PRODUCTION OF IRON AND IRON-ALLOY POWDERS

A Dissertation
submitted in partial fulfilment
of the requirements for the degree
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MASTER OF ENGINEERING
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METALLURGICAL ENGINEERING
(Extractive Metallurgy)

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CERTIFICATE

CERTIFIED that the dissertation entitled 'PRODUCTION OF IRON AND IRON-ALLOY POWDERS' which is being submitted by Mr. Chandra Shekhar in partial fulfilment for the award of Master of Engineering in Metallurgical Engineering (Extractive Metallurgy) of University of Roorkee, Roorkee is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for award of any other degree or diploma.

This is further to certify that he has worked for a period of seven months from January, 1972 to July, 1972 for preparing this dissertation at this University.

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P_R_E_F_A_C_E

The nature gave us an idea of powder metallurgy. The erosion of big stones into sand can be said to have inspired the mankind to develope this new technology- Powder Metallurgy. The technique of powder metallurgy led to the development of metals possessing excellent properties which cannot be obtained by other techniques. As in all the metals, iron and steel are most widely used, same is also true for iron and its alloy powders because these are easily processed, cheap and versatile. Although a numb-er of methods are available for the production of iron and iron-alloy powders but with the increase in demand and man's natural curiosity led to the birth of new techniques of powder production.

In the present work " Production of Iron and Iron-Alloy Powder" an attempt has been made to produce the iron and iron-alloy powders of high purity economically from iron wastes. The iron bearing materials eg. scrap, turnings etc. were dissolved in hydrochloric acid and super saturated solution was formed at higher temperature. On cooling this solution, the crystals of ferrous chloride were obtained which after compressing were reduced by hydrogen. The hydrochloric acid produced during reduction was recovered. The effect of time and temperature on reduction were studied.

The report has been divided into four chapters.

Chapter I deals with the general introduction, advantages and limitations of powder metallurgy and its applications.

Chapter II includes literature review. A critical survey of the methods of iron powder production was done and reviewed in this chapter with the characterstics of the powder produced by various methods. The mechanism and kinetics of the reduction of ferrous chloride is also discussed together with the factors affecting the rate of reduction.

Chapter III deals with the description of experimental set up and procedure followed in the present investigation. The crystals of ferrous chloride and alloy chlorides were made and after processing were reduced in a stainless steel tube reactor. The hydrochloric acid produced during reduction was collected and its recovery was measured by titrating against 1.0N - NaOH solution. The ferrous chloride crystals were reduced at 400°, 450°, 500°, 550°, 600° and 650°C and the crystals of iron-alloy chloride namely Fe-Ni, Fe-Cr and Fe-Ni-Cr were reduced at 600°C only. The crystals and powder were chemically analysed to know the percentage recovery of hydrochloric acid and percentage reduction. The shape of the particles of the powder produced was also studied.

Results obtained from the experiments carried out and a discussion on them constitutes the subject matter of Chapter IV. It is found that the reduction of iron and iron-alloy chloride crystals takes place topochemically. The increase in temperature increases both the percentage reduction and recovery of hydrochloric acid. The nature of the reduction of ferrous chloride and iron-alloy chloride crystals is same. Presence of Ni^{2+} ions increase the rate of reduction whereas Cr^{2+} ions reduce it.

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LIST OF SYMBOLS

q = Reduction rate in moles HCl, cm^{-2} sec^{-1}

r = Rate of advance of reaction front

C_o = Bulk density

D = Diffusion coefficient of HCl through the H_2

R' = Universal gas constant

γ = Porosity factor

T = Absolute temperature

x = Thickness of diffusion zone

p_o = Thermodynamic equilibrium partial pressure of HCl in the reacting pellet.

p = HCl partial pressure in the bulk hydrogen stream.

x_o = Thickness of reaction zone in the absence of bulk pressure.

f = Fractional reduction

t = Time of reduction in minutes

d = Pellet diameter

ρ_{Fe} = Weight of Fe (initially present as chloride)

R_x = Fractional reduction of particle.

θ = Time of reduction in minutes

$d\rho$ = Diffusion of hydrogen chloride in H_2, ft^2 per minute

X_1 = Fractional concentration of HCl

X_o = Fractional thermodynamic concentration of HCl at equilibrium at reaction temperature.

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CHAPTER - I

INTRODUCTION

I.1 GENERAL

Powder metallurgy is not a new concept to man, although much of its development has taken place during the present century. It has its origin at least 6000 years ago, when primitive techniques for the reduction of iron and copper ore to sponge and powder allowed the fabrication of untensils and weapons. The first recorded use[1] was by the ancient Egyptians who were able to produce sponge iron by reducing iron oxide with charcol for making swords and implements. About 1600 years ago, the smiths of India managed to produce a real masterpiece, namely the famous Delhi Pillar, weighing 6½ tons. Later the Hittites[2] used a similar process, but it was really in the early 19th century, with Wollaston's[3] work on platinum and the later endeavours in the field of ductile tungsten wire and cemented carbides by Coolidge[3], Schwarzkoff[4] and others, in the 1920's, that the foundation of the present state of the industry were laid.

Powder metallurgy has been defined[3] as the art and science of manufacturing useful articles from metal powders and of producing these powders. Such articles may be in the form of ingots, semifinished or finished shapes. It permits the production of metallic or metal like bodies of simple or complicated shapes without the use of the orthodox metallurgical practices such as melting, casting, ingot solidifcation, metal working and shaping by machining operations . It provides a means of obtaining a wide range of characteristics in a variety of metallic compositions and at reasonable costs. By this method it is possible to produce parts of two or more elements, capitilising on the special properties of each in a powder metal compact, where such elements could not be fabricated into an alloy since they perhaps may be partially or completely immiscible in the molten and/or solid state.

During the past decade, [illegible], improved techniques for the manufacture of powder metallurgy parts have been developed throughout the industry which has contributed the acceptance and growth of the process. More complex and critical parts are now being produced and with the availability of new powders and the development of new fabrication techniques, one can expect continued rapid growth in the industry. An indication of the rate of this growth can be gained from the fact that the production of iron powder has doubled over the past five or six years. Table-I shows the production[4] of iron powder by the various. companies in different countries in the year 1970.

Some of the unique advantages[3,6] of powder metallurgy are as follows:

1. Powder metallurgy is used to manufacture products which can be made in no other way and those which could be made by another method but for which powder metallurgy is more convenient and more economical.

2. Saving in labour and materials, elimination of capital investment in machines, reduction in overhead and tool

time, greater end product value and better performance are among the other important considerations in the decision of powder metallurgy.

3. The powder metallurgy process can be more convenient and more economical because

i) it does not involve the handling of molten metal

ii) its end products seldom require subsequent machining or finishing operations.

iii) porosity of products can be controlled over wide range.

iv) it allows the rapid mass production of metals in precision dies.

4. There are few other reasons which makes the process economical such as

i) mass production techniques employed

ii) the reduction or elimination of scrap losses

iii) reduction or in many cases, the complete elimination of machining or finishing operations.

5. Since there is substantial reduction of machining and scrap losses, powder metallurgy is ideally suited to the production of complex and intricate shapes. Control of porosity and density is an important factor in parts such as filters or counter-balances.

The powder metallurgy techniques have also certain limitations[1,3] which are as follows

1. Only small size products can be produced

2. Due to more free surface area, the reactivity of powders is increased. So greater care is needed in handling.

3. Because of high cost of powders, dies and tooling, the powder metallurgy method is not inexpensive and will only pay off where there is a large volume of parts involved or parts simply cannot be made by any other technique.

I.2 APPLICATIONS OF POWDER METALLURGY

The major applications[1,2,3,4,5-9] of powder metallurgy can be classified as follows:

1. Structural applications
2. Porous and frictional materials
3. Machine and tool appliances
4. Electrical and electronic appliances
5. Manufacture of chemicals
6. Miscellaneous applications

(1) STRUCTURAL APPLICATIONS[1,2,16]

These include various kinds of small structural parts such as gears, cam and connecting rods. In the past, such parts have been made by casting, forging and machining but at present these are made by powder metallurgical techniques. These are finding a growing application in the motor industry with the increased popularity of automatic transmission.

(2) POROUS AND FRICTIONAL MATERIALS[3,5,6]

The manufacture of self lubricating bearings from iron, brass, bronze and aluminium alloys have to be a major application of this process. These are used in small motors of fractional horse power. Porous alloys made of bronze compounded with iron possess stable frictional characterstics and hence are use as materials for engine clutch plates and brake lining of tractors, automobiles, aircrafts etc. Various metallic filters made of stainless steel powders are use for the filtration of various fluids.

3) MACHINE AND TOOL APPLIANCES[1,3,6]

Commercial cemented carbide, a product made by powder metallurgy technique, is used for machine and tool parts where high resistance to wear is of utmost importance. It also enhances the ability to produce cemented carbide tool bits of high hardness and wear resistance. Grinding wheels and drills are made by combining diamond dust or carbide dust with softer metals.

4) ELECTRICAL AND ELECTRONIC APPLIANCES[4,5,6]

During last two decades, powder metallurgy has made a great inroad in electrical and electronic field. Sintered iron powder products are especially significant for magnetic materials and cores. Cores made of pure iron, iron silicon and iron nickel are used in motor pieces and generator armatures. Powder metallurgy has been successfully used in the manufacture of electrical contacts which are usually composed of tungsten or molybdenum plus silver or copper to enhance desired properties like electrical conductivity and resistance to heat incorporated in one piece. These properties cannot be obtained by any other way. Manufacture of lamp filaments is another application of powder metallurgy.

Another product of increasing importance made by powder metallurgy is tiny memory cores for computers, about the size of the head of pin. These are made of powdered ferrites. Oxide magnets are, especially, adopted in radio and television receivers, communication equipments, telephone, etc for their excellent magnetic properties.

5) MANUFACTURE OF CHEMICALS[3,4,9]

The paint and pigment industry is probably the largest and most important consumer of metal powders. Flake stainless steel powders have found applications in paints for bottom of ships and fan blades of exhaust fans to remove nitric acid fumes.

6) MISCELLANEOUS APPLICATIONS[27]

Welding electrodes are often coated with iron powders to deposit more metal in the weld to increase the efficiency of the operation. Recently powder iron is introduced into oxygen stream of a cutting torch to allow the flame to penetrate the refractory oxides in high alloy stainless steel. This process is also applicable to the cutting of cast iron and high strength materials.

Above are the few applications of powder metallurgy process. In future, it is expected that more new applications will come-up. Though, there are some limitations to the applications of powder metallurgy process, but with an understanding of these limitations, the process will successfully continued.

CHAPTER - II

LITERATURE REVIEW

II.1 INTRODUCTION

During the past few decades powder metallurgy is rapidly coming into prominence because of its versatility in fabricating complex shapes and production of special parts like self lubricating bearings and other sintered components, electrical contacts, composite materials, magnetic components etc. It also helps to eliminate the numerous costly machining operations and material losses in addition to the reduction of other costs such as tooling, inspection and quality control. Of all the metal powders, iron powder is easily processed, cheap and versatile. In recent years sintered iron powder components have succeeded in replacing the traditional materials such as copper, brass,bronze etc. As a consequence its applications have reached a new height and is being manufactured in the large quantities. During the past twenty years the growth rate throughout the world has been considerably increased. The Table-II shows the consumption[5] of iron powder in various years in the world.

The largest consumption of iron powder is in the production of sintered iron powders. With the development[4] of direct rolling of strip from powder, the consumption of iron powder will increase tremendously. Besides automobile industry, other major fields of application of iron powder include welding electrodes, flame cutting, magnetic and electronic components, magnetic seed cleaning and chemical industries. The expansion of the use of iron powder for those applications will depend on a considerable reduction in the price of powder.

In order to be an acceptable product for the powder metallurgy industry, iron powder must have certain physical and chemical characteristics[7,9], and the important ones are given below:

1. The composition i.e. purity, extent of oxide contents, acid insolubles and nonmetallic inclusions - on which the extent of deformation depends and also the density of the green and sintered parts.

2. Microstructure
3. Particle size and shape
4. Flow rate and compressibility
5. Reproducibility

II.2 METHODS OF IRON POWDER PRODUCTION

There are a great many methods[1,3-5,9] of producing iron powder, each being capable of making products with distinctive chemical and physical characteristics. These methods may be classified under five main headings:

1. Reduction
2. Carbonyl decomposition
3. Atomization
4. Electrolytic
5. Hydrometallurgical

Generally speaking, each method of the powder production yields a specific product with definite qualities which may or may not make it suitable for particular applications. Sometimes several entirely different methods of production results in powders equally well adopted to process to same type of industrial article. Usually each application requires a powder with special properties which can be obtained only by a particular method of powder production.

Instead of this, in addition to the incentive of producing a more acceptable product at lower cost, the availability of a particular raw material has had a major influence on the process selection. The Table -III shows the world production[5] of iron powder in 1970 by each of the main process groupings and the raw materials which can be used.

II.2.1 REDUCTION METHODS

These processes involve the reduction of iron oxide in the form of an ore concentrate or mill scale by a solid or gaseous reductants. These are normally used for the production of pure iron powder. A fairly uncomplicated, these produces the least dense type of powder. A number of reduction processes are available but the most common are described below:

1) HÖGANÄS PROCESS

This process[2,4,6,9-15] was firstly developed by Sieurin of Sweden in 1903 for the production of sponge iron. Later the

Höganäs company extended it for the production of iron powder. In this process rich magnesite ore averaging 70% of Fe is mixed with powdered lime stone and coke breeze. This mixture is packed in cylindrical refractory containers known as 'saggers' and heated to 1200°C (i.e. at a temperature below the melting point of iron) in a tunnel kiln through which the saggers slowly progress. Because reduction by solid carbon is a slow process and also because of low temperature employed, the process is a protracted one taking several days to complete. At the end of the reduction, the saggers are cooled to 200°C and the product, in the form of sponge iron cake, is taken out mechanically As a consequence of low temperature, absorption of impurities from the flux and the reductant are at a minimum, the product being a high purity iron (+ 97.5%) with a phosphorus and sulphur content below 0.015%. This is ground to powder and the iron is separated from impurities magnetically. Further annealing is done under hydrogen atmosphere as required in order to produce desirable particle characteristics. The flow sheet of the process is given in fig-1.

Various modifications have been introduced to this process from time to time to improve the quality of the product and economics. The important ones are discussed below:

1) USE OF SILICON CARBIDE/METALLIC CYLINDERS: These cylinders[14] have high thermal conductivity which permits a fast rate of heating and cooling and thus results in less overall time, better utilisation of fuel and possibility of quenching from high temperatures.

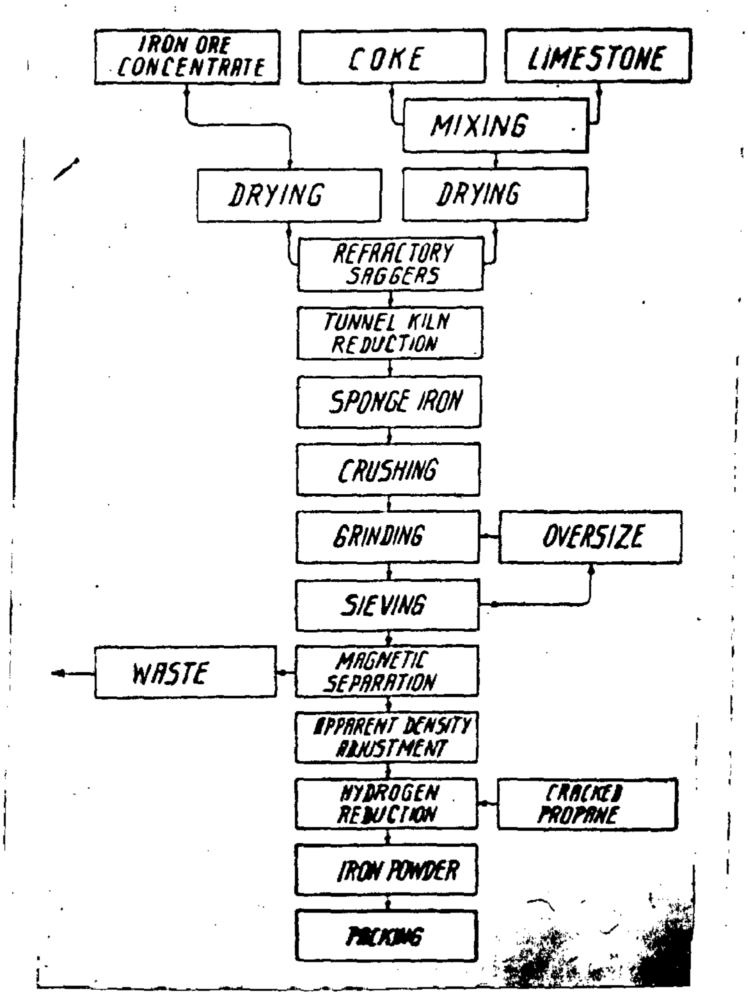


FIG.1. Höganäs Process: A typical flow sheet.[13]

ii) USE OF CALCIUM CARBIDE: It can function both as a reducing agent and a fluxing agent. The reaction is exothermic so low thermal energy is required to carry out the reduction.

iii) USE OF MIXTURES OF REDUCING AGENTS: At the Brovary steel plant[16] in USSR, the use of both wood charcol and gaseous reducing agents are practised.

2) H- IRON PROCESS

This process[2,15,17,18] was developed by the Bethlehem steel Co and Hydrocarbon Research Inc. in 1959. In this process sized iron ore is preheated to a temperature of 480°C and is fed to the top of a reactor vessel (fig.2). Reduction is carried out in three different zones of fludized beds and the ore is transferred from bed to bed and finally discharged at the bottom of a hopper. Preheated hydrogen is used as the reducing agent and it enters at a pressure of 35 atmosphere at the base of the reducer and passes through there three beds which are in series, reducing the iron ore to iron. The reduced mass is annealed under nitrogen atmosphere at 800-850 °C.

3) PYRON PROCESS

In this process[4,5,9,15] iron oxide is reduced with gaseous reductants such as hydrogen, water gas etc. Here the mill scale containing < 0.5% Si is dried in a drier, crushed to 100 μ and oxidised in a rotary gas fired heating furnace at 870-930°C. Heated and oxidized powder thus obtained is kept on a conveyor belt into an electrically heated furnace at

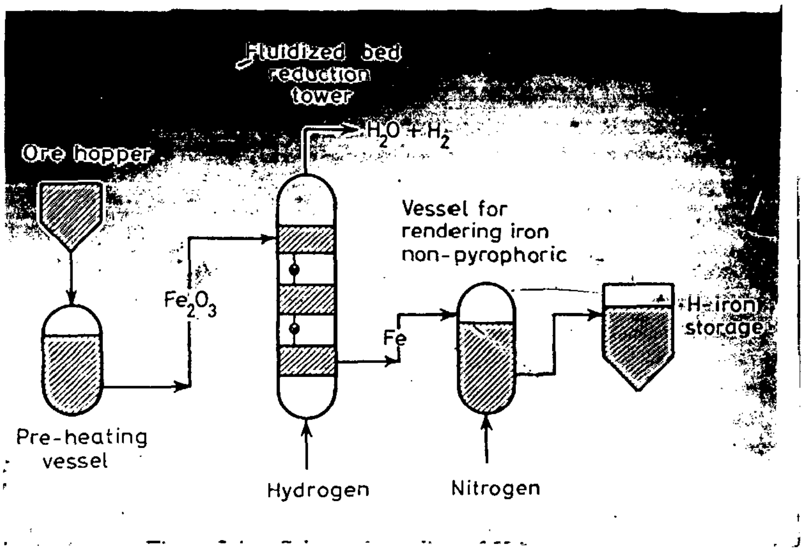


FIG.2: A Schematic outline of H-Iron process.[2]

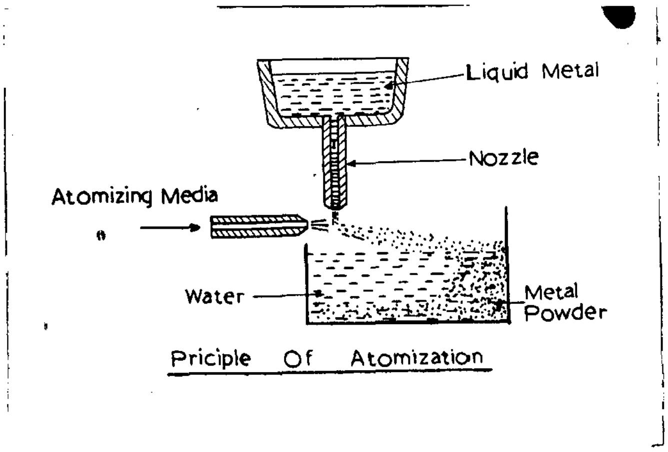


FIG.3: The principle of atomization

980°C in hydrogen atmosphere. The resulting material is processed to give the desired powder properties. The process is comparatively cheap due to short time of reduction, low carbon content of powder and reduced labour and maintenance costs.

The following two important modifications in the Pyron process are recommended.

i) USE OF OTHER CHEAP REDUCING AGENTS: In Japan water gas and in USSR converted natural gas are used as reducing agents. Recently it has been reported that methane[19] can also be used as the reducing agent.

ii) PRODUCTION OF ALLOY POWDERS: Instead of mill scale, the alloy scale can be used to produce alloy powders. In France[20] the alloy iron scale containing 3% Chromium and Aluminium is used for the production of powders.

4) CHEMICOMETALLURGICAL PROCESS

In this method[21] the iron ore concentrate is first calcined at 800°C to burn out carbon and sulphur and then it is mixed with commercial calcined coke amounting 3 to 4 times than theoritically required followed by grinding to 50-60 μ size. This mixture is then loaded into a vertical steel tube retorts with a hermetic lid and have iron pans arranged one over the other in the form of stack. Hydrogen is supplied from the bottom of the retort to reduce the charge.

The resulting product is in the form of a cake which a porous spongy mass and this is coold under hydrogen atmosphere. After this the cake is ground in steel ball mill containing water. It was then leached with acidified hot water (pH 3-3.6) and finally the powder is washed with water and dried in vaccum drier at 60-80°C. This powder has successfully been utilised for sintered magnets, magnetic cores etc.

6) CARBIDE- OXIDE REACTION PROCESS

This process is based on the interaction of high carbon iron powder with relatively pure iron oxide at suitable temperatures to yield iron powder. At Ferrum company of Canada[9], an electric furnace is used to melt synthetic cast iron which is then shotted and mixed with iron oxide to decarburise. By controlling atmosphere during annealing and employing more degree of gaseous reduction a considerable flexibility can be introduced in the process. The iron powder obtained by this process can be compacted to high densities. This is because of the removal of carbon by oxide from the surface of particles as carbonmonoxide to give a soft ferrite layer at the surface which improves compactibility of the powder.

POWDER CHARACTERESTICS[3,4,6]

Reduction processes tend to give spongy irregular shaped particles having a relatively low oxygen content. A fairly high amount of impurities are present. These powders have a relatively low apparent density and compressibility which tends to be reduced by the impurities present. These impurities also tend to increase die wear. Powders produced by reduction of mills scale are smooth and spherical and have a high flow ratio.

These powders serve as starting materials for many magnetic and electronic components, coating for welding electrodes and for many other small size sintered parts of intricate design. High purity iron powder is used in the automobile industry for making parts like magnetic clutches, parking rings, valve, tappet bodies and castle clutch cylinders[22].

II. 2.2 CARBONYL DECOMPOSITION METHOD

This method[3] has its origin in Germany, where I.G. Fabren Industrie produced commercial quantities of iron powder and then it was developed by International Nickel Co. in U.K. for the production of both nickel and iron powders. The process is based[1,3,9] on the formation and then decomposition of iron carbonyl $Fe(CO)_5$ which is liquid at room temperature but boils at 103°C. The iron carbonyl is obtained by passing carbon monoxide over the powdered or spongy iron in a pressure chamber at pressures of 70-200 atmosphere and temperature 200°C followed by condensation and storage under pressure. During the decomposition, the temperature of the chamber is maintained at 200°C so that the liquid carbonyl boils. As the pressure is reduced to 1 atmosphere, the iron carbonyl vapours decomposes and deposit as metal powder in the hot space. The decomposition can be facilitated by mixing the iron carbonyl with a stream of hot inert gas such as nitrogen. After decomposition, the powder can be mechanically ground if further reduction of size is required.

In USSR it has been claimed that very fine particles of size 0.5-1.0 μ can be obtained by thermal decomposition of iron carbonyl with atomisation using centrifugal nozzles of tangential or screw type.

POWDER CHARACTERISTICS[4,5,23]

Carbonyl particles are regular and spherical in shape. The powder is of high purity and has a finer particle size, narrow particle size distribution and a higher particle density. Indeed carbonyl powders, generally, are the most dense of any iron powder. They have excellent sintering properties. These are best suited for permanent magnets, high frequency iron cores coils and various other magnetic applications.

II. 2.3 ATOMIZATION METHODS

Atomisation[1,3-5,9,24-27] is becoming the most widely used commercial method for the production of iron powder. In this method the raw material is normally high grade scrap which is melted in an arc or induction furnace. The molten metal is forced to come out of a nozzle and then subjected to heavy blast of high pressure air, inert gas or liquid jets either through the common nozzle or nozzles provided separately. The resultant stream of molten metal is disinto-grated into fine droplets which are frozen either by further passage through air or by quenching in a water tank. The solidified particles are dried and finally annealed to give the required product powder. The basic principle of the process is shown in fig.3. The various processes developed in different countries by different workers are described below:

1) MANNESMANN PROCESS

The process is used by Mannesmann[4,5,24] in Germany and Easton in USA and it utilises a high carbon melt and compressed air as atomizing agent. During atomization the powder is partially oxidised which is reduced by carbon during annealing. In Canada the process utilizes high purity pig iron which is atmomised by water. Reduction is carried out in a protective atmosphere. The high carbon granules formed by atomization are ground and reacted with mill scale (Fe_3O_4) at elevated temperature The carbon in the iron and oxygen in the mill scale react to produce a powder having the required properties.

2) QUEBEC METAL POWDER PROCESS

This process[5,27] is developed in Canada and uses the molten iron produced during the titanium bearing slag. Molten iron is first transferred into a furnace and superheated. On reaching the appropriate temperature, it is atomised into fine solid particles by impact of high pressure water. Powder particles of proper size are then treated at high temperature in a controlled atmosphere furnace in order to remove final traces of carbon and oxygen. During furnace treatment particles have a tendency to agglomerate and sinter to some extent. This sinter cake is broken down by a series of attrition mills.

3) D.P.G. PROCESS

In this process[4,6] the stream of molten metal is broken up into small droplets by impingment of a rotating disc.

4) A.O. SMITH PROCESS

This process[6] was developed in U.S.A. Here consistent high grade scrap is used and subsequent annealing of atomized particles reduces carbon and oxygen to very low level.

POWDER CHARACTERISTICS[3-6]

Atomisation processes can be operated to give spherical or irregularly shaped particles. Atomised powder is characterised by high apparent density and flow rate. Good compressibility is obtained by having very pure fully annealed particles. When prealloyed powders are made, each particle have the same composition as that of the melt from which it was made.

II.2.4 ELECTROLYTIC METHODS

Small quantities of electrolytic[3-6,9,28-31] iron powder are produced in several countries. The process is becoming less popular due to higher cost of production compared to other methods. There are two methods of producing iron powder electrolytically.

1. Electrolysis of aqueous solutions
2. Electrolysis of fused salts.

1) ELECTROLYSIS OF AQUEOUS SOLUTIONS

In this method[1,3,4] ferrous wastes, scrap, mill scale as well as low grade ore can be used as starting material. Ferrous sulphate or ferrous chloride is used at the electrolytes. The sulphate bath produces more refined product while chloride bath at high temperature results in a greater rate of deposition. Generally chloride baths are preferred as their cell voltage is lower and separation of iron powder is easier. Anode is made of impure iron, steel or cast iron. There are two methods for the production of iron powder by this process which are as follows:

a) ELECTRODEPOSITION WITH SOLID CATHODE: In this method the cathodes are usually of stainless steel sheet. The cells are acid resistant. Upon electrolysis pure iron particles are deposited on the stainless steel sheets as a spongy or solid mass, leaving impurities in the solution. The deposits are washed and milled to desired screen size and then annealed to soften and to eliminate hydrogen remaining from the electrolysis of iron. The particle size can be controlled by changing the current density.

b) ELECTRODEPOSITION WITH LIQUID CATHODE: Iron is electrodeposit from aqueous ferrous sulphate solution on a liquid mercury cathode. Though the solubility of iron in mercury is [illegible] is only of the order of 10^{-40} percent, it is easily wetted by mercury. Separation of iron and mercury is carried out by filteration, centrifuging or by magnetic means followed by distillation.

2) ELECTROLYSIS OF FUSED SALTS

In this method[31] pig iron or sponge iron is used as the soluble anodes and either sodium chloride is used as an electrolyte or a mixture of sodium and potassium chlorides. The electrolyte is prepared by melting sodium chloride and anhydrous iron chloride in a nickel vessel in an argon or nitrogen atmosphere at 800-900°C. After weighing the anode material is charged into the anode basket which is tightly closed and purged with nitrogen. It is then heated to require temperature and the required level of fused electrolyte is established.

The cathode made of stainless steel is immersed in the fused electrolyte and direct current is switched on. After electrolysis, the cathode deposit is cooled and discharged from the cathode to a chamber purged with inert gas.

The cathode deposits and anode residue are processed hydrometallurgically. The deposits are then annealed under hydrogen atmosphere at 800°C to remove oxide films on the surface of particles.

This method is superior to aqueous solution electroof insoluble iron compounds from aqueous solutions. An acid solution of $FeCl_3$ containing a polysaccharide such as dextran is added in the form of drops or sprays or by violent mixing to an alkaline precipitating solution like ammonia. The formation of the gelatinous precipitate of ferric hydroxide normally obtained is completely supressed with the production of gel. The amount of modifying agent and the method of mixing control the size and shape of the gel particles. The gels are then aged and washed thus effecting substantially the purification, these are then air dried and pass into a reducing furnace at 600-700°C and are reduced by hydrogen or CO/CO_2 mixture. The resultant product is obtained in the form of iron powder.

The outstanding characterstics of this process are its simplicity, its versatility in the preparation of metal powders from the more easily reducible oxides and the great range of size and shape of the powders that it makes possible.

2). IRON SULPHATE REDUCTION PROCESS

In this process[33] an acidic solution of ferrous sulphate obtained as waste pickle liquor from pickling of iron and steel is treated to give crystals of $FeSO_4.7H_2O$ containing some pro acid and moisture. The ferrous sulphate is dried at 60-100°C to yield particles of size 0.2 to 1 mm diameter and then treated in a fluidised bed at 200-300°C to remove water of recrystallization. The dehydrated salt is further. treated at 800°C to convert practially pure Fe_2O_3 which is heated in lumps of black graphite to yield iron powder.

3.) IRON CHLORIDE REDUCTION PROCESS

In this method[4,5,34-44] any iron bearing material such as iron ore, scrap, pickle liquor, low grade scrap etc. can be used. The iron bearing feed stock is first leached with hot hydrochloric acid to give a solution containing ferrous chloride. Hydrogen gas evolved is recovered for subsequent use. Impurities are removed by filtration and the ferrous chloride solution is sent to crystalliser where it is heated to flash off water and hydrochloric acid. On cooling the concentrated liquor yields pure ferrous chloride tetrahydrate ($Fe Cl_2.4H_2O$) crystals. These crystals are flash dried and compacted. The compacted mass is subsequently reduced by hydrogen in a reactor. After reduction, the sponge iron briquettes are produced which are then cooled and ground to powder.

Based on this method Wood-all Duckham Ltd of England in association with Peace River Mining and Smelting Co. of Canada and Research Council of Alberta have planned[36,37,40-42] to build a commercial iron powder plant near Windsor. The flow sheet of the process is given in fig.4. This plant is expected to produce very high purity of powder which can be directly converted into the foil or powder metallurgy parts. In this process carbon level can easily be controlled and alloy can be produced without adding much cost.

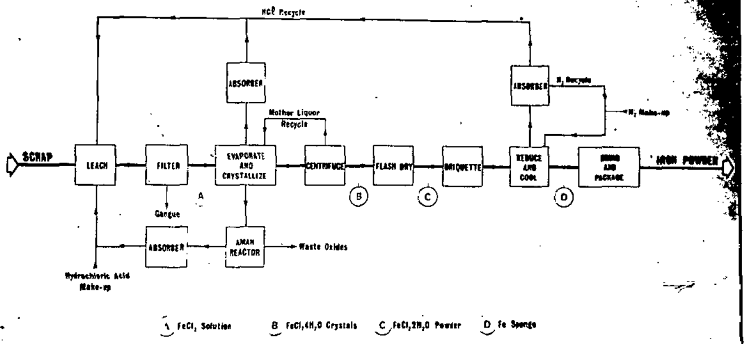


FIG. :.—Iron powder process: flow diagram.

FIG:4: Flow diagram: Iron powder production by Chloride reduction method.[42]

POWDER CHARACTERSTICS[4,6,37,42]

The powder produced is irregular in shape and spongy, each particle consisting of agglomerates of micron size sub particles. These are extremely pure and no annealing is required. The powder has moderately high apparent density and flow rate together with excellent compressibility. The powder is used for fillers, gears, pumps cams, brake drums and connecting rods in automobile industry.

II.3 MECHANISM OF DISSOLUTION OF STEEL SCRAP IN HYDROCHLORIC ACID

It is well established[45,46] that the corrosion of iron in aqueous media is reasonably well represented by the following steps:

1. Anodic dissolution, especially at grain boundaries

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

2. Cathodic liberation of hydrogen via the following stages:

i) Migration of hydrogen ions by diffusional and convective processes from the bulk of the solution into the electric double layer surrounding the cathodic areas

$$(H_3O^{+})_B \longrightarrow (H_3\,O^{+})_E$$

ii) Discharge of hydrogen ions in the electric double layers followed by adsorption of the resultant H-atom on the iron surface (M)

$$(H_3O^{+}) + \overset{-}{e} + M \longrightarrow M\text{-}H + H_2O$$

iii) Combination of the adsorbed H-atoms

$$2M\text{-}H \longrightarrow 2M + H_2$$

iv) Secondary discharge of hydrogen ions

$$(H_3O^+)_E + M\text{-}H + \overset{-}{e} \longrightarrow M + H_2O + H_2$$

The absence of any effect due to agitation of the solution confirms the findings of the Lochharev[47] that the dissolution of iron in HCl is not limited by the process 2(i) but is controlled by the diffusion of hydrogen ions into the metal surface. The effect of ferrous chloride on the reaction rate may be due to change in character[46] of the electric double layer at the cathodic areas leading to a lowering of the hydrogen overpotential and a consequent increase in the rate.

Although the dissolution reaction is moderately exothermic

$$Fe + 2HCl_{(aq)} \longrightarrow H_2 + Fe\,Cl_{2(aq)} \; ; \; H = -21.0 \text{ K Cal/mole}$$

it is found[48] that, under typical condition of operation, the heat required by the acid and iron feeds to reach the operating temperature almost balances the reaction heat. Heat losses from the equipment and the evaporation of water as a result of hydrogen evolution require that external heat must be supplied to the system to maintain the temperatue. It has been found that the rate of dissolution is maximised at 85 °C.

II.4 MECHANISM AND KINETICS OF THE REDUCTION OF FERROUS CHLORIDE WITH HYDROGEN

The reduction of ferrous chloride with hydrogen has been studied as a possible commercial route to iron. Although a considerable work[49] has been done on the thermodynamics of ferrous chloride reaction in the past but the study on the kinetics of the reaction has started in 1963 with the feasibility of commercial production of iron powder[60] by Research Council of Alberta. Rigg and Coworkers[61-64] and Yannopoulos[65] and Themelis have investigated the Kinetics of the reaction and proposed mechanism.

It has been well established[61,63,65] that the reduction of ferrous chloride occurs at the sharply defined reaction front which advances linearly with time under conditions of constant gas temperature and composition towards the centre of the pellet. In this type of topochemical reaction, the hydrogen first come in contact with the pellet surface, reduces it to iron and hydrogen chloride comes out. In this way the reaction front moves towards the centre. The model is shown in fig.6.

II.4.1 RATE CONTROLLING STEPS

The overall reaction involves the following steps:

1. Transfer of the reactant gas and product gas through the boundary layer around the particle.
2. Diffusion of these gases through the reduced layer.
3. Chemical reaction at the interface which is initiated at the surface of the particle and then recede inwards as reduction progresses.

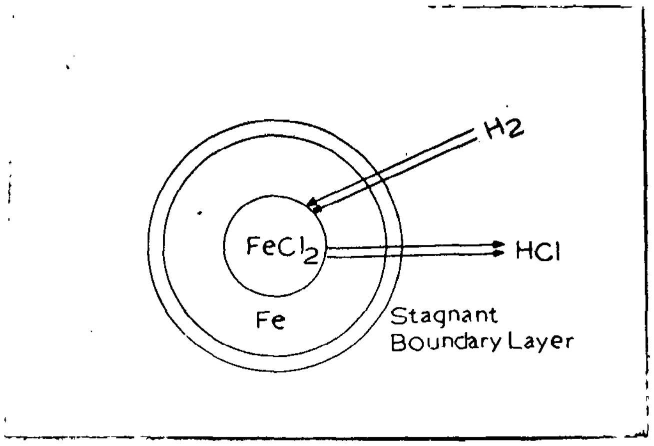


FIG.5: Topochemical model for the reduction of ferrous chloride pellet.

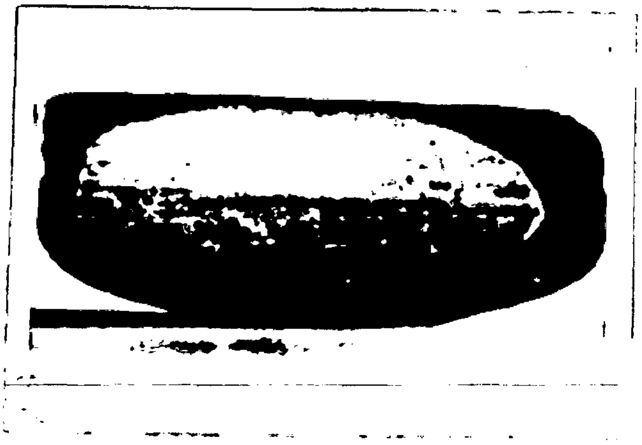


FIG.6: A cross sectional view of partially reduced ferrous chloride pellet.[50]

The results, produced by the investigators, gave conflicting evidence as to the nature of the reaction. The conflict is essentially a question whether the rate of reaction, under the range of conditions in which the experiments were carried out, was controlled either by diffusion (step 1 and 2) or by chemical reaction (step 3) or by a combination of both.

II.4.2 DIFFUSION CONTROL

Sections of partially reduced pellets showed a distinct interface between product and apparently unreacted core[61] as shown in fig.6. In porous pellets a sharp interface exists only for the case of a chemical reaction. But even if the reaction is not fast, it can still be confined to a narrow zone surrounding an unreacted core.

The mass of iron formed in sixty minutes was found to be inverse function of the concentration of hydrochloric acid in the feed. This was explained by Rigg[61] that the reaction rate was proportional to the difference between the equilibrium partial pressure of hydrogen chloride at the reaction interface and the partial pressure of hydrogen chloride in the hydrogen stream. It also confirms that the topochemical mechanism of the reaction exists. The reaction rate per unit area of the reaction interface for the following reaction

$$\mathrm{Fe\,Cl_2\,(s) + H_2\,(g) = Fe\,(s) + 2HCl(g)} \qquad \ldots\ldots(1)$$

is given by the expression

$$q = 2VC_e = \frac{D\gamma(p_e - p)}{R'\,Tx} \qquad \ldots\ldots(2)$$

By calculating x values from equation (2), it was suggested that the reaction rate was subjected to simple chemical control but on this basis some features of the reduction system could not be explained. For example it was found that hydrogen pressures upto 1.4 Kg/Cm^2 do not affect the rate of reaction appreciably ; where as decreasing the partial pressure of hydrogen produces a decrease in the reaction rate. Further more the course of the reaction was appeared to be somewhat dependent on temperature gradient in the reaction zone. To explain these processes, it was suggested that the reduction does not proceed by the direct route implied by the net equilibrium equation (1) but involves ferrous chloride vapours according to the equations

$$Fe\,Cl_2\,(s) = Fe\,Cl_2\,(\text{vapour}) \quad \ldots\ldots \quad (3)$$

$$Fe\,Cl_2\,(\text{vapour}) + H_2\,(g) = Fe(s) + 2HCl(g) \ldots\ldots (4)$$

The ferrous chloride vapours can diffuse unhindered by the HCl equilibrium barrier into the interior of the reaction zone so that it can react under steady state conditions where $p < p_0$. It was concluded that the flow rate of ferrous chloride vapours into the reaction zone was essentially proportional to the difference in HCl partial pressure existing across entire reaction zone. A factor B, to account for the increased effective resistance to diffusion encountered by HCl, is introduced in Eq. (2)

$$q = 2\,VC_0 = \frac{D\,\gamma\,(p_0 - p)}{R'\,T\,Bx} \quad \ldots\ldots (5)$$

so there are two means of slowing down the reaction:

(i) decreasing the partial pressure of hydrogen such that stagnation of gas takes place

(ii) increasing the back pressure of HCl

Hence the rate equation for this case will be

$$q = 2\,VC_o = \frac{D\sqrt{p_o}}{R\sqrt{T}\,Bx_o}\;\frac{(p_o - p)}{p_o} \qquad \ldots\ldots(6)$$

Bx_o represents a constant diffusional resistance under constant pressure and isothermal conditions and is equal to $Bx\,(p_o - p)/p_o$. B is the resistance factor and is approximately equal to the ratio of $FeCl_2$ saturated vapour pressure and equilibrium HCl partial pressure, p_o.

If the above mechanism is the principal rate controlling process in the reduction of the pellets of $FeCl_2$, the reaction front will advance at a constant rate towards the centre of the pellet and the plots of fractional penetration of reaction front versus the reaction time will yield straight lines at various temperatures as shown in fig.7.

Rigg[63] gave the rate equation in terms of fractional penetration as :

$$\frac{\ell}{t} = \frac{76.8}{\rho_{Fe}\,d}\left(\frac{p_o - p}{p_o}\right) e^{-15{,}600/RT} \qquad \ldots\ldots(7)$$

The values of apparent energy of activation for the reaction were obtained from experimental plots of Arrhenius type by various workers as 19.9[61], 15.6[63] and 16.8[64] K Cals/mole. These values suggest that diffusion plays a significant role in determining the rate.

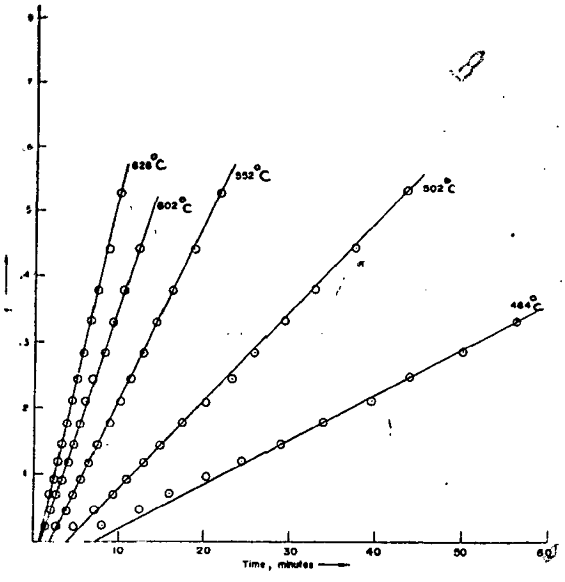


FIG.7: Typical fractional reduction VS time plots for the reduction of ferrous chloride pellet at various temperatures.[54]

II.4.3 CHEMICAL CONTROL

Before being reacted with hydrogen pellets of Fe Cl_2, containing 1.7 to 2.5 moles of water per mole of chloride, pellets were brought to reaction temperature in nitrogen atmosphere.[51,54,55] After the water had driven out the pellet remained which was porous enough throughout and might be expected to offer a little or no resistance to the diffusion of hydrogen and hydrogen chloride.

It has been observed that traces of iron oxide present in the pellets of Fe Cl_2 is readily reduced. This shows that the hydrogen gas can penetrate quickly into the pellet at least in the initial stages. Plots of fractional penetration of the pellets by the reaction interface indicates a constant rate of advance of the interface. This usually, though not unequivocally taken as evidence of chemical reaction control. Yannopoulos and Themelis[55] gave the rate equation for the chemical reaction control as follows:

$$\left[1-(1-R_x)^{\frac{1}{3}}\right]/\theta = (3.5\times10^5/d\rho)\,e^{-27,500/RT}\left(\frac{p_0-p}{p_0}\right)\ldots(8)$$

$$\text{or } \frac{\delta}{t} = \frac{3.5\times10^5}{d}\left(\frac{p_0-p}{p_0}\right)e^{-27,500/RT} \qquad \ldots\ldots(9)$$

They[55] calculated an activation energy of 27.5 K Cal/mole. This figure of activation energy is more in keeping with chemical reaction rate controlled, but still it is on the lower side.

It is not clear from the above evidence whether the reaction should be regarded as chemical reaction or diffusion controlled. Recently Miriyala and Brown[53] study the Kinetics of reduction of single pellet of Fe Cl_2 in hydrogen by thermogravimetric method and they observed that a significant resistance exists to the diffusion of gas through the particle of which the pellets are composed. They carried out the experiments at temperatures low enough for chemical reaction to be controlling and obtained an activation energy of 39 K Cal/mole of ferrous chloride.

II. 4.4 FACTORS AFFECTING THE RATE OF REDUCTION

The following factors affect the rate of reduction of ferrous chloride.

(1) EFFECT OF HYDROGEN FLOW RATE

The hydrogen flow rate affects the kinetics of the reduction of ferrous chloride. It has been reported[54] that a variation in hydrogen velocity upto 10 Cm/Sec has very little effect on the rate of reduction of Fe Cl2. However below 1.0 cm/Sec. the reaction rate is strongly dependent on the gas velocity as shown in fig. 8. Gases form a stagnant boundary layer around the pellet. As the flow rate of the reducing gas is increased, the thickness of the stagnant boundary layer is reduced and the state is reached when the stagnant boundary layer is not critical. Increase in flow rate beyound this limit will not have any effect on the reduction rate. At lower velocities this stagnation gives rise to serious HCl back pressure which affects the Kinetics of the process.

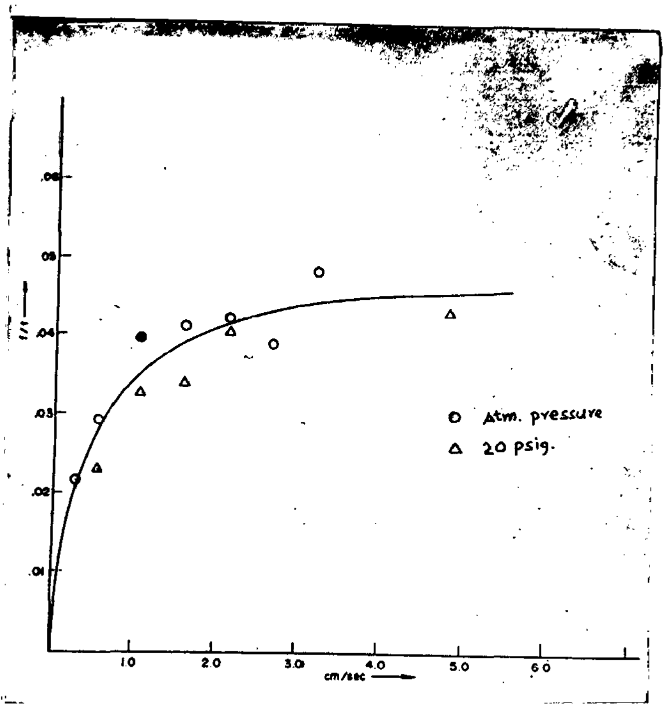


FIG.8: Effect of gas velocity on hydrogen reduction of ferrous chloride pellet.[54]

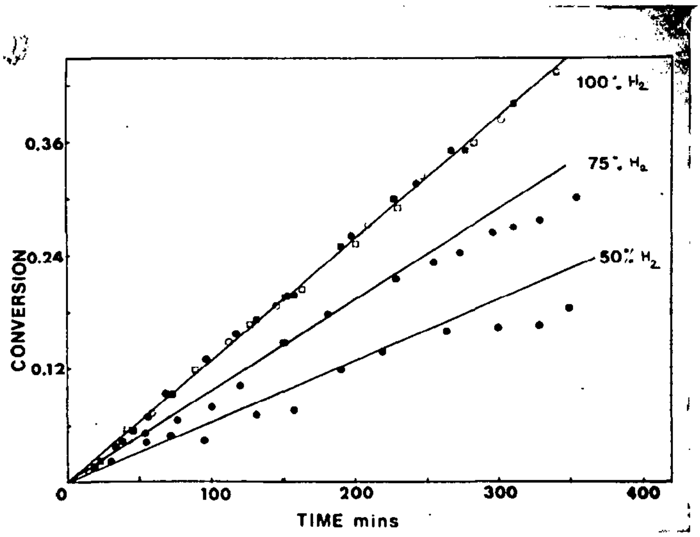


FIG:9: Effect of gas composition on hydrogen reduction of ferrous chloride pellet.[56]

(2). EFFECT OF GAS COMPOSITION

As the partial pressure of hydrogen gas is reduced by increasing the partial pressure of nitrogen in a gaseous mixture of H_2 and N_2, the rate of reduction is also reduced and the fractional reduction is decreased for the same interval of time because nitrogen acts as diluent and it reduces the sites for the adsorption of hydrogen gas on the crystal surface. The effect of gas composition on the fractional reduction is quite clear from the work of Miriyala and Brown[56] and is shown in fig.9.

3) EFFECT OF PELLET SIZE

It has been[54,56] observed that pellet size has no significant effect on the rate of fractional conversion. It indicates that HCl and H_2 gases move through the pellet without difficulty.

4) EFFECT OF PELLET POROSITY

It was thought that interpellet porosity might be affected by the pressure used to pelletise. Miriyala and Brown[56] used four pressures upto 140 Kg/cm^2 for pelletizing, but no significant difference was observed in the subsequent reduction and it was found that even at the heighest pressure the pellets were of a sufficiently open structure after dehydration which makes easier the diffusion of the reactant and the products. Thus the dehydration increases the porosity of the pellets and compacting pressure will have least effect on it.

olysis because the permissible current densities during electrolysis in fused salts are higher than in aqueous solutions. Apart from this, in contrast to fused salts, it is difficult to obtain powder with a predetermined particle size is aqueous solutions.

POWDER CHARACTERSTICS[4,5,28-30]

The most usual shape of electrolytically produced powders is dendritic although this can be changed by alteration of processing variables. The particles are near solid and extremely pure. Subsequent annealing softens the powders. These particles have high apparent deensity, excellent compressibility and medium green strength. The powders are suitable for the production of magnets, magnetic cores, high density constructional parts and alloys with special electric, magnetic and physical properties.

II.2.5 HYDROMETALLURGICAL METHODS

It has long been recognised that if hydrometallurgical[4,5,32-44] processes could be applied economically to steel making, a close control over quality can be obtained and consequently low grade scrap can be used to produce high purity products. A few attempts have been done during last decade. Some of those are described below:

1). GEL PRECIPITATION PROCESS

A novel process[32] has been developed for producing gels

5) EFFECT OF TEMPERATURE

Reduction of ferrous chloride is a thermally activated process, therefore, the rate increases with increase in temperature. Rigg and coworkers[51,52,54] found a regular increase in the rate of reduction in the temperature range of 450°-628°C and similar nature was also confirmed by Yannopoulos and Themelis[55] and Miriyala and Brown[56]. The effect of temperature on the rate of reduction is shown in fig.7.

6) EFFECT OF PRESSURE

The effect of hydrogen pressure[54] on the rate of reduction of ferrous chloride is small and is shown in fig.8. This insensitivity of pressure is attributable to several opposing factors. For instance, the diffusion coefficients of HCl gas and F_e Cl2 vapours are inversely proportional to the total pressure while the equilibrium partial pressure of HCl gas increases with the square root of total pressure. Thus the decreased diffusion coefficient is counterbalanced by the increased value of equilibrium partial pressure of HCl gas and the decreased value of diffusional resistance factor. This infers that the growth of iron particles may be somewhat restricted at elevated pressure but not definite expenditure evidence has so far been observed.

CHAPTER - III

EXPERIMENTAL WORK

III.1 INTRODUCTION

As it has been described in Chapter II that there are several methods available for the production of iron powders having their own merits and demerits but the choice of a particular method depends on the following factors:

a) economical considerations

b) availability of raw materials

c) purity and properties required.

Taking into consideration the above factors, hydrometallurgical methods can be applied economically for the production of high purity iron powder with a close control over the quality. This method can be used to any type of iron bearing materials by dissolving in hydrochloric acid for the production of iron and iron-alloy powders. The aim of the present work is to produce iron and iron alloy powders by reducing iron chloride and mixture of chlorides of iron and alloying elements by hydrogen. For this, the work was planned as below:

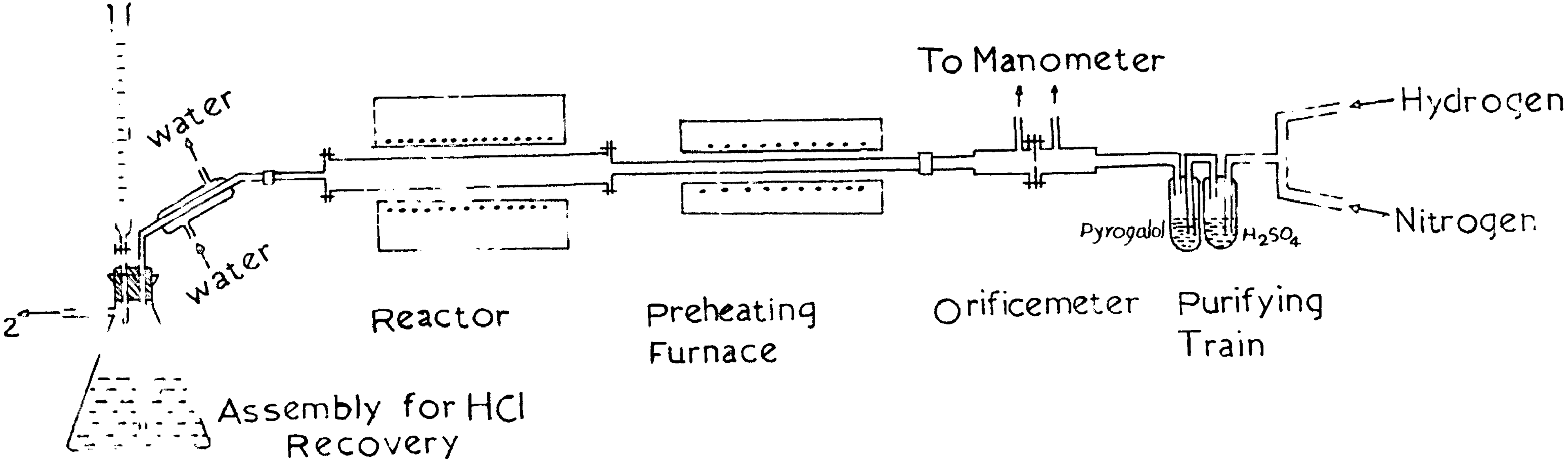
i) Production of ferrous chloride crystals

ii) Drying and making of pellets of the crystals

iii) Reduction of the pellets with hydrogen at various temperatures.

III.2 EXPERIMENTAL SET UP

The apparatus used for the reduction of the pellets of ferrous chloride crystal is shown in fig.10. The apparatus



(A)

FIG:10 EXPERIMENTAL SET UP

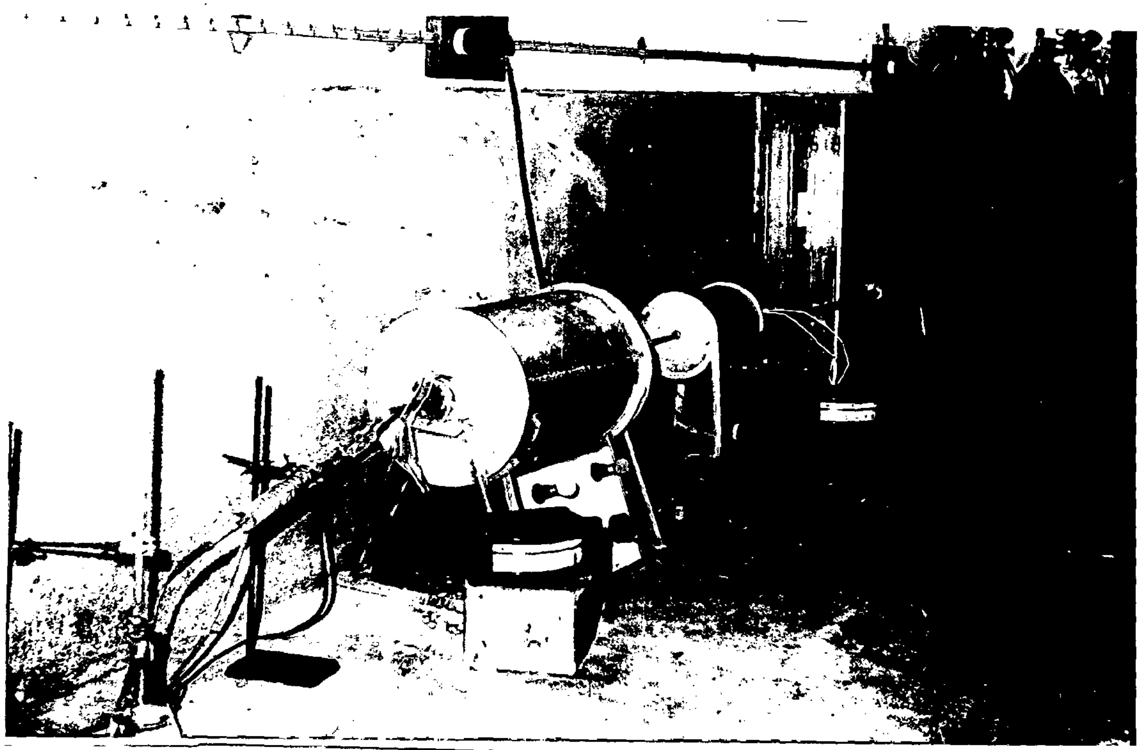


FIG.10B: A general view of Experimental Set-up can be divided into the following three main parts:

i) Reactor for the reduction of ferrous chloride pellets
ii) Preheating furnace for the heating of gases
iii) Assembly for the recovery of hydrochloric acid.

III.2.1 THE REACTOR

It consists of a 18/8 stainless steel tube with an internal diameter of 3.8 cm and overall length of 80 cm. The tube was heated in a 3.2 KW muffle furnace covering 55 cm of its length. The muffle was externally wound by 18 SWG Kanthal Wire. The temperature in the tube was controlled within the limits of ± 5°C by means of a chromel-alumel thermocouple and a Honeywell 'Servotrovik' controller. At outward end a stainless steel tube of 6 mm diameter and at the inward end a mild steel tube of 12.5 mm diameter were attached by means of flanges.

III. 2.2 THE PREHEATING FURNACE

It consists of a mild steel tube of 12.5 mm diameter and overall length of 100 cm. It was placed in a 1.1 KW silliminite tube furnace of 2.54 cm diameter. The temperature in the tube was also controlled by chromel-alumel thermocouple and controller within the limits of ± 5°C.

III. 2.3 THE ORIFICEMETER

To measure the hydrogen flow rate, an orifice meter was constructed and was calibrated against a wet test gas meter.

The design of the orifice meter is shown in fig.11.

III.2.4 ASSEMBLY FOR HYDROCHLORIC ACID RECOVERY

It consists of a spiral condenser and an absorption flask. The absorption flask contained distilled water and was fitted with a burette to intoduce Na OH solution for titrating HCl collected. Methyl red was used as an indicator.

III.3 MATERIALS USED

The materials, used for experimental work, are given below:

i) Iron scrap
ii) Nickel metal turnings
iii) Chromium metal turnings
iv) Stainless steel (18/8)turnings
v) Hydrochloric acid commercial grade purity
vi) Hydrogen gas
vii) Nitrogen gas
viii) Sodium hydroxide 1-N solution
ix) Methyl red solution

III.4 EXPERIMENTAL PROCEDURE

The various steps involved in the experimental procedure are described below:

III.4.1 PREPARATION OF CHLORIDE CRYSTALS

The cleaned iron scrap was dissolved in hydrochloric

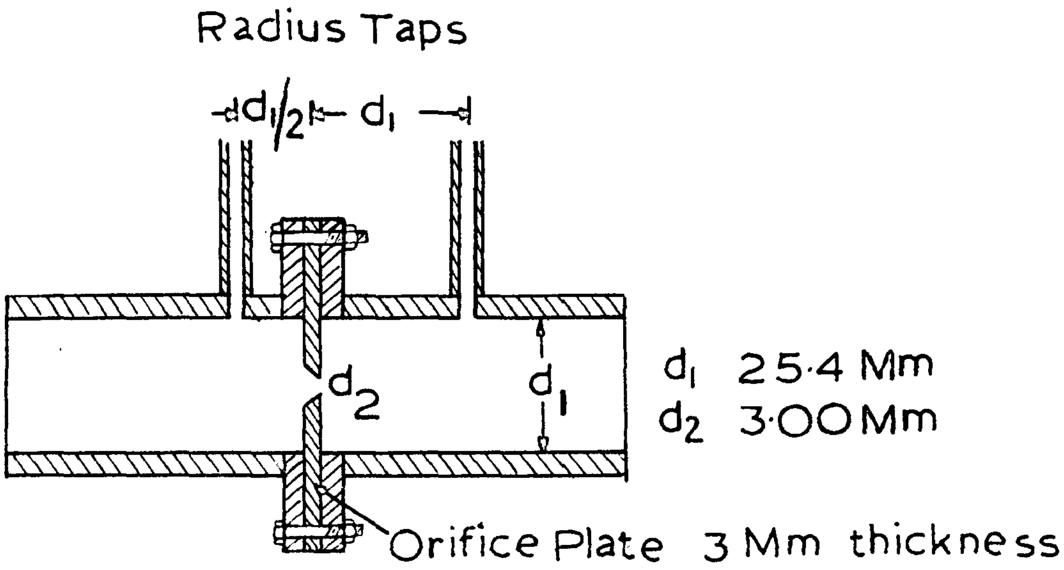


FIG: 11 DESIGN OF THE ORIFICEMETER

acid at 83°C. It went into the solution readily and hydrogen gas was evolved. This ferrous chloride liquor was filtered through a pressure edge filter to remove the insoluble impurities. The filtered solution was heated to increase the concentration of $FeCl_2$ in the solution. This hot liquor was then cooled. By concentration and cooling of the liquor, crystals of $FeCl_2 4H_2O$ were formed. The crystals were taken out the mother liquor and were washed with water to remove adhered HCl from the surface.

To prepare iron alloy crystals, weighed amount of iron scrap and the alloying elements, viz. nickel, chromium etc. were dissolved in hot hydrochloric acid and the crystals were produced in the similar fashion as discussed above.

The tetrahydrate crystals were, then, dried on a stainless steel plate placed on an electric hot plate and was ground to a fine size. The dry crystal powder was analysed by conventional chemical analysis method for iron to determine water-molecules associated with crystals after dehydration.

III.4.2 MAKING OF PELLETS

The dihydrate ferrous chloride crystals were pressed in a cylindrical die of diameter 1.66 cm to produce pellets same in diameter and height. The finished pellets were weighed and stored in an air tight container. These were taken out immediately before introducing into the reactor to avoid any chance of oxidation. The pellets are shown in fig.12.

III.4.3 REDUCTION OF THE PELLETS

The reduction of ferrous chloride pellets was carried out in the reactor at various temperatures viz. 400°, 450°, 500°, 550°, 600° and 650°C. The pellets were kept in a silliminite boat. When the reactor attained the temperature 100°C less than the required reduction temperature, systems was purged by nitrogen gas and after ten minutes, four pellets were introduced in the reactor. The reactor was heated to the required reduction temperature. As the reactor attained the required temperature, the nitrogen was replaced by hydrogen. The hydrogen was first passed through the preheating furnace, maintained at the reactor temperature, so that it may not cool the reactor. The hydrogen flow rate was 3 litre/minute which was kept constant in all the experiments.

The course of the reaction was followed by titration of the evolved HCl against 1.0-N NaOH solution using methyl red indicator to know the amount of HCl recovered.

As the reaction reached to completion, the power was switched off. The hydrogen was continued to pass for a decrease of 100°C in temperature. Then the hydrogen was

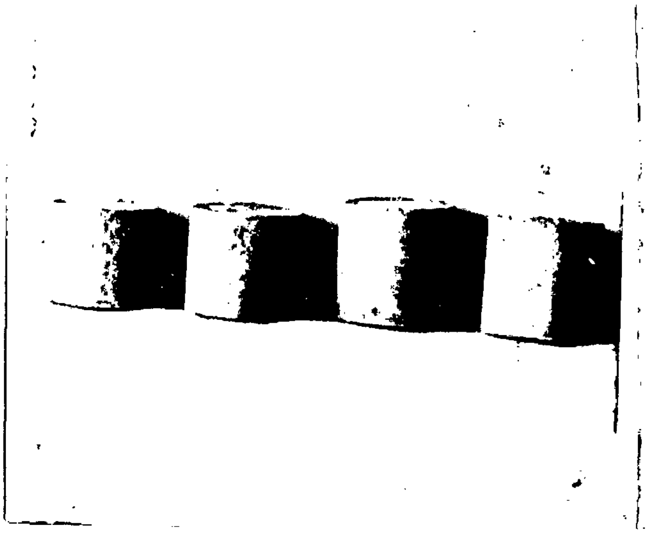


FIG.12: A view of unreduced ferrous chloride pellets.

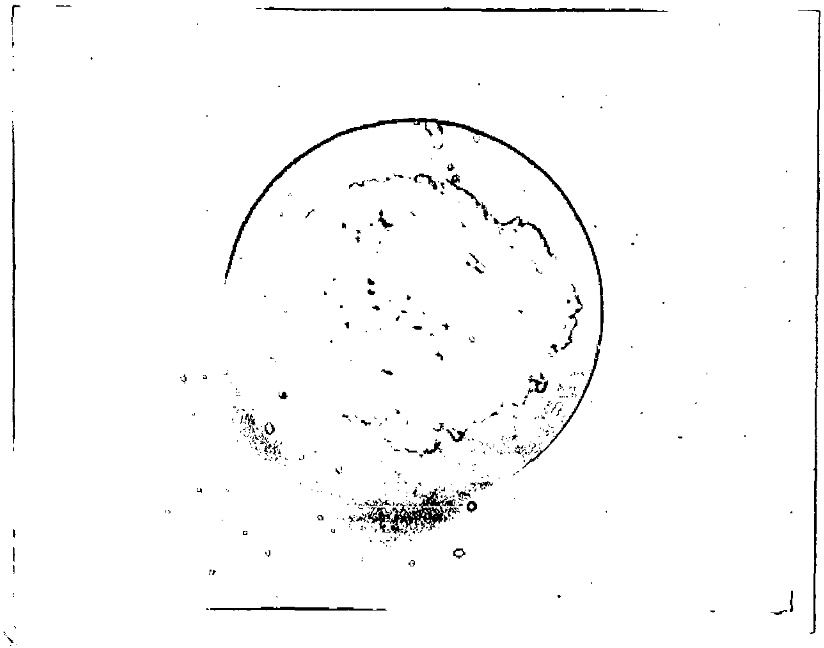


FIG.13: A cross sectional view of partially reduced ferrous chloride pellet at 450°C.

replaced by nitrogen for cooling the reduced mass until it reached to room temperature. The reduced samples were analysed for iron content to know the percentage reduction.

III.4.4 STUDY OF THE SHAPE OF POWDER PARTICLES

The shape of the particles of various powders was also studied by using Neophot-2 microscope.

CHAPTER IV

RESULTS AND DISCUSSIONS

IV.1 RESULTS

In the present investigation, the ferrous chloride and iron-alloy chloride crystals were reduced by hydrogen for the production of powders. The ferrous chloride crystals were reduced at temperatures 400°, 450°, 500°, 550°, 600°, and 650°C whereas the alloy chloride crystals were reduced only at 600°C. The samples were analysed before and after the reduction to know the composition of the powder produced and the extent of reduction.

The experimental results for the reduction of ferrous chloride crystals at various temperatures are tabulated in tables 4 to 9 and for alloy chloride crystals in Table 11 to 13. The percentage reduction and the percentage recovery of HCl at the end of reduction in each case are also plotted graphically. Figs.14,18,19 and 20 are the plots of HCl recovery in c.c. versus time in minutes for the reduction of ferrous chloride and alloy chloride crystals.

In fig.16 and 17 percentage reduction and percentage recovery of HCl are plotted against time in minutes for ferrous chloride crystals. A comparision of HCl recovered in c.c versus temperature at fixed time is also made and is shown in fig.15. The percentage of HCl recovered was calculated by using the following formula:

$$\%\ \text{Recovery of HCl} = \frac{\text{HCl recovery in c.c. practically}}{\text{HCl recovery in c.c. theoritically}}$$

The comparison of percentage reduction and percentage recovery of HCl in the reduction of ferrous chloride and various alloy chloride for 120 minutes at 600°C is shown in figs.22 and 23. And the comparison of actual HCl recovered at this temperature is shown in fig.21.

The physical examination of samples after reduction revealed the presence of an inner core where the pellet remained unreduced. Cross section of partially reduced pellet of ferrous chloride crystal is shown in fig.13.

The shape of the particles of various powders was studied by using Neophot-2 microscope. The photograph of these particles were taken and are shown in figs.24 and 25.

IV.2 DISCUSSIONS

The ferrous chloride crystals were reduced at temperatures in the range of 400° to 650°C where as the alloy chloride crystals were reduced at 600°C only by hydrogen. The experimental results are shown in figs. 14 to 22, and are discussed below.

(1) REDUCTION OF FERROUS CHLORIDE CRYSTALS

The reduction of ferrous chloride crystals at various temperatures is shown in fig.14. It shows the amount of HCl recovered in c.c versus time of reduction in minutes for various temperatures. It is clear from the figure that as the temperature increases the amount of HCl recovered is also increased with

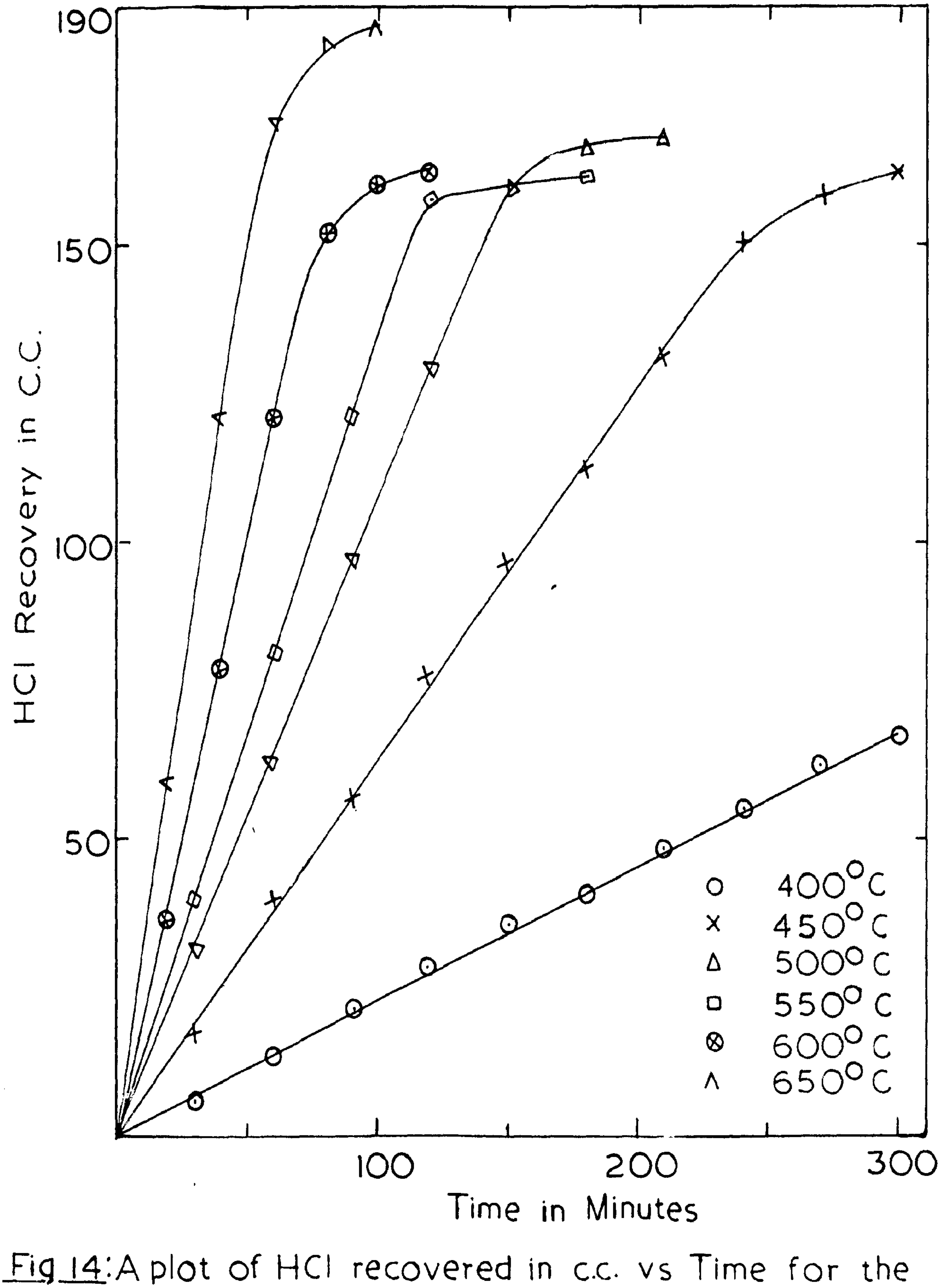


Fig 14: A plot of HCl recovered in c.c. vs Time for the reduction of ferrous chloride crystals at various temperatures.

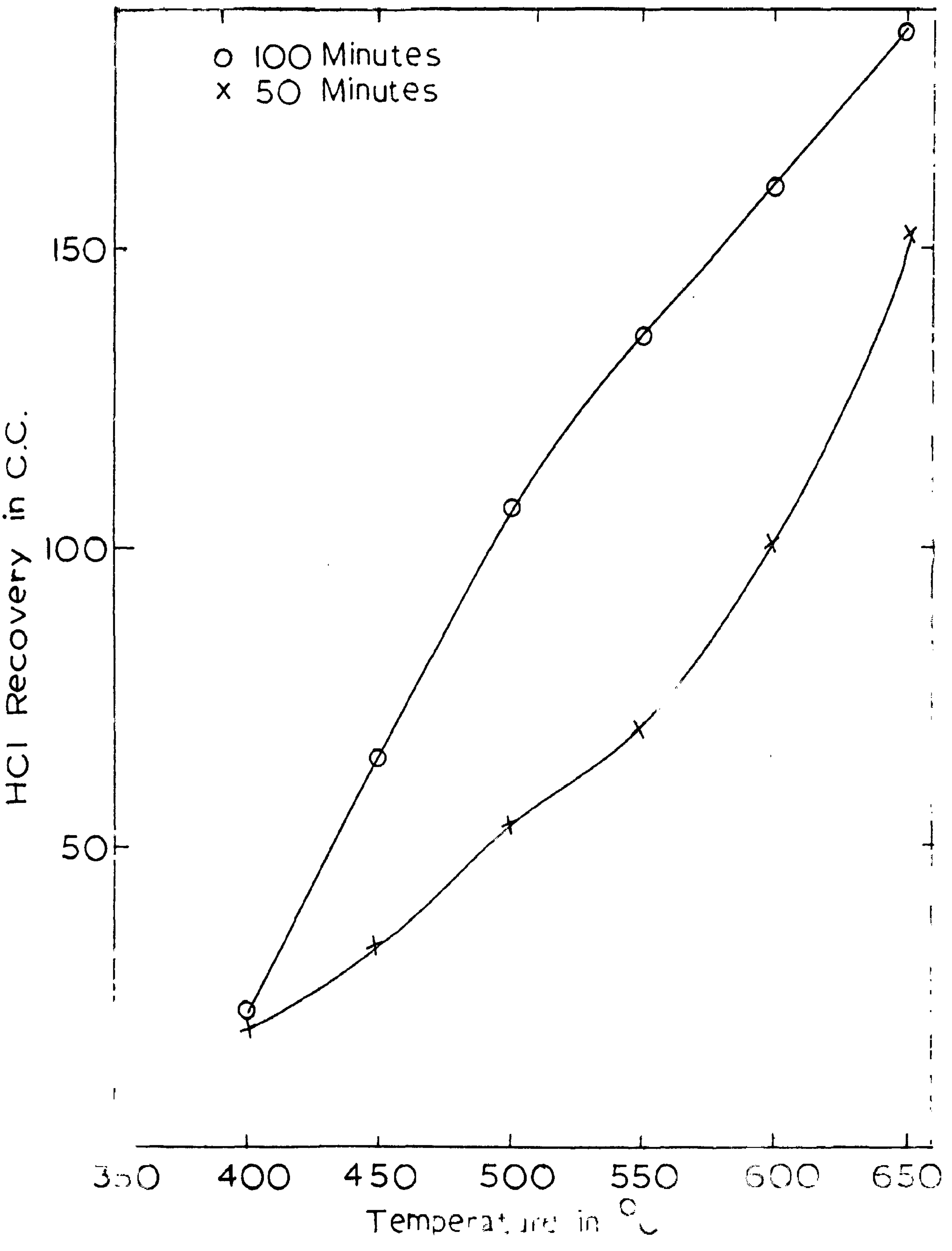


Fig 15: Comparision of HCl recovered in c.c. vs. Temperature for reduction of ferrous chloride pellets at fixed times.

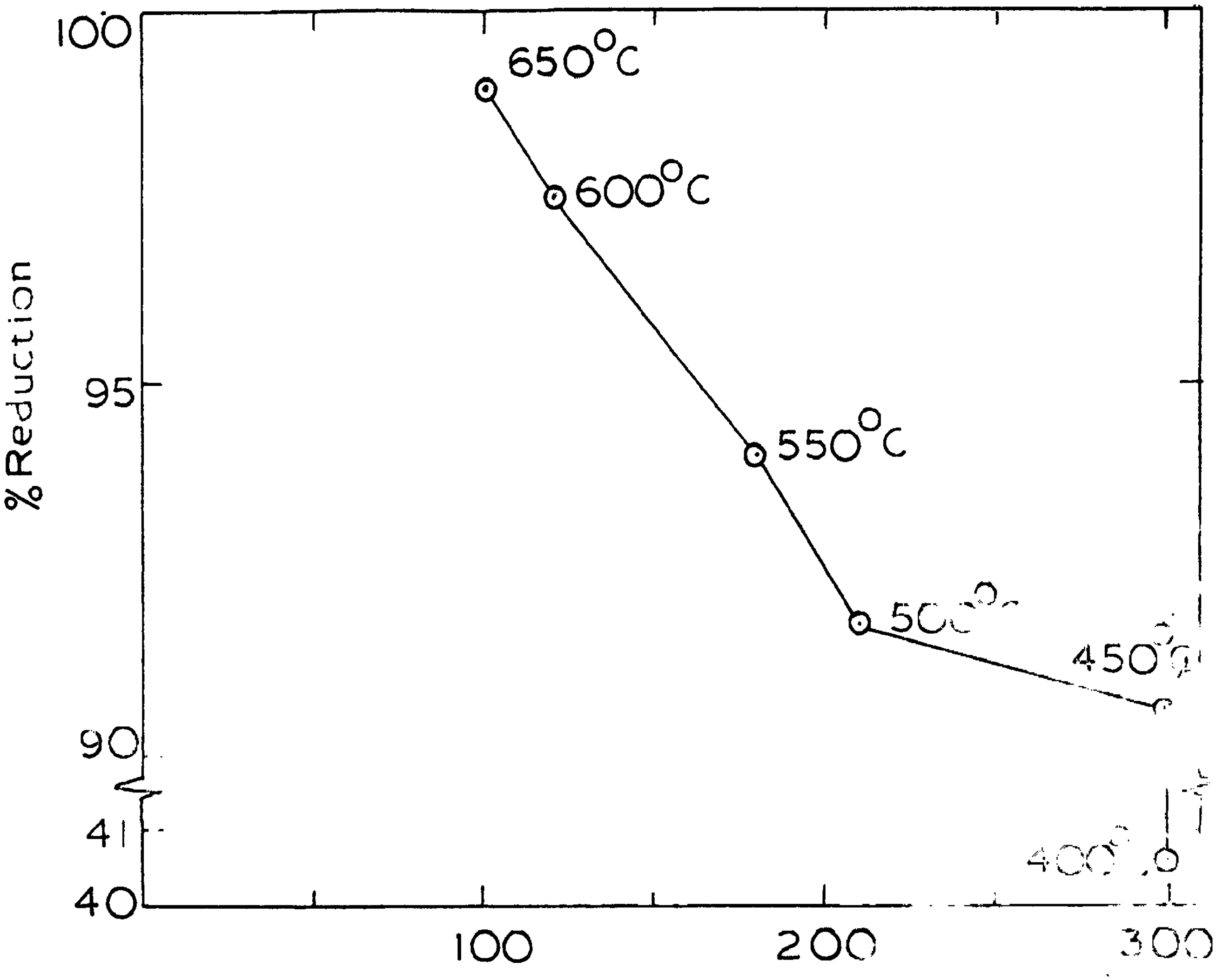


Fig.16: A plot of Percentage Reduction at the end of reduction of ferrous chloride crystals at various temperatures

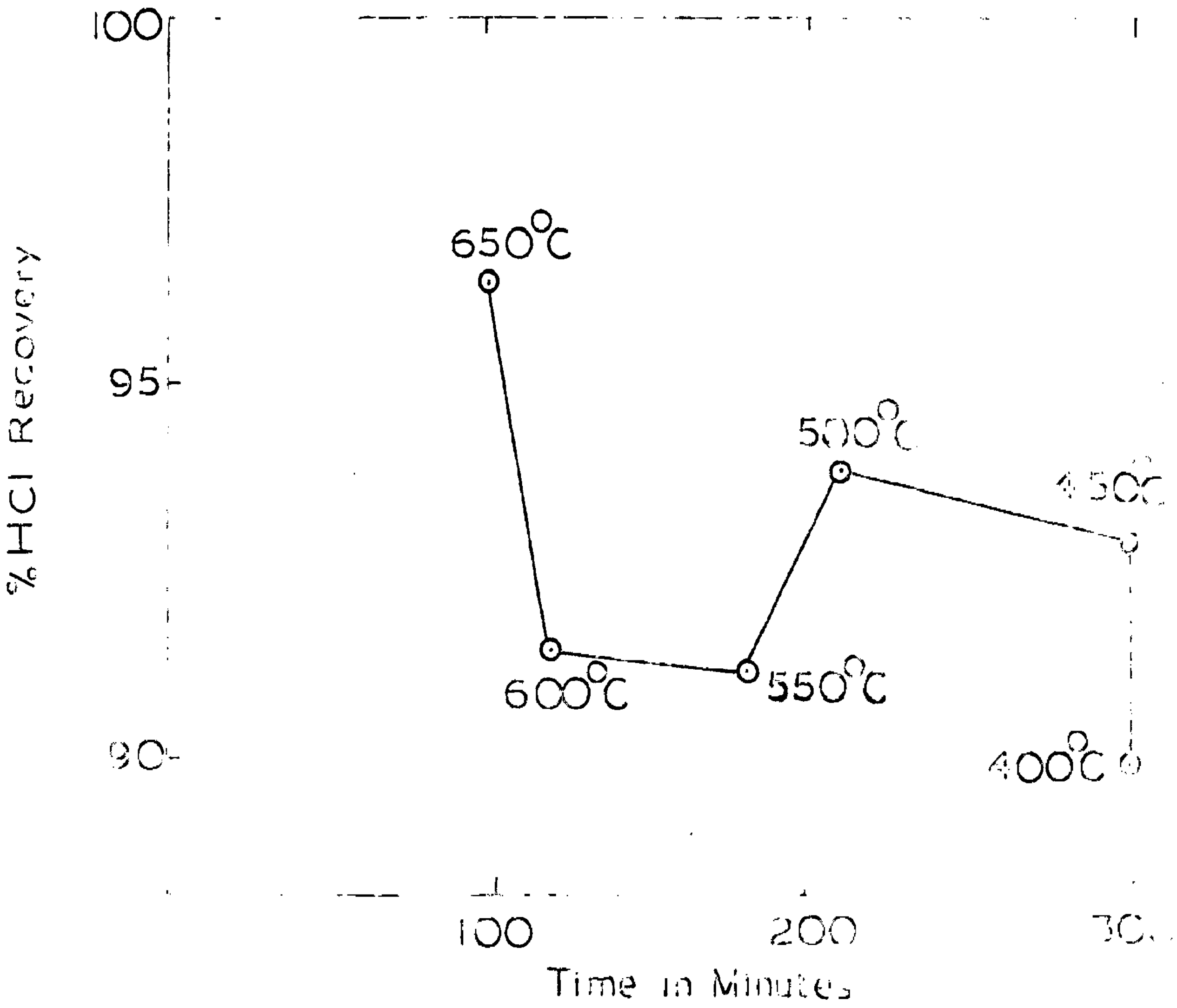


Fig.17: A plot of Percentage HCl Recovered at times of reduction of ferrous chloride crystals at various temperatures.

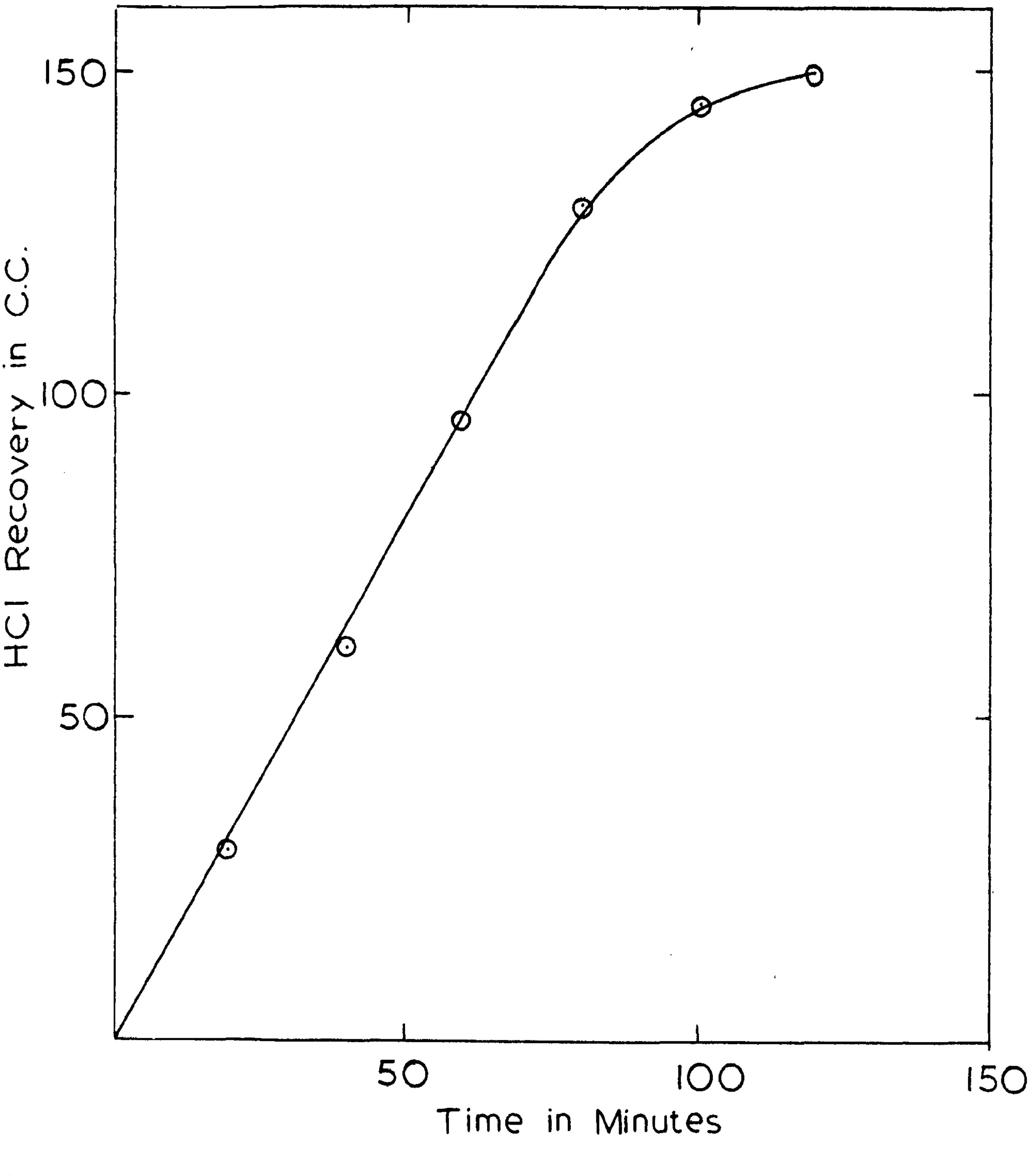


Fig 18. Plot of HCl recovered in c.c. vs Time for the reduction of Fe-Cr chloride crystals at 600°C

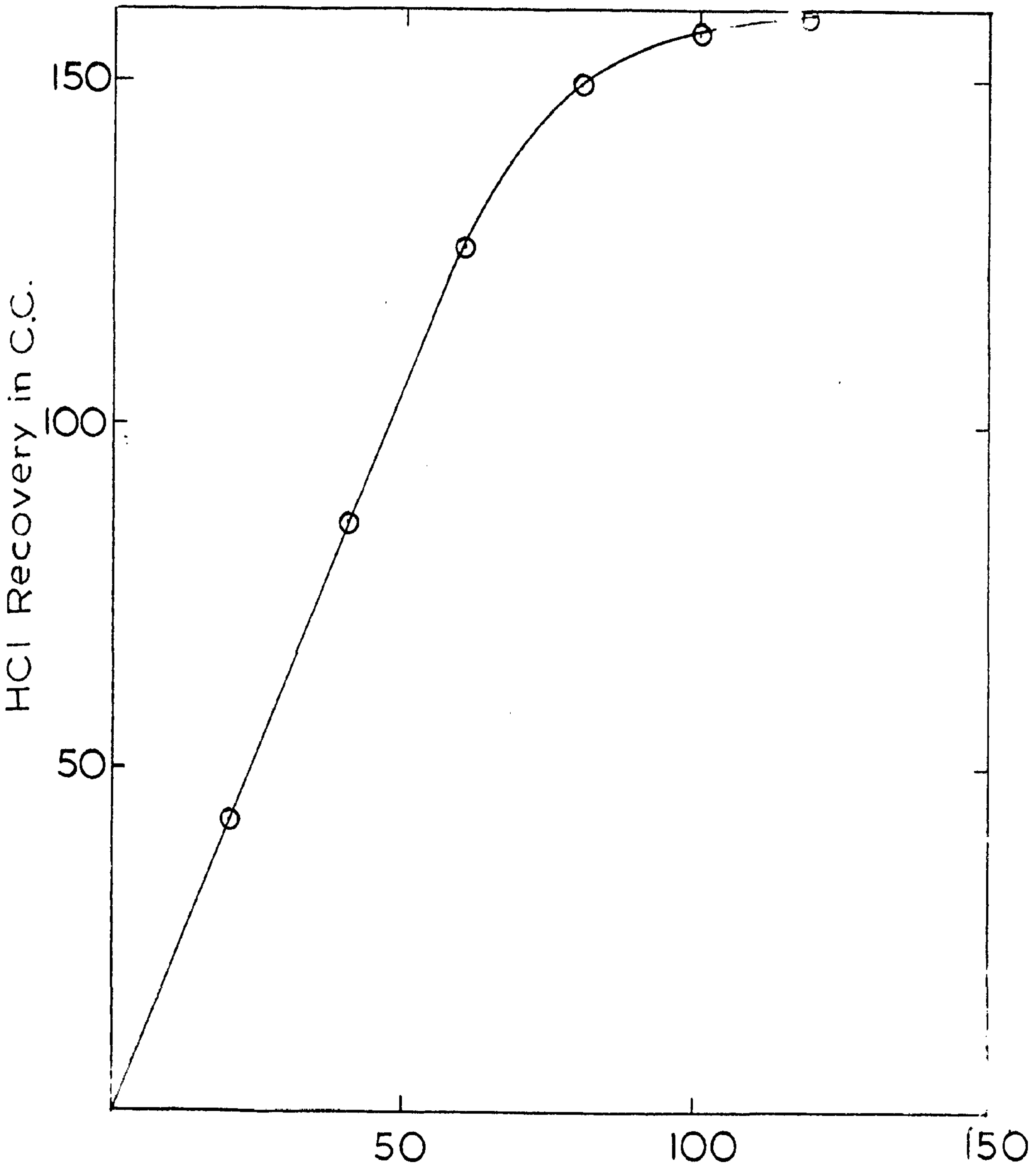


Fig 19: A plot of HCl recovered in c.c. vs Time for the reduction of Fe-Ni chloride crystals at 600°C

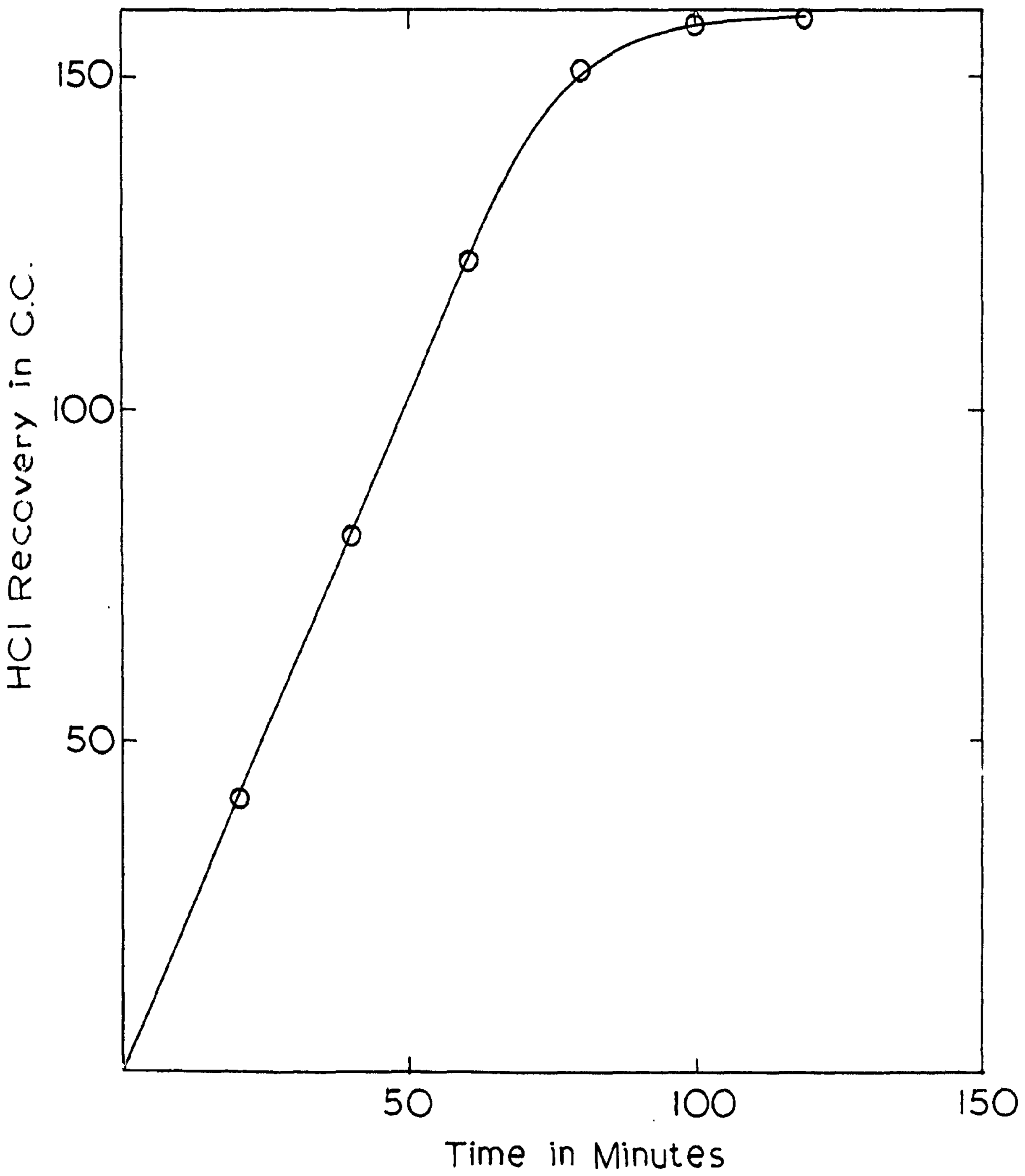


Fig 20. A plot of HCl recovered in c.c. vs Time for the reduction of Fe-Cr-Ni chloride crystals at 600°C

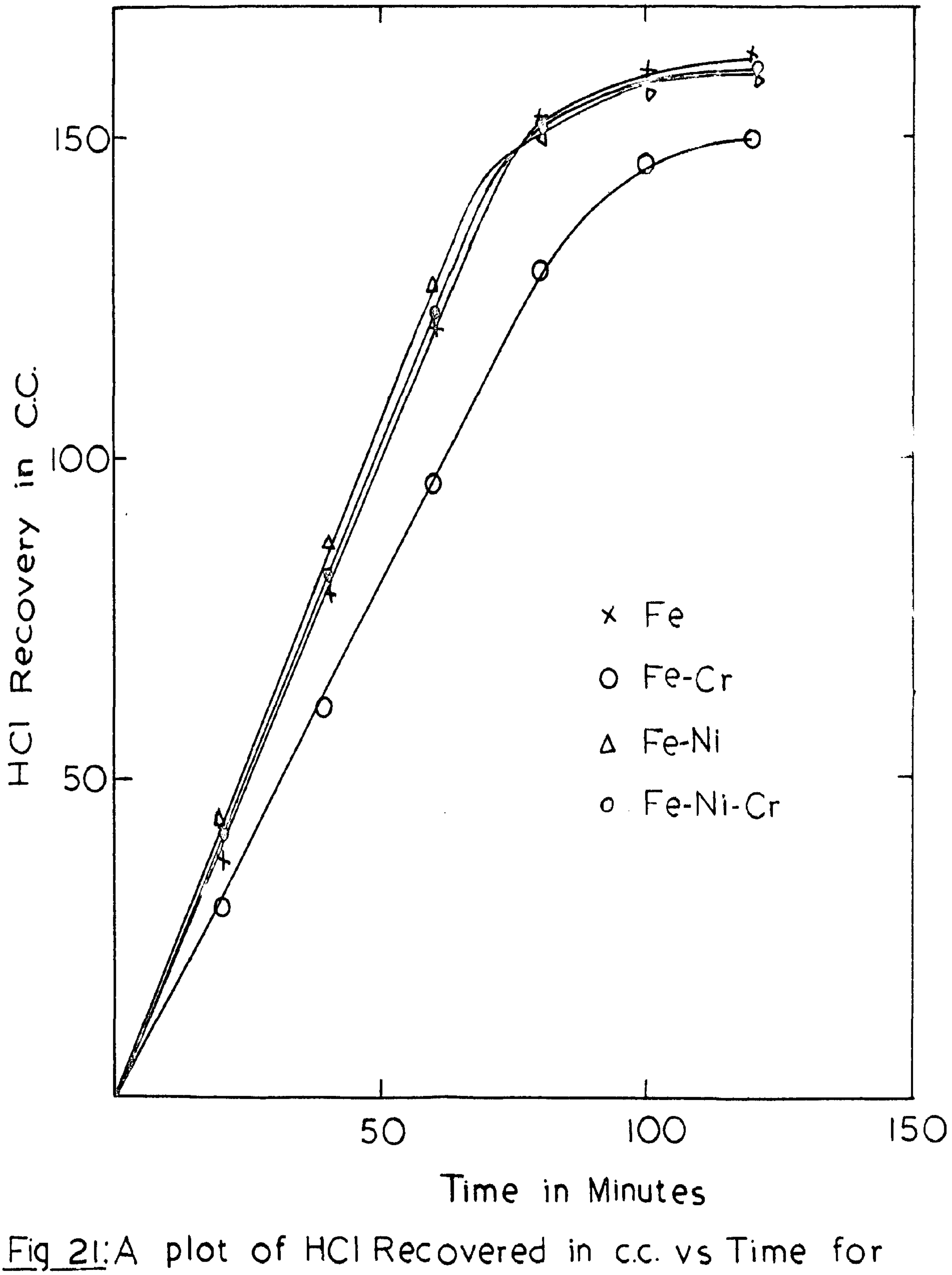


Fig 21: A plot of HCl Recovered in c.c. vs Time for the reduction of ferrous and alloy chloride crystals at 600°C.

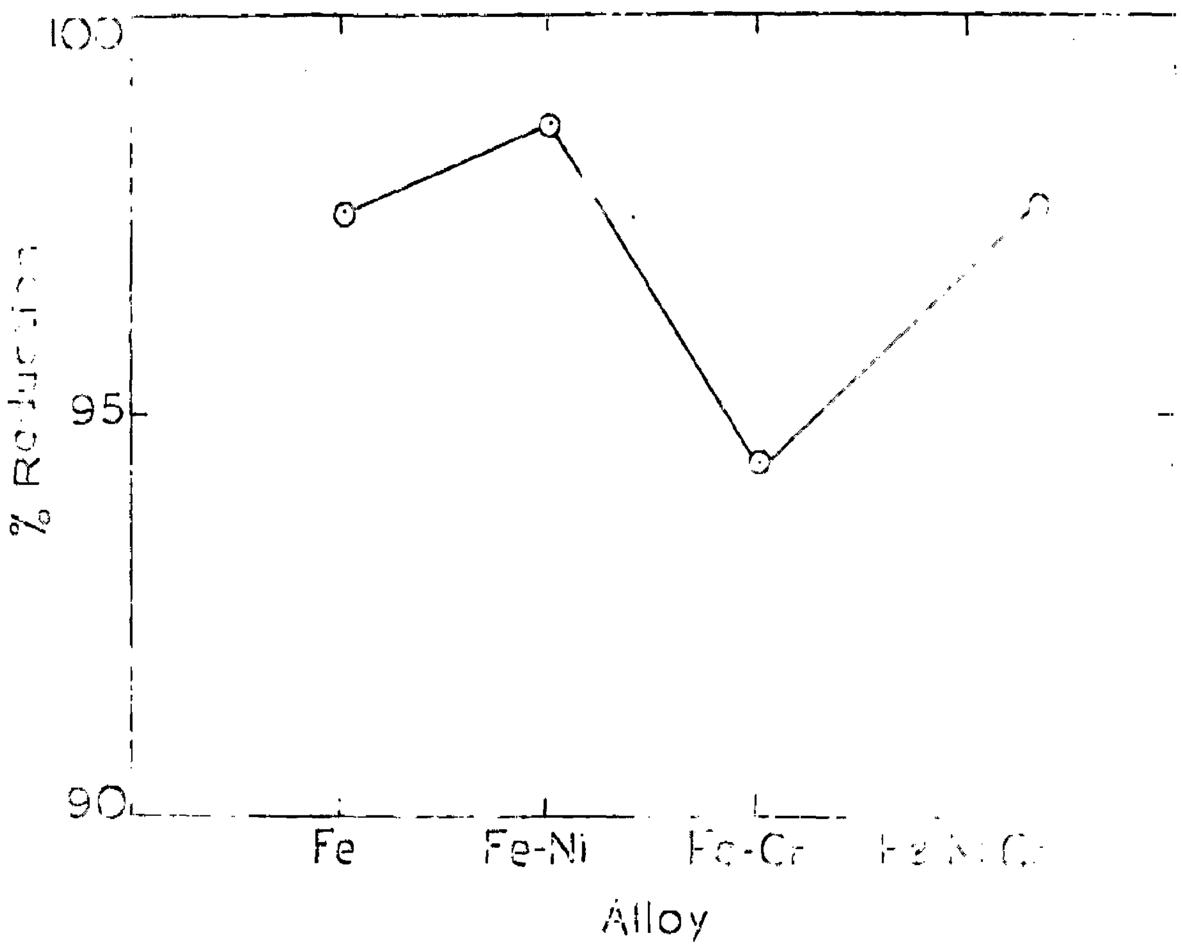


Fig.22:A plot of Percentage Reduction in 120 at 600°C for various alloy chloride slurry [illegible]

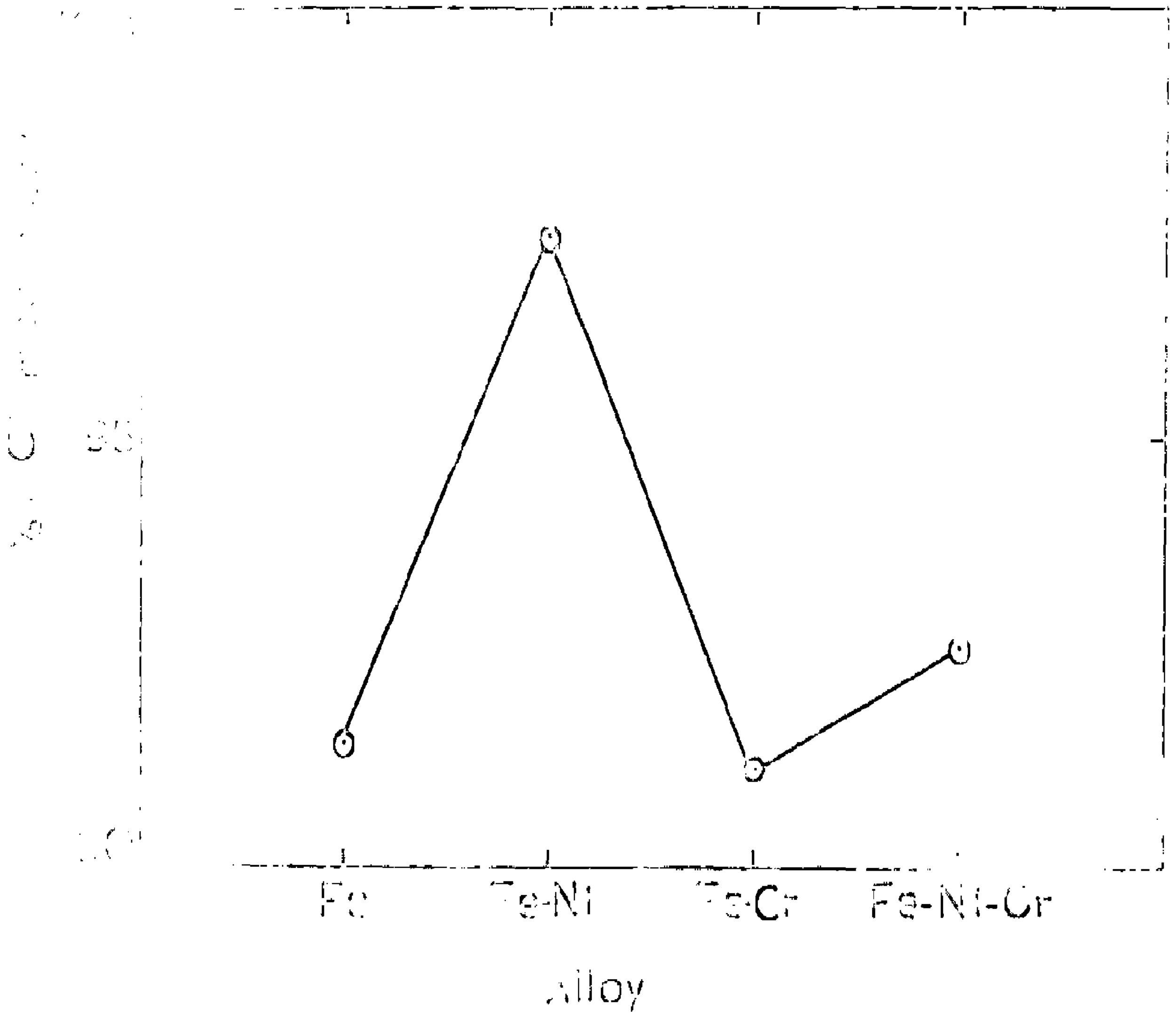
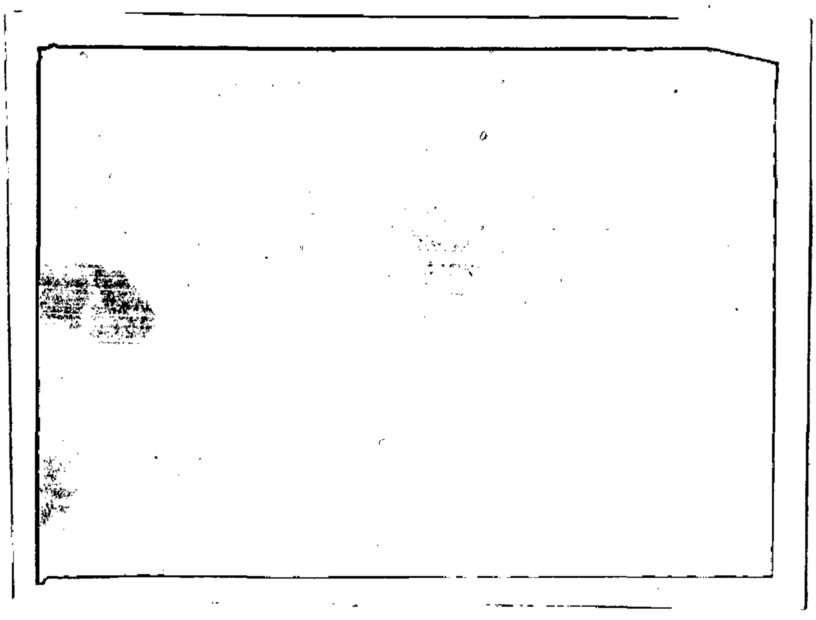


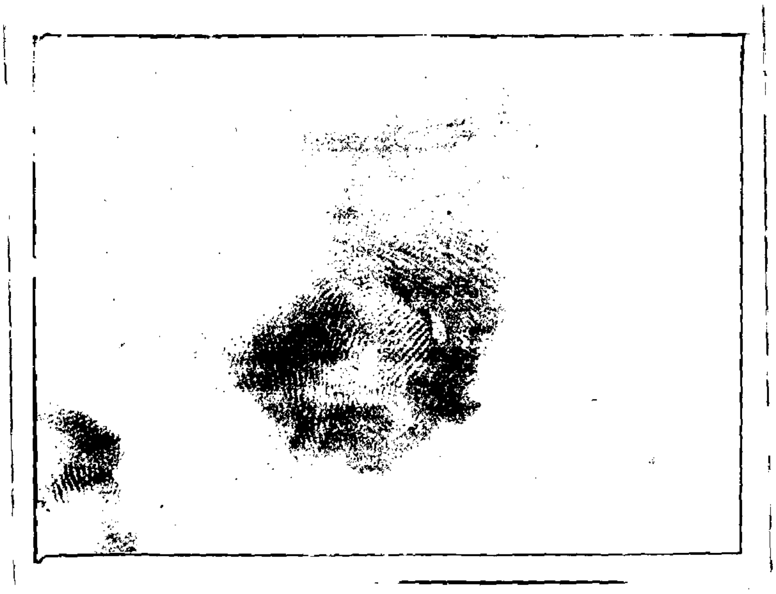
Fig. [illegible]A Plot of Percentage HCl Recovered in 120 minutes at 600°C for various alloy chloride cryst

Temp. 600°C 80 X

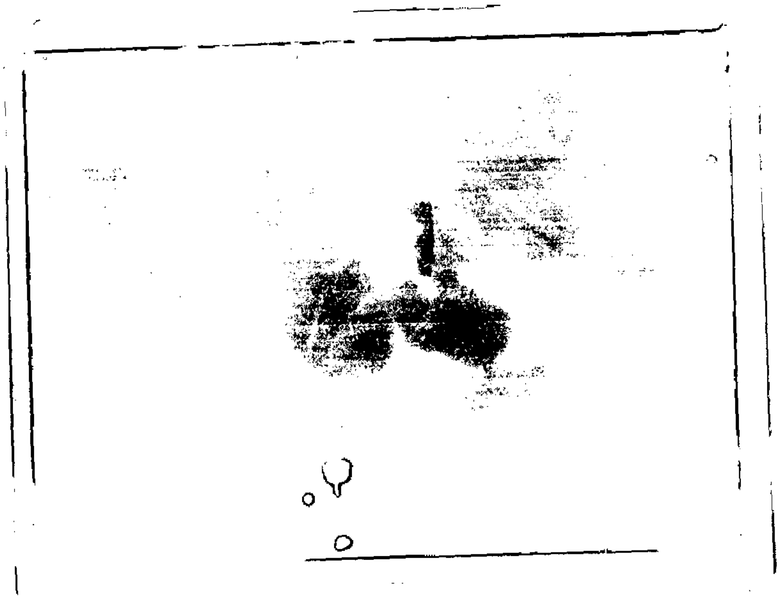


Temp. 650°C 80 X

FIG.24: Shape of iron powder particles obtained at various temperatures.



Fe - Ni Alloy 80 X



Fe - Cr Alloy 80 X

FIG.25: Shape of various iron-alloy powder particles

decrease in reduction time. So it can be well argued that the amount of HCl produced and thus the rate of reduction is extremely temperature sensitive. This is further clarified from fig.15 in which a comparison of HCl recovered in c.c. versus temperature for reduction of ferrous chloride crystals at fixed time is made. It is found that at the end of 60 minutes the recovery of HCl at 400°C is 20 cc while with an increase of 100°C it becomes 43 cc. With an further increase in temperature upto 650°C the recovery of HCl becomes 164 cc. Similarly at the end of 100 minutes the recovery of HCl at 400°C is 22 cc while at 650°C it is 187 cc.

The percentage reduction of ferrous chloride crystals is calculated from the analysis of reduced sample at various temperatures and is plotted against time in fig.16. This shows that the percentage reduction of ferrous chloride crystal is increased in lesser time with increase in temperatures. At 400°C the percent reduction is 40.68 while at 650°C it is 98.9 in times 300 and 100 minutes, respectively.

From the percent reduction data, the theoritical amount of HCl produced was calculated and the percentage recovery was found out. This is compared in fig.17 for various temperatures which shows that the percentage recovery of HCl is not same at all temperatures.

The cross section of an partially reduced pellet of ferrous chloride crystal is shown in fig.13 which shows the presence of an unreduced core and confirms that the reduction of the ferrous chloride crystal takes place in a topochemical manner. In this case there is a gas diffusion boundary layer at the outer surface of the pellet. But this boundary layer is not critical when the gas flow rate is beyound a particular optimum flow rate (1 litre/min). In the present investigation the flow rate of hydrogen gas was kept 3.0 litre/min. Therefore the foundary layer was not critical.

2) REDUCTION OF IRON-ALLOY CHLORIDE CRYSTALS.

The reduction of various iron-alloy chloride crystals viz. Fe-Ni, Fe-Cr, Fe-Ni-Cr was carried out at 600°C and the experimental results are shown in figs.18 to 20. The percentage reduction of these alloy chloride crystals was calculated from the knowledge of the analysis of the crystals and powders. With the help of these reduction data the theoritical HCl recovered was also calculated to know the percentage HCl recovery and hence loss of HCl. These data, percentage reduction and percentage HCl recovery for various alloys, were compared in figs. 22 and 23.

The reduction of ferrous-nickel chloride was 99.6% whereas the reduction of ferrous-chromous and ferrous-nickel-chromous chloride crystals were 94.4% and 97.0% respectively. The maximum reduction was obtained in case of Fe-Ni alloy powder at the same temperature and in the same time but is minimum in case of Fe-Cr alloy powder. It indicates that the presence of Ni^{2+} ions increase the rate of reduction and Cr^{2+}

ions decreases which is quite evident from the reduction data of Fe-Ni-Cr chloride crystals. This figures falls in the range of the reduction data of Fe-Ni-and Fe-Cr alloy chloride crystals.

A comparison among various alloy chloride crystals is also made in fig.21 where true HCl recovery in c.c. is plotted against time. A true comparison cannot be made due to variation in weights of the pellets but the nature of the curves can be compared. The shape of the curves are similar to that of iron chloride.

3) SHAPE OF THE POWDER PARTICLES

The shape of iron and iron-alloy powders are shown in figs 24 and 25. In both cases the shape of the powder particles is irregular and the particles are spongy in nature.

CONCLUSIONS

On the basis of results and discussions explained in chapter IV, the following conclusions can be drawn

1. The reduction of ferrous chloride crystals by hydrogen takes place in a topochemical manner.
2. The increase in temperature increases the percentage reduction for the reduction of ferrous chloride crystals by hydrogen.
3. The increase in temperature also increases the HCl recovery for ferrous and various alloy chloride crystals.
4. The nature of the reduction of ferrous chloride and alloy chloride are same.
5. The presence of Ni^{2+} ions increase the percentage reduction whereas the presence of Cr^{2+} ions decrease.
6. The shape of the iron and alloy powders is irregular and spongy.

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APPENDIX

TABLE -1

PRODUCTION OF IRON POWDER BY VARIOUS PRODUCERS IN THE WORLD IN 1970

Country/company	Location	Estimated capacity (Metric ton/year)	Basic method	Feed stocks	Remarks
SWEDEN					
Hoganas AB	Hogans	176,000	Carbon reduction, atomisation	Sponge iron	
Husquarna Vapenfabricks AB	Huskvarana	1,000	Electrolysis	$FeCl_2$/NH_4Cl electrolyte	
U.K.					
Jand J.Makin Ltd.	Rochdale, Laus		Atomisation followed by comminution	Car pressing offcuts	Output about 3500 ton.could be expecte to 10,000 ton per yr
George Cohen	London E.6	1,000	Electrolysis		
Round Oak Steel works	Brierley Hill	16,000	Atomisation		Planned for 1970
WESTERN GERMANY					
Hartmetall 'AG		11,000	Comminution in N_2 atm.	Carbon steel wire	Hametag process
Mannesmann Pulvermetall	Monchengladbach	11,000	Atomisation	Scrap and pig iron	
Metallhutten-werke Lubeck	Lubeck	7,000	Atomisation	Pig iron & steel	Iron & alloy powders

Country/Company	Location	Estimated capacity (Metric ton/year)	Basic method	Feed stocks	Remarks
CANADA					
Domfer	Quebec	10,000	Atomisation	Hot metal from Quebec	High compres ibility.Thro ugh out probably abo 10,000 ton/ year, UK agents Powd Metallurgy Ltd.
Quebec Metal Powders Ltd.	Tracy, Quebec	70,000	Atomisation	Iron & Ti.	
Fine Metals	Montreal	16,000	H_2 Reduction	Concentrates	
PRMS	Windsor Ontario	50,000	Hydro-metallurgical	Car Pressing off cuts.	Started in early 1970

TABLE -2

CONSUMPTION OF IRON POWDER IN VARIOUS YEARS

Year	Iron Powder consumption in the world
1947	10,000 tons
1951	30,000 tons
1967	150,000 tons
1973	500,000 tons (expected)

TABLE -3

IRON POWDER PRODUCTION IN 1970

Type of Process	% of World Production	Suitable raw material
Reduction	28	High grade iron ore or Mill scale.
Carbonyl decomposition	Small quantity	Spongy iron, powdered iron
Atomization	60	High quality of scrap or Hot metal
Electrolytic	2	low grade steel plate, cast iro
Hydrometallurgical	10	Any iron bearing raw material including scrap, ilmenite, pickle liquor.

TABLE-4. EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORIDE CRYSTALS AT 400°C

****

Weight of pellet	Time in Min	HCl Recovery in C.C.	% Reduction	HCl Recovery (Theo.)cc	% HCl Recover
15.0144 gm	30	5.1			
	60	13.6			
	90	21.1			
	120	28.3			
	150	35.9			
	180	41.3			
	210	48.4			
	240	55.5			
	270	62.9			
	300	67.1	40.65	74.82	89.8

TABLE -5

EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORRIDE CRYSTALS AT 450°C

Weight of fellet	Time in Min	HCl Recovery in cc	% Reduction	HCl Recovery (Theo.) in c.c	% HCl Recovery
15.9784 gm	30	17.8			
	60	39.9			
	90	57.9			
	120	77.3			
	150	96.4			
	180	112.3			
	210	131.1			
	240	150.3			
	270	159.0			
	300	162.2	90.61	174.9	92.8

TABLE-6: EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORIDE CRYSTALS AT 500°C

Weight of pellets	Time in Min	HCL Recovery in Cc	% Reduction	HCl Recovery (Theo.) in cc	% HCl Recovery
16.0010 gm.	30	30.8			
	60	62.9			
	90	97.1			
	120	129.0			
	150	160.3			
	180	167.0			
	210	168.0	91.79	179.0	93.8

TABLE-7: EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORIDE CRYSTALS AT 550°C

Weight of pellets	Time in Min	HCl Recvoery in cc	% Reduction	HCl Reccovery (Theo.) in cc	% HCl Recovery
15.450 gm	30	39.6			
	60	80.8			
	90	121.4			
	120	157.9			
	150	159.9			
	180	161.3	94.09	177.72	91.1

TABLE-8: EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORIDE CRYSTALS AT 600°C

Weight of Pellets	Time in Min	HCL Recovery in cc	% Reduction	HCl Recovery (Theo.) in cc	% HCl Recovery
14.9216 gm.	20	36.6			
	40	78.7			
	60	120.8			
	80	152.3			
	100	160.1			
	120	162.9	97.5	178.6	91.4

TABLE 9: EXPERIMENTAL DATA FOR THE REDUCTION OF FERROUS CHLORIDE CRYSTALS AT 650°C

Weight of pellets	Time in Min.	HCl Recovery in cc	% Reduction	HCl Recovery (Theo in cc)	% HCl Recovery
16.1470 gm.	20	59.6			
	40	120.2			
	60	171.3			
	80	184.8			
	100	193.9	93.9	193.9	93.4

TABLE -10

ANALYSIS OF FERROUS CHLORIDE CRYSTALS AND POWDERS

Crystals (% Fe)	Powder	
	Temperature in °C	Analysis (% Fe)
34.02	400	66.7
	450	94.8
	500	96.4
	550	96.7
	600	98.6
	650	99.4

TABLE-11 EXPERIMENTAL DATA FOR THE REDUCTION OF Fe-Ni CHLORIDE CRYSTALS AT 600°C

Weight of Pellet	Time in Min.	HCl Recovery in cc	% Reduction	HCl Recovery (Theo.) in cc	%.HCl Recovery
13.900 gm.	20	42.5			
	40	86.3			
	60	125.8			
	80	149.8			
	100	158.2			
	120	159.9	98.6	104.2	97.3

TABLE -12: EXPERIMENTAL DATA FOR THE REDUCTION OF Fe-Cr CHLORIDE CRYSTALS AT 600°C

Weight of pellet	Time in Min.	HCl Recovery in cc	% Reduction	HCl Recovery (Theo.) in cc	% HCl Recovery
14.010 gm	20	29.7			
	40	63.6			
	60	96.6			
	80	129.5			
	100	145.4			
	120	149.8	94.4	166.2	91.1

TABLE 13: EXPERIMENTAL DATA FOR THE REDUCTION OF Fe-Cr-Ni CHLORIDE CRYSTALS AT 600°C

Weight of Pellets	Time in Min	HCl Recovery in cc	% Reduction	HCl Recovery (Theo.) in cc	% HCl Recovery
14.3410gm	20	41.6			
	40	81.3			
	60	122.6			
	80	151.2			
	100	158.2			
	120	160.0	97.6	173	92.5

TABLE 14: ANALYSIS OF CRYSTALS AND POWDERS OF VARIOUS ALLOYS AT 600°C

Alloy	Crystals			Powders		
	Fe	Cr.	Ni	Fe	Cr	Ni
Pure Fe	34.02%	-	-	98.6%	-	-
Fe-Ni	28.65%	-	5.64%	83.4%	-	15.78%
Fe-Cr	30.3%	3.62%	-	87.7%	9.1%	-
Fe-Cr-Ni	25.4%	6.2%	2.92%	73.1%	17.76%	7.80%