactory, however, to control the bath temperature manually, using the input power to the radio frequency generator where a temperature of $1600^{\circ}\text{C} \pm 10^{\circ}\text{C}$ could be obtained with ease.

g) Exhaust Gas Analysis.

The carbon dioxide concentration of the exhaust gas after having passed through the platinised asbestos furnace was measured by means of a Grubb Parson Infra-Red Analyser. The instrument had three concentration ranges and was calibrated by means of "Wosthoff Gas Mixing Pumps". These are precision piston pumps, various mixing proportions being obtained by means of a gear train having changeable driving wheels. Two pumps were used in series. The first pump produced a 10% CO_2 mixture in argon and the second reduced this concentration to a series of values of 1% and less in order to obtain a calibration curve. The various inaccuracies existing in the pumps have been referred to by the manufacturers 112.

The error in mixing for the two pumps was given as 0.06% and 0.024% respectively. There were also inaccuracies caused by using gases of different molecular weight and small differences in the inlet pressures of the gases but these were similar in magnitude to the mixing errors.

A daily check on the analyser was made using a standard argon/0.8% carbon dioxide gas mixture supplied by British Oxygen, the correct setting having been obtained immediately after the analyser had been calibrated.

As shown in Appendix 3, a curve fitting technique was used on the calibration curve.

The output from the analyser was registered on a high-speed recorder and a computer programme was used to integrate the area under the curve using the calibration equation, in order that events occurring in the reaction tube could be related to a bath carbon content as recorded on the chart. It took about a one minute delay for events in the bath to appear on the print-out and comments in Figure 22 refer to the actual

time they occurred and not to the time they appeared on the chart.

(iv) Analytical Techniques.

a) Preparation of fume containing ejections.

For all experiments where carbon was a constituent in the bath, there were some ejections thrown up out of the bath and where the oxygen partial pressure in the inlet gas was above 15% these ejections were considerable in number. They were usually deposited on the walls of the tube together with large quantities of fume.

In order that the fume could be analysed, the fume and ejections were brushed out of the reaction tube and dispersed in a beaker of water placed in an ultra-sonic cleaning bath. The large particles fell to the bottom and the fume suspension was decanted off and filtered. Random microscope analyses showed that particles having a diameter greater than 5μ did not appear in the fume sample and no fume remained in the residue

b) Fume Analysis.

The fume was always analysed as a weight of iron which would eliminate differences caused by the various oxidation states in which it could have existed.

The fume from the glass-wool plugs and filter paper was dissolved in concentrated hydrochloric acid, reduced with stannous chloride and titrated against $\frac{N}{10}$ potassium dichromate.

c) Carbon Analysis.

R.T.B. Aylesbury.

i) For carbon contents of less than 0.5%, the sample was melted using a R.F. generator and the CO_2 produced, when a known volume of oxygen was passed over, was analysed using a Hilger and Watts I.R. Analyser. Accuracy $\pm .0005\%$

ii) For carbon contents greater than 0.5%, the samples were analysed using a gravimetric technique as laid down in B.S 1121 Part 11. Estimated accuracy $\pm .01\%$.

S.C.O.W Division, Port Talbot.

All samples were analysed for carbon by a method based on the non-aqueous titration with tetra-n-butylammonium hydroxide of the carbon dioxide evolved by combustion of the sample in a stream of oxygen.

The carbon dioxide was absorbed in a solution of formdimethylamide 113,114

Estimated accuracies:-

<u>% Carbon</u>	<u>95% of samples between \pm</u>
3.000	.022%
0.100	.003%
0.0010	.0002%

4. The Effect of Gas Composition on the Vaporization
of Pure Iron at 1600°C.

(i) Introduction.

Turkdogan et al ⁴⁸ have shown that by passing a reactive gas (eg. oxygen) over a molten iron surface, enhanced vaporization occurs, which increases with increasing partial pressure of reactive gas until a cut-off occurs, caused by the formation of an oxide layer on the metal surface. Since the equipment used in this investigation was similar to that used by Turkdogan, the aim of these experiments was to reproduce that part of his work concerned with molten iron and see if matching results were obtained.

ii) Procedure.

For these tests, high purity vacuum refined iron was used with a carbon content of .003% and oxygen content .004%. Approximately 13g of the material was used in each experiment and was melted out under an atmosphere of argon. With the preheater on at its maximum setting, the required argon/oxygen mixture was passed through the tube for ten minutes, after which it was replaced by pure argon and the power switched off. Any fume deposited inside the tube was cleaned out with cotton wool which together with the glass wool filter was analysed for total iron.

Table 4.

(iii) Results

Area of metal surface:- = 2.52 cm^2

Gas Flowrate:- = 4 litres/min N.T.P.

Test Duration:- = 10 mins

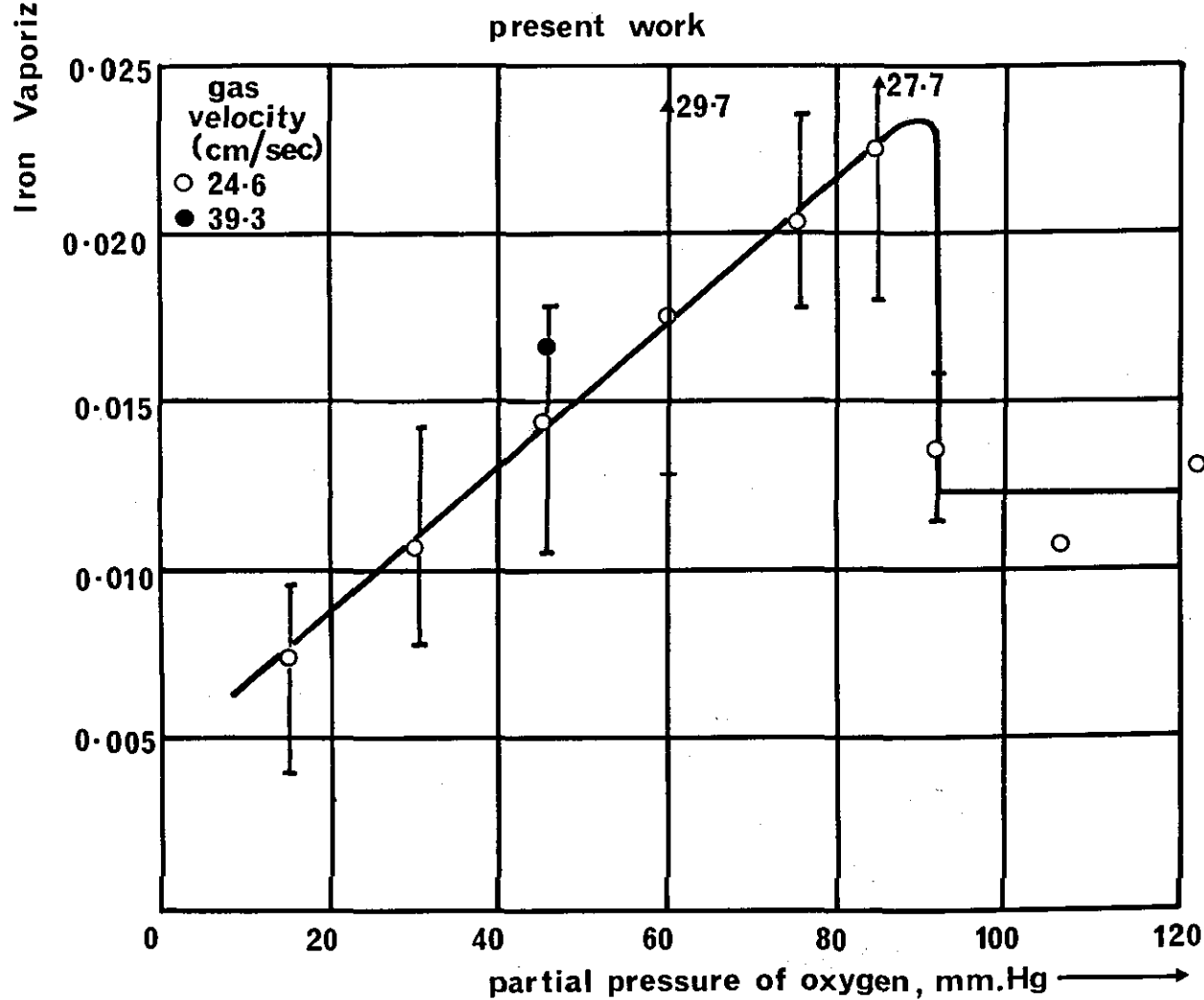
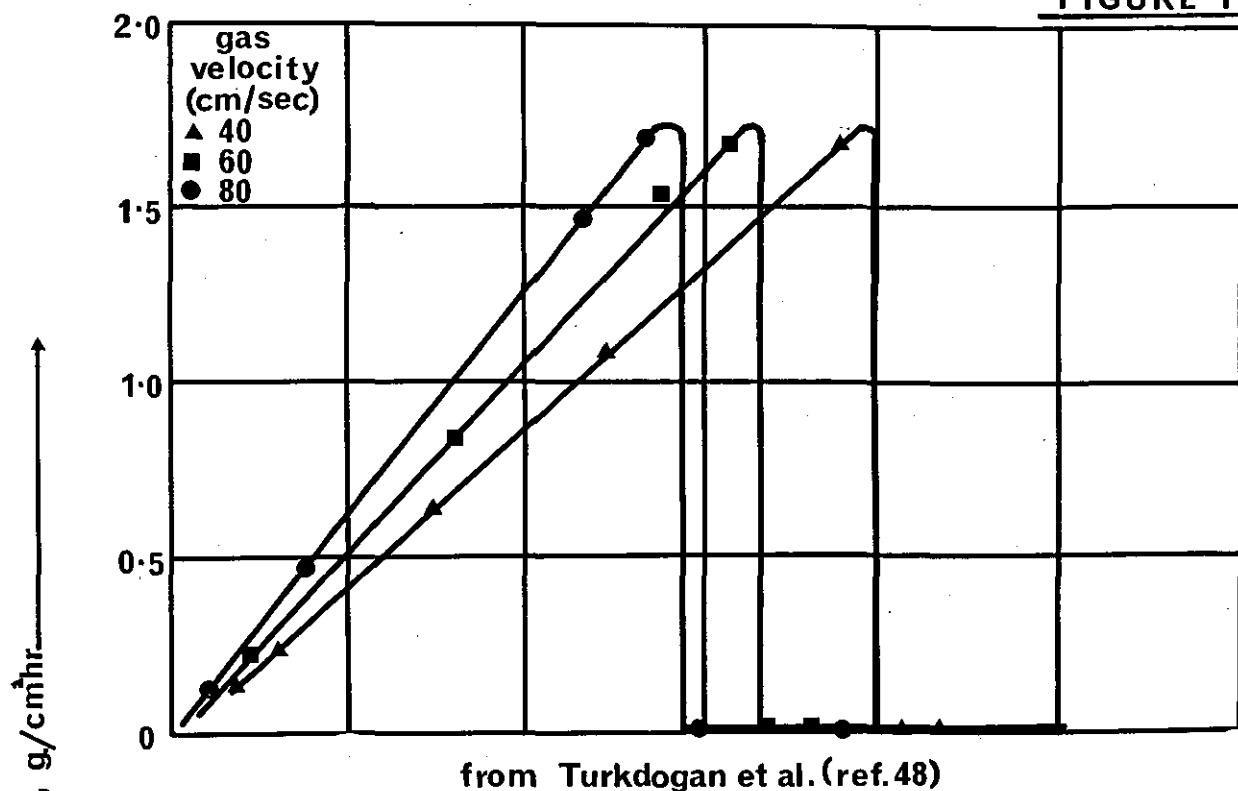
Test Number	Gas Composition (%O ₂)	Wt.of iron (g.)	Wt.of Fume (mg.of Fe)	Average fume weight (mg.)	Fume Rate g./cm ² .hr.
58	2	11.74	1.5	3.1	X 10 ³
61	2	12.68	3.5		7.4
62	2	12.40	4.0		
80	2	13.49	3.5		
59	4	12.13	3.25	4.4	10.6
63	4	12.26	3.5		
64	4	12.97	6.0		
81	4	12.35	5.0		
60	6	12.66	7.5	6.1	14.6
65	6	11.48	7.0		
66	6	11.10	4.5		
82	6	12.66	5.5		
50	8	11.86	7.0	7.4	17.6
52	8	12.77	6.0		
67	8	12.14	6.0		
68	8	12.35	12.5		
83	8	12.82	5.5		

Table 4 (cont.)

Test Number	Gas Composition (%O ₂)	Wt. of iron (g.)	Wt. of fume (mg. of Fe)	Average fume weight (mg.)	Fume Rate g./cm ² .hr. X 10 ³
71	10	11.43	10.0	8.5	20.2
72	10	12.26	7.5		
84	10	12.97	8.0		
73	11	12.44	7.5	9.5	22.6
74	11	13.42	11.5		
75	12	12.31	7.0	5.7	13.6
76	12	12.19	5.0		
85	12	11.64	5.0		
78	14	13.48	4.5	4.5	10.7
79	16	12.06	5.5	5.5	13.1

EFFECT OF OXYGEN PARTIAL PRESSURE ON THE RATE OF VAPORIZATION OF IRON AT 1600°C

FIGURE 11



(iv) Discussion

As can be seen from Figure 11, these experiments were not able to substantiate the results of Turkdogan. The results show an increased vaporization with increasing partial pressure of oxygen up to 11% for the conditions used but the degree of increase is relatively very small.

The cut-off region was noted visually, by a flickering effect on the melt surface presumably due to oxide being swept under by the R.F. generator. This resulted in a slow build up of oxide at the edge of the boat.

For his experiments, Turkdogan used velocities of 40, 60 and 80 cm/sec which were measured in the $1\frac{1}{2}$ inch diameter section of the tube and was equivalent to 3.5, 5.2 and 7.0 litres/min. at N.T.P. In these experiments 4.0 litres/min. were used which was equivalent to a velocity of 24.6 cm/sec. at 730°C.

A number of tests at varying conditions were undertaken in an effort to pin-point any error in equipment or technique. The effect of preheater temperature on vaporization rate is discussed in the equipment design section and showed that varying the temperature had no effect in spite of the decreased velocity of gas flow.

In test number 91, the metal sample was melted out under an atmosphere of argon/10% hydrogen to ensure a clean surface free of oxide. 6% oxygen was passed at a flowrate of 6.38 litres/min. (39.3 cm/sec.). The fume formed was 7.0 mg. eliminating the possible errors of surface contamination and difference in velocity.

Since it is shown in an earlier section that convection losses from the bath only amount to 9.5% of the total heat loss, it is difficult to consider the small fume figures in terms of an inability to provide sufficient preheat and it is only in this section that any difference in technique took place.

It must be concluded that no adequate explanation can be given for the difference in results obtained.

-44-

5.(i) General Description of the Effect of Oxygen Partial Pressure on Iron/Carbon Melts.

Figure 12 shows the effect of oxygen partial pressure on an iron/carbon alloy at 1600°C having an initial carbon content of 4.5%. Tests were of ten minutes duration or less, this being the life span of the thermocouple sheath at the temperature used.

It can be seen that two different effects have taken place.

Provided that the carbon content of the alloy was above a certain value for the conditions under consideration, the initial period of decarburization occurred on the surface of the metal and resulted in vaporization of iron similar in visual effect to that occurring in pure iron melts. This proceeded until the flux of carbon to the metal surface was insufficient to prevent oxide formation. Clearly, the higher the oxygen partial pressure used, the higher was the carbon content of the melt at which oxide formation occurred. At some time after oxide formation, a boil commenced, resulting in considerable fume formation and if left long enough, also resulted in the majority of the melt finishing up on the roof of the glass tube in the form of small droplets having diameters up to approximately 1000 microns. The time lapse before the boil commenced was not constant even for identical experimental conditions but was usually in the order of ten seconds.

Figure 12 shows that within the ten minute period, no boil occurred until 15% oxygen was used, and that for 20% oxygen the reaction was so violent that the test was stopped after ten minutes with the boat almost empty.

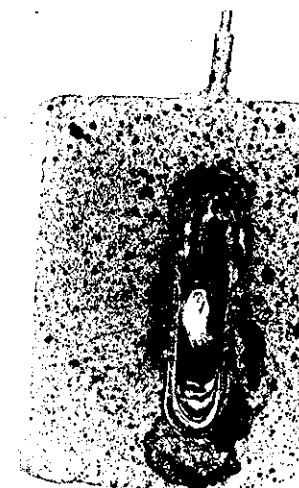
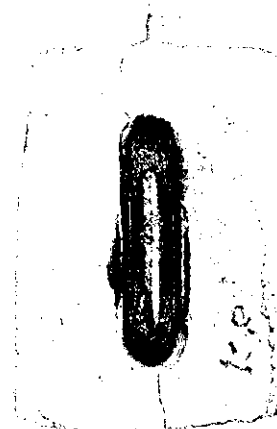
The infra-red analyser was not able to accurately predict bath carbon contents after vigorous boiling had commenced because a) the programme for computing carbon content was geared to a constant bath weight and could not utilise data from a bath that was losing metal in the form of ejections to an unknown varying degree and b) the boil caused considerable pressure fluctuations within the system which in turn influenced the analyser's accuracy, the infra red detection system being extremely sensitive to pressure variation.

Figure 12

Effect of Oxygen Partial Pressure on the Appearance
of the Bath after a 10 minute run.

0 - 10% oxygen:	no boil occurred.
15% oxygen:	boil occurred.
20% oxygen:	bath almost empty after 10 minutes.

INITIAL CARBON — 4.50 PCT.



GAS COMPOSITION (O₂)

0 PCT.

5 PCT.

10 PCT.

15 PCT.

20 PCT.

The analyser was able to show, however, that the period of oxide formation and boil commencement did not represent the change of control mentioned in the literature survey on decarburization, but that the control changes from oxygen supply in the gas to carbon supply in the metal, some seconds later, shown by the falling decarburization rate. This was also found by Distin ⁸⁴.

Figure 13

Appearance of Bath, before and during a Boil.

Gas Composition : 100% oxygen flowing from
 right to left.

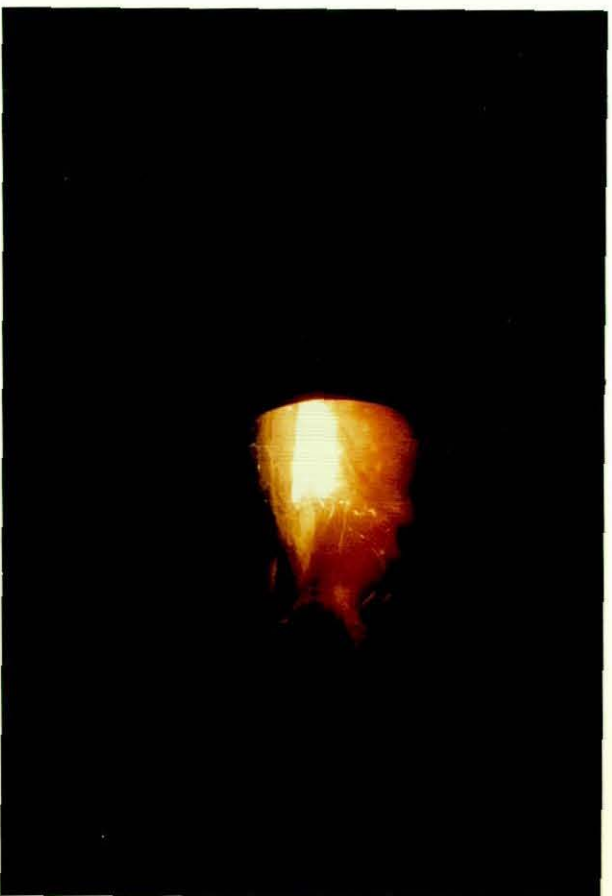
Metal Temperature: 1600°C

A. Before Boil. (Bath reflection can be seen
 above the bath).

B. During Boil.



A



B

ii) High Speed Photographic Examination of the
"Boiling" Period.

a) Introduction.

From initial tests, it was seen quite clearly from visual observation that for appreciable quantities of fume to be formed, it was necessary to have a boil taking place which in turn required the presence of an oxide skin over the melt.

The aim of the photographic investigation was to observe fuming under "boiling" conditions and determine, if possible, any effect influencing its formation. The camera used was a Fastax WF3T with a speed of 5000 frames/second. The boat was observed from upstream in order to reduce the masking effect of the fume formed.

b) Observations.

As can be seen from the series of photographs in figures 14 and 15, the boil caused ejections to be thrown into the zone above the bath where a number of them exploded into fume. From an analysis of the ejections which did in fact explode, it appears that there was no single factor which determined which ejections should explode - certainly size was not the only factor.

c) Discussion.

These observations together with those of Baker⁴ appear to give a clear picture of the reactions taking place.

When the ejections leave the bath, their high area/volume ratio means that they will rapidly solidify unless some source of additional heat is supplied. Oxygen with its exothermic reaction properties provides this heat. While in the oxidizing atmosphere, the ejections decarburize until an oxide layer is formed on their surfaces. This in turn gives rise to gas nucleation within the droplets which causes the explosions to take place.

Figure 14.

High Speed Photographs showing the Formation.
of Ejections due to Bubble Bursting.

Frame speed: 5000/second.

Gas composition: 100% oxygen.

Metal temperature: 1600°C.

Gas flow is from right to left.

A



B



C



D

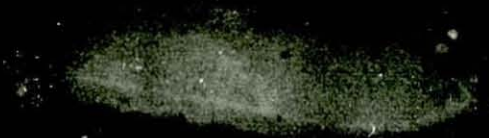


Figure 15.

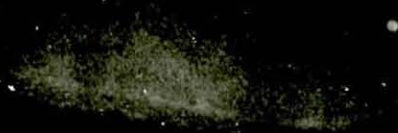
High Speed Photographs showing
the Disintegration of an Ejection.

Frame Speed: 5000/second.
Gas Composition: 100% oxygen.
Metal Temperature: 1600°e.

A



B



C



D

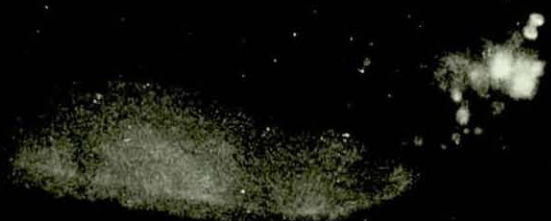


Figure 16.

High-Speed Photographs showing the
Growth of an Ejection before it Disintegrates.

Frame speed: 5000/second.

Gas composition: 100% oxygen.

Metal temperature: 1600°C.

Gas flows from right to left.

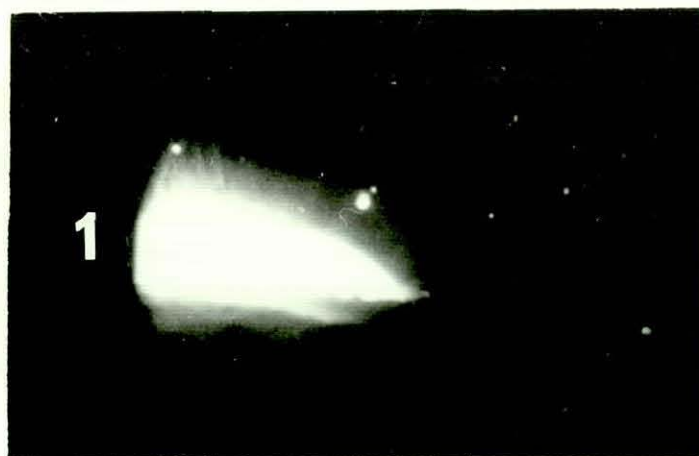


Figure 16 shows the growth of an ejection just prior to it exploding. When carbon dioxide was used in place of oxygen in a series of qualitative experiments, an oxide layer appeared on the surface of the melt causing the ejection of droplets as before, but these immediately solidified and no fume was observed.

Clearly, from the above model, there are a number of factors which will determine whether a droplet will explode.

origin of gas bubbles in melt.

A bubble originating at the bottom of the bath will grow as it rises to the surface and will also increase in speed. Newitt¹⁰⁴ has shown that by increasing the depth of bubble generation, the size of the large ejections will also be increased, and Garner⁹⁶ has shown that increasing the bubble diameter also increases the droplet size.

speed at which ejections pass into the oxidising atmosphere above the bath. An ejection will first have to pass through an atmosphere containing carbon monoxide and carbon dioxide which will reduce its temperature before it reaches the oxygen. Clearly, the extent of this will depend on the type of equipment or plant being used. In the L.D. for example, some particles are certainly ejected from the crater wall directly into the jet and so will not have to pass through this non-reactive atmosphere. size of droplet. Clearly large droplets will take longer to decarburize and reach the point of oxide formation than small ones and will therefore have less chance of exploding.

time lag after oxide formation before nucleation takes place. If heterogeneous nucleation of carbon monoxide within the droplet is assumed, there will be a random time lag between the formation of the oxide layer on the droplet and a portion of this layer being swept inside the droplet to act as a nucleation site. This effect will be similar to that observed on the surface of the metal just before the boil commenced.

oxygen partial pressure.

High oxygen partial pressures will decarburize more quickly and cause oxide formation at a higher carbon content. This will increase the probability of explosions taking place.

The picture which emerges is one in which statistics play a major part with particles of different diameters being emitted at different velocities into a reactive atmosphere where they may disintegrate to a varying degree and in a varying time interval. It would appear that maximum fuming is caused by high oxygen partial pressures and small particle size of ejections indicative of bubble formation close to the surface of the metal.

An ejection thrown up into an exothermic atmosphere will gain heat by chemical reaction and lose heat chiefly by radiation. An analysis of this heat balance was carried out using a computer (Appendix 7). Droplets with diameters ranging from a micron to a millimetre were considered at 1600°C radiating to a surface at 100°C . Carbon monoxide was considered to be the reaction product. The analysis showed that a micron droplet at 4.5% carbon reached a carbon level of 0.35% in approximately 10^{-2} - 10^{-3} seconds depending on oxygen composition, which was increased to 1.7 - 17 seconds for a millimetre droplet. All the droplets, however, dropped in temperature. A micron droplet, for example, reacting with 100% oxygen had its temperature reduced by 250°C in 10^{-11} seconds compared with a millimetre droplet which lost 0.26°C in 10^{-3} seconds. This certainly did not appear to be the case from visual observations of the high-speed film, although the formation of oxide with its higher emissivity, on the surface of the droplet would have given the effect of an apparent rise in temperature. This very simple model took no account of the CO/CO_2 flame front close to the metal surface. Turkdogan⁴⁹ quotes data giving the temperature of the flame front obtained by complete combustion of CO by a stoichiometric amount of O_2 as 2930°C when the reactants are initially at room temperature. Clearly the existence of a flame front to any extent will reduce radiation losses as will the fact that half the droplet will be viewing the steel melt and will not therefore be radiating to a surface of 100°C .

Nevertheless, the comparatively large times predicted for oxide formation on the larger particles would indicate that for ejected droplets, the reaction rates are much faster than for equivalent bath conditions,

caused by a reduced boundary layer and hence faster diffusion rates. Baker⁸ obtained decarburization rates of 6.6% C/second for $1\frac{1}{2}$ mm droplets in free fall through oxygen compared with 2.5%C/second for the 1mm droplets in the model.

The effect of steel particle explosions can be observed in a different field to that of steel manufacture. A simple means of testing various metals for composition is by observing the sparks produced when using a grinding wheel. In a review of this topic, Tschorn⁶³ has shown spark photographs for different steels. The sparks, which were all molten at a distance of 20cm from the wheel, gave a coloured streamline and, in many cases depending on the composition, finished by exploding into small fragments, provided that there was carbon in the material. High carbon sparks took longer to explode than equivalent low carbon sparks.

It is very likely that the reactions taking place were qualitatively similar to those occurring with ejected droplets from a steel bath.

iii) Examination of Fume using the Electron Microscope.

The fume produced during the surface vaporization and during the boiling periods were examined using the Philips EM 300 electron microscope and some of the results are shown in Figures 17 and 18.

It can be seen that two distinct types of fume were produced. During the vaporization period, fume particles were produced, the majority being within the size range $.05\mu - .15\mu$ and octagonally shaped in cross-section. The sample was obtained by passing argon/6% oxygen over a 4.5% C/Fe alloy at 1600°C . The results are similar to those of Desforges and Charles⁶⁹ who obtained octagonal particles by vaporising iron (0.02% C) in oxygen, and Meldau⁶². The non-uniform colour intensity indicates a three-dimensional structure, possibly a di-octagonal pyramid referred to by Meldau.

The sample produced during the boiling period was obtained by passing 100% oxygen over a 4.5% C/Fe alloy, also at 1600°C . The large particles (greater than 5μ) were separated by the method described earlier.

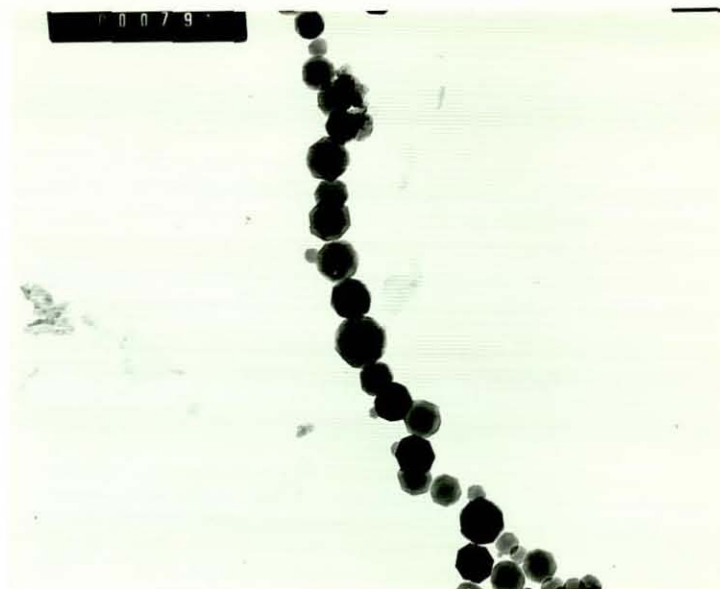
It can be seen that a completely different picture is obtained. The fume is much larger in size with a wide size range, from approximately 3μ downwards. The octagonal shape is no longer apparent and is replaced in the main by spheres. It is this form of fume that is widely reported in the literature as having originated from commercial steelmaking processes 1,11,12,61.

Figure 17

Electron Microscope Photographs of Fume produced
during the "Vaporization" Stage.

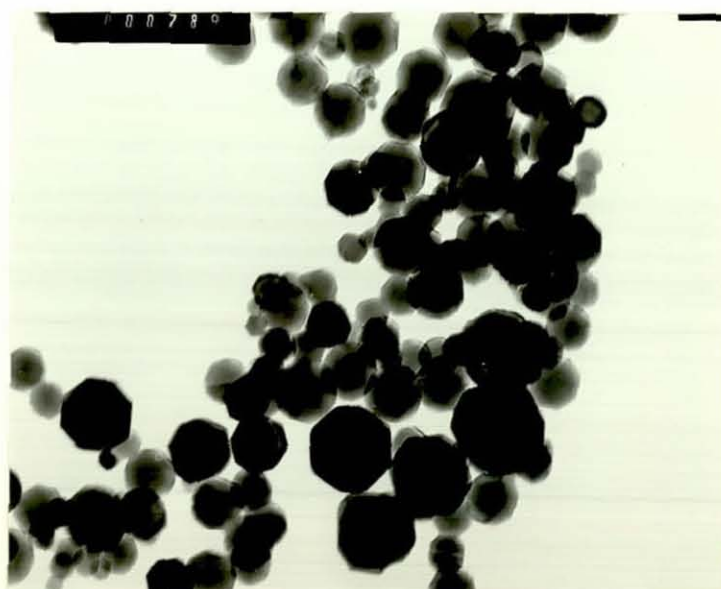
Magnifications.

A.	x47,000
B.	x73,000
C.	x73,000
D.	x73,000
E.	x167,000
F.	x167,000



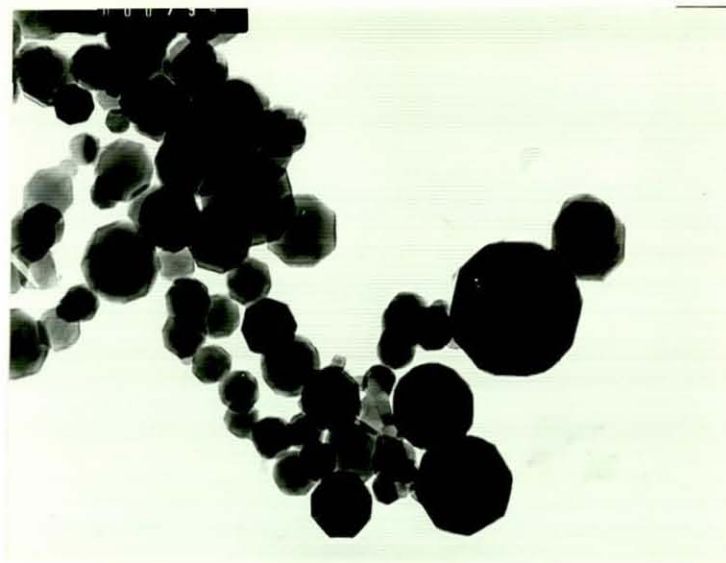
.21 μ

A



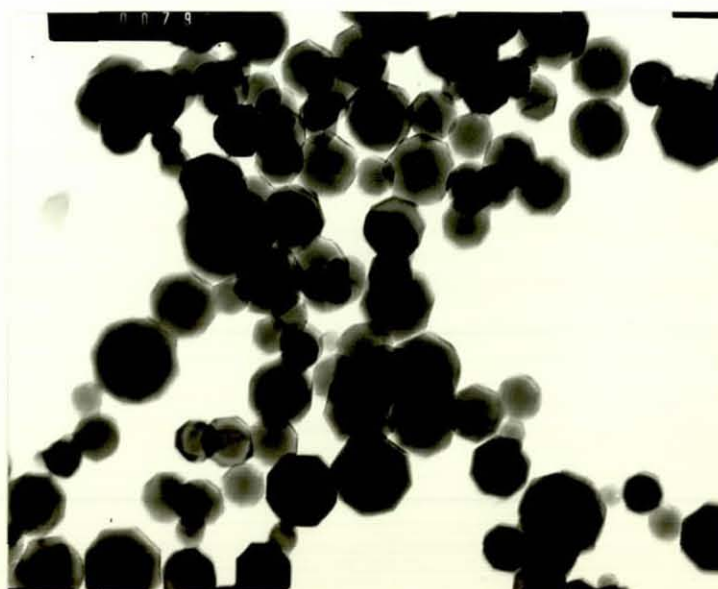
.14 μ

B



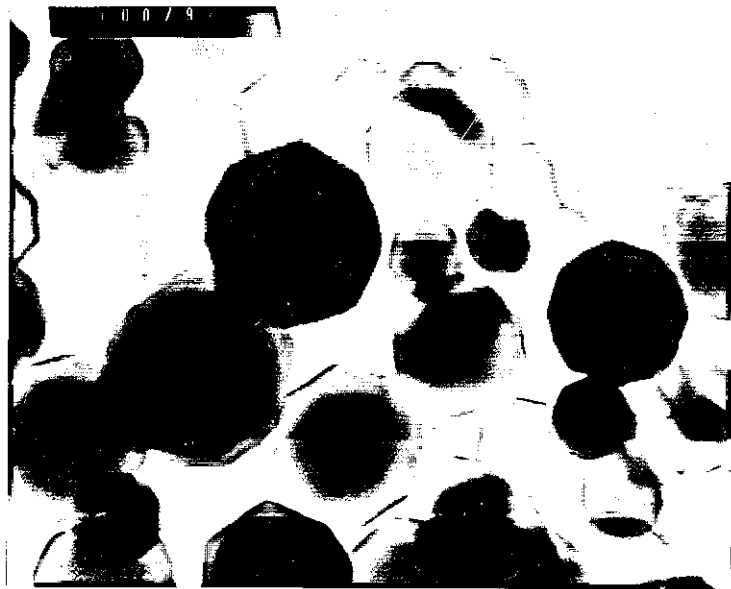
.14 μ

C



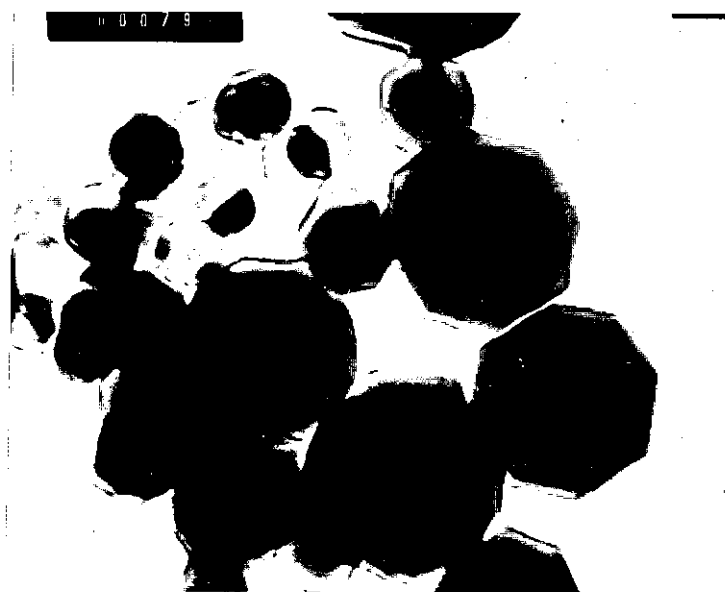
.14 μ

D



.06 μ

E



.06 μ

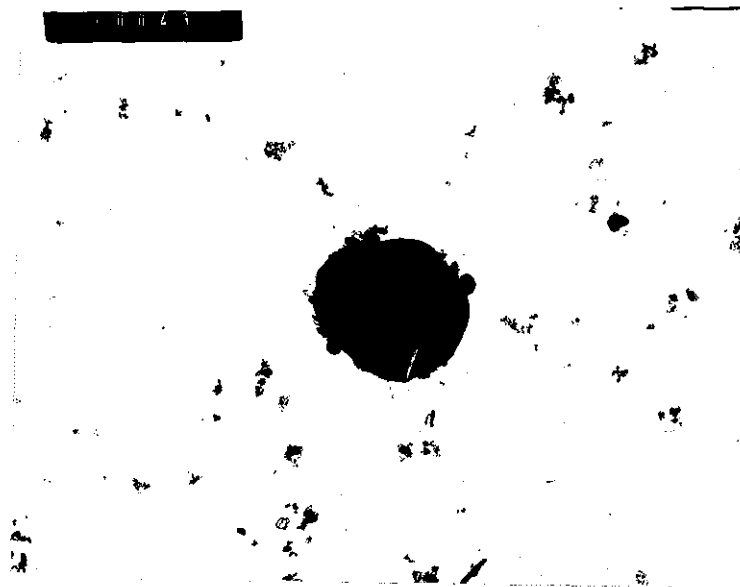
F

Figure 18.

Electron Microscope Photographs of Fume produced
during the "Boiling" Stage.

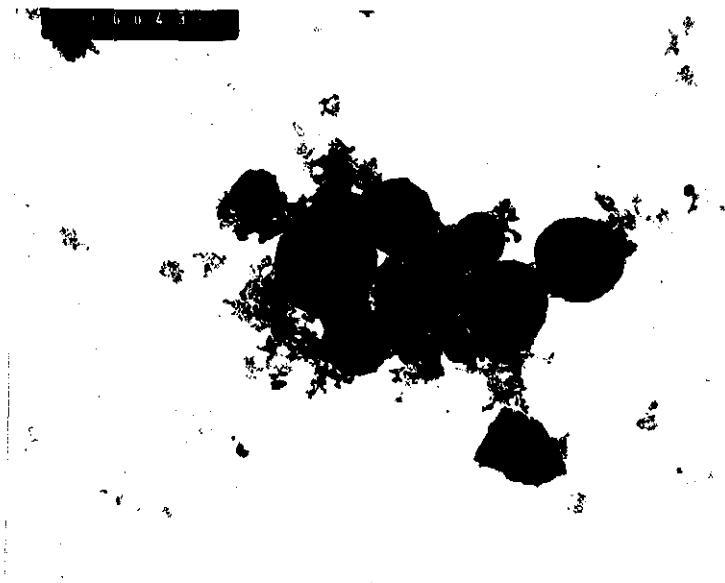
Magnifications.

- A. X6,000
- B. x6,000
- C. x15,000
- D. x30,000
- E. x30,000



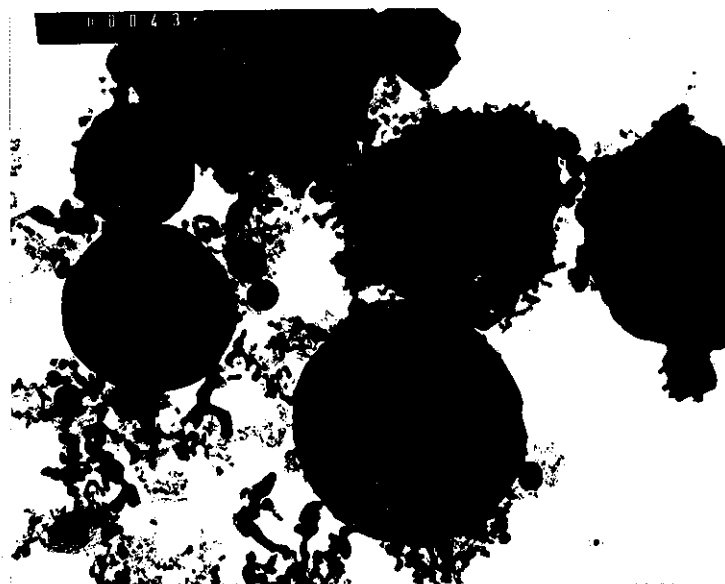
1.67 μ

A



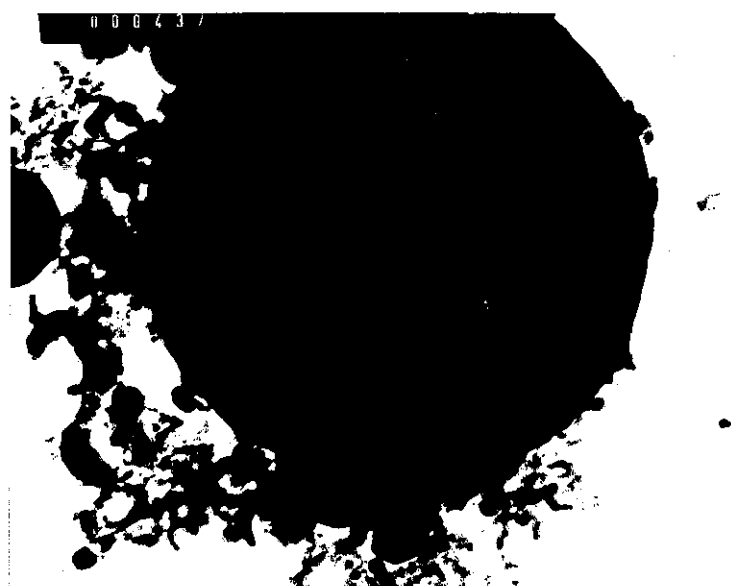
1.67 μ

B



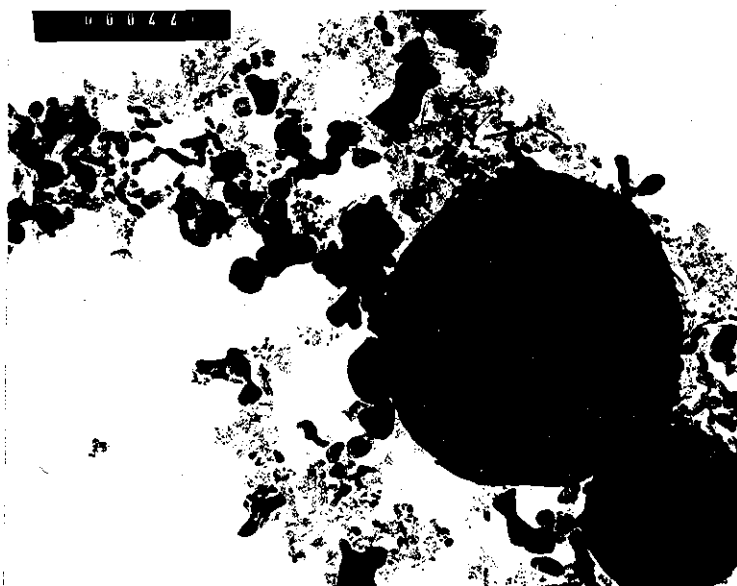
.67 μ

C



.33 μ

D



.33 μ

E

iv)

Examination of Fume using a Scanning
Electron Microscope.

As before, the different types of fume produced before and during the boiling period were examined, this time using a Cambridge Stereoscan.

The examination took place at the onset of the investigation into the boiling period and the presence of some large spheres greater than 5 microns in the sample necessitated the use of an efficient separation technique for all later work.

The difference in particle size is clearly seen in the photographs (figs. 19, 20). The fine fume is in the form of agglomerates and the highest practicable magnification (x10,000) was insufficient to determine individual particle shape. The highest magnification on the Philips electron microscope is 167,000.

Figure 19.

Stereoscan Photographs of Fume Produced
during the "Vaporization" Stage.

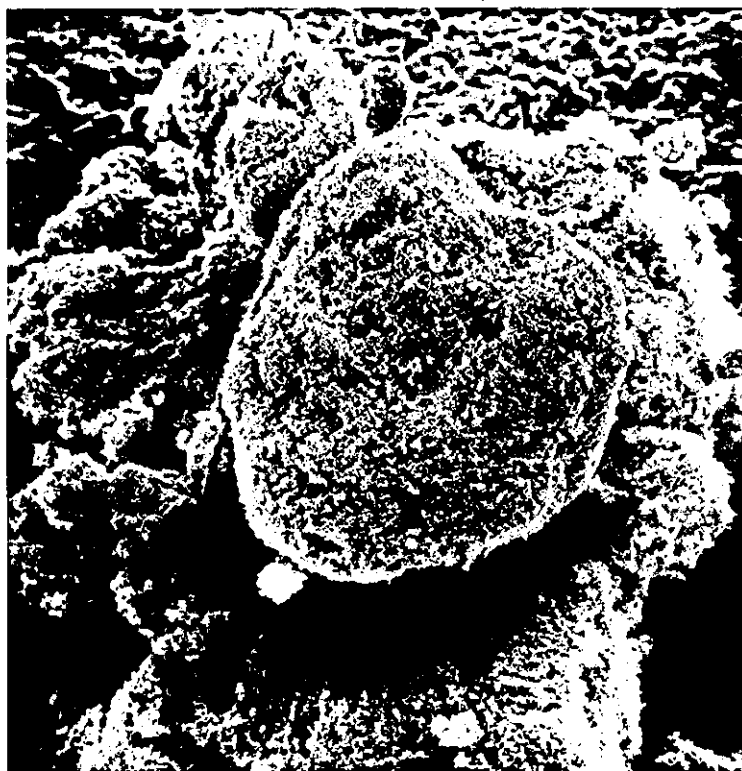
Magnifications.

- A. x200
- B. x1000
- C. x2000



50 μ

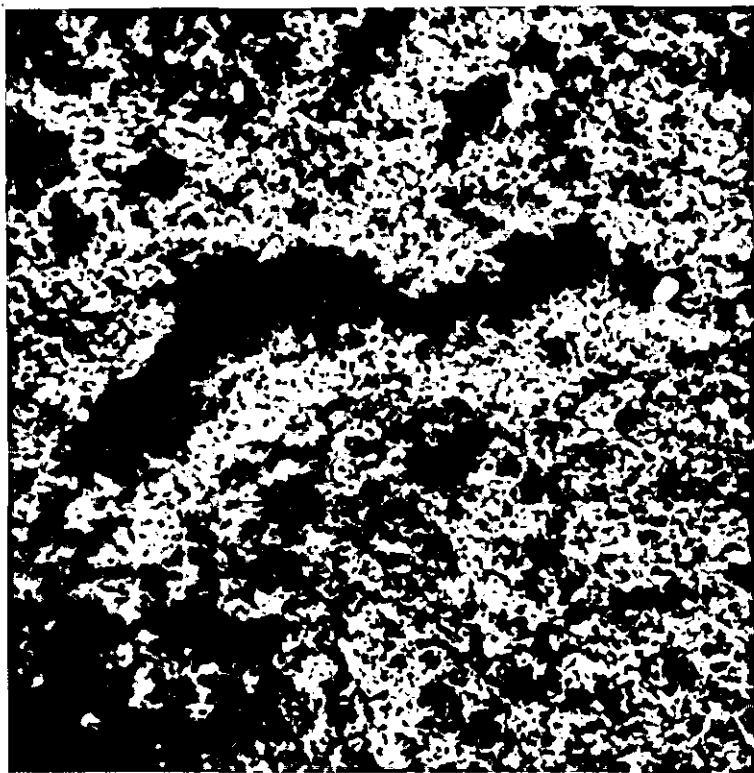
A



10 μ

B

5 μ



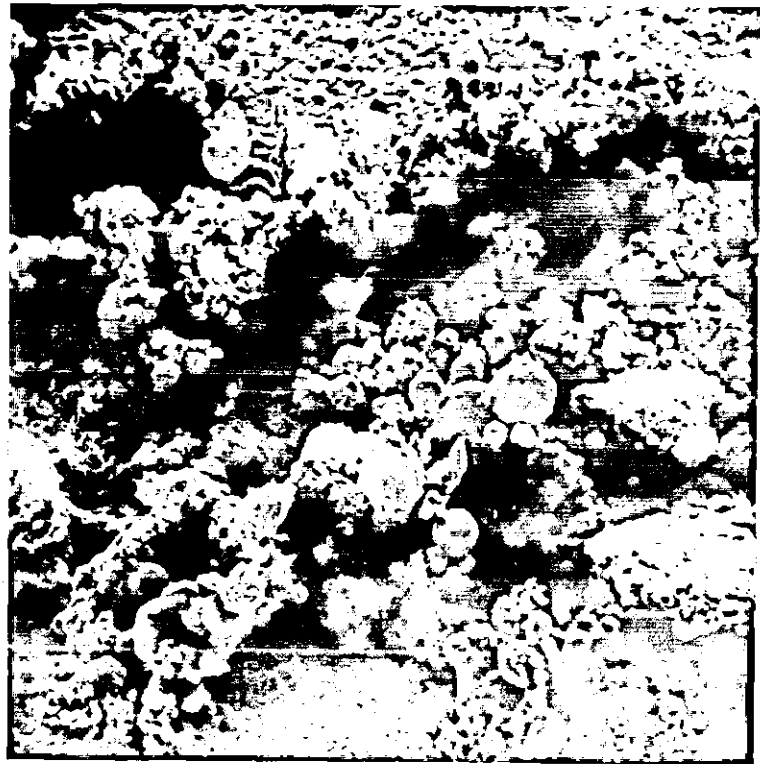
C

Figure 20

Stereoscan Photographs of Fume Produced
during the "Boiling" Stage.

Magnifications.

- A. x500
- B. x2000 (showing the centre of A.)
- C. x10,000 (showing one sphere from B.)
- D. x2,500 (industrial fume sample from
 electric arc furnace.)



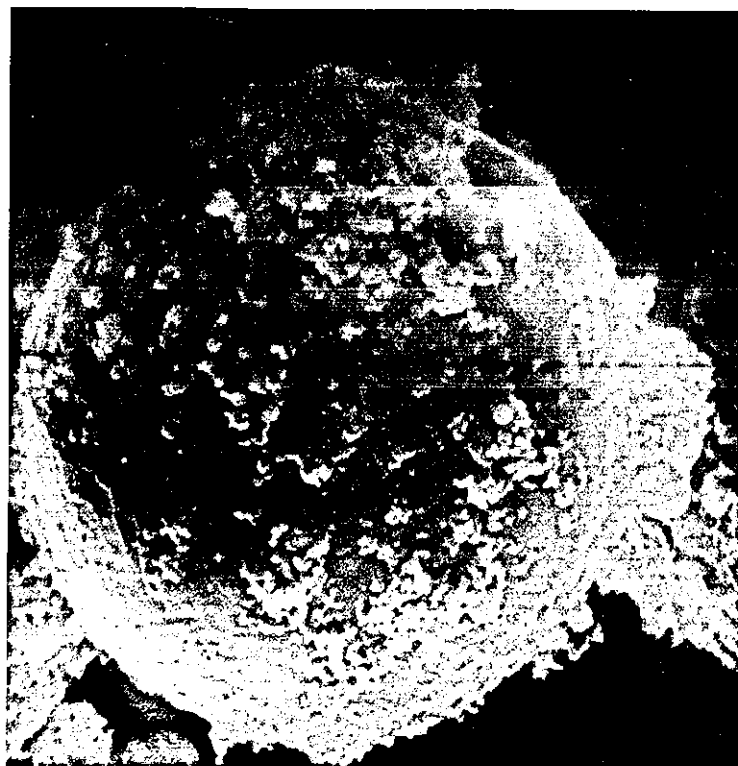
20 μ

A



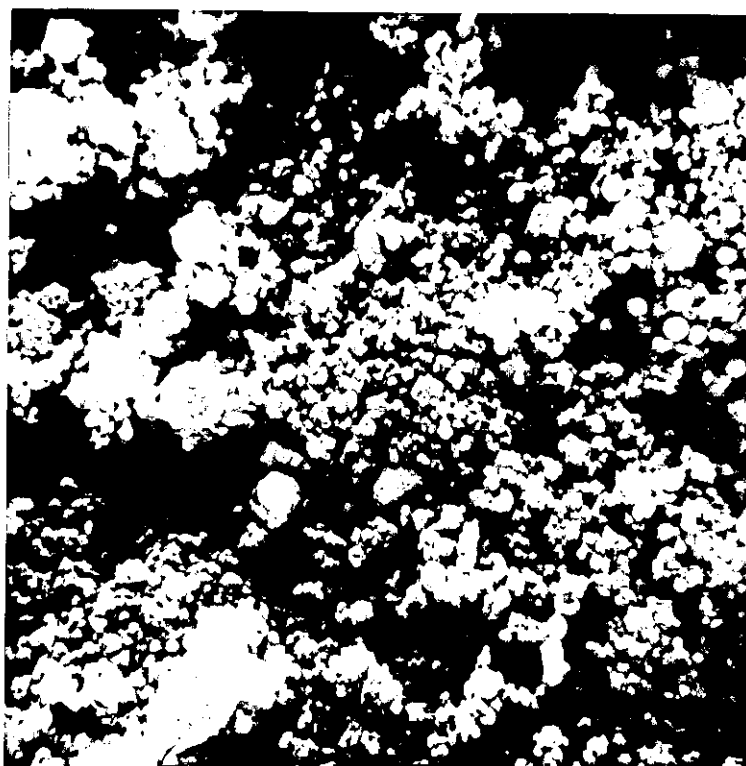
5 μ

B



1μ

C



4μ

D

(v) Effect of Oxygen Partial-Pressure on the Decarburization
Rate during the Non-Boiling Period.

The effect of oxygen partial pressure on the rate of decarburization was investigated in a series of tests using a 4.60% C starting material. The results are shown in Table 5 and the graph in Figure 21, and verify the theory that initial decarburization is controlled by the supply of oxygen to the metal surface.

When boiling commenced, pressure surges occurred in the system causing rapid variations in the rotameter readings indicating the dilution ratio of the gases going into the analyser. This reason, coupled with the fact that the analyser was sensitive to even slight changes in pressure, meant that the chart print out after boiling commenced was subject to possible error. It did indicate, however, that the initial boiling period maintained the decarburization rate at approximately the same level, indicating that the total surface area being decarburized was similar in size before and just after the start of the boil.

The fall-off in CO_2 composition after 6 minutes when using 20% oxygen was probably due to a loss of metal from the bath rather than a change of control since the computed figure for the bath composition at the start of the fall-off (2.28%C) is far higher than any published figures. The bath was nearly empty at the end of the run.

The print-out obtained by passing pure argon over the molten sample shows the reaction occurring between the alumina boat and the metal. The initial surge before START was characteristic of all runs and occurred during melt out. The print out shows a gradual fall-off in CO_2 evolution during the whole run. If the reaction occurring in run 113 was alumina reacting with dissolved carbon, the quantity of carbon removed from the bath (0.08%) should have been replaced by an aluminium content of 0.12% by weight. Analysis of the melt and of the base material for a similar run was unable to show any increase at all in the aluminium content.

An estimate of the kinetics of this reaction can be obtained from

Table 5.

Effect of Oxygen Partial-Pressure on Decarburization Rate.

Starting Material: 4.60% carbon at 1600°C.

Gas Flowrate: 4 litres/minute.

Test No.	Initial Mass Of Sample (g.)	Oxygen Partial Pressure (%)	CO ₂ conc ⁿ in plateau region(%)	Average CO ₂ conc ⁿ in plateau region(%)	Final C content (analysis) (%)	Final C content (computer print-out) (%)	Rate of Decarburization (g.moles/sec.)x10 ⁴	Average Rate of Decarburization. (g.moles/sec.)x10 ⁴
105	13.37	5	0.92	0.94	3.23	3.33	0.27	0.28
106	13.43	5	0.96		3.36	3.37	0.29	
107	13.36	10	1.71	1.80	2.12	2.16	0.51	0.54
108	13.66	10	1.89		2.07	2.07	0.57	
109	13.64	15	2.77	3.07	0.30	0.72	0.83	0.92
110	13.58	15	3.38		0.087	0.089	1.01	

Table 5. (contd.)

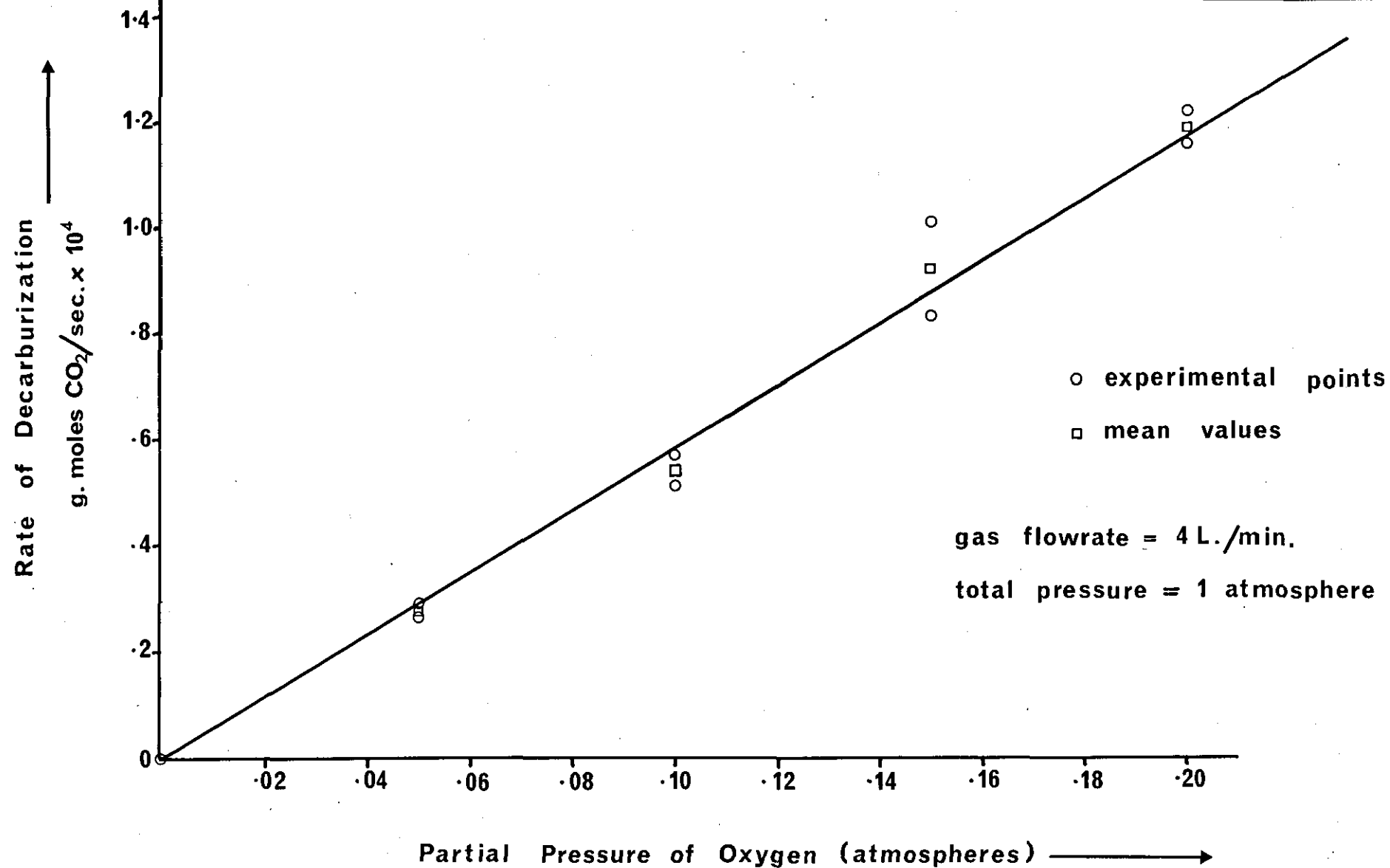
Test No.	Initial Mass of Sample (g.)	Oxygen Partial Pressure (%)	CO ₂ conc ⁿ in plateau region(%)	Average CO ₂ conc ⁿ in plateau region(%)	Final C content (analysis) (%)	Final C content (computer) print-out (%)	Rate of Decarburization (g.moles/sec.)x10 ⁴	Average Rate of Decarburization. (g.moles/sec.)x10 ⁴
111	13.62	20	4.10	3.99	⊕	⊕	1.22	1.19
115	12.43	20	3.87		⊕	⊕	1.16	
113	13.28	0	*	*	4.50	4.52	*	*
114	13.50	0	*		4.55	4.51	*	

* no plateau region.

⊕ no figures possible since boat empty at end of test.

EFFECT OF OXYGEN PARTIAL PRESSURE ON
THE RATE OF DECARBURIZATION AT 1600 °C

FIGURE 21



the results of Simkovich et al.¹¹⁸ who studied the rate of dissolution of alumina in carbon-saturated liquid iron at 1600°C. They dipped an alumina rod 0.29 inches diameter, $1\frac{1}{2}$ inches into 600 grams of molten iron/carbon alloy. After 83 hours, the aluminium content of the melt increased from .003 to .038% compared with a final aluminium content of .053% in 48 hours if the melt was rapidly rotated. This was equivalent to an aluminium transfer rate of 7×10^{-4} grams/cm².hr. The transfer rate required to explain the print-out for 0% oxygen is 10^{-2} grams/cm².hr.

It would seem much more likely particularly from the shape of the print-out, that the reaction was between carbon and air which was trapped in crevices on the boat surface. The fall-off would then represent a reduction in the air available for reaction.

The decarburization rate averaged out to 9.5×10^{-5} grams C/cm².min. The subject of crucible reaction is discussed by Fujii⁵⁹ who obtained a figure of 2.42×10^{-4} grams C/cm² min. using a magnesia lining, which he found to be constant with time and independent of carbon composition down to 0.2% .

Figures 22 (a - e).

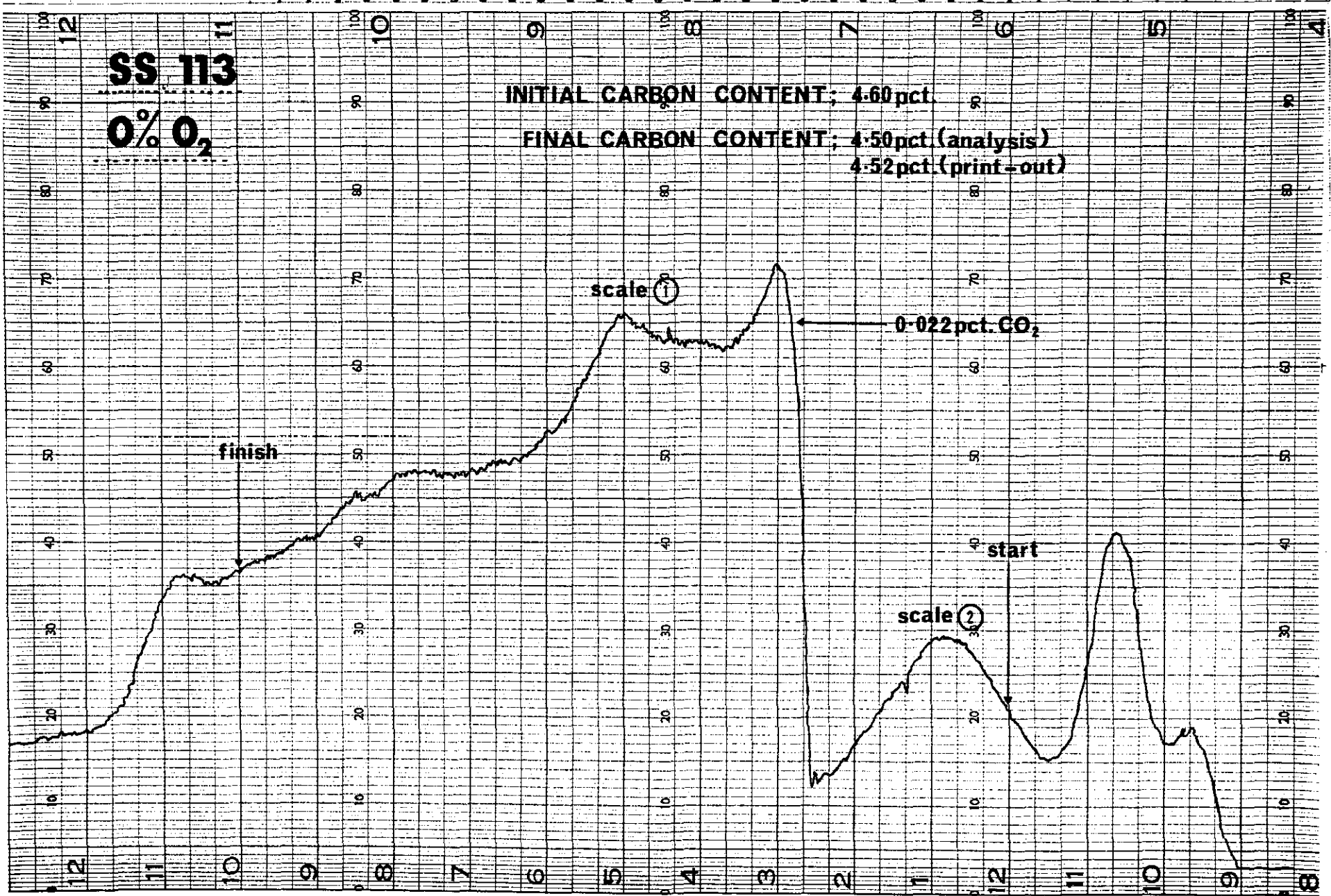
TYPICAL PRINT-OUTS FROM THE
INFRA - RED ANALYSER.

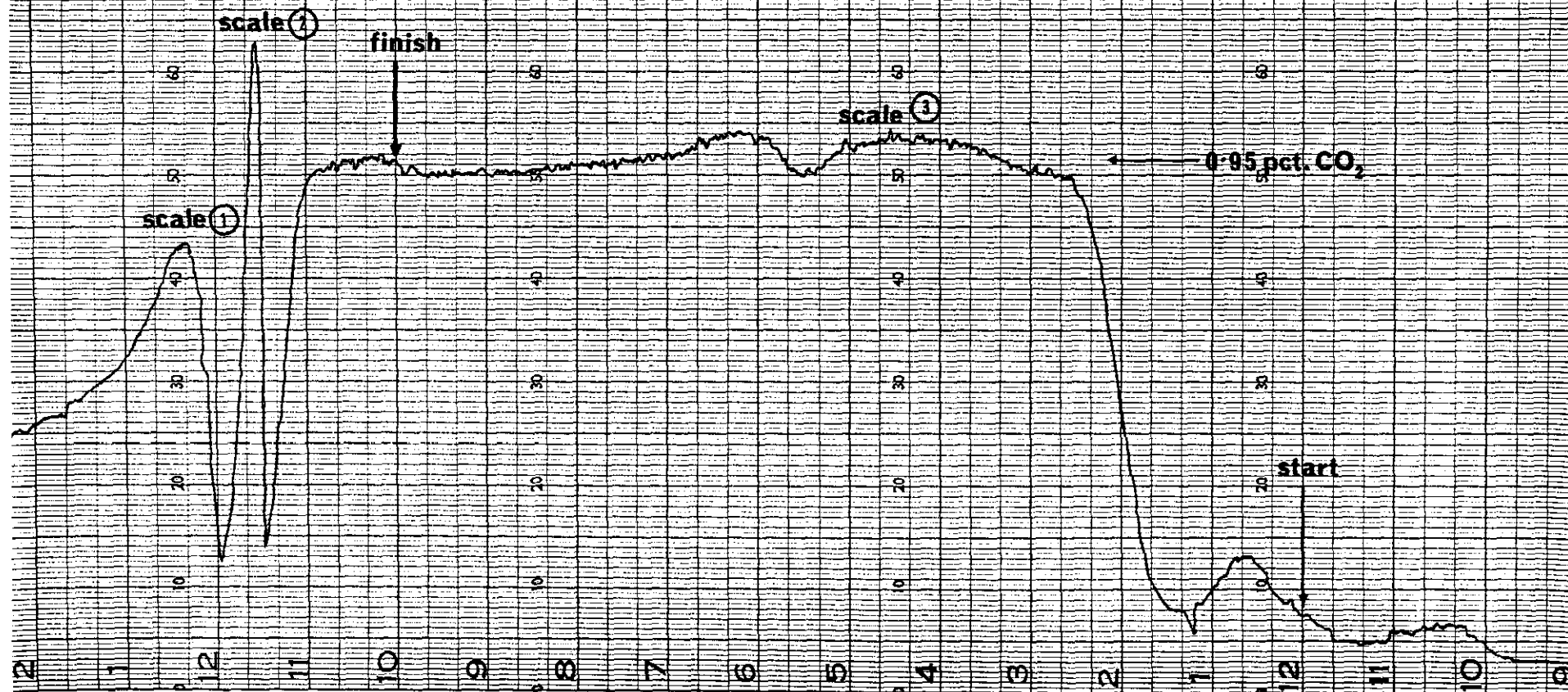
SS 113

0% O₂

INITIAL CARBON CONTENT; 4.60 pct

FINAL CARBON CONTENT; 4.50 pct (analysis)
4.52 pct (print-out)



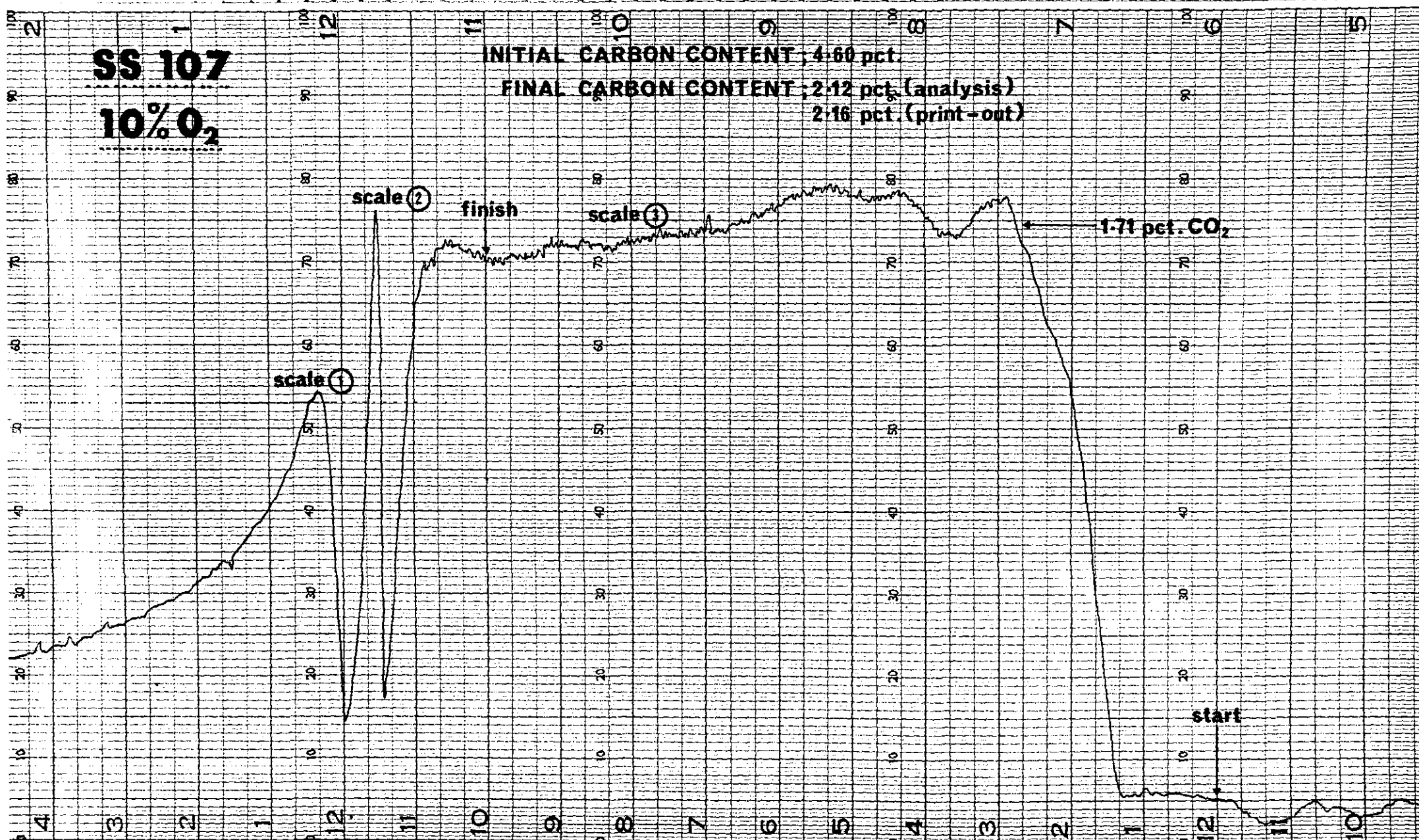
SS 106**5% O₂****INITIAL CARBON CONTENT ; 4.60 pct.****FINAL CARBON CONTENT ; 3.36 pct. (analysis)
3.37 pct. (print-out)**

SS 107

10% O₂

INITIAL CARBON CONTENT : 4.60 pct.

**FINAL CARBON CONTENT : 2.12 pct. (analysis)
2.16 pct. (print-out)**

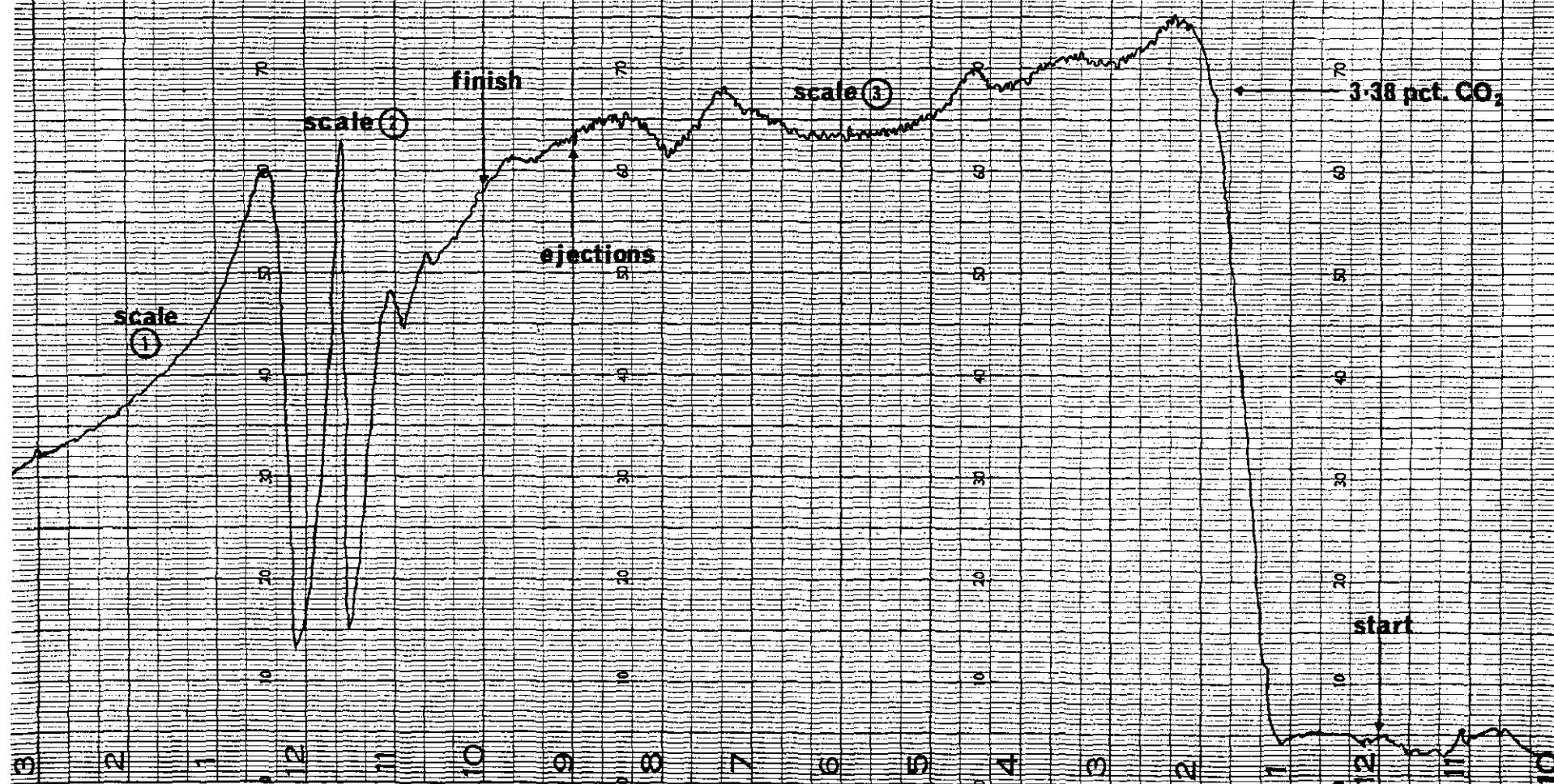


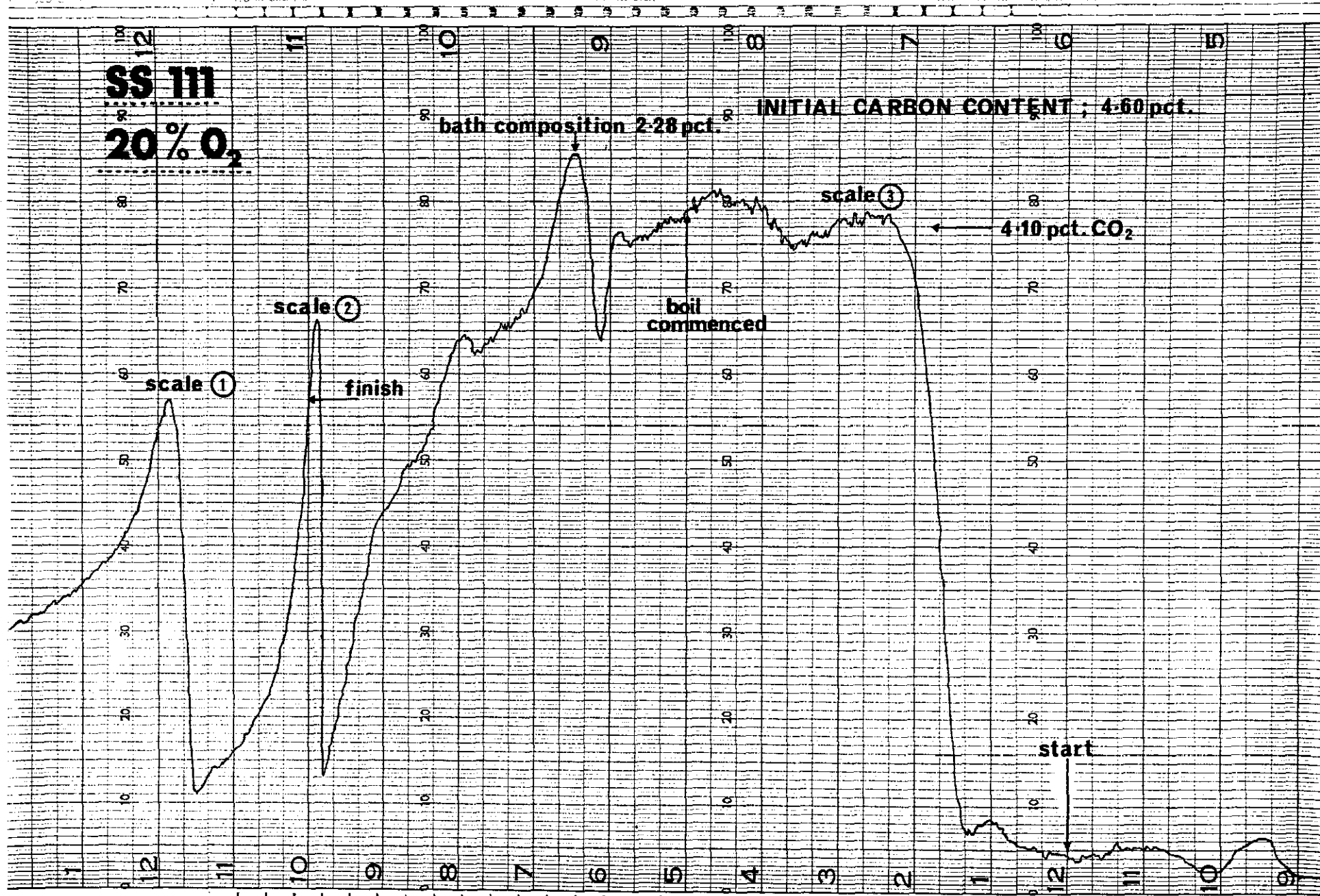
SS 110**15% O₂**

INITIAL CARBON CONTENT ; 4.60 pct.

FINAL CARBON CONTENT ; 0.087 pct. (analysis)

0.089 pct. (print-out)





(vi) The Effect of Oxygen Partial Pressure on the Formation of an Oxide Phase.

a) Introduction.

Preliminary tests had shown that fume formation was dependent upon the formation of an oxide phase. The aim of these tests was to determine the effect of oxygen partial pressure on the bath composition at which an oxide phase appeared.

b) Procedure.

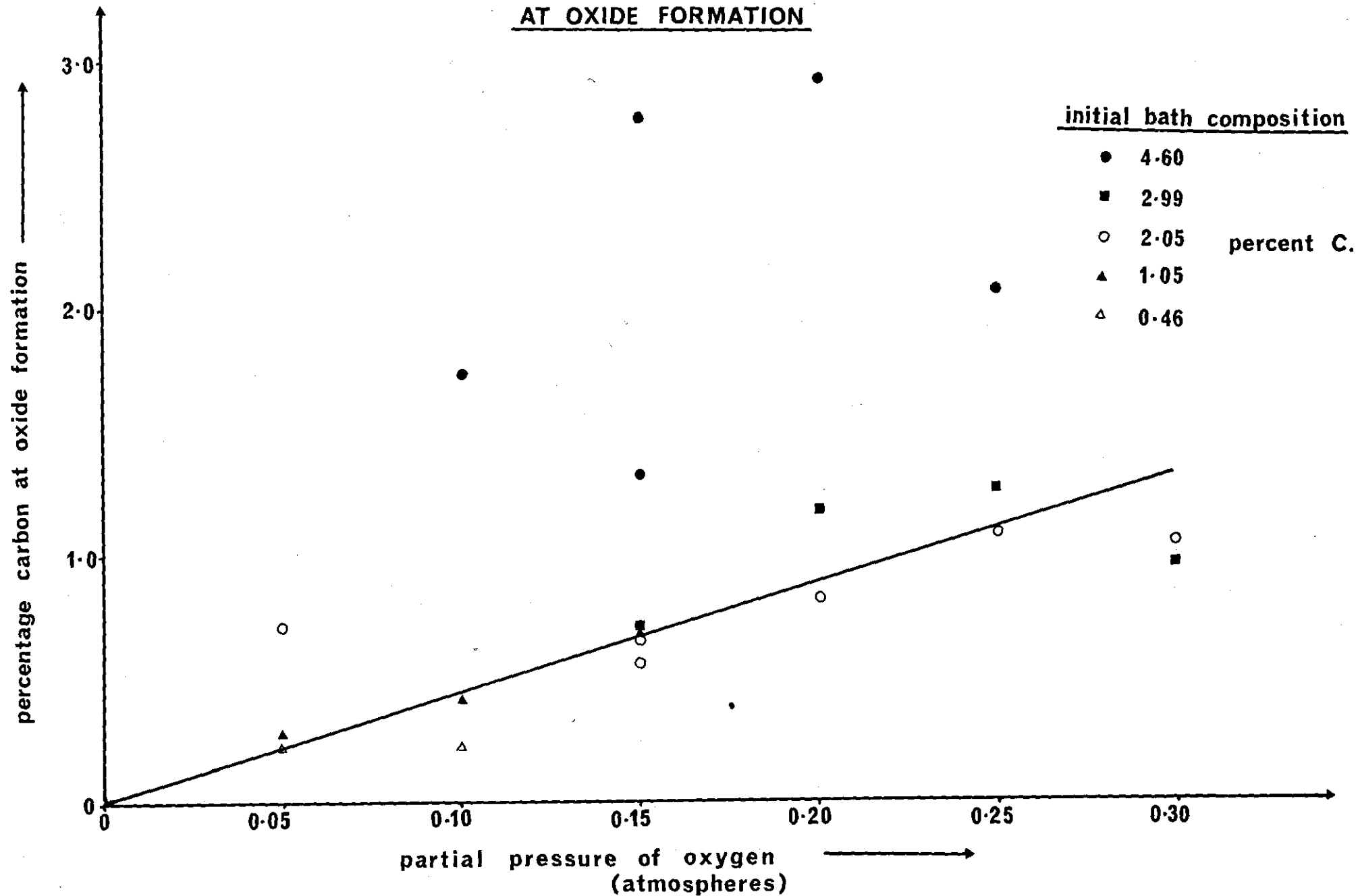
A range of iron/carbon alloys were melted out at 1600°C. Oxygen/argon mixtures with a maximum of 30% oxygen were passed over the alloys until an oxide phase appeared, when the experiment was stopped and the alloy analysed for carbon.

Wherever possible, the surface was completely covered with oxide before the test was stopped. This was the case for all alloys except the 4.6% carbon alloy which always started to boil before a clearcut oxide phase occurred. In those cases, oxide particles appeared and probably nucleated a boil while the bath carbon content was still high. Since the 4.6% C alloys passed the composition range of the alloy below (2.99% C) before a boil commenced, it is difficult to explain why the erratic behaviour occurred in the high carbon alloy only.

c) Results.

The results are given in figure 23 and show as expected that as the partial pressure of oxygen increases, there is a corresponding increase in the percentage carbon in the bath at oxide formation.

EFFECT OF OXYGEN PARTIAL PRESSURE ON THE BATH COMPOSITION
AT OXIDE FORMATION



(vii)

Calculation of Overall Mass Transfer Coefficients.

From the graphs of percentage carbon at oxide formation and percentage carbon dioxide, against percentage oxygen, it is possible to obtain values of the overall mass transfer coefficients for the transport of oxygen and carbon from the bulk phases through the respective diffusion boundary layers. Precise interpretation is not possible from the data obtained since the reaction of carbon and oxygen produces both the monoxide and dioxide. Previous workers^{5,84}, using levitated drops in oxygen have shown that the overall reaction was in producing carbon monoxide. Baker⁵ obtained CO/CO_2 ratios of 6.17:1 using 10% oxygen compared with ratios ranging from 8:1 to 14:1 using pure oxygen obtained by Distin⁸⁴.

In the present investigation, the CO/CO_2 ratio was about 0.5 : 1 measured by the infra-red analyser when using and when bypassing the converter which converted CO to CO_2 . This ratio was irrespective of oxygen partial pressure up to 20% oxygen. It is possible that this CO/CO_2 ratio does not represent the gas composition leaving the boundary layer with some conversion having taken place in the bulk gas phase. At 1600°C the equilibrium constant for the conversion of carbon monoxide to dioxide is 5.44×10^3 and thus a kinetic restraint must exist to prevent virtually complete conversion taking place.

In the calculation, extreme values for the coefficients are obtained by assuming CO is produced at the metal surface, with values obtained assuming that CO_2 is the main product, given in the discussion.

In the system under consideration, a ternary mixture of oxygen, argon and carbon monoxide exists with argon being static. The possible presence of carbon dioxide further complicates the picture which means that the application and integration of standard diffusion equations is not feasible.

If N_{O_2} is the flux of oxygen moles/ $\text{cm}^2 \cdot \text{sec}$, h_{O_2} is the mass transfer coefficient for oxygen transfer and P_{O_2} is the bulk phase oxygen partial pressure, applying the standard mass transfer equation for the diffusion of oxygen:-

$$N_{\text{O}_2} = \frac{h_{\text{O}_2}}{RT} (P_{\text{O}_2})$$

assuming that the oxygen partial pressure at the metal surface is zero.

The validity for this relationship is shown in Figure 21 where the decarburization rate (proportional to N_{O_2}) is linearly related to oxygen partial pressure.

From Figure 21 it can be seen that:-

$$20\% O_2 \cong 0.000118 \text{ moles/sec } CO_2$$

If it is assumed that the CO_2 is formed outside the boundary layer, then

$N_{CO_2} = N_{CO}$ and the flux of oxygen is half the flux of CO.

$$\therefore N_{O_2} = \frac{0.000118}{2 \times 2.52} = .0000236 \frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}}$$

$$\therefore h_{O_2} = \frac{.0000236 \times 82.05 \times 1873}{0.2}$$

$$\therefore h_{O_2} = 18.28 \text{ cm/sec}$$

\therefore The Overall Mass Transfer Coefficient for the transport of oxygen through the gas boundary layer is 18.28 cm/sec.

At the occurrence of oxide on the metal surface, it is assumed that the carbon content at that position is zero.

Thus the flux of carbon to the surface:-

$$N_C = h_C C^*$$

where h_C is the overall mass transfer coefficient for the transfer of carbon from the bulk metal to the surface and C^* is the bulk carbon content.

Taking the density of steel at $1600^\circ C$ to be 7.16 g./cc^{119}

$$\begin{aligned} \therefore C^* &= \frac{7.16 \times .01}{12} \text{ grm moles/cc at } 1\% C \\ &= 0.005967 \text{ grm moles/cc.} \end{aligned}$$

From figure 23, partial pressure of oxygen causing oxide formation at 1% C bulk composition = .228 atmos.

\therefore Oxygen concentration

$$\begin{aligned} &= \frac{.228}{82.05 \times 1873} \\ &= 0.00000148 \text{ grm moles/cc.} \end{aligned}$$

$$\text{But } N_o = h_c C^{\ddagger} = 2N_{o_2} = \frac{2h_{o_2} p_{o_2}}{RT}$$

$$\therefore \frac{h_{o_2}}{h_c} = \frac{C^{\ddagger} RT}{2 p_{o_2}}$$

$$\therefore \frac{h_{o_2}}{h_c} = \frac{.005967}{.00000148 \times 2} = 2015.9$$

$$\therefore h_c = \frac{18.28}{2015.9} = 0.009 \text{ cm/sec}$$

\therefore The Overall Mass Transfer Coefficient for the transport of Carbon through the metal boundary layer is 0.009 cm/sec.

Discussion.

The mass transfer coefficient for carbon transfer is 0.009 cm/sec. assuming fast reaction occurring at the liquid gas interface and the coefficient for oxygen transfer is 18.28 cm/sec. assuming CO formation, a figure which becomes 36.6 cm/sec if CO₂ formation is assumed. Distin⁸⁴ obtained a mass transfer coefficient of 0.032 cm/sec. for carbon transfer in a levitated drop at 1770°C also using the position of oxide formation to obtain his result. A higher figure is to be expected for levitated drops since the greater degree of stirring occurring would result in a correspondingly thinner boundary layer. For oxygen transfer his results gave a coefficient of 9.9 cm/sec. for a gas velocity of 16 cm/sec. N.T.P. assuming CO as the overall product. Baker's results⁵ give an oxygen transfer coefficient of 44.7 cm/sec. at 1660°C for a gas velocity of 12.56 cm/sec. making similar assumptions. It can be seen that good agreement is obtained between these results and those obtained from the present investigation.

(viii) Effect of Oxygen Partial Pressure on the Quantity of Fume Produced.

A series of tests were undertaken to determine the effect of oxygen partial pressure on the quantity of fume produced. Since it had been found that appreciable fuming only occurred after bubbling had commenced, the fuming rates have been represented as fume per minute of bubbling, and the fume produced before the boil started is included in the figure obtained for the boiling period. This time delay varied from a few seconds at 100% oxygen to nearly 5 minutes for 15% O_2 . In some of the tests particularly at the lower oxygen levels, the boil was spasmodic, and the time of boiling was obtained using a cumulative stop-watch.

Results.

The results are given in Table 6 and Figures 24 and 25.

It can be seen that an increase in the oxygen partial pressure resulted in a corresponding increase in the rate of fume production during the "boiling" period.

A reduction in the percentage oxygen will influence fume formation in four different ways. It will cause oxide formation to occur at a lower carbon content. This, applying the observations of Morris⁵⁰, will produce larger ejections indicative of a deeper nucleated boil. These larger ejections will take longer to decarburize and hence have less chance of reaching the conditions required for disintegration to take place.

Secondly, it will decarburize the ejections at a lower rate which will increase the time before gas nucleation occurs inside the droplet.

Thirdly, oxide formation on the droplet will occur at a lower carbon content, further increasing the time before a possible explosion could take place, and finally reduced oxygen partial pressure will reduce the exothermic nature of the gas and increase the chance of droplet solidification. It can be seen that statistics play an important part in the relationship between fume emission rates and oxygen partial pressure; nevertheless, a reasonable linear correlation is obtained. A reduction in the initial bath carbon content produced less fume per minute, 100% oxygen and 1.05% carbon giving the same fume production.

Table 6.

Effect of Oxygen Partial Pressure on the Quantity of Fume Produced

Gas Flowrate: 4 litres/minute N.T.P.

Metal Temperature: 1600°C.

Total Pressure: 1 atmosphere.

Test No.	Initial Carbon Content (wt.%)	Oxygen Concentration (vol.%)	Total time of run (secs)	Time of boil (secs)	Fume Produced (mg.)			Fume per Minute of Boiling (mg.)
					Tube.	Filter	Total	
142	4.60	100	75	60	995.0	55.5	1050.5	1050
171	4.60	90	46	28	422.0	21.0	443.0	950
172	4.60	80	88	69	905.0	16.5	921.5	801
143	4.60	70	95	70	607.0	115.5	722.5	619
127	4.60	70	130	100	1055.0	86.0	1141.0	685
173	4.60	60	74	40	371.0	7.0	378.0	567
144	4.60	40	105	45	320.5	33.0	353.5	471
166	4.60	35	125	40	265.5	7.5	273.0	409
167	4.60	30	165	41	192.5	7.5	200.0	292
168	4.60	25	130	43	115.0	11.0	126.0	176
169	4.60	20	150	58	97.0	8.0	105.0	109
170	4.60	15	367	80	35.0	9.0	44.0	33
159	2.05	100	46	28	398.0	10.5	408.5	875
160	2.05	70	52	32	250.0	18.5	268.5	503
158	2.05	40	80	38	110.0	16.0	126.0	199
165	1.05	100	20	14	165.5	7.0	172.5	739
164	1.05	70	30	18	135.0	12.0	147.0	490
163	1.05	40	55	45	70.5	8.5	79.0	105

FIGURE 24

EFFECT OF OXYGEN PARTIAL PRESSURE ON THE RATE OF FUME FORMATION

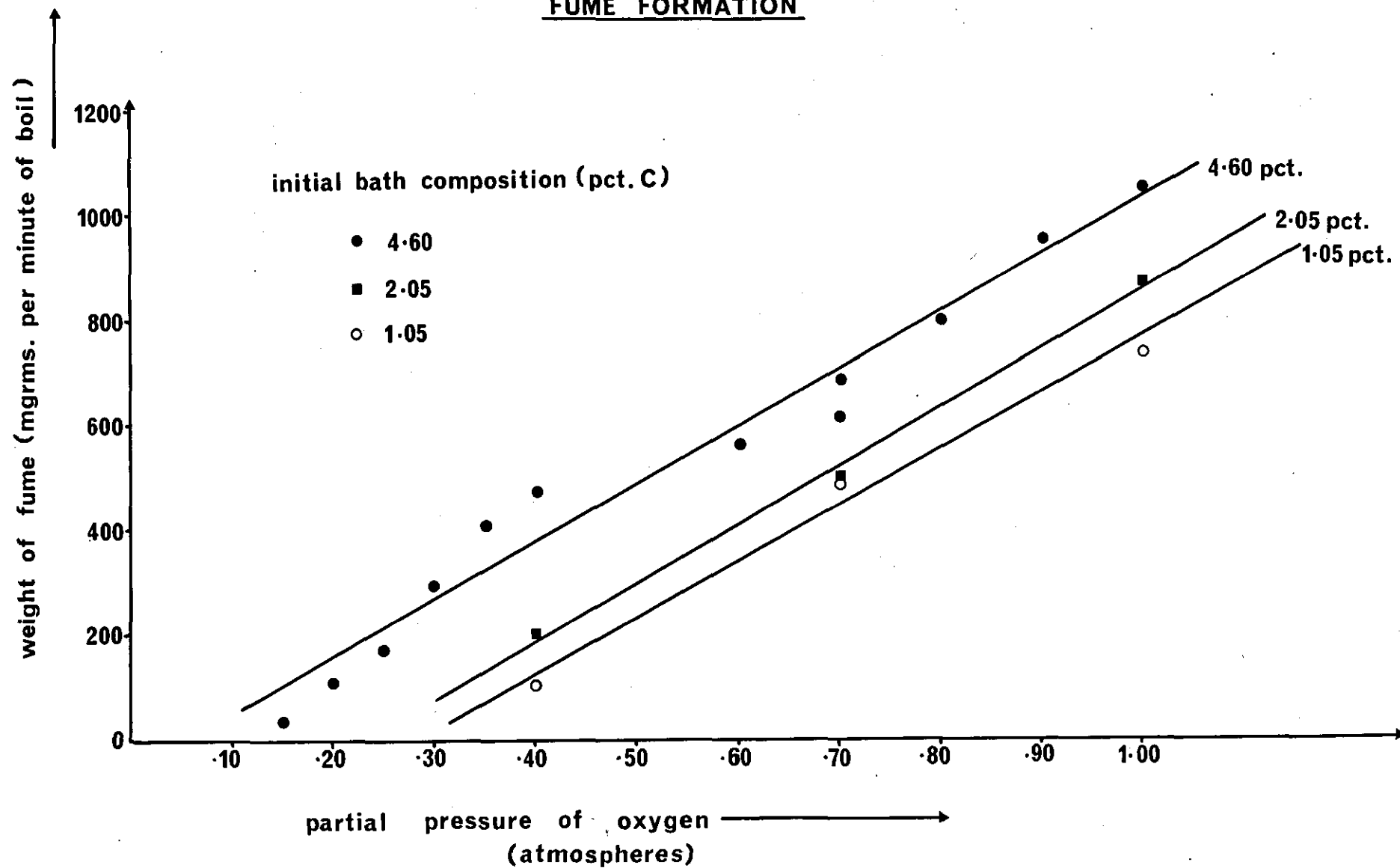


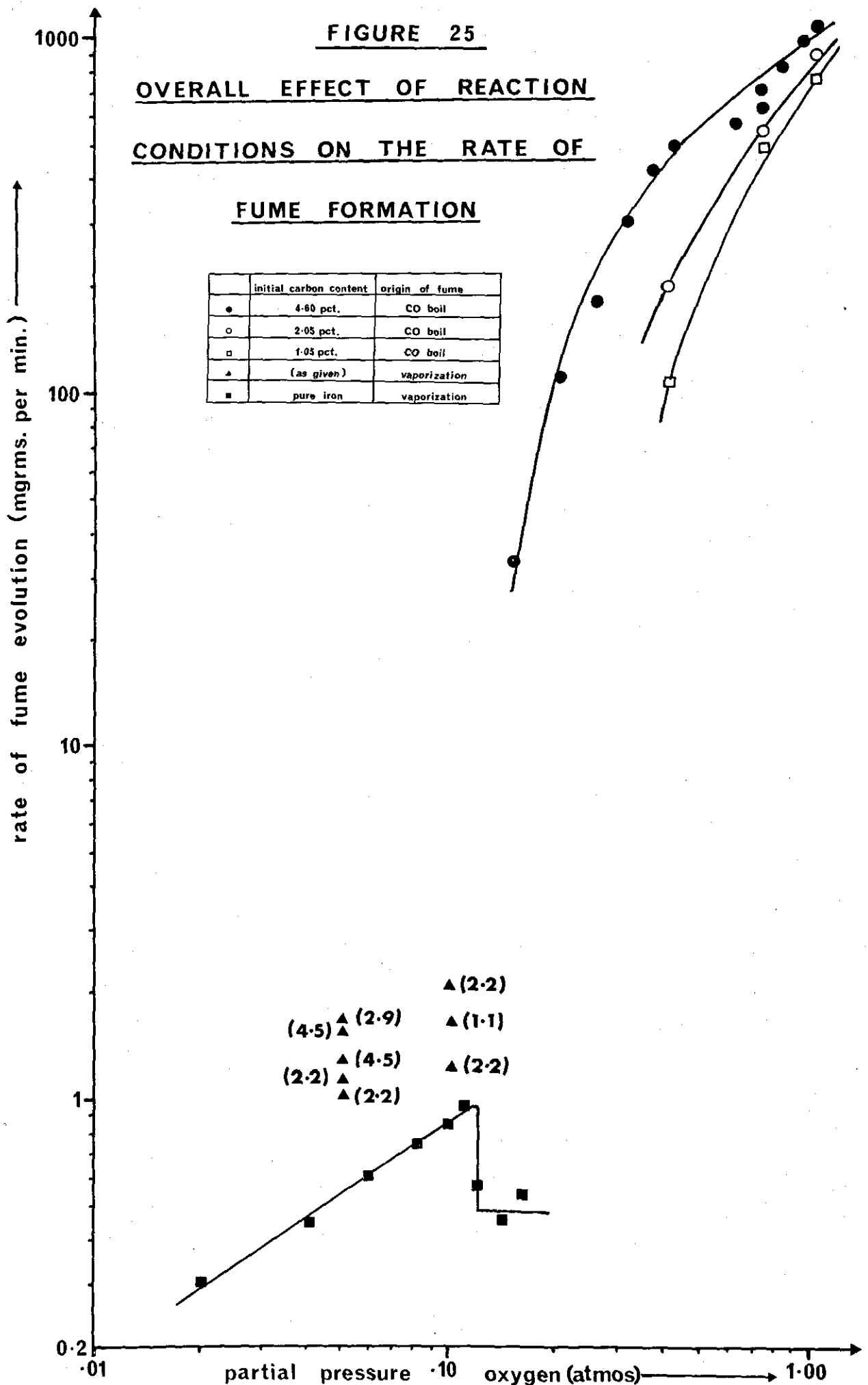
FIGURE 25

OVERALL EFFECT OF REACTION

CONDITIONS ON THE RATE OF

FUME FORMATION

	initial carbon content	origin of fume
●	4.60 pct.	CO boil
○	2.05 pct.	CO boil
□	1.05 pct.	CO boil
▲	(as given)	vaporization
■	pure iron	vaporization



rates as 75% oxygen and 4.60% carbon. It would appear that a lower bath carbon content produced larger ejections observed by Morris⁵⁰, which statistically should give less fume.

It is difficult to estimate accurately the error in including "vaporization" fume in the value obtained from the boil. Table 7 gives typical fume values obtained from runs in which a boil did not take place.

Observations made at the time of each run showed that occasional bubbling did take place during the course of the ten minute period even with 0% oxygen, due almost certainly to a crucible reaction but any ejections produced from the bubble bursting did not give the spark-like flashes which were characteristic of bubbling from a boil. This was probably due to the low oxidising power of the gas used since it was not possible to do a satisfactory run without ejections at greater than 10% oxygen. The quantities of fume produced were too small to attempt a separation of any ejections above 5/16 in size produced from the crucible reaction and also when some bubbling took place in the final minute (shown by an asterisk). Nevertheless, the fume values/minute are very low compared to those obtained from a boiling period and it is fair to assume that including vaporization fume produced before the boil in the value obtained from the boil, has not produced an appreciable error and will not effect the overall picture.

Certainly, the effect of including the "vaporization" fume will be within the experimental error in obtaining the fume rates during the boiling period.

Figure 25 shows the overall effect of reaction conditions on the rate of fume formation. It can be seen that there is up to a three orders of magnitude increase in fuming rates during a boil compared to during the "vaporization" stage and stresses the significance of a boiling bath as a necessary condition for appreciable fuming to take place.

Table 7.

Quantity of Fume Produced in the Absence of a Boil.

Period of run: 10 minutes.
 Metal temperature: 1600°C.
 Gas flowrate: 4 litres/minute N.T.P.
 Total pressure: 1 atmosphere.

Test No.	Oxygen concentration (vol.%)	Wt. of sample (grams)	Initial Carbon Content (wt.%)	Final Carbon Content (wt.%)	Fume Produced (mgrms)
9	0	11.70	.014	.008	1.7
15	0	10.79	.006	.002	2.5
16	0	12.79	.003	.0025	2.8
25	0	10.28	4.37	4.32	9.8
28	5	12.62	4.55	3.60	12.5
30	5	11.99	3.34	2.31	8.0
33	5	11.77	2.24	1.29	11.0
34	5	11.70	2.24	1.21	10.0
37	5	11.90	1.10	0.14	13.5
38	5	11.50	1.10	0.07	9.5 *
35	10	11.98	2.24	1.03	12.0
36	10	11.93	2.24	0.04	20.5 *
39	10	12.17	1.10	0.02	16.0 *
107	10	13.36	4.60	2.12	8.0
108	10	13.66	4.60	2.06	5.0

* bubbling in final minute after oxide appearance.

6. The Effect of Gas Composition on Iron Alloy
 Melts containing Manganese.

Introduction.

It is well known that at 1600°C, the vapour pressure of manganese is 45.0mm while that of iron is 0.058mm.⁵⁰ If fuming is primarily a consequence of ejections thrown up out of the bath which in turn explode, then the concentration of an alloying element in the fume should be equivalent to that in the bath, even in the case of a highly volatile element like manganese. The aim of this series of tests was to determine the ratio of iron to manganese in the fume compared to that in the bath for conditions where bubbling took place and where only vaporization occurred.

Table 8

The Effect of Reaction Conditions on the Manganese Ratio in Fume.

Test No.	Gas Composition % O ₂ (vol.)	Time of run (mins)	Bubbling in Tube ?	BATH COMPOSITION				FUME COMPOSITION		
				% C (wt.) in melt	%Mn (wt.) in melt	% Fe (wt.) in melt	Fe/Mn in melt (wt./wt.)	Wt. Mn in fume (mgrms)	Wt. Fe in fume (mgrms)	Fe/Mn in fume (wt./wt.)
98	6	5	No	3.91	4.31	91.78	21.29	7.5.	5.0	0.67
99	40	2	Yes	3.86	4.43	91.71	20.70	2.7	64.0	23.70
101	40	1½	Yes	4.28	4.65	91.07	19.58	4.1	106.0	25.85
102	6	4	No	4.31	4.47	91.22	20.41	9.4	3.0	0.32
103	6	4	No	4.17	4.49	91.34	20.34	10.1	3.0	0.30
145	0	3	No	4.35	4.20	91.45	21.77	11.1	4.0	0.36
146	0	3	No	4.24	4.17	91.59	21.96	10.1	3.0	0.30
161	0	5	No		4.12	95.88	23.27	7.0	2.0	0.29
162	0	5	No		4.22	95.78	22.70	11.5	3.0	0.26

Procedure.

Alloys of iron, manganese and in some cases carbon were prepared by placing pre-weighed quantities of the three components in an alumina boat and melting out under an atmosphere of argon. The Radyne setting required to obtain a temperature of 1600°C was noted since it was not possible to remelt with the thermocouple in position because of shearing of the sheath. The sample was then cooled, the tube cleaned to remove a small amount of vaporization during melt-out and the impactor and filter fitted in position. The power was then switched on and after heating the sample to the correct setting, the required gas composition was passed into the tube for a set time after which the power was switched off and the tube purged out with argon. The results are shown in Table 8.

Discussion.

The results show as expected that there is a considerable difference in the iron/manganese ratio in the fume depending on the reaction conditions occurring in the tube.

When boiling has occurred the following correlation was obtained:-

$$\frac{\text{Fe}}{\text{Mn}} (\text{fume}) = 1.23 \frac{\text{Fe}}{\text{Mn}} (\text{melt}) \dots\dots 1$$

which is in good agreement with a value close to unity expected if fume is primarily a consequence of boiling and subsequent oxidation of the ejected droplets.

When a boil was absent using 6% oxygen, the correlation coefficient for equation 1 was 0.02 compared with 0.013 when vaporizing into pure argon.

When vaporization is occurring, there is a possibility of manganese depletion at the metal-gas interface. If it is assumed that transport of manganese from the bulk metal to the interface is fast, compared to the vaporization process, then:-

$$\left[\frac{N_{\text{Fe}}}{N_{\text{Mn}}} (\text{fume}) \right]_{\text{Minimum}} = \frac{p_{\text{Fe}} [a_{\text{Fe}}]_{\text{metal}}}{p_{\text{Mn}} [a_{\text{Mn}}]_{\text{metal}}}$$

where a refers to the activity, and N is the mole fraction. Manganese

forms an ideal solution with iron, hence at 4.17% Mn :-

$$\left[\frac{\text{Fe (fume)}}{\text{Mn}} \right]_{\text{Minimum}} = \frac{.058 \times 95.83}{45 \times 4.17} = 0.029$$

$$\text{and } \left[\frac{\text{Fe (fume)}}{\text{Mn}} \right]_{\text{Minimum}} = .0013 \frac{\text{Fe (melt)}}{\text{Mn}}$$

It can be seen that the coefficient is an order of magnitude smaller than that obtained for vaporization into argon, showing that manganese transport was relatively slow. The addition of 6% oxygen to the inlet gas had no apparent effect on either the composition or quantity of fume produced.

Morris⁵⁰ investigated the distribution of tracer elements between the bath and fume. In general, elements more volatile than iron increased in concentration in the fume and vice versa. The spread, however, between the highest and lowest distribution ratios was very narrow (a factor of 7) considering the wide range of volatilities of tracers investigated. He concluded that the results strongly suggested that fume consisted of mechanically produced particles. His results gave the relationship:-

$$\frac{\text{Fe (fume)}}{\text{Mn}} = (0.25 - 0.14) \frac{\text{Fe (metal)}}{\text{Mn}}$$

depending on the temperature for a bath manganese content of 0.18%. It can be seen that his coefficient is much nearer the unity value expected from a boiling reaction, than .0013 expected from vaporization.

Bogdandy and Panke¹⁴ found a correlation between the manganese concentration in the bath and the Fe/Mn ratio in the fume, for bottom-blowing.

From their results, it can be determined that for a bath manganese content of 0.2%

$$\frac{\text{Fe (fume)}}{\text{Mn}} = 0.008 \frac{\text{Fe (metal)}}{\text{Mn}}$$

Their data is insufficient for meaningful interpretation to be made, but it appears that the results were taken during the after blow. During this period the fume production in bottom-blowing is at a maximum with carbon at a low level. Thus one would have expected that their

-118-

coefficient should have been much larger instead of being similar in magnitude to the vaporization coefficient of 0.0013.

7. General Discussion.

The large quantities of fume emitted by modern oxygen steelmaking processes have previously been explained by any of four different mechanisms. The earliest was the theory that a volatile compound was produced, immediately decomposing to give iron which would then oxidize to produce fume. No concrete evidence was ever produced to verify this theory and Belton's thesis was unable to support it. It was then suggested that fume was a consequence of the hot spot produced where an oxygen jet hit the metal surface. Fume measurements showed that a temperature of about 2300°C would be required in all the issuing gases to support this mechanism. The theory was unable to explain a) fume produced under endothermic reaction conditions of $\text{FeO}+\text{C}$, and b) the dependence of fume on bulk carbon content and the absence of fume when blowing oxygen onto pure iron.

The third theory considered that there was a gas/metal-vapour reaction close to the metal surface within the boundary layer. This provided a sink for both reactants setting up steep concentration gradients with a consequent enhancement in the vaporization rate. The results for carbon-free iron supported the theory which was extended to include the effect of carbon. The maximum evaporation rates predicted in this theory were obtained in practice assuming temperatures of about 2000°C but the theory failed to explain the finite slope of the graph of carbon content against fume evolution rates.

The final theory was concerned with the ejection of droplets caused by the bursting of carbon monoxide bubbles. Although experimental evidence on this theory was qualitative, there were no apparent contradictions when applying the mechanism to known observations.

The results were obtained on equipment very similar to that used by Turkdogan, and the effect of oxygen partial pressure on the vaporization of pure iron was initially obtained. It was seen that an enhancement was obtained with increasing oxygen concentration but the quantities of iron obtained as fume were about 1/50th of that obtained by Turkdogan. The only apparent difference in technique in

the present investigation was an inability to obtain the preheat gas temperature of 1600°C . It was shown that a variation in the preheater temperature up to a maximum of 1000°C had no effect on the quantity of fume produced.

The effect of oxygen on iron/carbon alloys was then investigated, and it was seen that the state of decarburization occurring had considerable influence on the nature and quantity of fume produced.

Provided that the carbon content of the metal was above a certain value depending on the oxygen partial pressure being used, decarburization occurred at the surface of the melt and was gas phase controlled, with vaporization similar in quantity and nature to that present with pure irons. When there was a change in control and an oxide layer formed on the metal surface, a carbon monoxide boil was nucleated which caused ejections to be thrown out of the bath, some of which exploded into fume. Fume measurements during this boiling stage showed that there was a three orders of magnitude increase in fume production rates compared with the vaporization stage. An examination of the fume under the electron microscope showed that vaporization fume was mainly octagonal in cross-section and within the size range of 0.05μ to 0.15μ while fume from a boiling bath was characteristically spherical and much larger in size, having a maximum diameter of 3μ .

The investigation into decarburization during the "vaporization" period showed that there was a linear relationship between the percentage oxygen in the bulk phase and the rate of decarburization as shown by the percentage CO_2 in the exhaust gases after conversion from CO had taken place. This period was observed as a plateau region on the print-out from the infra-red analyser and the fall off from this plateau occurred soon after the appearance of an oxide phase on the metal surface. The carbon content of the bulk metal at oxide formation was found at various oxygen partial pressures and it was seen that a linear correlation existed, with an increasing oxygen concentration causing oxide to appear at a correspondingly higher bulk carbon content.

From the graphs of percentage carbon dioxide and percentage carbon

at oxide formation against percentage oxygen, the overall mass transfer coefficients for the transport of carbon and oxygen through the boundary layers were obtained.

It was found that $h_{O_2} = 18.28 \text{ cm/sec.}$ and $h_C = 0.009 \text{ cm/sec.}$ assuming that carbon monoxide was formed at the metal surface within the boundary layer. The value for h_C is doubled if carbon dioxide was the only product within this region. These values are similar to those obtained from the results of Distin and Baker. Gas analyses showed a CO/CO_2 ratio of about 0.5:1 but since this ratio is much lower than other published values, some conversion could have taken place outside the boundary layer - clearly equilibrium was not reached to any extent since purely equilibrium conditions indicate almost complete conversion to CO_2 .

Finally, the distribution of a highly volatile component, manganese, between fume and metal was investigated. With fume from a boiling bath, the ratio $(Fe/Mn)_{\text{fume}} / (Fe/Mn)_{\text{metal}}$ was 1.23 compared with the expected value close to unity while a vaporizing bath gave a ratio of 0.02 with 6% oxygen and 0.013 with pure argon, compared with a value of 0.0013 expected if vaporization occurred without depletion of manganese at the surface. The order of magnitude difference indicates that this was not the case.

These results indicated that the two key stages in the production of fume were the generation of ejections by the bursting of carbon monoxide bubbles at the melt surface, and the reaction of these droplets in an exothermic atmosphere. The removal of either of the stages would cause the rate of fume formation to be drastically reduced. This was shown by using carbon dioxide as the reacting gas instead of oxygen, and is applied on the commercial scale with the process known as fumeless refining.

Thus, from the difference in the nature and quantity of fume produced in the "bubbling" and "vaporization" stages, it is concluded that bubble bursting and the subsequent oxidation of ejected iron droplets in an exothermic atmosphere is the major cause of fume

formation in oxygen steelmaking.

APPENDIX I

Large Scale Research Work

(i) Introduction

When the initial programme of research was drawn up, it was decided that the work should take place not only on the small scale (approx. 10 gram samples) where boundary conditions were accurately known and where fume formation could be observed, but also on a larger scale, where the conditions would more closely simulate industrial practice.

It was realized that in the latter case, inaccuracies would be much greater than in the small scale, but it was hoped that these could be estimated and eliminated where possible.

(ii) Experimental Programme

It was considered that when designing equipment on this scale to follow a particular programme, progress in any of a number of directions would depend on previous results, thus necessitating a flexible range of equipment that could readily be arranged to perform different types of tests.

It was hoped that information could be obtained on the relevance of the various theories that existed at the onset of the project and to remove various anomalies which existed in the literature (e.g. effect of temperature and CO_2 on fume formation)

The initial programme would be to obtain a correlation of fume formation against carbon content of the melt which would calibrate the equipment in terms of other literature values.

An investigation into the bubble bursting theory would then follow. It was hoped to inject various gases into the melt to simulate carbon monoxide generation, with various atmospheres above the melt and see if appreciable quantities of fume could be obtained.

It was further hoped that high speed photography could be used to examine reactions taking place above the melt surface.

(iii) Apparatus

The work was carried out at the Central Research Laboratories of R.T.B. at Whitchurch, Aylesbury and an EFCO 40 KV high frequency air induction furnace was provided to melt out samples of required composition. The charge weight was 1 cwt.

The furnace was lined with "Basic A" material supplied by Pickford Holland Ltd. This contained 86.76% MgO, 6.55% SiO₂ and 2.23% Fe₂O₃.

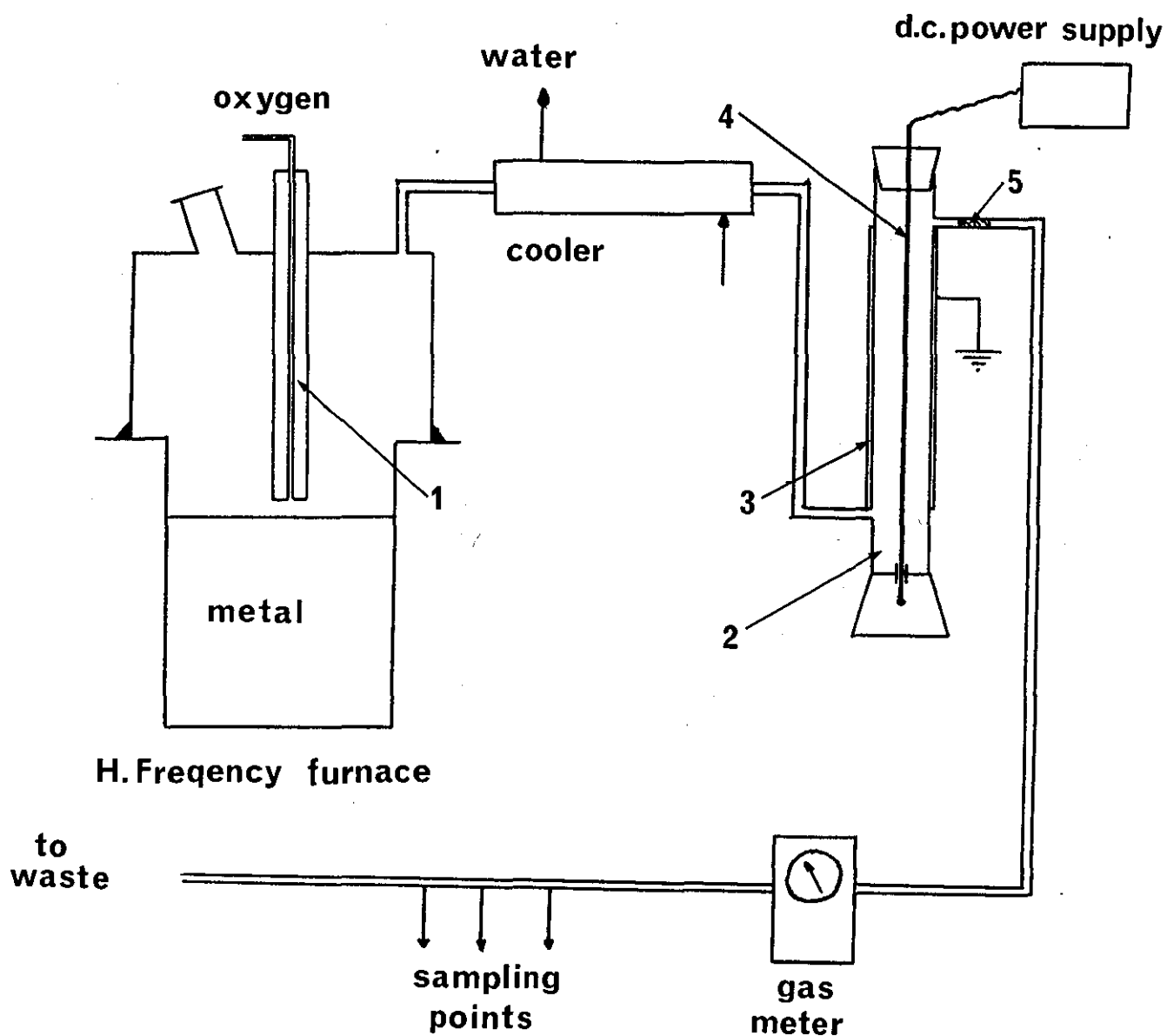
It was essential for the system to be gas-tight and in order to enclose the gases and fume above the melt, a hood was built. This had provision for gas inlet, outlet and sampling, and a window, with a wiper, to observe the melt.

Two hoods had to be built; the first was a mild steel shell lined with Marinite which was found to be unsatisfactory because moisture was driven off from the Marinite when it got hot, and condensed in the fume separation system.

The Marinite was replaced by light-weight silica bricks but these had to be bolted into the shell individually and extensive leakage occurred through the bolt holes, even when asbestos gaskets were used.

In addition it was found impossible to seal the hood to the refractory top plate of the furnace.

It was also observed that cracks occurred just above the metal level in the lining material. Expansion figures for Basic A refractory were then obtained, and it was seen that at about 1200°C, the percentage linear expansion changed from positive to negative. It is likely that this temperature existed in the vicinity of the crack.



- 1 water cooled lance
- 2 electrostatic precipitator
- 3 collecting electrode
- 4 discharge electrode
- 5 glass wool plug

FIGURE 26

LARGE SCALE EQUIPMENT

REVISED FURNACE AND HOOD DESIGN

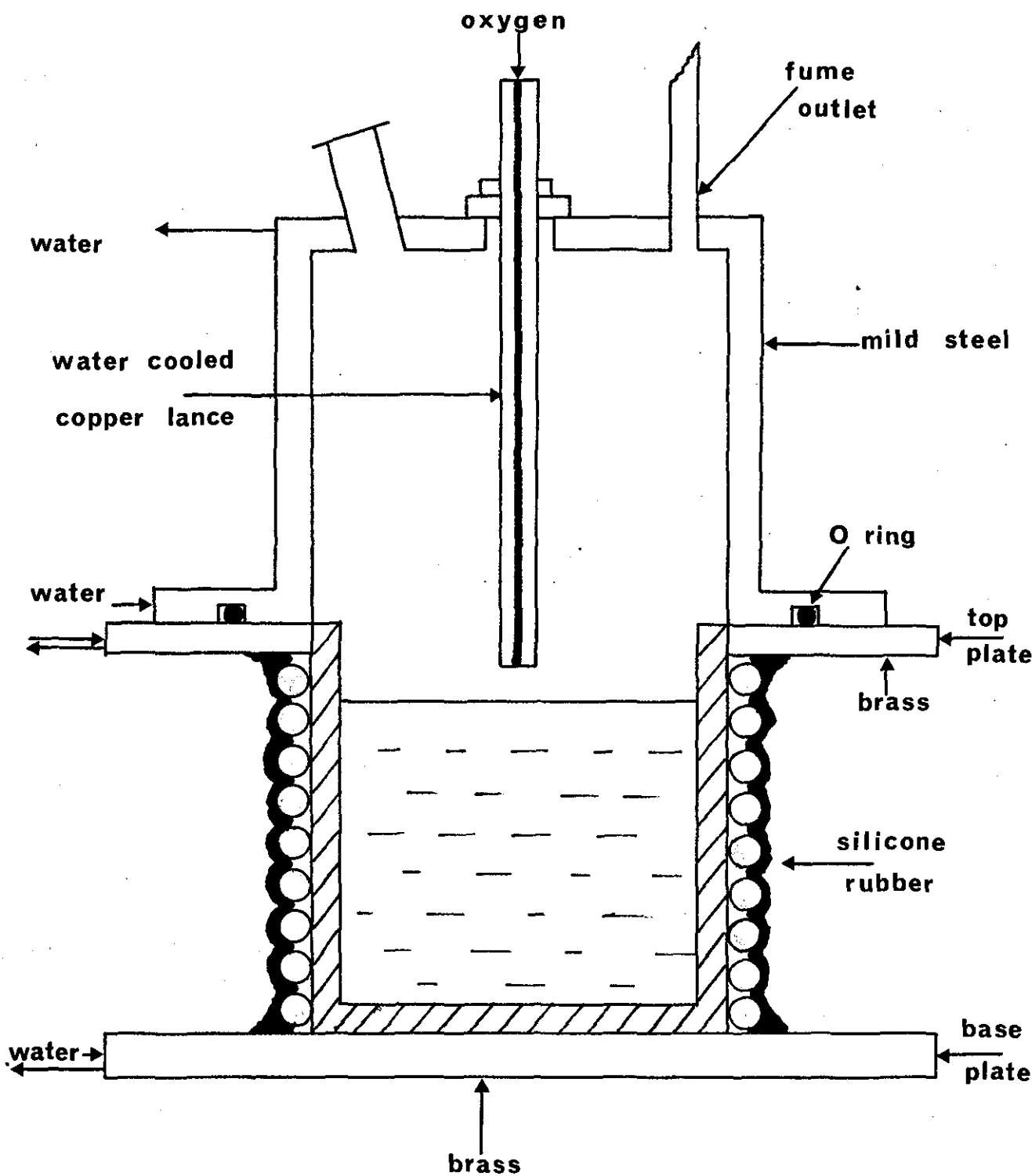
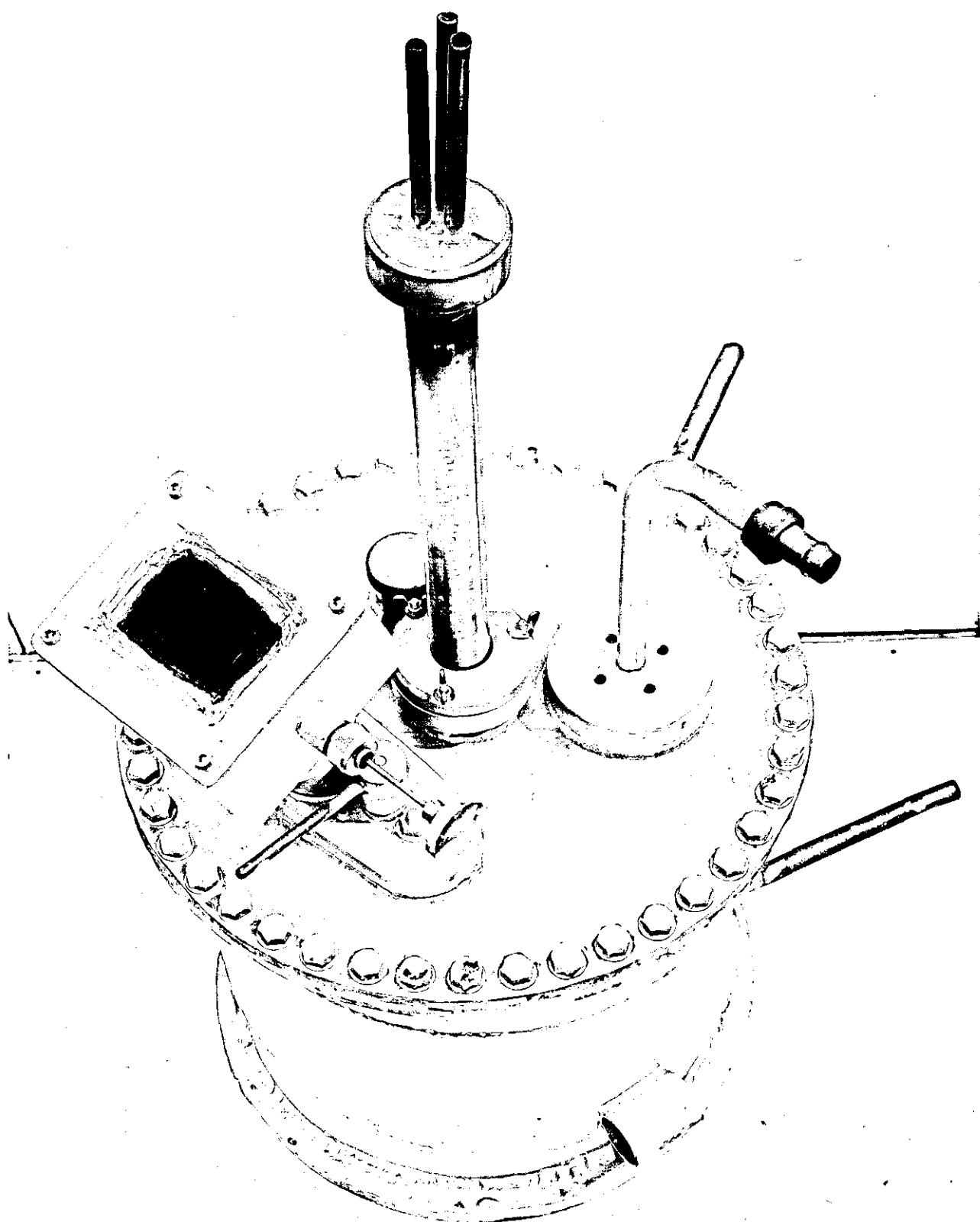


FIGURE 27

FIGURE 28

Photograph of Hood used for Large Scale Programme



Because of these difficulties, the hood and furnace top plate were scrapped and redesigned.

A brass water-cooled bottom plate was made for the high-frequency coil to sit on and another water-cooled brass plate was clamped on top of the coil. The entire coil was then coated with a silicone rubber compound, (Silastoseal B made by Midland Silicones).

The new hood was made of mild steel and was water-cooled. It had an "O" ring inset into its base and two clamps secured the hood to the top plate. This system proved to be completely gas-tight.

Gas entry was by means of a lance placed $1\frac{1}{2}$ inches from the metal surface. Various refractories were tested as possible lance materials.

Both silica and recrystallised alumina melted when blowing oxygen onto the metal surface and zirconia and magnesia failed immediately due to thermal shock. For this reason thoria was not tried. A water-cooled copper lance was then tried and found to be entirely successful.

After leaving the hood, the fume and gases were cooled in a concentric copper tube cooler which led to the fume separation equipment.

Various methods of fume separation were considered and it was decided, because of its low pressure drop, to use an electrostatic precipitator.

From the results of previous work³⁴⁻⁴¹, a high voltage unit was built which could develop 30KV d.c. through a negative discharge electrode placed down the centre of a 1 inch I.D. pyrex tube, 12 inches long.

Trials were conducted to determine the relative effectiveness of various discharge electrodes including copper, platinum, and platinum with barbed spikes.

Very little difference was observed in the coronas produced, and consequently a copper wire, .015 inches diameter, was chosen.

In addition, collecting electrodes were tried both inside and outside the glass tube. In view of the analysis requirements on the collected fume, it was decided to use aluminium foil, wrapped outside the tube. The precipitator tube was put inside a wooden cage with a perspex front, in view of the possible explosion risk mentioned by Drinkler³⁴.

A small glass-wool plug was put in the gas line just beyond the precipitator to remove any fume entrained into the exit gases.

The precipitator unit was tested and found to be completely efficient in separating the fume, with a very small percentage appearing in the glass wool. A second plug put downstream from the first showed no evidence of fume collection.

The remainder of the equipment included a dry gas-meter and provision for collecting gas samples for orsat analysis.

(iv) Experimental details.

The base material used was Swedish Iron, with its very low impurity content (0.05% maximum element) and tests were carried out to determine the most satisfactory means of carburizing up to its saturation point. Top-dipping carbon rods into the molten metal was very violent and somewhat hazardous for the person concerned due to the high oxygen content of the base material. When the carbon was charged into the furnace with the cold metal initially, however, and the bath brought to temperature, the process was much quieter. High purity carbon powder with a total impurity of 150 p.p.m. was supplied by Cabot Carbon Co., Ltd.

When the water-cooled modifications were made to the furnace and hood, the possibility of an explosion due to water coming into contact with molten steel became very real, and special aluminised asbestos suits were obtained for use when working on the furnace.

In order that metal samples could be taken easily, glass vacuum sample tubes were tried out, similar to those described by Strathdee⁴³. These were about 6 inches long and $\frac{1}{4}$ inch diameter. When the tip was immersed below the steel surface, it melted and a thin rod of steel was sucked up the tube, which contained aluminium to remove the oxygen in the sample. Samples from different parts of the rods were used in analysis. Samples were always taken with the hood in position. Metal temperatures were determined using a platinum/platinum 13% rhodium thermocouple which was put through the sampling point in the roof of the hood.

(v) Analysis of Fume

The fume produced in the large scale equipment was black and characteristic of the Japanese O.G. process which also operates with a closed hood system.

Samples taken from the precipitator were examined by the X-ray powder diffraction technique. This showed that the fume contained predominantly wustite with traces of α -iron and also between 5 and 10% iron borate. The existence of boron was confirmed by spectrographic analysis and traced to the Basic A lining of the furnace. A sample of this was analysed and found to contain 0.89% boron.

At the conclusion of the project, a new boron-free lining had been chosen and was being put into practice. An analysis of O.G. fume from the Sakai plant in Japan gave 83.9% FeO and a total iron content of 68.2%.

(vi) Electron Microscope Examination of the Fume

A sample of the fume taken from the precipitator was examined using a Philips EM 300 electron microscope and some of the results are shown in Figure 29.

The majority of the fume is spherical with a maximum diameter of 0.5μ . Measurements from the Sakai O.G. plant in Japan gave a typical particle size of 0.2μ .

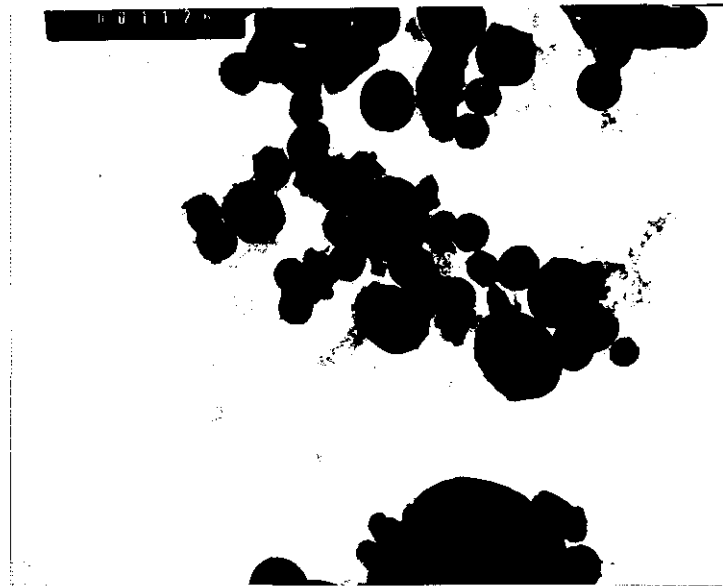
FIGURE 29

Electron Microscope Photographs of Fume produced

From the Large Scale Equipment

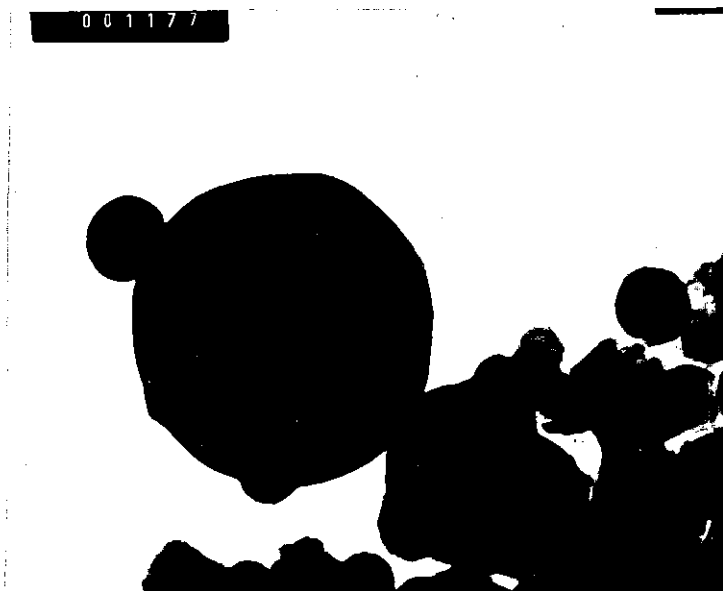
Magnifications

A.	x23,000
B.	x47,000
C.	x47,000
D.	x60,000



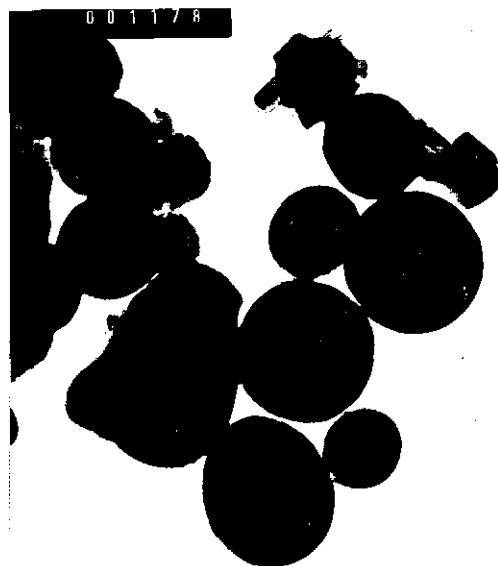
.43 μ

A



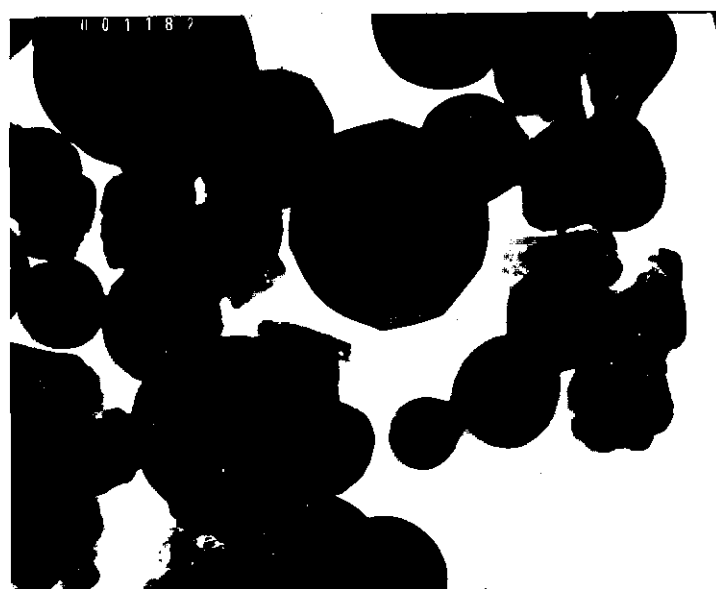
.21 μ

B



.21 μ

C



.17 μ

D

(vii) Project Conclusion

In July 1968, it was announced that the Central Research Laboratories of R.T.B were closing as part of the reorganization due to steel nationalisation.

In order that inconvenience should be reduced to a minimum, the project was immediately transferred to the Steel Company of Wales Division, Port Talbot, and the move made in August.

The moving of the High-frequency equipment presented considerable difficulties and necessitated a delay of several months. In view of this and the fact that the small scale equipment was then in working order, it was decided that the large scale work should be put in abeyance.

APPENDIX 2

Fume Suppression

(a) Introduction

It has been widely reported in the literature that various additions to the oxygen stream can suppress fume formation to a considerable degree e.g. 76. Bengstorff^{54,56} studied the effect on the 21b scale with both bottom blowing and top blowing and found that hydrogen, methane and steam had a noticeable effect on the quantity of fume produced. One explanation suggested^{31,33,79} was that the additions reduced the temperature of the "hot-spot" so reducing the quantity of iron evaporating.

Carbon dioxide has had a confusing effect in that reports of good suppression, when using it as an addition,^{1,51} have accompanied reports showing it to have no effect e.g. 54.

The fume suppression effects have been incorporated into a commercial process known as Fumeless Refining^{33,91,109}. Both oxygen/fuel oil and oxygen/town gas have been used with a substantial reduction in fume¹¹⁷ (figure 30) and only a slightly longer refining time. Miller⁸³ has given results showing typical fume loadings of 0.05 grains/s.c.f. over 200 blows. This is within the requirements set out by the Alkali Inspector¹¹⁰. The process has been put into production by B. S. C. Midland Group in Sheffield using oxygen/fuel-oil but has had little success in refining stainless steels. Excessive chromium loss into the slag was always experienced accompanied by a severe hydrogen pick-up and an inability to reach the desired specification of 0.06% carbon¹⁰⁸. The subject of fume suppression has been reviewed by Munro⁸⁶.

FIGURE 30

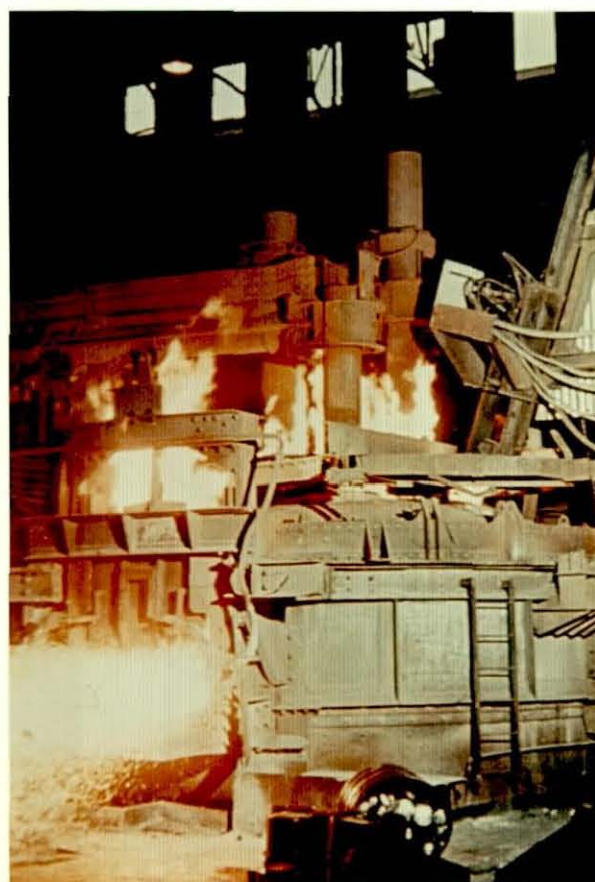
Photographs of Fume Suppression trials on a 30 - ton
Furnace at English Steel Corporation Ltd.

- A. Refining with an Oxygen Lance.
- B. Refining with an Oxy-Fuel Burner.

(by courtesy of Shell Mex and B.P Ltd)



A



B

(b) Explanation of Fume Suppression

Since the hot-spot theory is not accepted in this thesis, as of major importance in fume formation, the effect of various additions in suppressing fume cannot be explained in terms of their cooling effect on the impact area.

In a series of qualitative tests on the small scale equipment, carbon dioxide was passed over iron/carbon alloys at 1600°C . As in the case of oxygen, an oxide layer formed over the melt in each case and this was followed almost immediately by a vigorous boil accompanied by copious ejections thrown into the atmosphere above the bath. However, no droplet explosions took place and no fume formation occurred. The droplets were considerably lower in temperature due to the endothermic nature of the gas used.

TABLE 9
Heats of Reaction at 1600°C ¹¹⁹

REACTION	Heat evolved at 1600°C calories/mole
$\text{Fe (l)} + \frac{1}{2}\text{O}_2(\text{g}) = \text{FeO (l)}$	+59,000
$\underline{\text{C}} + \frac{1}{2}\text{O}_2(\text{g}) = \text{CO(g)}$	+33,000
$\underline{\text{C}} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	+99,500
$\text{Fe (l)} + \text{CO}_2(\text{g}) = \text{FeO} + \text{CO}$	- 7,500
$\underline{\text{C}} + \text{CO}_2(\text{g}) = 2 \text{CO(g)}$	-33,500
$\text{Fe(l)} + \text{H}_2\text{O(g)} = \text{FeO(l)} + \text{H}_2$	- 1,200
$\underline{\text{C}} + \text{H}_2\text{O(g)} = \text{CO(g)} + \text{H}_2(\text{g})$	-27,200

Thus the addition of, for example, fuel oil to the oxygen jet removes a key stage in the formation of fume, that of the supply of an exothermic atmosphere to the zone above the bath without which fume cannot be formed in appreciable quantities.

APPENDIX 3

Computer Programme for Output from Infra-Red Analyser

The aim of this programme was to integrate the infra-red analyser output as shown on the recorder, in order that events in the vicinity of the bath could be related to a bath composition. The analyser had three scales i.e. 0 - .01% CO₂, 0 - .1% CO₂ and 0 - 1% CO₂ and a calibration curve was obtained, using Wosthoff calibration pumps, of infra-red reading against gas composition.

The De La Rue Time-Sharing Computer Service was used and one of their standard programmes, POLFT~~3~~ *** was able to curve fit the calibration graph so that the maximum error on any calibration point was 0.14%.

The recorder print-out was divided into 15 second time intervals and the carbon losses indicated by the ordinate values were integrated using Simpson's Rule, which assumes that the points on the ends of the ordinates are joined by parabolic curves. This is sufficiently accurate for data which also depends on the accuracy of analysis of the starting material.

Nomenclature

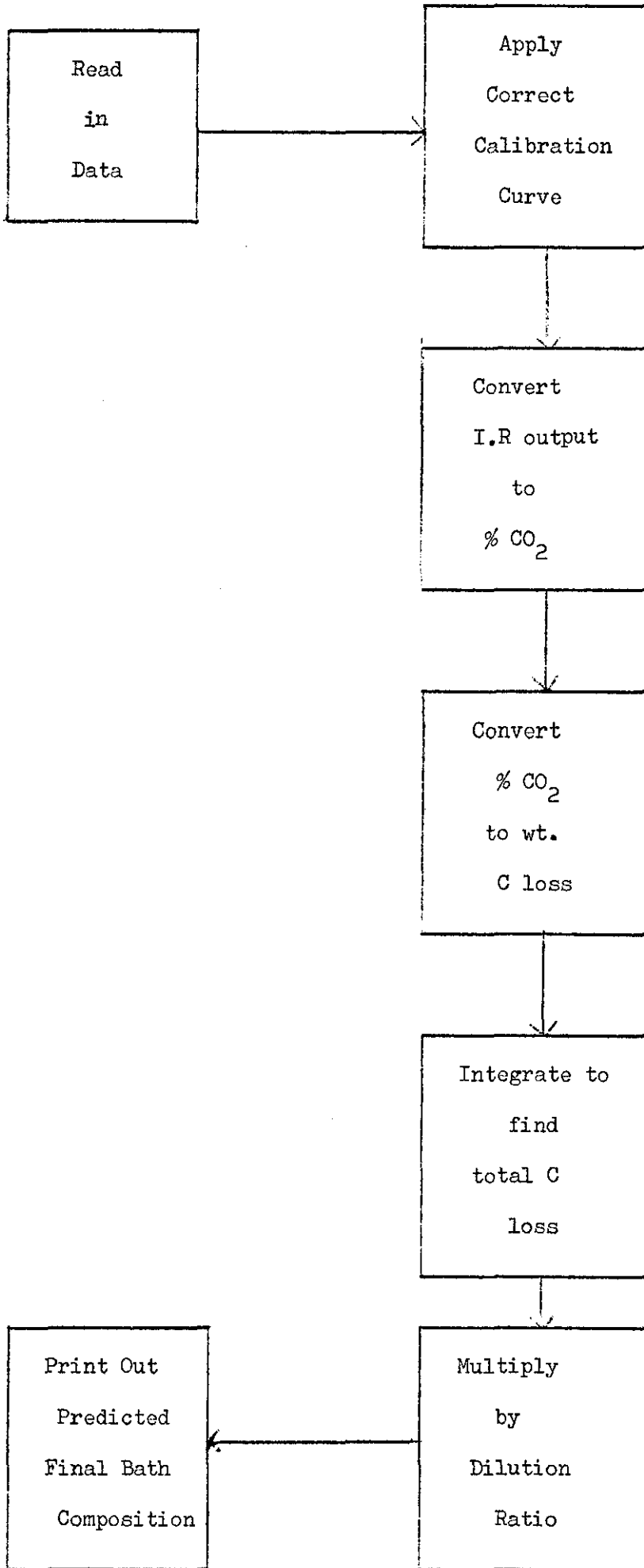
- Z = total number of sets of data
- B~~3~~ = specimen number
- H = interval between ordinates
- V = speed
- W = initial mass of sample
- Y₁ = initial carbon content
- E = dilution ratio
- N = total number of ordinates
- N₁ = total number of ordinates to date
- N₂ = number of ordinates for each calibration curve
- C = calibration curve i.e. 1,2 or 3

-143-

(1 represents 0 - .01%)

(2 represents 0 - .1%)

(3 represents 0 - 1.0%)



DECARB

```
10 READ Z
15 LET K=0
20 LET D=0
21 LET H=0
22 LET V=0
23 LET W=0
24 LET Y1=0
25 LET E=0
26 LET N=0
30 LET D=D+1
40 READ BS,H,V,W,Y1,E,N,
50 DIM X(3,201)
60 MAT X=ZER
90 LET G=0
95 LET G=1
105 READ N1,N2,C
110 LET P=0
120 LET Q=0
130 LET R=0
140 LET S=0
150 LET T=0
160 LET O=0
170 FOR P=G TO N1 STEP 1
180 READ X(1,P)
190 NEXT P
200 IF C=2 THEN 310
210 IF C=3 THEN 390
220 FOR Q=G TO N1 STEP 1
230 LET X(2,Q)=.49051207E-10-.17331038E-2*X(1,Q)+.42124818E-3*X(1,Q)+2
240 LET X(2,Q)=X(2,Q)-.39901208E-4*X(1,Q)+3+.20548211E-5*X(1,Q)+4
250 LET X(2,Q)=X(2,Q)-.64076376E-7*X(1,Q)+5+.12656669E-8*X(1,Q)+6
260 LET X(2,Q)=X(2,Q)-.15945110E-10*X(1,Q)+7+.12423375E-12*X(1,Q)+8
270 LET X(2,Q)=X(2,Q)-.54567221E-15*X(1,Q)+9
280 LET X(2,Q)=X(2,Q)+.10333303E-17*X(1,Q)+10
290 NEXT Q
300 GO TO 460
310 FOR Q=G TO N1 STEP 1
320 LET X(2,Q)=.50515014E-9-.17331040E-1*X(1,Q)+.42124821E-2*X(1,Q)+2
330 LET X(2,Q)=X(2,Q)-.39901211E-3*X(1,Q)+3+.20548213E-4*X(1,Q)+4
340 LET X(2,Q)=X(2,Q)-.64076381E-6*X(1,Q)+5+.12656670E-7*X(1,Q)+6
350 LET X(2,Q)=X(2,Q)-.15945111E-9*X(1,Q)+7+.12423376E-11*X(1,Q)+8
360 LET X(2,Q)=X(2,Q)-.54567225E-14*X(1,Q)+9+.10333303E-16*X(1,Q)+10
370 NEXT Q
380 GO TO 460
390 FOR Q=G TO N1 STEP 1
400 LET X(2,Q)=.54427431E-8-.17331040*X(1,Q)+.42124822E-1*X(1,Q)+2
410 LET X(2,Q)=X(2,Q)-.39901212E-2*X(1,Q)+3+.20548213E-3*X(1,Q)+4
420 LET X(2,Q)=X(2,Q)-.64076382E-5*X(1,Q)+5+.12656670E-6*X(1,Q)+6
430 LET X(2,Q)=X(2,Q)-.15945111E-8*X(1,Q)+7+.12423376E-10*X(1,Q)+8
440 LET X(2,Q)=X(2,Q)-.54567226E-13*X(1,Q)+9+.10333304E-15*X(1,Q)+10
```

DECARB CONTINUED

```
450 NEXT Q
460 FOR O=G TO N1 STEP 1
470 LET X(3,0)=(4*12*X(2,0))/(100*22.4)
480 NEXT O
485 IF N1=N THEN 520
500 LET G=G+N2
510 GO TO 105
520 LET F=0
530 LET L=0
540 LET F=X(3,1)
550 LET L=X(3,N)
560 LET S=F+L
570 FOR R=2 TO N-1 STEP 2
580 LET S=S+4*X(3,R)
590 NEXT R
600 FOR T=3 TO N-2 STEP 2
610 LET S=S+2*X(3,T)
620 NEXT T
630 LET A=(H/V)*S/3
640 LET A=A*E
650 LET M1=W*Y1/100
660 LET M2=M1-A
670 LET Y2=(M2*100)/(W-M1+M2)
680 PRINT TAB(15);"TEST NUMBER ";BS
690 PRINT
700 PRINT "INITIAL MASS OF SAMPLE = ";W; " G"
710 PRINT
720 PRINT "INITIAL CARBON CONTENT = ";Y1;" PCT"
730 PRINT
740 PRINT "FINAL CARBON CONTENT = ";Y2;" PCT"
750 PRINT
760 PRINT
770 PRINT
780 IF D<Z THEN 30
9999END
```

Format of Computer Print Out

DECARB 15:41 MANCHR 27/03/69

TEST NUMBER SS106

INITIAL MASS OF SAMPLE = 13.4285 G

INITIAL CARBON CONTENT = 4.6 PCT

FINAL CARBON CONTENT = 3.37219 PCT

DECARB 15:43 MANCHR 27/03/69

TEST NUMBER SS107

INITIAL MASS OF SAMPLE = 13.3625 G

INITIAL CARBON CONTENT = 4.6 PCT

FINAL CARBON CONTENT = 2.15911 PCT

DECARB 10:07 MANCHR 28/03/69

TEST NUMBER SS110

INITIAL MASS OF SAMPLE = 13.5778 G

INITIAL CARBON CONTENT = 4.6 PCT

FINAL CARBON CONTENT = 8.87001E-02 PCT

DECARB 10:09 MANCHR 28/03/69

TEST NUMBER SS113

INITIAL MASS OF SAMPLE = 13.2806 G

INITIAL CARBON CONTENT = 4.6 PCT

FINAL CARBON CONTENT = 4.51862 PCT

APPENDIX 4

Nucleation of Carbon Monoxide Bubbles From

Within a Steel Melt (refs 23-25)

The mechanism of carbon monoxide bubble nucleation has received considerable attention in recent years and has been widely publicised ^{22,82} .

The nucleation of a bubble from within a homogeneous liquid is very difficult since in addition to atmospheric and ferrostatic pressure, a gas bubble is under an excess pressure given by:-

$$p = \frac{2\gamma}{r} \quad (\text{ref 23})$$

Where γ is the surface tension, approx. 1500 dynes/cm at 1600°C.

r is the bubble radius ,

Thus a bubble of 1 μ diameter is subject to an excess pressure of 61 atmospheres and clearly bubbles containing a few molecules of carbon monoxide will be subject to pressures which can never be exceeded by the supersaturation of molten iron with respect to carbon and oxygen because both have limited solubilities. The classical experiments of Korber and Oelsen ¹⁹ who when using glazed crucibles, were able to hold molten steel with supersaturations approaching 10 atmospheres of carbon monoxide, verify that homogeneous nucleation is most unlikely.

The most widely accepted mechanism has been that carbon diffuses to crevices in the refractory material where it reacts either with trapped air or with oxygen that has also diffused from the bulk metal. The pocket of gas grows outwards from the crevice until it detaches itself and while rising to the surface, it grows due to reaction at its surface.

In this study of fume formation, nucleation of carbon monoxide appears to occur at two different stages - in the melt and within the ejected droplets.

While a detailed examination of the droplets in the vapour space is difficult to achieve, it is certain both from the present investigations and from observations of Distin⁸⁴ that for the bath to boil, there must be an oxide layer (either complete or partial) on the metal surface. The mechanism by which this oxide layer promotes nucleation has been discussed in detail by Distin. If a portion of the oxide is swept beneath the surface by a circulating eddy, large equilibrium CO saturations could be attained but it seems more likely that nucleation takes place heterogeneously in crevices on the oxide particles. Once nucleation has taken place, the boil is so violent that gas could well be trapped under the surface and promote a chain of reactions as the boil becomes more intense. Meyer^{88,90} has reported on an investigation into the slag-metal emulsion region above the bath. An examination of metal ejections in this region revealed internal cavities and surface blowholes due to gas evolution and a microprobe analysis showed the presence of iron oxide within the droplet.

For interpretation of his bursting drop experiments, Baker⁴ considered that homogeneous nucleation had taken place due to an oxidised surface being swept beneath the surface. He considered that a supersaturation of 50 atmospheres of CO could be obtained which is similar to the figure obtained by Baker et al⁵ of 55 atmospheres.

APPENDIX 5

Fume Formation in Bottom Blowing

Any theory proposed to explain the mechanism of fume formation in oxygen steelmaking must take into account the remarkable difference between top and bottom-blowing. The difference is shown in Figure 31 and it can be seen that with top-blowing the highest fume production rates are associated with the highest carbon levels, and a reduction in the bath carbon content results in a corresponding decrease in fume, whereas with bottom-blowing the majority of fume occurs at the end of the heat at low carbon levels.

An explanation of this effect is as follows:-

When oxygen is bottom-blown at high carbon levels, a rising oxygen bubble removes carbon at the bubble wall and the reduced oxygen partial pressure within the bubble indicates that an oxide film at the bubble interface is unlikely. As the carbon level drops, an oxide film will be produced at an earlier stage in the passage of the bubble, i.e. at a higher oxygen partial pressure. This will cause droplets to be ejected into the bubble where they may explode to a degree depending on the exothermic nature of the gas within the rising bubble. Thus the substantial quantities of fume will be produced at the lowest carbon levels where an oxide film is quickly formed and where surface decarburization only takes place to a very small degree.

Clearly the above picture is much simplified from that which occurs in practice. The concept of discrete bubbles originating from a submerged orifice is not probable ¹ and a more likely system is one of metal drops, streamers, and globules suspended within a gas stream.

TYPICAL EFFECTS OF CARBON CONTENT OF IRON
BATH ON SMOKE EVOLUTION IN BOTH TOP AND
BOTTOM BLOWING

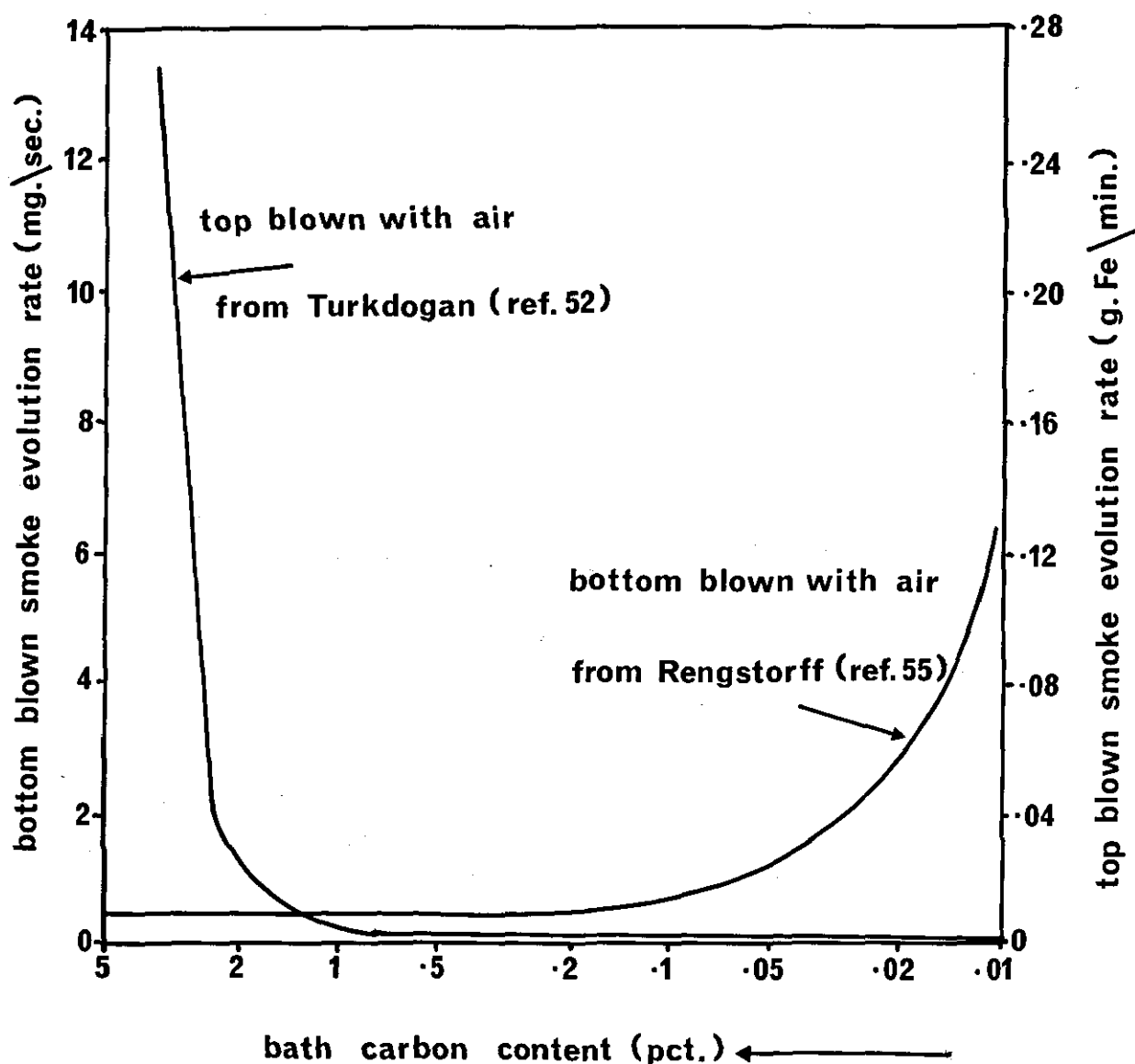


FIGURE 31

APPENDIX 6

Heat Losses From Molten Iron at 1600°C

Radiation

$$\text{Heat loss } Q = e\sigma (T_1^4 - T_2^4)$$

where e is the emissivity (assumed = 0.4)

σ is the Stefan - Boltzmann constant

$$= 1.01 \times 10^{-8} \text{ lb-cal/hr-ft}^2 \text{ } ^\circ\text{K}^4$$

T_1 is the molten iron temperature = 1600°C

T_2 is the ambient temperature = 15°C

Inserting Values

$$\begin{aligned} Q &= \underline{49692 \text{ lb-cals/hr - ft}^2} \\ &= \underline{6.74 \text{ g. cal/sec - cm}^2} \end{aligned}$$

Convection (Ref 111)

$$\text{Heat loss } Q = hA (T_1 - T_2)$$

where h is the heat transfer coefficient

For Streamline Flow:-

$$h = 0.31 \left(\frac{\Delta T}{l} \right)^{\frac{1}{4}}$$

where l is the length of convection path = $1\frac{1}{2}$ inches

Inserting Values

$$\begin{aligned} Q &= \underline{5228 \text{ lb - cal/hr - ft}^2} \\ &= \underline{0.71 \text{ g. cal/sec - cm}^2} \end{aligned}$$

Thus % heat loss due to convection

$$= \frac{5228}{54920} \times 100$$

$$= \underline{9.5\%}$$

APPENDIX 7

Computer Programme For Heat Balance on

Ejected Droplets

Nomenclature

C1 = initial carbon content
P1 = partial pressure of oxygen
T1 = time
T2 = droplet temperature
T3 = time for oxide formation
T4 = temperature rise in droplet
Q1 = heat loss by radiation
Q2 = heat gained by chemical reaction.
D = droplet diameter
J = flux of oxygen/unit area
A = droplet area
V = droplet volume.

1 PRINT " TEMPERATURE EFFECTS ON MOLTEN EJECTIONS"

2 PRINT

3 PRINT

10 LET C1 = 4.5

15 LET P1 = 0.1

20 LET T2 = 1873

25 LET D=.0001

30 LET T1= 0

35 LET A = 3.14*D*2

40 LET V = (3.14/6) *D* 3

50 LET J = (18.3*P1)/(82.05*T2)

60 LET T3 = (V*7.16*(C1-0.35))/(2*J*A*100*12)

70 LET Q1 = 0.5*A*1.36E-12*(T2*4-373*4)

```
80 LET Q2 = J*A*33000
90 LET Q = Q2-Q1
100 LET T4 = (Q*.001) / (V*7.16*0.144)
110 PRINT P1,T2,T1,D
120 LET T1 = T1+.001
122 IF T1 .01 THEN 150
125 LET T2=T2+T4
127 IF T2 1800 THEN 150
130 IF T1 T3 THEN 50
133 PRINT
140 PRINT "OXIDE FORMATION OCCURRED"
150 PRINT
160 PRINT " TIME FOR OXIDE FORMATION = ";T3;" SECS"
170 PRINT
180 LET D = 10*D
190 LET T2=1873
200 IF D .1 THEN 30
205 LET P1=P1+0.1
207 IF P1 1.05 THEN 25
210 END
```

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