

SOLID CARBON—THE MOST EFFECTIVE REDUCING AGENT

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THE reducibility of metal oxides is usually characterized by the amount of oxygen removed from the unit weight of oxide by the reducing agent in the unit of time. However, higher oxides are not reduced directly to metal but pass through all possible intermediate oxide stages /e.g. Fe_2O_3 is reduced to Fe_3O_4 , this to FeO and metallic iron is always formed from FeO /.

In reducing hematite / Fe_2O_3 / to wustite / FeO / 33 pct of the total oxygen is removed without obtaining any metal; for magnetite this value is 25 pct and still hematite is easier to reduce. This is because the oxygen atoms are not bonded uniformly; it is easy to transform higher oxides to lower ones /e.g. by thermal dissociation in the case of Ni or Cu/ but the production of metal from the lowest oxide is usually difficult and only possible by using a reductant.

The reducibility of iron ores is usually given for 80 pct oxygen removal; this corresponds to the transformation of higher oxides to wustite and to the formation of metal and gives the global rate of oxygen removal for several processes.

Several basic methods may be used to study the progress of reduction reactions:

1. Microscopic study of the sample after "freezing

in" during the reduction.

2. Measuring the enthalpy variation of the processes.

3. Measuring the weight variation of the sample.

4. Determining the amount and type of gaseous products.

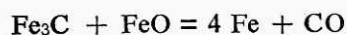
5. Measuring the variation of crystal structure of the oxide.

The first method has the advantage of being simple and showing the variation of the material structure; however, the test is periodic and fixes a not exactly definable state. The other methods permit a continuous measurement but it is hard to separate the reactions which overlap or occur simultaneously. For this end the various measurements would have to be carried out simultaneously in the same sample. The "Derivatograph" developed by the Hungarian scientists F. Paulik, L. Paulik and L. Erdey — supplemented with a gas analyzing apparatus — has realized the simultaneous and continuous measurement of the temperature, enthalpy variation, weight variation, the rate of weight change and the type of gases formed during the reactions in the same sample as a function of temperature.

First I shall show some tests carried out by "freezing in".

Figure 1. shows 0.2—0.3 mm magnetic grains at a magnification of 200 x, reduced at 800 deg. C with hydrogen. All surfaces and pores accessible to hydrogen are covered by a metal layer. Reduction has slowed down appreciably because the gas cannot penetrate the 4 μ deep metal layer.

Figure 2. When coke breeze was mixed with the ore and hydrogen was used again for reduction the primary metal layer was disrupted and another reaction front started towards the interior of the ore, only to stop after the formation of another continuous metal layer. This is due to the fact that the metal layer in contact with solid carbon is transformed to Fe_3C ; this in turn reduces the internal oxide according to



evolving a pressure within the metal membrane which disrupts the membrane and opens new paths to the reducing gas.

Figure 3. shows a briquette from Fe_2O_3 / 50 x / reduced in coal breeze at 1150 deg. C. No coal was mixed with the oxide. The formation of metallic iron started at the surface. The metal/oxide boundary is sharp, no intermediate partly reduced layer can be detected. No metallic iron is visible on the internal surface of the ore pores, showing that gas did not take part in the reduction which occurred by solid carbon penetrating inside by diffusion.

Figure 4. When a small amount of graphite powder was mixed with the ore before briquetting and reduction was carried out in coal breeze, reduction started not only at the outside but also around the coal particles inside the briquette. The pores show no metal formation which might be due to gaseous reduction. This shows that carbon reduces directly, without any gaseous phase. This test has recorded the existing situation without furnishing any information on the actual reaction mechanisms. These latter may be studied much more suitably with the Derivatograph.

Since the mechanism of iron oxide reduction is rather complicated we shall start with the derivatograms of some simpler oxides.

Figure 5. shows the dissociation of silver oxide $[\text{Ag}_2\text{O}]$ in air. The graph has been registered as a function of time.

Curve t shows the temperature variation
 Curve DTA shows the enthalpy variation
 Curve TG shows the weight variation and
 Curve DTG shows the changes of the rate of weight variation.

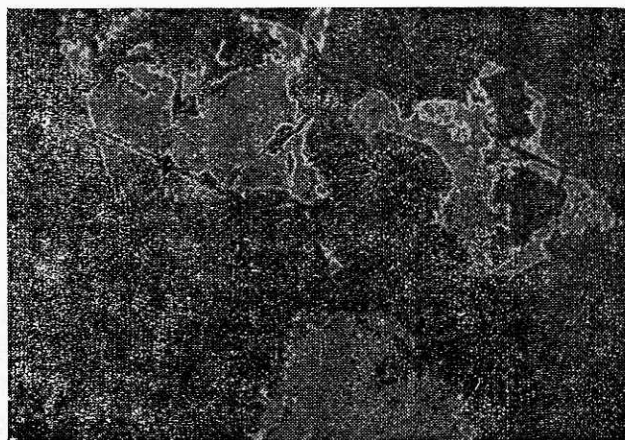


Figure 1

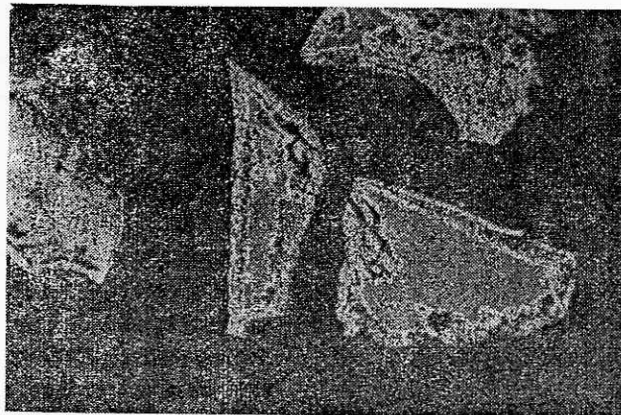


Figure 2

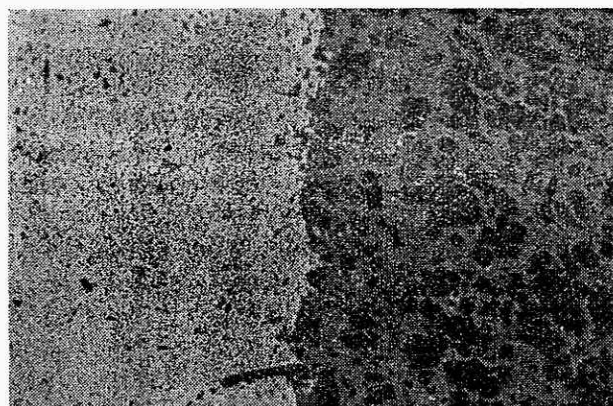


Figure 3

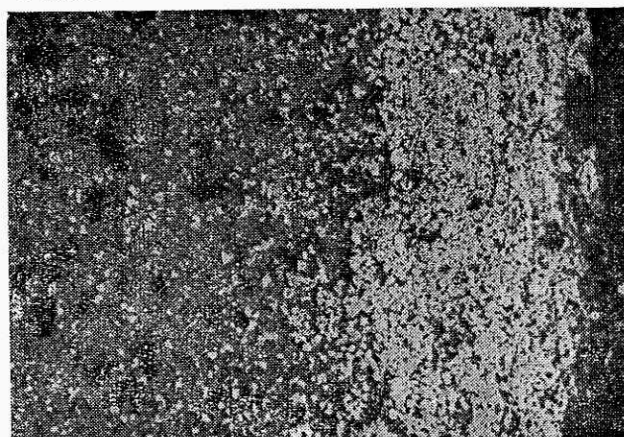


Figure 4

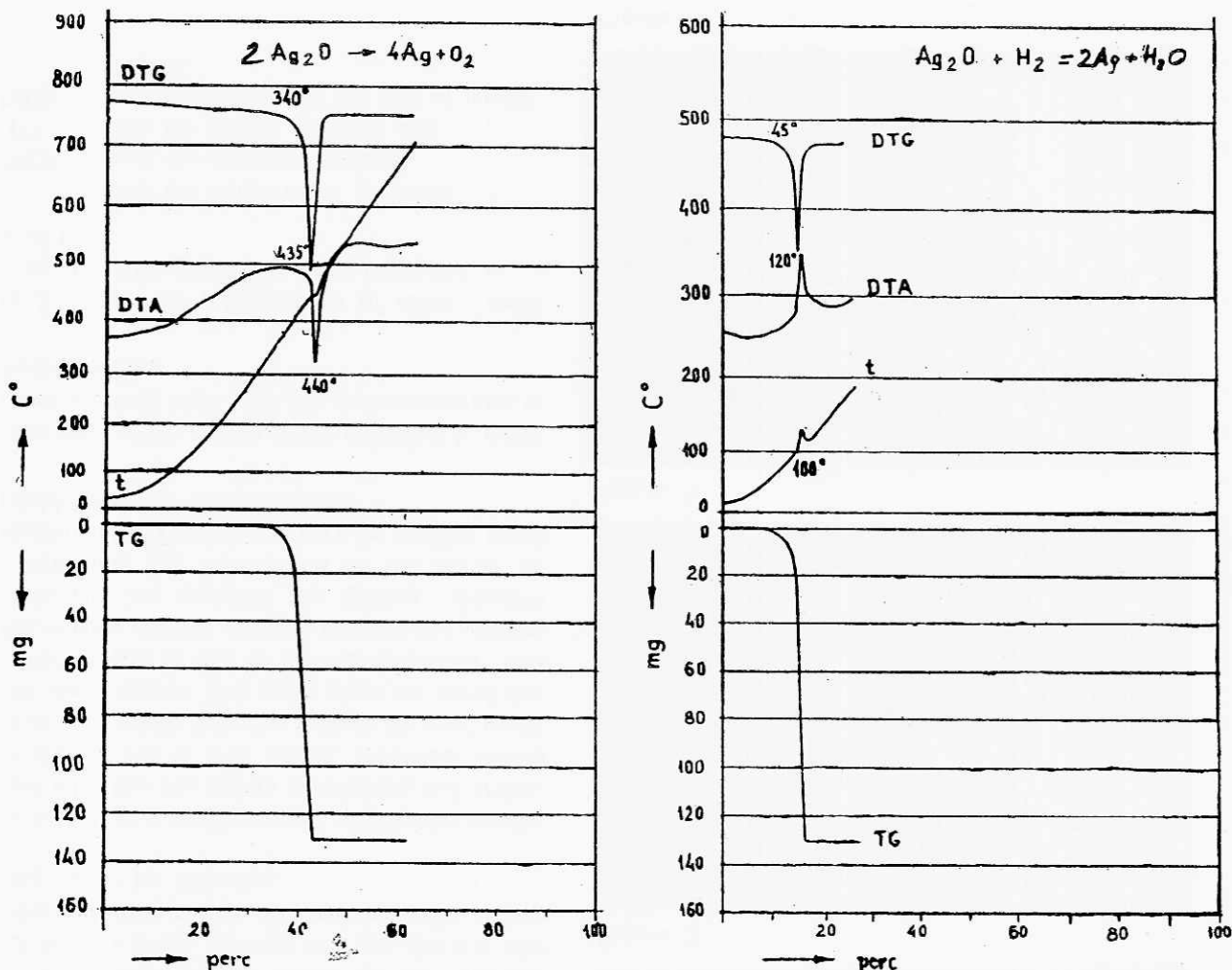


Figure 5

The DTG curve is the derivative of the weight variation and its minimum marks the highest rate of the process.

When the temperature rises at the rate of 13,8 deg. C per minute, the weight reduction—the thermal decomposition — of silver oxide begins with an endothermic heat effect at 340 deg. C. According to the DTG curve the maximum of oxygen elimination is at 440 deg. C. The measurable weight loss corresponds exactly to the oxygen removal of the endothermic process $2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2$ $\Delta H_0 = 7300 \text{ cal/mol}$. The maximum rate of dissociation — characterized by the weight of removed oxygen — is 14,3 Mg oxygen per gramme Ag_2O per minute at 435 deg. C.

When silver oxide was heated in flowing hydrogen the removal of oxygen started with an endothermic heat effect at 45 deg. C and its maximum rate was 34 mg oxygen per gramme Ag_2O per minute at 120 deg. C. Hydrogen reacts with oxygen at far lower tempera-

tures than the dissociation of Ag_2O requires; the actual reduction proceeds according to

$2\text{Ag}_2\text{O} + \text{H}_2 \rightarrow 4\text{Ag} + \text{H}_2\text{O}$ $H_0 = -52050 \text{ cal/mol}$ at a rate much higher than the rate of pure thermal dissociation. The reduction of Ag_2O to metal by CO starts at even lower temperatures, below 0 deg. C.

Figure 6. shows the dissociation of Ni_2O_3 in a nitrogen atmosphere. The removal of oxygen starts at 100 deg. C and is completed at 650 deg. C. the weight of the sample remains constant up to 1100 deg. C. From the weight reduction the residual Oxide is NiO ; however, the oxygen removal — according to the DTA and DTG curves — occurs in three steps through the oxide stages



The black sample turns light green.

When Ni_2O_3 is mixed with graphite and heated in nitrogen dissociation takes place — as in the absence

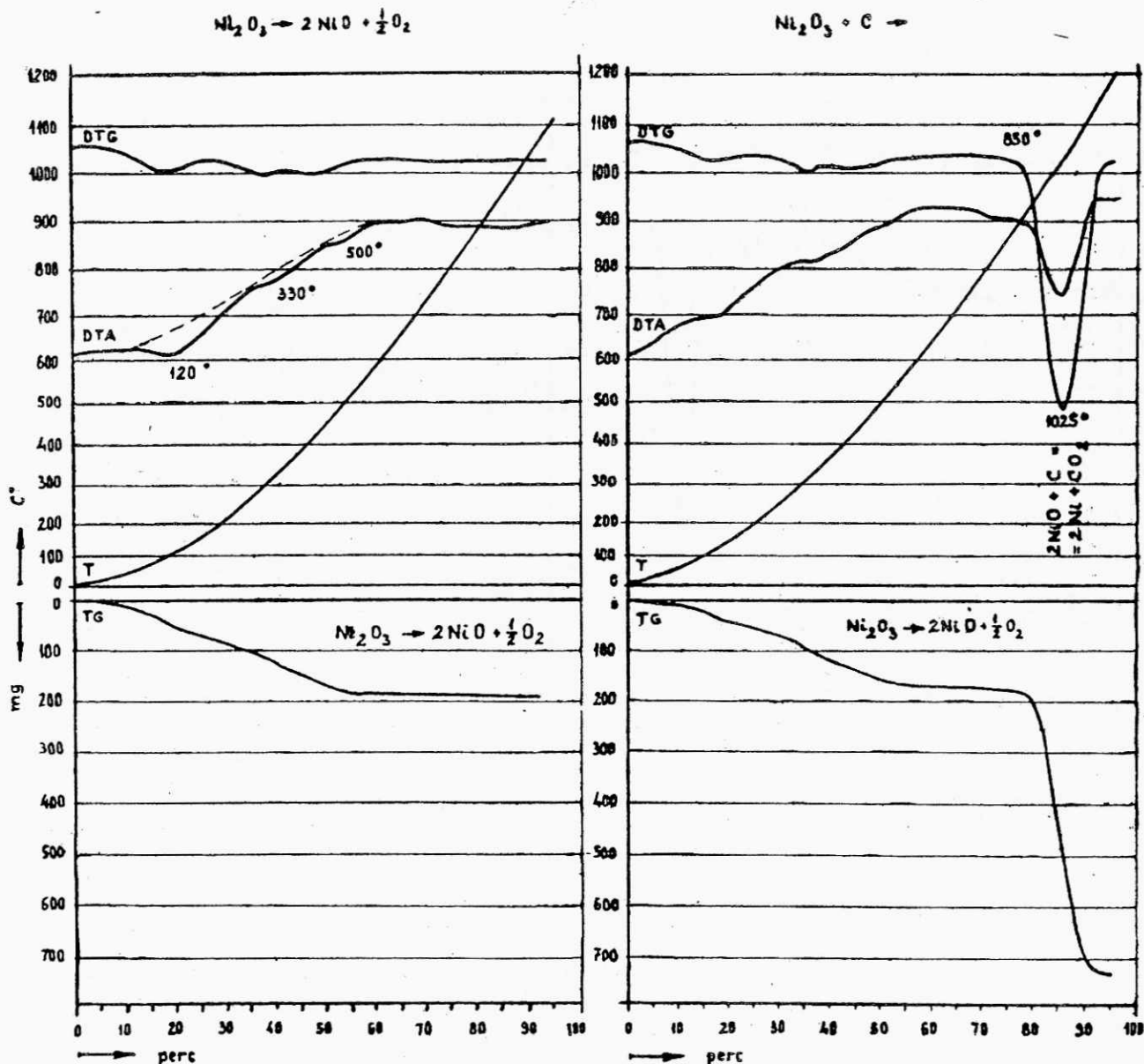


Figure 6

of graphite — but at 850 deg. C an endothermic begins, corresponding to $2 \text{NiO} + \text{C} \rightarrow 2 \text{Ni} + \text{CO}_2$

$$H_o = 2170$$

cal/mole./from the consumed carbon, the weight loss and the gas analysis. The reduction of NiO to nickel metal was accompanied by the formation of CO_2 .

The reduction of Co_3O_4 is similar, although Co_3O_4 does not dissociate to lower oxide; CoO is obtained by reduction.

Figure 7. shows the reduction of Co_3O_4 by solid carbon in argon. The weight is constant up to 650 deg. C when an exothermic process starts; this is a rate maximum at 790 deg C and is conducted at 830 deg. C. The sample weight is again constant up to 880 deg C;

here an endothermic process commences leading to an even higher weight loss.

From the weight losses, the analysis of the reduced sample and the gas the processes are as follows:

- I. at 650–830°C $2 \text{Co}_3\text{O}_4 + \text{C} \rightarrow 6 \text{CoO} + \text{CO}_2$
 $H_o = -23113$ cal/mole
- II. at 880–1200°C $6 \text{CoO} + 3\text{C} \rightarrow 6 \text{Co} + 3 \text{CO}_2$
 $H_o = + 10 30$ „

The rate of process I at 790 deg. C is

14,8 mg CO_2 or 10,8 mg O_2 per gramme Co_3O_4 per minute. The rate of process II at 1120 deg C is 34,4 mg CO_2 or 25 mg O_2 per gramme Co_3O_4 per minute.

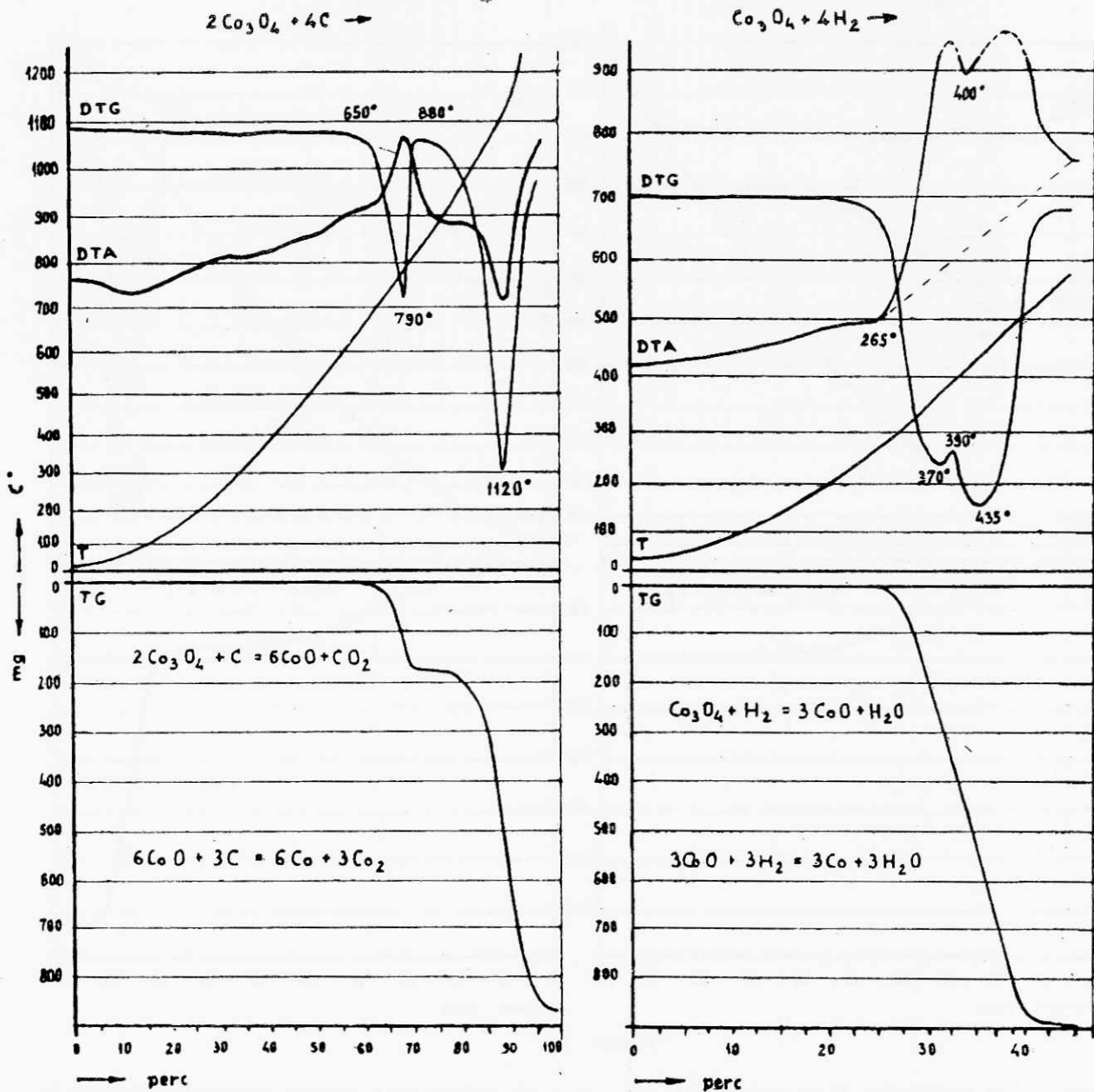
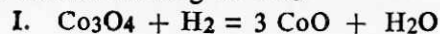


Figure 7

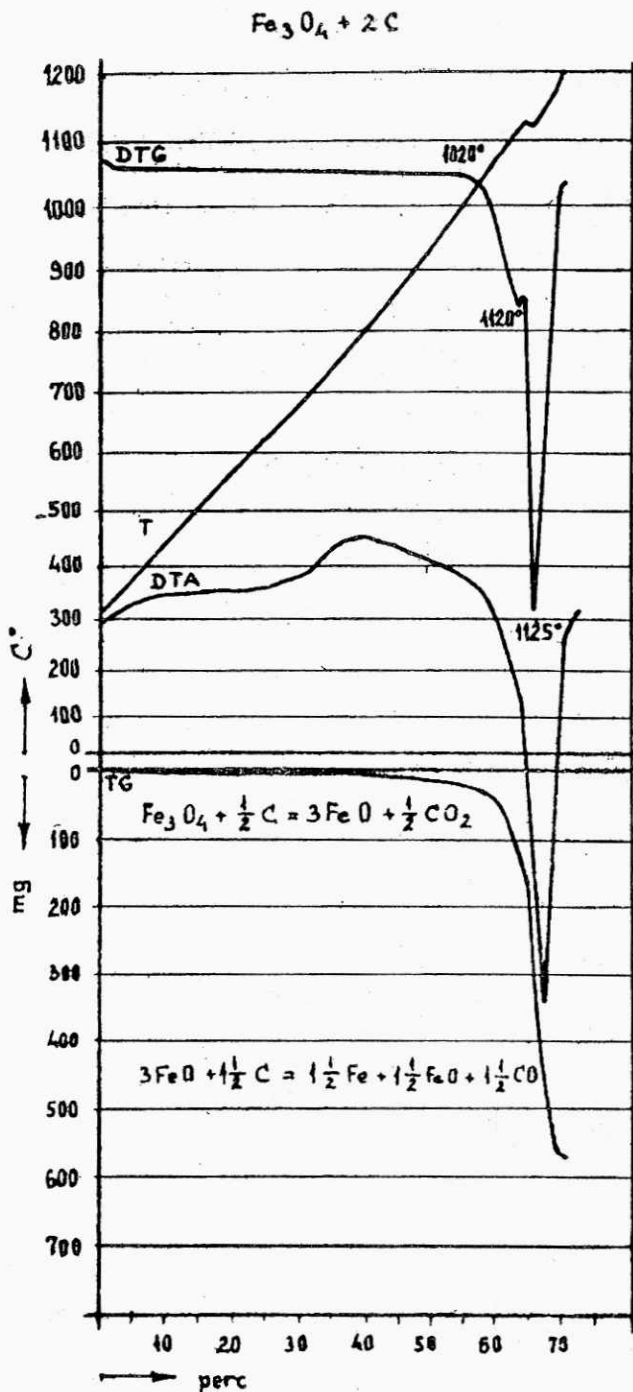
Co_3O_4 has been reduced to metal in two separate steps at different temperatures; metal formation started only when the whole sample had been transformed to CoO . The reduction of CoO starts at a temperature 230 deg. C higher than the reduction of Co_3O_4 this shows that the stabilities of the oxide stages differ widely.

When Co_3O_4 is reduced with hydrogen reduction again occurs in two stages but these overlap strongly and cannot be distinguished on the TG curve.

The first reaction leading to CoO



begins at 265 deg. C but before its completion the second reaction II. $3 \text{CoO} + 3 \text{H}_2 = 3 \text{Co} + 3 \text{H}_2\text{O}$ starts. This overlapping is equally detectable in the DTG and DTA curves: the rate maximum of process I is detected at 370 deg C, that of process II at 435 deg. C. Contrary to the reduction with carbon, both reductions start with small temperature differences and run in parallel from about 300 deg. C. That is why pure CoO cannot be obtained by reducing with hydrogen.



The derivatograph has the advantage of separating such closely overlapping reactions and detecting the individual weight losses and rates.

The above considerations prove that oxides are always decomposed through all possible intermediate oxide stages. The reduction of the highest oxide starts at the lowest temperature and the lower oxides are reduced at increasing temperatures. If the starting temperatures of reduction stages lie close to each other

several reactions may run in parallel. For all metals which are not oxidized by CO_2 — e.g. Co, Ni, Cu — the direct reduction to metal produces gaseous CO_2 the reduction is independent of the composition of the gas phase and the metal can be obtained in an atmosphere of CO_2 .

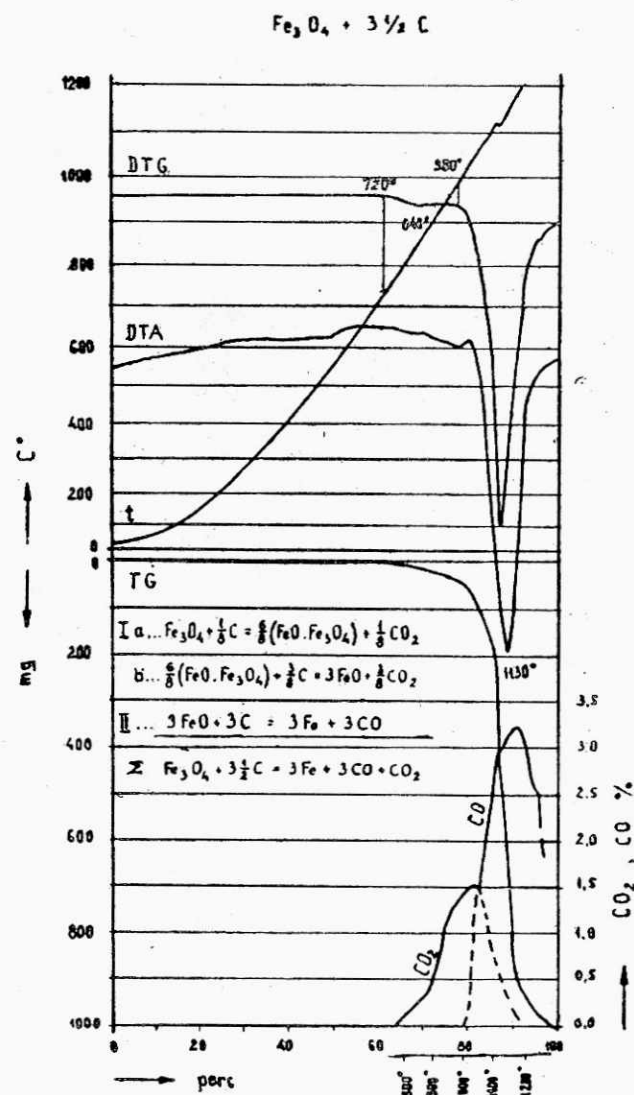
The reduction of iron oxides

The oxygen removal from iron oxides also takes place in several stages and iron metal is always obtained from the lowest oxide, wustite. The initial temperature of the reduction stages lie close together and therefore several reactions run in parallel at a given temperature and are difficult to separate.

We started by studying the reaction of the mixture $\text{Fe}_3\text{O}_4 + 2\text{C}$ in argon. The carbon would be sufficient for complete reduction according to the reaction Fig. 8

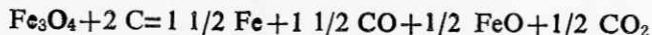
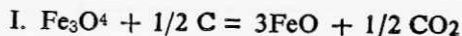


However, the reduced sample contained merely 45.1



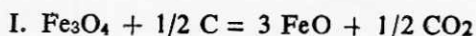
pct metallic iron and 0.15 pct carbon showing that magnetite had been reduced only partially to metal although carbon had been completely consumed. The diagram shows two stages of reduction, the first starting at 1020 deg. C with a rate maximum at 1120 deg. C; before its completion another reaction starts with a rate maximum at 1125 deg. C. Both processes are strongly endothermic. The gas analyzer at first only detected CO₂ and Co appeared at 1100 deg. C. CO₂ decreased rapidly and towards the end of the test the

atmosphere was pure CO.



Therefore the reduction of magnetite [Fe₃O₄] occurs in two stages leading to wustite and metallic iron respectively and strongly overlapping. The first stage is accompanied by the evolution of CO₂ and the second by the formation of CO.

According to Figure 9 the detailed mechanism of metallic iron formation from magnetite is as follows:



In spite of the strong overlapping it is possible to determine the rates of the two processes from the diagram. The rate of process II is at 1130 deg. C $v_{\text{max}} = 35$ mg oxygen per gramme FeO per minute.

Figure 10. shows the derivatogram of the reaction of a mixture of Fe₃O₄ with 3 1/2 C in CO₂ gas. Reaction I occurred in the same way as in argon — undisturbed by the presence of CO₂ — and process II /metal formation/ also started; however, after reaching the maximum rate and the evolution of CO decreased the oxidation of metallic iron commenced according to $\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO}$ as shown by the rapid weight increase of the sample.

The reduction mechanism of hematite was studied first in a mixture of 2 Fe₂O₃ + 3 C in argon. This amount of carbon was sufficient for complete reduction with CO₂ as the sole gas product.

Reduction actually occurred according to Figure 11 in two readily distinguished steps. Process I started at 900 deg. C and reached its highest rate at 1085 deg. C; simultaneously another reaction started with an endothermic minimum at 1130 deg. C.

The weight loss, gas analysis and the analysis of the reduced sample lead to the following reactions:

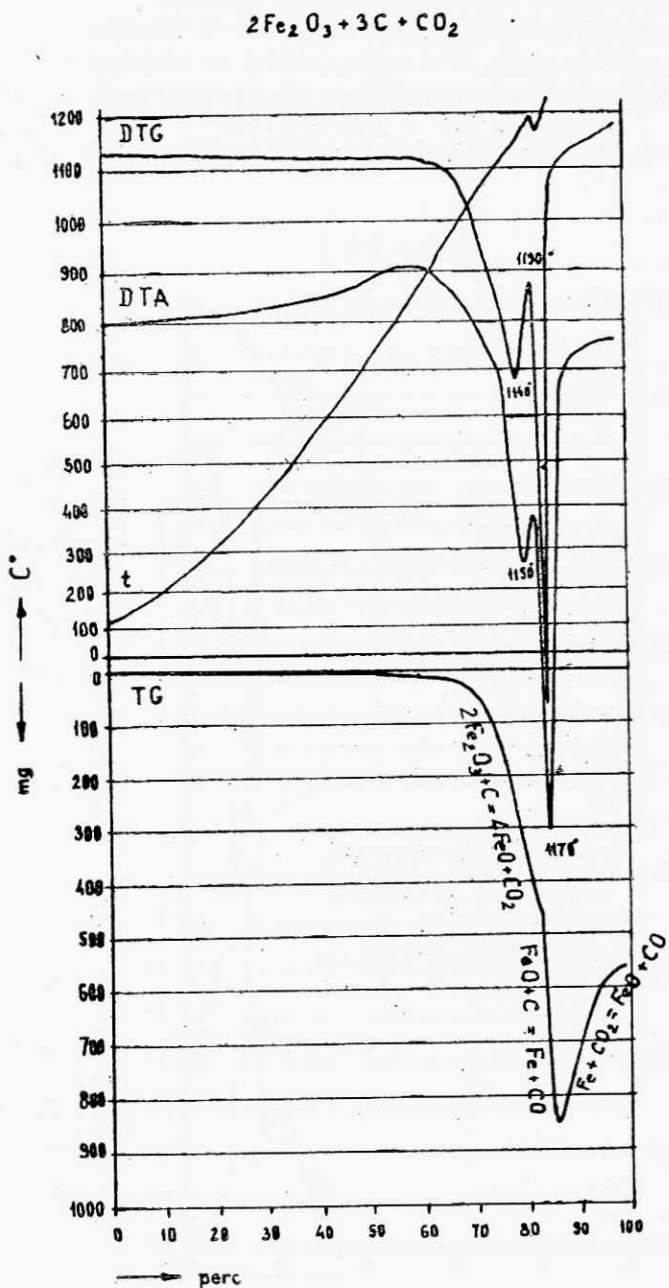
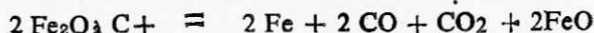
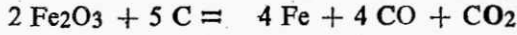


Figure 10

5 moles of carbon are needed for the full reduction of two moles of F_2O_3 .



The reduction of hematite with solid carbon in CO_2 gas is shown in Figure 12. Process I proceeds stoichiometrically and the start of process II /metal formation/ is sharply discernible.

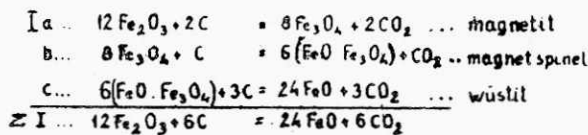
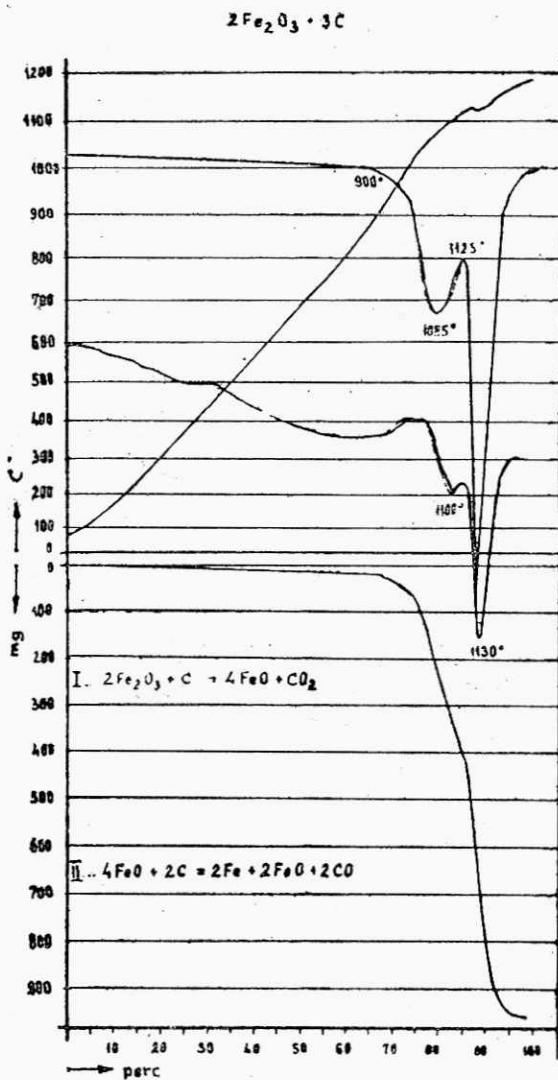


Figure 11

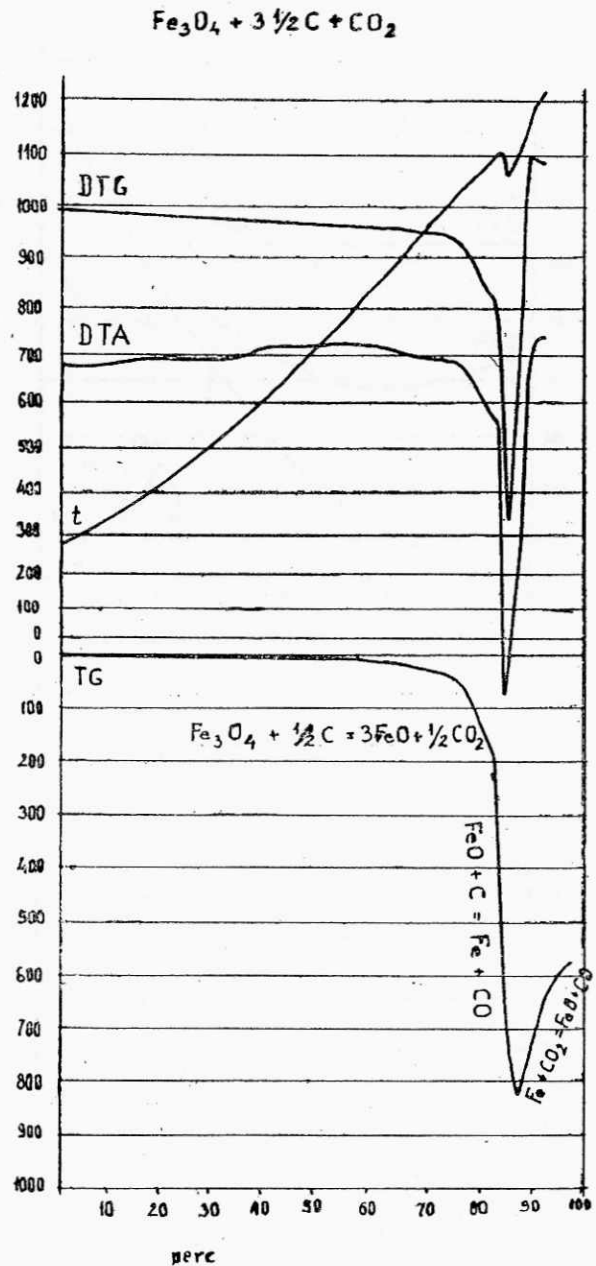


Figure 12

This reduction proceeds at a high rate until the oxidizing effect of CO_2 takes over, transforming the reduced metal to FeO , according to the weight increase. The rate of metal formation at 1130 deg. C is 33 mg oxygen per gramme FeO per minute.

Our tests have shown that the molar mechanism is the same when CO and H_2 are used as reductants; the initial temperatures and rates of the reduction stages are different however.

Figure 13. shows the reduction of hematite with hydrogen with a heating rate of 25 deg. C per minute.

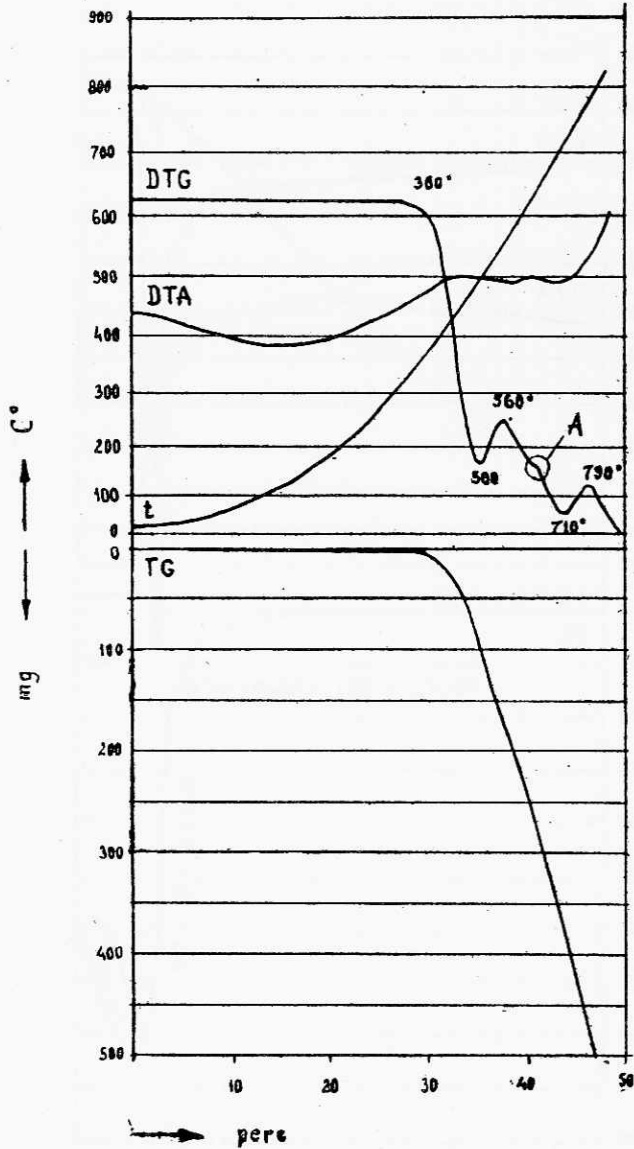
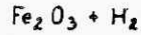


Figure 13

Process I starts at 360 deg. and leads to Fe_3O_4 . Process II has a rate maximum at 710 deg. C and terminates at 790 deg. C leading to FeO . However, the reactions overlap even more than in reductions with carbon. The formation of metallic iron also begins meanwhile.

In the reduction of magnetite with hydrogen we were unable to achieve a 100 pct reduction. At a grain size of 0,1-0,2 mm reduction practically stopped at 595 pct degree of reduction, grain size of 20 μ the final degree of reduction achieved was 89 pct. This is due to the lattice structure of magnetite being more dense than

that of hematite and covered by a dense 4 μ thick metallic iron layer through which hydrogen cannot penetrate. On hematite this layer is much more porous, reduction starts at the surface of the underlying crystals and also in their interior since hydrogen can penetrate into the porous hematite lattice. To reduce magnetite completely it must be roasted previously to hematite or ground to 8-10 μ grain size.

Reduction with CO begins at lower temperatures. According to Figure 14, reduction of hematite with CO starts at 290 deg. C with a heating rate of 4,3 deg. C per minute and an exothermic heat effect. After the rate maximum at 350 deg C another exothermic pro-

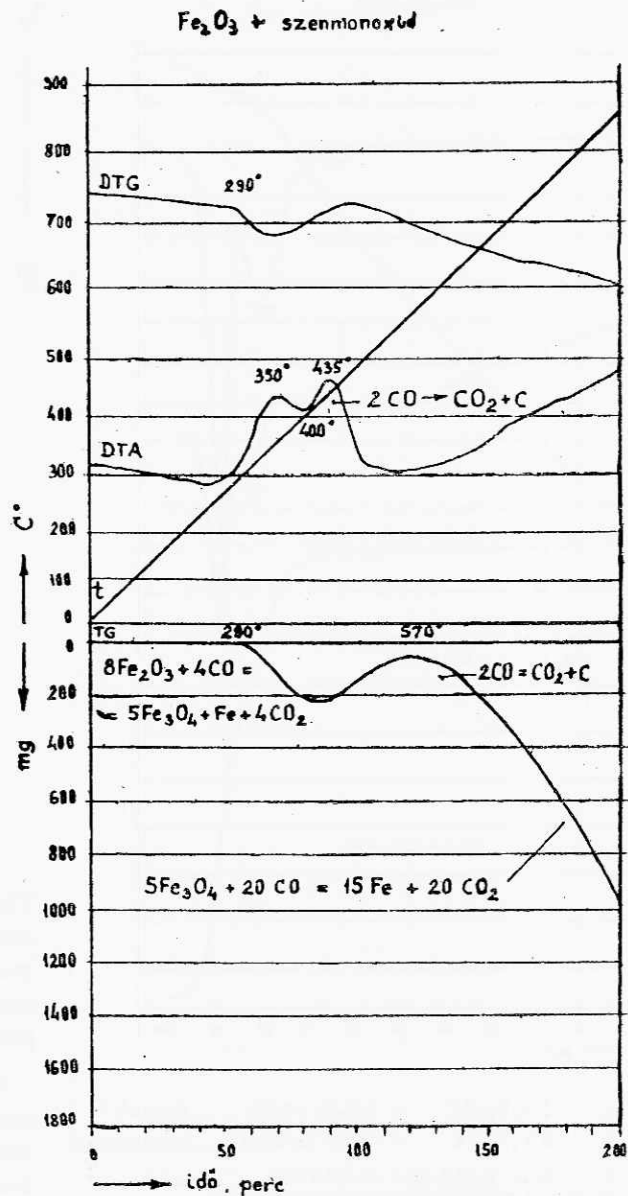


Figure 14

cess starts on the DTA curve, accompanied by a weight increase. Since much carbon was found in the cooled sample this must have caused the weight increase. The exothermic maximum of carbon precipitation is observed at 435 deg. C. At 570 deg. C the rates of carbon precipitation and oxygen removal are equal and above this temperature reduction is the more rapid process. Due to the continuous carbon precipitation other stages of reduction cannot be distinguished.

The start of carbon precipitation is simultaneous with the appearance of metallic iron. In this test the formation of metallic iron started at 380 deg. C. With rapid heating carbon precipitation was reduced, probably because the formation of metallic iron was displaced towards higher temperatures.

To exclude the interference of carbon formation the samples were heated in argon to the desired temperature and reduction was studied at constant temperature. We were able in this way to detect the individual stages of reduction and to measure their rates. This technique was also employed in reductions with hydrogen.

Figure 15 shows the rates of oxygen removal measured at constant temperature; we show the measured weight losses $\mu = \text{mg oxygen per gramme of oxide per minute}$ in a logarithmic scale as a function of $1/T$ on Arrhenius straights.

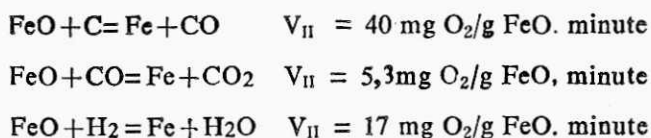
The rate of reduction with hydrogen is always higher at a given temperature than the rate of reduction with CO and the increase of the reduction rate with temperature is also higher for hydrogen. This could lead to the conclusion that only hydrogen-bearing gases should be injected into the blast furnace to accelerate the reduction processes.

For reductions with solid carbon much higher rates of oxygen removal were measured above 1000 deg. C. than for gaseous reductions. The rate equation for the direct reduction $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$ with a heating rate of 13, 6 deg C per minute is

$$V_{II} = 1,32 \cdot 10^9 \exp / - \frac{48600}{RT} /$$

The Arrhenius straight for this equation is also shown in Fig. 15.

Accordingly the rates of oxygen removal at 1150 deg. C are:



Fémeszképződés II. reakciósebesség.
Kétfázisú anyag bontás.

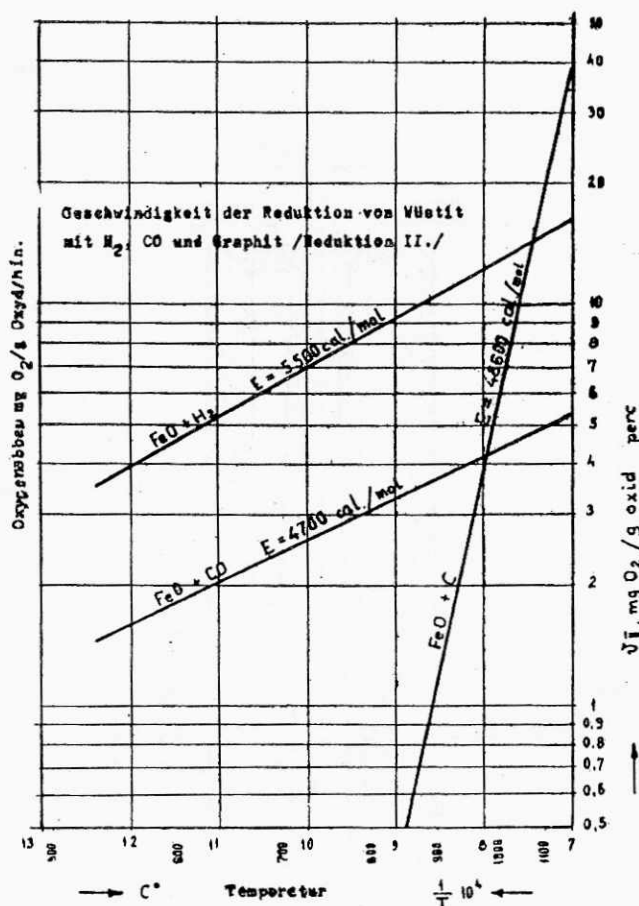
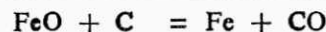
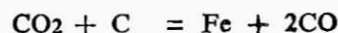
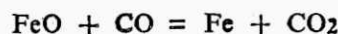


Figure 15

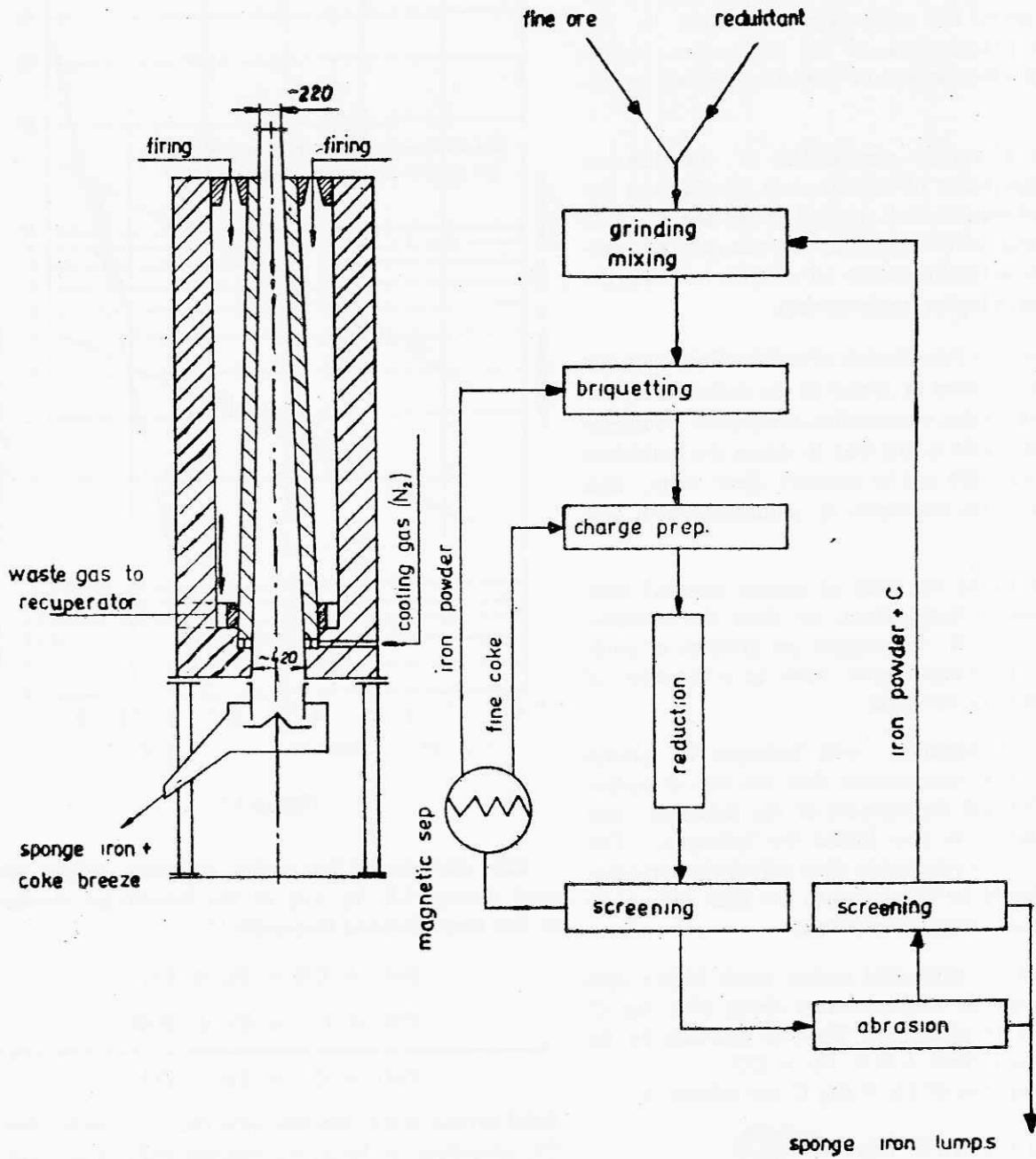
This also shows that direct reduction cannot proceed through CO by way of the Boudouard reaction, as has been assumed frequently**



Solid carbon reacts directly with the solid oxide. Since CO according to the above reaction reduces at a ratio about eight times lower than the actually measured rate in the presence of carbon. At this temperature carbon reduces about 2,5 times faster even than hydrogen.

From the measured reduction rates the optimal reduction mechanism of sponge iron production may be

* Kohl H., Marincek B.: Archiv f. d. Eisenhüttenwesen 1965, No.12.p.854



RETORT FURNACE

PROCESS OF CARBOTERMIC SPONGE
IRON PRODUCTION

Figure 16

derived

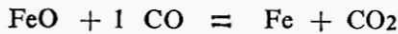


However, as we have seen, such a reaction does not exist. Metallic iron is always obtained from wustite—in the case of a reduction with carbon above 1000 deg. C with the evolution of CO. The final stage of reduction is therefore



This reduction is not complete, leaving 1 mole of unreduced FeO.

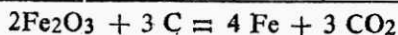
For full reduction /4 Fe/ only 3 moles FeO should arrive in this reduction zone; one of the above 3 moles of CO should be utilized to reduce 1 mole of FeO to metallic iron.



After reduction the gas composition is: 33,4 pct CO₂ + 66,6 pct CO. This gas composition permits a reduction below 700 deg. C. Reduction to wustite must be carried out with the CO₂ + CO of the above composition. This is perfectly possible thermodynamically, since this stage of reduction also proceeds in an atmosphere of CO₂.

The partial processes may be arranged in the order of increasing temperatures as follows:

1. above 280°C $2\text{Fe}_2\text{O}_3 + 2\text{CO} + \text{CO}_2 = 4\text{FeO} + 3\text{CO}_2$
v = 5 mgO₂/g. minute
2. At 700°C $4\text{FeO} + 3\text{CO} = \text{FeO} + 3\text{FeO} + \text{CO}_2 + 2\text{CO}$
v = 2,4mgO₂/g. minute
3. Above 1000°C $\text{Fe} + 3\text{FeO} + 3\text{C} = 4\text{Fe} + 3\text{CO}$
v = 22 mgO₂/g. minute



For convenience of calculating with whole molecules the stage of magnetite formation has been omitted here.

The above combination of direct and indirect reductions supplies the optimal mechanism of sponge iron production with the utilization of the reduction potential of carbon.

This mechanism should be investigated also, however, from the point of view of kinetics, i.e. productivity.

The time for complete reduction is governed by the slowest reduction No. 2. Since the rate of this reaction is 2, 4 mg O₂ per gramme per minute /at 700 deg C/

as compared to the rate for reaction 3/: 22 mg O₂ per minute /at 1100 dge. C/ the ore must stay about ten times longer at 700 deg. C than at 1100 deg. C. Accordingly the 700 deg. C zone must be ten times larger the productivity must be limited to the rate of reaction 2.

From the practical point of view it could be better to reduce all four moles of FeO with carbon according to the following optimal reactions of reduction:

for hematite $2\text{Fe}_2\text{O}_3 + 4\text{C} = 4\text{Fe} + 2\text{CO}_2 + 2\text{CO}$

for magnetite $\text{Fe}_3\text{O}_4 + 3\text{C} = 3\text{Fe} + \text{CO}_2 + 2\text{CO}$

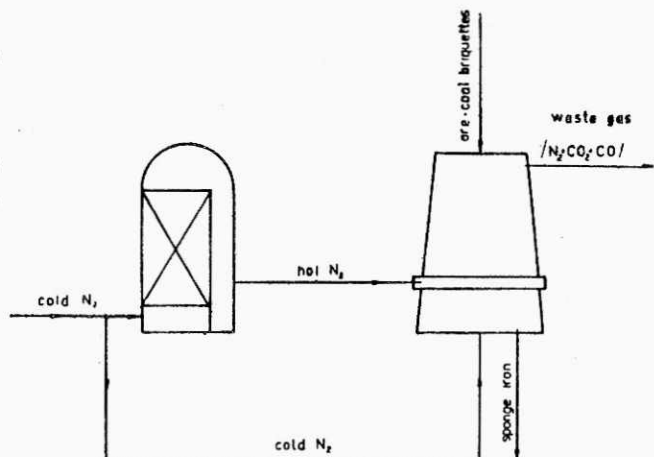
In this case the productivity depends on how rapidly one is able to heat the ore-carbon mixture to 1100 deg. C.

The requirements in reducing carbon are:
150 kg carbon per ton of hematite /215 kg carbon per ton of Fe/.

156 kg carbon per ton of magnetite /215 kg carbon per ton of Fe/.

When carbon is employed as reductant the reduction proceeds in the same way with hematite and magnetite; roasting of magnetite to hematite before reductions is not necessary.

To achieve a high productivity and rapid reduction the process must be carried out at sufficiently high temperature — 1100 deg. C — and the thermal requirements of the endothermic process must be supplied at this temperature. Any success in reducing the tem-



KILN

Figure 17

perature of reduction represents a significant economy in fuel. The reduction with charcoal requires about 1000 deg. C and the presence of activating substances /e.g. K_2CO_3 , $NaNO_3$ reduces the temperature of metallic iron formation still further, to 900—950 deg. C. The thermal requirements amount in this case — without heat loss—to 2,500.000 cal per ton of sponge iron with 95 pct Fe and for the reduction at 1100° C to 3,800.000 cal per ton of sponge iron.

The heat cannot be supplied with waste gases containing CO_2 , therefore one must either employ external heating — similar to vertical coking retorts — or supply the heat to the system with a hot inert gas, e.g. preheated nitrogen. The nitrogen can be heated to 1350 deg. C in hot blast stoves and this hot gas can be used in shaft furnaces, in large pans — similarly to the HyL process or in rotary furnaces to heat the ore-coal mixture to the temperature of reduction. The nitrogen requirements are about 5500—6000 m³ per ton of sponge iron.

To provide the necessary close contact, the mixture of ore, coal and activating agents should be briquetted or pelletized. In shaft furnaces the briquettes should be mixed with coke breeze, to prevent sticking; this coke breeze does not participate in the reaction and may be recirculated repeatedly.

The flowsheet and equipment of this process are very simple:

1. Grinding the raw materials to < 1 mm.
2. Briquetting to 20 mm dia. lumps.

3. Reduction in kilns or pans.

4. Separation of the sponge iron and coke breeze by screening.

5. Removal of the coke adhering to the surface by tumbling of the sponge iron.

When hot nitrogen is used for heating the waste gas only contains a little CO_2 and CO ; it cannot be utilized but may be evacuated into the atmosphere with any regenerating equipment.

We have developed the process in a pilot plant consisting of an externally heated retort with a volume of 0.44 m².

We achieved a 90—95 pct degree of reduction and an output of 5 to 6 tons per m³ per day. In a shaft furnace — with its better heat transfer — an output of 10 tons per m³ per day would have been possible.

The sponge iron produced with coke breeze as reductant had the following composition.

Total Fe	83,40 pct
Metallic Fe	82,37 ..
C	1,44 ..
S	0,092 ..
SiO ₂	9,14 ..
Al ₂ O ₃	3,06 ..

Figure 16 shows a possible mode of realization of the retort process. In Figure 17 you see the shaft furnace variant with nitrogen injection.