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GENERAL REVIEW OF DIRECT REDUCTION PROCESSES

by

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Summary:

A general review of the basic theoretical factors involved in the various direct reduction processes for iron ore is given, e.g. equilibrium conditions, kinetics of the reactions, and thermal problems. A brief account is also given of the metallurgical and economic characteristics of some of the more important types of direct reduction processes.

The prereduction of iron ore for production of pig iron in electric furnaces and the melting of sponge iron for steelmaking in different types of furnaces is discussed.

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1. Introduction

The blast furnace process is not always the best process for reduction of iron ore to metallic iron. If coking coals are lacking but there is a plentiful supply of cheap water power, pig iron can be produced in electric furnaces instead of blast furnaces.

There are also a great number of processes invented for the production of sponge iron instead of pig iron. Such processes may be useful for certain types of ore or certain types of fuel or for the production of a high-grade raw-material for steelmaking in electric arc furnaces or open-hearth furnaces, where the sponge iron can be used as a substitute for commercial steel scrap, which is often contaminated with impurities, which cannot be removed during the steelmaking process. Sponge iron can also be used for the manufacturing of iron powder for powder-metallurgical purposes.

Reduction of iron ore can also be carried out by adding the ore to a liquid bath of hot metal or steel containing carbon in solution. The dissolved carbon acts as a reducing agent and can be replaced by adding also carbonaceous material to the liquid bath.

2. Equilibria in gaseous reduction of iron oxides

The production of sponge iron is always carried out by gaseous reduction of solid iron ore. Even if the ore is mixed with solid fuel, the reduction takes place by diffusion of reducing gases into the pores of the ore. The most important reducing gases are carbon monoxide, hydrogen and methane.

Fig. 1 Fig. 1 shows the well-known equilibrium diagram for the reduction of iron oxides with carbon monoxide and hydrogen. At 820°C carbon monoxide and hydrogen have the same reducing power. At lower temperatures carbon monoxide is the stronger reducing agent. At higher temperatures hydrogen is stronger than carbon monoxide.

If Fe_2O_3 is reduced, Fe_3O_4 is first formed, and in this reaction both carbon monoxide and hydrogen can be completely converted to CO_2 or H_2O.

In the further reduction of Fe_3O_4 metallic iron is formed directly at temperatures below 570°C but at temperatures above 570°C wustite (FeO) is obtained as an intermediate product.

If the reduction is carried out with carbon monoxide at temperatures above 700°C, austenite is formed. The carbon content of this austenite is higher, the lower the CO_2 content of the reducing gas. If the carbon monoxide is pure enough, the austenite may be saturated with carbon and also free cementite (Fe_3C) may be formed.

At reduction temperatures below 700°C FeO is reduced by carbon monoxide directly to Fe_3C without the formation of metallic Fe as an intermediate product. At low reduction temperatures the reduction of iron ore with carbon monoxide is disturbed by deposition of free carbon, if metallic iron is present as a catalyst for the reaction.

$$2\,CO = C + CO_2$$

This carbon deposition has a maximum at about 550°C. Formation of austenite, cementite or free carbon can also take place, if the ore is reduced with a gas containing CH_4 or other hydrocarbons.

Reduction of iron ore with pure hydrogen is sometimes carried out at low temperatures down to 480°C. At such low temperatures the equilibrium conditions are unfavourable. If reduction of Fe_3O_4 to Fe with hydrogen is carried out at 480°C, it is not possible to utilize more than 16 per cent of the gas volume for reduction.

3. Kinetics of gaseous reduction of iron oxides

The velocity of the reduction of iron ore to sponge iron is dependent on many different factors, e.g. the physical nature and chemical composition of the ore, the temperature, the composition and velocity of the reducing gas, the heat supply, etc.

Reduction of hematite (Fe_2O_3) to metallic Fe is a faster reaction than the reduction of magnetite (Fe_3O_4) to metallic Fe, in spite of the fact that more oxygen has to be removed.

Fig. 2 The influence of the temperature on the velocity of the reduction of Fe_3O_4 with hydrogen and carbon monoxide is shown in fig. 2. Magnetite with a grain-size of 2 mm was reduced with pure hydrogen or pure carbon monoxide at different temperatures and the amount of oxygen removed during two hours reduction was determined.

Reduction with hydrogen has a maximum velocity in the temperature range 500-600°C. With increasing temperature the reaction velocity decreases. The reason for this is that the very porous metallic iron has a tendency to recrystallize and form more or less gastight layers around the remaining unreduced FeO particles. After a minimum at about 700-750°C the reduction velocity increases again, and at 1000-1100°C it has reached about the same value as it had at 500-600°C.

If reduction with hydrogen is carried out below about 550°C, the metallic iron formed has such a high microporosity that it is pyrophoric. The pyrophoric sponge iron can be passivated by compression and recrystallization at 750-850°C in hydrogen or nitrogen.

Reduction with carbon monoxide is at low temperatures a much slower reaction than reduction with hydrogen, and the carbon deposition is also a difficulty, if carbon monoxide is used for reduction at low temperatures.

At high temperatures, above 900°C, reduction with carbon monoxide is a faster reaction than reduction with hydrogen, and it is easier to get complete reduction with carbon monoxide than with hydrogen. Reduction with carbon monoxide in shaft furnaces is, therefore, carried out at the highest possible temperature, which is about 850-1000°C. The upper limit is the temperature at which the tendency of the sponge iron pieces to weld together causes operating difficulties.

If the ore is mixed with an excess of solid reducing agent, a somewhat higher temperature can be used without sticking difficulties.

At high temperatures, mixtures of carbon monoxide and hydrogen reduce faster than the pure gases used separately. The hydrogen speeds up the reduction during the preliminary stages and the carbon monoxide during the final stage.

4. Thermal problems in reduction of iron oxides

Reduction of iron oxide with carbon or hydrocarbons are strongly endothermic reactions, and heat must be supplied to the reduction furnace, even if the ore and reducing agent are preheated to reduction temperature.

Reduction of iron oxide with carbon monoxide is slightly exothermic and with hydrogen slightly endothermic. The heat of reaction at 900°C is zero, if a mixture of carbon monoxide and hydrogen with 48% hydrogen is used. If normal heat losses from the reduction furnace are considered, a constant temperature of 900°C can be maintained in the furnace, if the reduction is carried out with a mixture of carbon monoxide and hydrogen, containing 35-40% hydrogen.

A higher hydrogen content may be used, if the ore and the gas are preheated to a higher temperature than the desired temperature of the sponge iron, or if extra heat is supplied by partial combustion of the gas with oxygen or preheated air.

If natural gas or other hydrocarbons shall be used for the reduction of iron ore, a good method is to reform them first into a mixture of carbon monoxide and hydrogen by means of steam oxygen or carbon dioxide in order to avoid too much heat supply to the reduction furnace.

5. Metallurgical and economic characteristics of some of the more important types of sponge iron processes

Of the many processes for the production of sponge iron, which have been invented and tried during the last fifty years, only very few have been economically successful and reached the industrial stage.

(a) Hoeganaes process

This process is carried out in a tunnel kiln, where layers of rich iron ore concentrates and coke breeze are heated to about 1200°C in saggers, made of silicon carbide, which are placed on cars. In the original process horizontal layers were used, but in modern furnaces a packing with vertical layers, either flat or tubular is used. The finished sponge iron is removed from the saggers as sintered cakes.

The Hoeganaes process is used in Hoeganaes and Oxelosund in Sweden and in Riverton, New Jersey, U.S.A., mainly for the production of iron powder for powder-metallurgical purposes, but some of the sponge iron is also used as melting stock for the production of high-grade steel in electric furnaces and open-hearth furnaces.

Per ton of metallic iron in the sponge is consumed:

Coke breeze (dry)	610 kg
Limestone	130 "
Fuel oil for tunnel kiln and drying of ore and coke breeze	100 "
Electric energy	80 kWh
Silicon carbide (for saggers)	16 kg
Labour	2 man-hours

(b) Wiberg process

The ore is heated in the top part of a shaft furnace to 900-1000°C by complete combustion of gaseous gas from the lower reduction zones with air. The ore is then reduced in two different stages in the middle and lower part of the shaft. In the middle part the ore is pre-reduced to a composition corresponding approximately to the formula FeO, and in the lower part the final reduction to metallic iron takes place. At the interface between the two reduction zones about two-thirds of the gas from the final reduction zone is removed from the shaft and is blown through a layer of coke or other fuel in an electrically heated gas producer (carburettor), where CO_2 and H_2O in the gas react with the carbon in the coke, thus producing the mixture of carbon monoxide and hydrogen which is used for the reduction of the ore in the shaft. The sponge iron is cooled and discharged continuously into closed containers.

The hydrogen content of the reducing gas is increased to about 30% by addition of hydrocarbons or coke-oven gas to the carburettor. The sulphur in the reducing gas is removed in a dolomite filter between the carburettor and the reduction furnace.

The Wiberg process is used in five furnaces in Sweden, and two furnaces are under construction in Japan. The Swedish furnaces are all using pellets made from rich magnetite concentrates, and the Japanese furnaces are going to use pellets made from iron sand. The sponge iron is used for the production of high-grade steel in electric arc furnaces or open-hearth furnaces.

Per ton of metallic iron in the sponge is consumed:

Coke	150 kg
"Gasol" (propane & butane)	65 "
Dolomite (raw)	100 "
Electrodes (Soderberg)	2 "
Electric energy	1,150 kWh
Labour	1.7 man-hours

The investment cost is about 40 dollars per annual ton for a plant with 12 furnaces and a total production of about 1,000 tons of sponge iron in 24 hours.

(c) HyL process

The world's largest sponge iron plant is located at Monterray, N.L., Mexico, where the HyL process produces 700 tons of sponge iron per day in the plant of Fierro Esponja S.A. This company is affiliated with Hojalata y Lamina S.A., from which the process derives its name and by whom it was developed in co-operation with the M.W. Kellogg Company in New York.

Lump ores (or agglomerates) are reduced in fixed bed batch reactors. The reducing gas is a mixture of carbon monoxide and hydrogen, prepared by the catalytic reforming of natural gas and steam. Naphta, other light hydro-carbons, or coke oven gas may be reformed in the same way.

The sponge iron is melted in electric arc furnaces for the production of low carbon steels. Open hearth furnaces can also be used for the same purpose.

Per ton of metallic iron in the sponge is consumed:

Natural gas	700 m^3
Labour	0.38 man-hours

The investment cost is about 37 dollars per annual ton for a plant with a production of about 500 tons of sponge iron in 24 hours.

Further information about the HyL process will be given in the paper B4-1, "The HyL Process", by Messrs. J. Celada and J. Skelly.

(d) H-iron, Nu-iron and Esso-Little processes

These processes, which are using fluidized beds for reduction of powdered iron ore with pure hydrogen or hydrogen-rich gases, have been tried in pilot plants in the U.S.A., but they have not proven economically feasible.

(e) RN and SL processes

The RN (Republic-National Lead) and SL (Steel Company of Canada - Lurgi) processes are both using rotary kilns for reduction of iron ore with solid fuels, magnetic separation of the sponge iron from excess fuel, which is recirculated, and introduction of air through tubes along the kiln for controlled combustion of the carbon monoxide resulting from the direct reduction of the ore with solid carbon.

In both processes, the kilns are heated by central burners for gas or oil at the discharge end of the kiln. The main difference between the two processes seems to be that in the SL process some gas is added also to the air tubes along the kiln, so that these tubes can act as gas burners.

(i) The RN process has been developed in a semi-commercial pilot plant at Birmingham, Alabama, U.S.A. Lump ores of different types and pellets, made from rich concentrates, have been tested. Depending on the purity of the raw materials, the reduced product may or may not be subjected to subsequent concentration and briquetting of the metallic iron before feeding to steel furnaces. As solid reductants have been used coke breeze, anthracite and char. A new process for charring coking as well as non-coking coal on a travelling grate has been developed. The hot char gases can be used directly as fuel in the rotary kiln. The total consumption of fuel per ton of metallic iron in the sponge is about 3 million kcal for high grade ore pellets (70% Fe) and 6 million kcal for low grade ore (35% Fe) which has to be concentrated after reduction.

(ii) The SL process has been developed in a semi-commercial pilot plant at the Steel Company of Canada, Hamilton, Ontario, Canada, in collaboration with Lurgi Gesellschaft für Chemie und Hüttenwesen m.b.H., Frankfurt (Main), West Germany. The tests have been carried out mainly with rich pellets, anthracite and natural gas. No concentration of the reduced pellets has been necessary, only briquetting of about 10 to 15% fines and dust formed during reduction. Pellets of 8 to 15 mm and rich lump ores of 8 to 20 mm have been proved to be favourable. The total consumption of fuel per ton of metallic iron in the sponge is about 3.5 million kcal.

Both the RN and SL processes are still in the experimental stage, but the results are promising and commercial size plants are being planned.

(f) Echeverria process

This process is used at the steelworks of Patricio Echeverria S.A., Legazpia, Guipuzcoa, Spain. It is a very simple method using externally heated vertical retorts for reduction of iron ore with charcoal, coke-breeze or anthracite.

Lump ores (or agglomerates) are mixed with the reducing agent and some limestone for sulphur removal. Anthracite with 25-30% ashes is generally used for the reduction.

The mixture is preheated in the upper part of the retort by burning some of the gas with air, and the sponge iron is continuously discharged into a water-cooled chamber. Excess reductant is separated from the sponge iron by magnetic separators and recirculated.

The heating of the retorts from the outside can be made with any solid, liquid or gaseous fuel. In Legazpia ordinary producer gas is used.

The plant in Legazpia has 40 retorts. Its capacity is about 18,000 tons of sponge iron per year.

Per ton of metallic iron in the sponge are consumed:

Anthracite (25-30% ashes)	400 kg
Bituminous coal (for heating)	900 kg
Limestone	60 kg
Electric energy	120 kWh
Labour	2.5 man-hours

The investment cost is about 30-40 dollars per annual ton for a small plant with a production of about 50-60 tons of sponge iron in 24 hours.

Further information about the Echeverria process will be given in the paper B4-2, "The Echeverria Sponge-Iron Process", by Mr. G. Cedervall.

(g) Electric pig-iron smelting

Most of the furnaces for electric pig-iron smelting are of the Tysland-Hole type and some are of the similar Demag type. The most common size is 10,000 to 30,000 kW units.

The reducing agent is a mixture of 30-50% gas coke and 50-70% coke breeze.

The best results have been obtained with self-fluxing sinter. The CO_2 content of the furnace gas, which is only about 10%, if lump ore is used, is increased to about 20-25%, if self-fluxing sinter is used.

The consumption per ton of pig iron in furnaces using self-fluxing sinter is:

About	2,000 kWh
About	370 kg of coke & coke breeze
About	15 kg of Soderberg electrodes
About	2 man-hours .

The heat value of the gas from electric pig iron furnaces, consisting mainly of carbon monoxide, is in the order of 1 million kcal per ton of pig iron. The gas can be used in chemical industry for production of methanol, urea and ammonia, but the main interest today concerns use of the gas for increasing the production of pig iron by preheating and prereduction of the charge.

Tests for such pretreatment of the charge have been carried out by Elektrokemisk Company, Oslo, Norway, in a rotary kiln or a shaft furnace, installed directly above the electric smelting furnace.

Preheating and prereduction is also used in the Strategic-Udy process with the utilization of a rotary kiln for the prereduction and a special technique for the smelting in the electric furnace. The process facilitates selective reduction of complex ores and direct production of semi-steel with medium or low carbon content.

Further information about the Strategic-Udy process will be given in the paper B5, "The Strategic-Udy Process", by Mr. K. Sandbach.

The conventional electric pig iron process operates with a power consumption in the range of 2,000 - 2,500 kWh per ton of pig iron, which hardly justifies a higher power price than 0.005 U.S. dollars per kWh.

By prereduction, it is possible to reduce the power consumption to the range of 1,000 - 1,500 kWh per ton. With this low power consumption, a higher power price may be tolerated, probably 0.007 - 0.008 U.S. dollars per kWh or more.

Very considerable advantage is gained by increased iron production for the same transformer capacity and furnace size. This gives increased iron production per man-hour and makes the electric process competitive with the conventional blast furnace process also in areas not favoured by water-power resources.

(h) Other Direct Reduction Processes

During the period from 1924 to 1930, the Flodin-Gustafsson method was tried in Sweden in electric arc furnaces provided with means for continuous charging of briquettes that were made of rich magnetite concentrates and charcoal powder with slaked lime as a binder. Also a mixture of sinter, charcoal in lumps and burnt lime could be used. Steel of high quality was produced, with a consumption per ton of steel of about 380 kg of charcoal, 200 kg of burnt lime, 2,700 kWh and 10 kg of electrodes. If the sinter was prereduced in a separate furnace, so that 60% of the total iron was in the metallic state, the consumption of electric energy was only 1,400 kWh per ton of steel. Tests were also carried out with coke instead of charcoal, but the sulphur content of the coke was too high to be eliminated economically in the steel-making furnace.

The drawback of the method was high power consumption, low furnace production, and the necessity of using charcoal as the reducing agent. It was found more economical to produce pig iron or sponge iron from the ore as a first step and then use the steel furnace only for melting and refining. It is possible, however, that direct steel making in electric furnaces may be of interest in countries where there are rich iron ores, cheap hydro-electric power and cheap fuel with a low sulphur content, especially if the rich gas from the furnace can be utilized for prereduction of the ore, thus lowering considerably the consumption of electric energy, fuel and electrodes and increasing production.

Another way of making steel directly from iron ore is to use it as charge ore or feed ore in open-hearth furnaces or electric steel furnaces, using a high percentage of pig iron. The ore is then reduced by the carbon in the molten iron, thus increasing the output of the furnace. This is the simplest and most commonly used method of making steel directly from iron ore.

Also in Bessemer and Thomas converters, ore can be added instead of scrap. A fairly large quantity of ore can be added and reduced in oxygen converters, especially in Kaldo converters, where the ore addition can be about 15% of the weight of the hot metal.

(i) Economic characteristics of the blast furnace process

For comparative cost calculations the following approximate figures for the production of one ton of hot metal from rich ores in an ordinary coke blast furnace, producing about 1,000 tons of hot metal in 24 hours, can be used:

Metallurgical coke	600 kg
Limestone	180 kg
Labour	0.8 man-hours
Investment cost (not including coke oven plant and sintering plant)	50 dollars/annual ton
Credit for gas and slag	2 dollars/ton hot metal

(j) Melting of sponge iron

Sponge iron can be used instead of scrap for the production of steel in all types of steel-making furnaces.

In electric arc furnaces, various amounts of sponge iron can be used, up to 100 per cent of the charge.

In high frequency induction furnaces, the gangue content of the sponge iron must be kept as low as possible, because it is difficult to melt large amounts of slag in an induction furnace.

In basic open-hearth furnaces about 25-50% sponge iron can be used with the normal melting technique, and up to 70% sponge iron and 30% scrap with a special melting technique. Sponge iron with high carbon content (1.5 - 2.5% C) is easier to melt in open-hearth furnaces than low carbon sponge iron (0.0 - 0.5% C).

In acid open-hearth furnaces, the normal addition of sponge iron is about 20-30%. More sponge iron can be used for the production of acid open-hearth steel, if a duplex process is used, with melting of the sponge iron in a basic arc furnace or a basic open-hearth furnace, and finishing the heat in an acid open-hearth furnace.

Sponge iron can also be melted in gas- or oil-fired rotating furnaces and in oxygen converters. In a Kaldo converter about 40% sponge iron with 1.5% carbon can be melted.

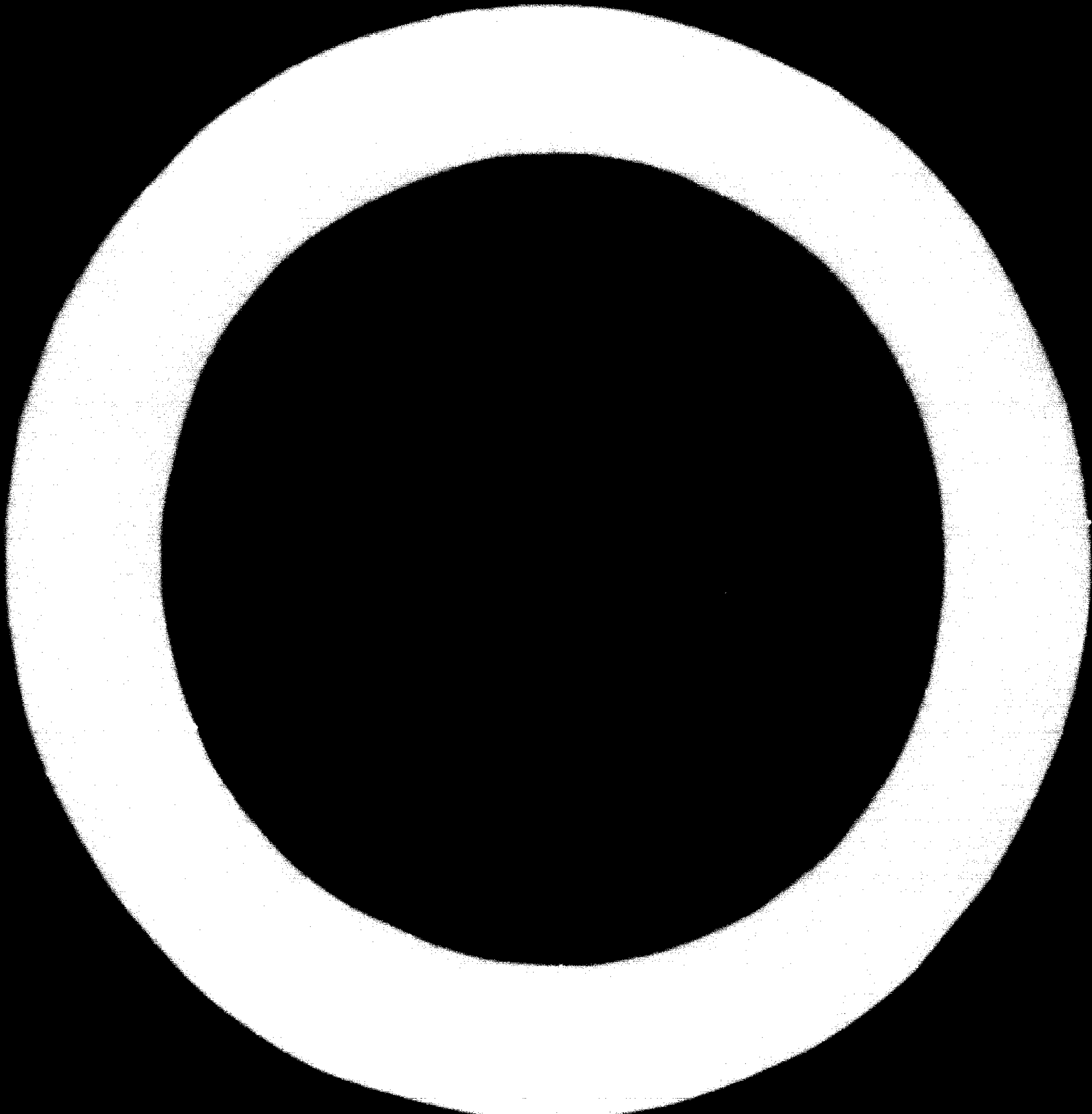
Due to the content of gangue and non-reduced FeO in the sponge iron, power or fuel consumption for melting sponge must necessarily be higher than for melting scrap. In an electric arc furnace, for instance, the extra power required for melting sponge can be calculated to be 0.76 KWh per kg of extra slag, and 0.95 KWh per kg of Fe combined with oxygen as FeO. For a good quality sponge iron, this extra power required is small, and for a sponge with 90% total Fe, 91% reduction and 7.5% slag, it is 130 KWh per ton of Fe.

(k) Comparison of different processes

The price of one ton of pig iron, hot metal or scrap cannot be directly compared with the price of one ton of sponge iron. Cost calculations for comparison of different processes should always be made for one ton of finished steel, and eventual differences [illegible] quality should also be considered.

[illegible] many other factors to be considered before the best method can be selected, for instance, the chemical and physical characteristics of the ore, its reducibility, [illegible] fines and [illegible] properties, the reducibility and [illegible] of the various [illegible] products, the availability and price of [illegible] energy, the scale of production, the manpower factor, the [illegible] products to be made, and market conditions. [illegible] must be studied separately by experts, [illegible] of methods or combinations of methods can be made.

FIGURES



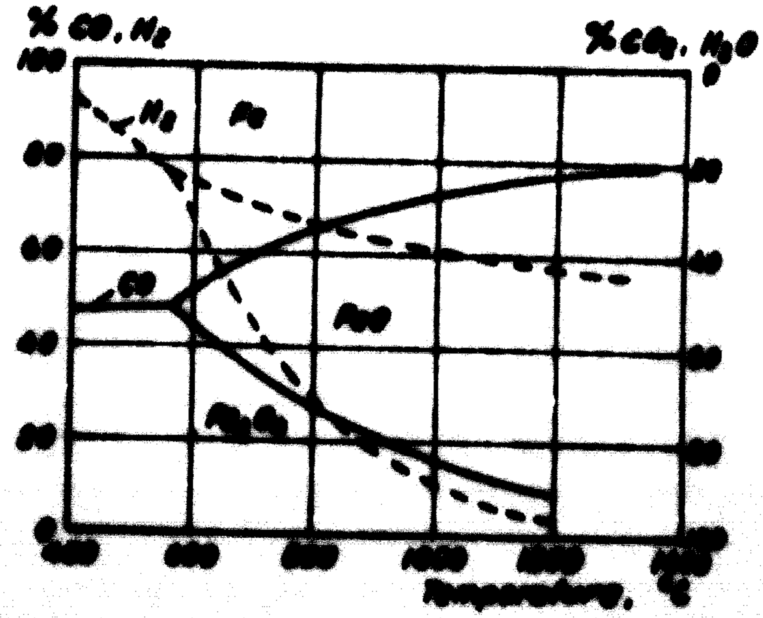


Fig. 1
Equilibrium diagram

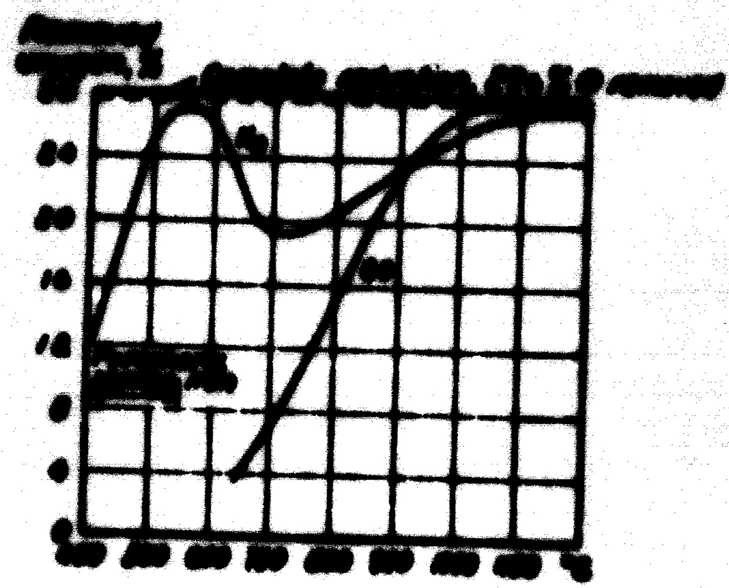


Fig. 2
Reduction velocity, expressed as per cent oxygen removed from 2 mm grains of Fe_3O_4 during 2 hours reduction with hydrogen or carbon monoxide.

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