

FACTORS WHICH INFLUENCE THE CONSTITUTION

OF IRON ORE SINTERS

T H E S I S

submitted to the  
UNIVERSITY OF GLASGOW  
for the Degree of  
DOCTOR OF PHILOSOPHY

by

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JUNE 1946

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## CHAPTER I

### Introduction.

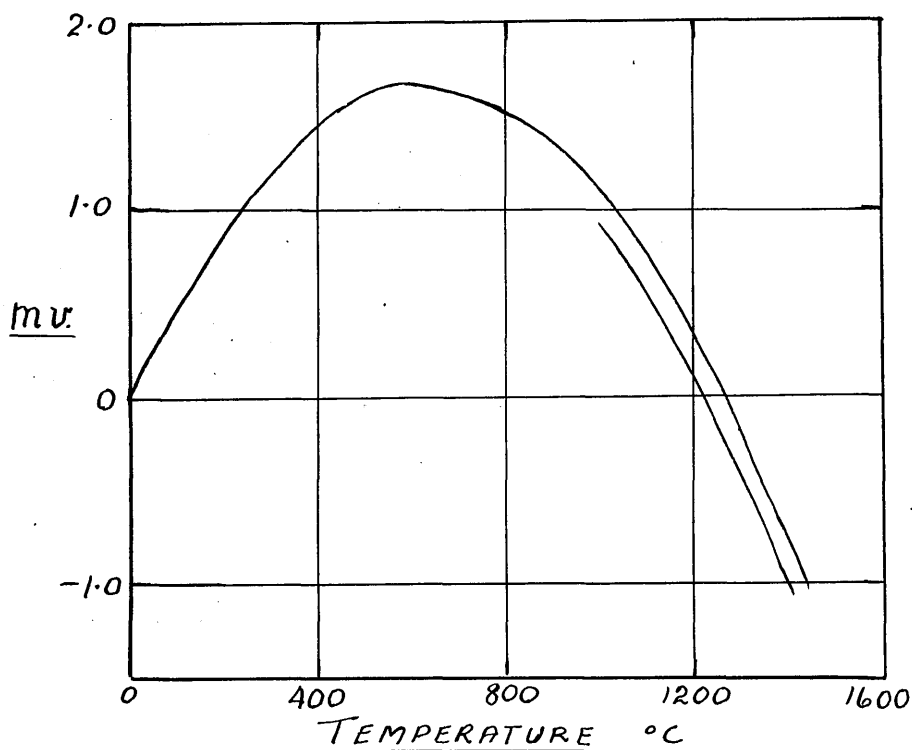
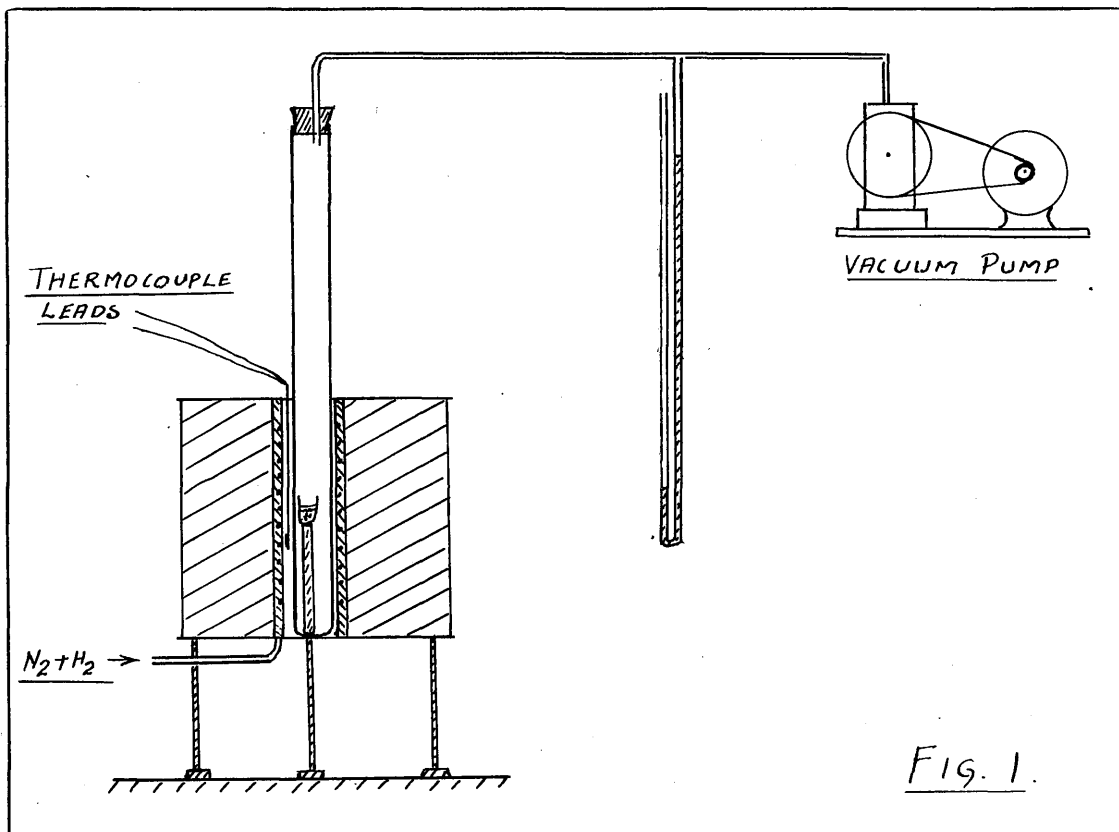
Sintering or agglomerating of iron ore was developed as a method of utilising fines in the blast furnace. It was obvious that fines could not be charged direct or they would impede the smooth flow of gases up the furnace resulting in channeling and slipping with consequent difficulty of control and the production of inferior iron. On the other hand if fines were allowed to go to waste the loss would be considerable especially as operators were beginning to realise the importance of crushing the charge to below a certain maximum size thus producing more fines. The first sintering machines developed were designed merely to agglomerate the fines into lumps of sufficient strength to withstand the superincumbent charge in the furnace. No thought was given to the actual reducibility of the sinter although the process attempted to produce a porous product with the object of exposing as large a surface as possible to the reducing gases. Thus for many years the only properties required of a sinter were strength and macro-porosity.

It is now a well known fact that iron ore sinters show a very much poorer rate of reducibility than iron ores, and from tests carried out on fourteen British sinters and several ores it can be stated that a dense ore with poor reducibility is more quickly reduced than a good industrial

sinter. The general result of this is that it is not generally found advantageous to use more than 30 to 40 per cent sinter in the furnace burden probably due to the different rates of reducibility giving rise to varying conditions in the shaft. The use of this percentage of sinter has its advantages such as keeping the burden open and utilising fines and flue dust. A good hard porous sinter can provide voids for gas flow and so give better gas distribution and more uniform pressure drop up the shaft with consequent smoother running and higher efficiency. According to Neustaetter's results<sup>(1)</sup> more coke is required to provide voids for the blast than that which is required for either the production of heat or reducing purposes. The use of a percentage of sinter eliminates this waste of coke. Elliot<sup>(2)</sup> found that coke consumption decreased with increase of sinter in the charge to about 34 to 39 per cent above which it again increased. Williams and Stubblefield<sup>(3)</sup> state that the general opinion of furnace operators in America is that the benefits of sinter begin to make themselves manifest with about 10 to 20 per cent sinter in the burden and continue to about 35 to 45 per cent. These figures are based on a high blowing rate. This seems to indicate that above about 35 per cent the poor reducibility of the sinter begins to outweigh the other advantages. It must not be forgotten however that blast furnaces have been run successfully on 85 to 100 per cent sinter provided the rate of blowing and other conditions are adjusted to suit the different requirements of an all sinter burden. The

strength of the sinter is also important, since if it crumbles much of the voidage will be lost with consequent detrimental results to gas distribution. Assuming that the function of coke and sinter in keeping the burden open is similar, an indication of the effect of a sinter which crumbles can be obtained from Neustaetter's results<sup>(1)</sup> which show that when a coke of stability index 43.6 per cent and average size 2.15 inches was replaced by a coke of stability index 47.9 per cent and average size 2.36 inches the volume of blast fell by 2000 c. ft. per minute due to the poorer strength in spite of the larger original size.

It can thus be seen that the advantages of sinter as it is made at present lie not in providing a good starting material for the production of iron but only in converting the fines to a form which can be suitably used in the blast furnace. With the ever increasing need for efficient and economic production the problem of producing a sinter which will be as reducible as a natural ore while retaining a sinter's property of strength for promoting good gas distribution becomes more and more acute. With this object in view the following work was undertaken to study the mechanism of formation, the micro and macrostructure, composition and reducibility of various classes of sinters.



## CHAPTER II

### Preliminary Work.

In order to understand sinters and sintering fully it was considered that the first necessity was an understanding of the mechanism of sintering. With this in view some preliminary tests were carried out. The usual method of sintering by mixing the ore coke and water and then igniting and sucking air through the mixture, was considered unsatisfactory for this work as the number of variables involved would make it very difficult to make a thorough examination of the results. Accordingly an attempt was made to produce sinter by mixing pure  $\text{Fe}_2\text{O}_3$  with carbon and heating in vacuum to a predetermined temperature. All heat was supplied externally, the carbon merely serving as a reducing agent for the  $\text{Fe}_2\text{O}_3$ . The apparatus used is shown in fig. 1. Heat was supplied by a molybdenum wound resistance furnace. A Salamander crucible containing the charge rested on alundum stools inside a Morganite tube which could be evacuated to a pressure of 0.0003 mm. mercury by a Hyvac pump. The temperature was measured by a tungsten molybdenum thermocouple situated outside the Morganite tube. This simplified the experimental work considerably as the thermocouple once placed in position did not have to be moved except for occasional repairs. The calibration was done and checked at regular intervals against a known platinum-platinum-rhodium thermocouple with its junction inside the Salamander crucible, so that



although the junction of the tungsten molybdenum 'couple was always higher than the crucible, the temperature of the charge could be measured accurately by it. Fig. 2 shows the true calibration curve along with a shorter curve which indicates the temperature inside the crucible over the working range.

The  $\text{Fe}_2\text{O}_3$  used was prepared by heating ferrous oxalate in air at about  $200^\circ\text{C}$  till it decomposed to black ferrous oxide and subsequently oxidised to brick red  $\text{Fe}_2\text{O}_3$  which was heated to  $1100^\circ\text{C}$ . for one hour in a stream of oxygen. It was then cooled in oxygen after which treatment the colour had deepened till it was almost black. This  $\text{Fe}_2\text{O}_3$  was now mixed with 5 per cent carbon and heated to  $1200^\circ\text{C}$ . for 60 minutes. On cooling the furnace and removing the charge a fairly dense sinter was found to have been produced. Several other sinters were now made in a similar manner using 2, 3, and 4 per cent carbon and various temperatures from  $1050^\circ\text{C}$ . to  $1300^\circ\text{C}$ . It was found that the charge did not sinter satisfactorily below  $1150^\circ\text{C}$ . An examination of the microstructure of these sinters proved unsatisfactory. No regular variation, as the carbon content increased, could be found and it was suspected that the Salamander crucible probably played a considerable part in the reduction. Accordingly for further work it was replaced by a platinum crucible. These first experiments however succeeded in their aim which was to investigate the possibility of sintering iron oxides below their melting point without any slag bond.

Fig. 3.

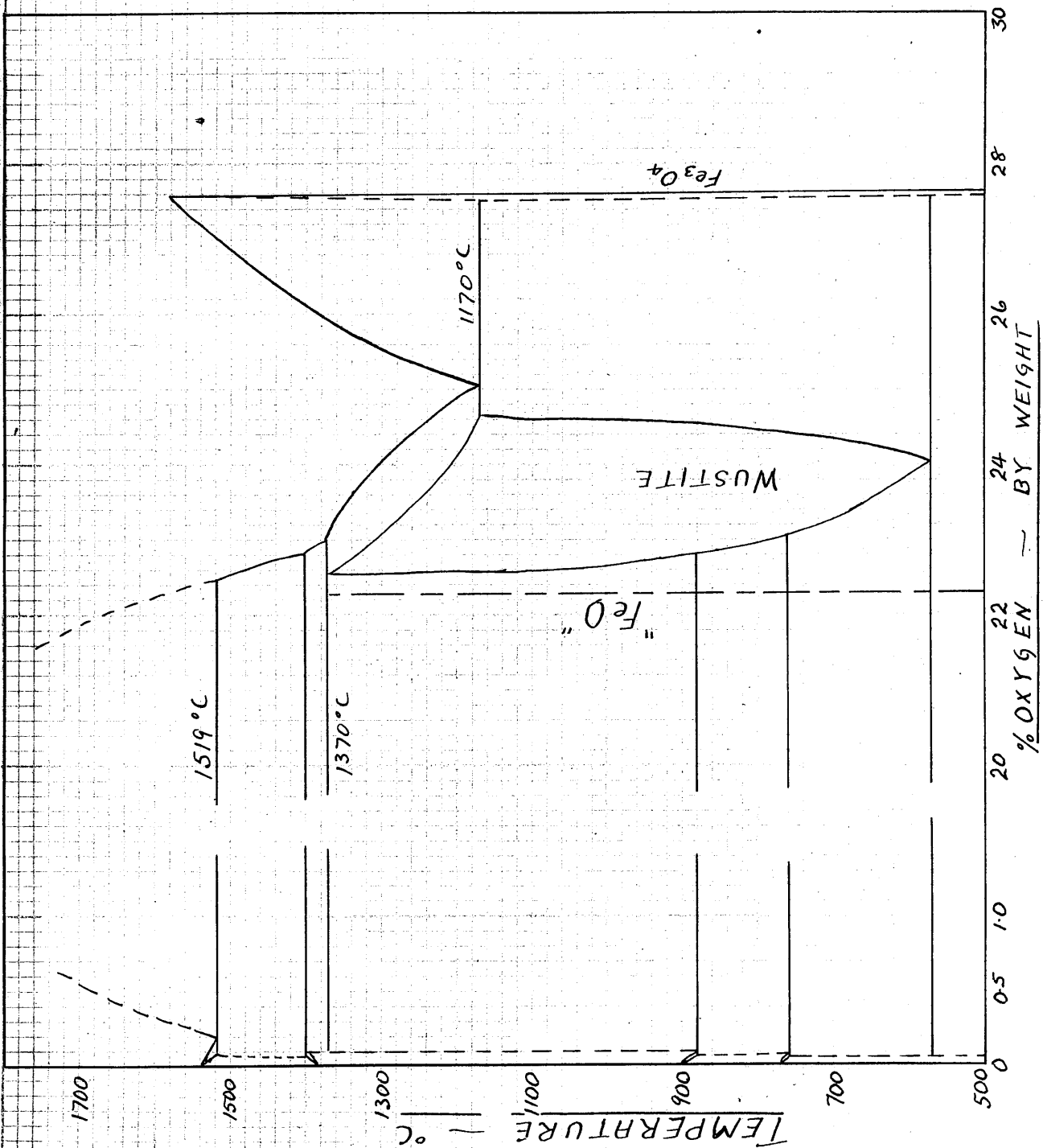
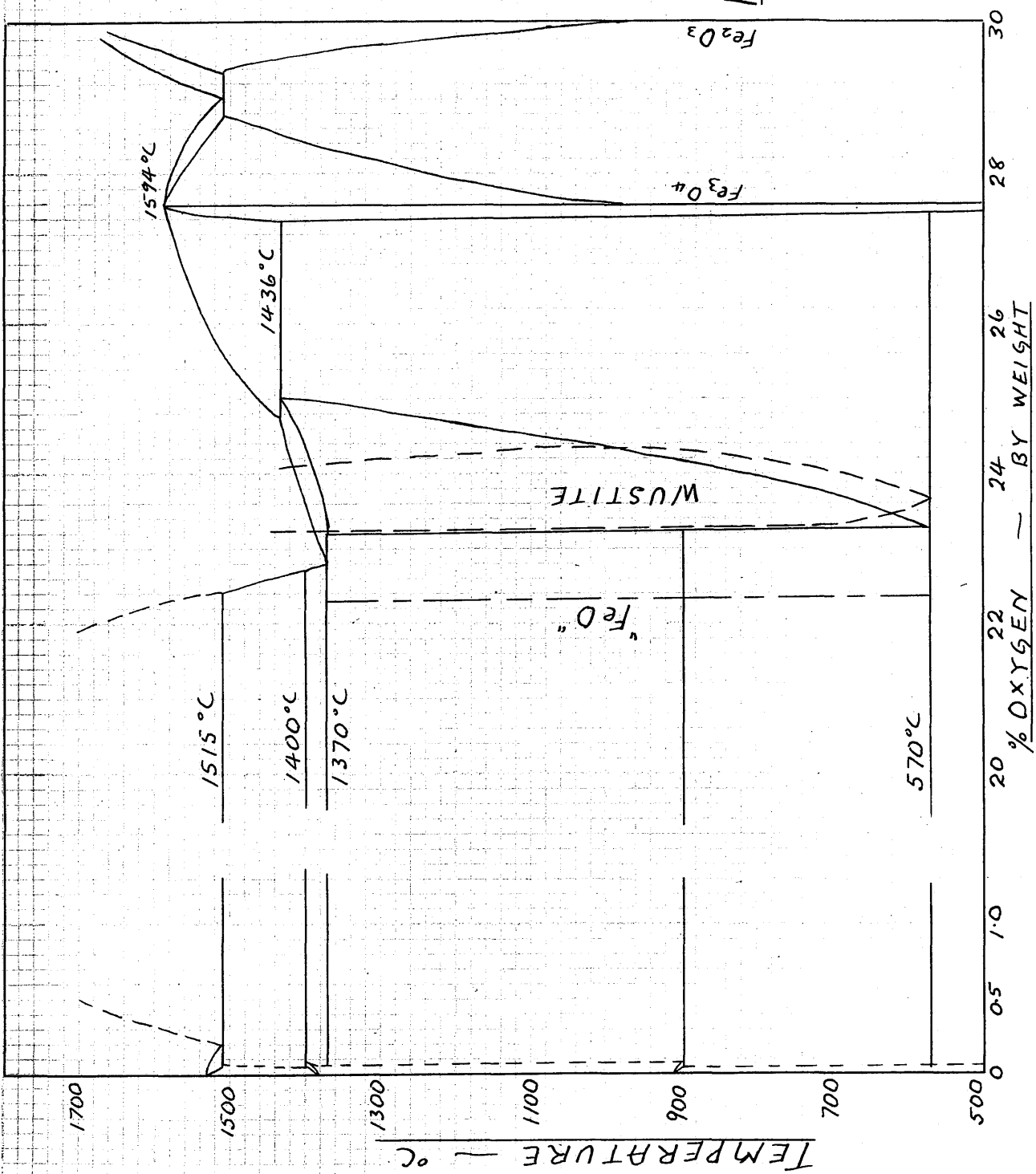


FIG. 4.



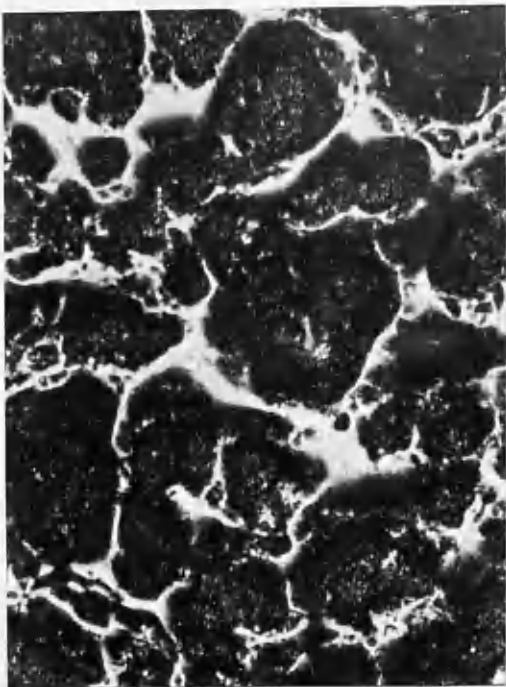
### CHAPTER III

#### Investigation of the Iron Oxygen Diagram and the Mechanism of Sintering Iron Oxides.

There are two main types of iron-oxygen diagrams published in current literature. Figure 3 was compiled by Matthewson Spire and Milligan<sup>(4)</sup> showing an eutectic at  $1150^{\circ}\text{C}$ . between wüstite and  $\text{Fe}_3\text{O}_4$ . A similar diagram by Benedicts and Lofquist<sup>(5)</sup> shows an eutectic at  $1200^{\circ}\text{C}$ . Figure 4 has been compiled from the work of Tritton and Hanson<sup>(6)</sup>, Jette and Foote<sup>(7)</sup>, Pfeil<sup>(8)</sup>, White Graham and Hay<sup>(9)</sup>, and White<sup>(10)</sup>. Both Jette and Foote's X ray results and Pfeil's thermal results for the wüstite range are shown, the former being dotted.

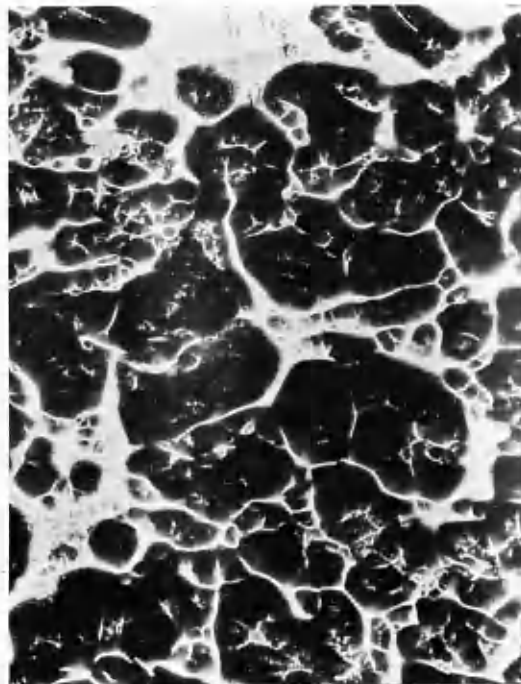
In a paper by Professor Hay and the author<sup>(11)</sup>, a micro photograph was shown which could be interpreted as showing the eutectic between wüstite and magnetite. It was further stated however that from examination of many sections the authors were inclined to take the view that no such eutectic existed, but that the structure shown was produced by crystallisation of magnetite from a supersaturated solution of ferrous oxide.

In order to determine which type of diagram was correct mixtures were made consisting of 64 per cent "FeO" and 36 per cent  $\text{Fe}_2\text{O}_3$ , which is the composition of the eutectic in figure 3. These mixtures contained in a platinum crucible were heated in vacuum to various temperatures above  $1170^{\circ}\text{C}$ . with the intention of obtaining a microsection of



MICRO 1

x 1000



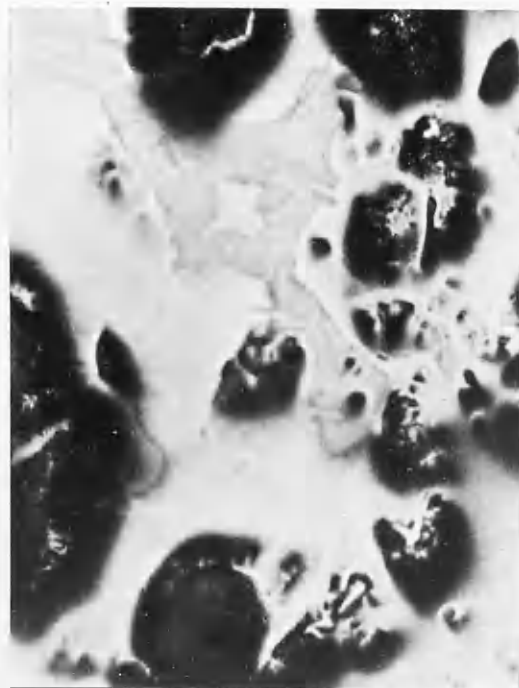
MICRO 2

x 1000



MICRO 3

x 1000



MICRO 4

x 1000

THE FORMATION OF SINTER.

the eutectic if it existed. In no case was melting obtained although temperatures as high as 1350°C. were used. Actually sinters were produced the microstructure of which showed the direct formation of crystalline material without any melting. Table I shows some of the data for these sinters.

TABLE I

Specimen No	Treatment	Remarks	Micro-structure
21	1200°C. for 20 mins.	Shrinkage 5% linear Soft	See Micro 1
22	1250°C. for 20 mins.	Shrinkage 15% linear Strength similar to Northants Ore.	See Micro 2
23	1300°C. for 20 mins.	Shrinkage 25% linear Strength good	See Micro 3
24	1350°C. for 20 mins.	Shrinkage 40% linear Very hard and strong	Wüstite and Magnetite See Micro 4
24a	1350°C. for 20 mins. Annealed at 1050°C for 4 hours in vac.	- do -	Wüstite and Magnetite.
24b	1350°C. for 20 mins. Annealed at 1000°C. for 1 hour in 1 cm. air pressure.	- do -	Magnetite and Fe <sub>2</sub> O <sub>3</sub> on surface of specimen.

Micro 1 which depicts a typical field from specimen 21, shows the formation of a crystalline phase among much unaltered powder which was just fritted together. Micros 2, 3 and 4 from specimens 22, 23 and 24 respectively show

the progressive formation of crystalline material. A thin section of specimen 24 was made and examined under transmitted light. No additional information was obtained however as the specimen was opaque under all conditions. It was not possible at this time to identify with certainty the crystalline phases but subsequent work described in Chapter IV made it possible to identify magnetite and oxygen-rich wüstite. Two more sinters were made in a similar manner from mixtures of 31 per cent "FeO" and 69 per cent  $\text{Fe}_2\text{O}_3$  which corresponds to magnetite composition. As was expected higher temperatures were required to sinter. Specimen 25 heated to  $1400^\circ\text{C}$ . for 30 minutes showed a microstructure similar to micro 1 while specimen 26 heated to  $1420^\circ\text{C}$ . for 60 minutes was similar to micro 2. The crystalline phase however was proved by subsequent work to be magnetite. Specimen 26 was given further treatment by heating to  $1000^\circ\text{C}$ . for 1 hour in 2 cm. pressure of air. Since the dissoceation pressure of  $\text{Fe}_2\text{O}_3$  at this temperature is negligible<sup>(12)</sup>, it was considered that this treatment would oxidise the magnetite to  $\text{Fe}_2\text{O}_3$  and so find out its appearance under the microscope. On polishing and examining the surface a phase lighter than magnetite was observed. On grinding thin layers off the surface and polishing and examining between each, the light phase was observed to decrease till only magnetite remained. It was thus concluded that the light phase was probably  $\text{Fe}_2\text{O}_3$ .

From a study of these and other specimens of "eutectic"

and magnetite composition it has been concluded that there is no eutectic between wüstite and  $\text{Fe}_2\text{O}_3$  and consequently figure 4 is probably the correct form of the diagram. Subsequent work on the microstructure of sinters described in Chapter IV also points to the same conclusion. It has also been concluded that the ideal formation of sinter occurs by diffusion and crystallisation in the solid state. Crystallisation probably starts from areas of maximum contact between particles, that is areas of greatest local pressure or finest state of division. It seems probable that when a certain temperature is reached the outer layers of ions in two neighbouring particles of iron oxide attain a sufficient degree of mobility to permit slight atomic rearrangement resulting in the welding together of the two particles into an imperfect crystal. This will provide nuclei for crystallisation waves which in a similar manner will spread throughout the mixture preferentially along the paths of most intimate contact. The assumption that ions rather than atoms are responsible for the link up has been made after consideration of the crystal structures. The structure of the crystals " $\text{FeO}$ " and  $\text{Fe}_3\text{O}_4$  consists of a regular arrangement of iron and oxygen ions surrounded by the electrons which hold the crystal together. No one of these electrons can be said to be attached to a particular ion. They will diffuse back and forwards throughout the crystal changing their influence from ion to ion, but always distributed so that the stability of the crystal is unaffected. Indeed, they may be regarded as



spheres or waves of influence holding the crystal together. The ions inside the crystal will thus be held in position by ionic forces all round, but those on the surface will be held only on one side, so that instead of even forces all round, there will be a concentration of forces at one side. When two such crystals are brought together they will touch at a number of points. At such points it seems probable that there will be a tendency for the electronic forces instead of concentrating on one side of the surface ion to spread round it and join with the electronic forces on the surface of the other crystal. It thus seems that with increasing temperature a state will be reached when the electrons will have attained sufficient energy to effect the above link. This will result in several weak points of attachment where the crystals have come into contact with each other, leaving spaces in between. The spaces will be gradually closed as the pull of the electrons causes iron and oxygen ions which are still in a position where the electronic forces act mostly on one side, to jump into a new position where the forces will more nearly act on all sides. This will continue till the crystals are welded together. The ions have been said to jump from one position to another as it is considered that when the forces become strong enough to pull an ion from its position it will swing rapidly into its new and more stable position. Micro 1 shows this process at an early stage while micro 4 shows it almost having reached completion, the dark areas being mainly holes. Such a process of crystallisation

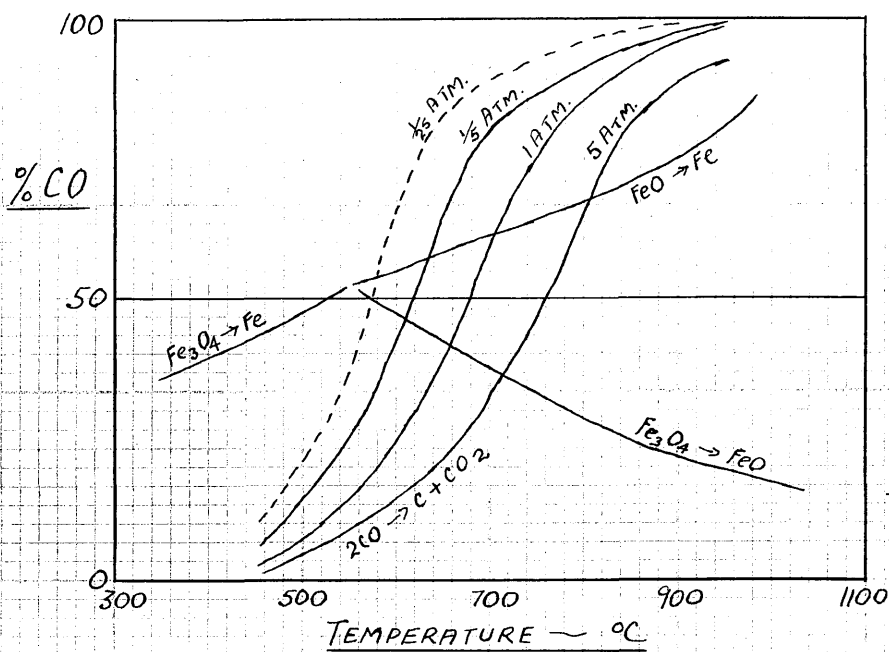


FIG. 5.

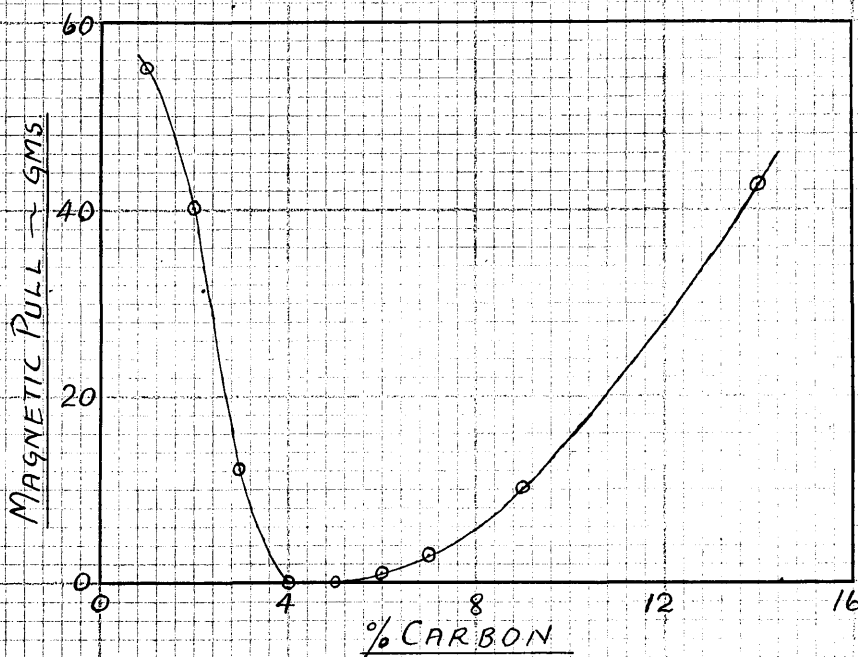
AFTER EASTMAN<sup>23</sup>

FIG. 6.

while being quite possible in a homogeneous powder will be speeded up by the presence of a chemical reaction. In the above sinters this was provided by the  $\text{Fe}_2\text{O}_3$  and the "FeO" reacting to give  $\text{Fe}_3\text{O}_4$ . In the case of subsequent sinters made from pure  $\text{Fe}_2\text{O}_3$  and carbon, the reducing action of the carbon will provide the reaction. It is not suggested that this is the main mechanism of bonding in industrial sinters as they are made at present. On the contrary macro examination of almost all the industrial sinters shows melting to have taken place.

The "FeO" used in making the above sinters was prepared in the following manner. Ferrous oxalate was heated in vacuum to  $1000^\circ\text{C}$ ., held at this temperature for 1 hour, cooled slowly to  $600^\circ\text{C}$ . and then as rapidly as possible to room temperature. The reaction taking place is  $\text{Fe}(\text{COO})_2 \rightarrow \text{FeO} + \text{CO} + \text{CO}_2$ . It can thus be seen that the  $\text{CO}:\text{CO}_2$  ratio is unity. Heating was carried out as rapidly as possible to above  $650^\circ\text{C}$ . above which temperature it can be observed from figure 5, "FeO" is the stable phase and a  $\text{CO}:\text{CO}_2$  ratio of unity is also stable. Below  $530^\circ\text{C}$ . "FeO" would tend to be reduced and below about  $575^\circ\text{C}$ . the CO would tend to give carbon deposition. Both these reactions were reduced to negligible proportions by the rapid heating and by the low gas pressure maintained by the vacuum pump even when the gas evolution was at its maximum. The "FeO" produced was found to be non-magnetic and analysed to 77.6 per cent iron. The dotted curve for the  $\text{CO}:\text{CO}_2$  equilibrium at  $1/25$ th atmosphere has been estimated from the known curves.

## CHAPTER IV

### The Microstructure of Iron Oxide Sinters

Having established the type of bond formation in pure iron oxide sinters it was then decided to investigate crystal structures obtainable in sinters on various degrees of deoxidation. Accordingly sinters were prepared from pure  $\text{Fe}_2\text{O}_3$  and varying proportions of carbon. Table II shows some of the mixtures employed, the temperature at which they were sintered and the time of sintering. As before, the sintering was carried out in a platinum crucible in vacuum, and the sinter was slowly cooled in vacuum. The chemical analysis of the sinter is given and from this the phases expected to be present were calculated. It will be seen that these agree well with the phases actually found by microscopic examination.

The magnetic pull of a standard magnet on the sinter was devised as a method of assessment of the degree of reduction of the iron oxide in the sinter. It was measured in the following manner. The pan of the balance was replaced by a platinum crucible containing 10 grams of finely ground sinter and the balance adjusted to equilibrium. A magnet was then fixed to the balance so that the bottom of the crucible just rested on the north pole. A relative figure for the magnetic pull on the sinter could then be obtained by finding the weight required just to pull the crucible off the magnet. Figure 6 shows the results in

TABLE II

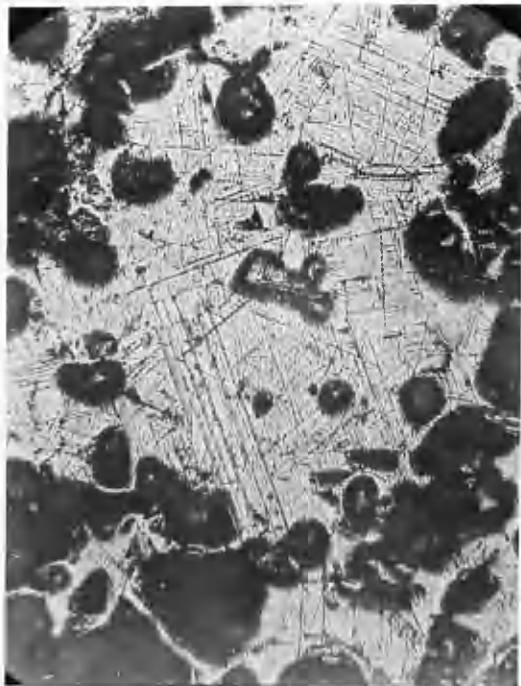
Sinter No.	%C	Temp °C	Time Mins	Analysis			Phases Calculated				Mag. Pull gms.	Micro Section
				Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	Wüstite	Fe		
40	1	1300	120	72.85	27.15	-	6.7	93.3	-		55	Magnetite with a few short thick lines at grain boundaries
27 39	2	1320 1300	60 120	64.4	35.6	-	-	80.3	19.7 *		40.5	Magnetite with a few crystals of wüstite showing a "martensitic" appearance.
28 38	3	1320 1300	60 120	39.7	60.3	-	-	34.7	65.3 *		12.7	Some magnetite, but mostly wüstite showing a "martensitic" appearance.
29 37	4	1320 1300	60 120	26.5	73.5	-	-	0.3	99.7 *		0	All wüstite showing a "martensitic" appearance.
30 41	5	1320 1300	60 120	11	89	-	-	-	99.75 $\phi$	0.25	0	Glossy wüstite crystals with a very little iron-wüstite eutectic at boundaries.
31 42	6	1320 1300	60 120	6	94	-	-	-	97.8 $\phi$	2.2	1.1	A few globules of iron in and around crystals of wüstite which show recrystallisation to be taking place.
32 43	7	1320 1300	60 120	0.5	99.5	-	-	-	96 $\phi$	4.0	3.0	Similar to above but more iron.
44	9	1300	120	-	82.5	17.5	-	-	79.4 $\phi$	20.6	10.0	Similar to above but more iron and some lines along the crystal planes of the wüstite.
45	14	1300	120	-	65.7	34.3	-	-	63.4 $\phi$	36.6	42.6	Much iron among wüstite which shows signs of iron tending to precipitate from it.

\* Containing 24.29% Oxygen

 $\phi$  Containing 23.21% Oxygen



MICRO 5                      x 200  
MAGNETITE AND WÜSTITE



MICRO 6                      x 200  
WÜSTITE (OXYGEN RICH)



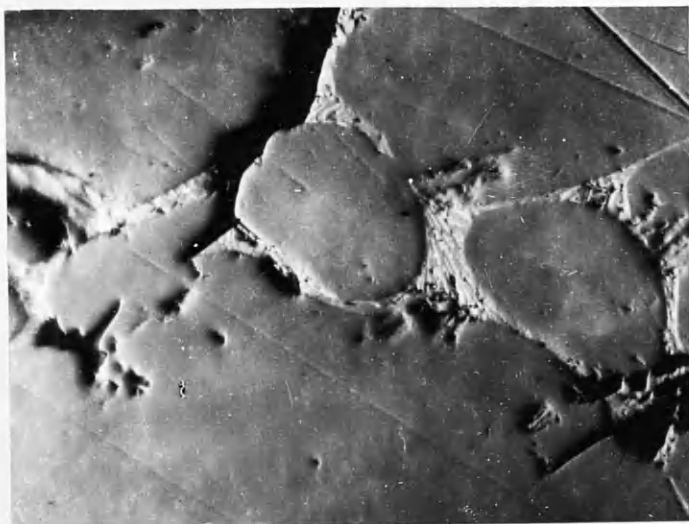
MICRO 7                      x 200  
WÜSTITE (IRON RICH)

graph form. The object of this test was to obtain a check on the relative amounts of magnetite and wüstite present and so provide a definite check on the interpretation of the microsections and chemical analysis which is given as  $\text{Fe}_2\text{O}_3$ , "FeO", and Fe. Since "FeO" does not exist as such these results were recalculated to  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , wüstite, Fe basis. For this purpose the iron-oxygen diagram shown in figure 4 was used, and the calculated results were then compared with the microsections.

Sinter number 40, 1 per cent carbon, according to the diagram could consist of magnetite with a very little eutectic of magnetite and ferric oxide. Its microsection showed massive magnetite which on etching with aqua regia showed a few deep black lines round the grain boundaries. No eutectic was found possibly due to the fact that the sintering temperature was very much below the eutectic temperature. Figure 4 shows that wüstite at its oxygen rich boundary contains 24.28 per cent oxygen and may be said to consist of 62.2 per cent "FeO" with 37.8 per cent  $\text{Fe}_3\text{O}_4$  in solid solution. The calculations of the phases to be expected in sinters 39, 38, and 37, containing 2, 3, and 4 per cent carbon respectively were made on the assumption that on cooling,  $\text{Fe}_3\text{O}_4$  stays in solution in metastable equilibrium. The microsections agree well with the calculated phases on this assumption. Micro 5 of sinter 39 shows much magnetite with a little wüstite, the black areas being holes. The micro of sinter 38 was similar except that

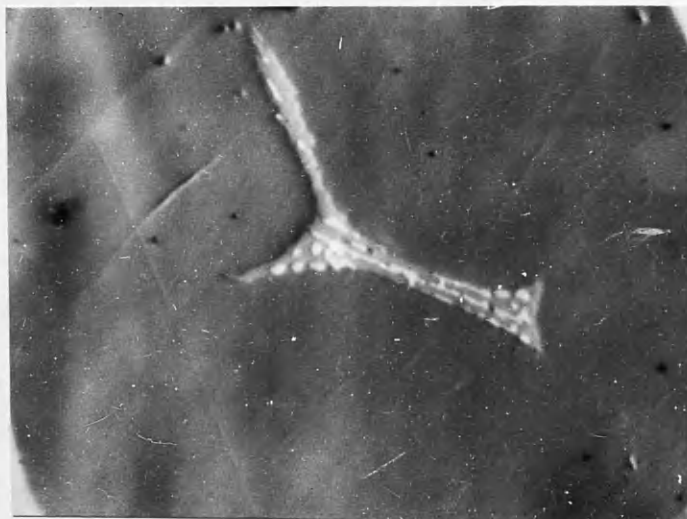
the wüstite was in excess of the magnetite. Sinter 37, 4 per cent carbon has a calculated composition of 0.3 per cent  $\text{Fe}_3\text{O}_4$  and 99.7 per cent wüstite containing 24.28 per cent oxygen which agrees with micro 6. On etching sinters 39, 38, and 37 with aqua regia, the wüstite in all cases took on the martensitic appearance seen in the micros. This was thought to indicate the tendency of magnetite to precipitate along the crystallographic planes of wüstite due to its decreasing solubility on cooling. It is interesting to note that Pfeil<sup>(13)</sup> obtained a troostite-like type of structure from a specimen of similar composition when quenched from the wüstite region while a martensitic type of structure was obtained in the present work on slow cooling. This variation is thought to be due to the very different previous treatment and method of formation of the wüstite. The polishing and etching of these specimens gave considerable trouble. During polishing fine particles of sinter tended to come out of the holes and cracks, resulting in bad scratching of the specimen on the cloth. When a high polish was obtained it was often found difficult to wet the specimen with the etching reagent especially if much magnetite was present. The following etching reagents were tried: 1 per cent nital, 25 per cent  $\text{HNO}_3$ , a mixture of 25 per cent  $\text{HNO}_3$  and 25 per cent  $\text{HCl}$ , 50 per cent  $\text{HCl}$ , Aqua Regia, molten potassium pyrosulphate, and molten sodium and potassium carbonate mixture. Aqua Regia generally gave the best results and was the most consistently used.





MICRO 8

x 500



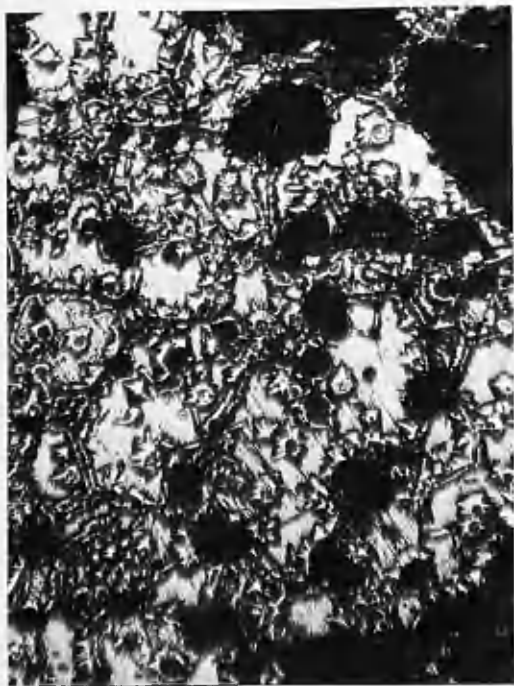
MICRO 9

x 1000

IRON - WÜSTITE EUTECTIC

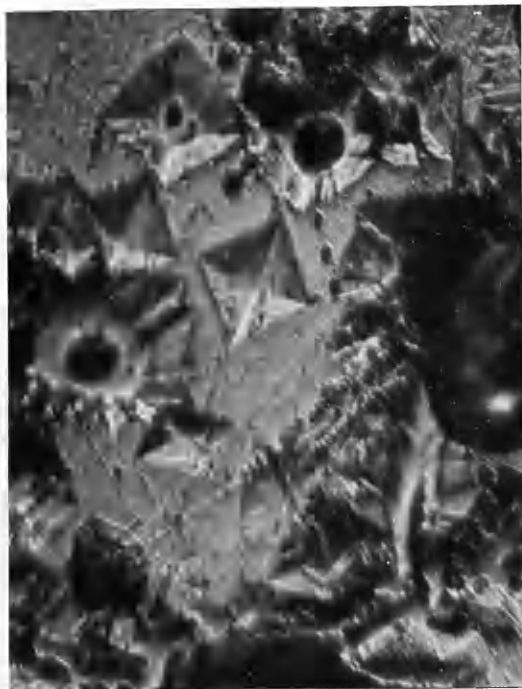
The drying of the specimen also presented considerable difficulty due to its porous nature. Acetone generally left the specimen so stained that the structure was almost completely hidden. Two methods were found satisfactory. One consisted of washing the specimen thoroughly in water followed by drying for at least an hour on top of a resistance box. The hot air from the box gradually dried the specimen thoroughly and expelled the moisture from the very fine pores. The other method consisted of placing the specimen in boiling alcohol for a few minutes followed by a few minutes drying on the resistance box. In both cases the specimen was finished off by a light polish on a clean dry Selvyt cloth. An attempt was made to avoid the above troubles by mounting the specimen in lucite. This proved a complete failure as the scratching was not reduced at all and the drying was even more difficult since alcohol could not be used.

The analysis of sinter 41, 5 per cent carbon indicates 99.75 per cent wüstite of oxygen content 23.21 per cent which is Jette and Foote's figure for the iron rich limit of wüstite. Micro 7, of this specimen heavily etched, shows plain crystals of wüstite with a distinct tendency to assume a hexagonal form. The lines across the crystals are scratches. On careful examination in the unetched condition, a few small areas of eutectic could be observed between the wüstite grains. Micros 8 and 9 show this eutectic which from appearance and analysis of the specimen appears to be the iron-wüstite eutectic. Very little



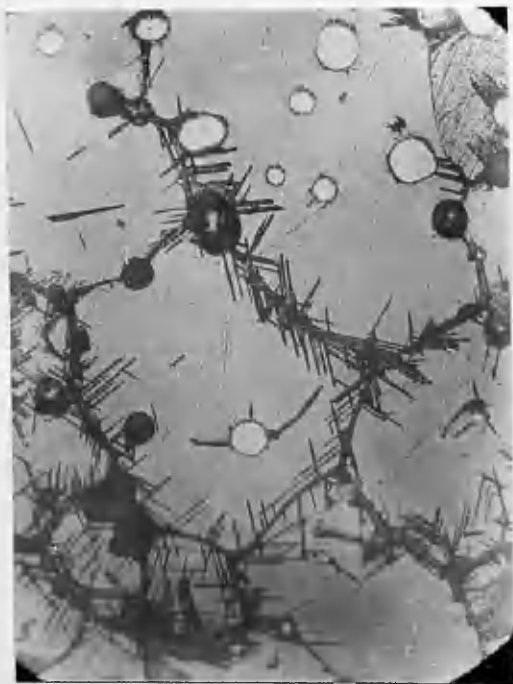
MICRO 10

x200



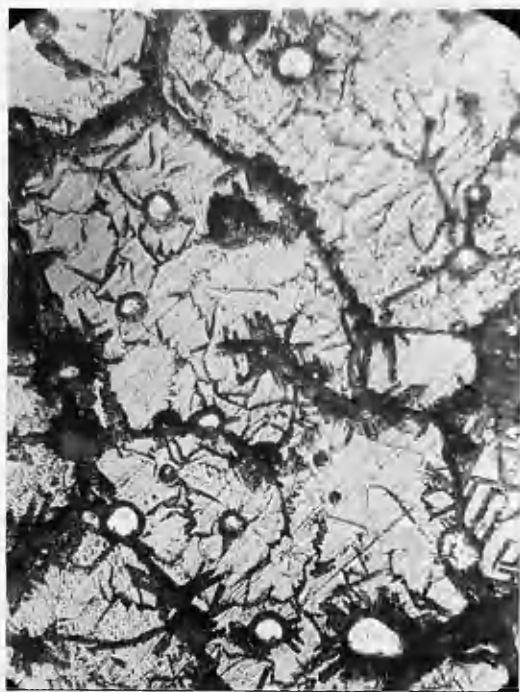
MICRO 11

x1000



MICRO 12

x200

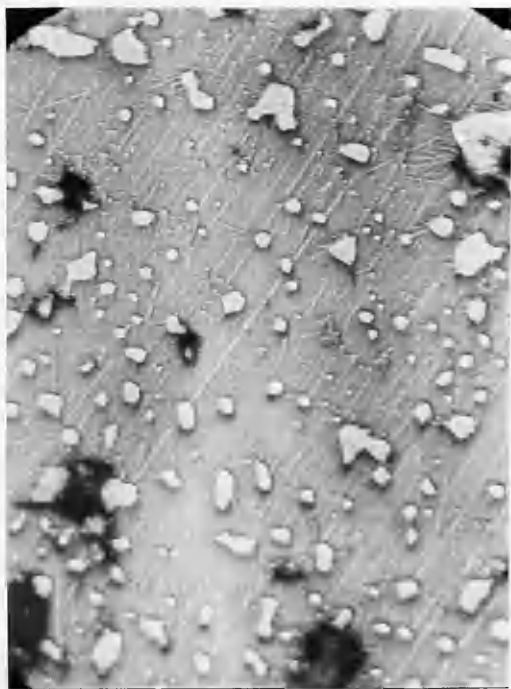


MICRO 13

x200

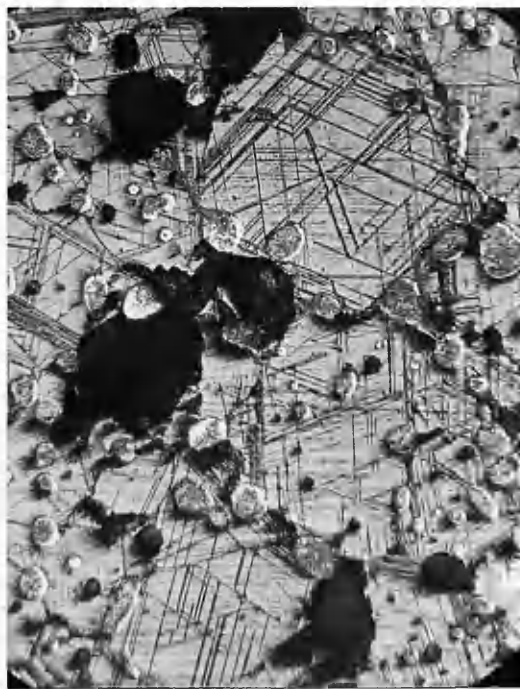
RECRYSTALLISATION IN WÜSTITE

eutectic was present in the specimen, the areas shown in the micros containing much more than the average. On etching with 1 per cent nital there was no appreciable change in the appearance but when aqua regia was used the eutectic was quickly attacked becoming very dark and undistinguishable, while the wüstite was unaltered, as shown in micro 7, except in a few non-representative areas where etching lines similar to those in micro 12 appeared. Sinters 42 and 43, 6 and 7 per cent carbon respectively, in the unetched condition, showed globules of iron in a plain matrix. On light etching it could be seen that the globules occurred both in and around the wüstite grains. On etching with aqua regia and then polishing lightly on a cloth, the microstructure appeared as shown in micros 10 and 11. These shows small globules of iron, some of which are darkened and pitted due to etching, and a general appearance of recrystallisation in the wüstite grains. The old grain boundaries can still be seen as broad dark lines roughly hexagonal in shape, while the new recrystallised wüstite appears to be growing from centres along these boundaries or from the iron globules. A few areas showed etching lines similar to those in micro 12, and micro 13 shows an area where both types of structure are present. It seems that the thick dark etching lines, which only appear on strong etching indicate the tendency of finely divided iron to precipitate from the supersaturated wüstite along the crystallographic planes. This in turn will give rise to the



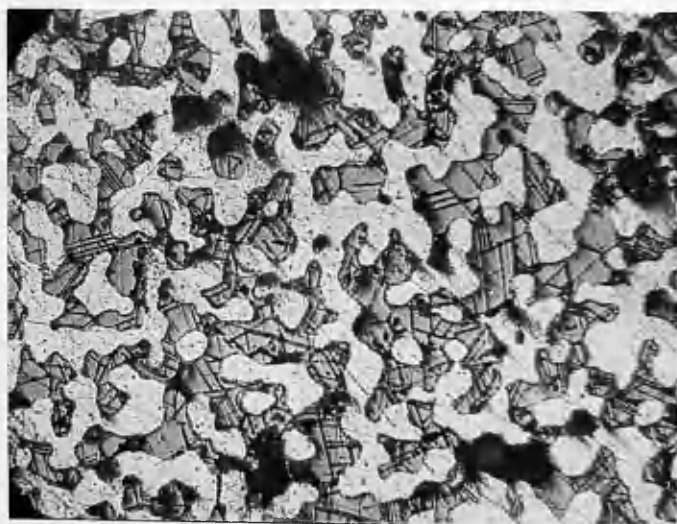
MICRO 14

x 200



MICRO 15

x 200



MICRO 16

x 200

WÜSTITE AND METALLIC IRON

recrystallisation which will be assisted by the very slow cooling rate. No eutectic was observed in these specimens which from analysis and reference to figure 4 would be expected to consist of a little free iron and eutectic of iron and wüstite. It seems probable that the eutectic iron has diffused and separated out into globules due to the length of time the specimens were held at 1300°C.

Sinters 44 and 45, 9 and 14 per cent carbon respectively show an increasing amount of iron and a decreasing amount of wüstite. Micro 14 of sinter 44 shows iron globules in a matrix of unetched wüstite. On etching and light polishing the wüstite showed lines along its crystallographic planes. This can be seen in micro 15 of sinter 44 and in micro 16 of 45. It will be noticed that these lines while similar to those in micro 12, are quite different from the etching lines obtained in oxygen rich wüstite which are of a much finer nature as seen in micro 6. This may be due to the finely precipitated magnetite being more resistant to the etching reagent, than the iron from the iron rich wüstite. Many of these sinters however on careful examination showed a recrystallisation type of microstructure, similar to that in micro 10, interwoven with the etching lines.

In no case was any indication of the decomposition of wüstite observed although slow cooling was always used. This is in agreement with the work of Kanz and Scheil<sup>(14)</sup> who found that wüstite must be held at a temperature of

500°C. for four days followed by a further four days at 480°C. before decomposition can be observed.

The solubilities of oxygen in pure iron, and wüstite in magnetite were neglected in the above calculations as no reliable figures are available and in any case they are thought to be small. Tritton and Hanson<sup>(7)</sup> give an estimated figure of 0.05 per cent for the solubility of oxygen in iron. Pfeil<sup>(8)</sup> in his diagram indicates a relatively high solubility of wüstite in magnetite based on microscopic examination of annealed specimens. There does not however seem to be any confirmatory evidence from any other source.

## CHAPTER V

### Determination of Reducibility

Most of the sinters made so far were quite satisfactory from a strength point of view but there was some doubt as to whether they would be easily reducible, as the macro-porosity was very small although with correct temperature control the micro-porosity appeared to be quite good. This lack of macro-porosity was not thought to be important as ores which generally have poor macro but good micro-porosity reduce more rapidly than industrial sinters which generally have good macro but often low micro-porosity as a result of glazing by slag. These variations between macro and micro-porosity in ores

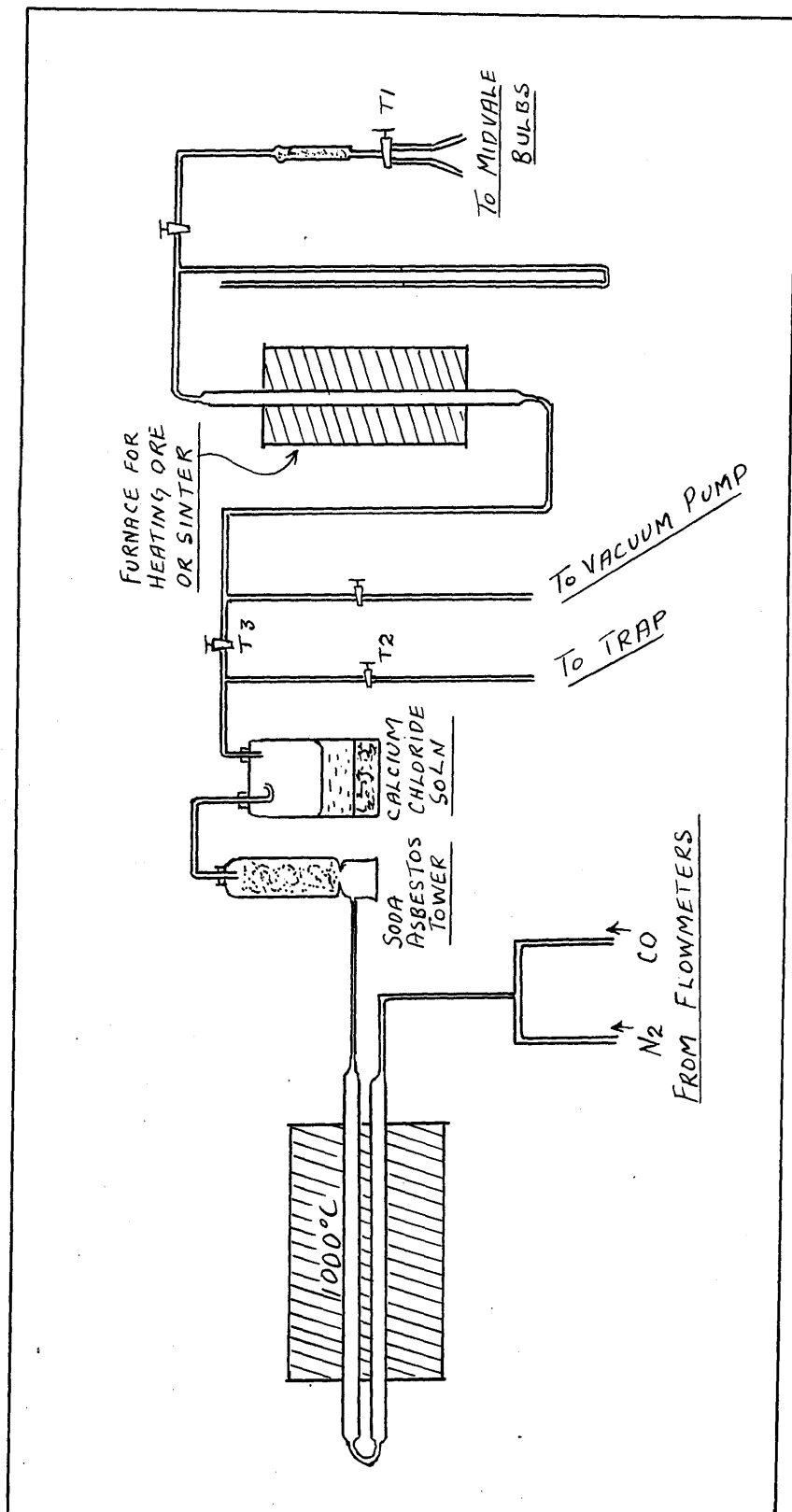


FIG. 7.

REDUCIBILITY APPARATUS



and sinters are shown graphically by Saunders and Tress<sup>(15)</sup>. To obtain more definite information on this point an apparatus for determining relative rates of reducibility was constructed. This apparatus which is shown diagrammatically in figure 7 is similar to that described by Elliot<sup>(16)</sup> but with certain modifications. The reducing gas consists of the so-called synthetic blast furnace gas which is a mixture of two parts of nitrogen and one part of carbon monoxide. These gases are measured out by flow meters to give a total flow of thirty litres of mixed gas per hour. This gas passes through a tube furnace at  $1000^{\circ}\text{C}$ . where any oxygen impurity in the gas reacts with carbon monoxide to form carbon dioxide which is then removed by the soda asbestos tower. From here it passes through a flask containing a saturated solution of calcium chloride from which it picks up 0.0053 grams of water per litre of gas. This procedure was adopted after some preliminary tests described below in which it was shown that moist gas reduces a sinter much more quickly than dry gas. The sample to be reduced is crushed to  $-\frac{1}{2}$  inch,  $+\frac{1}{4}$  inch since this is the largest size which can be conveniently handled and it is considered that the smaller the pieces the greater the errors introduced. The reason for this is that the crushing of the sinter exposes many new surfaces to the action of the reducing gases. In addition to increasing the area of the exposed surface these new surfaces will probably be of a better type for reduction since being

originally unexposed they will not be subject to the same degree of glazing as the primary surface. Also the distance through which the reducing gas must diffuse to reach the centre of the sinter is much reduced by crushing. This is still true in spite of the effect of macro pores which diminish the distance especially in larger pieces. The rate of diffusion which is probably one of the most important factors in the reduction of an ore or sinter is discussed in a subsequent chapter. A convenient amount of sinter is weighed out and placed on a perforated porcelain disc supported by an alundum stool in the vertical tube furnace which during a test is maintained at the desired temperature by a manually controlled resistance. The furnace is wound to give a uniform hot zone of eight inches. The reducing gases pass up the furnace tube then through a magnesium perchlorate bulb to remove moisture and finally through a midvale bulb containing soda asbestos to absorb the carbon dioxide formed by the reduction of the iron oxides in the sinter or ore. The two way tap T1 allows the gas to pass to either of two midvale bulbs so that while one is absorbing carbon dioxide the other can be weighed and thus a constant check can be maintained on the carbon dioxide being evolved. To start a test a weighed sample is placed on the porcelain disc and the furnace is evacuated for a few minutes after which nitrogen is admitted and the furnace heated to the desired temperature. Meanwhile the reducing gas is allowed to pass to waste through tap T2

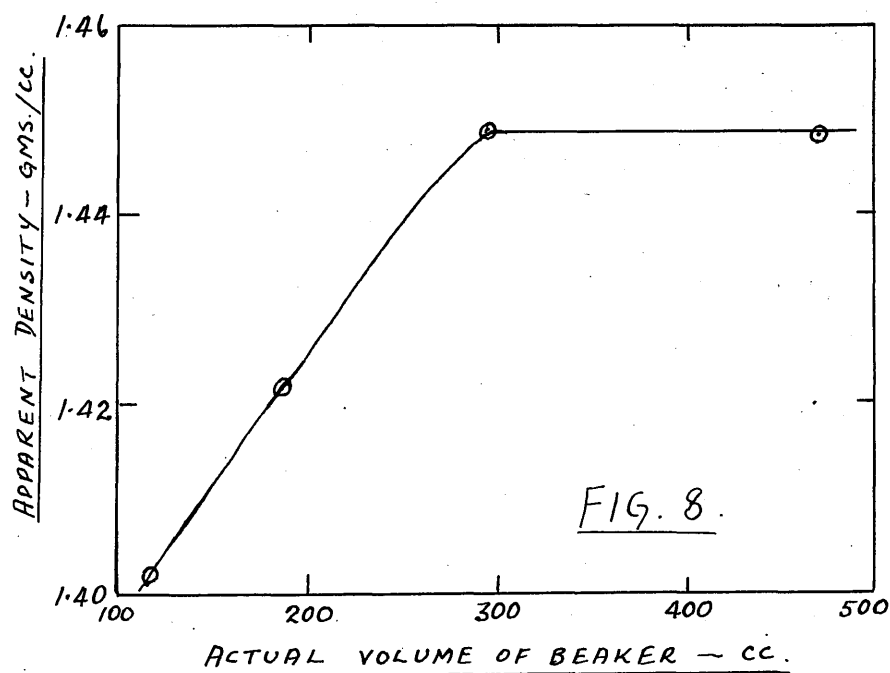
When a constant temperature has been attained tap T3 is opened and T2 closed thus directing the gases through the furnace. An indication of the rate of reducibility is obtained by the heat generated in the midvale bulbs and one of these is changed at intervals varying from five to fifteen minutes depending on the rate. Thus the amount of carbon dioxide evolved in a given time is obtained, from which the percentage reduction in any required time can be calculated and plotted graphically. After a few preliminary trials it was found possible to obtain very consistent results and so a few ores and industrial sinters were first tested to form standards against which the laboratory sinters could be compared. An attempt was also made to discover whether or not any relationship existed between such factors as porosity, silica content, lime-silica ratio etc. and the rate of reducibility.

Samples of sinter from fourteen industrial sources were given the following treatment. All large lumps were broken down and the sample was reduced to 25 lbs. by coning and quartering. This 25 lb. was crushed and about 1000 grams of  $\frac{1}{2}$  inch pieces were removed by hand picking. All experimental work was done on this 1000 grams. The reason for selecting  $\frac{1}{2}$  inch pieces has already been discussed.

The density and porosity of the sinters were determined by a test which was devised to assess voidage as well as pores and so take into account packing density.

TABLE III

Beaker size cc.	Actual volume cc.	Weight of sinter gms.	Apparent density gms./cc.
100	115	161	1.402
150	185	263	1.422
250	294	426	1.449
400	470	681	1.448



The test consisted of filling a 294 cc. beaker level to the top with  $\frac{1}{2}$  inch pieces. This quantity of sinter was weighed in air, placed under paraffin in a vacuum dessicator for 24 hours and finally weighed in paraffin.

$$\text{Thus } \frac{\text{Loss in weight}}{\text{Specific Gravity of paraffin}} = \text{Actual volume of 294 cc. of sinter}$$

from which the porosity can be calculated. The density was simply calculated from the weight of sinter divided by the volume of paraffin displaced. These figures take account of the voids between the pieces of sinter as well as the open pores but take no account of the enclosed pores which seems to be in order since in the blast furnace or the reducibility apparatus the reducing gas fills the voids and open pores but only enters the enclosed pores by the slow process of diffusion through the solid walls. A 294 cc. beaker was chosen as after tests with 100, 150, 250, and 400 cc. beakers this was found to be the smallest size in which the surface of the bottom and sides did not introduce an error. Porosity was found to be high when the 100 cc. beaker was used and the figure fell consistently till the 250 cc. size was used after which it remained constant within the limits of experimental error. These results are shown in Table III and figure 8. The actual volume of the beaker was measured by filling it to the top with water. The weight of sinter is the average of several samples. With careful filling and shaking down it was found the variation in weight seldom exceeded 2 grams and generally

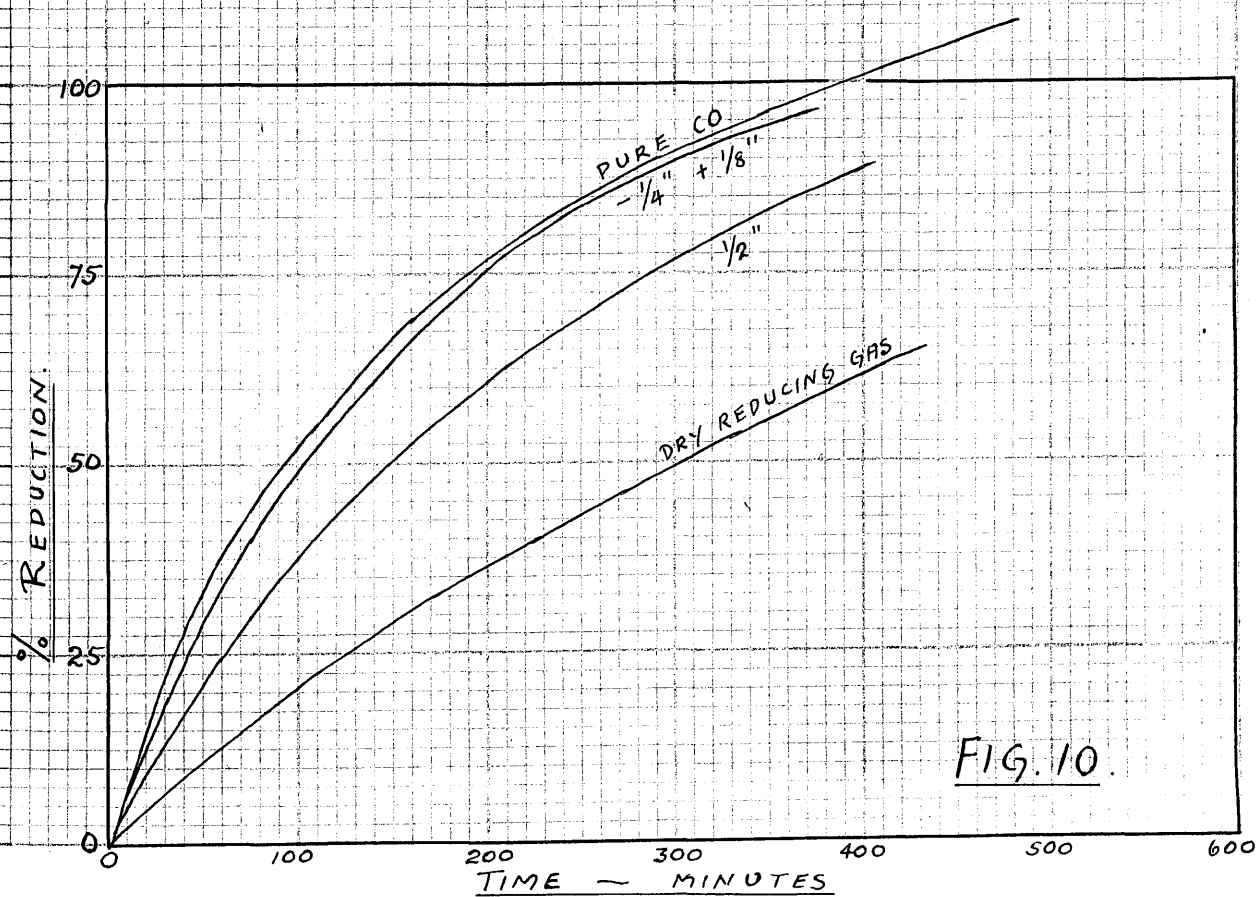
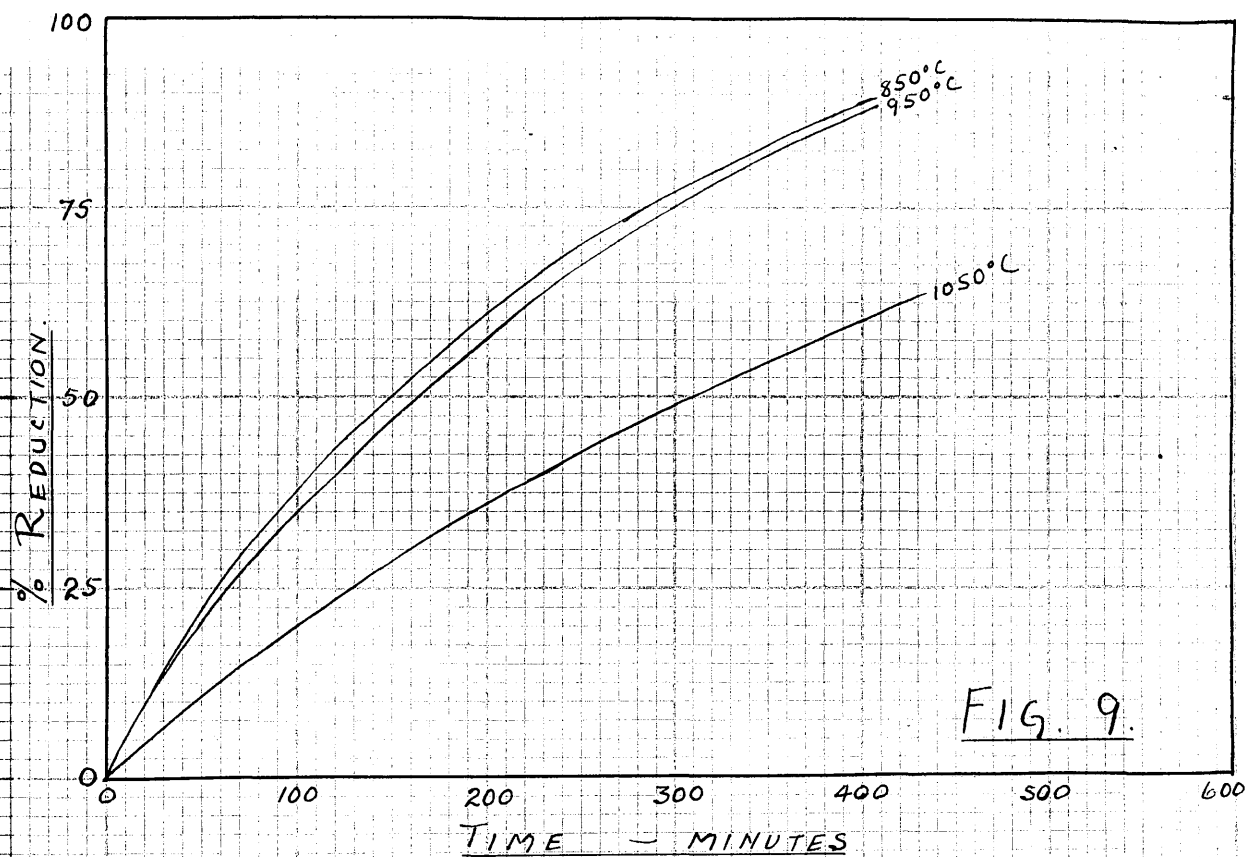
a weight could be repeated to within  $\frac{1}{2}$  gram. This type of test was used as it was not found possible to make a standard piece of sinter such as a 1 inch cube for tests. In any case such a cube would have machine cut surfaces which would present a different system of pores compared to a natural or broken surface since the former would remove glazed surfaces and expose additional micro pores. Figures for density and porosity are shown in Table IV which also gives some chemical analysis figures kindly supplied by the Clyde Iron Works of Messrs. Colville Ltd.

For preliminary reducibility tests a sinter was selected at random. To ensure uniformity it was decided to take 20 cc bulk volume of sinter, as this was the largest volume which could be conveniently handled. The decision to measure out the sinter by volume instead of by weight was taken since the amount of sinter in the blast furnace is a function of volume. Hence a poor sinter with a lot of gangue has a better CO:CO<sub>2</sub> ration for a given rate of driving than a good sinter. As any attempt to measure out 20 cc. by a measuring cylinder would result in considerable error due to the surface effect of the cylinder walls, it was decided that greater accuracy could be obtained by calculating the weight of 20 cc. from the weight of the 294 cc. used for porosity, and so weighing out 20 cc. It was subsequently discovered that the flow of CO in the reducibility apparatus was sufficient to make this precaution unnecessary.

TABLE IV

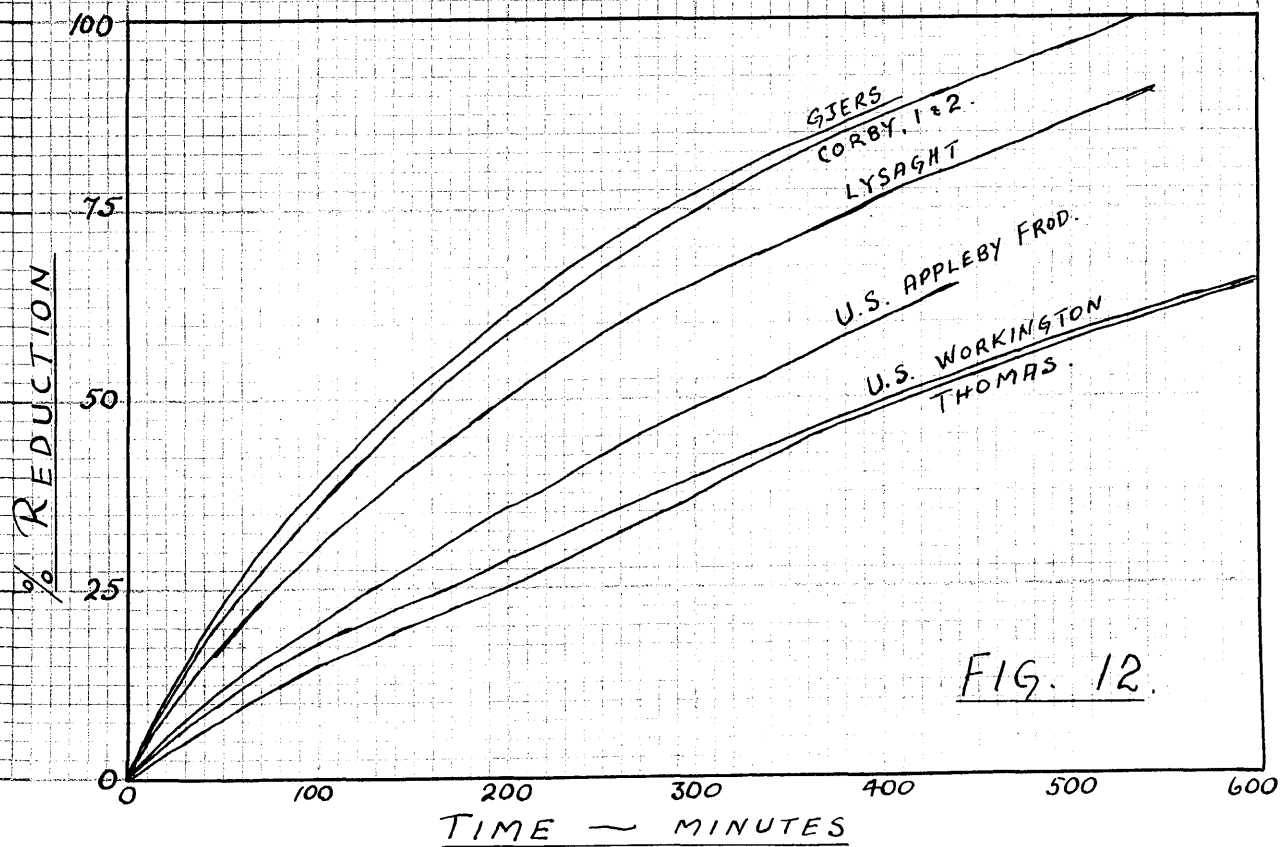
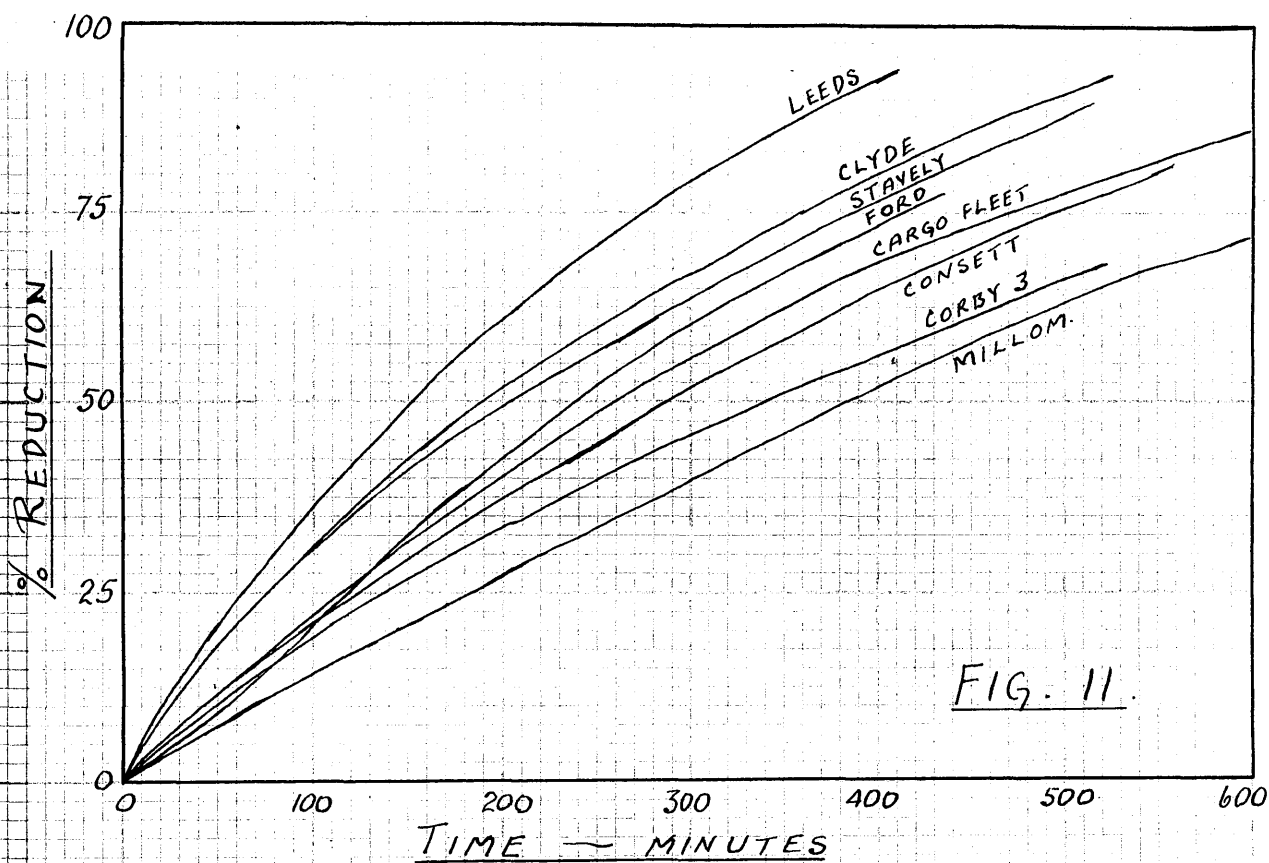
Sinter	Ref.No. in fig.	Wt.of 20 cc gms	Porosity %*	Density %	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	Time to 70% reduction Mins.	Mins.for 1% reduction at 70%
Gjers	1	29	69.4	4.7	6.37	0.70	0.57	4.37	23.92	65.43	250	11.7
Ford	2	27.7	68.3	4.37	5.94	1.0	0.32	1.31	22.88	66.86	370	14.0
Clyde	3	22.4	68.4	3.54	13.64	3.0	0.87	11.13	13.0	57.43	326	14.5
Consett	4	29.4	63.9	4.03	17.06	4.0	0.95	6.84	23.14	46.85	450	17.5
Stavely	5	21	67.9	3.23	17.2	12.4	1.25	7.99	14.56	41.00	350	16.2
Leeds	6	25.3	71.3	4.45	6.79	1.50	0.70	7.47	18.2	64.3	250	10.3
Millom	7	30.7	59.2	3.76	13.44	3.4	tr	1.81	18.2	61.43	585	24
Cargo Fleet	8	25.2	63.2	3.43	16.2	9.3	0.94	9.3	11.7	47.57	420	19.5
Lysaght	9	20.4	58.7	3.08	21.92	7.74	1.32	14.84	18.2	34.3	343	16.2
Corby 1 & 2	10	24.7	66.4	3.65	13.4	9.72	2.18	10.11	21.06	42.3	267	12.5
Corby 3	11	25.3	64.9	3.60	15.2	7.34	1.98	13.31	23.7	37.3	545	21.5
Thomas	12	24.8	63.6	3.42	22.16	4.5	1.84	10.96	30.16	28.0	675	20
Worthington (U.S.)	13	33.7	61.4	4.38	11.1	2.72	tr	7.75	13.0	65.14	665	24.5
Appleby Piddingham (U.S.)	14	25.7	63.2	3.49	15.2	8.4	0.32	13.9	28.6	29.14	480	17

\* Including voidage.





The first tests were carried out to determine the best temperature for reduction. These were carried out at 850, 950, and 1050°C. The reducibility curves obtained are shown in figure 9 from which it can be seen that fastest reduction is obtained at 850°C. with that at 950°C. almost as good. Slight glazing at 1050°C. is probably the cause of the slower reduction. It should be noted that all subsequent reducibility results for industrial sinters, ores and laboratory sinters are plotted on the same scale as figure 9 so that direct comparison of the results is possible. Further tests were now carried out at 850°C. to determine the effect of moisture and particle size. When the gas was dried by magnesium perchlorate and phosphorus pentoxide before entering the reduction furnace, the rate was much slower. Bone<sup>(17)</sup> obtained similar results on ores using calcium chloride dry gas and gas containing 2 per cent moisture. His results however show only a slight difference in the rate of reducibility but it is probable that the difference between calcium chloride and phosphorus pentoxide dry gas will account for this. The effect of size was shown by using a sample crushed to between the limits -  $\frac{1}{4}$  inch, +  $\frac{1}{8}$  inch. As expected this showed much more rapid reducibility, due to the greater surface area exposed, and also to the much less depth of diffusion required for penetration to the centre of the pieces. Figure 10 illustrates these results. The other curve in this figure indicates the results obtained when pure



carbon monoxide flowing at a rate of 20 litres per hour was tried as the reducing gas. Considerable carbon deposition was observed which explains why the curve rises so rapidly to above the 100 per cent reduction limit.

As a result of these preliminary tests the routine tests were now carried out at  $850^{\circ}\text{C}$ . using moist reducing gas and 20 cc. of  $\frac{1}{2}$  inch pieces. The sinter was weighed out and placed in the furnace which was then evacuated. Nitrogen was introduced and the sinter heated to  $850^{\circ}\text{C}$ . in a nitrogen atmosphere. When steady temperature conditions had been obtained, the reducing gas was admitted and the rate of reduction followed by the carbon dioxide formed. The percentage reduction for each reading was calculated from a knowledge of the total oxygen content of the sample and the results plotted in figures 11 and 12.

As can be seen from the graphs the good sinters reduce about twice as fast as the poorer ones but all may be classed as poor since the best sinter takes over eight hours for complete reduction. It seems fairly certain that most sinters will reach the bosh of the furnace in a partially reduced condition leading to the reducing and melting reactions taking place simultaneously with consequent decreased efficiency if the amount is excessive since the reduction of "FeO" by either carbon or carbon monoxide is endothermic thus taking heat which would be better employed in melting and superheating the

metal and slag. When considering this loss in thermal efficiency, caused by direct reduction, it must be remembered that the iron content of the burden and the temperature of the blast must also be taken into account. Thus for a rich burden it has been shown<sup>(18)</sup> that if all the reduction is done indirectly by carbon monoxide, excess carbon over that required to provide heat for melting the metal and slag must be burnt to provide sufficient carbon monoxide for complete reduction. In such a case it is obvious that a certain amount of direct reduction, which incidentally produces carbon monoxide for indirect reduction, will be beneficial. This applies mainly to American practice where rich concentrates are used and there is little slag to be melted. In the case of a burden low in iron with a consequent increase in the amount of slag formed, extra coke is required to provide heat for melting this slag resulting in increased carbon monoxide production, and since there is less iron oxide to reduce it is probable that there will be sufficient carbon monoxide for 100 per cent indirect reduction. In such a case it follows that 100 per cent indirect reduction is the ideal condition for maximum efficiency. The temperature of the blast also plays an important part. If by more efficient stoves it can be increased, then the amount of coke required to be burnt to provide heat is reduced with a consequent decrease of the carbon monoxide from this reaction. Thus a burden which would give maximum efficiency on 100 per cent indirect reduction

with a blast temperature of  $600^{\circ}\text{C}$ . might require a certain proportion of direct reduction if the blast temperature were raised to  $800^{\circ}\text{C}$ . This of course does not mean that there is a possibility of increased efficiency by charging a small quantity of poor reducibility sinter which will not be completely reduced till it reaches the bosh where it will be reduced by carbon. Such an addition to the burden is a disadvantage as far as thermal efficiency is concerned since it does not reduce at the same rate as the majority of the charge and the furnace is being driven at a rate to suit this rate of reducibility. If a high proportion of this type of sinter was used in the charge it would be expected that the iron loss to the slag would tend to be high due to melted " $\text{FeO}$ " or  $\text{FeO}\cdot\text{SiO}_2$  running down to the hearth before it is reduced unless the furnace was driven at a slower rate to suit the requirements of sinter. Such is found to be the case in practice. Elliot<sup>(19)</sup> states that when sinter was increased above 38 per cent the furnace worked much colder. At 50 per cent sinter the amount of iron leaving the slag notch was almost incredible and the furnace ran so persistently cold that the experiment was discontinued. He also states that above 38 per cent sinter it was difficult to control sulphur even with slags of very high basicity unless silicon was allowed to reach about 1.1 or 1.2 per cent. It thus appears that the cooling effect of the unreduced sinter prevents the formation of a sufficiently fluid

FIG. 13.

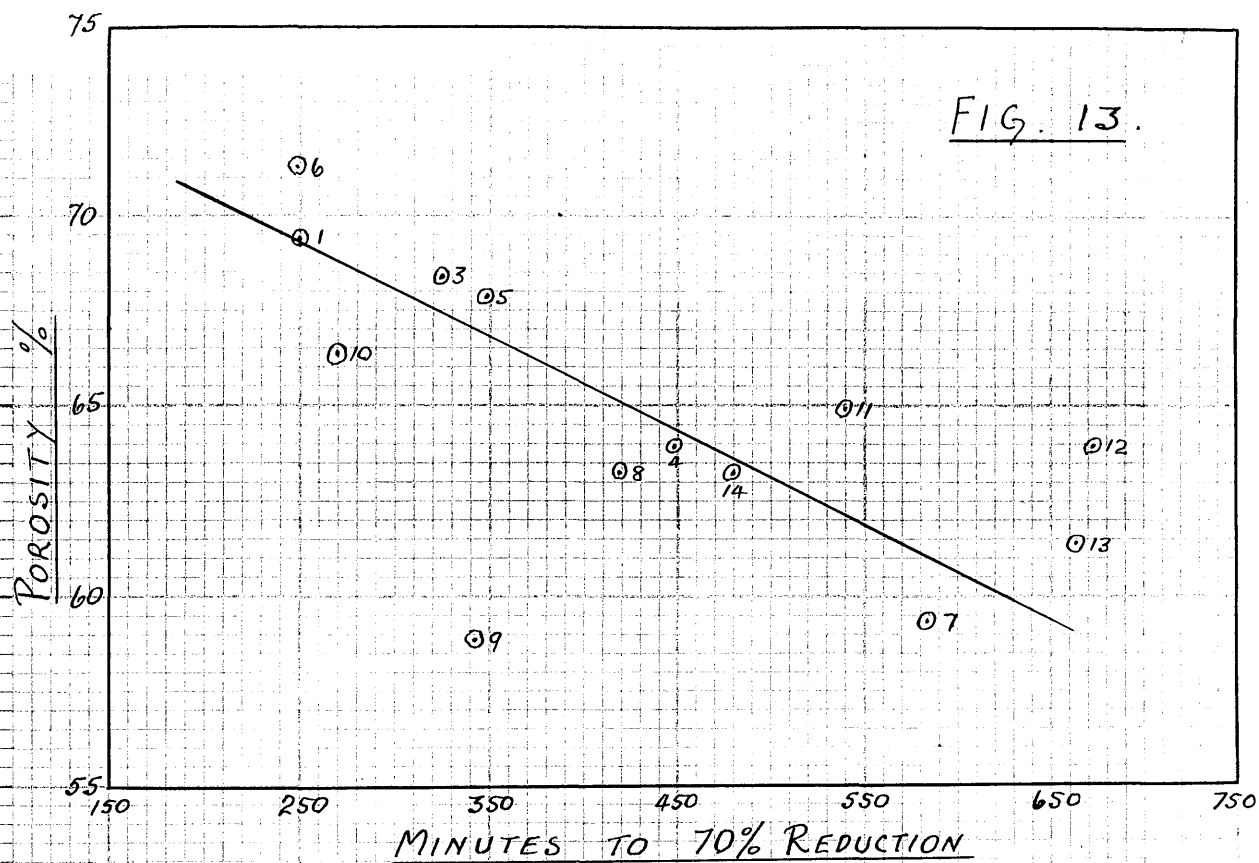
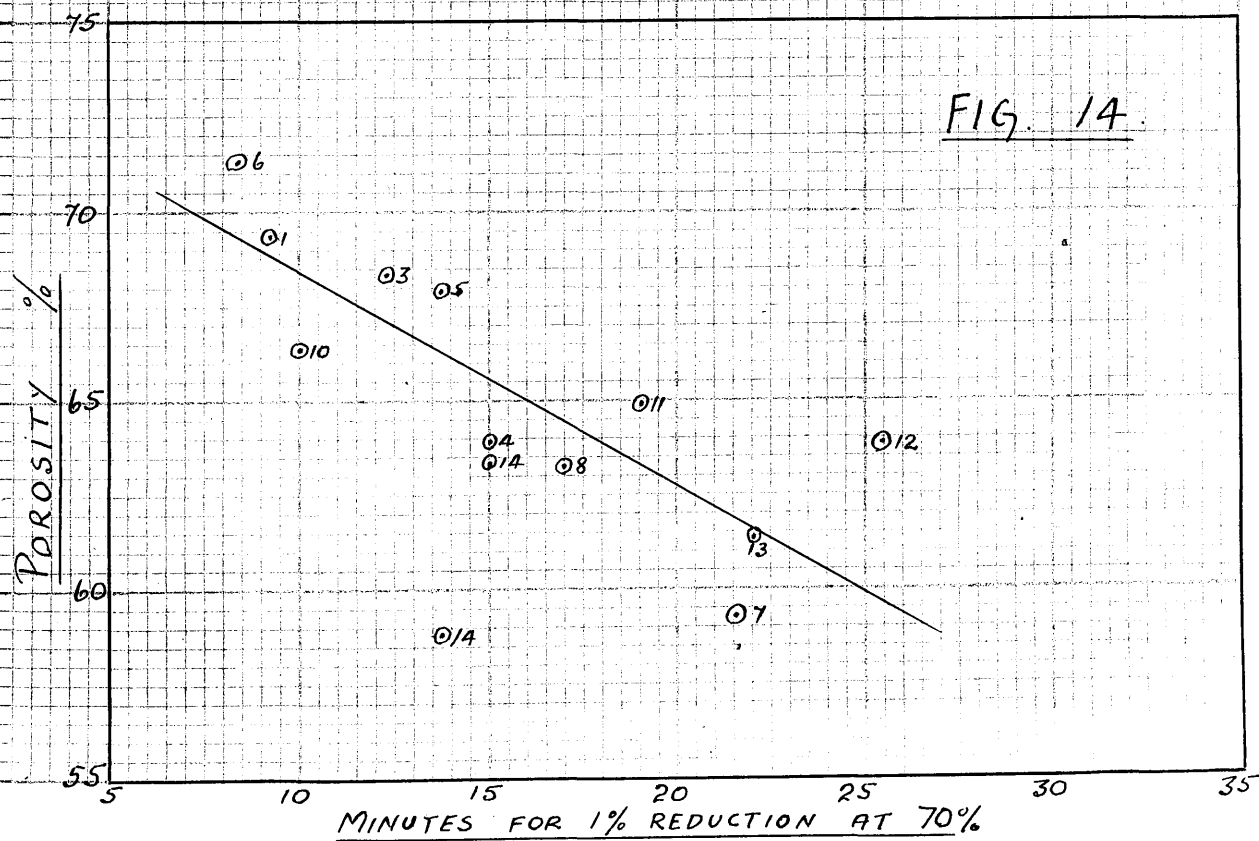


FIG. 14.



slag for sulphur removal unless additional coke is added to maintain the heat, which results in the reduction of considerable silica.

An attempt was made to correlate the rate of reducibility with porosity. Table IV shows the time taken to 70 per cent reduction and also the time for 1 per cent reduction at 70 per cent which may be taken as an indication of the rate of reduction at 70 per cent. Figures 13 and 14 show these figures plotted against porosity. It can be seen that there is a fairly good relationship in spite of the great differences in the previous treatment of the sinters. The relationship is to be expected considering that greater porosity means greater surface area and less depth of penetration required to reach the centre of the specimen. The time to 90 or 100 per cent reduction would have been a better figure to take but it can be seen from the graphs that it would have been impossible to obtain either of these figures in a reasonable time. Figures for the S.K. porosity test on these sinters were supplied by Dr. Saunders but no relationship whatever could be found between these figures and reducibility possibly due to the varying conditions under which different sinters were made. It was considered that there should be a relationship between the reducibility and such factors as  $\text{CaO}:\text{SiO}_2$  ratio, the total percentage of slag present, and the "FeO" content. No such connection could be found either simply or when more than one factor was taken into

account at once. That this was probably due to such factors as differences in time and temperature of sintering was subsequently proved when good relationships were obtained in synthetic sinters. Macro examination of the unpolished surface through binoculars showed that in general the sinters with the poor reducibility had the most glazed surface and it was possible, on examining each sinter individually, to see that there was a distinct connection between lime, silica, ferrous oxide, reducibility and degree of glazing.

A similar situation arises in refractory materials where Kanz<sup>(20)</sup> found that the physical constitution produces greater changes in permeability than chemical nature. Table V shows his results.

TABLE V.

Type of substance	Permeability Range (cc/sec/cm <sup>2</sup> /cm/cm of water pressure)
Fireclay product	0.00278 - 0.476
Silica product	0.0158 - 0.132
Magnesite product	0.0275 - 0.265
Chromite product	0.147 - 1.42
Insulating product	0.00597 - 0.539

While it must be noted that such a result for refractories is far from being unexpected, the magnitude of the permeability range is remarkable.



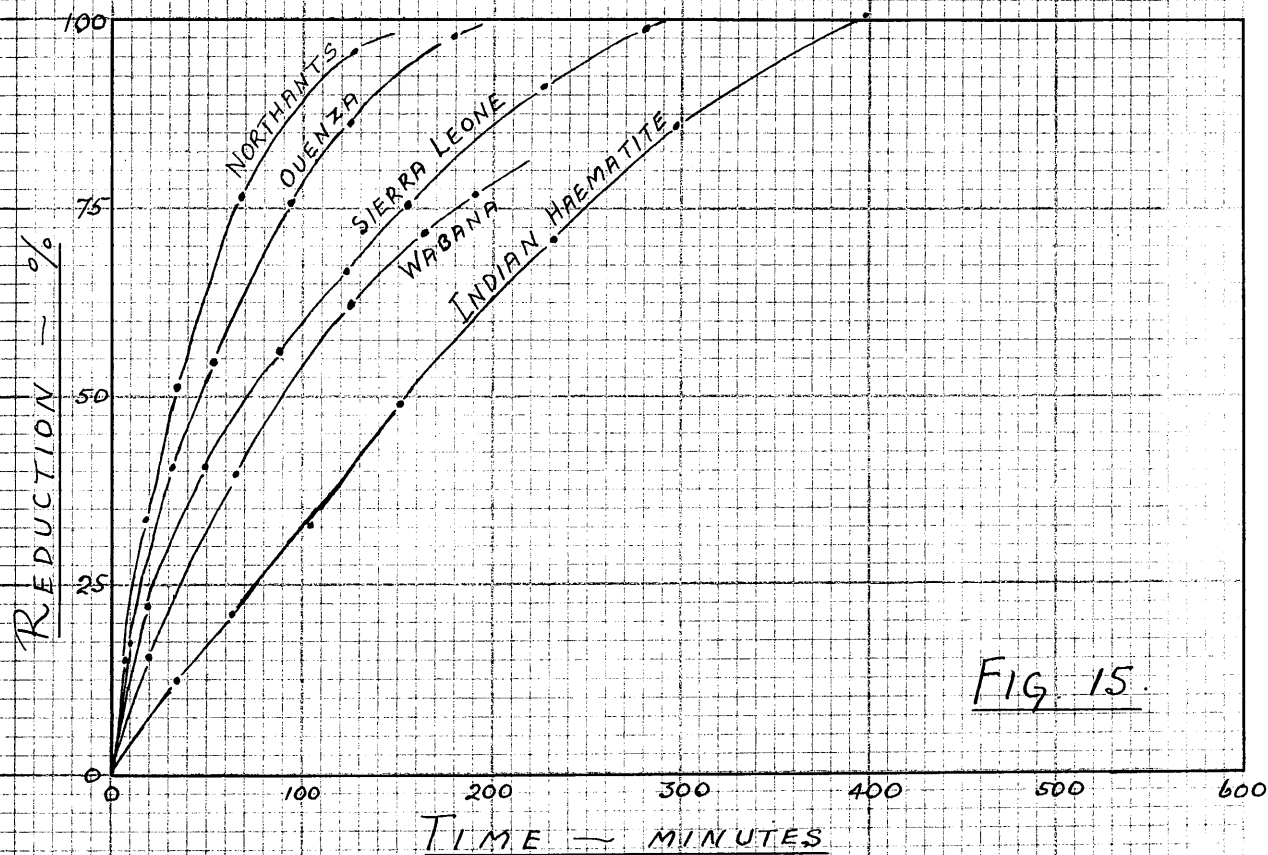


FIG 15.

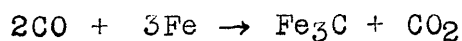
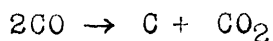
Several ores were now tested in a similar manner, the results of which are shown in figure 15 while Table VI gives the chemical analysis.

TABLE VI

Ore	%Fe	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>	%CaO	%MgO	%Mn
Sierra Leone	53.7	3.81	7.0	0.30		0.39
Ouenza	52.7	3.03	0.1	5.76	0.19	1.79
Northants	42.9	10.3	9.5	6.9	1.36	0.34
Wabana	51.1	10.8	5.2	3.6	0.73	0.57
Indian Haematite	65.5					

By comparison it can be seen that a poorly reducible ore such as the Indian haematite reduces faster than a good sinter. The testing of these ores raised an unexpected source of error. When tested all the ores passed their 100 per cent theoretical limit and it was only by continuing the test till the reducibility curve became a straight line that the actual 100 per cent reduction figure could be ascertained. This usually occurred at about 120 per cent. This blank was considered to be due to carbon deposition and carburisation both of which give rise to excess carbon dioxide. If this is so it is probable that the blank is small at first but increasing later as more metallic iron is formed. It is interesting to note that in Elliot's results<sup>(21)</sup> the curves for

Zaccar and Ouenza ores both meet the 100 per cent reduction limit at a steep angle and it appears that if the test had been carried further they would certainly have exceeded the 100 per cent reduction figure. There was thus a varying and indefinite blank during the tests. No allowance has been made for this in the sinter results in figures 11, 12 and 16 as there was no way of finding the true 100 per cent figure, and in any case the blank is thought to be small during the first part of the reduction. Also carbon deposition is less for sinters than ores as seen from figure 17. It can be remembered however when considering these figures that the actual rate of reducibility is somewhat less than that indicated. The results for the ores in figure 15 have been corrected by carrying on the test till the ore was completely reduced which occurred at about 120 per cent theoretical and then altering the scale to make this read 100 per cent. This procedure is not strictly accurate since it assumes the blank to be constant. The only method of making an accurate check on the blank seemed to be by measuring the ingoing reducing gases and the waste gases accurately by meters. When the known changes in volume due to reduction were allowed for the blank could be calculated from the unaccounted for reduction in volume since as can be seen from the following equations both carbon deposition and carburisation result in a reduction in volume with the accompanied production of carbon dioxide.



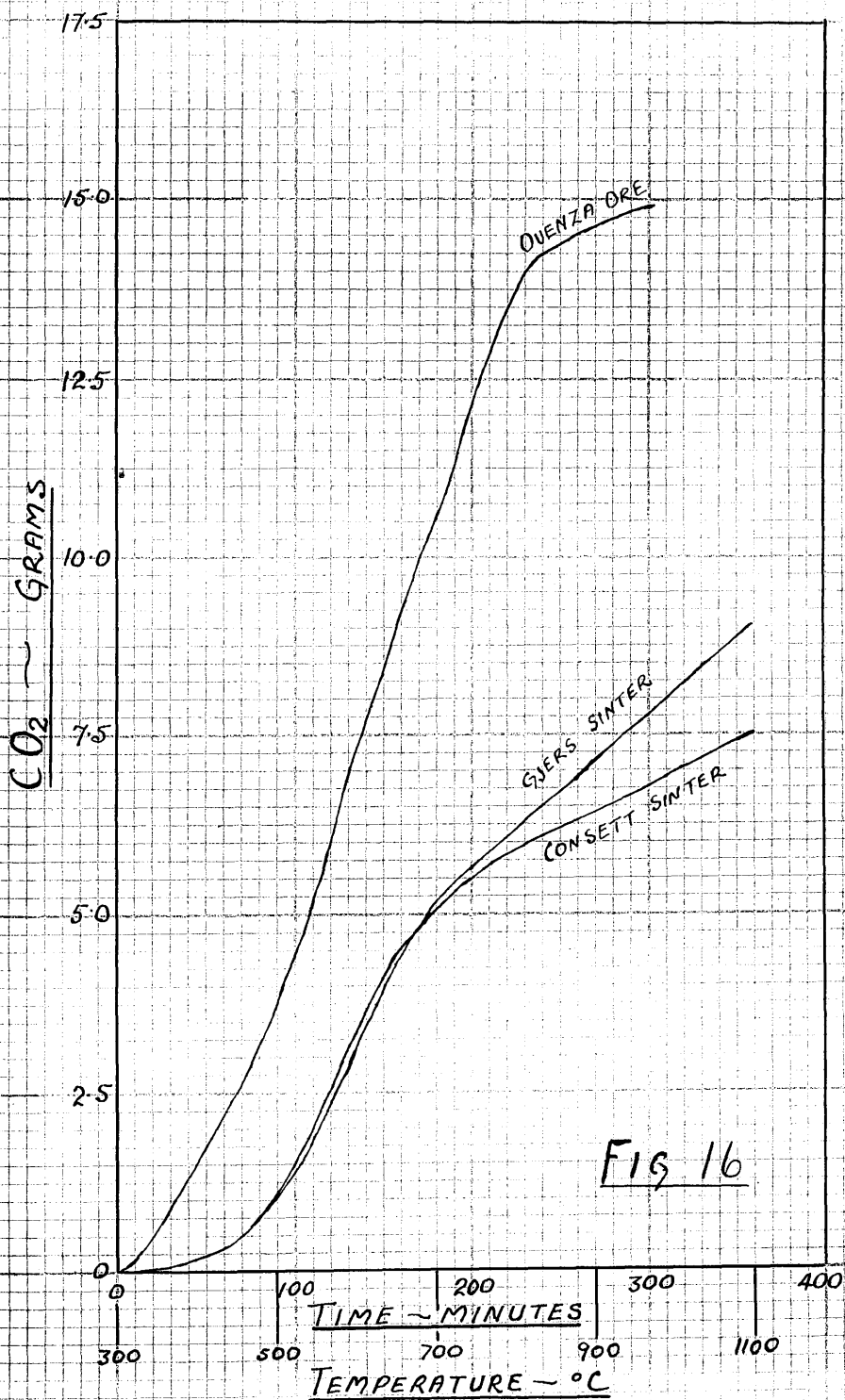


Fig 16

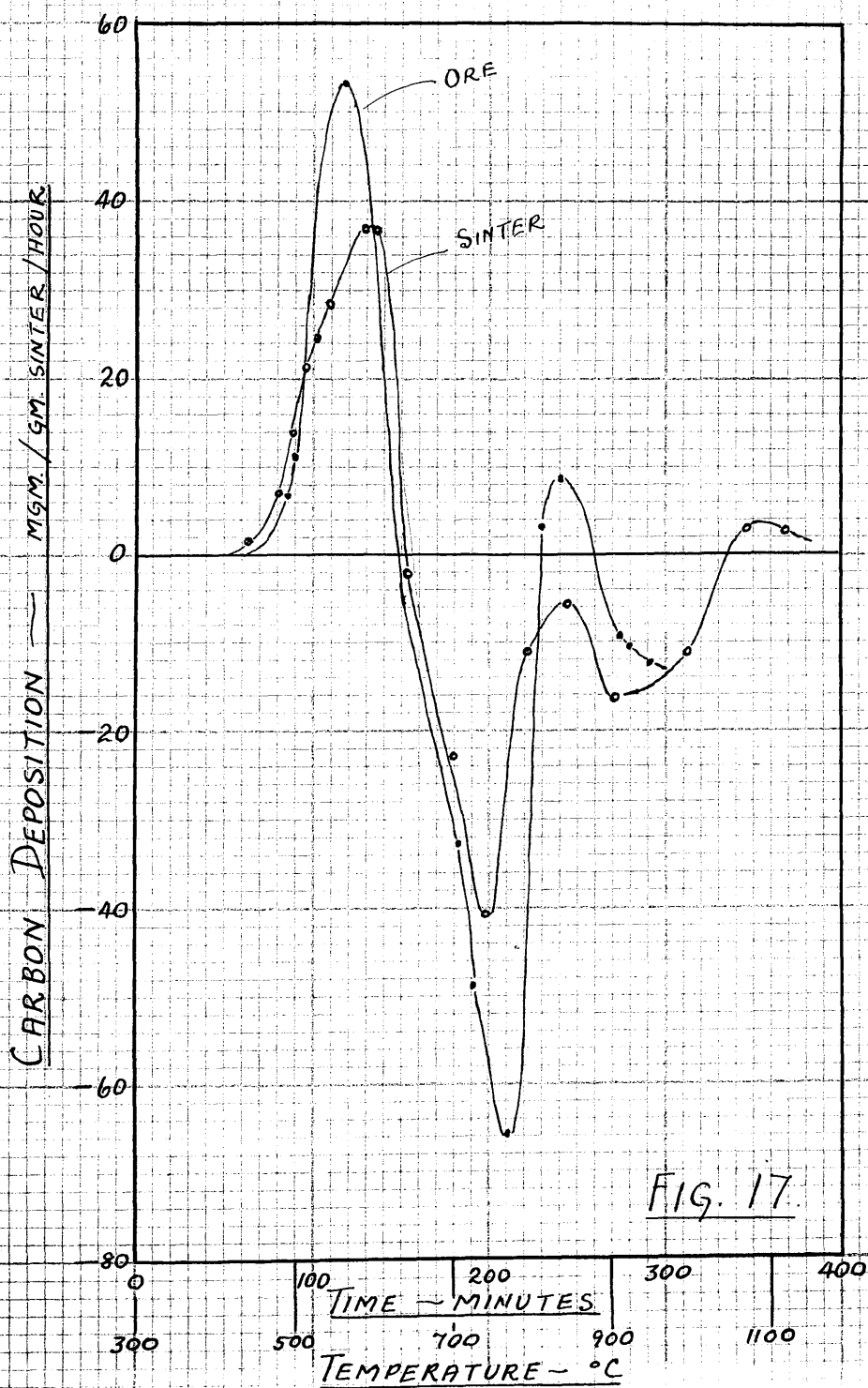


FIG. 17.

As two accurate meters were not available at the time this method was not possible.

The strength of these ores varied considerably and it is interesting to note that the Indian haematite and the Wabana which have the slowest reducibility were the strongest while Northants which has the best reducibility was the weakest.

The above type of test while being quite satisfactory for comparison purposes makes no attempt to reproduce actual blast furnace conditions. Accordingly a modified form of the test was carried out using a rising temperature instead of the steady temperature of  $850^{\circ}\text{C}$ . The test was started with the sinter or ore at about  $300^{\circ}\text{C}$ . and during the test the temperature was raised steadily at the rate of about  $135^{\circ}\text{C}$ . per hour which approximates to modern blast furnace conditions. Figure 16 shows the results obtained for two sinters and an ore. It will be noticed that carbon deposition appears to start at about  $360^{\circ}\text{C}$ . in the case of the sinter and  $300^{\circ}\text{C}$ . for the ore. It appears to stop or become smaller at  $650^{\circ}\text{C}$ . for the sinter, which is in accordance with figure 5 which indicates that above this temperature the  $\text{CO}:\text{CO}_2$  ratio required for ore reduction is smaller than that required for carbon deposition so that ore reduction predominates. The graph for the ore continues to rise steeply to about  $800^{\circ}\text{C}$ . and it does not indicate where carbon deposition stops. Figure 5 may not hold strictly for reducing conditions since after the initial

period of reduction the reducing gas has to diffuse into the mass to carry on the reduction. There is thus the possibility that even above  $650^{\circ}\text{C}$ . there may be local conditions favouring carbon deposition at the surface although further in conditions will not permit it. In such a case the amount of carbon dioxide collected in the midvale bulbs would probably indicate that the state of reduction had not advanced far enough to permit carbon deposition above  $650^{\circ}\text{C}$ . and thus it might be wrongly assumed that there could be no blank from this cause.

An attempt was made to measure the carbon deposition by measuring the volume of gas entering and leaving the apparatus. As stated before accurate meters were not available and so the ingoing gases were measured by the flowmeters which were calibrated before and after each test while the waste gases were measured by collecting at frequent intervals in a 1000 cc. graduated flask over water allowance being made for temperature, pressure and water vapour. Carbon deposition involves a decrease in volume as can be seen from the equation  $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ . Thus the amount of carbon deposited can be measured by the volume difference between the ingoing gases, and the total of the waste gases and the carbon dioxide collected in the midvale bulbs. The results obtained for Gjers sinter and Ouenza ore, shown in figure 17, while being far from accurate give a general indication for the reaction. The first sign of carbon deposition was observed at about  $400^{\circ}\text{C}$ . rising to a maximum at about  $600^{\circ}\text{C}$ ., falling to



MICRO 21

x 400

WÜSTITE



MICRO 22

x400

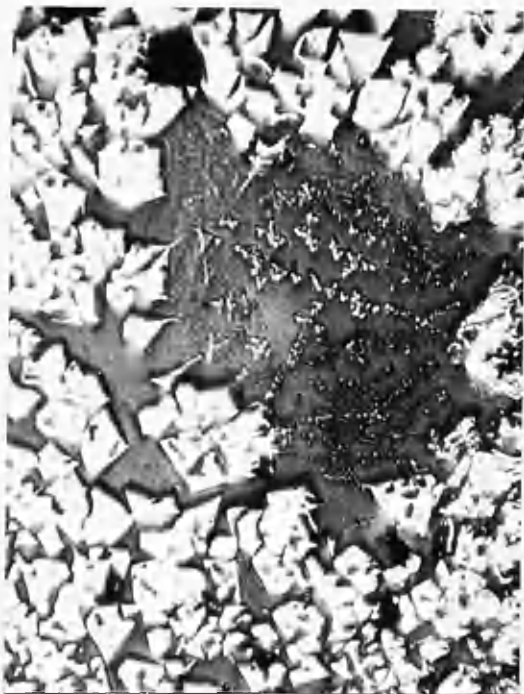


MICRO 23

x400

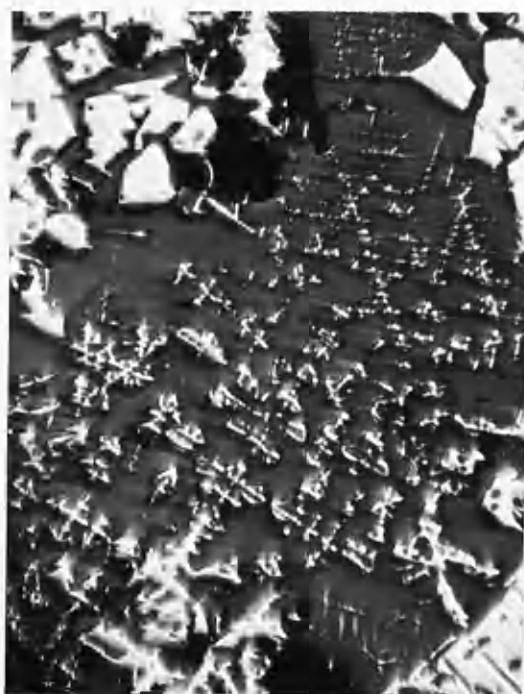
PROGRESS OF REDUCTION





MICRO 17

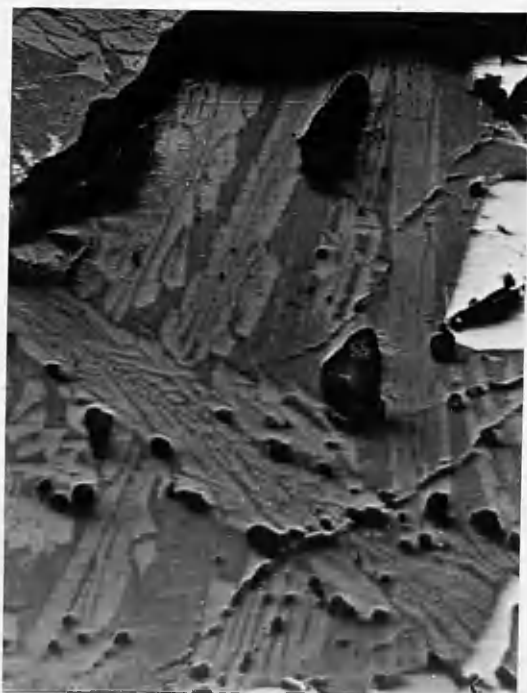
x 400



MICRO 18

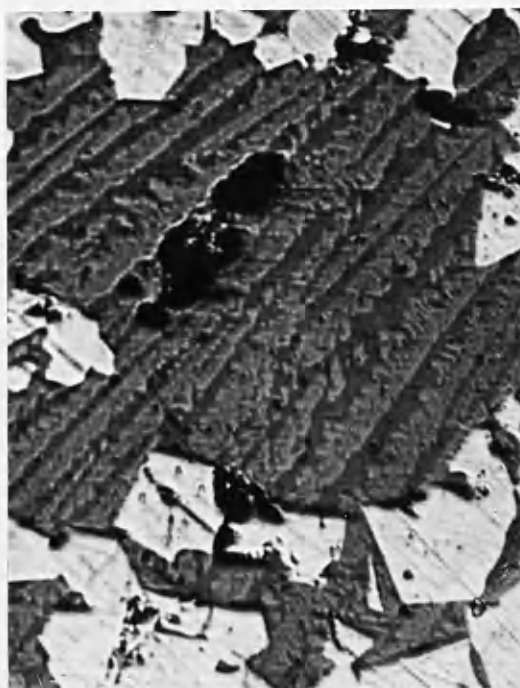
x 400

MAGNETITE



MICRO 19

x 400



MICRO 20

x 400

CRYSTALLISATION OF GLASS

zero around  $640^{\circ}\text{C}$ . and thereafter an excess volume of gas indicated the possibility of carbon reduction taking place according to the equation  $\text{C} + \text{FeO} \rightarrow \text{CO} + \text{Fe}$ , or  $\text{C} + \text{Fe}_3\text{O}_4 \rightarrow \text{CO} + 3\text{FeO}$ . This carbon reduction seems to reach a maximum at  $750^{\circ}\text{C}$ . and thereafter fall to a minimum at  $850^{\circ}\text{C}$ . The reason for this minimum in carbon reduction is not obvious. It may be real or it may be only apparent, a result of some other reaction such as carbide formation causing a reduction in the gas volume according to the equation  $2\text{CO} + 3\text{Fe} \rightarrow \text{Fe}_3\text{C} + \text{CO}_2$ . Bone<sup>(22)</sup> found that at  $750^{\circ}\text{C}$ . deposited carbon was a more powerful reducing agent than carbon monoxide.

The microstructure of all the sinters tested was examined. The most common feature was magnetite both in massive angular crystals and in fine dendritic form as seen in micros 17 and 18. In one case a lighter phase, thought to be ferric oxide was observed round the edges of the magnetite grains. The glass in most cases was non-crystalline but micros 19 and 20 show two good examples of crystallised glass. Micro 21 shows evidence of a recrystallisation process taking place round the grains of wüstite, similar to the synthetic sinter number 43 seen in micro 10. Micros 22 and 23 of partly reduced sinters are interesting, since they show the process of reduction as the reducing gases penetrate the mass. In 22 the white crystals are metallic iron while the grey crystals in the centre where the reducing gases have not penetrated so rapidly, are wüstite. It is interesting

to note that the characteristic magnetite form persists. Micro 23 again shows crystals which were originally magnetite. Most are only reduced to wüstite but in some crystals the actual change from wüstite to metallic iron is obvious.

## CHAPTER VI

### The Reducibility of German Sinters.

Since the cessation of hostilities, samples of three German sinters have been received and tested for reducibility. No porosity determinations could be carried out as the sample was not large enough. Table VII gives some general data.

TABLE VII

Sinter	%FeO	%Fe <sub>2</sub> O <sub>3</sub>	%Fe	Time to 70% Redn.	Strength
Hermann Goering	15.1	38.8	42	245 mins.	Poor
Bochum (D.L.)	21.8	54	58.7	278	Fairly good
Barbech (Grwt.)	16.3	52.3	53.2	160	- do -

The strength of the Hermann Goering sinter was poor. When put through the jaw crusher a considerable quantity of fines was produced and the strength of the small pieces ( $\frac{1}{2}$  inch) was poor compared to either British or the average laboratory sinter. Both Bochum and Barbech were stronger,

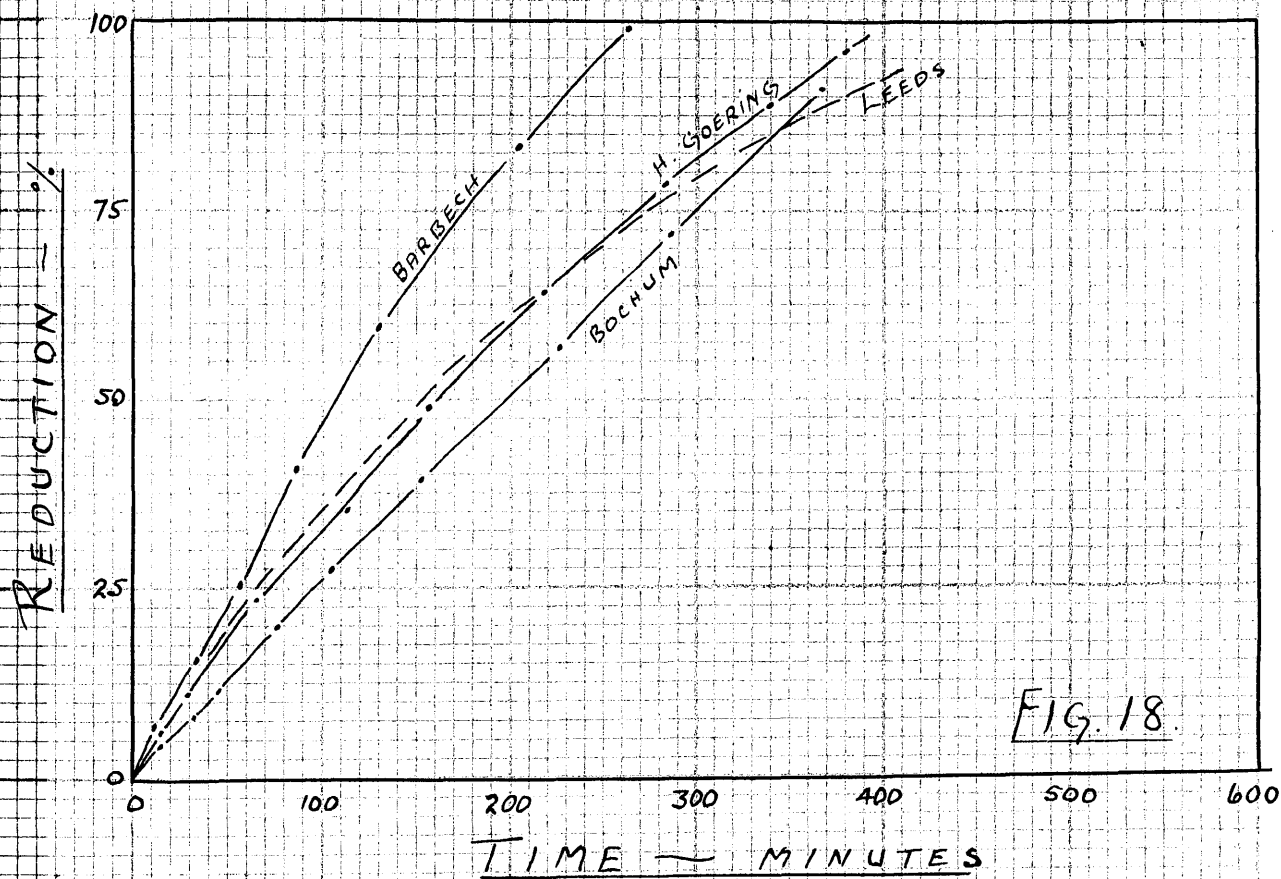


FIG. 18

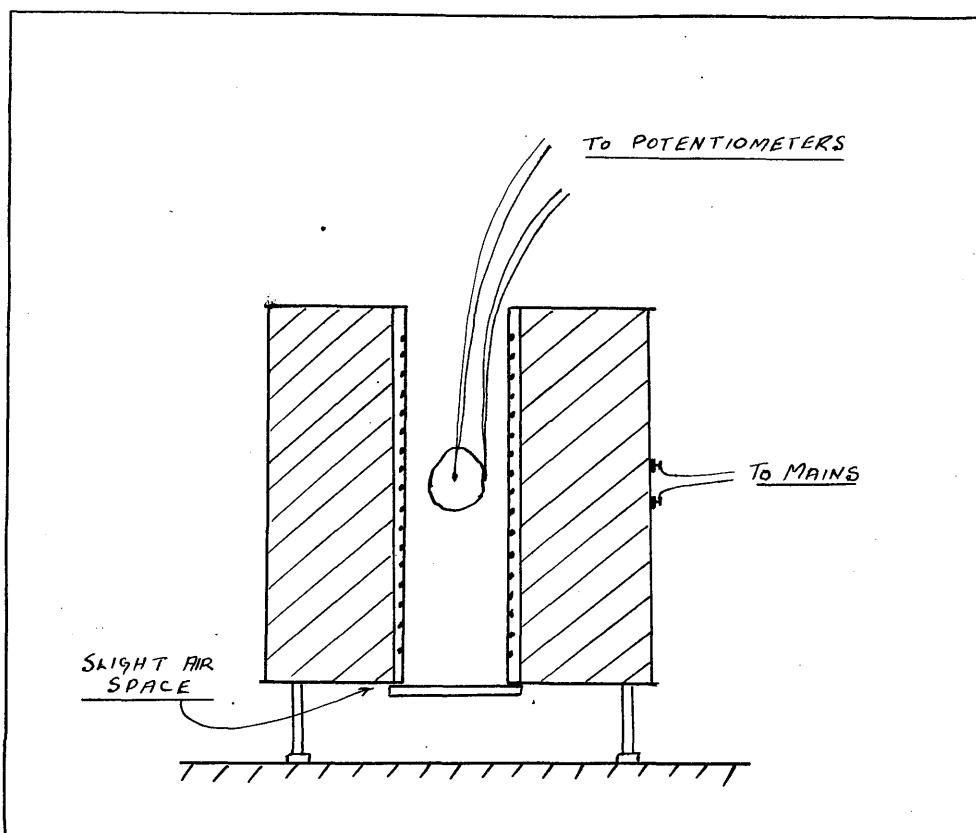


FIG. 19

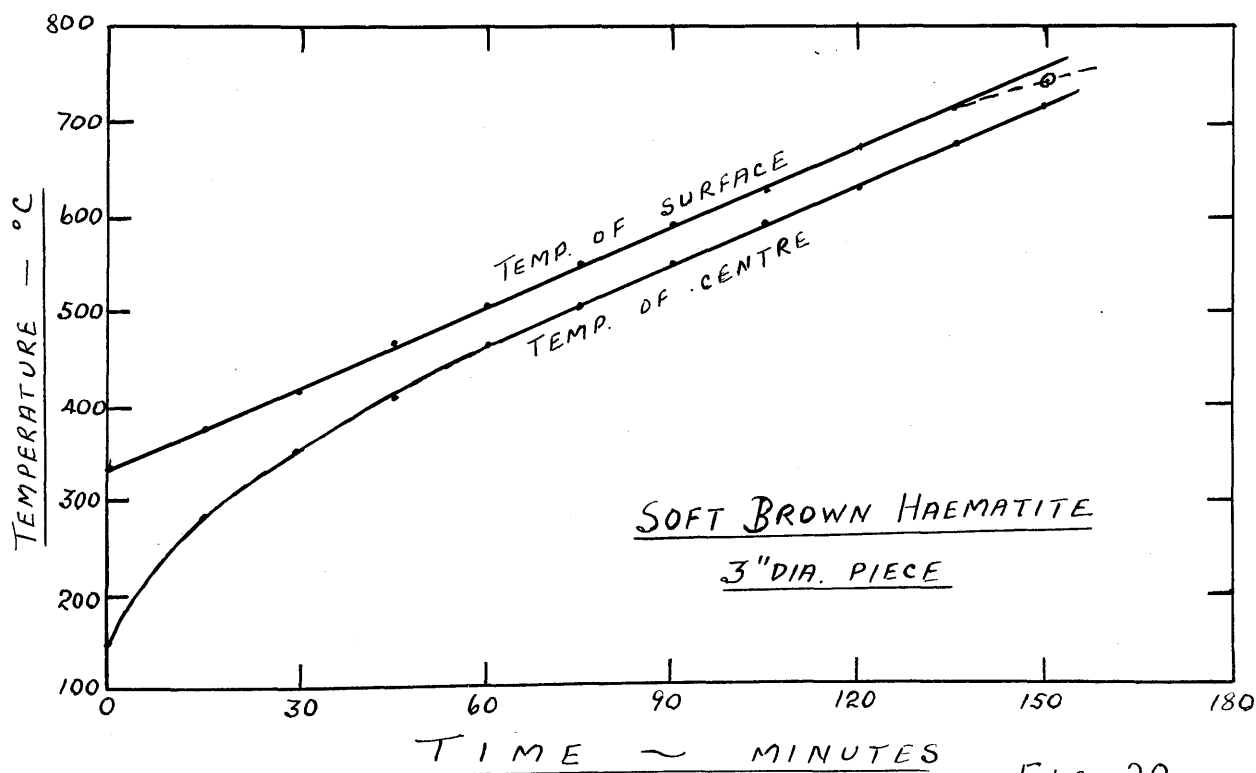


FIG 20

probably about equal to the average British or laboratory sinter or perhaps slightly weaker. The macro structure of these sinters appeared to be good. There was a tendency to glazing on the outside but apart from this the structure was granular and generally did not appear to have been badly melted. It would appear that a better temperature control has been maintained over the German plants than has generally been done in this country resulting in the production of sinter about equal in general quality to our best industrial sinters except in the case of Hermann Goering which is too soft.

Figure 18 shows the reducibility curves of the above sinters. The dotted line for Leeds is included for comparison purposes.

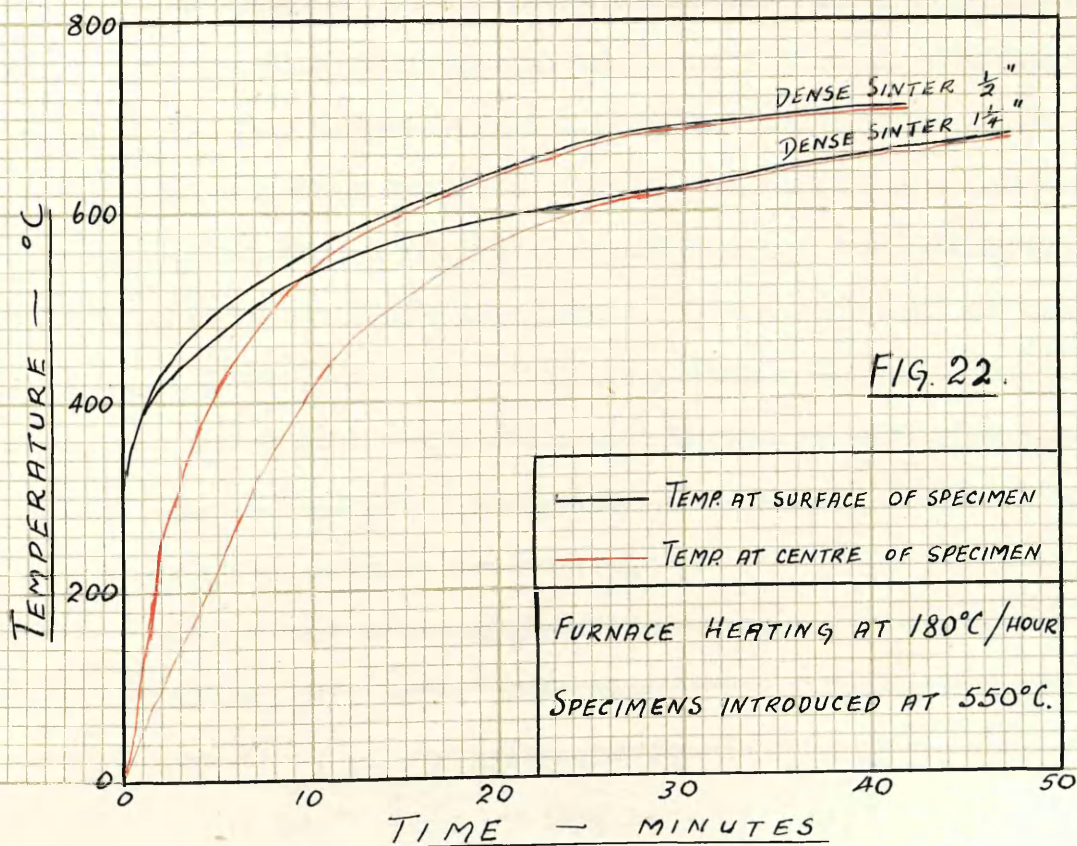
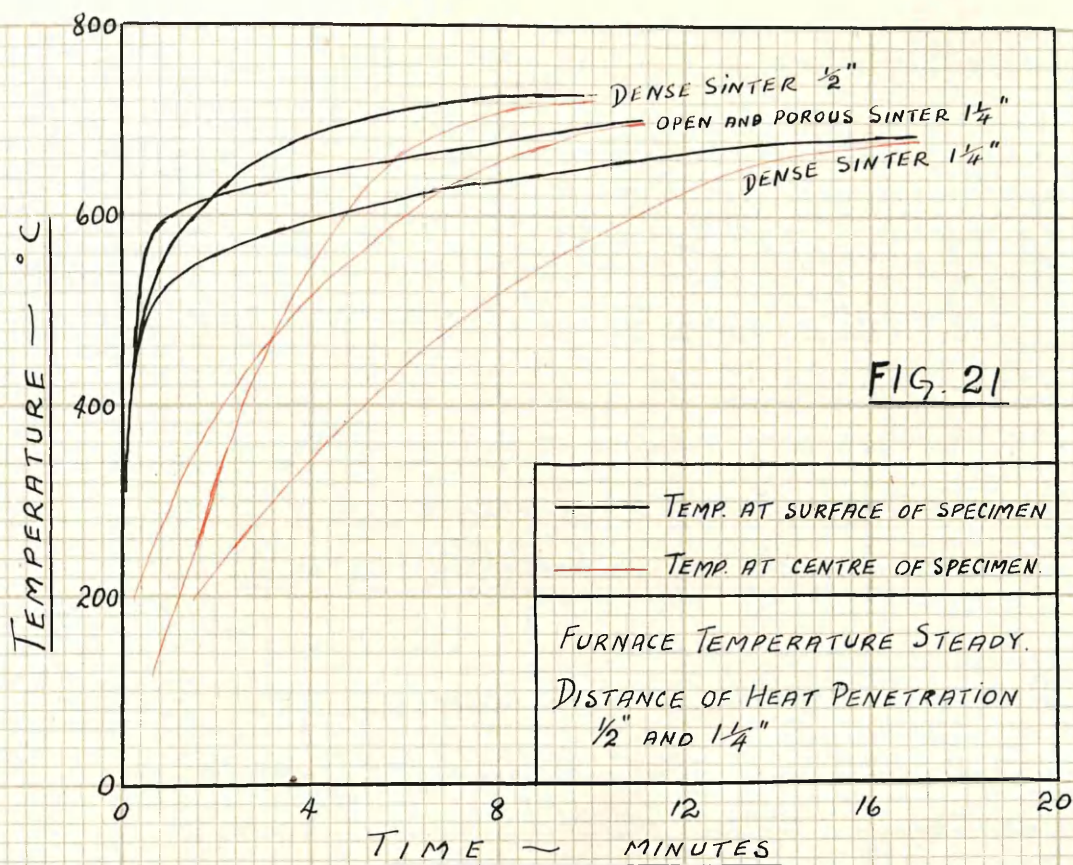
## CHAPTER VII.

### Effect of Rate of Heat Penetration in Ores and Sinters

One of the factors involved in the reduction of ores and sinters is the rate of penetration of heat from the surface to the centre of each piece, to give the temperature necessary for reduction. A test to assess the practical importance of this factor was carried out. The apparatus, shown in figure 19 consists of a resistance wound furnace in which the specimen is suspended by a wire cage. Two thermocouples are attached to the specimen, one at the surface and one in a hole

drilled to the centre. The bottom of the furnace is only partly closed so that there is an air draught up the furnace. The specimen is thus heated partly by radiation and partly by rising hot gases which is similar to the conditions in the blast furnace. Figure 20 shows the results for a soft brown haematite. The specimen was a rough sphere of 3 inch diameter which meant that the heat had to penetrate a distance of  $1\frac{1}{2}$  inches to reach the centre. This was placed centrally in the furnace which was then heated as rapidly as possible to  $350^{\circ}\text{C}$ . after which it was heated at the steady rate of  $180^{\circ}\text{C}$ . per hour. The reason for introducing the specimen when the furnace was cold rather than at  $350^{\circ}\text{C}$ . was that a preliminary run had been done to check if it was centrally placed, by heating to  $800^{\circ}\text{C}$ . and holding there till both thermocouples registered the same temperature. Actually there was a difference of two degrees which has been allowed for in figure 20. Thus having got the specimen centrally placed in the furnace it was not considered advisable to disturb it before the actual test. This test it was considered would give conditions worse than ever encountered in a blast furnace as the rate of heating even in fast driving does not reach  $180^{\circ}\text{C}$ . per hour. Temperature readings on both thermocouples were taken every 15 minutes. It can be seen that within 60 minutes the centre was only  $43^{\circ}\text{C}$ . behind the surface which difference was maintained to above  $700^{\circ}\text{C}$ . when the surface temperature began to fall off, shown by the dotted line,







due to the inability of the furnace to maintain the heating rate. This indicates that while the ore is still in the carbon deposition zone and before it reaches the zone where reduction is rapid, the temperature throughout a 3 inch lump is even enough not to interfere materially with good reduction. It seems probable however that

for larger pieces of about 6 inch diameter or over, there is danger of a great enough temperature lag at the centre to seriously retard the reaction of the reducing gases.

It was thought that the temperature difference between the surface and centre of a piece of sinter would be much less than in an ore due to the macro porosity allowing better heating by convection but tests were carried out to verify this. The first experimental procedure adopted was to lower the piece of sinter with thermocouples attached into the furnace which was at a steady temperature and note the time taken for the centre to reach a temperature near that of the outside.

Figure 21 shows the results obtained in three tests. It will be noted that for a  $2\frac{1}{2}$  inch piece of open porous sinter the temperature at the centre was only about  $5^{\circ}\text{C}$ . below that at the surface after about ten minutes. For a dense sinter the corresponding figures for a  $2\frac{1}{2}$  inch piece were  $5^{\circ}\text{C}$ . after fifteen minutes, and for a one inch piece,  $5^{\circ}\text{C}$ . after nine minutes. Figure 22 shows the result of introducing the specimen into the furnace at about  $550^{\circ}\text{C}$ . and heating at about  $180^{\circ}\text{C}$ . per hour. When

conditions had steadied up and heating of the outside was constant, the temperature difference in the case of a  $2\frac{1}{2}$  inch piece of dense sinter was only 6 to 7°C. while that of a one inch piece was about 4 to 5°C.

These results indicate that while the temperature lag in the centre of a piece of ore may or may not be of importance depending on its size, in the case of a sinter it is quite definitely negligible, due no doubt to heat carried into the macro pores by the gases.

## CHAPTER VIII

### Production of Sinters from Pure Ferric Oxide.

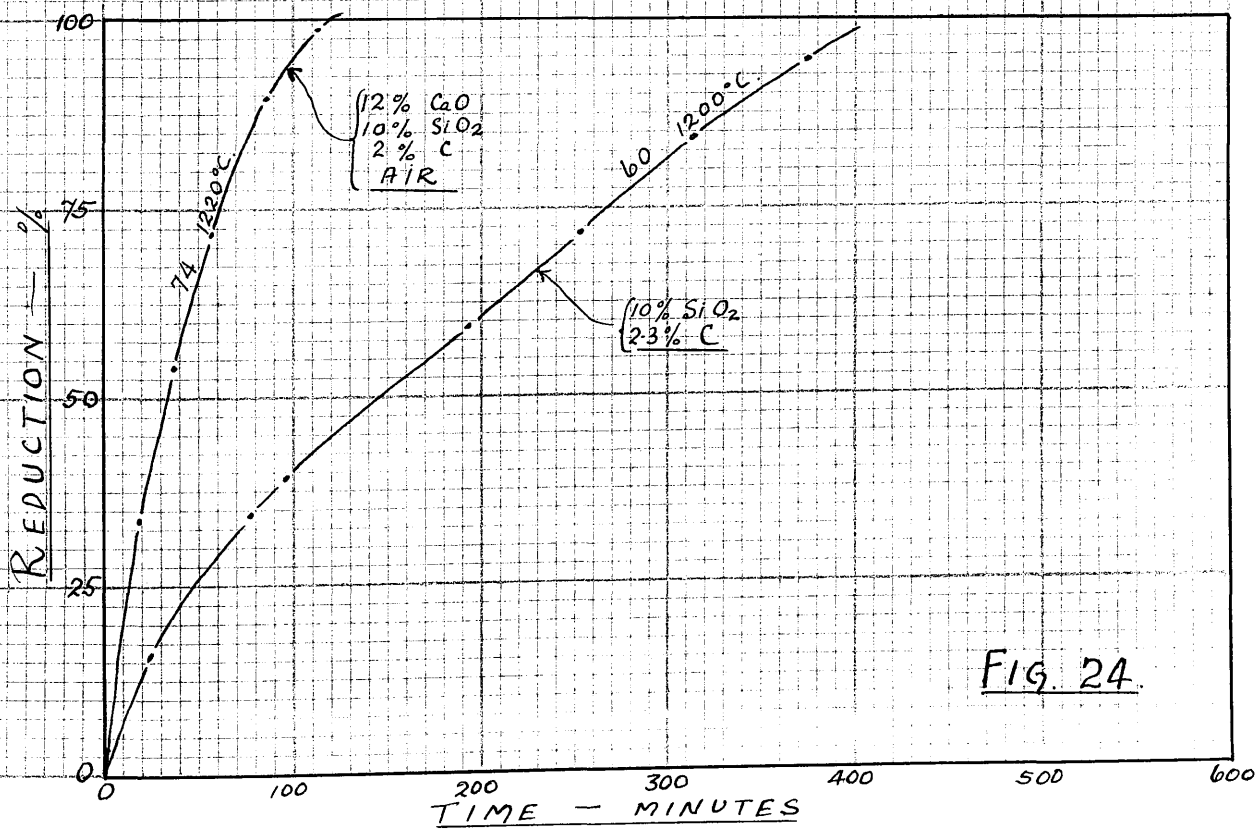
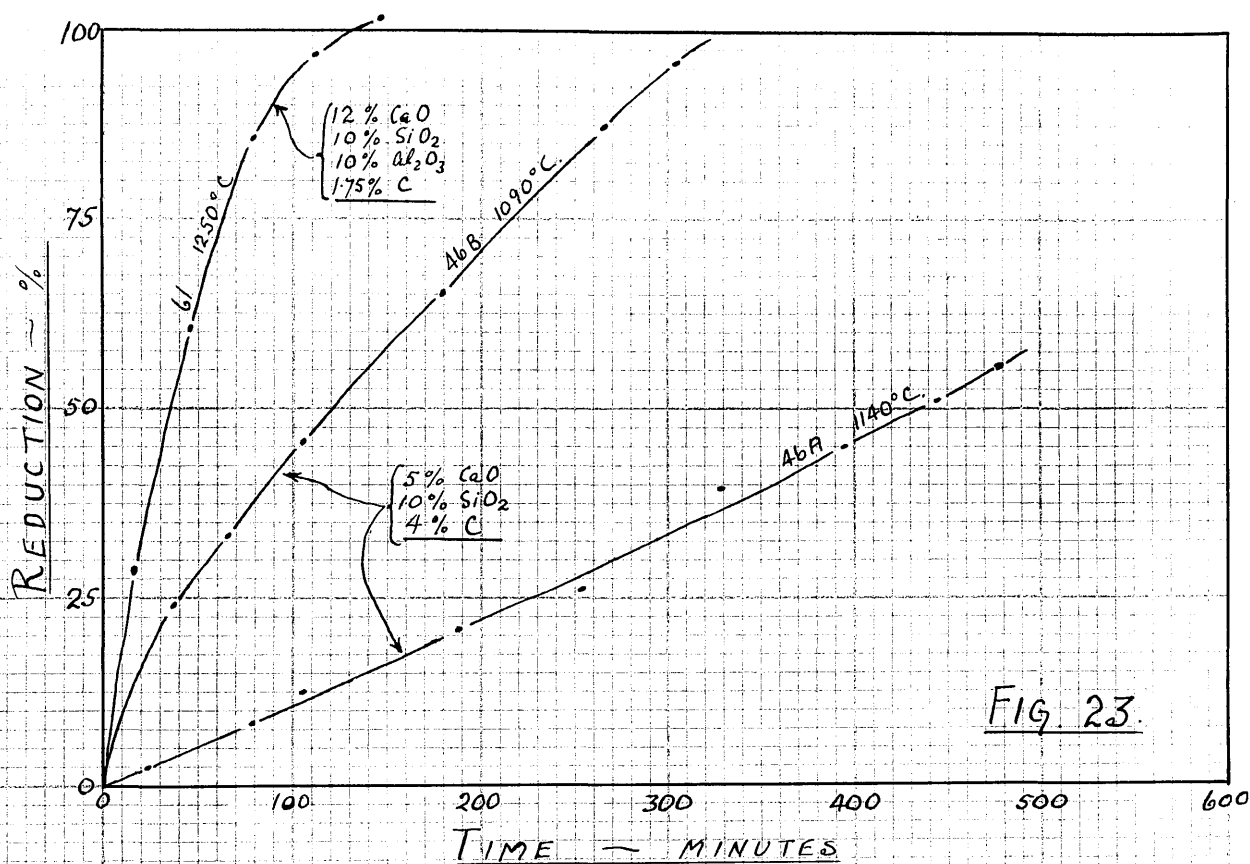
An attempt was now made to produce a laboratory sinter as strong as an industrial sinter but with reducibility as good as or better than ores. Sinters were made from pure ferric oxide with varying additions of carbon, silica, lime and alumina, and at a range of temperatures as shown in Table VIII. Two per cent carbon was generally employed as it was considered that this, while being sufficient to cause enough reduction for fairly rapid sintering, would not produce much ferrous oxide, with a consequent lessening in the liability to form low melting point compounds such as fayalite and hedenbergite. In most cases the lime-silica ratio was greater than unity. This was done in an attempt to raise

TABLE VIII

Sinter No.	%C	%SiO <sub>2</sub>	%CaO	%Al <sub>2</sub> O <sub>3</sub>	Temp °C	Sintering Time mins.	Redn. Time Mins.		Method of Packing	Remarks.
							To 70%	To 95%		
46	4	10	5	-	1050	10			T	Poorly fritted, weak.
46A	4	10	5	-	1140	10	(570)	-	T	Glazed, very hard.
46B	4	10	5	-	1090	10	197	300	T	Strength poor.
53	2	10	12	-	1170	7	48	92	R	Strength poor.
55	2	10	12	-	1200	7	62	139	R	Strength fairly good.
56	2	10	12	-	1250	7	111	217	R	)
57	2	10	12	-	1300	7	100	174	T	) Strength very good,
59	2	10	12	-	1340	7	150	252	T	) increasing with
64	2	10	12	-	1320	7	133	231	T	) temperature.
65	2	10	12	-	1320	7	150	284	R	)
58	1.75	10	12	10	1200	7			T	Strength fairly good.
61	1.75	10	12	10	1250	7	57	103	T	)
65	1.75	10	12	10	1320	7			T	) Strength good.
62	2.3	10	-	-	1160	7			T	)
60	2.3	10	-	-	1200	7	250	385	T	Made in air.
74	2	10	12	-	1220	7	57	102	T	

T Mixture tapped down into crucible.

R Mixture rammed down into crucible.



the melting point of any silicates present by replacing as much "FeO" as possible by CaO. It was also thought that the free "FeO" would reduce more easily than the combined "FeO". The ratio could not be allowed greatly to exceed unity because of the danger of dusting due to the formation of calcium orthosilicate ( $2\text{CaO} \cdot \text{SiO}_2$ ). The time of sintering was kept to a minimum in order to approximate to industrial conditions. Some sinters such as numbers 46, 46A, 46B, 60 and 62 were made from a mixture which it was thought would give a poor sinter similar to many industrial sinters and thus provide a basis for the assessment of the advantages of the low carbon and high lime theory stated above. Sintors number 46, 46A, and 46B were made with a mixture containing 4 per cent carbon which would reduce most of the iron to the ferrous state, and with a silica content in excess of the lime. As can be seen from the table a sintering temperature of  $1050^\circ\text{C}$ . resulted in unsatisfactory bonding while  $1140^\circ\text{C}$ . gave a strong sinter but with poor reducibility. An intermediate temperature of  $1090^\circ\text{C}$ . gave a sinter with poor strength, but with good reducibility. The curves for both these sinters can be seen in figure 23. From these results it appears that a usable sinter could be made under critical temperature control at about  $1100^\circ\text{C}$ . As it is quite impossible to control the temperature of an industrial sintering plant with such accuracy, and the majority of industrial sinters contain silica in excess of the lime, it is not surprising

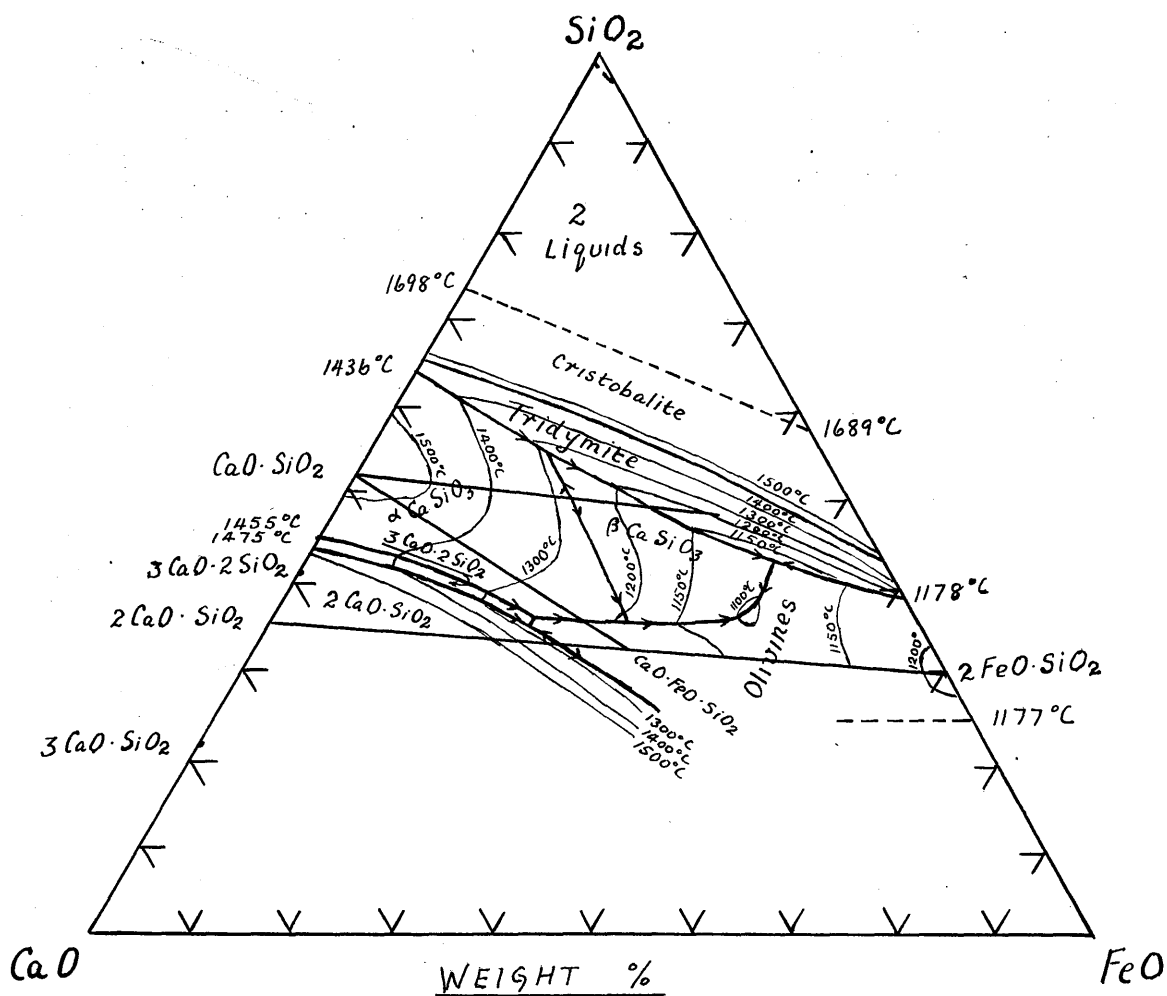


Fig. 25.

BOWEN AND OTHERS<sup>24</sup>

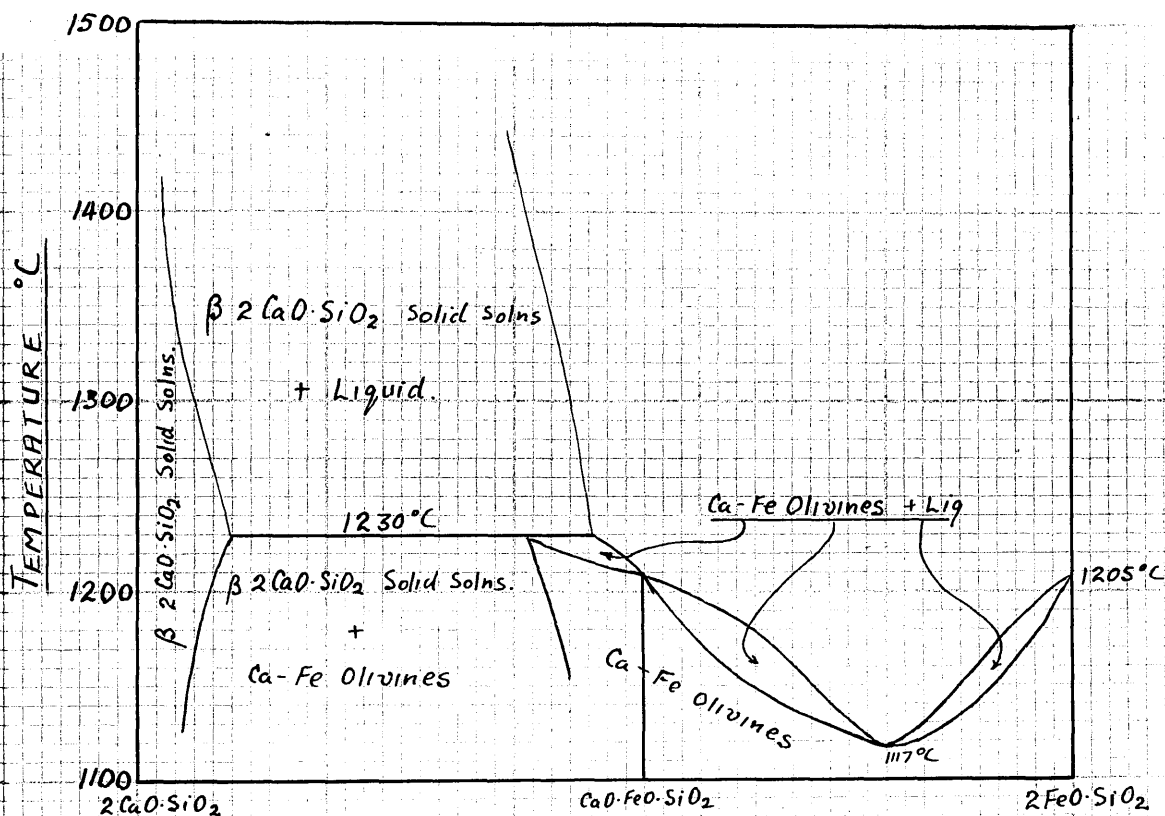


FIG. 26.

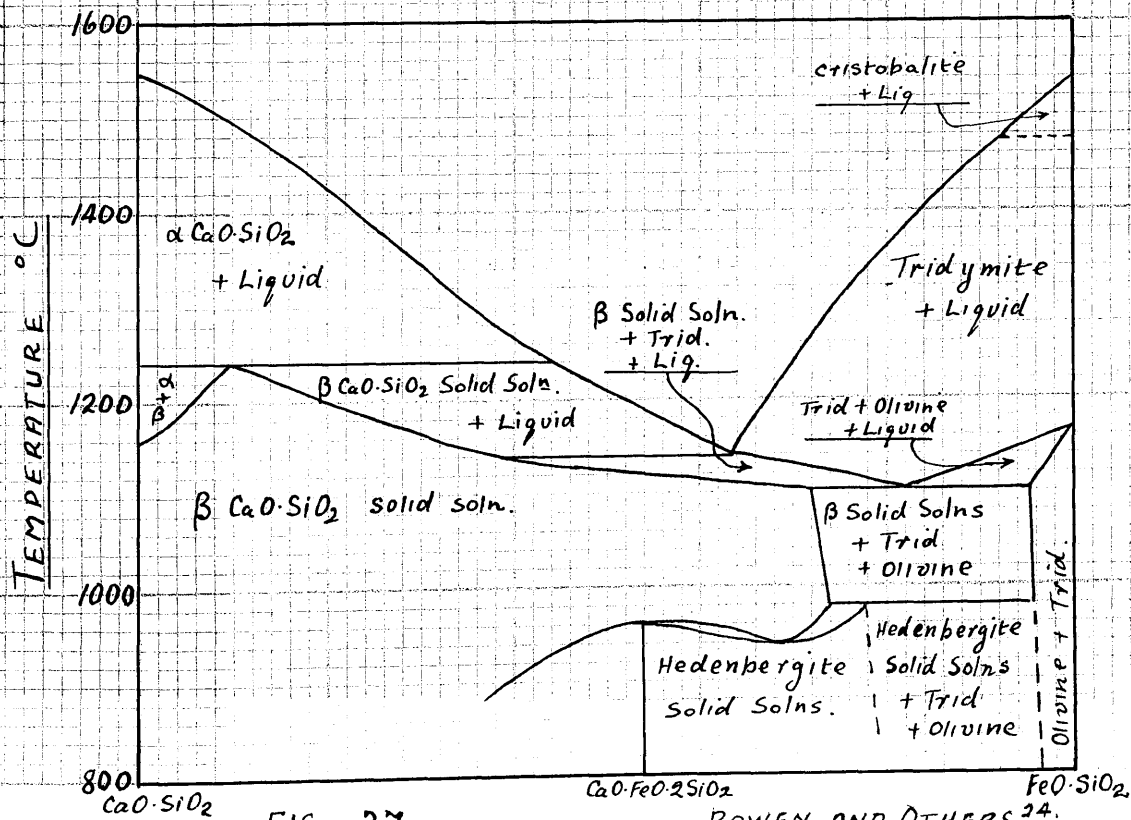
BOWEN AND OTHERS<sup>24</sup>.

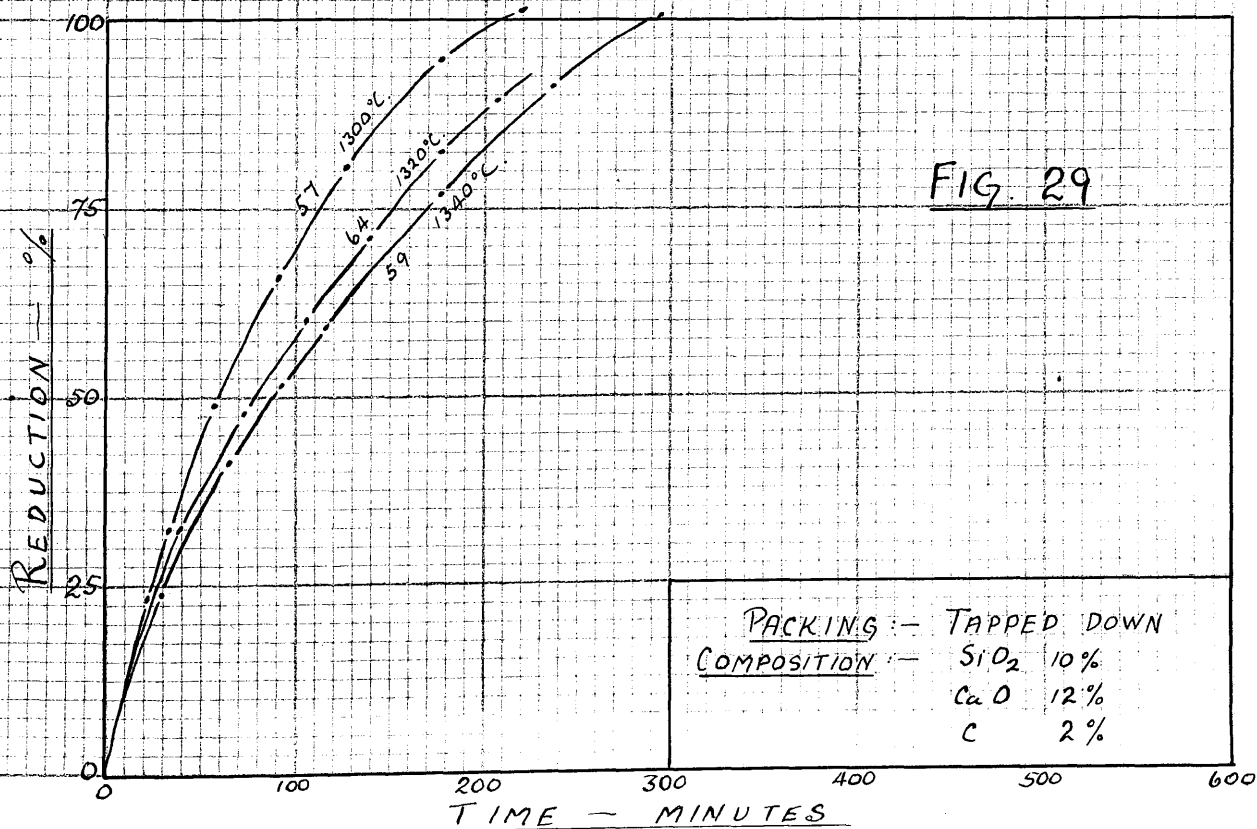
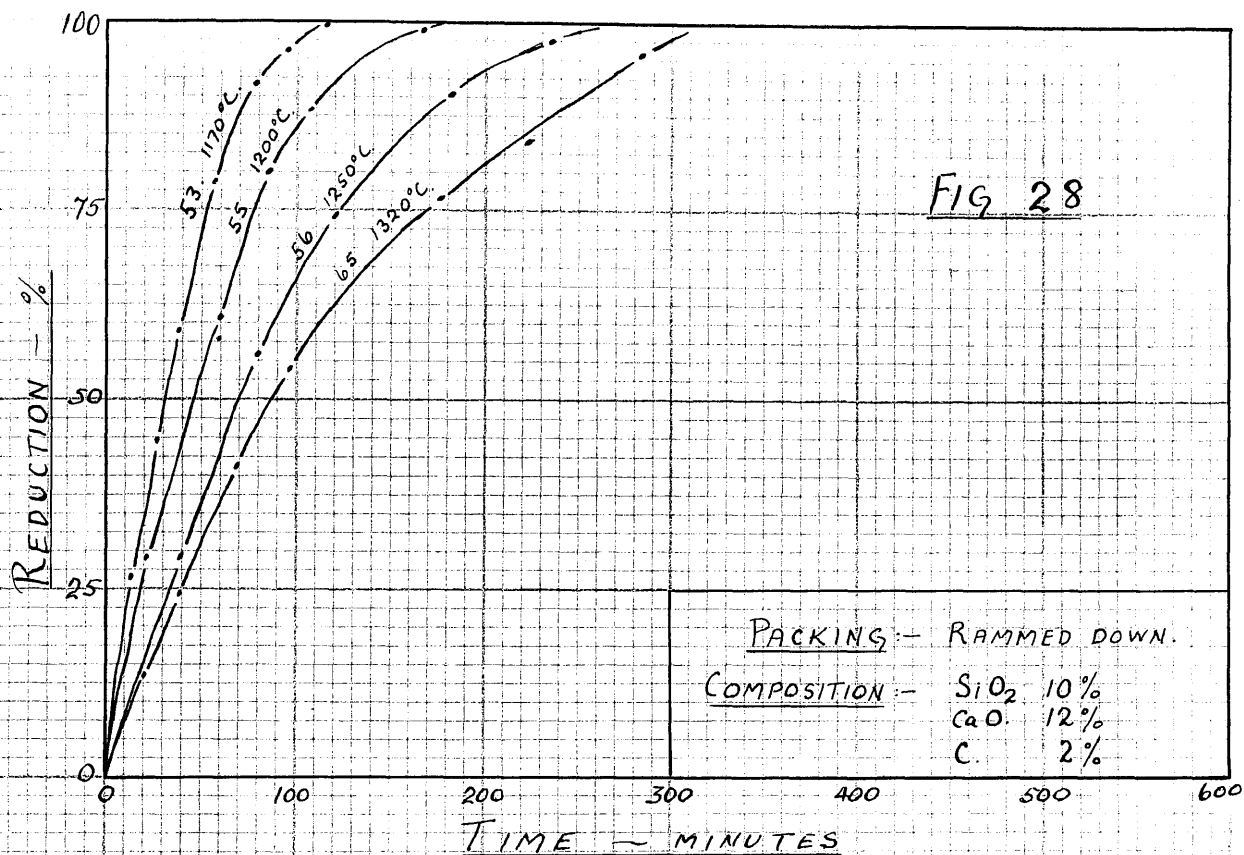
FIG. 27.

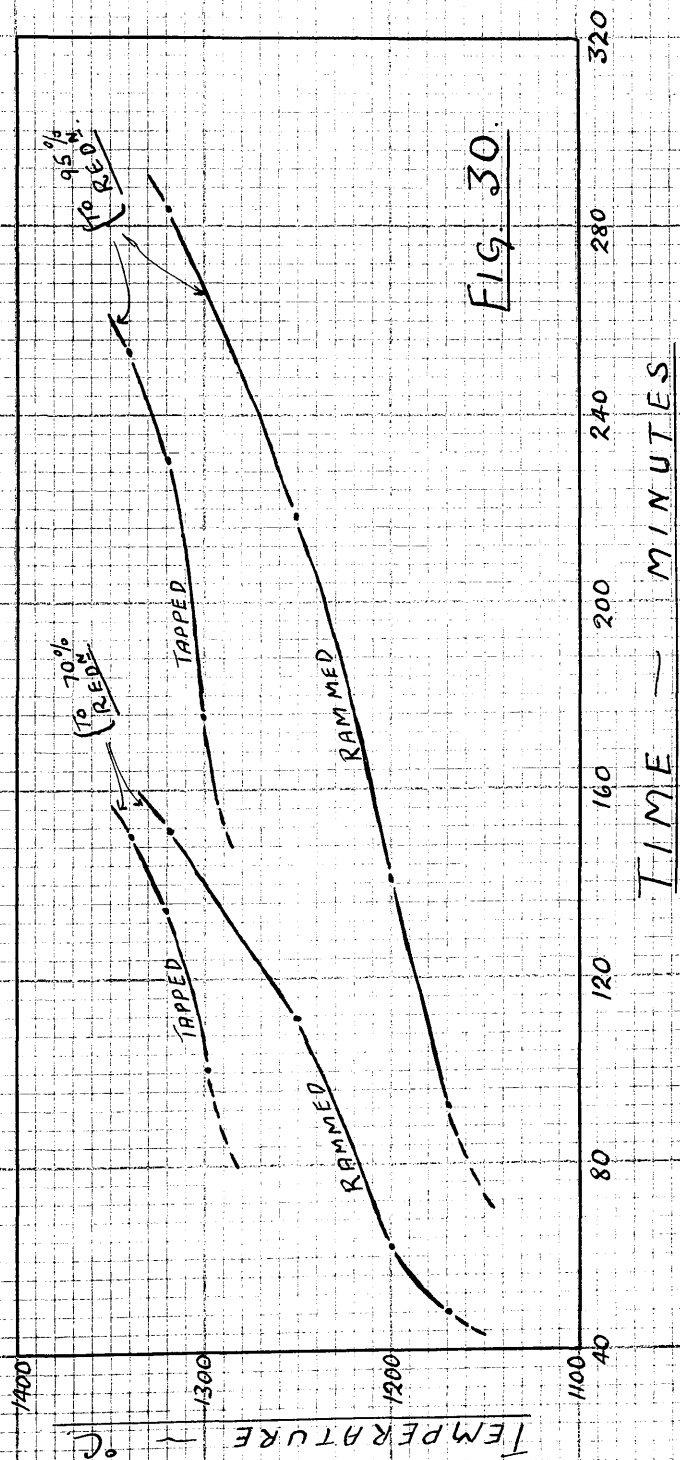
BOWEN AND OTHERS<sup>24</sup>.

that these are all characterised by poor reducibility. It is more difficult to assess the exact effect of the carbon in industrial sinters. At the start of the process the carbon is always above 4 per cent but it is difficult to assess how much of it reduces the oxides of iron and how much is merely burnt by the blast. It is not even possible to estimate it by analysis of the final product since considerable oxidation must occur during cooling while the blast is still being sucked through the bed.

Referring back to Table I it can be seen that in the absence of carbon the pure iron oxide bond starts to form slowly at about  $1200^{\circ}\text{C}$ . With carbon present it forms at a slightly lower temperature but the rate of formation is slow. From this it follows that in the above three sinters the pure iron oxide bond played little or no part in the sintering together of the particles. The  $\text{CaO} - \text{FeO} - \text{SiO}_2$  ternary system, figure 25 with the  $2\text{CaO} \cdot \text{SiO}_2 - 2\text{FeO} \cdot \text{SiO}_2$  and the  $\text{CaO} \cdot \text{SiO}_2 - \text{FeO} \cdot \text{SiO}_2$  pseudo-binary joins, figures 26 and 27 make clear what has taken place. "FeO" has combined with the CaO and excess  $\text{SiO}_2$  to form a ceramic bond with a composition probably between Ca-Fe olivine ( $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$ ) and fayalite ( $2\text{FeO} \cdot \text{SiO}_2$ ) and with a melting point of just over  $1100^{\circ}\text{C}$ . Thus in making sinter 46B the temperature of  $1090^{\circ}\text{C}$ . was not high enough to cause slag formation and hence the poor strength and good reducibility results, but in sinter 46A the temperature was above the melting point of the slag matrix resulting in a strong sinter with poor reducibility







due to the sealing of the micro pores by slag.

Having shown the disadvantages of high carbon and low lime, the carbon content was now reduced to 2 per cent and the lime increased to 12 per cent to minimise the amount of silica free to form low melting point compounds. The resulting series of sinters in Table VIII showed that strength became fairly good when a temperature of  $1200^{\circ}\text{C}$ . was used for sintering which suggests the presence of the iron oxide bond since as shown previously, this is the temperature at which such a bond begins to form. This was accompanied by excellent reducibility. As the temperature of sintering was progressively increased to  $1340^{\circ}\text{C}$ . the strength showed a corresponding increase while the reducibility steadily became slower. It was found that the original packing of the mixture in the crucible had a definite effect on the product. When the powder was packed down merely by tapping the crucible on the bench, the reducibility was better and the strength poorer than when the powder was rammed down into the crucible with a pestel, always provided the same sintering temperature was used. The effect of varying temperatures and the effect of both methods of packing can be studied in figures 28 and 29, and in figure 30 which shows the temperature of sintering plotted against the time taken to reach 70 and 90 per cent reduction. This figure however does not take the strength into account and as a result wrong conclusions might easily be drawn from it. It might be assumed that since for any given temperature

the sinters made from the rammed mixtures reduce very much slower than those from the tapped mixtures, the latter are the more desirable. This is not the case as the rammed mixtures produced a very much stronger sinter. Indeed sinters of similar reducibility invariably had similar strength, so that if the mixture was rammed instead of tapped down, a sinter as good in all respects could be made at a considerably lower temperature. It is interesting to note that these sinters compare favourably with the ores in figure 15 both in respect of reducibility and strength.

The obvious success of lime additions to the sinter mixture led to the making of three further sinters, the only difference being the addition of 10 per cent alumina. The strength of these was similar or if anything perhaps slightly weaker than the previous series when made at corresponding temperatures. The reducibility was improved as shown by the curve for sinter 61 in figure 23.

Two further sinters, numbers 62 and 60 were made containing 10 per cent silica and 2.3 per cent carbon but without any lime or alumina, with the object of obtaining more accurate information on the precise benefit of lime additions. 2.3 per cent carbon was used instead of 2 per cent since due to the lack of lime the ferric oxide percentage was also higher. Their reducibility, as shown by the curve for sinter 60 in figure 24, was poor compared to those containing lime. It may be noted however that it is considerably better than sinter 46A

which contains 5 per cent lime and was made at a temperature  $60^{\circ}\text{C}$ . lower. Number 46A contained 4 per cent carbon which would give rise to considerable quantities of ferrous oxide while number 60 only contained 2.3 per cent. The improvement in the latter case must therefore be attributed to the different carbon contents. It thus seems that the carbon content may be as important if not more so than the lime addition.

As all sinters so far had been made in vacuum, it was now thought advisable to check the effect of making them in air. Several such sinters were made and tested as seen from the results of sinter 74 in Table VIII and figure 24, there was little if any change in reducibility and the strength was unaffected. As a result of these tests, all subsequent sinters were made in air.

When adding lime, the danger of dusting due to the 10 per cent volume change when  $\beta 2\text{CaO}\cdot\text{SiO}_2$  changes to the  $\gamma$  form at  $674^{\circ}\text{C}$ ., must be borne in mind. Several tests were made to discover the lime:silica ration necessary to cause dusting. The lime:silica ratios by weight of the silicates likely to occur are as follows:-

$\text{CaO}\cdot\text{SiO}_2$	0.933
$3\text{CaO}\cdot 2\text{SiO}_2$	1.4
$2\text{CaO}\cdot\text{SiO}_2$	1.866

To obtain the limiting ratio above which dusting took place, the following sinters shown in table IX were made.

TABLE IX

Sinter No.	Temp. °C.	Time mins.	%C	%CaO	%SiO <sub>2</sub>	Remarks *
98	1250	7	2	14	10	Just dusted
97	1250	7	4	12	10	Dusted
99	1200	7	4	10	10	Part dusted
49	1200	7	4	10	10	Not dusted

\* In no case was proper dusting observed. In this Table dusted must be taken as meaning disintegration with some fines and some pieces up to a size of  $-\frac{1}{4} + \frac{1}{8}$  inch produced.

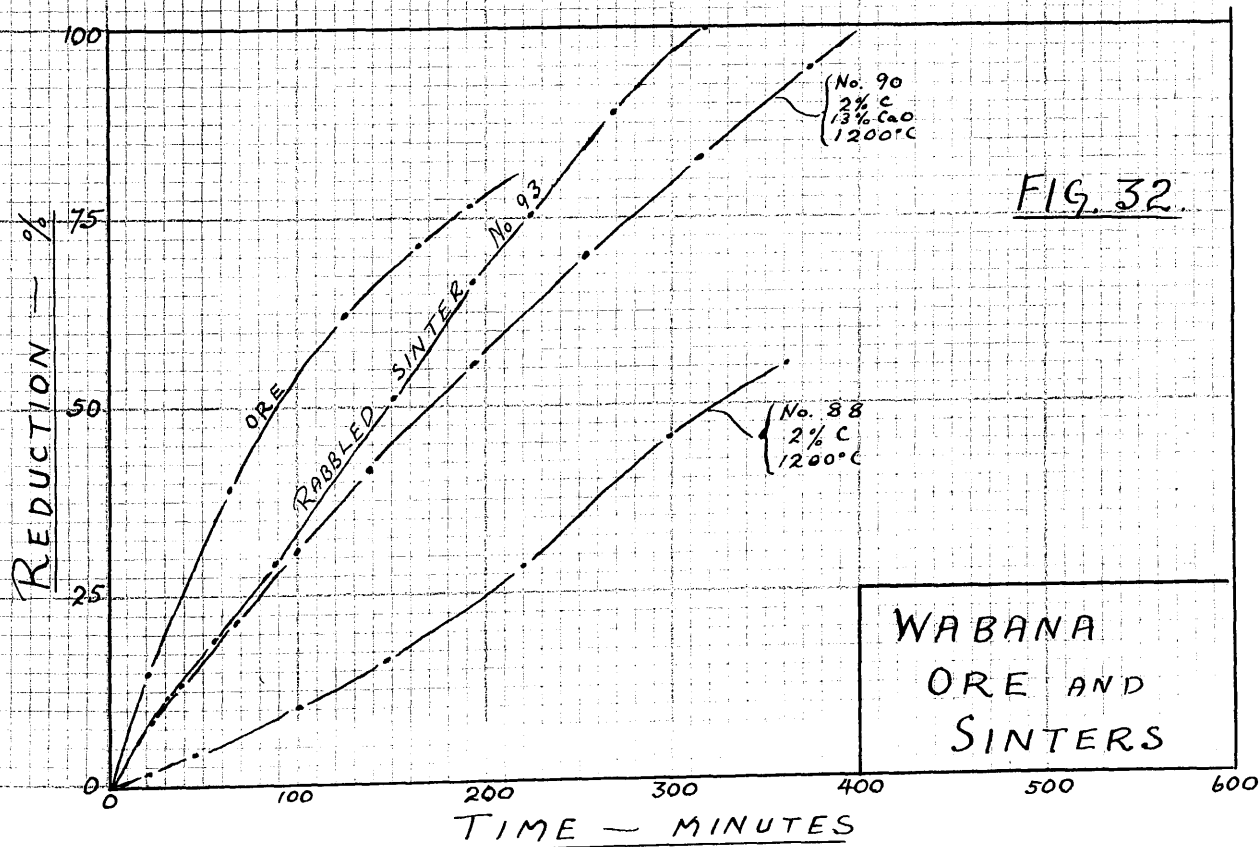
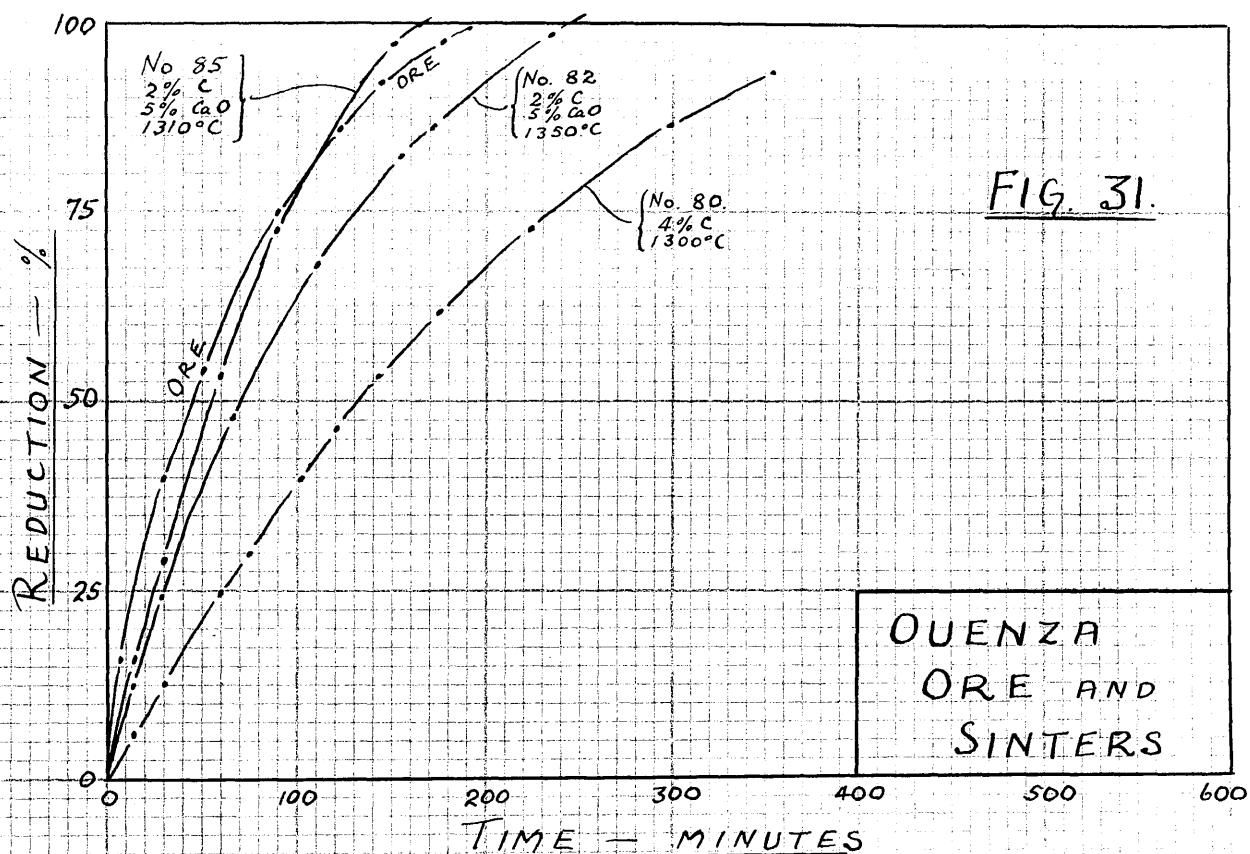
It had already been observed that sinters of 2 per cent carbon, 12 per cent lime and 10 per cent silica showed no sign of dusting so for the first trial with 2 per cent carbon the lime content was increased to 14 per cent. The resulting sinter when cold disintegrated after about ten minutes, but did not dust badly. From this it was concluded that the limiting ratio must be about 14 per cent lime to 10 per cent silica which is 1.4. Theoretically there should be no dusting with this composition as only  $3\text{CaO} \cdot 2\text{SiO}_2$  should be present. It must be remembered however that with 2 per cent carbon the reduction of the ferric oxide proceeds beyond the magnetite stage so that a little ferrous oxide will be present. This will have the effect of reducing the silica free to react with the lime. As the amount of silica is limited the reactions will tend to equilibrium between  $\text{CaO} \cdot \text{SiO}_2$  ( or  $3\text{CaO} \cdot 2\text{SiO}_2$  ),  $2\text{CaO} \cdot \text{SiO}_2$  and  $2\text{FeO} \cdot \text{SiO}_2$ . There is not much free "FeO" present with 2 per cent

carbon and so it would be expected that most of the silica would go with the lime. This appears to have been the case since dusting took place only at a slightly lower ratio than would have been expected without the presence of "FeO". That is it took place at a ratio of 1.4 instead of over 1.4. When 4 per cent carbon was used the position was quite different. Dusting took place readily with 12 per cent lime and 10 per cent silica but with 10 per cent lime and 10 per cent silica one specimen did not dust while another just fell apart into fairly large pieces with very little dusting. From this it was assumed that the limiting ratio was unity. This shows very clearly the effect of ferrous oxide. Four per cent carbon in the sinter mixture reduces all the iron to the ferrous state. Thus since there was 76 per cent  $\text{Fe}_2\text{O}_3$  present in the mixture, the resulting "FeO" content of the sinter allowing for carbon and oxygen loss will be 75.7 per cent. It seems that this "FeO" has prevented about 3 per cent silica from reacting with the lime thus allowing the ratio to reach 10/7 or just over 1.4 resulting in slight disintegration. The importance of this in sintering ores high in lime is obvious. If a sound sinter is to be produced the carbon must be kept to a minimum.

From a study of the work carried out so far it becomes obvious that the rate of diffusion through solids is probably one of the most important factors in the reducibility of ores and sinters. This diffusion may be

divided into two stages. First there is the diffusion of the reducing gas into the macro and micro pores which will be fairly rapid although slowed down to some extent by the fact that all the carbon dioxide formed must diffuse out again. Also the nitrogen will continually diffuse in and out merely acting as a diluent and consequently a hindrance to the process of reduction. This however only reaches the surface of the solid oxides and consequently to effect reduction in depth diffusion in the solid state becomes operative. This takes place when the outer layers become reduced by the carbon monoxide thus setting up an oxygen concentration gradient into the solid. The oxygen will then start to diffuse outwards. As diffusion in the solid state is always a slow process the distance between the open pores becomes very important. In a lump of ore which generally has good micro porosity this distance is small which is one of the factors contributing to the good reducibility of ores. In the case of industrial sinters micro porosity is low due to much melting and glass formation, resulting in the reducing gases having to diffuse through the solid for a much greater distance before complete reduction can be effected. This is reflected in the poor results obtained for these sinters. Sintors made in the laboratory confirmed these views. So long as precautions were taken against melting the reducibility was good. The effect of this micro porosity was also very obvious when polishing sections. Industrial sinters polished easily but laboratory sinters which had





not been melted gave considerable trouble in drying as already mentioned due to moisture slowly oozing out of the pores.

## CHAPTER IX

### Production of Laboratory Sinters from Ores.

Having established the main factors leading to poor reducibility and the means of avoiding them, attempts were now made to make good sinters from natural ores. A sample of Ouenza was obtained from a local sintering plant. A rough grading analysis gave the following results.

	+ 10 mesh,	6.03%
- 10 mesh,	+ 20 " ,	23.75%
- 20 " ,	+ 50 " ,	33.12%
- 50 " ,	+ 100 " ,	34.55%
- 100 " ,		2.55%

As this was very coarse compared to the ferric oxide previously used, there was some doubt about producing as good a sinter. The first trials, using the ore with 2 per cent carbon at temperatures of 1200 and 1250°C., produced a sinter which was too weak especially to abrasive stress. Sinter number 80, made with 4 per cent carbon at 1300°C. had fairly good strength but the reducibility was unsatisfactory as shown in figure 31. Accordingly the next sinters to be made contained 5 per cent

lime and the carbon content was reduced 2 per cent. Sinters 82 and 85 made at 1350 and 1310°C. respectively, show very satisfactory results from this change. In figure 31 it can be seen that sinter 85 gave a reducibility curve slightly better than the ore. It is thought however that this may be false due to a slightly higher rate of carbon deposition on the sinter. It is certain however that if the sinter is not better than the ore, it is not much poorer. The strength of sinters 82 and 85 was as good if not better than the ore which is fairly strong as ores go. It would be interesting to know the result of a complete investigation on the effect of grading the sinter mixture for use in the ordinary sintering machine. Close grading should give maximum voids which in turn would lead to more even air suction and temperature over the bed. If the variations in temperature between different parts of the bed could be reduced by this means, better control and a much more uniform sinter would result. In this respect it must be remembered that the lowest temperature attained in any part of the bed must be as high as the minimum sintering temperature, from which it follows that if there is too great a variation in the bed some parts will be liable to be fused and others not sintered.

While the above confirmed the benefits of low carbon and added lime, it was considered desirable that tests should be carried out with an ore containing more silica than Ouenza which contains only 3 per cent. Accordingly

Wabana, containing 10.8 per cent silica and 3.6 per cent lime was chosen. The first sinters made from this ore with 4 per cent carbon at 1250°C. melted almost completely and with 2 per cent carbon at the same temperature considerable melting took place. It was found that the temperature for this ore was fairly critical when mixed with carbon only. If it was much below 1200°C. the strength was poor and if it was much in excess, melting took place presumably due to Olivines. The addition of 13 per cent lime to the sinter mixture resulted in the considerable improvement in reducibility shown in figure 32, in which lime has been added to sinter 90 but not to 88. Another valuable effect of the lime addition was that satisfactory sinters could be produced over a temperature range from about 1160 to 1250°C. which was considerably better than without lime. The form of the graph for sinter 88 is interesting. It starts slowly, then gradually rises more steeply but finally starts to fall off again. This is similar to the result for the Ford sinter. When these sinters were examined under binoculars (X 15) it was noticed that both seemed to be quite good internally but the surface was covered with a thin film of melted material. It is probable that the poor reducibility at the beginning is due to this glassy film, but when it has been reduced it will not offer so much resistance to gas penetration hence the gradual improvement followed later by the natural falling off of the rate:

Table X gives the general data on the above sinters.

TABLE X

Sinter No.	Ore	Temp °C	Time mins	%C	%CaO	Redn. Time		Remarks.
						70%	95%	
80	Ouenza	1300	7	4	-	210	370	Very strong " " Strength useless reducibility excellent.
82	"	1350	7	2	5	122	210	
83	"	1320	7	4	5			
84	"	1260	7	4	5			
85	"	1310	7	2	5	85	142	Very strong.
100	"	1250	7	2	5			-
88	Wabana	1200	7	2	-	(500)		Very strong.
90	"	1200	7	2	13	250	375	Strength similar to ore.
93	"	1220	15	4	13	204	295	Made in gas muffle Hand rabbled Strength variable
93A	Nassington	1220	15	4	13			

In order to check the effect of particle size on sintering temperature some Ouenza ore was ground to - 50, + 100 mesh and a sample taken. This was sintered at various temperatures with 5 per cent lime and 2 per cent carbon. It was found that the strength of sinter number 100 made at a temperature of 1250°C. was of similar strength to number 85 made at 1310°C. from the coarser ore. It would appear that in the sinters made from the coarser ore the larger pieces, probably those above 20 mesh, prevented intimate contact to such an extent that a temperature of about 60°C. higher was required to give

similar strength.

All sinters so far had been made in a platinum crucible in a vertical tube furnace. The small scale of these tests and the fact that the maximum distance of heat penetration was  $\frac{1}{2}$  inch raised some doubt about the success of applying the principles on a larger scale. A small gas fired muffle furnace of the type in which the flame plays over the inside of the roof arch, was available and so some tests were carried out in it. A thin steelplate container was used to hold the sinter mixture which consisted of ore, lime and carbon. Mixtures 93 and 93A are examples of the compositions and temperatures employed. The furnace was heated to a steady temperature. The container, filled to a depth of about four inches, was placed in the furnace. After about five minutes, the charge was rabbled to assist heat penetration. Considerable care was necessary during this operation otherwise much of the fine material was liable to be blown out of the container by the blast. Rabbling was repeated at about three minute intervals until a total sintering time of fifteen minutes had elapsed when the container and sinter was withdrawn. The sinter was mostly in pieces between half and one inch in size except round the sides of the container where it formed a continuous layer. About 75 per cent of the mixture was sintered there being an unsintered cone left in the centre which was probably due to inefficient rabbling. The strength was variable but that of the small pieces was as good as the ore. The

test was repeated without rabbling in order to assess its value in assisting the penetration of heat. The product showed melting to have taken place on the surface under which there was a half inch layer of sinter. The remainder of the charge was still in powder form proving the necessity for rabbling. It was thought that with more efficient rabbling and a slightly higher temperature, the sintering time could be reduced to the order of about seven minutes. The reducibility of sinter 93 was tested and is shown in figure 32. It is not as good as the ore and from the curve it appears that carbon deposition has taken place from about 150 minutes onwards.

These tests show that great improvement is possible on the present sinter plant technique with a consequently improved product. Whether or not it will prove practicable to alter the existing methods and plant without making the project economically unsound remains for industry to find out. Several changes however could be made without much trouble. Separate bedding bins for different types of ore would make it possible to dilute those which were easily fusible like Wabana, with those which have a wide sintering range like Ouenza. The silica content could be easily calculated and hence the optimum amount of lime to be added could be estimated. The only expense involved if this was adopted would be for bedding bins and for efficient mixing plant such as a tube mill which would incidently do some crushing. A second alteration would be the incorporation of crushing

and grading plant. It has been shown that finer particle size permits a lower sintering temperature which is of great importance with easily fusible ores. The temperature control on the present industrial plant however is so vague that it is possible that this improvement would not be economically sound till improved plant is used. Also the danger of too fine a charge preventing even suction with consequent channeling and hot spots has to be remembered. The use of low carbon with the object of forming as little ferrous oxide as possible is difficult as long as the plant uses the carbon for the dual purpose of reduction and the provision of heat.

To produce ideal sinter it would of course be necessary to design a new machine or at least make considerable alterations to the present types. The considerable extra expense of such a plant would have to be recovered in reduced blast furnace costs. Blending of sinter and ore would be important. If variable types of ore were used and two furnaces were in operation, it should be possible to run one on fast reducing ore and sinter and the other on slow reducing ore and sinter. Then as the burden would all reduce at the same rate, the furnace could be driven at the rate of maximum efficiency for the reducibility of the charge without any fear of unreduced material reaching the crucible as happens at present if the sinter in the charge is too high. If properly carried out this should reduce the coke required for thermal and



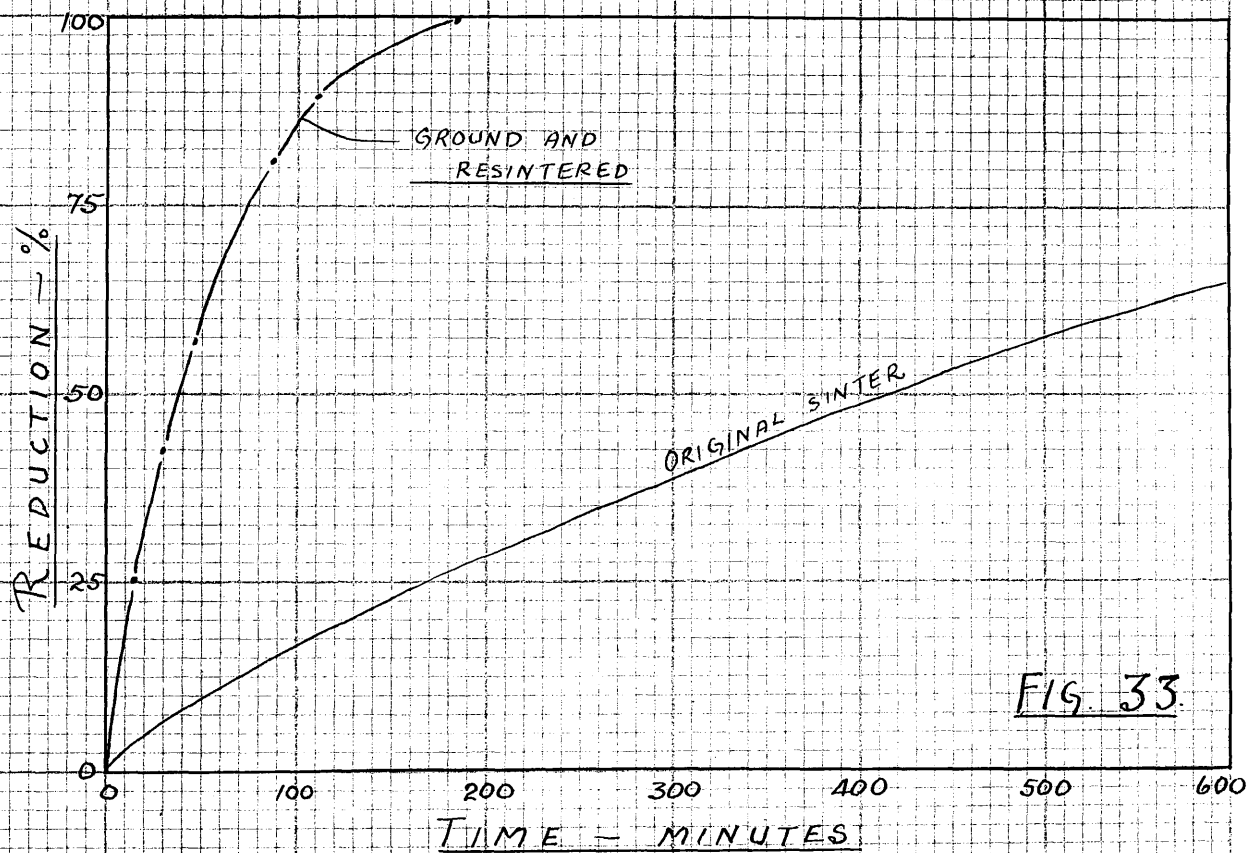


FIG. 33

reducing purposes to a minimum, and if this quantity along with the sinter was insufficient to keep the charge open, the economics of either adding more coke, which is obviously a wasteful process, or adding more sinter would have to be considered. To add more sinter, fines would have to be obtained either by buying them in natural form or in concentrates, or by crushing ore. It must be remembered that if excess coke is added it amounts to a dilution of the burden whereas extra sinter has a considerable enriching effect which must reduce the final cost of the pig iron. As mentioned in Chapter I, according to Neustaetter, the possibility of the coke required to keep the burden open being in excess of that required for reduction purposes does exist. Thus when considering whether or not it is economical to make and use more sinter this important factor must be borne in mind.

To verify the conclusion that the poor reducibility of industrial sinters was due to unsatisfactory production methods, a sample of Workington sinter was ground up and resintered in a platinum crucible with 2 per cent carbon and 12 per cent lime at a temperature of  $1150^{\circ}\text{C}$ . The reducibility of the resulting sinter was excellent but the strength, which was about equal to Northants ore, was not very satisfactory. From previous results it seems certain that a somewhat higher temperature would give a strong sinter with only slightly poorer reducibility. A comparison of the new sinter with the original in figure 33 leaves no doubt about the benefits derived from scientifically

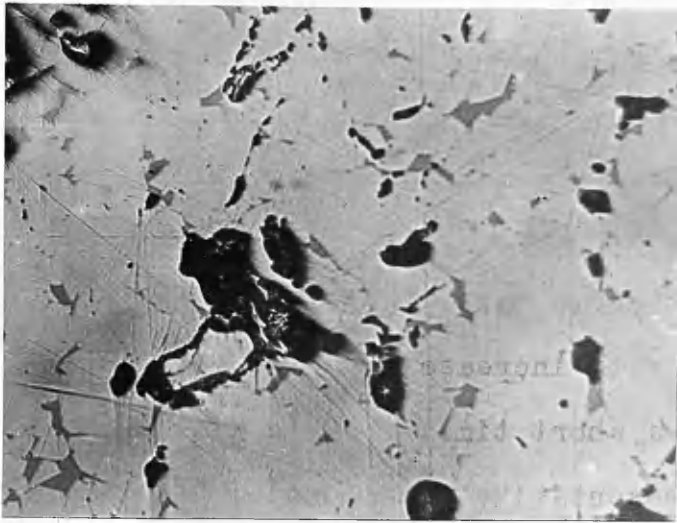
controlled production.

## CHAPTER X

### The Function of the Lime Addition.

An attempt was now made to prove the exact function of the lime in the formation of a sinter. Many slags containing lime, ferrous oxide and silica in varying proportions were made and examined. A platinum crucible was used as container and heating was carried out in a nitrogen atmosphere. The slag forming materials were heated just to the softening point and held there for ten minutes. This procedure was adopted in preference to pure sintering since it was considered that in most industrial sinters, when made properly, the slag forming constituents will almost melt, or in the case of troublesome sinters such as Wabana, the melting point will probably be exceeded.

A series of ferrous silicates were first made by mixing silica with ferric oxide plus the requisite amount of carbon to form ferrous oxide. That all the iron was in the ferrous state was proved by the specimen being non-magnetic and a check was made by making a further similar specimen using slightly more carbon which resulted in the appearance of a few specs of metallic iron. Specimens corresponding to the compositions  $1\frac{1}{2}\text{FeO}\cdot\text{SiO}_2$ ,  $1\frac{3}{4}\text{FeO}\cdot\text{SiO}_2$ , and  $2\text{FeO}\cdot\text{SiO}_2$  were made at  $1180^\circ\text{C}$ . and subsequently



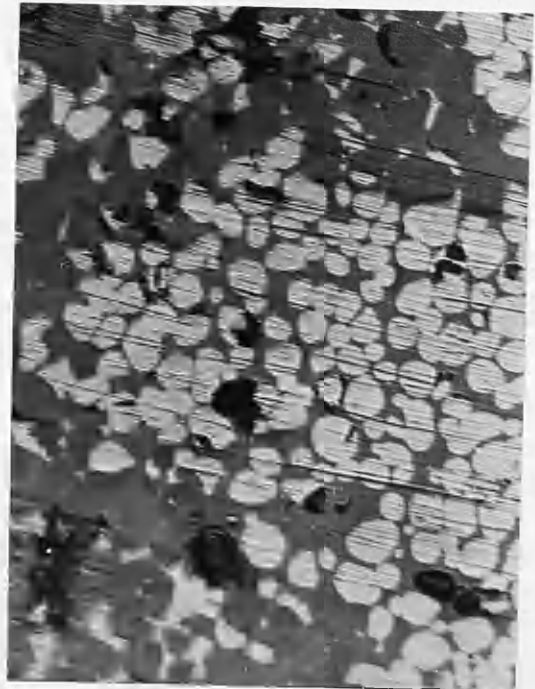
MICRO 24

x 250



MICRO 25

x 250



MICRO 26

x 250

examined. Under the microscope the first two appeared similar. Micro 24 depicts a typical area of specimen 119, of composition  $1\frac{3}{4}\text{FeO} \cdot \text{SiO}_2$ . The fayalite specimen, number 115, showed globules of free wüstite probably due to the short time of soaking at  $1180^\circ\text{C}$ . not allowing complete interaction to take place. It was not considered desirable to increase the time since industrial sintering employs a short time. Table XI gives some data on a few representative specimens.

TABLE XI

Specimen No.	Composition	Temp. $^\circ\text{C}$	Time Mins	Microstructure
115	$2\text{FeO} \cdot \text{SiO}_2$	1180	10	Globules of wüstite in fayalite matrix.
119	$1\frac{3}{4}\text{FeO} \cdot \text{SiO}_2$	1180	10	As in Micro 24
129	$1\frac{1}{2}\text{FeO} \cdot \text{SiO}_2$	1180	10	Similar to Micro 24
121	$1\frac{3}{4}\text{FeO} \cdot \text{SiO}_2 \cdot 1\frac{1}{5}\text{CaO}$	1280	10	Similar to Micros 25 and 26
131	$1\frac{1}{2}\text{FeO} \cdot \text{SiO}_2 \cdot 1\frac{1}{5}\text{CaO}$	1280	10	- do -
133	Fayalite + CaO	1280	10	As in Micros 25 and 26

The effect of lime additions was now investigated. Specimen 121 was made from ferric oxide + carbon, silica and lime to give a composition of  $1\frac{3}{4}\text{FeO} \cdot \text{SiO}_2 \cdot 1\frac{1}{5}\text{CaO}$ . It was observed that the temperature required to cause softening was about  $1280^\circ\text{C}$ . which is  $100^\circ\text{C}$ . higher than that for pure ferrous silicate. Since  $2\text{FeO} \cdot \text{SiO}_2$  is the limiting ratio in which ferrous oxide can combine with silica it was thought that if, as would be expected from

its greater basicity, the lime would to a certain extent combine preferentially with the silica, then some ferrous oxide would be thrown out of solution. If this were the case then it follows from the  $2\text{CaO}\cdot\text{SiO}_2 - 2\text{FeO}\cdot\text{SiO}_2$  diagram, figure 26, that the softening temperature of specimen 121 would probably be about  $1230^\circ\text{C}$ . since the  $\text{CaO}\cdot\text{SiO}_2$  ratio was just in excess of unity. Actually as mentioned above it was slightly higher probably due to time lag in the interaction of the constituents. This was borne out by the fact that if the temperature was not lowered immediately softening took place, complete melting resulted. The micro section of this specimen, which was very similar to micros 25 and 26, showed both globules of wüstite in a matrix of calcium iron olivines and what appears to be an eutectic between wüstite and calcium iron olivines. Specimen 131 was similar in all respects.

These results seem to indicate that the advantages of lime addition to sinter are due to the displacement of ferrous oxide from silicate compounds by the lime thus freeing it and converting it to a form more easily reduced and also to the raising of the softening point of the slag constituent of sinter resulting in less melting with consequently less glazing to cover micro pores.

Specimens 121 and 131 do not however prove what happens when lime is added to the sinter mixture of an ore in which the ferrous oxide and silica are already combined. Accordingly specimen 133 was prepared consisting of a

PLATE A



PLATE B

211  
210  
 $\beta$   
200  
111  
 $\beta$   
110  
100  
 $\beta$

COPPER  $K_{\alpha}$  RADIATION

9cm. CAMERA

weighed quantity of finely ground ferrous silicate (specimen 119 was used) and a lime addition so that the lime:silica ratio was 1.2. The behaviour on sintering and the microstructure of this specimen did not vary from that of specimens 121 and 131. The microstructure is depicted in micros 25 and 26.

As microscopic examination did not prove definitely that the light phase was wüstite a check was made by X rays. Three powder photographs were taken, of specimen 133, of iron rich wüstite, specimen 41, and of oxygen rich wüstite, specimen 37, the latter two being for comparison purposes. It can be seen by comparing plate A of specimen 133 with plate B of specimen 41 that iron rich wüstite is present in specimen 133. In the actual film of specimen 133 all the wüstite lines except the 2,0,0 line were visible but on printing neither of the very weak lines have come up.

Tables XII and XIII show the calculated results for the two wüstite specimens (41 and 37). It can be seen that the approximate lattice spacings are  $4.304\text{Å}$  for the iron rich wüstite and  $4.285\text{Å}$  for the oxygen rich wüstite. Jette and Foote<sup>(7)</sup> give the following lattice spacings.

Wüstite at iron side of the solid solution	$4.302\text{Å}$
Wüstite at eutectoid composition	$4.290\text{Å}$
Wüstite at oxygen side of the solid solution	$4.272\text{Å}$

It would thus appear that the composition of the wüstite in the oxygen rich specimen lies between the eutectoid and oxygen limit of the solid solution, figure 4. This would confirm the view expressed previously that the lines along the crystallographic planes, seen in micro 6, were due to



TABLE XIIIron rich wüstite (Copper K $\alpha$  radiation)

Strength	Distance Apart	$\theta$	d	h,k,l	a
W	5.68	18.04	2.484	-	-
M	6.60	20.96	2.151	100	4.301
M	9.57	30.39	1.521	110	4.300
W	11.48	36.46	1.295	-	-
W	12.06	38.30	1.242	111	4.301
WW	14.38	45.67	1.076	200	4.303
WW	16.19	51.41	0.9845	-	-
W	16.72	53.10	0.9622	210	4.303
W	19.25	61.14	0.8786	211	4.304

M Medium

W Weak

WW Very Weak

TABLE XIIIOxygen rich wüstite (Copper K $\alpha$  radiation)

Strength	Distance Apart	$\theta$	d	h,k,l	a
W	5.74	18.23	2.461	-	-
M	6.65	21.11	2.137	100	4.274
M	9.64	30.62	1.511	110	4.279
W	11.52	36.59	1.262	-	-
W	12.12	38.49	1.236	111	4.281
WW	-	-	-	200	-
WW	16.25	51.61	0.9818	-	-
WW	16.83	53.46	0.9578	210	4.284
WW	19.41	61.64	0.8747	211	4.285

magnetite precipitating with falling temperature due to its decreasing solubility. The lattice measurements indicate that this precipitation has not reached completion.

## CHAPTER X

### Summary.

It has been shown that the poor reducibility of industrial sinters is due to the formation of too much liquid during sintering. It is possible to overcome this by critical temperature control, or better, by avoiding the formation of low melting point compounds, which allows a temperature variation of over  $100^{\circ}\text{C}.$ , while still producing a strong and easily reducible sinter. Moisture appears to be unnecessary for sintering. It may cause the formation of macro pores by steam pressure but it has been shown that these pores are not of primary importance. However as long as sintering is done by drawing air or other gases through a bed of fines, it appears that some moisture will be necessary in order to obtain maximum voidage and so allowing easy gas penetration.

The most desirable bond in a sinter is that formed by diffusion between particles of iron oxide. It is not possible to completely avoid a slag bond, but it can be greatly minimised by the precautions stated above, and the effect on the rate of reducibility can be immediately seen.

The slag bond can be formed almost  $100^{\circ}\text{C}$ . below the minimum temperature for the iron oxide diffusion bond and so a sinter made at a temperature of about  $1200^{\circ}\text{C}$ . or lower is stronger if the slag bond is present. When precautions are taken to avoid or minimise the slag bond, the temperature must be over  $1200^{\circ}\text{C}$ . or over  $1250^{\circ}\text{C}$ . if the grading is coarse, to form an oxide diffusion bond of sufficient strength, but in spite of this increase in temperature a faster reducing sinter results. The strength of this bond when properly formed appears to be better than the slag bond probably mainly due to the fact that it is not so brittle. The poor reducibility of industrial sinters is largely due to the above precautions not being observed. That they have been sintered at an excessively high temperature is shown by the presence of a considerable proportion of slag material.

It should be possible to obtain improved results in the blast furnace especially with respect to smooth running and coke consumption and the resulting more uniform grade of iron, if improved sinter was used. The extra cost of producing such a sinter would have to be balanced against the saving in furnace costs.

### ACKNOWLEDGEMENTS

In conclusion I should like to thank Professor R. Hay, Ph.D., F.R.I.C., for suggesting the subject under investigation in this thesis and for his continued advice and encouragement during the course of the work.

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