PRODUCTION OF IRON POWDER FROM IRON OXIDE (MILL SCALE)

A thesis submitted to the Department of Metallurgical Engineering, Bangladesh University of Engineerings and Technology, Dhaka, in partial fulfilment of the requirements for the degree of Masters of science in Engineering (Metallurgical).

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CONTENTS

DECLARATION

This is hereby declared that neither this thesis nor any part therein has been submitted or is being concurrently submitted any where else for the award of any other degree or diploma.

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ABSTRACT

The present study was undertaken with a view to study the kinetics of reduction of mill scale by coal and to study the possibilities of producing iron powder from the reduced masses. Another aim was to estimate the activation energy of reaction after evaluating the reaction mechanism. Mill scale from Chittagong Steel Mills Ltd.(CSM),Bangladesh and coal from India were used in the present study. Mill Scale and Coal were placed by two ways within the crucible. Firstly, a central column of mill scale was surrounded by coal and secondly, an uniform layer (disc) of scale was sandwiched by a bottom and a covering layer of coal. The mixtures were reduced isothermally at four different temperature levels from 1173 to 1323K.

Nearly complete reduction of the mill scale was obtained in about 120 - 150 minutes at 1050°C for a particle size of -165 to + 200 micron and a coal : oxide ratio of 0.9. Higher temperature increases, the reduction rate and a decrease in the particle size shows negative effect on the reduction rate, whereas an increase in coal : oxide ratio has little effect on the rate. The kinetic data of reduction fits the spherical i.e, chemically controlled reaction model for both arrangements (column and disc).

$$G(\alpha) = 1-(1-\alpha)^{1/3}$$

Between the two arrangements, column is better fitted because of its lower activation energy (40 kJ/mol) in compare to disc (55 kJ/mol). For the same temperature and time the degree of reduction was always higher in a central column of mill scale surrounded by coal than that of a central disc of mill scale sandwiched by coal.

Higher reduction temperature and time produce better sintering of the reduced masses.

CHAPTER ONE

INTRODUCTION

POWDER METALLURGY has been defined as the art and science of producing fine metal powders and objects finished or semi finished shaped from individuals, mixed, or alloyed metal powders with or without the inclusion of non-metallic constituents.It is that branch of metal working processes, which in its simplest form, consists of preparing and mixing of metal powders, compacting and simultaneous or subsequent heating (or sintering) at elevated temperature in a furnace under a protective atmosphere with or without fusion of a low melting point constituent only so as to develop metallic or metal like bodies with satisfactory strength, density, and without losing the essential shape imparted during compaction[1].

Powder Metallurgy is an art which has been part of human story from the earliest times[2]. Powder Metallurgy industry has enjoyed an above average growth rate for the past four decades - derives from its ability to mass-produce complex structural parts with savings in labour, material, and/or energy. In recent years, an entirely new dimension has been added with the achievement of full density and improved control of purity and microstructure. This has resulted in the fabrication of high performance materials, permitting extending service life or more efficient use. Examples of commercial uses include aerospace super-alloy, low-alloy steels, dispersion - strengthened alloys and tool steels. These developments have added considerable diversification to the conventional press-and-sinter technique and are opening up new markets beyond the traditional ones of the automotive, farm, lawn and garden and office equipment industries[3]. The importance of powder Metallurgy in the development of modern technology is so much that the powder Metallurgy part is said to be "ubiquitous"[4,5].

Powder must posses the required physical and chemical characteristics for use in the various powder Metallurgy consolidation process and applications. Generally, Powders in current uses are cleaner ranges. Improved and more complete powder characterization is certain to become more important.

The primary characteristics of a metal powder are :-

(i) Chemical composition and purity,
(ii) Particle size and it distribution,
(iii) Particle shape,
(iv) Particle porosity, and
(v) Particle microstructure.

Specific surface, apparent density, tap density, flow rate as well as its compacting and sintering characteristics are the other characteristics which are dependent entirely or to a large extant on the above primary properties of metal powders. Primary properties such as the particle size distribution and the important secondary properties such as apparent density and flow rate are most widely used in specification and control routine. The success of a powder Metallurgy processing technique depends to a great extend on understanding and evaluating the physical and chemical properties of metal powder both as individual particles and in bulk form. Relationships between these powder properties and their behaviour during processing (for example, compressibility, dimensional change during sintering),in most cases are qualitative in nature.

There are various methods of manufacturing metal powders and consequently there is a wide range in their characteristics. A choice regarding the suitability of manufacturing techniques of metal powders can be made only after considering the required finished product for a specific job.

Because of its increasing use in structural parts during world war II, iron powder has become the single most important powder in the powder Metallurgy industry. High compressibility is of prime importance for the production of structural parts by pressing and sintering. This constitutes the major use of iron powders. Other advantages of iron powder for which it leads in commercial powder Metallurgy application[6] are (i) it is inexpensive to produce (ii) it has a favourable strength-to-weight-cost ratio (iii) It alloys readily (iv) it possesses superior properties and (v) it is available in sufficient quantity.

Upto 1965, most of the iron powders used were made by reduction of oxides or ore. Due to significant advances in atomization technology in the 1950's and 1960's, most iron powder is currently produced by atomization techniques. Atomized iron powders have enjoyed increased usages because they offer excellent compressibility and high purity. Before 1965, electrolytic iron powder was used widely because of its unsurpassed compressibility. Water atomized low-carbon iron provides a less expensive substitute of almost equal compressibility. With the development of techniques such as powder forging that achieve full density, powder purity has become equally important for the achievement of maximum dynamic properties.

The development of mechanical alloying and the demand for finer powders in recent years have led to the use of high energy milling. Full-dense sintering of high - alloy steels and injection moulding processes have led to the use of much finer powders conferred to conventional powder Metallurgy processes. Powder producers who supply metal powders to the Powder Metallurgy Industry also supply metal powders for manufacturing paints, inks catalysts, peripheries, explosives food additives, and welding electrodes and for use in plasma and flame spraying. Manufacturing process for these powders are similar to those used for producing powder for structural parts.

A major break-through is the manufacture of powder directly from ore. It is now possible to prepare larger and higher strength materials from new powders possessing the superior properties. Iron powder has also been produced from oxide ore, pure oxides or a cheap initial product such as mill scale by reducing with carbon, hydrogen or natural gas[7].

Production of iron powder by the reduction of iron oxide, and in particular the reduction of iron ore by carbon, is the oldest method of producing iron powder. The Swedish sponge iron process, which was developed in Höganäs, Sweden in the early 1900's, was originally intended to produce metallic iron in sponge form as the raw material for steel making . A modified version of the process is still one of the important industrial methods of producing iron powder and is practiced in Sweden and in the United State. A similar adaptation also is used in Soviet Union[8]. The Swedish sponge iron process is one of many developed for the direct reduction of iron ore to metallic iron at temperatures below the melting point of iron. However, metallic iron produced by most of the direct reduction process are not suitable for use as iron powder in the production of powder metallurgy iron and steel products, because they contain too high a percentage of impurities.

In Bangladesh, there is no reserve of iron ore but large quantities of mill scale are produced in the re-rolling mills every year. Only in Chittagong steel Mills Ltd, 3600 tons of mill scale are produced every year[9]. Most of these scales are wasted. Since the mill scale is a high grade iron oxide, there is a great scope to develop a process by which sponge iron can be produced from these mill scale.The final sponge iron, of very high purity, can be used in powder metallurgy. Coal dust can be used as a reducing agent which is produced during transportation and storage. These fines are usually wasted.

The present study is undertaken with a view to study the kinetic of reduction of mill scale by coal and to study the possibilities of producing iron powder from the reduced masses.Another aim was to estimate the activation energy of reaction after evaluating the reaction mechanism.

The reduction of iron oxide by carbonaceous materials is not only of great industrial significance for the production of pig iron and sponge iron but is also of considerable theoretical interest.

CHAPTER TWO

LITERATURE REVIEW

2.1 POWDER MANUFACTURE PROCESS :

Metal powder production has always been influenced greatly by cost and quality requirements of powder consolidation techniques and applications. This interrelation ship has led to the development of many powder - producing processes. Manufacturing methods must be cost effective; powders must possess the required physical and chemical characteristics for use in the various powder Metallurgy consolidation processes and applications.

The powder manufacture process is a very broad topic and the commonly employed commercial methods for making metal powders are : milling, atomization, thermal decomposition, reduction of oxides, gaseous reduction of solutions, electrolysis. Practically any material can be made into a powder by using one or more of these methods. The particular method chosen depends upon the types of raw materials readily available[10]. However , newer production techniques especially applicable to highly alloyed system have been developed in recent years, powder manufacture processes can be divided into following two headings[11]:

Mechanical processes: powder production by mechanical disintegration is widely employed in Powder Metallurgy. Mechanical process include : a. Machining, b. Crushing, c. Milling, c.Shotting, d.Graining, and e. Atomization. These are time taking processes rendering low yields.

Physico-Chemical processes: include (a) Condensation, (b) Thermal decomposition, (c) Reduction, (d) Electrodeposition, (e) Precipitation from aqueous solution, (f) Precipitation from fused salt, (g) Hydrometallurgical or gaseous reduction, (h) Intergranular corrosion, and i.Oxidation and decarburization methods.

2.2 Mechanical Processes :

Machining : This method is employed to produce fillings, turning, scratchings, chips, etc, which are subsequently pulverized by crushing and milling. Relatively coarse and bulky powders entirely free from fine particles are obtained by this method[11].

Crushing: This method is mostly used for the disintegration of oxides (subsequently reduced to metal powders) and brittle materials. Any type of crushing equipment such as stamps, hammers, jaw crushers or gyratory crushes may employed for crushing brittle material[12].

Milling: Milling of materials, whether hard and brittle or soft and ductile, is of prime interest and of economic importance to Powder Metallurgy industry[13]. Milling or Mechanical Comminution is the most widely used method of powder production for hard metals and oxide powders. In most cases, the objective of milling is particle size reduction. During milling , Four types of forces act on particular material; impact, attrition,shear, and compression. The milling action is carried out by the use of a wide variety of equipments such as ball mill,rod mill, impact mill, disc mill, eddy mill, vortex mill etc. The main disadvantages of milling are work hardening, excessive oxidation of the final powder, particle welding and agglomeration[14].

Shotting : This method consists essentially in pouring a fine stream of molten metal through a vibrating screen in to air or neutral atmosphere. In this way, molten metal stream is disintegrated into a large number of droplets which solidify as spherical particles during its free fall. All metal and alloys can be shotted[11].

Graining : Graining involves the same procedure as the shotting the only difference being that the solidification is allowed to take place in water . In similar manner, other pulverization method are used for the production of very fine powders[11].

Atomization : Atomization may be defined as the break up of a liquid into a fine droplets, typically smaller than 150 micron.

For large particles this process is referred as "shooting". Consequently , any material available as a liquid can be atomized. The break up of a liquid stream brought about by the impingement of high pressure jets of water or gas is referred to as "water" or "gas" atomization respectively. The use of a centrifugal force to break up of a liquid stream is known as :centrifugal atomization". Atomization into a vacuum is known as "vacuum" or "soluble gas atomization". The use of ultrasonic energy to effect break up is referred to as "ultrasonic atomization".

Atomization technology has grown steadily and has become more sophisticated since large scale production of atomized iron powder first began during World War II. High quality powders from aluminum, brass, and iron powders to stainless steel, tool steel, and superalloy powders - in combination with new consolidation techniques, have lead to many new applications and to properties that are sometimes superior to wrought counterparts[15,16].

<u>Cold stream process :</u> Cold steam process relies upon the brittleness of certain metals and alloys at low temperatures. The starting material is coarse particles. This is conveyed in a high velocity, high pressure air stream through a vertical nozzle and strikes on a target in an evacuated blast chamber. At the nozzle pressures drop occurs at once and this results in a very quick temperature drop to the zero. The brittle raw material shatters

against the target into an irregular shaped powder having very little surface contamination and excellent pressing characteristics. The resulting powder is separated into suitable size using a classifier[17].

2.3 Physico-chemical processes :

Condensation : This process in fact may be considered as a modification of the usual distillation process employed for refining zinc. Zinc dust, at least 97% pure, is produced very large tonnage in this way[18].

Thermal decomposition (or gaseous pyrolysis method) : The thermal decomposition of vapour produces metal powders which has achieved industrial importance particularly in the manufacture of ferrous and nickel powder by the decomposition of their carbonyl. Other metals such as Zn, Mg, Co, W, Mo, and Cr can also form respective carbonyl which at certain temperature and pressure can decompose to give a gas and a metal[19].

Carbonyl are volatile liquids. They are produced by allowing carbon monoxide to pass over spongy or powdered metal at suitable temperature and pressure. At reduced pressure and elevated temperature all of those carbonyl decompose to reform both metal and the carbon monoxide. The latter being recycled aud reemployed again to produce more carbonyl liquid and continue to process[20].

Electrodeposition : Metal powder can be produced by electrodeposition from aqueous solution and fused salts. This method is reversed adaptation of electroplating. As many as thirty metals have been prepared as powder by electrolysis of aqueous solutions accompanying simultaneous refining, but this technique is mainly employed for the commercial production of metal powders such as copper, beryllium, iron, zinc, tin, nickel, cadmium, antimony, silver and lead. The process has a great number of advantages[21].

Precipitation from aqueous solution : The principle of precipitating a metal from its aqueous solution by the addition of a less noble metal which is higher in the electromotive series has been applied in numerous metallurgical process. This process permits the production of very fine metal powders of low apparent density which are occasionally used for sintering purpose[11].

Precipitation from fused salts : Powders, particularly of reactive metals are also prepared by precipitation from fused salts. Several intermetallic compounds have been prepared in powder form by reacting two amalgams[11].

Hydrometallurgical or gaseous reduction process : Metal powders are precipitated on commercial scale by hydrometallurgical method by the reduction of aqueous solution or slurries of salts of metals with hydrogen when subjected to the correct combination of high pressure and temperature. A distinct virtue of the process is that it can be operated on the low grade ores[22].

Intergranular Corrosion : This process is based an the fact that the grain boundaries of the heat treated alloys are more susceptible to chemical attack, then the grains, thus freeing particles of bulk material. The powder particles possess angular shape and the final particle size ia determined by the grain size of the sensitized material[23].

Oxidation and Decarburization : This method has been developed for the production of pure reactive metal powders by react metal carbide with metal oxide vacuum at elevated temperature so that both oxygen and carbon are removed as CO[11].

Reduction Process : Its great importance is understood by the fact that the production of the largest quantities of metal powder is undertaken by the Powder Metallurgy industry[24]. This is a convenient, economical and extremely flexible method for controlling the properties of the product regarding size, shape and porosity over the wide range. It is extensively employed for the manufacture of Fe, Cu, Ni, W, Mo and Co, though Ta, Th, Zr, Ti and even Al and Cr are also being produced. This process yields extremely fine powders with irregularity shaped particles and considerable porosity. Gases such as hydrogen, dissociated NH3, CO Coal gas, enriched blast furnace gas, natural gas, partially combusted hydrocarbons or alkali, metal vapours, Carbon and metals are used as reducing agent; but the choice of reducing agent is made from the view point of convenience and economy of operation.

Carbon is the cheapest reducing agent, but with its use difficulties have been experienced is closely controlling the carbon content of the final powder. Hydrogen, dissociated ammonia and other atmospheres rich in hydrogen are used conveniently but they are expensive. Metallic reducing agents are also used for reduction of various metallic oxides involving exothermic thermit reaction as carbon and other reducing gases are unable to reduce them economically[25,26,27].

By varying (i) the degree of purity, (ii) particle size, and shape of the raw material (vi) temperature and time of reduction (iv) the type of reducing agent, and (v) in case of gaseous reduction the pressure and flow rate of the gas, close control over the purity; particle size and shape, apparent density and related properties of the deposited metal powder and completeness of reduction can be obtained. Since oxides are generally brittle and easily comminuted to the desired degree of fineness, it is possible to obtain very fine metal powders. Decreasing the reduction temperature also results in the production of very fine powders. When the reduction process are carried out at higher temperatures the final metal powder particles sinter together into a 'sponge' that is easily crushed and committed to powder for use in Powder Metallurgy.

Production of iron powder by the reduction of iron oxide, and in particular the reduction of iron ore by carbon, is the oldest method of producing iron powder. The Höganäs process[28] uses pure magnetite Fe_3O_4 ore found in northern Sweden, which has an iron content of approximately 71.5%. The impurities present in small amounts are not in solid solution in the oxide, but exist as discrete phases. The ore is of consistent quality and is available in sufficient quantities for continued usages. Coke breeze or another carbon source that provides the reducing agent is required to produce sponge iron powder. Additionally lime stone is used to react with the sulfur contained in the coke. The ore and the coke-limestone mixer are then charged into ceramic tubes. A pair of concentric steel charging tubes is lowered to the bottom of the ceramic tubes. The ore is fed between the steel tubes. The coke - limestone mixture is fed within the inner of the two concentric charging tubes and between the outer charging tube and the inner wall of the ceramic tube. The charging tubes are then withdrawn from the ceramic tube, leaving the ore and the reduction mixture in contact with one another, but not intermixed.

Within the hot zone of the tunnel kiln to a temperature of 1200 C, several chemical reactions occur. Decomposition of limestone generates carbon di oxide, which oxidises the carbon in the coke to form carbon monoxide. carbon monoxide reacts with magnetite to form additional carbon di oxide and ferrous oxide. The ferrous oxide is further reduced by the carbon monoxide to metallic iron. Metallic iron particles are sintered together to form sponge iron cake.

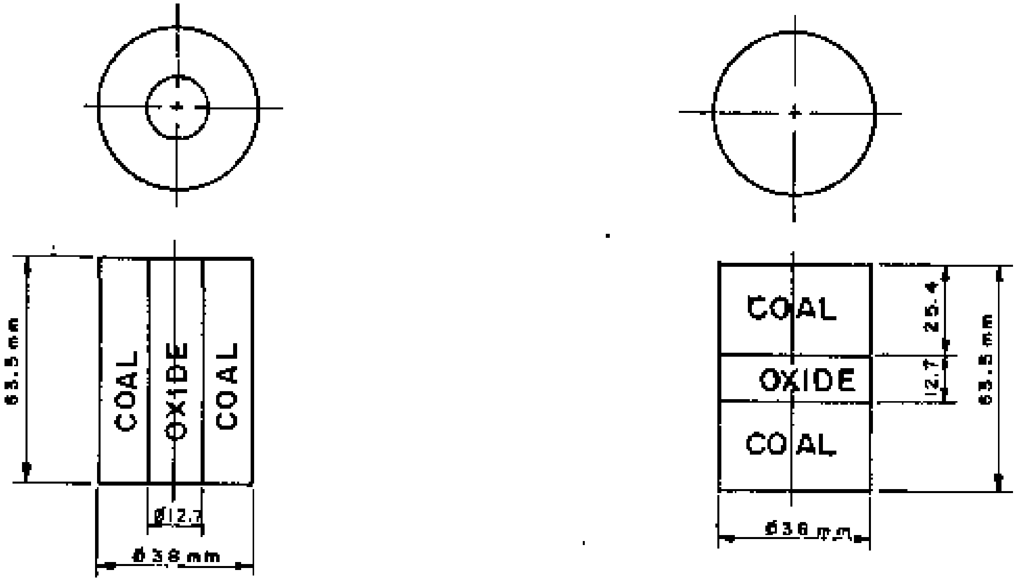
The thermodynamics and the kinetics of the process by which iron oxide is reduced to metallic iron have been studied repeatedly. It has been found that 96% of the oxide has been reduced to iron and the iron contains 0.3% C. For powder metallurgy purposes 65% of the powder should passes through a -100 mesh is generally required.

Production of iron powder by the Pyron Process[29] provides an alternative for the production of iron powders by the reduction of oxides. Instead of using ground iron ore as the raw material for reduced iron powders, the Pyron Process usages mill scale taken from steel mills that produce plain carbon steel products, such as sheet, rod, wire, plate, and pipe. Mill scales containing alloying elements other than mauganese are not used. Mill scale is grounded to -100 mesh in a continuous ball milling operation. Careful control of this operation ensures desired particle size distribution. Hydrogen reduction is done in electric furnace.

CHAPTER THREE

EXPERIMENTAL :

The oxides and reductant were placed in the crucible by two ways. Firstly, a central column of mill scale was surrounded by coal and secondly, an uniform layer (disc) of scale was sandwiched by a bottom and a covering layer of coal. The arrangements of mill scale and coal within the crucibles are shown in Fig.3.1.



A. OXIDE PLACED AS A CENTRAL COLUMN. B. OXIDE PLACED AS A CENTRAL DISC.
FIG. 3 1. DIFFERENT ARRANGEMENTS IN REDUCTION SYSTEM.

3.1 RAW MATERIAL USED :

Mill scale from Chittagong Steel Mills Ltd.,Bangladesh and coal from India were used in the study. The analysis of mill scale and coal are given in tables 1 and 2 respectively.

Table - 1

Chemical Analysis of mill Scale used

Mill Scale wt.	
Fe_{tot}	72.56%
Fe_3O_4	52.60%
FeO	44.36%
SiO_2	2.42%
MnO	0.54%
S & P	0.08%

Material and analysis supplied by CSM Ltd.Chittagong, Bangladesh & Regional Research Laboratory, Bhubanessar, India, respectively.

Table - 2
Proximate analysis of coal used

Coal wt.	
Moisture	3.57%
Fixed Carbon	52.60%
Volatile Material	34.08%
Ash	9.75%

3.2 REDUCTION PROCEDURE :

Reduction experiments were carried out in mild steel crucible of diameter 38mm and height 63.5mm. Mill scale and coal of same particle sizes were used in the experiments, were not mixed thoroughly but kept separate. No load was applied for compaction, only mild tapping were applied in each case. The crucibles containing the reduction mixture were heated in an electrically heated muffle furnace. A reducing atmosphere was maintained by placing some extra crucibles full of coal in the furnace.

After predetermined times the samples were taken out from the furnace and quenched in a water tray placing in such a way that they were half immersed. To prevent re-oxidation the top of the crucibles were covered with mild steel sheets. After cooling, the reduced masses were separated from the char. The mass was then crushed to -150 micron size and then analyzed chemically to estimate the percentage of total iron using standard volumetric method[30,31].

3.3 ESTIMATION OF TOTAL IRON :

Total iron was estimated by volumetric method using potassium dichromat as titrating agent.

Solution required :

1. 0.1N standard $K_2Cr_2O_7$ solution .
2. $SnCl_2$ solution : 50 ml $SnCl_2$ was dissolved in 200 ml concentric HCl and then made upto 1 litre by adding water.
3. A saturated solution of $HgCl_2$ in water at room

temperature.

4. Diphenylamine indicator: 1 gm in 100 ml concentric H_2SO_4.

5. Acid mixture : H_2SO_4 + H_3PO_4 + H_2O (15:15:70)

At first 0.5 gm sample was weighed out and dissolved in 25 ml (1:1) HCl. After one hour digestion the solution was cooled and diluted to a volume of 250 ml. 25 ml of the solution was taken out in a conical flask, heated to boiling and few drops of HCl were added. Then stannous chloride solution was added drop by drop with constant shaking till the yellow colour changes to almost colourless.The flask was then cooled quickly to avoid oxidation. 20 ml of $HgCl_2$ solution was added. A silky white precipitate was formed. 20 ml of acid mixture was added followed by 2 to 3 drops of diphenylamine indicator and the solution was titrated with 0.1N $K_2Cr_2O_7$ solution. The end point was indicated by the appearance of deep blue colour.

The reactions which take place during the determination are as follows:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + Cr_2Cl_6 + 7H_2O$$

1ml of 1N $K_2Cr_2O_7$ = 0.05583 gm of Fe

% Fe_t = 11.17 x Vol. of 0.1N $K_2Cr_2O_7$ solution consumed.

ESTIMATION OF THE DEGREE OF REDUCTION :

Degree of reduction is the ratio of weight of oxygen removed to that of the initial total oxygen present in the oxide in combination with iron. For the estimation of degree of reduction, α, it is necessary to estimate the exact percentage of different valance states of iron in the reduced mass. Although standard volumetric methods for these analysis are available, estimation of α using these methods are lengthy and associated with uncertainties. To avoid these difficulties the degree of reduction, α, was calculated from the total iron analysis only using the formula suggested by Chernyshev et al[32]. The formula is written as :

$$\alpha = K\left(\frac{\%Fe_t^{r} - \%Fe_t^{i}}{\%Fe_t^{r} \times \%Fe_t^{i}}\right) \times 100$$

Where K = ratio of weight of iron to that of oxygen in initial iron oxide.

$\%\ Fe_t^{i}$ = Percentage of total iron in initial oxide.

$\%\ Fe_t^{r}$ = Percentage of total iron in reduced mass.

The formula suggested by Chernyshev et. al[32] is based on the assumption that loss of weight for the oxide mass is caused by oxygen removal from the iron oxides only. This formula is also supported by Gonzales et al[33] who proposed a similar formula for the estimation of α. This equation was successfully used by other workers[34,35].

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 PRELIMINARY SELECTION OF PROCESS VARIABLES :

The process variables of the present experiments were the following :

(i) temperature
(ii) mill scale and coal particle size and
(iii) coal/mill scale ratio

It has been mentioned earlier that scale and reductant were not mixed but kept in separate layers in two ways (a) the reductant surrounding a central column of scale and (b) the reductant sandwitching a central disc of scale.

The experimental ranges were selected after some preliminary studies. As shown in fig.4.1(a) and 4.1(b), the rate of reduction increases with increasing particle size but decreases after certain size. Maximum reduction can be observed for -160 to +200 micron size particles both at 1273°K and 1323°K. Fig.4.2 shows that an increase in mill scale/coal ratio increases the rate of reduction but beyond a value of 0.9 it has a little effect on degree of reduction. From the above studies finally an average particle size of -160 to + 200 micron and scale/coal ratio of 0.9 were selected for the kinetic studies. This is because, a reasonable degree of reduction has been achieved after reducing the scale under given parameters at 1273° K for 2 hours. For both arrangements of scale and reductant, an appreciable change in the degree of reduction has been observed. So in the both cases kinetic studies were carried out separately for the evaluation of activation energies.

Kinetic studies are aimed to determine the influence of various process parameters on a reaction and also to explain the reaction mechanism. When a kinetic law is established and the variation of rate constant with temperature is studied then it become possible to obtain a value of activation energy which is said to indicate the reaction mechanism. So the main aim of the study was to establish a kinetic law and calculate the activation energy of the reaction.

4.2 KINETIC STUDY FOR CENTRAL COLUMN OF SCALE SURROUNDED BY COAL:

To establish the reaction mechanism, isothermal kinetic studies were carried out at four temperature levels namely 1173, 1223, 1273, and 1323 K. The results are shown in Fig.4.3. It shows plots of the degree of reduction (α) of the mill scale against time (t).

It was observed that the reaction mass took about 10 to 25 minutes to reach the reaction temperatures. Although the temperature profile is not truly isothermal in the initial stage of reaction, the kinetic plots seem to be quite smooth passing through the origin. This is due to the reason that from about 500°C to onwards the coal begins to liberate volatile matter. It is well known that volatile matter contributes to the reduction of iron oxides to some extent even at low temperatures[36]. Due to this compensating effect the plots are quite smooth.

In order to get an initial idea about the kinetic law, reduced time plots were used which is shown in Fig. 4.4 Preliminary identification of the reaction mechanism is possible using the reduced time plots[37,38]. Although such plots have widely been used in the analysis of solid state reaction but their application in the chemical metallurgy has been limited[39]. This method can be used to ascertain the reaction mechanism and hence the appropriate function $G(\alpha)$.

In reduced time plots, the kinetic relationships are rewritten in terms of dimensionless time using the following procedure[40].

We have : $G(\alpha) = kt$ (1)

Now, if $t_{0.5}$ is the time required to obtain 0.5 fraction reacted i.e. $\alpha = 0.5$ then $g(\alpha) = kt_{0.5}$ (2)

Dividing equation(1) by (2) one obtains a modified form.

$$G(\alpha) = \alpha \, . \, t/t_{0.5} \qquad (3)$$

$$G(\alpha) = B \, (t/t_{0.5}) \qquad (4)$$

where B is a constant which depends on the form of the function $G(\alpha)$. Eq. (4) is dependent on kinetic rate constant and is dimensionless. Thus for a particular reaction mechanism, a single equation of the type of Eq.(3) represents all kinetic data irrespective of the nature of the system, temperature or other factors which affect the reaction. Thus each mechanism has a unique reduced time plot. Keattach and Dollimore[40] have described the method of using the reduced time plots and have given the values of $t/t_{0.5}$ for different values for some of the reaction mechanism.

The method initially involved tabulation of the functional values $G(\alpha)$ for various reaction mechanisms for different α values. These $G(\alpha)$ values are used to calculate the $t/t_{0.5}$ values. Later plots of the various reaction mechanisms are obtained by plotting the α values against the calculated values of $t/t_{0.5}$. Reduced time plots of experimental data are superimposed on these master plots and the mechanism is identified by observing which one of the theoretical expression fits the experimental data.

The reduction of a lump oxide involves gas -solid reaction at a sharp interface between the unreacted core and product layer. The reaction kinetics is generally determined by the diffusion of the reducing gases through the product layer or chemical reaction at the core-product layer interface.It should be noted that gaseous diffusion is involved even when the reductant is solid. Solid-solid reaction between oxide and carbon plays only a minor role and reduction is mostly achieved via gaseous intermediates[11]. In the case of oxide coal mixtures, there can be no sharp reaction interface, the reaction proceeds throughout the bulk simultaneously. The reaction which is known to follow First order kinetics, may be called the total internal reduction[12]. However the kinetic equation is written as :

$$-\ln(1-\alpha)=kt. \qquad (5)$$

where k is the rate constant and t is the time. Again in some systems where oxide and coal are placed separately, the chemically controlled reactions or the diffusion controlled reactions may be the probable mechanism. The probable chemically controlled reaction mechanism is spherical and that of diffusion controlled reaction is Ginstling-Brounsthein model whose equations are given below respectively.

$$1-(1-\alpha)^{\frac{1}{3}}=kt \qquad (6)$$

$$1-(\frac{2}{3}\alpha)-(1-\alpha)^{\frac{2}{3}}=kt \qquad (7)$$

From Fig.4.4 it can be seen that out of three commonly suggested models such as Spherical, First order reaction and Ginstling-Brounsthein for iron oxide reduction, the Spherical equation seems to be the appropriate one to fit the data obtained in these studies.

Based on the findings from the reduced time plots, the data of Fig.4.4 were plotted according to the Spherical equation.

$$G(\alpha)=1-(1-\alpha)^{\frac{1}{3}}=kt \qquad (8)$$

The plots are shown in Fig.4.5.

4.3 EVALUATION OF ACTIVATION ENERGY (E) VALUE (column):

During a reaction all the particles in the system do not undergo transformation at one and the same time. Reactants and products coexist throughout the transformation and at any instant only a small fraction of the available particles can be in the process of transformation for the simple reason that only a fraction of the particles have free energy in excess of the mean and, therefore, energetically suitable for transformation. Those with insufficient free energy must wait until they receive the necessary activation energy from thermal fluctuations. So it can be said that activation energy is that energy which is required to initiate a chemical reaction or transformation[43], Kinetic data can be analyzed in two ways for the evaluation of the activation energy (E) i.e integral approach and differential approach.

<u>Integral approach :</u> At first this approach was used to estimate the value of E. During isothermal kinetic studies the progress of a reaction is generally measured in terms of degree of reduction (α).Degree of reduction means the ratio of oxygen removed from the feed to the total oxygen combined with iron in the feed. It varies from zero to unity. Values of α were plotted against time (t) for the given temperatures. Subsequently these data were fitted into an appropriate form of integral kinetic equation i.e $G(\alpha)=1-(1-\alpha)^{1/3}=kt$, which is shown in Fig.4.5. Integral expression of kinetic equations for some reaction mechanisms are well known[42]. In these expressions an appropriate function of α, which is known as $G(\alpha)$ is proportional to time (t). From the slope of $G(\alpha)$-t the reaction rate constant k can be obtained for various temperatures.

Generally reaction rates increases exponentially with increase in temperature.If the temperature range is not too wide, the temperature dependence of the rates of most reactions obey the Arrhenious type exponential equation[44,45] which is as follows :

$$k= A\ \exp^{-E/RT} \qquad (9)$$

Activation energy is said to depend on the reaction mechanism, Pre-exponential factor A depends on many factors . R is the gas constant and T is the temperature in degree kelvin. Eqn (9) is often applicable to both homogeneous and heterogeneous equation. The temperature dependence of the rate constant can be expressed as

$$\ln k = \ln A - E/RT \qquad (10)$$

Hence, a plot of "lnk" against 1/T should give a straight line whose slope will be E/R. The slope of this linear plot gives the value of activation energy. The pre-exponential factor is obtained from the intercept. This approach is called integral approach.

For the present study, the reaction rate constants (slope of the lines) of various temperatures (1323,1273,1223 and 1173 K) were obtained from the linearised plots of Fig.4.5 and then plotted according to the Arrhenious type equation shown in Fig.4.6.

The apparent activation energy of the process estimated from Fig.4.6 (slope = - E/R) is found to be about 40 kJ/mole.

Differential approach :

The apparent activation energies at different levels of reaction were also estimated using a differential approach where prior knowledge of the kinetic equation is not essential. At any time the reaction rate is a function of temperature (T) and α .Therefore, the differential form of the rate expression is:

$$d\alpha/dt = k(T) . f(\alpha) \qquad (11)$$

where K(t) is the temperature dependent rate constant and f(α) is an appropriate function of α. Substituting the value of k(T) from equation (10) we get:

$$\frac{d\alpha}{dt}=A.\exp^{-E/RT}.f(\alpha) \qquad (12)$$

Hence

$$\ln\left(\frac{d\alpha}{dt}\right)=-E/RT+\ln A+\ln f(\alpha) \qquad (13)$$

Thus it can be seen from eq. (13) that a plot of ln (dα/dt) against 1/T should give a straight line with a slope of − E/R provided α is fixed at a given value and f(α) is kept constant. In this method, the value dα/dt is obtained from the α-t plots of for various temperatures at fixed value of α.

The E value thus can be estimated without the necessity of finding a kinetic model. The major disadvantage of this approach is that one has to calculate (dα/dt) values from α-t plots, and calculation of these values often involve uncertainties. This problem can be solved by using second differential approach. Eq. 12 can be rewritten as :

$$\int d\alpha/f(\alpha)=k\int dt=A\int \exp^{-E/RT}dt \qquad (14)$$

For any given level of α ,the left hand side integral,with limits of 0 and α , has a constant value .The right hand side integral has the value t_α i.e time required to obtain the given value of α at the given temperature.Thus it can be written as

$$t_\alpha = \text{constant}/\exp^{-E/RT} \qquad (15)$$

$$\ln t_\alpha = \text{constant} + E/RT \qquad (16)$$

So plots of $\ln t_\alpha$ versus 1/T should be linear and the slope should yield the value of E which is shown in Fig 4.7. The values of t_α i.e time required for various degree of reduction were calculated from Fig.4.3.

The values of the apparent activation energies were in the range of 34 to 43 kJ/mole for α values in the range of 0.2 to 0.9. it is thus found that apparent activation energy obtained by the different approaches are nearly identical . This is an evidence to support the kinetic law identified . It is also found that variation of E values with α is minor . This is due to the fact that the reaction mechanism remains practically unaltered as the reaction proceed.

4.4 KINETIC STUDY FOR DISC OF SCALE SANDWICHED BY COAL:

To establish the reaction mechanism for this reduction system, isothermal kinetic studies were carried out at four temperature levels like the previous system i.e. column of scale surrounded by coal. Plots of the degree of reduction (α) in the mill scale-coal mixture against time (t) is shown in Fig. 4.8.

In order to obtain an initial idea about the kinetic law, redneed time plots were used which is shown in Fig.4.9. It can be seen that like the previous system spherical (chemical controlled reaction) model seems to be the appropriate one to fit the data obtained in these studies.

Based on the findings from the reduced time plots, the data of Fig.4.8 were plotted according to spherical equation;

$$G(\alpha)=1-(1-\alpha)^{\frac{1}{3}}=kt$$

The plots are shown in Fig.4.10.

4.5 EVALUATION OF ACTIVATION ENERGY (E) VALUE (DISC):

Here also kinetic data were analyzed in two ways for the evaluation of activation energy (E). At first, the integral approach was used to estimate the value of E . In this method , the reaction rate constants of various temperatures were obtained from the linearised plots of Fig.4.10 and then plotted according to the Arrhenious type equation. This is shown in Fig.4.11. The apparent activation energy of the process is thus estimated from the Arrhenious type plot (slope = - E/R) as 55 kJ/mole.

Secondly , the apparent activation energies at different levels of reaction were estimated using differential approach. For this purpose t_α values at different levels of α were estimated from the plots of Fig.4.8. Then the α versus 1/T plots were plotted, which are shown in Fig.4.12. The values of the apparent activation energies were in the range of 55 to 59 kJ/mol for α values in the range of 0.2 to 0.8. Here it is also found that apparent activation energy obtained by the different approaches are nearly identical. This can be taken as an evidence to support the kinetic law identified.

Activation energy required for the reduction of iron ore, which is mainly higher oxide of iron (Fe_2O_3), by coal is generally in the range of 120-150 kJ/mol[36,46]. However, in this study, lower value may be due to the reason that mill scale does not contain any Fe_2O_3.

It contains considerable amount of lower oxides, such as Fe_3O_4 and FeO. Lower activation energy for the reduction of lower oxides of iron was also reported by other workers[41,47].

4.6 PHOTOGRAPHY

Photography of the reduced masses both for column and disc are shown in Fig.4.13. It shows the effect of time and temperature on its sintering. Better sintering of the reduced masses observed with higher reduction temperature and time.

Chapter 5

Conclusions

1. Nearly complete reduction of the mill scale can be achieved in about 120-150 minutes at 1323°K for a particle size of -166 to +200 micron and coal : oxide ratio of 0.9.

2. Higher temperature will increase the reduction rate, a decrease in the particle size has negative effect on the reduction rate whereas an increase in coal : oxide ratio has little effect on the rate.

3. For the same temperature and time the degree of reduction is always higher in a central column of mill scale surrounded by coal than that of a central disc of mill scale sandwitched by coal.

4. The kinetic data of reduction of mill scale by coal fits the spherical i.e, chemically controlled reaction model for both arrangements (column and disc).

   $G(\alpha)=1-(1-\alpha)^{1/3}$

5. The apparent activation energy for the reduction of a central column mill scale by coal is about 40 kJ/mol whereas that of a central disc of mill scale by coal is about 55 kJ/mol.

6. Higher reduction temperature and time produce better sintering of the reduced masses.

5.1 SUGGESTIONS FOR FUTURE WORK

For complete reduction i.e. for 100% pure iron production furnaces with controlled atmosphere can be used instead of muffle furnaces. Flux or additives can be used to reduce the activation energy of the reaction.

REFERENCES

1. A.K. Sinha: Powder Metallurgy, Dhanpat Rai & Sons, New Delhi, India (1976), p 01.
2. I. Genkins: Powder Metallurgy Techniques and application, Metallurgic, Dec. 1957, Vol. 56, No. 3.38, p 271.
3. Erhald Klar, ASM Powder Metallurgy Handbook, 1990, Vol. 7, Edition 9, p-v.
4. Powder Metallurgy: A way of Make Almost Any Part Steel, Vol. 153, No. 23, Dec 1963, p 49.
5. K.H. Roll: Handbook of Metal Powders, (ed. A.R. Poster), Reinhold, New York, 1966, p 3.
6. Firtz V. Lenel: "Production of Iron Powder" ASM Handbook, Ninth Edition, 1990, Vol. 7, p 79.
7. Erhard Klar: Chemical Methods of Powder Production, ASM Handbook,1990, Vol. 7, Edition 9, p 52.
8. L. Bogdandy and H. Engell; Vosstanoulenie Gelesnich Rud, Metallurgia, Moscow, 1971, p 197.
9. Production report, Chittagong Steel Mills Ltd. (CSM)., Bangladesh April 1990.
10. P.U. Gummeson: Powder Metallurgy, Vol.15, No.29, 1972, p 67.
11. A. K. Sinha: Powder Metallurgy , published by Rai & Sons 1976 India, chapter 3, p 4.

12. F.S. Badger, Jr. and W.O. Sweemy, Jr.: Symposium on Materials for gas turbines, ASTM, 1946, p 99.

13. William E. Kuhn and Ira L. Friedman; " Milling of Brittle and Ductile Materials"; ASM Handbook,Vol.7, Ninth Edition,1990,p 56.

14. Harrish, C.C., On the Limit of Comminition, Trans. 50c Minning Engg. , March 1967, p 17.

15. Erhard Klar and James W. Fesko : " Gas and Water Atomization" SCM Metal Products Vol.7, Edition 9, ASM Handbook,1990, p 25.

16. J.F. Watkinson; P.M. No. 1/2, (1958), pp 13-23.

17. David L. Houck: "Spray Drying of Metal Powders" by Vol. 7, Edition 9, ASM Handbook, 1990 p 73.

18. Don O. Noel: Powder Metallurgy (Ed. John Wulff), ASM,1942,p 112.

19. H.E. Carlton and W.H. Goldberger; J. of Metals, June, 1965, p 611

20. G.V. Samsonov and S.Ya. Plotkin; Proizvodstvo Zheleznogo Poroshka, Moscow,1957.

21. P.U. Gummeson; Powder Metallurgy, Vol.15, No.29, 1972, p 94.

22. T.P. Forbath; Chem, Engg. Jan. 1957, p 194.

23. J.Wulff in Powder Metallurgy, (J. Wulff Ed.), ASM, Cleaveland, (1942) pp 137.

24. F.D. Richardson and J.H.E. Jeffs, Journal of the Iron and Steel Institute, Vol. 160, 1948, p 268.

25. Alan Arias: Powder Metallurgy, Vol. 11, No. 22, 1968, p 411.

26. G..Meiter; Metal Progress 53, (4) 1948, p 515.

27. B. P. 675933

28. E. Sieurin : HÖGANÄS PROCESS , vänn, 13 (1910-1912) p 195

29. Harold T. Harrison: " Production of Iron Powder by the Pyrone process" Vol.7 Edition 9, ASM Metal Handbook,1990, p 82.

30. G.E.F. Lundell, J.I. Haffman and H.A Bright : Chemical Analysis of iron and Steel, New York, John Wiley and Sons Inc.,1950, p 530.

31. R.S Yong : Chemical phase analysis, London, Charles Griffin and Co,1974, p 42,49.

32. A.M Chernnysher, N.K. Karnilava, and Yu.V Terasenko : Steel USSR, 7(8), 1977,133.

33. O.G. Dam Gonzales and J.H.E. Jeffes : Iron making and Steel making 14(5), 1987, 217.

34. R. Haque, H.S. Ray and A Mukherjee : Proc. 7th Nat. Symp : Thermal analysis, Srinagar, India, 23-25 October, 1989,p 62

35. S. Mookherjee, A. Mukherjee, B.K Dhindaw and H.S Ray : Trans., ISIJ, 1986, 26, 101.

36. S. Mookherjee, H.S. Ray, And A. Mukherjee: Iron making and Steel making, 13,1986, p 227.

37. J.H. Sharp, G.W. Brindley and B.N. Narhari : J. Amer. Ceram. Sec. 46, 1963, 364.

38. A. Giess : J Amer. Ceram. Sec, 46, 1963,364.

39. H.S Ray : Trans., IIM 36(11), 1983, 11

40. G.J. Keattach and D. Dollimore : An Introduction to Thermogravimetry. 2nd.Ed. Heyden (London), ch.5.1975.

41. S.B. Sarkar, H.S. Ray and I. Chatterjee; Journal of Thermal Analysis, 35, 1989,2461.

42. S.Paul and S. Mukherjee; Iron making and Steel making,No.3, 19, 1992,p 190.

43. H.S. Ray : Kinetics of Metallurgical Reactions, Oxford and IBH Publishing Co., New Delhi, India, 1993, p 3.

44. H.S. Ray : Proc. Int. Conf. on Advances in Chemical Metallurgy, Vol.2, ICMS - 79, BARC Bombay, 1979.

45. Rene Cypres and Claire Soudan - Moinet : Fuel,60, Jan,1981, 33.

46. R. Haque, H/S. Ray & A. Mukherjee : Iron making and Steel making 19, 1992, 31.

47. A.K.M. Matiur Rahman: Production of Mill Scale by Coal - Kinetic Study and effect of Process Variable, M.Sc. Engg. Thesis, Dept of Met.E, BUET, May 1993, p 24.

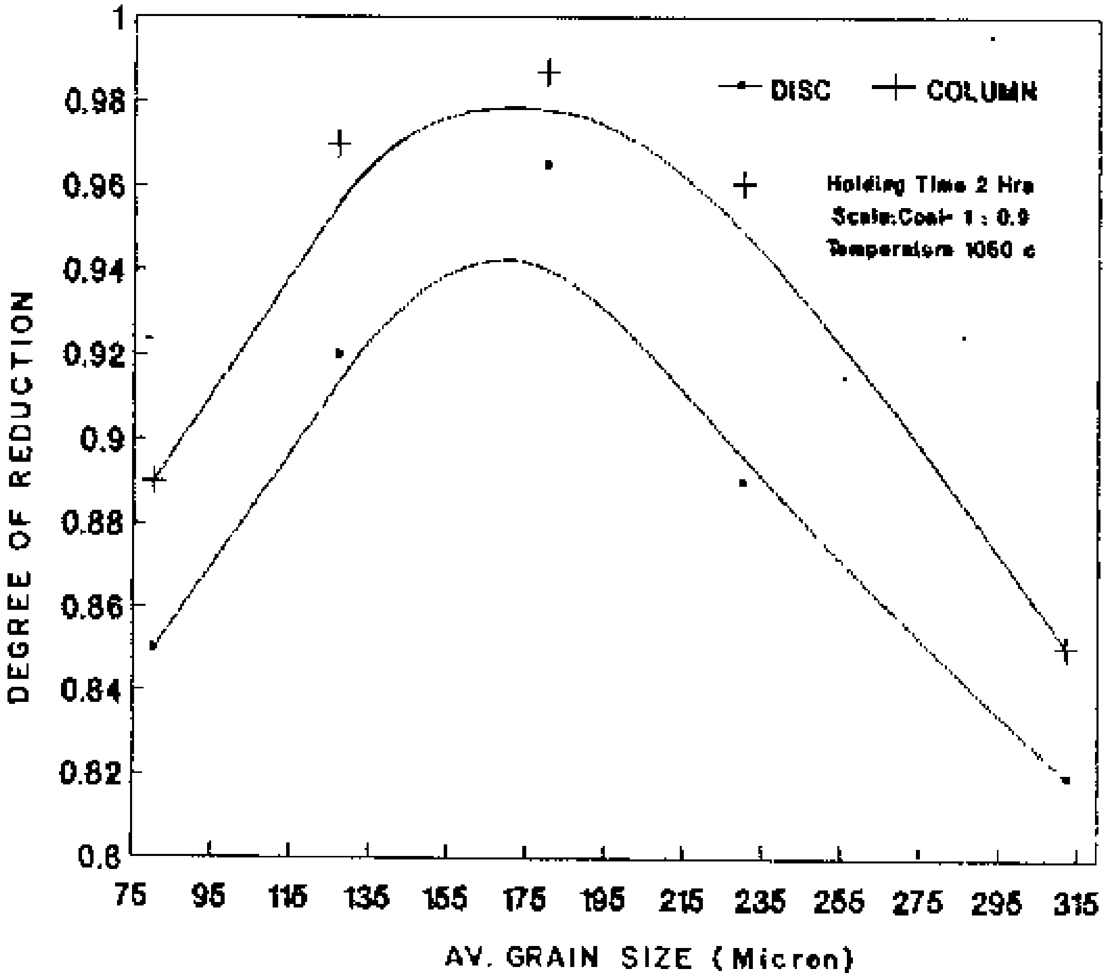


FIG. 4.1.(a) Effect of average particle size on the degree of reduction.

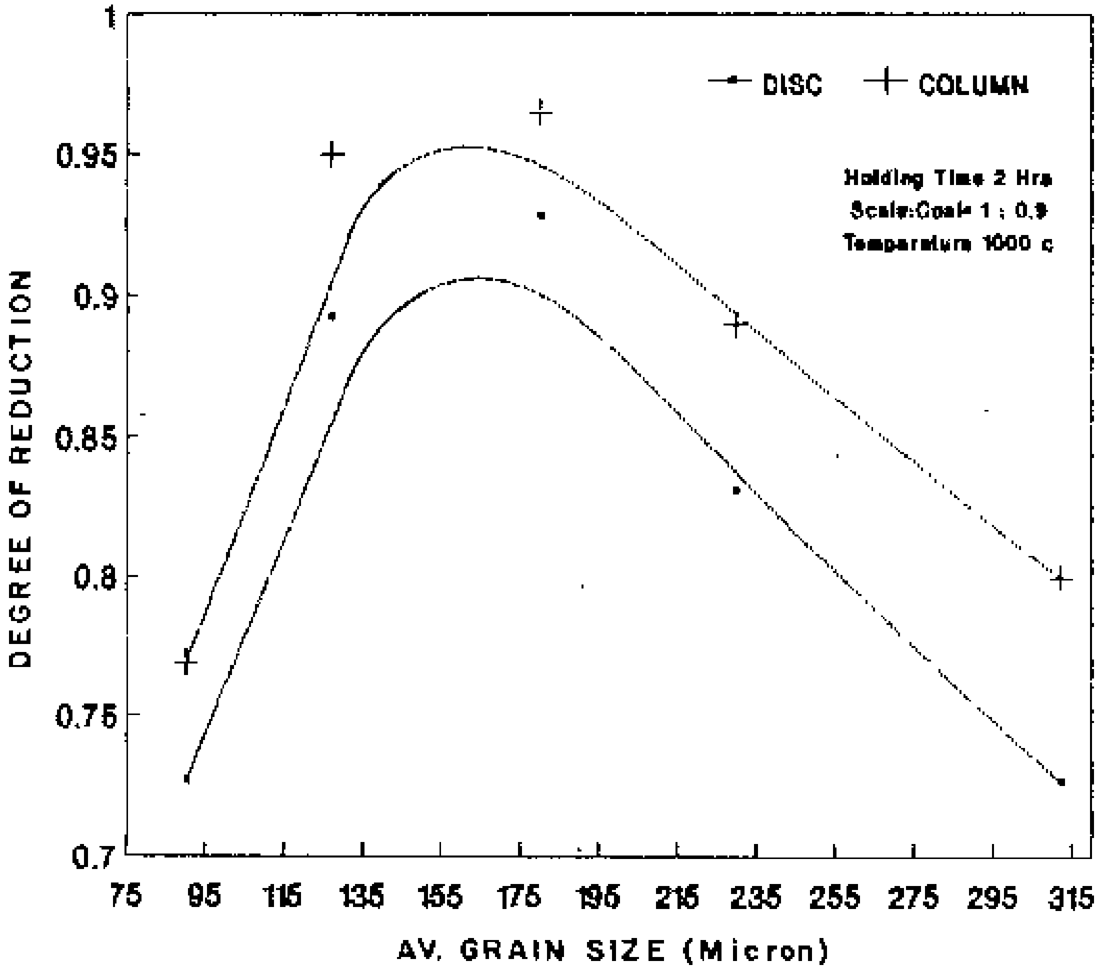


FIG. 4.1.(b) Effect of average particle size on the degree of reduction.

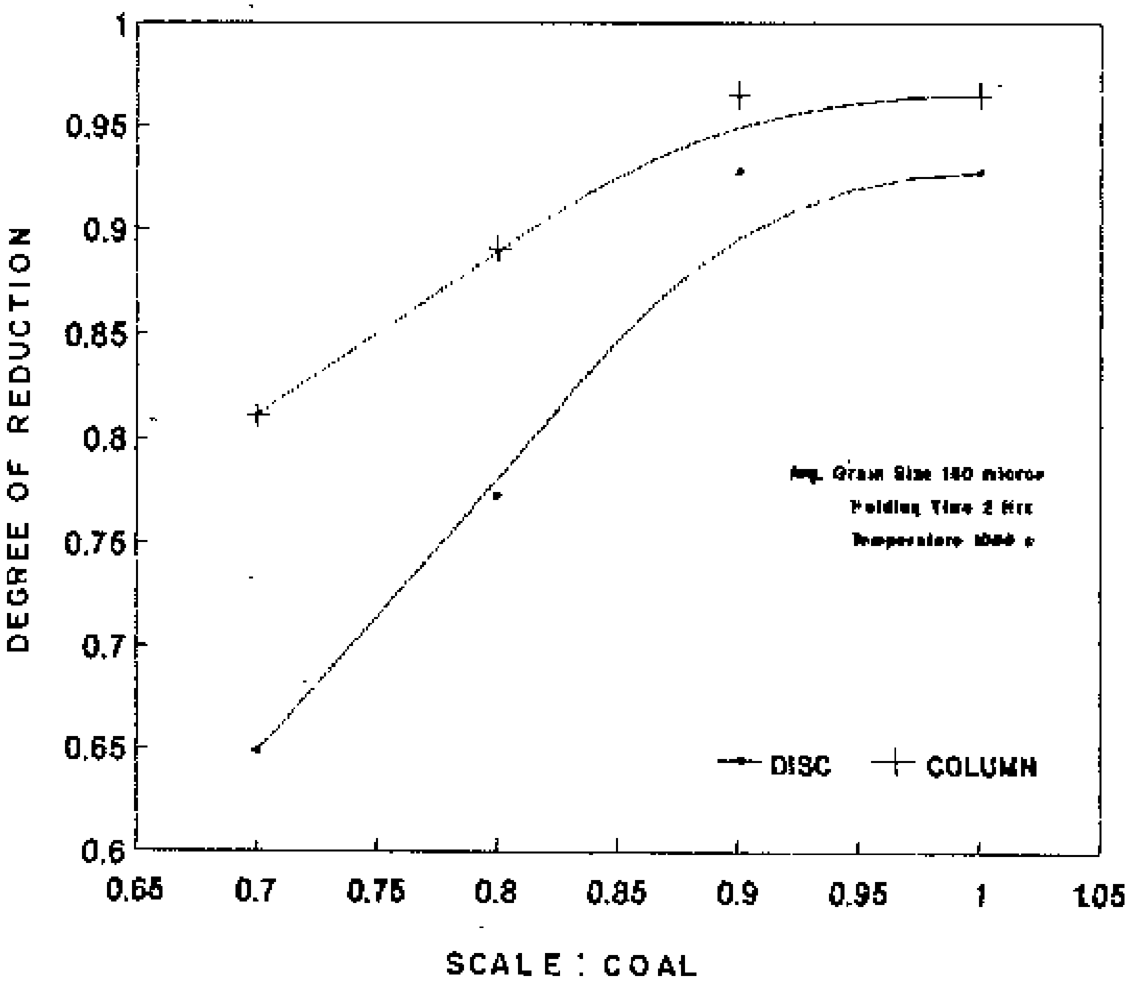


FIG. 4.2. Effect of mill scale : coal on the degree of reduction.

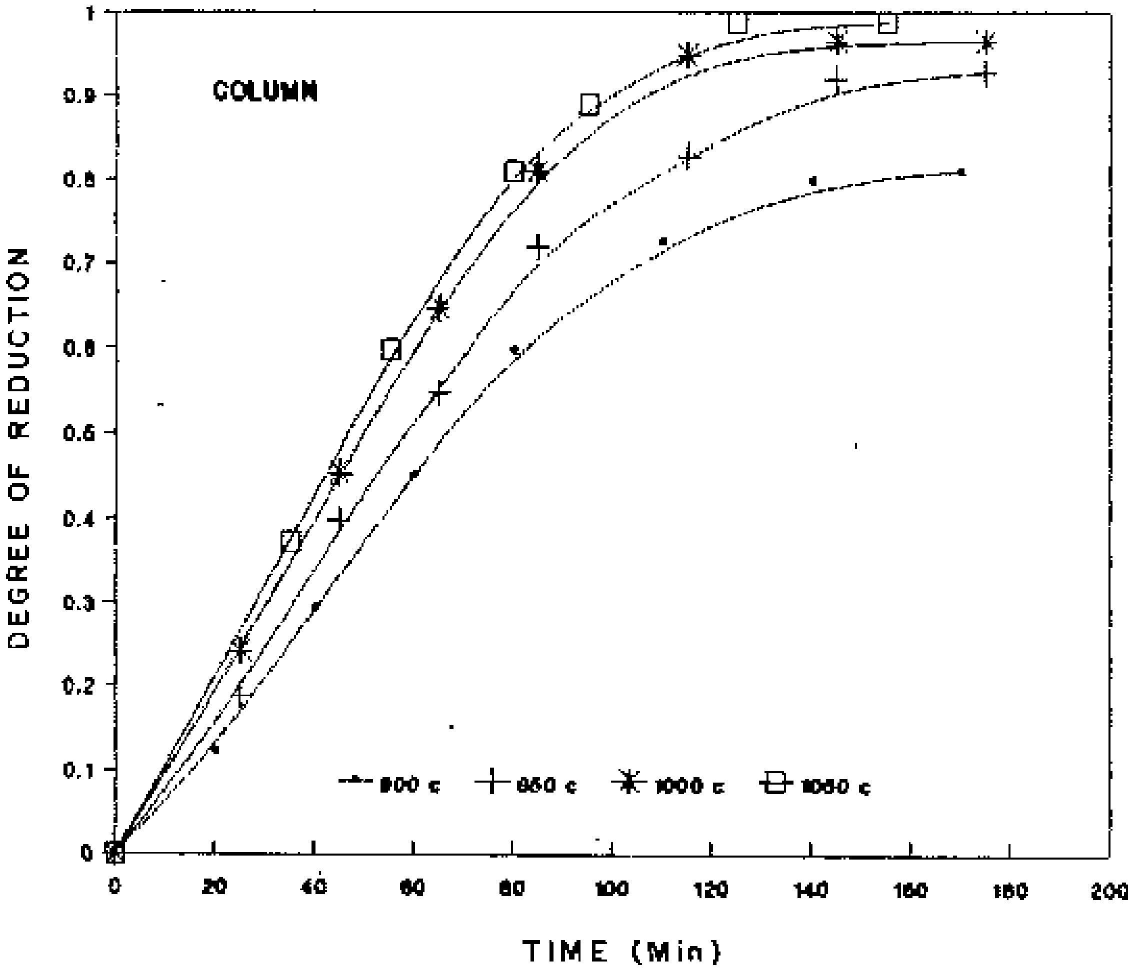


FIG. 4.3. Kinetics of isothermal reduction of mill scale by coal (column)

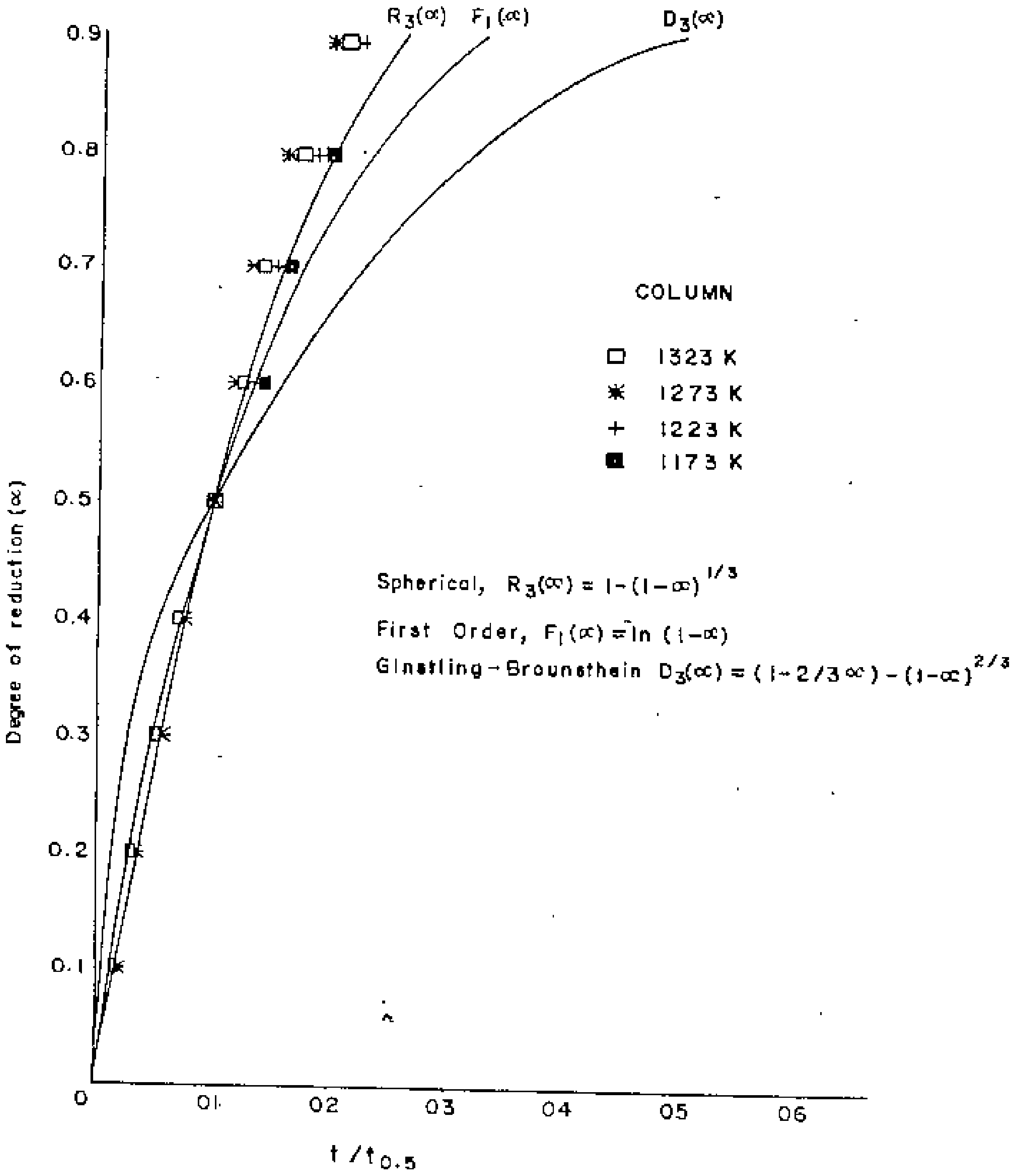


Fig 4.4 Reduced time plot for isothermal kinetic data shown in fig 4.3

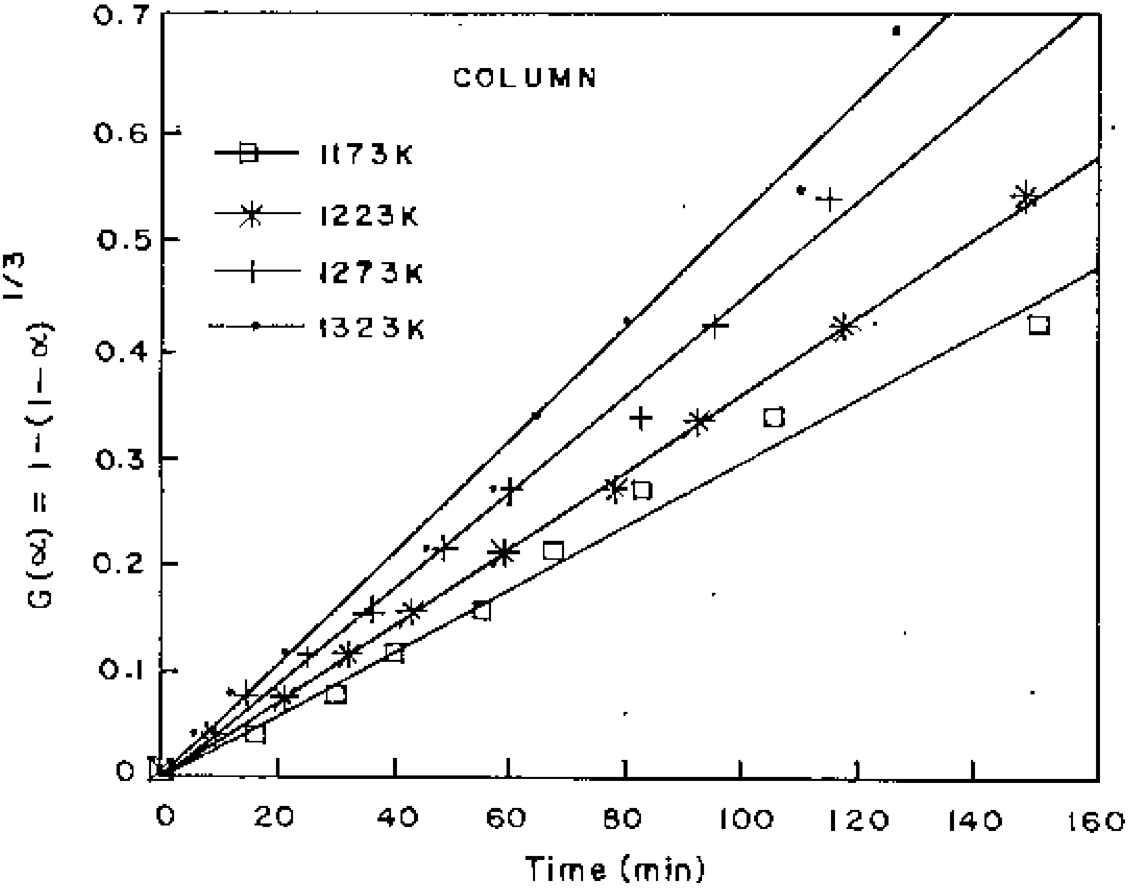


FIG. 4.5. Plots for isothermal kinetic data according to spherical reaction.

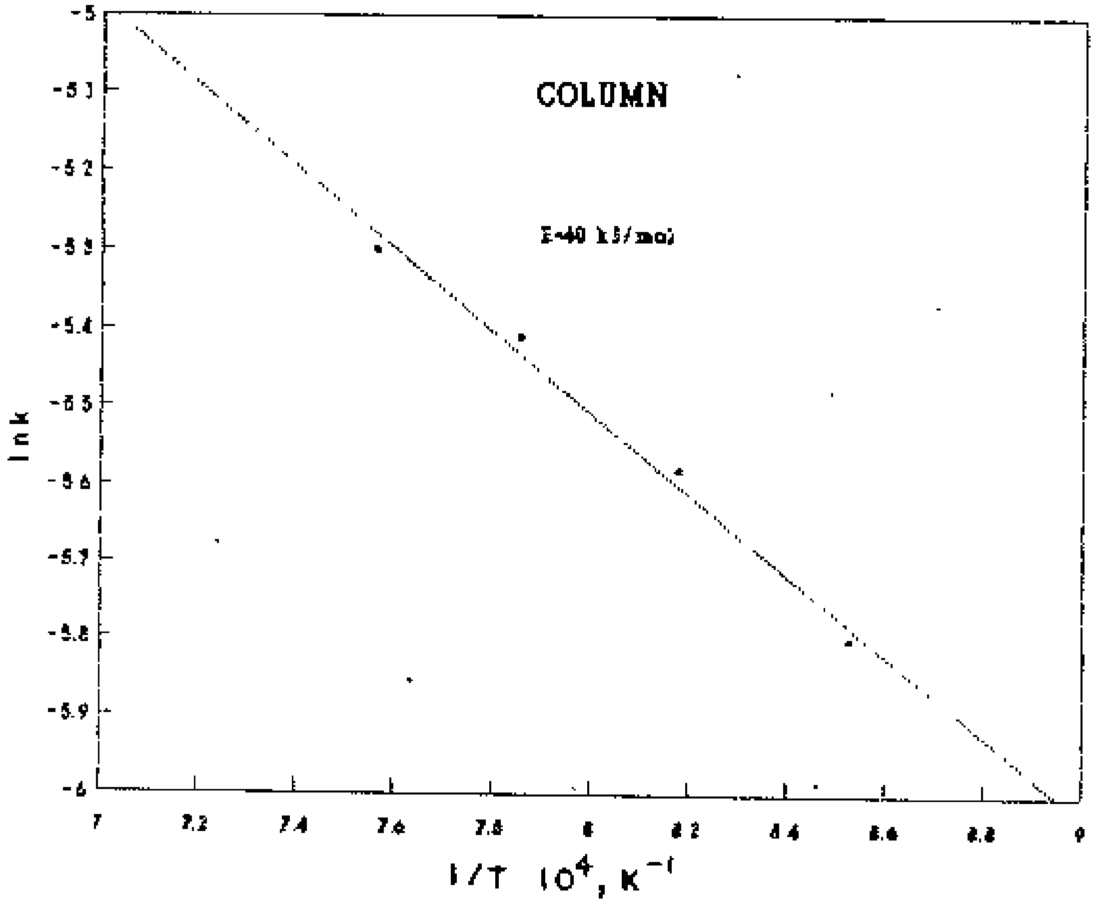


FIG. 4.6. Arrhenius type plots for kinetic data of fig. 4-5.

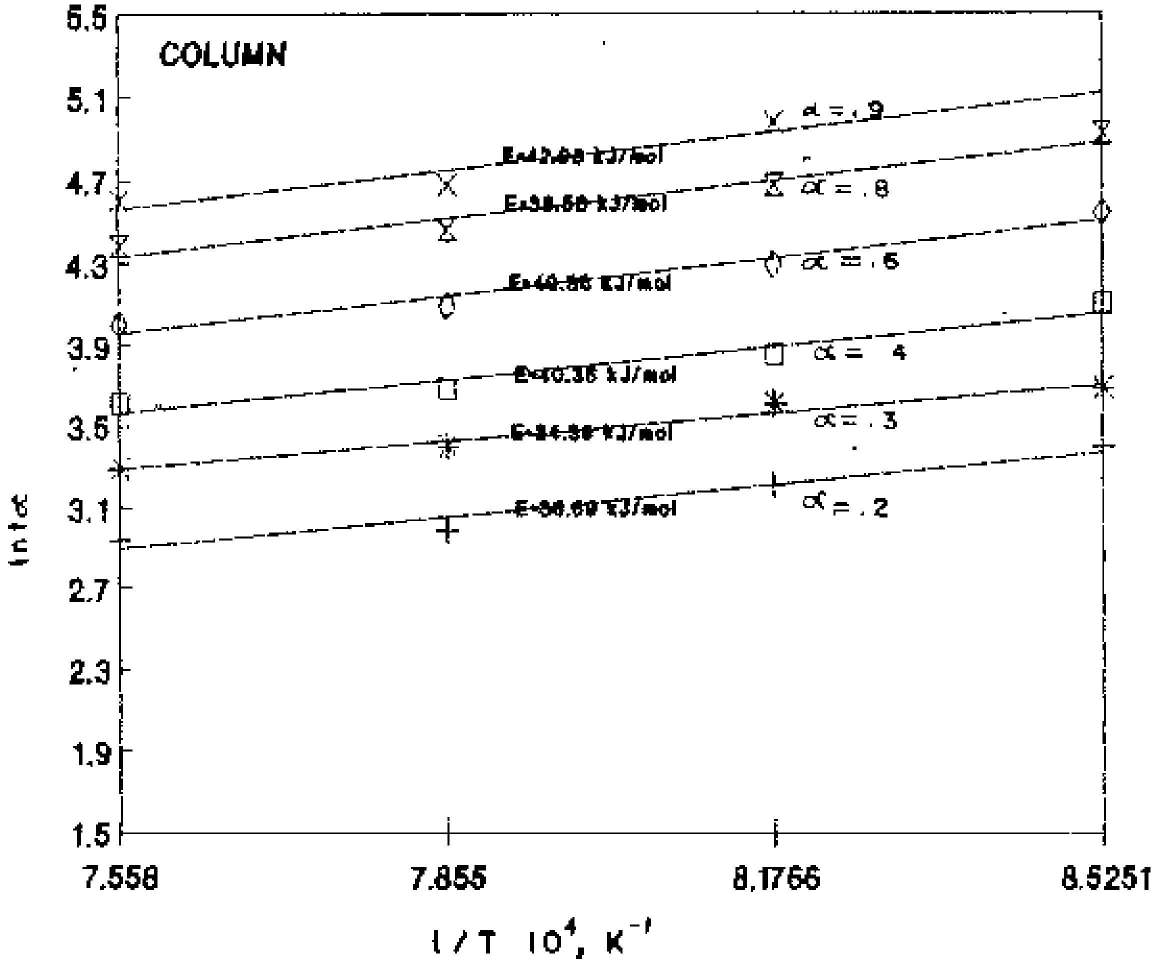


FIG. 4.7. Plots for calculation of apparent activation energy using the differential approach.

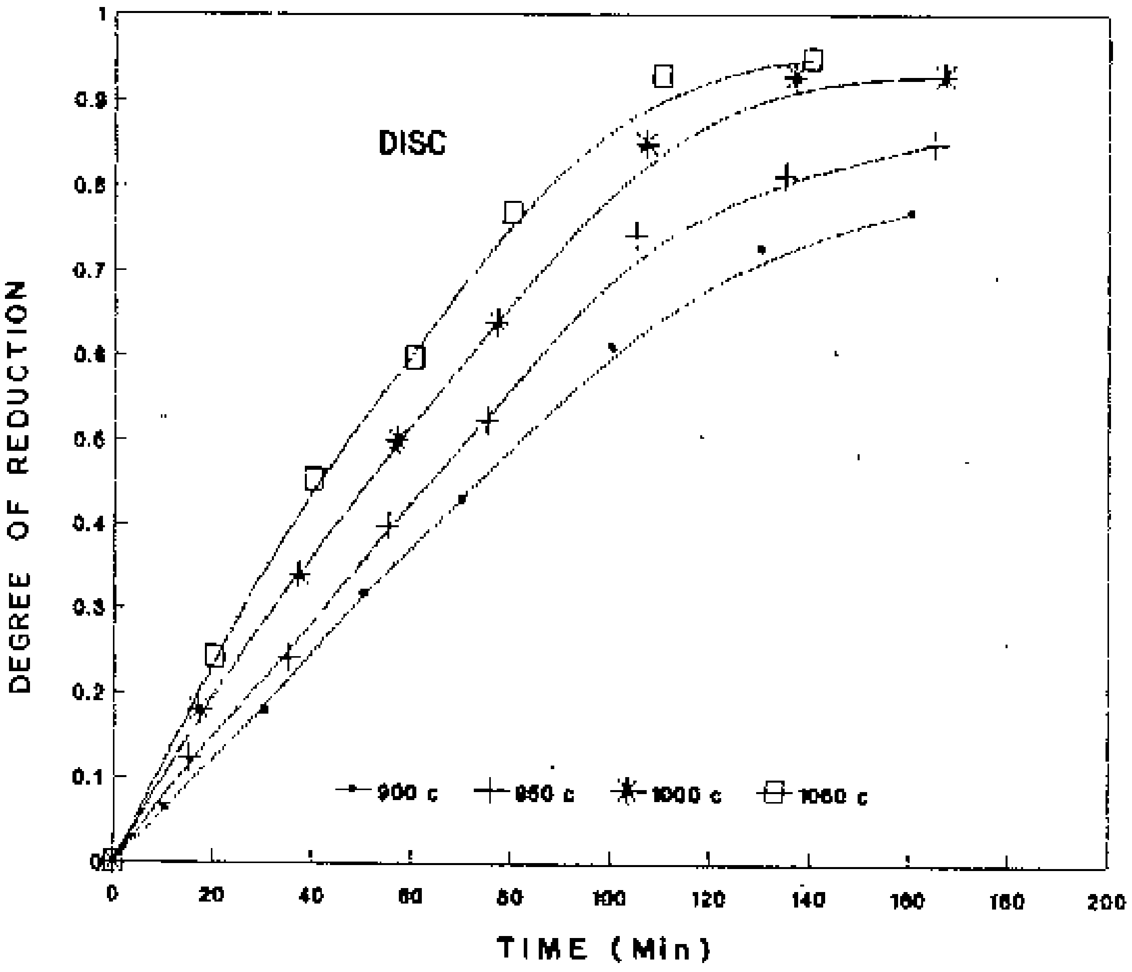


FIG. 4.8. Kinetics of isothermal reduction of mill scale by coal (Disc).

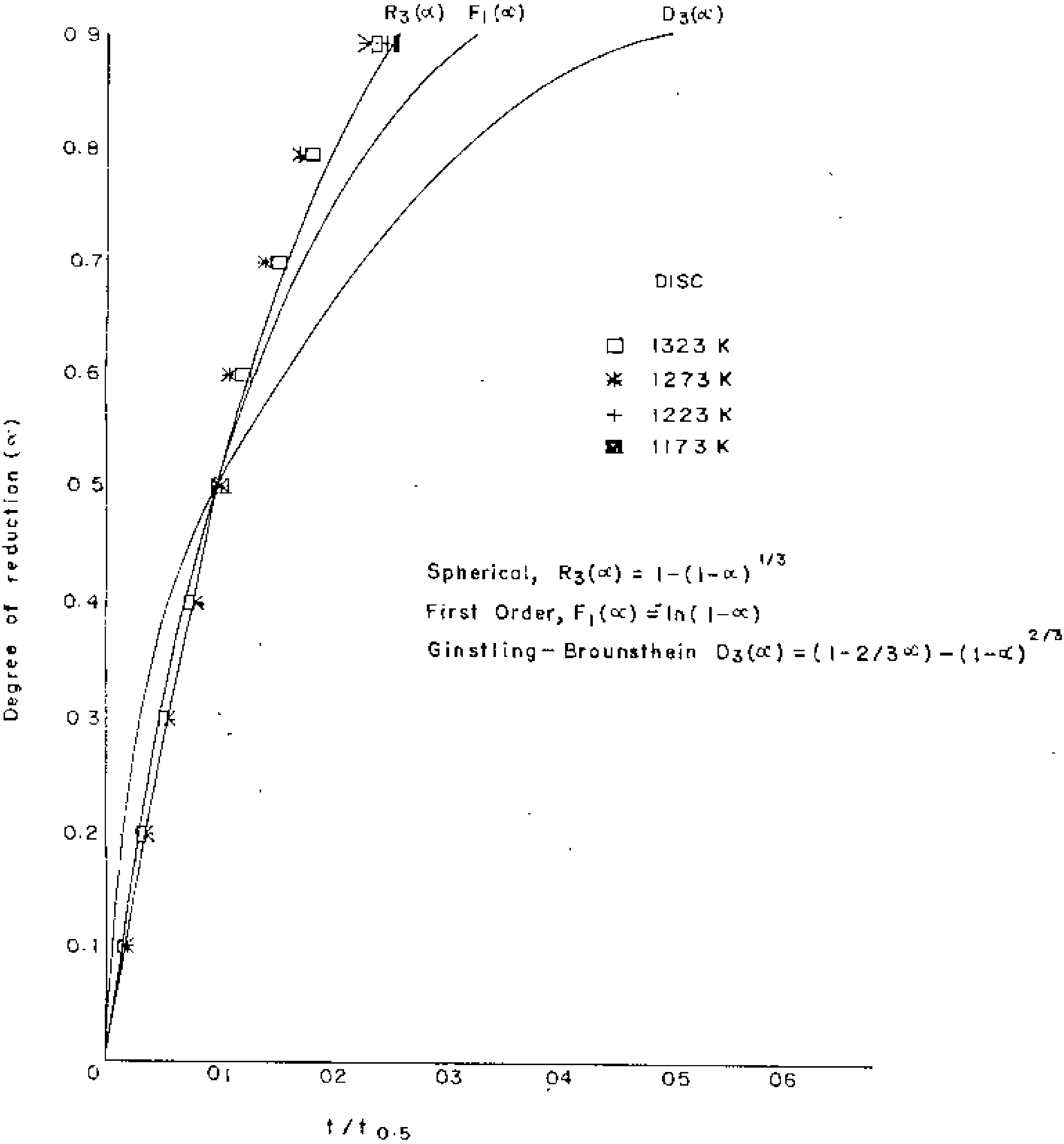


Fig 4.9 Reduced time plot for isothermal kinetic data shown in fig 4.8

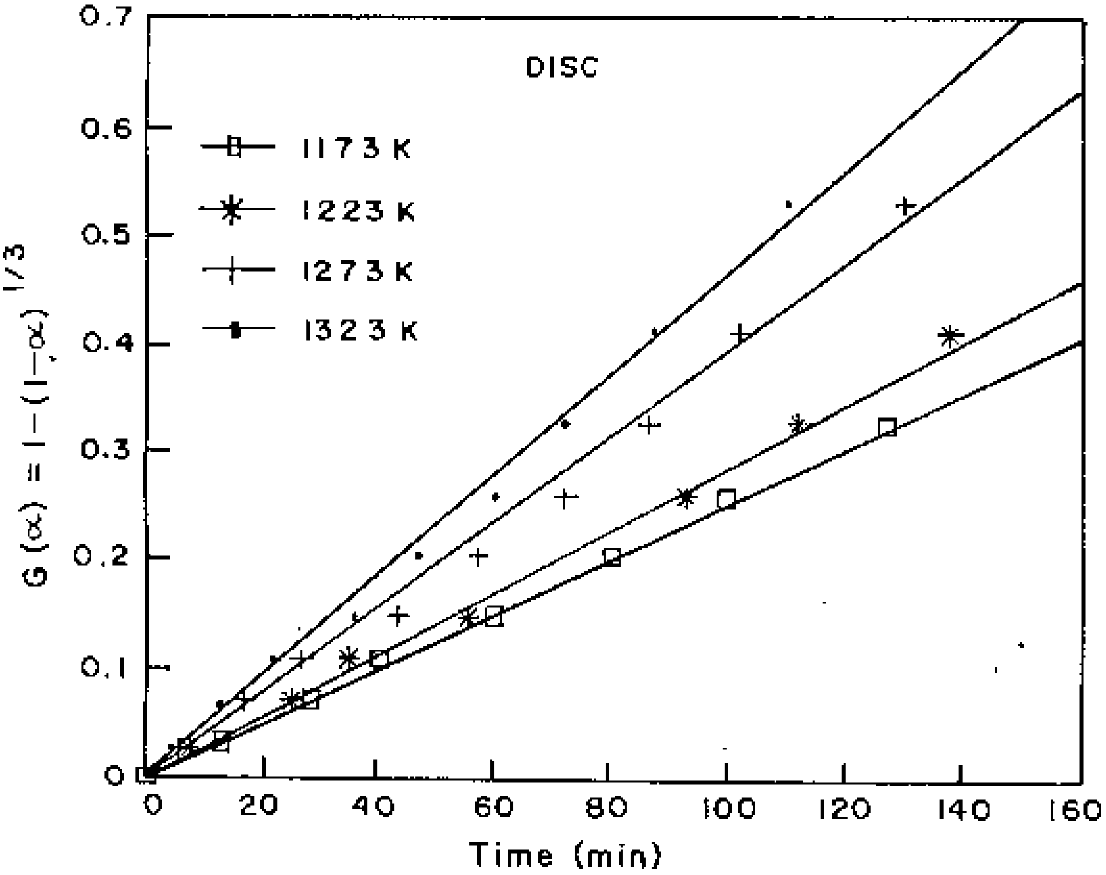


FIG. 4.10. Plots for isothermal kinetic data according to spherical reaction.

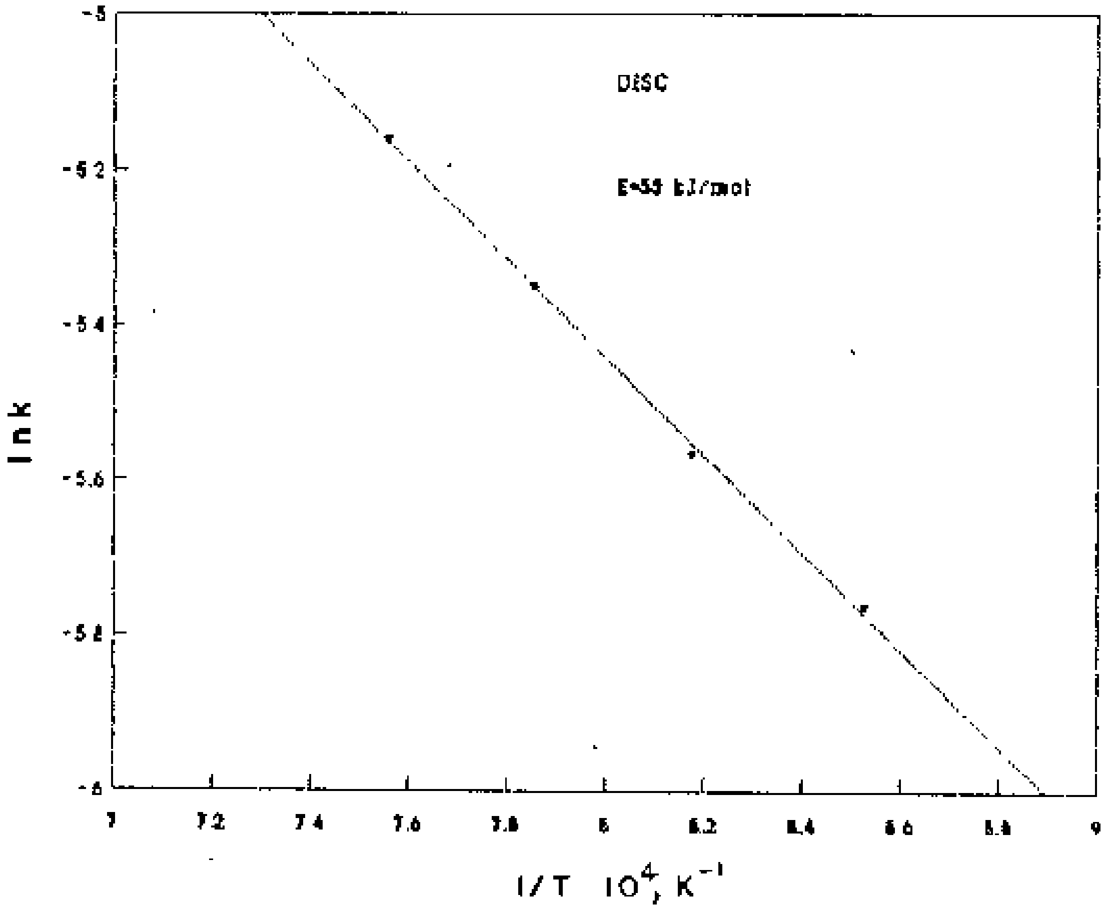


FIG. 4.11. Arrhenius type plots for kinetic data of fig. 4.10.

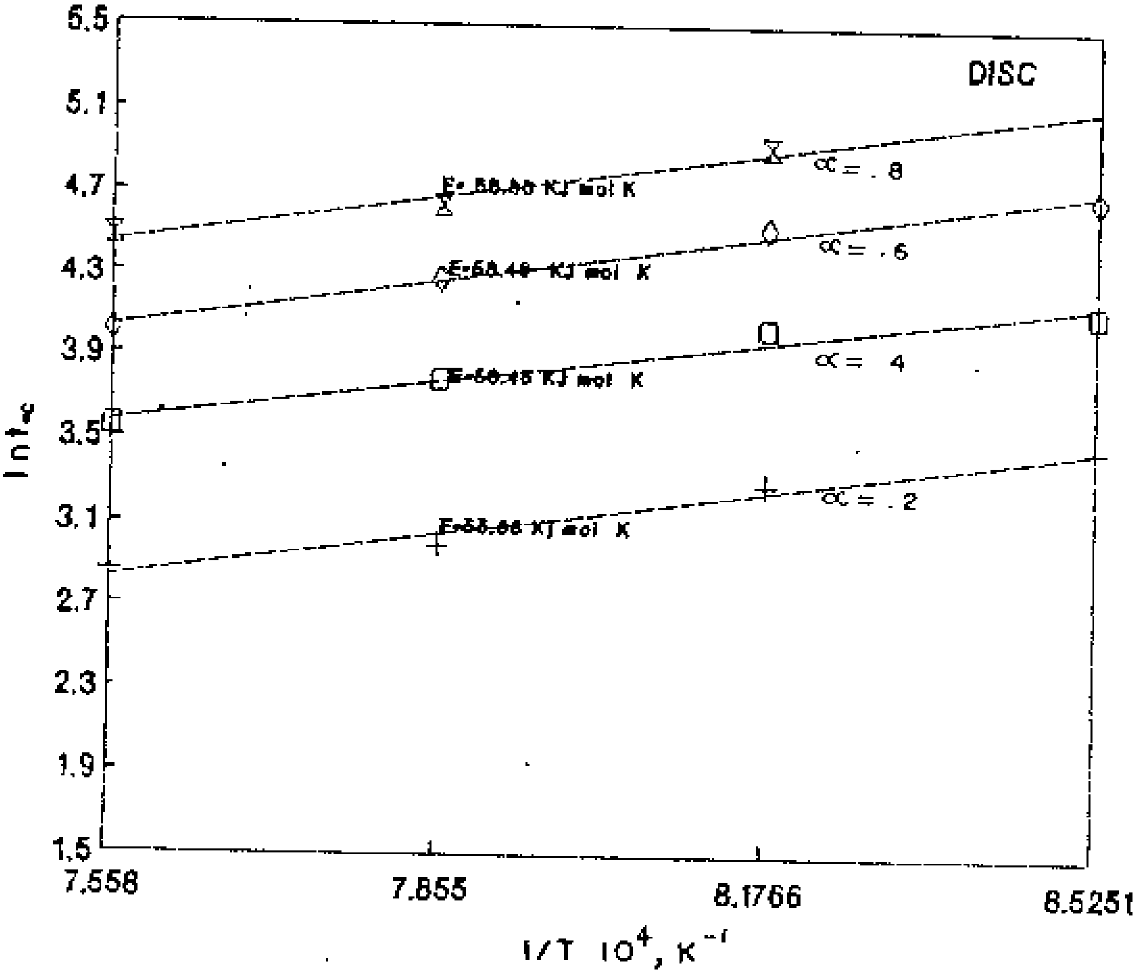
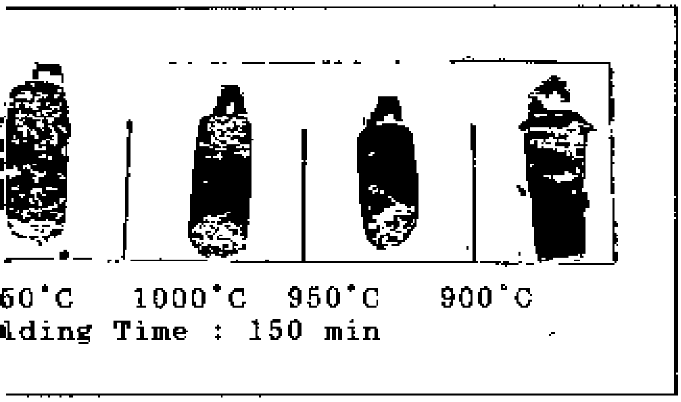


FIG. 4.12. Plots for calculation of apparent activation energy using the differential approach.



to 1 : Effect of temperature on degree of reduction (column).

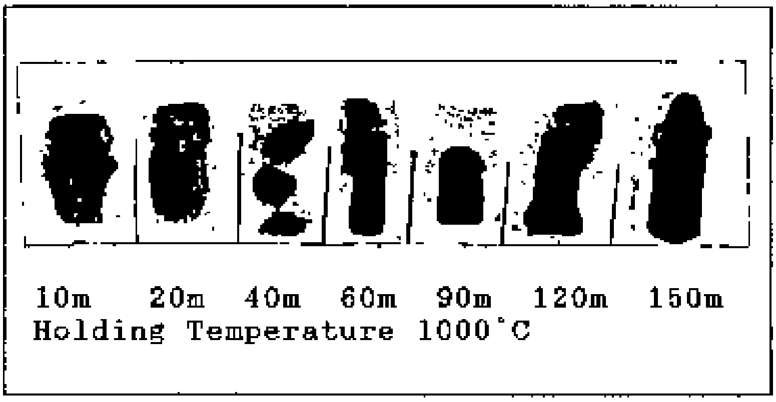


Photo 2 : Effect of time on degree of reduction (column).

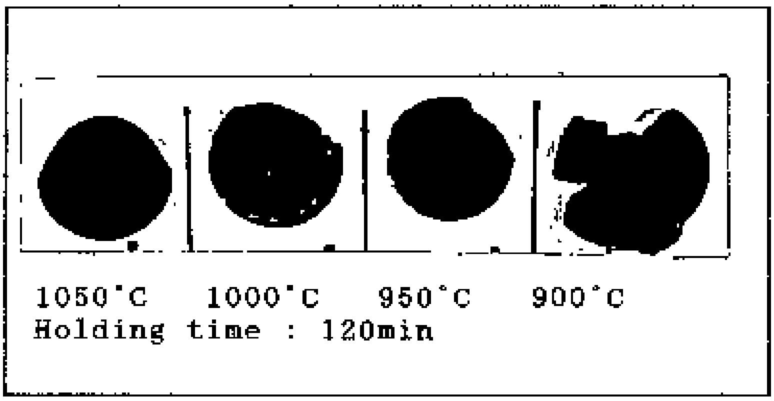


Photo 3 : Effect of temperature on degree of reduction (disc).

4.13 Photography of reduced masses.