# KINETICS OF PRE-REDUCTION OF IRON ORE BRIQUETTES USING LOW GRADE FUELS

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

*By*

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# CERTIFICATE

CERTIFIED that the dissertation entitled 'Kinetics of pre-reduction of iron ore briquettes using low grade fuels', which is being submitted by Mr. Kamlesh Chandra in partial fulfilment for the award of Degree 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 degree or diploma.

This is further to certify that he has worked for a period of ten months from January, 1971 to November, 1971 for preparing this dissertation at this University.

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# PREFACE

Now-a-days iron is the measure of Economy and Show-viz. of sound footing of any country. Thus the successive developments in the technology of iron production has occurred as to cope-up with the quest of increasing world demand for iron and steel. Because of the limitations of the high grade reserves of iron and good quality of coking coals needed for the iron production in blast furnace, the present day research in blast furnace technology aims mainly at increasing productivity and decreasing the coke rate. The use of pre-reduced burden in blast furnaces is one such significant development reported in recent years. Many countries e.g. Japan, Canada, U.S.A., etc. have reported highly encouraging results on the use of pre-reduced burdens in the blast furnace on pilot plants as well as commercial scales. But, very little work has been done, in India towards production and utilization of pre-reduced agglomerates.

Indian iron ore reserves are reported to be around 21,140 million tons. Due to the soft nature of Indian iron ores and mechanised mining, huge amounts of iron ore fines are produced. The suitable grade coking coal reserves are limited to about 1600 million tons out of a total of 103,000 million tons of coal. Hence, in order to improve the economics of iron ore mining and smelting operations, the utilization of iron ore fines and low grade fuels are highly desirable.

In addition to the above facts, the existing blast furnaces are not able to cope-up with country's requirements for iron and steel. These are two ways to increase the production of iron, first by errecting new blast furnaces and second, to increase the productivity of the existing blast furnaces. Errection of new blast furnaces requires huge amount of capital which is a handicap considering the economic situation of our country. Therefore, use of pre-reduced burden is highly desirable to improve the existing capacity of Indian blast furnaces. This requires to develop a suitable process which can produce pre-reduced agglomerates, economically, and development of any process requires the study of the thermodynamic and kinetic factors affecting the process.

Hence, this investigation has been undertaken to thoroughly investigate the effect of process variables e.g. temperature of reduction, time of reduction, type of reductant, etc. on rate of reduction of iron oxide by taking Indian iron ore fines and low grade coke and wood charcoal as reductants.

This dissertation has been divided into four chapters. Chapter I deals with a short review of the literature pertaining to the various factors affecting the rate of pre-reduction and describes the kinetic studies by various workers in the field of solid state reduction of iron ore by carbon. The advantages of carrying out pre-reduction under Indian conditions and that of under reduced pressure have also been pointed out.

Chapter-II deals with the detailed description of the materials with the method of their analysis, the experimental set-up and the procedure for conducting the experiments for kinetics studies of pre-reduction of iron ore briquettes.

In Chapter-III, the results of the kinetic studies on the pre-reduction of iron oxide in the briquettes consisting of iron ore fines and stoichiometric, 3% and 5% excess than stoichiometric amounts of low grade coke and wood charcoal under reduced pressure (0.1 mm of Hg) have been discussed. It has been found that upto about 30% reduction, the reduction reaction is surface controlled and highly sensitive of temperature. After 30% and upto 85% reduction, the reduction reaction proceeds in accordance with the semilogarithmic relationship $r = C \log t + X$, where r is the percent reduction, t is the time of reduction, C and X are constants. This relationship is found to be valid for both types of reductants (low grade coke and wood charcoal) at all the percentages (stoichiometric, 3% and 5% excess than stoichiometric). The activation energy values for briquettes reduced with stoichiometric, 3% and 5%

excess then stoichiometric amounts of low grade coke and wood charcoals are 50.2 ± 2.7, 51.4 ± 1.1, 50.2 ± 1.2 , 52.5 ± 1.1, 50.2 ± 0.8 and 52.5 ± 1.4 Kcals/gm. mole respectively. From the reported values of activation energy, the diffusion of iron through $Fe_3O_4$ is suggested to be the rate controlling step. Beyond 85% reduction, the relationship $r = C \log t + X$ has been found to be valid, but within the scope of experimental data, exact mechanism could not be elucidated.

Chapter-IV summarises the applications of the pre-reduced briquettes in iron and steel-making processes. It has also been pointed out that the pre-reduced briquettes should possess sufficient physical strength and should not swell when exposed to high temperatures. This chapter has been concluded with the remark that these pre-reduced briquettes are an excellent feed to improve the productivity of Indian blast furnace.

Further work on the studies of the kinetics of reduction of iron oxide with wood charcoal and low grade coke beyond 85% reduction and preparation of pre-reduced briquettes on pilot plant scale have also been suggested.

# ACKNOWLEDGEMENTS

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# CONTENTS

III- RESULTS AND DISCUSSIONS

IV- APPLICATIONS OF PRE-REDUCED BRIQUETTES

# CHAPTER -I

# INTRODUCTION

1.1 Since the blast furnace is the only versatile unit for production of pig iron, every effort has been made in recent years to increase its productivity and to decrease the coke rate. Factors contributing[1,2] to these improvements were, the use of high top pressure, humidification of blast, fuel injection through tuyeres, oxygen enrichment etc. The technology of these improvements have been very well established and the reported results on the increase in production and decrease in coke rate have exceeded beyond predictions. As a result, the production capacity[3] of the blast furnace has increased to a mark of 6000 tons/day while productivity of the blast furnace has crossed the mark of 2.33 tons/$m^3$/day. Japan has almost tripled her productivity from 0.81 tons/$m^3$/day in 1955 to 2.33 tons/$m^3$/day in 1967. U.S.A. has decreased the requirement of iron ore, coke and flux from 3 tons per ton of pig iron in 1957 to 2.5 ton per ton of pig iron produced in 1966.

However, the quest for increasing productivity and decreasing coke rate may be coped up by improving the blast furnace burden in the following two ways:

(i) Improving the burden size i.e. the size of iron ore, coke, flux etc. The trend now a days is to charge blast furnace with ore in the size range of 50 to 8 mm, instead of 40 to 10 mm.

(ii) Establishing the quality and composition of raw materials charged through blast furnace. Use of self and super-fluxed sinter has resulted in remarkable decrease in coke rate. Besides, sintering and pelletising, briquetting has also been used for utilization of ore fines of a wide size range. The uniform size and shape of briquettes confer desirable properties, especially for melting. Moreover, briquettes have higher green and hot strength as compared to sinter and pellets. Still, another approach to improve the quality of burden is to partially reduce the iron bearing materials prior to charging them in blast furnace. The partial reduction of iron bearing material is called pre-reduction which is recent innovation in the blast furnace technology.

Attempts have been made to achieve considerable reduction during agglomeration of iron ore bearing fines by the use of low grade fuels either externally or internally mixed to iron ore. Theoretical calculations by IRSID[3] show that for every 30% metallization, productivity would increase by 7% but above this the reward of pre-reduction decreases due to insufficient heat utilization. The Steel Company of Canada[4] has achieved a 23% increase in productivity and 20% decrease in coke rate by charging pre-reduced pellets (88.7% Fe and 90.6% metallization) which comprises of

30% of the total charge. Republic Steel, USA[5] has obtained 4% increase in production and 11.3% decrease in coke rate by charging metallized briquettes (71% Fe and 84% metallization) comprising of 14% of the total charge. Hegachida Plant, Yawata[4] (Japan) reported 18.4% increase in production and 18% decrease in coke rate by charging sponge iron (69% Fe, 58% metallization) comprising of 40% of the total charge. The highly reduced (over 92%) and metallized (over 90%) iron ore briquettes may also be used as a substitute for steel scrap in steel making.

In view of the limited reserves of high grade coking coal and limited capacities of our blast furnaces, use of pre-reduced burden is highly desirable.

## I-2 FACTORS AFFECTING PRE-REDUCTION OF IRON ORE BRIQUETTES

Rate of pre-reduction of iron oxide with solid fuels is affected by many factors such as type of reductants used, the temperature, particle size etc. The effect of each factor on rate of pre-reduction can be summarised as follows.

### 1.2.1 EFFECT OF THE TYPE OF REDUCTANT USED

The wood charcoal, lignite coke and low grade coke have decreasing effectiveness in the given order in bringing about the reduction of iron oxide[6]. This is because of the difference in reactivity of carbon of wood charcoal, lignite and low grade coke.

### 1.2.2 EFFECT OF TEMPERATURE

The rate of iron ore reduction are found to be very much dependent on the reduction temperature. Yun[7] studied on 'direct reduction of ferric oxide by solid carbon in vacuum' and the results indicated a marked increase in degree of reduction at the temperatures above than 900°C, as shown in Fig.1.1(A). While the extent of reduction occurred at 700 and 800°C was found to be extremely small, reaching only 10 to 20% even after 5 hours. As shown in Fig.1.1(B) and Fig.1.1(c). The maximum percentage reduction obtained was even less than 50% if the reduction temperature is below 987°C, while the percentage reduction increases remarkably if the reduction temperatures employed were above 987°C when the investigation on kinetics of iron ore reduction by carbon was carried out under nitrogen atmosphere[8]. As shown in Fig.1.1(D), the higher fractional weight losses were observed at 1100°C than those at 900°C for the iron ore pellets reduced even with different lignite coke percentages[9].

### 1.2.3 EFFECT OF PARTICLE SIZE DISTRIBUTION OF THE CONSTITUENTS

The kinetics of pre-reduction of iron oxide with solid carbon is largely affected by the particle size of the reactants. It has been reported that for a constant hematite particle size and a $Fe_2O_3/C$ ratio e.g. 1/3, the observed time for half complete reduction with coarse, medium and fine size of carbon particles at 1037°C is 34, 27 and 8 minutes[8]. The results are summarised in Fig.1.2.

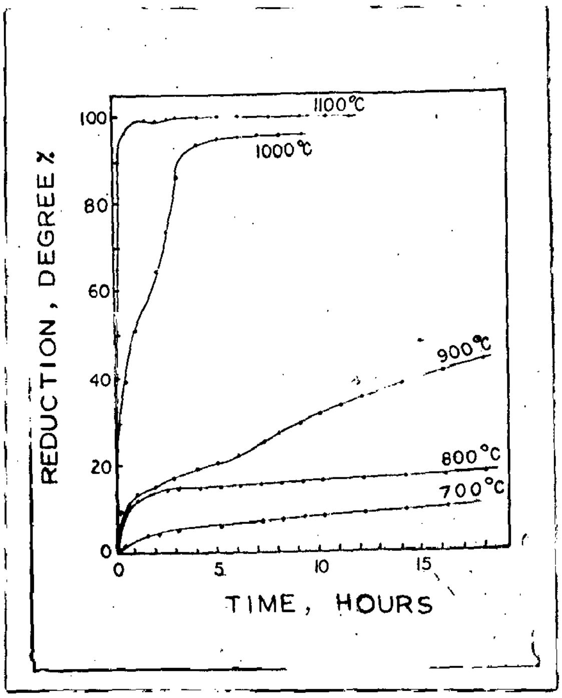


Fig.1.1(A). The effect of temperature on the direct reduction of hematite by carbon.

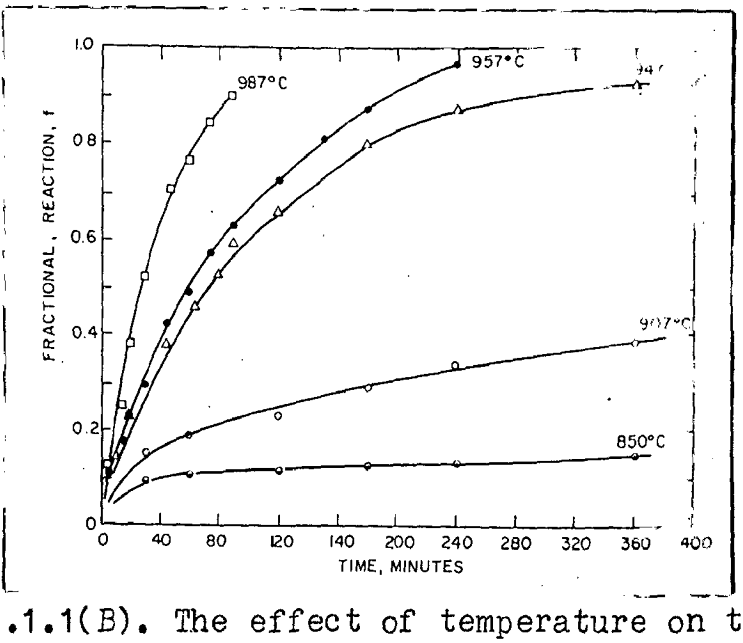


Fig.1.1(B). The effect of temperature on the reduction of hematite by carbon (temperatures of reduction are below 987°C)

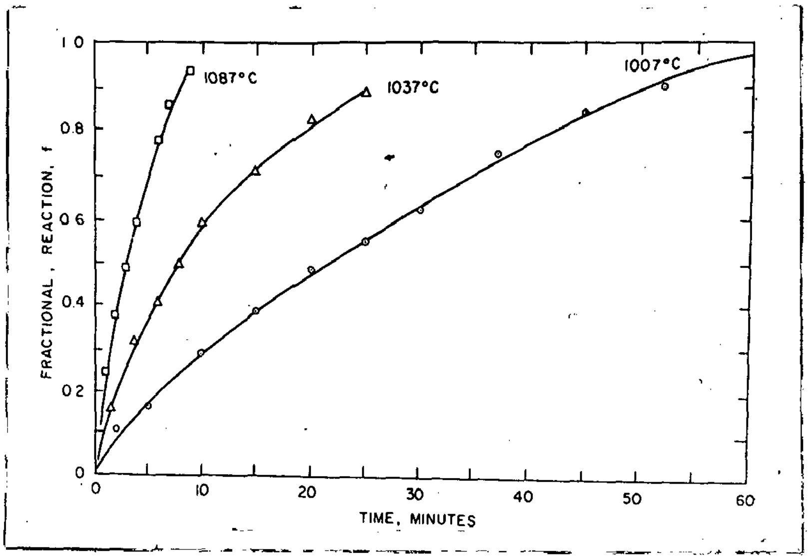


Fig.1.1(C). The effect of temperature on the reduction of hematite by carbon (tempetatures of reduction are

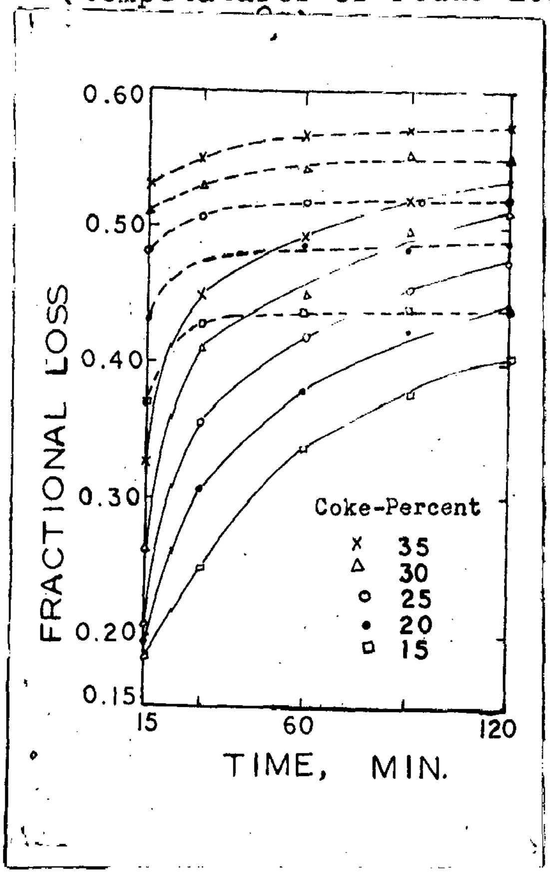


Fig.1.1(D). Weight loss of pellet with time at temperatures 900°C (cotinuous lines) and 1100°C (dotted lines).

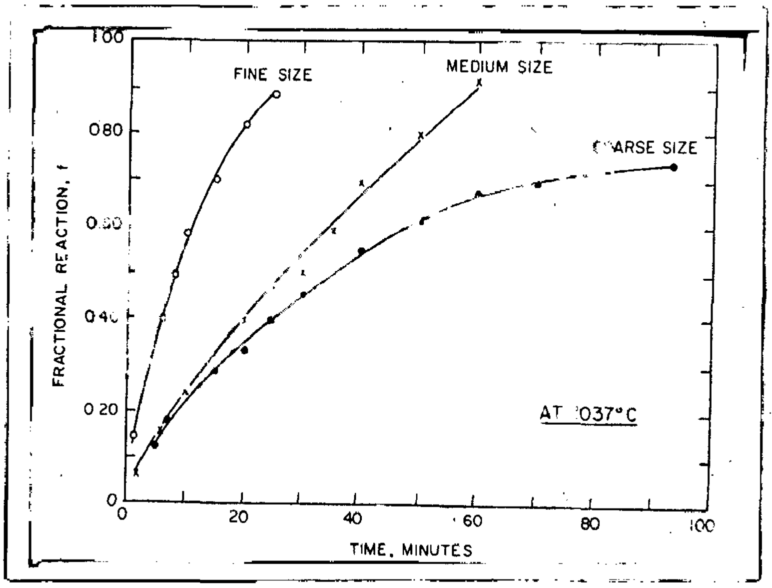


Fig.1.2. The effect of particle size of carbon on the reduction of hematite.

### 1.2.4 EFFECT OF HEMATITE/CARBON RATIO

The reduction rates of iron oxide are also affected by the amount of carbon used for carrying out the reduction. This amount of carbon is calculated on the basis of complete reduction and termed as stoichiometric requirement. By using carbon more than stoichiometric requirement the reduction rate increases. Studies carried out by Ghosh and Tiwari[9] with different percentages of lignite coke as reductant in the range from 15 to 35% as shown in Fig.1.3 (A) suggest that the higher amount of carbon increases the reduction rate. Similar results have also been reported by Rao[8] where the $Fe_2O_3/C$ ratio was varied between 1/1.5 and 1/9 as shown in Fig.1.3(B).

### 1.2.5 EFFECT OF NITROGEN GAS ATMOSPHERE AND VACUUM

Baldwin[10] carried his experiments on reduction of iron oxide with solid coke under nitrogen gas atmosphere at different nitrogen gas flows. A pronounced effect of the variation of the gas flow through the reduction bed is observed. With increasing gas flow the rate of removal of oxygen decreases until a point is reached where further increase has no effect on the rate as shown in Fig.1.4.

According to Le-Chatellier's principle, the use of

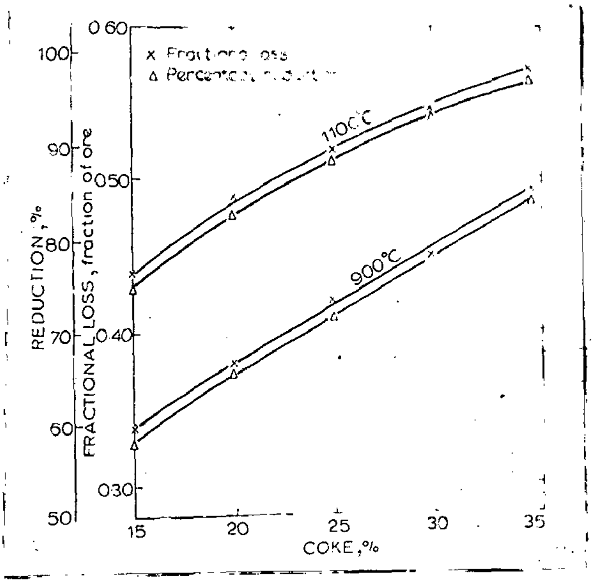


Fig.1.3(A). Weight loss of pellets in 1 hr.using different coke ratios.

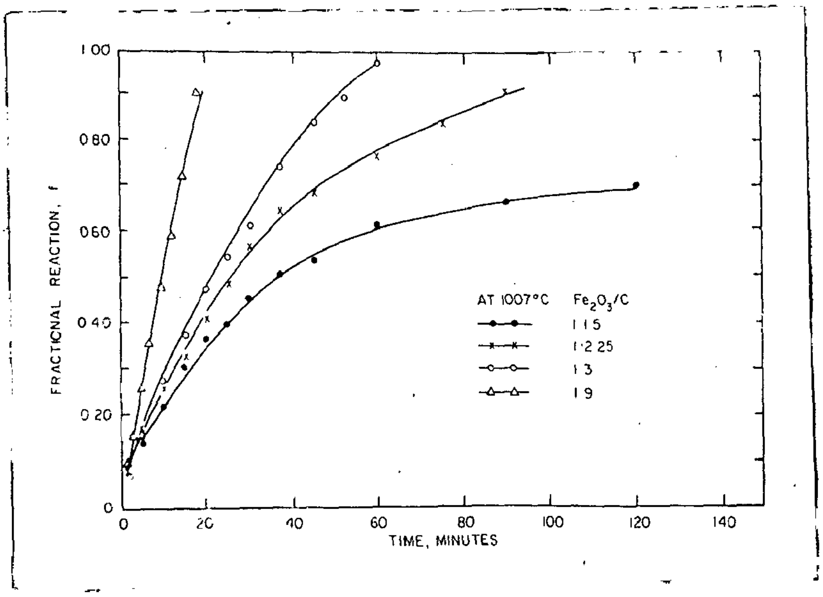


Fig.1.3(B). The effect of the '$Fe_2O_3/C$' ratio of the mixture on the reduction of hematite.

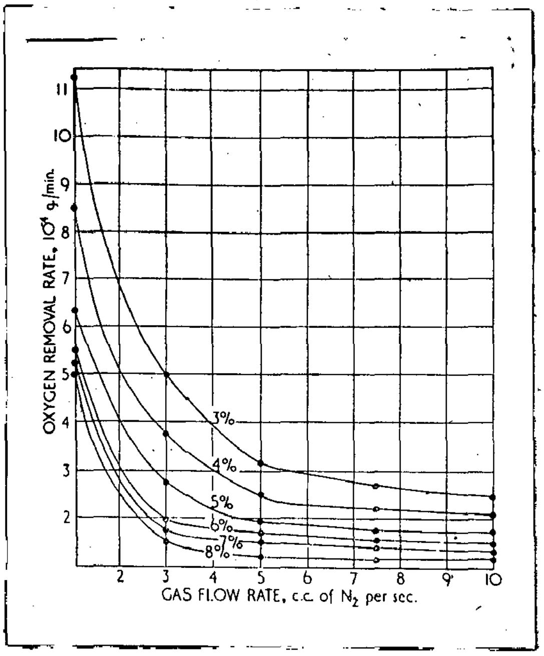


Fig.1.4. Effect of variation in the flow of nitrogen on the reduction occuring in a bed of 8-10 mesh ore and coke at 1000°C for various percentages of oxygen removal.

vacuum favours the forward reaction,

$$MO + C \longrightarrow M + CO$$

where MO is any metal oxide. Thus a higher percentage of reduction and metallization may be observed when reduction is carried under high vacuum.

### 1.2.6 EFFECT OF THE ADDITIONS OF PROMOTIVE AND INHIBITIVE AGENTS

As shown in Fig.1.5, the rate of reduction of hematite plus carbon mixtures is dramatically increased when 5% by weight of $Li_2O$ (known as promotor for solution loss reaction) is added to the mixtures and a noticeable decrease in the rate of reduction occurred in mixtures containing 5% by weight of FeS (known as inhibitor for solution loss reaction)[6].

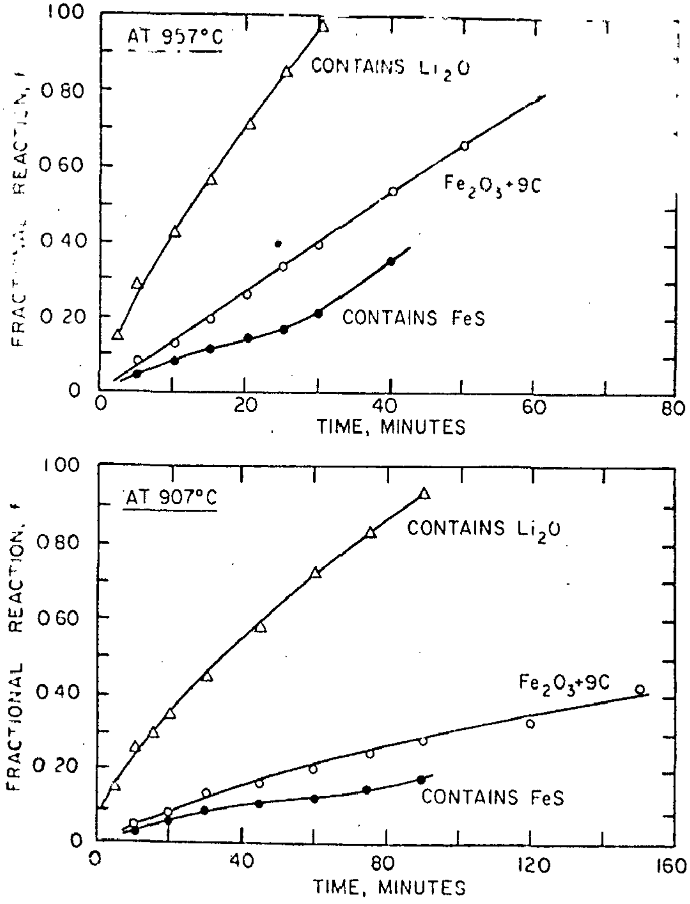


Fig.1.5. The effect of promotive ($Li_2O$) and inhibitive (FeS) agents on the reduction of hematite with carbon.

## 1.3 KINETICS OF PRE-REDUCTION

The gaseous reduction of iron oxide has been studied extensively[11,12,13] and ample experimental data are available for equilibrium conditions as well as for the reaction velocity, but comparatively little work[7,8] has been reported in the field of solid state reduction. This is due to the difficulties encountered in measuring solid-solid interaction compared with gas-solid interaction. Moreover, the effect of gaseous phase during solid state reduction can not be avoided. The reaction between iron oxide and carbon may be represented by the equation,

$$Fe_2O_3 + XC \longrightarrow 2Fe + Y\,CO + Z\,CO_2 \qquad \ldots (i)$$

Thus carbon-monoxide and dioxide are formed, setting free the metal, The gaseous products thus formed may react with the metal oxide or carbon itself, ie. carbon dioxide may react with carbon to form more carbon monoxide or carbon monoxide may react with the iron oxide to give rise to more carbon dioxide. The step controlling the rate of iron oxide reduction with carbon will mainly depend on the experimental conditions i.e. whether the gaseous products of equation (i) are being continuously removed from the reaction site and only the solid/solid interaction is taking place , or otherwise the gas/solid interaction is also taking place together with solid/solid interaction. Thus the two hypotheses[10] have been proposed to explain the reduction of iron oxide when it is intimately mixed with solid reductants, like coke, charcoal etc. These can be represented as follows;

$$Fe_xO_y(S) + C(s) \longrightarrow Fe_xO_{y-1}(s) + CO(g) \quad \ldots (1)$$

(direct reduction)

$$\left.\begin{array}{ll} Fe_xO_y(s) + CO(g) \longrightarrow Fe_x\,O_{y-1}(s) + CO_2(g) & \ldots(A) \\ CO_2(g) + C(s) \longrightarrow 2CO(g) & \ldots(B) \end{array}\right\} \ldots (2)$$

where $x = 1, 2,$ or $3$

when $y = 1, 3,$ or $4$

Thermodynamic considerations cannot assist in deciding which reaction is taking place, as the total reaction is identical in both cases. The view most widely held is that the two-stage hypothesis(2) is the more probable[14]. However, Tamman and Zvoruikin[15], Baukloh et al[16] and Yun[7] supported the first hypothesis. They claimed to have overcome the great difficulties associated with thorough degassing of the reacting substances and the interaction of the products of reduction. The preliminary dissociation of the oxide to give oxygen, which then combined with the carbon, was proposed by Tamman and Zvoruikin[15]. Baukloh and Durrer[17] suggested that diffusion of solid carbon was the rate determining process.

### (A) KINETICS STUDIES ON DIRECT IRON ORE REDUCTION

In the direct reduction, carbon is assumed to react directly with iron oxide, producing carbon monoxide along with a certain amount of carbon dioxide. Stoichiometrically the process may be represented by equations

$$Fe_xO_y(S) + C(S) \longrightarrow Fe_xO_{y-1}(S) + CO(g)$$
$$2Fe_xO_y(S) + C(S) \longrightarrow 2Fe_xO_{y-1}(S) + CO_2(g)$$

where x and y are assigned the same values as before.

The direct reduction may be visualized as beginning at the points of contact between iron oxide and carbon particles, and as the oxygen is removed from the solid in the form of CO or $CO_2$, islets of reduced iron appear on the oxide surface and eventually join together to form a continuous shell around the still unreduced oxide. Further reduction is assumed possible by diffusion of carbon atoms, through the reduced iron shell to the iron/oxide interface. The interfacial chemical reaction involving oxide and carbon is presumed to occur relatively rapidly as compared to the diffusion process. Consistent with these views, Baukloh and Durrer[17] and Yun[7] have proposed that diffusion through the product layer, i.e. reduced iron shell, is the rate limiting step. Direct reduction of iron oxide by carbon is possible only when the gaseous products of reactions, i.e. CO and $CO_2$, are removed from the reaction system as fast as these are generated. Thus Baukloh et al[17], Arkharov et al[18] and Yun[7] have conducted direct reduction experiments in a vacuum of $2 \times 10^{-2}$ mm Hg, $1 \times 10^{-3}$ mm Hg and $5 \times 10^{-4}$ mm Hg respectively and claimed to have overcome the problem of removing the gaseous products.

It has been observed by Jander(cited by Yun[7]) that endothermic reactions in the solid state follow the general diffusion laws that are applicable to crystalline materials. Hence the temperature at which a reaction begins is closely related to the thermal vibration of the atoms or molecules in the crystal lattices. The theoretical equations for the dependence of intersolid reactions on time, particle size and temperature were developed by Jander[19], Gristling and Brounshtein[20] and Carter[21] by applying the diffusion laws.

$$\left[1-(1-f)^{1/3}\right]^2 = \frac{2D\,Co}{r^2}\,t = K\,t \quad \text{(Jander)} \qquad \ldots (3)$$

$$\left[1-\frac{2}{3}f-(1-f)^{2/3}\right] = K\,t \qquad \text{(Ginstling et al)} \quad \ldots (4)$$

$$\frac{Z-\left[1+(Z-1)f\right]^{2/3}-(Z-1)(1-f)^{2/3}}{2(Z-1)} = K\,t \quad \text{(Carter)} \ldots (5)$$

where D is the (carbon) diffusion coefficient, Co is the initial concentration of diffusing element, $r$ is the initial radius of the oxide particle and f is the fraction reacted at time t, and Z is the ratio between the volume of the final product and that of an equivalent amount of the initial reactant(=0.47 for 2Fe : $Fe_2O_3$).

These three equations were derived on the common understanding that

i) the reacting particles remain spherical during the course of the reaction,

ii) the reaction is diffusion-controlled and obeys Fick's law, and

iii) One of the reactants diffuses into the particles of the other.

In deriving equations (3) and (4) it is further assumed that the size of the particle remains unchanged during the reaction. In addition to these, Eq.(3) also assumes that the diffusion takes place through a plane surface. Although Eq.(5) derived on a more rigorous basis, may seem preferable, nevertheless it has been shown that Eqs.(3) and (4) are equally satisfactory in fitting the data[22], and a plot of $\left[1-(1-f)^{1/3}\right]^2$ Vs 't' must have a constant slope, if the reduction reaction is carbon diffusion controlled.

In Fig.(1.6), the direct reduction kinetics determined by different investigators are shown according to Eq.(3). The experimental results of Baukloh and Durrer[17] are found to be in good agreement with the predicted linear behaviour. Working especially with a a high vacuum of $5\times10^{-4}$ mm Hg, Yun[7] obtained direct reduction results which, as shown in Fig. 1·6 , deviate considerably from the linear relationship. Thus it has been stated that diffusion of iron atoms instead of

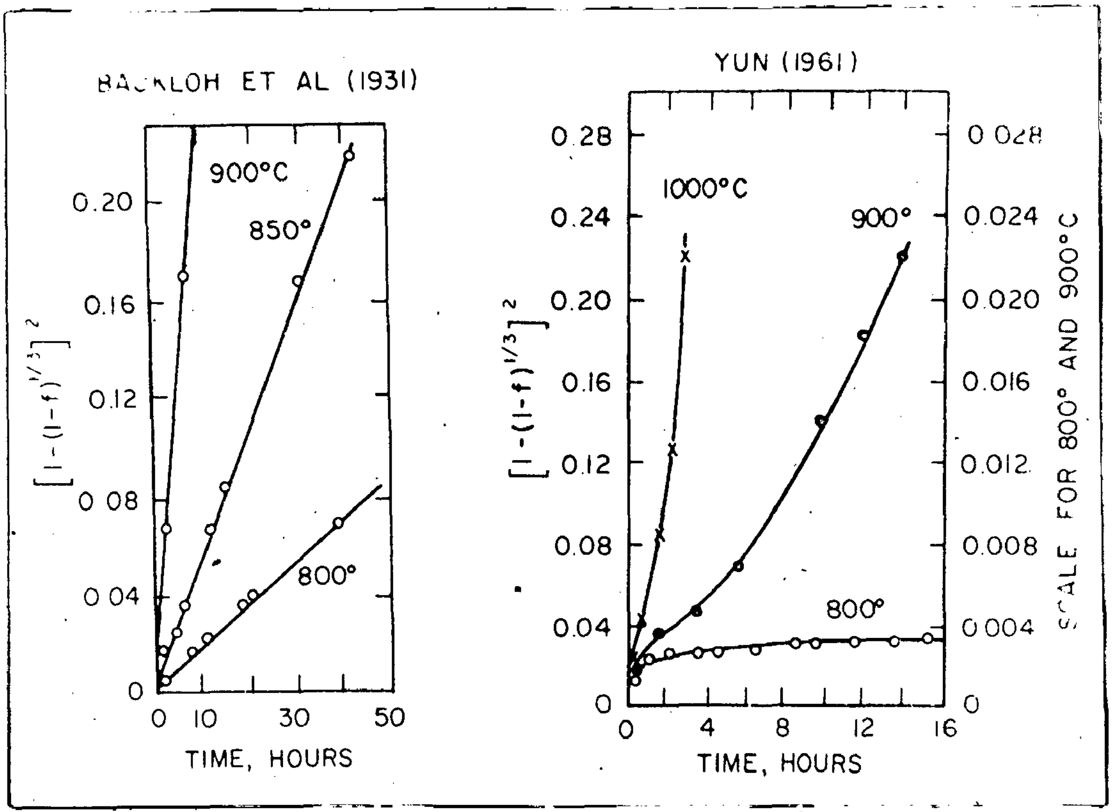


Fig.1.6. Comparision of $1-(1-f)^{\frac{1}{3}}\ ^{2}$ - time relationship in the direct reduction of $Fe_2O_3$ by carbon.

carbon within the oxide crystal is the rate determining process. This statement was based on the fact that the rate of reduction is nearly constant at constant composition of the gaseous phase in the course of reduction of wustite to metallic iron.

The diffusion of iron atoms in the oxide crystal is the rate determining process, could be better understood by knowing change of crystal structure during reduction in accordance with the stage of reduction. In the reduction sequence,

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe$$

the second and third steps are known to be autocatalytic, on completion of first step, a minimum reduction velocity is usually observed, after which a distinct increase of the reaction velocity occurs. Referring to Fig.(1.7) the transformation of ferric oxide, $\alpha\ Fe_2O_3 \longrightarrow \gamma\ Fe_2O_3$, takes place prior to the reduction of oxide between 200°C and 400°C. In this transformation, the metastable ferromagnetic spinel ($\gamma$-$Fe_2O_3$) is formed from stable $\alpha$-$Fe_2O_3$. A high concentration of Fe at the surface layer of this spinel is setup as the result of interaction between the carbon and oxygen (from the external oxide layer), producing a gradient of Fe-concentration through the spinel layer. As iron ions diffuse inside, a layer of magnetite grows from the $\gamma$-$Fe_2O_3$ with the advanced degree of reduction,

$$4\ Fe_2O_3 + Fe \longrightarrow 3\ Fe_3O_4$$

In this instance ferric oxide is completely converted

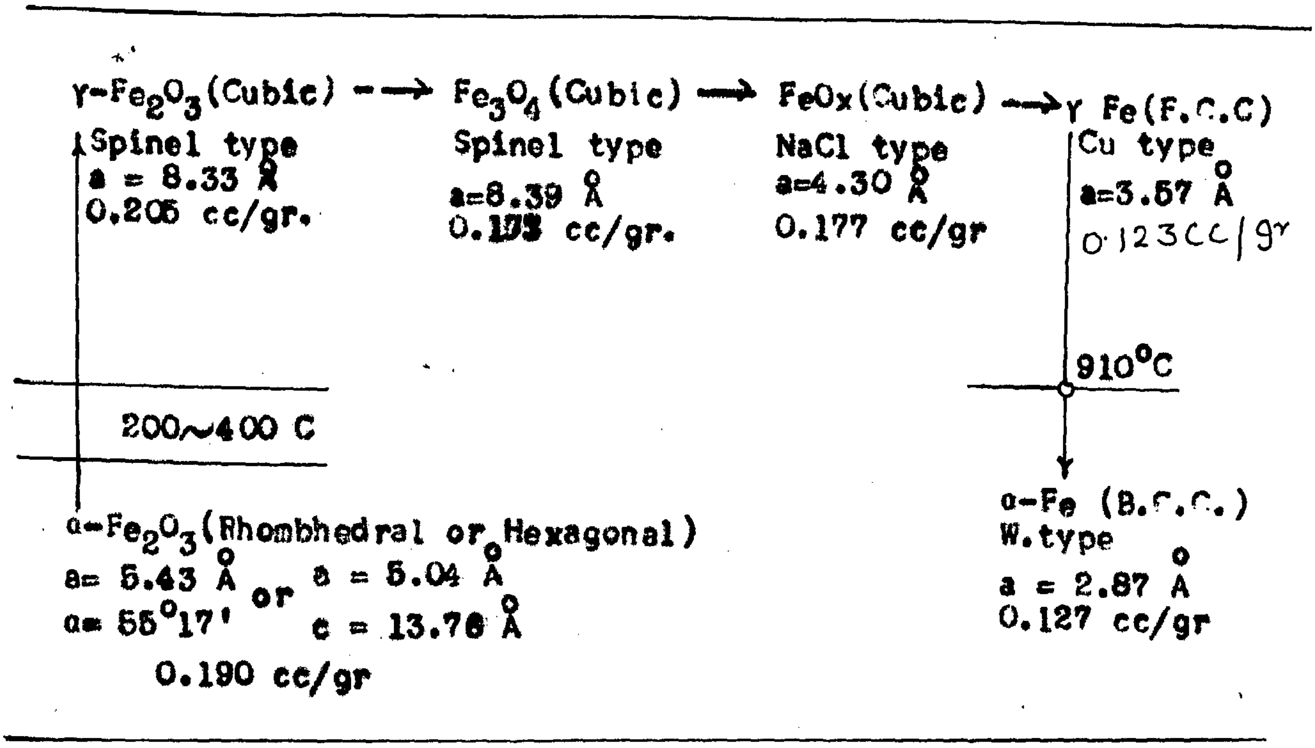


Figure 1.7- Change of Crystal Structure and Specific Volume in the Course of Reduction of Ferric Oxide

into magnetite at about 11% reduction. In accordance with the successive interaction between ferrosoferric oxide and graphite, wustite will be formed on the surface of magnetite, and further reduction ($Fe_3O_4 \longrightarrow FeO$) takes place, as a result of continuous transfer of iron ions through the wustite to the interface with magnetite, the magnetite will be converted to FeO according to the reaction,

$$Fe_3O_4 + Fe \longrightarrow 4\ FeO$$

The lattice orientational resemblance between the $Fe_3O_4$ and FeO lattices facilitates the above transformation. After magnetite is transformed completely to wustite, Fe-ions are continuously created on the external surface of wustite and they begin to raise the Fe-concentration throughout whole wustite layer by diffusing inward, filling in the vacancies of iron ion sites of the lattice. Upon reaching the maximum concentr tion of Fe-ions in FeO (i.e. filling all Fe-ion vacant sites in wustite), there is no place for the excess iron ion to diffuse, thus causing a minimum point on the reduction rate curve vs reduction degree (Fig.1.8). No minimum appears below 800°C because there is no metallic iron reduced from the oxide.

The transformation of,

$$Fe_3O_4(\text{sp.gr.}0.2\ \text{c.c./gm}) \longrightarrow FeO(0.19\ \text{c.c./gm})$$

is considerably easier than,

$$FeO(\text{sp.gr.}0.177\ \text{c.c./gm}) \longrightarrow \gamma\ Fe(0.123\ \text{c.c./gm.})$$

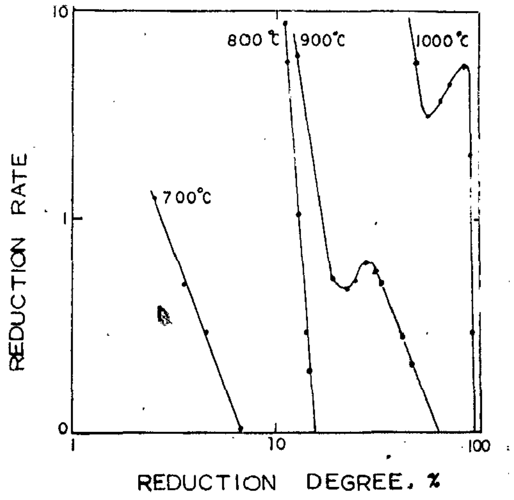


Fig.1.8. Reduction rate vs reduction degree at indicated temperatures, showing the minima at 900°C and 1000°C.

since here the decrease in sp.volume is comparatively large than in first case.

Thus the diffusion of Fe-ions within the oxide crystal is established as the rate determining process in the direct reduction of ferric oxide by carbon.

## (B) KINETICS STUDIES ON IRON OXIDE REDUCTION PREDOMINANTLY WITH CARBON MONOXIDE

According to this hypothesis of iron oxide reduction, carbon passes through the intermediate stage of carbon monoxide formation prior to reacting with the oxide. Further, the direct reduction contribution involving solid/solid interaction is regarded as relatively small compared to the magnitude of the gaseous reaction. This iron oxide reduction mechanism may be considered in two-stages viz. the reduction of hematite to iron by carbon monoxide i.e. equation 2(A), and the solution loss reaction i.e. equation 2(B). In the first stage of reduction process, the slowest step is the reduction of wustite to iron by carbon monoxide. As postulated by Khalafalla and co-workers[23], it is supposed that CO is first adsorbed on the oxide lattice according to reaction,

$$CO(g) \longrightarrow CO^{\circ} \text{ (adsorbed on oxide)} \qquad \ldots (a)$$

which is followed by the reactions according to following scheme.

$CO^*(ad) + CO(g) \longrightarrow CO_2^*(ad) + C^*$ (Free carbon atom) .. (b)

$C^* + FeO(S) \longrightarrow CO^*(ad) + Fe$ .. (c)

$CO^*(ad) \longrightarrow CO(g)$ .. (d)

$CO_2^*(ad) + Fe(S) \Longrightarrow FeO(S) + CO^*(ad)$ .. (e)

$CO_2(ad) \longrightarrow CO_2(g)$ .. (f)

For the mechanism of reduction of wustite by CO, reaction(b) was shown to be the slowest and rate-determining step[23].

In the second stage of the reduction process, it is postulated that $CO_2$ is first adsorbed on C-particles

$CO_2(g) \longrightarrow CO_2^*$ (adsorbed on carbon) .. (g)

and is followed by the reactions,

$CO_2^*$ (ad. on C) + $C \longrightarrow 2CO^*$ (ad. on C) .. (h)

$CO^*$ (ad. on C) $\longrightarrow CO(g)$ .. (i)

The activation energy for the reaction (b), the slowest step in the first stage, is found to be in the vicinity of 50 Kcals/mole[23]. For the reaction (h), the so-called solution-loss reaction, Meyer (as cited by Rao[8]) determined the kinetics and found it to be a zero-order reaction with an activation energy of 90 K.Cal./mole Rao[8] concluded that, reaction (h) , the so-called solution loss reaction , may be the rate controlling step in the overall reduction process, because of the proximity of its activation energy to the values determined during his experiments.

## 1.4 IMPORTANCE OF INVESTIGATION UNDER INDIAN CONDITIONS

India is fortunate enough in having large reserves of high grade iron ores, the basic raw material for iron and steel making. The reserves are reported[24] to be about 21,140 million tonnes with an average iron content of 52% and above, out of which the proved reserves are around 5400 million tonnes. Due to the mechanised mining and soft nature of Indian iron ores, as high as 40 to 50% fines are produced. This percentage is likely to increase when mining is carried out at the greater depths. On the contrary, the metallurgical grade coking coal reserves[24] are very much limited, about 1500 million tonnes. Their distribution is localised mainly in Bihar and Bengal regions. The non-coking coal and lignite coke reserves are about 103,000 million tonnes and distributed uniformly all over the country.

The iron bearing fines and low grade fuels, as such cannot be used as a part of blast furnace charge due to apparent disadvantages. These iron ore fines can be partially reduced with the help of low grade solid fuels, either externally or internally mixed with them. These pre-reduced agglomerates can prove an excellent blast furnace charge and thus the problem of utilization of these fines and low grade fuels may be reduced to a minimum. Therefore, it is advisable to pay sufficient attention to find out the possibilities of producing pre-reduced briquettes from low grade fuels which in turn can explore new possibilities in the technology of iron and steel production.

The primary need under Indian conditions is to develop an efficient process which can produce pre-reduced agglomerates of constant physical and chemical qualities economically. It is, therefore, worthwhile to thoroughly investigate and develop an economic process of pre-reduction utilising indigeneous low grade raw materials like lignite coke, anthracite, wood charcoal etc. as their reserves are comparatively more than that of coking coal.

In an attempt to produce pre-reduced pellets from Indian iron ore by using 35% lignite coke as reductant in the pellet, Ghosh and Tiwari[9] had achieved 90% reduction but no metallization has been reported, Koria and Jena[6] in their work on production of pre-reduced briquettes from Indian ore fines, intimately mixed with lignite coke or wood charcoal, could produce 100% reduced and more than 90% metallized briquettes.

The problem of association of iron ore minerals with gangue can be solved by using pre-reduced agglomerates after subjecting it to magnetic seperation. This sort of treatment removes the iron bearing fines from the gangue and thus fine iron powders can be produced, which can either be injected through tuyers to the blast furnace or used as a coolant material in the steel making process.

In the present investigation, the studies on the kinetics of the pre-reduction have been made to elucidate the mechanism of reaction for knowing the exact influence of the experimental variables, such as to achieve maximum possible pre-reduction and metallization of iron ore briquettes reduced with low grade coke and wood charcoal. Hence, this investigation has been under taken to study the effect of different amounts and type of reductants, temperature and time of reduction on rate of reduction and percent metallization.

# CHAPTER II

# EXPERIMENTAL WORK

The present chapter deals with a detailed description of the raw materials with methods of their analysis (chemical and proximate), the method of briquettes preparation, the experimental setup and procedure used for carrying out the reduction with different percentages of low grade coke and wood charcoal.

## 2.1 RAW MATERIALS

The raw materials used for the present investigation were iron ore fines in the size range -100 to +150 mesh and reductants, low grade coke and wood charcoal in the same size range.

### 2.1.1 IRON ORE

The iron ore fines were screened and the fractions between -100 to +150 mesh size were stored in dry beakers after chemical analysis.

#### (a) SIEVE ANALYSIS

Sieve analysis of the iron ore fines was performed in a Denver sieve set having sieves arranged according to Taylor's series. A 500 gm. ore sample was put on to the top of 100 mesh sieve and a 120 mesh sieve was placed in between 100 mesh and 150 mesh sieve. This assembly was then transferred to the sieve shaking machine and shaken for 15 minutes. The amount retained on each sieve was weighed. The results are reported in table-I(A).

## (b) CHEMICAL ANALYSIS OF IRON ORE[25]

### MOISTURE DETERMINATION

5 gms of ore sample was weighed onto a watch glass and heated in an oven at 105°C till constant weight was obtained. It was then cooled in a dessicator and weighed. From the loss in weight measurement, the moisture percentage in the ore fines was calculated.

### LOSS ON IGNITION

One gm. of ore sample was first ignited to 500°C for 5 minutes and then at 1000°C for 60 minutes till constant weight is obtained. From the loss in weight, percentage loss on ignition was calculated.

### IRON DETERMINATION

The iron percentage determination in the ore fines was done by titrating a reduced solution of the ore in hydrochloric acid against a standard solution of potassium dichromate.

0.5 gms of the ore sample was weighed and transferred into a 250 ml. conical flask. To this, 10 ml. of conc. HCl was added and heated gently for 10-15 minutes and then rate of heating was increased to bring to a gentle boil. The solution was evaporated to dryness and then about 10 ml. of conc.HCl and 40 ml. of cold water was added. The diluted solution was heated to boiling and then reduced by adding stannous chloride solution till the red colour of ferric iron was completely disappeared. A few excess drops of $SnCl_2$ solution was added and the flask was cooled quickly to room temperature by putting it under running tap water. To this about 10 ml. of mercuric chloride ($HgCl_2$) solution was added and the solution was diluted to 200 ml. with distilled water. The diluted solution was titrated against a standard solution of potassium dichromate, stirring all the times with a glass rod. Two to three drops of an internal indicator consisting of a solution of one gm. diphenylammine in 100 ml. conc. $H_2SO_4$ was added which gave an intense violet-blue colour at the end point. From the consistent readings of the volume of potassium dichromate consumed, the percentage iron in the ore sample was calculated.

The chemical analysis of the iron ore fines used in this investigation is given in table I-(B).

### 2.1.2 SOLID REDUCTANTS (Low grade coke and wood charcoal)

The solid reducing agents used in this investigation were low grade coke and wood charcoal. These were crushed and sieved. Fines in the range of -100 to +150 mesh were stored in dry beakers covered with watch glass. Sieve analysis and proximate analysis were then performed on the reductants.

### (a) SIEVE ANALYSIS

Sieve analysis of low grade coke and wood charcoal powders were performed in the similar way as described in 2.11(a) and the results are summarised in table II(A).

### (b) PROXIMATE ANALYSIS[25]

It consisted of heating coal under standard conditions and determining the amounts of moisture, volatile matter and ash.

### MOISTURE DETERMINATION

1.0 gm. sample of low grade coke or wood charcoal was weighed in a silica dish and distributed uniformly on the dish with the help of nickel wire loop. Sample sticking to the wire loop was transferred to the dish with the help of camel hair brush. The dish without the lid was placed in an oven adjusted to 105°C and heated for an hour or till the constant weight is obtained. The dish was then covered with lid, cooled in a dessicator and weighed. The loss in weight expressed as percentage of total weight of coke or charcoal sample before heating, gave percent moisture.

### VOLATILE MATTER DETERMINATION

One gm. of coke or charcoal sample was weighed and taken in a silica crucible provided for the purpose of volatile matter determination. The crucible was then heated in an electric furnace to 900 ± 25°C for seven minutes. It was then taken out from the furnace, cooled in a dessicator and then weighed. From the percent weight loss, the percentage of volatile matter was obtained by subtracting the amount of percent moisture.

## ASH DETERMINATION

One gm. of coke or charcoal sample was weighed in a silica dish and it was then placed in an electric muffle furnace at room temperature. The furnace temperature was raised to 400°-450°C and this temperature was maintained for 30 minutes. The dish with open lid was then transferred to another furnace maintained at 775° ± 25°C. After heating to about an hour, or till the black particles were burnt, the dish was covered with lid, removed from the furnace and cooled in a dessicator. From the weight of the residue, the percentage of ash in the coke or charcoal sample was calculated.

## FIXED CARBON DETERMINATION

The fixed carbon percentage in the reductants were determined by subtracting the sum of the percentages of moisture, volatile matter and ash from 100.

The proximate analysis of, as received, low grade coke and wood charcoal used in this investigation is given in table -II(B).

### 2.1.3 METHOD OF REMOVING VOLATILE MATTER FROM WOOD CHARCOAL

A preliminary treatment had been given to wood charcoal powder to remove volatile matter. About 300 gms of wood charcoal was put in graphite crucible. The graphite crucible with the open end closed by the lid was heated to $900^{\circ} \pm 25^{\circ}$C in an electric muffle furnace for about 180 minutes. The cruicible was then taken out and cooled in a dessicator.

The proximate analysis of this treated wood charcoal was done in a similar way as described in 2.1.2(b). The results are reported in Table II-(B).

## 2.2 BRIQUETTES PREPARATION

For the present investigation, the briquettes were made on 'Specimen mounting machine'.

The briquettes were made with stoichiometric, 3% and 5% excess than stoichiometric amounts of each reductant out of low grade coke and treated wood charcoal. The stoichiometric requirement of the reductants was calculated on the basis that reduction product is 100% carbon monoxide. The iron ore fines and the reductant were taken in desired proportion and thoroughly mixed. To this mixture, a little amount (about 5 ml. per 100 gms. of mixture) of water is added. This mixture is filled in cylindrical die of 1.3 cm. internal diameter and 7.6 cm. length and the mixture was pressed with the help of plunger on 'Specimen mounting machine' to a pressure, 452 kgs./cm$^2$. The briquettes were 1.3 cm. in dia. and 1.0-1.5 cm. in length.

### 2.2.1 DRYING OF BRIQUETTES

The briquettes were first air dried and then in an oven, at about 120°C for a day. This time was found to be enough for complete removal of moisture.

## 2.3 EXPERIMENTAL SET-UP

The experimental set-up used for reduction of iron ore briquettes is shown in Fig.2.1. The whole assembly can be divided into three main units namely, (a) Drying unit, (b) Vacuum unit, (c) Reduction furnace.

### (a) DRYING UNIT

It is an oven used for drying the briquettes which were kept in different pyrex beakers for different amounts of different reductants. A significant absorption of moisture from atmosphere was found and so to eliminate this moisture, the briquettes were dried time to time, and then used for reduction studies.

### (b) VACUUM UNIT

This unit consists of a rotary oil vacuum pump and connection tubes. The vacuum pump is connected with the reduction tube through a three way cork through which the reduction tube can either be connected to vacuum pump or to the atmosphere for vacuum release.

The evacuation which was achieved with the rotary

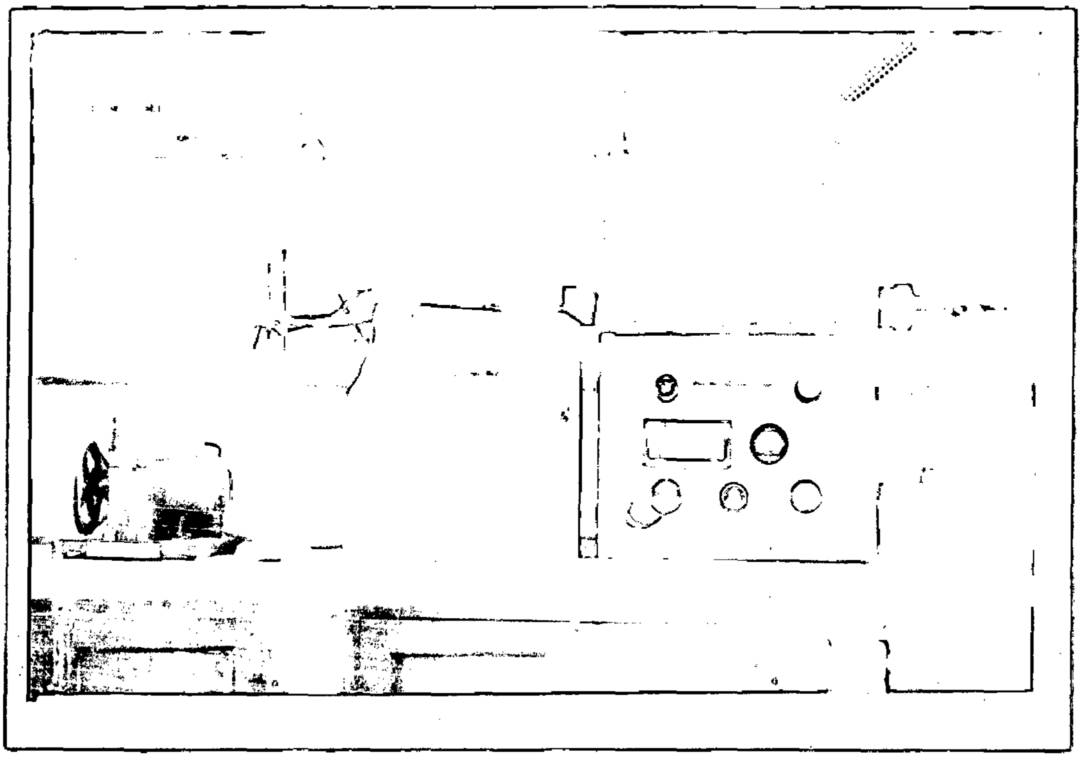


Fig.2.1. Experimental Set-up.

vacuum pump employed for present investigation, was of the order of 0.1 mm of Hg.

(c) REDUCTION FURNACE

The reduction furnace has the following specifications,

| | |
|---|---|
| (i) TYPE | Single phase resistance muffle tube horizontal furnace. |
| (ii) DIAMETER OF ALUMINA MUFFLE | 3 inches. |
| (iii) LENGTH OF ALUMINA MUFFLE | 24 inches. |
| (iv) LENGTH OF UNIFORM TEMPERATURE ZONE | about 10 inches from closed end |
| (v) RESISTANCE OF WINDING | 35 ohms. |
| (vi) POWER INPUT | 1.785 KW |
| (vii) MAXIMUM OPERATION TEMPERATURE | 1250°C |

An energy regulator for temperature control, a temperature indicator for temperature measurement and an ammeter were provided on the control board with the furnace. An autotransformer for controlled voltage supply to the furnace has also been employed.

The sockets were provided at both the alumina muffle ends, to close any one or both of its ends as desired. A Pt-Pt/13% Rh thermocouple was calibrated and then used for temperature measurements.

An alumina tube (0.75 inch in dia. and 24 inches in length) closed at one end was used as a reaction tube. The open end of reaction tube was connected to vacuum pump through a solid rubber cork.

Semicylindrical stainless steel boat, 15 cm. long and 1.5 cm wide was used for keeping the briquettes in the reaction tube.

## 2.4 PROCEDURE FOR CARRYING OUT PRE-REDUCTION OF IRON ORE BRIQUETTES

The briquettes made out of compacting the desired proportions of iron ore and low grade coke or wood charcoal fines (stoichiometric, 3% and 5% excess than stoichiometric amounts of reductants) followed by removal of moisture, were weighed in a chemical balance. Six briquettes each of different amounts and nature of reductants at a time were kept in stainless steel boat and the boat is then inserted into the alumina reaction tube. The open end of the tube was connected to the vacuum pump through a solid rubber cork. After proper evacuation (0.1 mm of Hg) the reaction tube containing the briquettes was then inserted into the furnace which was adjusted to the desired temperature. The furnace temperature was kept 5°C higher then required, as this was found to be temperature difference between the outside and inside the reaction tube. The time of introduction of the reaction tube was considered to be the starting of reduction reaction. After keeping the briquettes at desired temperature and period, the reaction tube was taken out from the furnace and cooled in atmosphere under vacuum. Then the vacuum seal was broken and the briquettes were taken out, weighed and analysed for residual carbon content by the method of carbon combustion to $CO_2$ and absorbing it in potassium hydroxide. In this way the experiments were performed at 950°C, 1000°C, 1100°C and 1150°C for different intervals of time (ranging from 5 minutes to 360 minutes) with stoichiometric, 3% and 5% excess than stoichiometric amounts of low grade coke and wood charcoal.

## 2.5 ANALYSIS OF THE REDUCED BRIQUETTES

The reduced briquettes have been analysed for determination of carbon percentage by strohlein apparatus. The oxidation of carbon is done at 1100°C in a stream of dry and pure oxygen to yield carbon dioxide. The whole volume of carbon dioxide plus excess oxygen from the combustion tube is treated with KOH solution to absorb $CO_2$. The amount of $CO_2$ absorbed by KOH solution is calibrated in terms of percentage of carbon on the measuring burette provided with the apparatus.

The carbon percentages left after reduction are reported in table V and table VI for the briquettes reduced with stoichiometric, 3% and 5% excess than stoichiometric amounts of low grade coke and wood charcoal.

# CHAPTER III

## RESULTS AND DISCUSSIONS

### 3.1 RESULTS

The percentage weight loss obtained and percentage carbon left for briquettes reduced with stoichiometric, 3% excess and 5% excess than stoichiometric amounts of low grade coke and wood charcoal in the temperature range (950 to 1150°C). For different intervals of time (5 minutes to 360 minutes) under reduced pressure (0.1 mm of Hg) are given in tables III to VI. From the weight loss measurements and carbon analysis, the percentage reduction of iron oxide in the briquettes is calculated. The results are given in tables VII and VIII and plotted in figures 3.1 to 3.6 at various percentages of low grade coke and wood charcoal. From these plots, it can be observed that the initial stage of reduction upto about 30%, is highly temperature sensitive and also depends on the nature of reductants. The wood charcoal is found to be highly reactive as compared to low grade coke.

In Figs. 3.7 to 3.12 log percentage reduction is plotted against log time for briquettes reduced with different amounts (stoichiometric, 3% and 5% excess than stoichiometric) of low grade coke and wood charcoal in accordance with the relationship $r = K t^n$, where r is percentage reduction, t is time of reduction, n is slope and K is a constant. If this law would have been obeyed than log (r) vs log (t) should give a straight line, but in the present investigation no straight line has been obtained.

From the plots 3.13 to 3.18 , the following relationship seems to hold good in the present investigation

$$r = C \log t + X \qquad (i)$$

where C and X are constants. In these plots the initial percentage reduction values upto about 30% reduction have not taken into consideration. The Eq.(i) is found to be valid for the reductants, low grade coke and wood charcoal at all temperatures ranging from 950 to 1100°C upto 85% reduction as the lines are nearly parallel to each other with the slope as shown in table IX. Beyond 85% reduction, the slope of the lines for various temperatures changes for both types of reductants as shown in the same table IX. The lines are again straight and parallel. The change in slope after 85% reduction is perhaps due to change in mechanism of iron oxide reduction.

The activation energy values for briquettes reduced with different amounts of low grade coke and wood charcoal are calculated in a similar way as adopted by Korio and Jono[6] in their work on production of pre-reduced briquettes where a similar relationship is reported. By differentiating with respect to t, the equation no.(1), we get

$$\frac{dr}{dt} = C\,\frac{1}{t}$$

or $$\frac{dr}{dt} \propto \frac{1}{t}$$

Hence according to Arrhenious equation, at all temperatures, the reciprocal of time for attaining a definite reduction r (value), should be proportional to $e^{-E/RT}$, where E, R and T are activation energy, gas constant and absolute temperature respectively. The $\log(\frac{1}{t})$ vs $\frac{1}{T}$ °K for briquettes reduced with stoichiometric, 3% and 5% excess than stoichiometric amounts of low grade coke and wood charcoal at the definite reduction percentages (20% , 30% , 40% and 80% reduction) are plotted in Figures 3.19 to Fig. 3.24. The activation energy values with their mean deviation have been calculated from the slopes of those curves and the values thus obtained are given in Table X. Beyond 85% reduction, the activation energy values could not be calculated because of insufficient data.

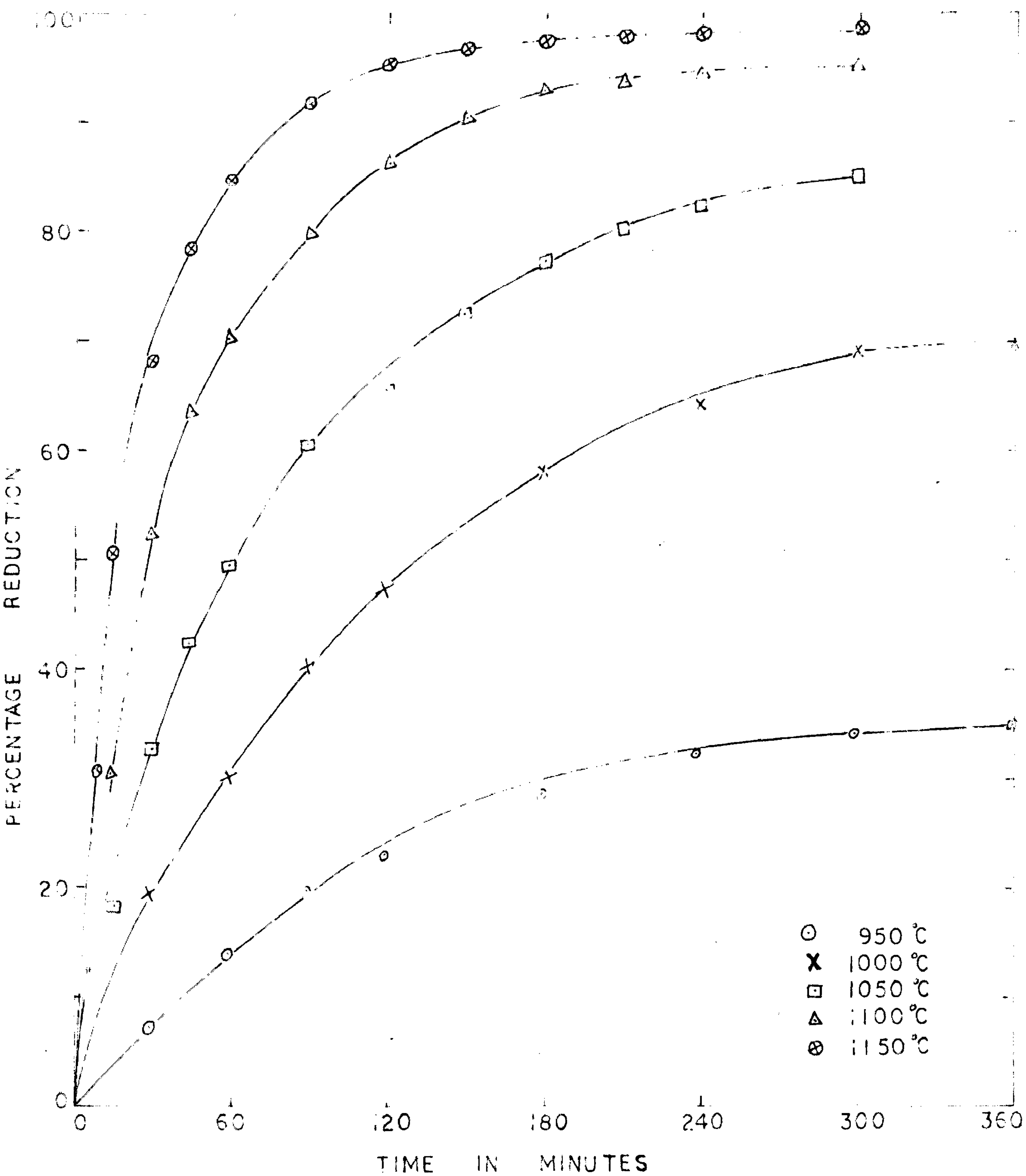


FIG.3·1 _ PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCE WITH STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1 mm OF Hg)

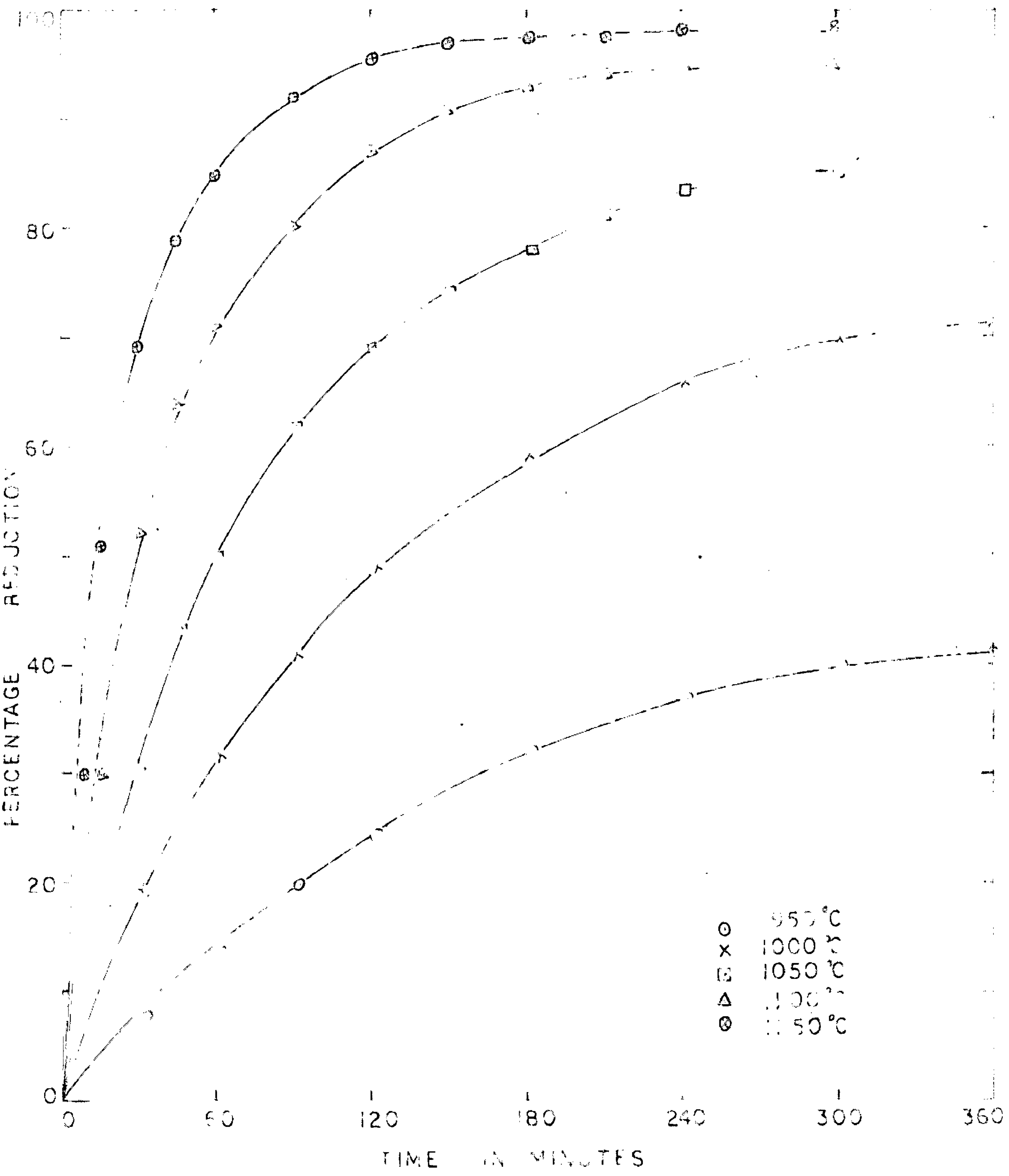
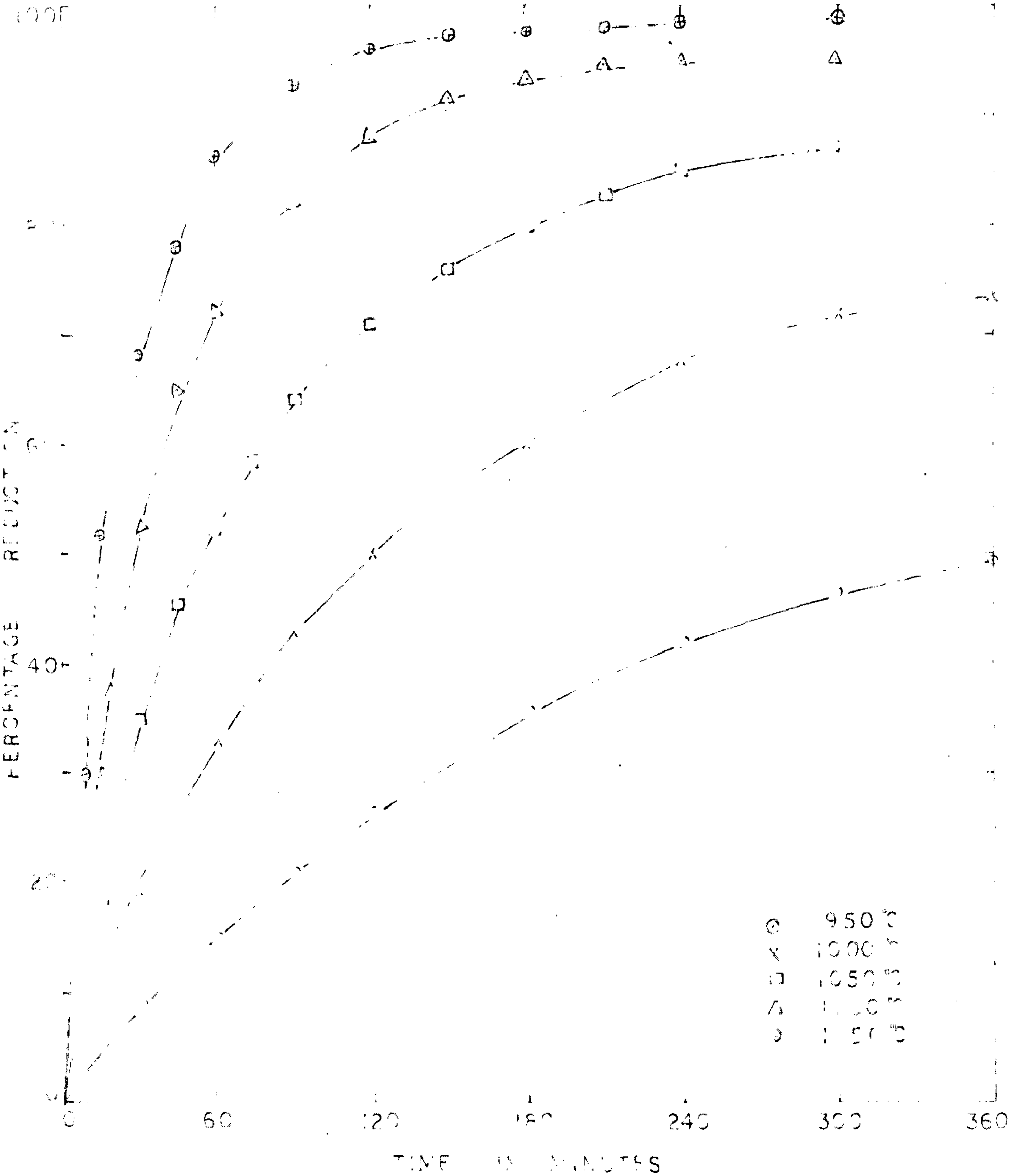


FIG.3.2_ PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1 mm OF Hg)



.3·3 _ PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1 mm OF Hg)

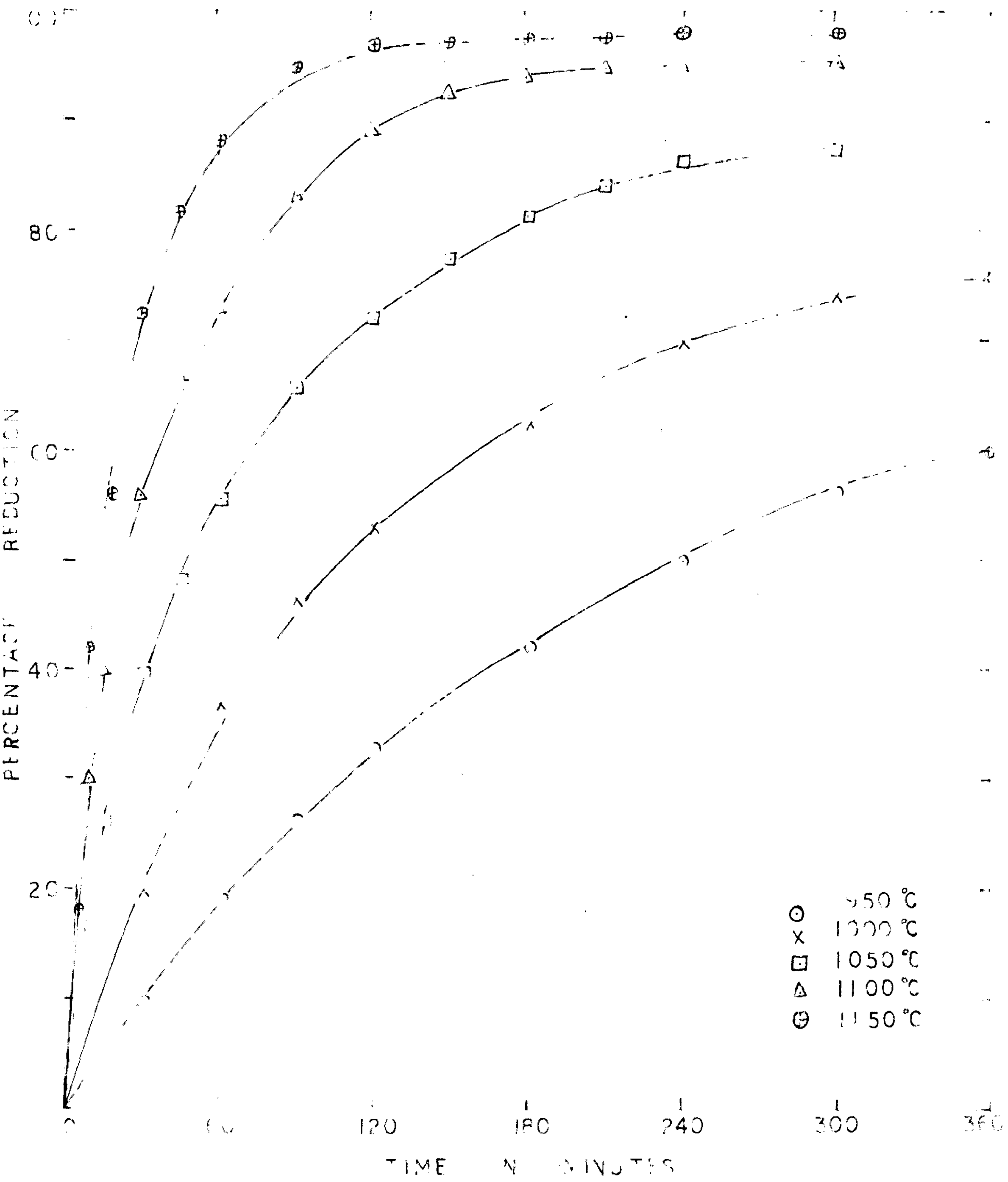


FIG.3.4 _ PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER RECDUCED PRESSURE (0.1 mm OF Hg)

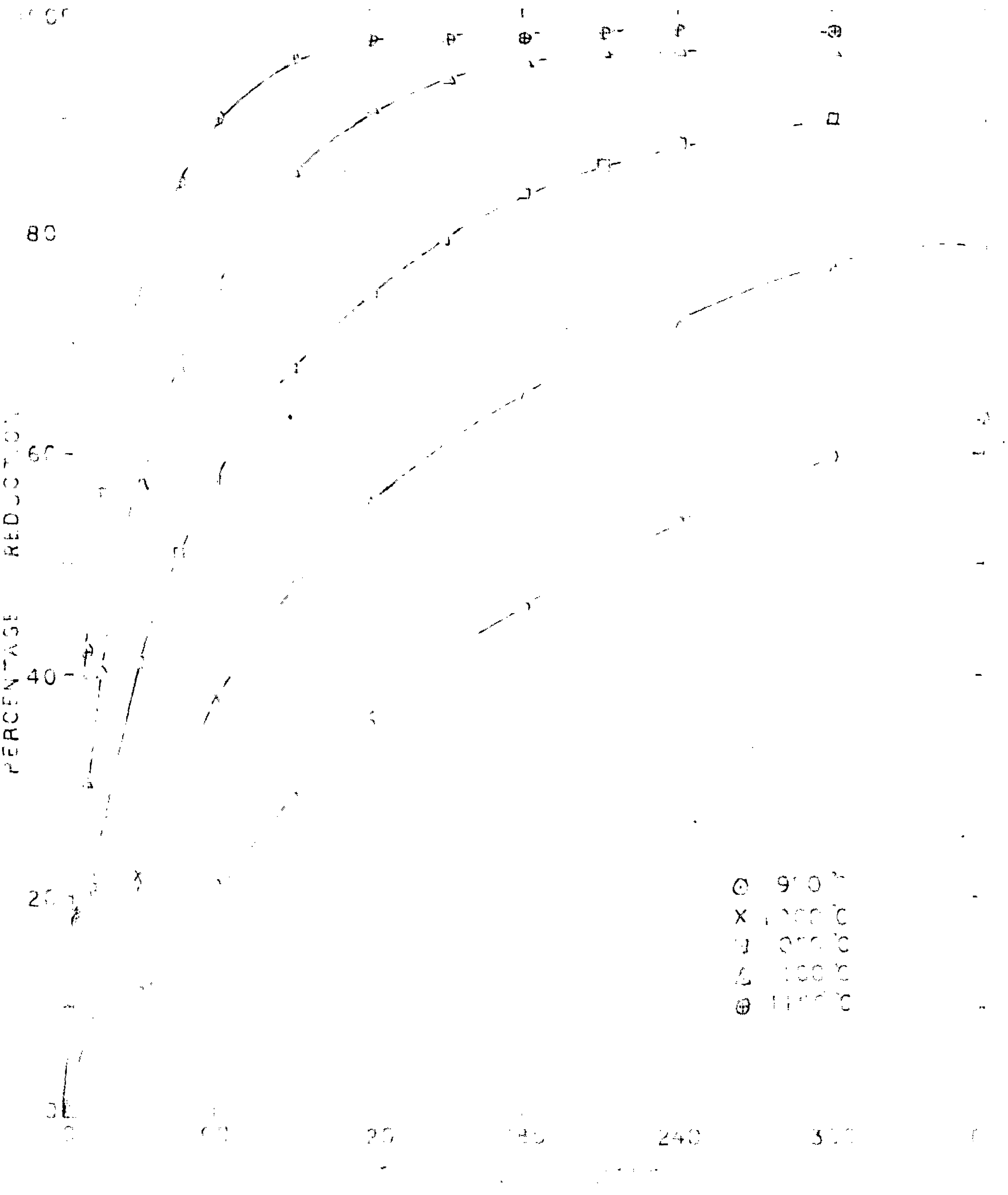


FIG. 3.5 – PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1 mm OF Hg)

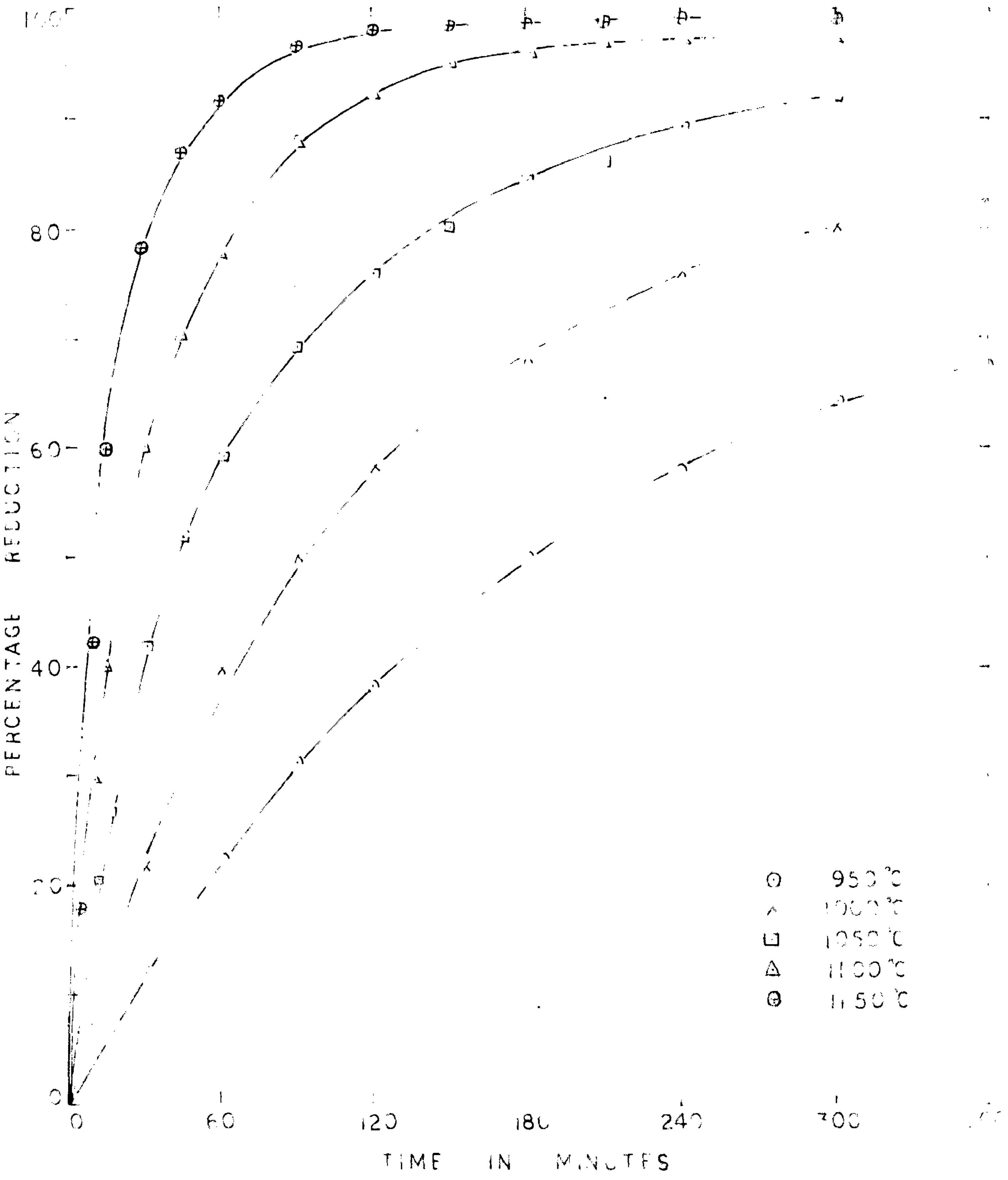


FIG.3.6 _ PLOT OF PERCENTAGE REDUCTION VS TIME FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1mm OF Hg)

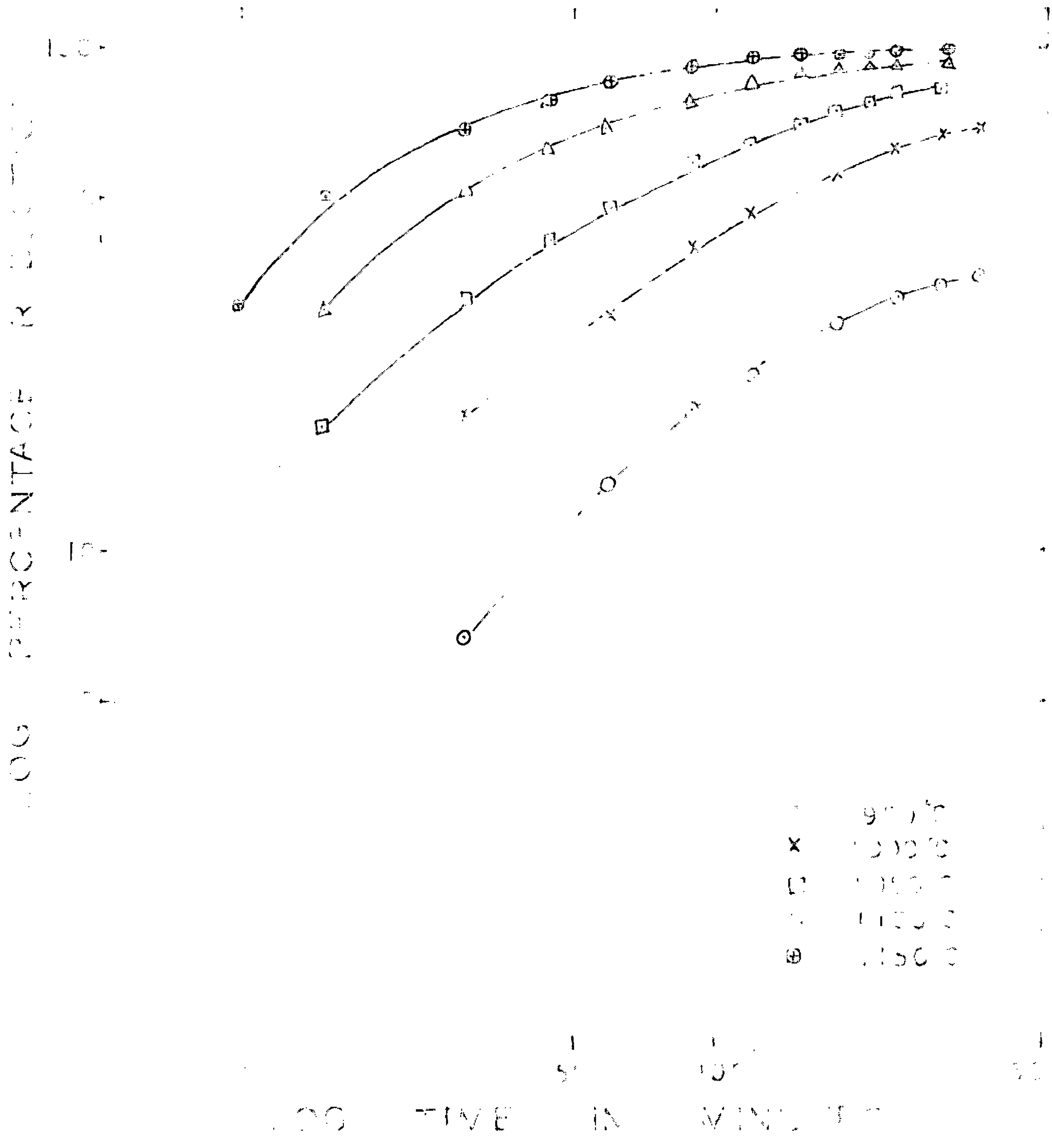


FIG. 7 _ PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1 mm OF Hg)

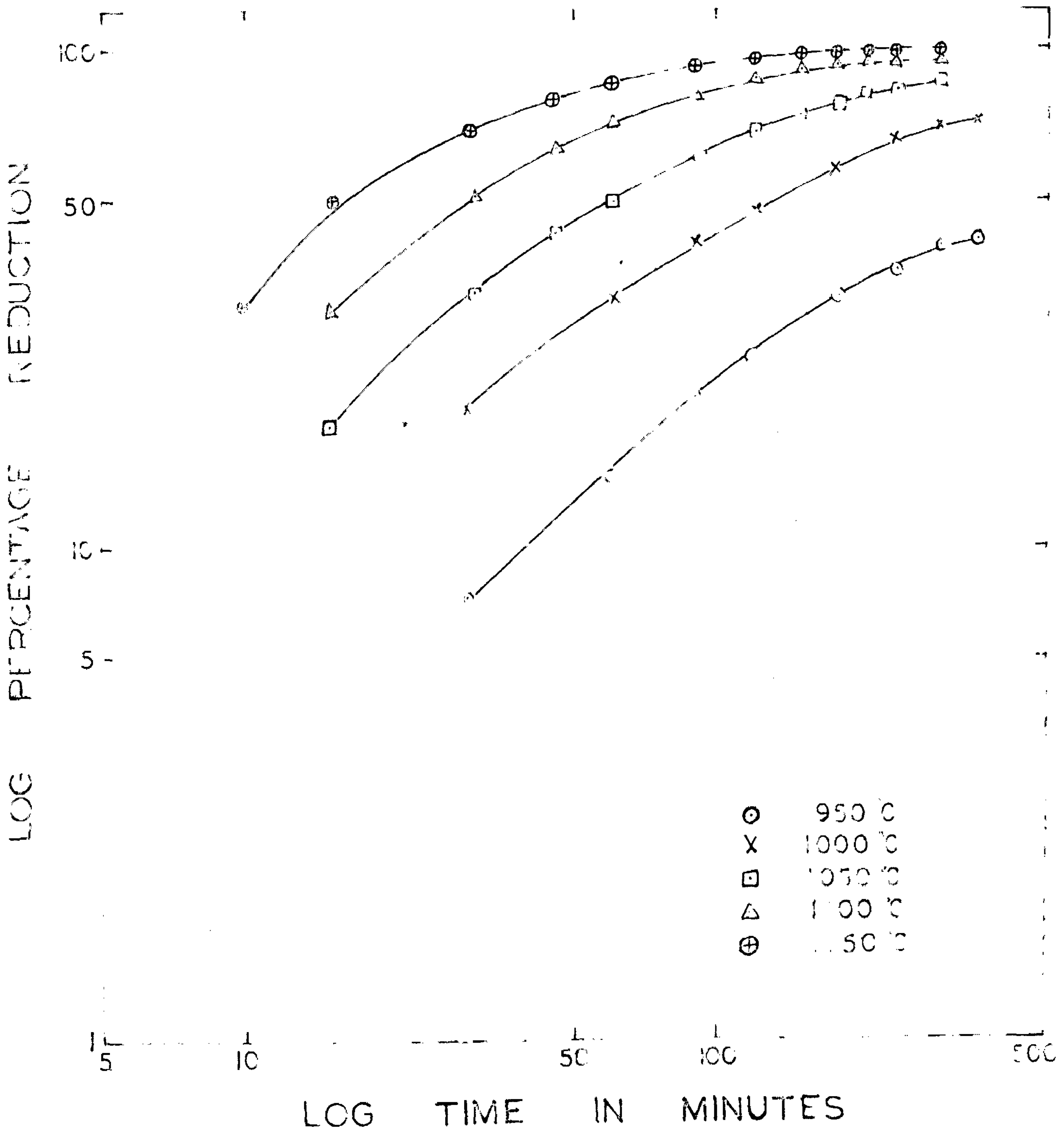


FIG.3.8_ PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1 mm OF Hg)

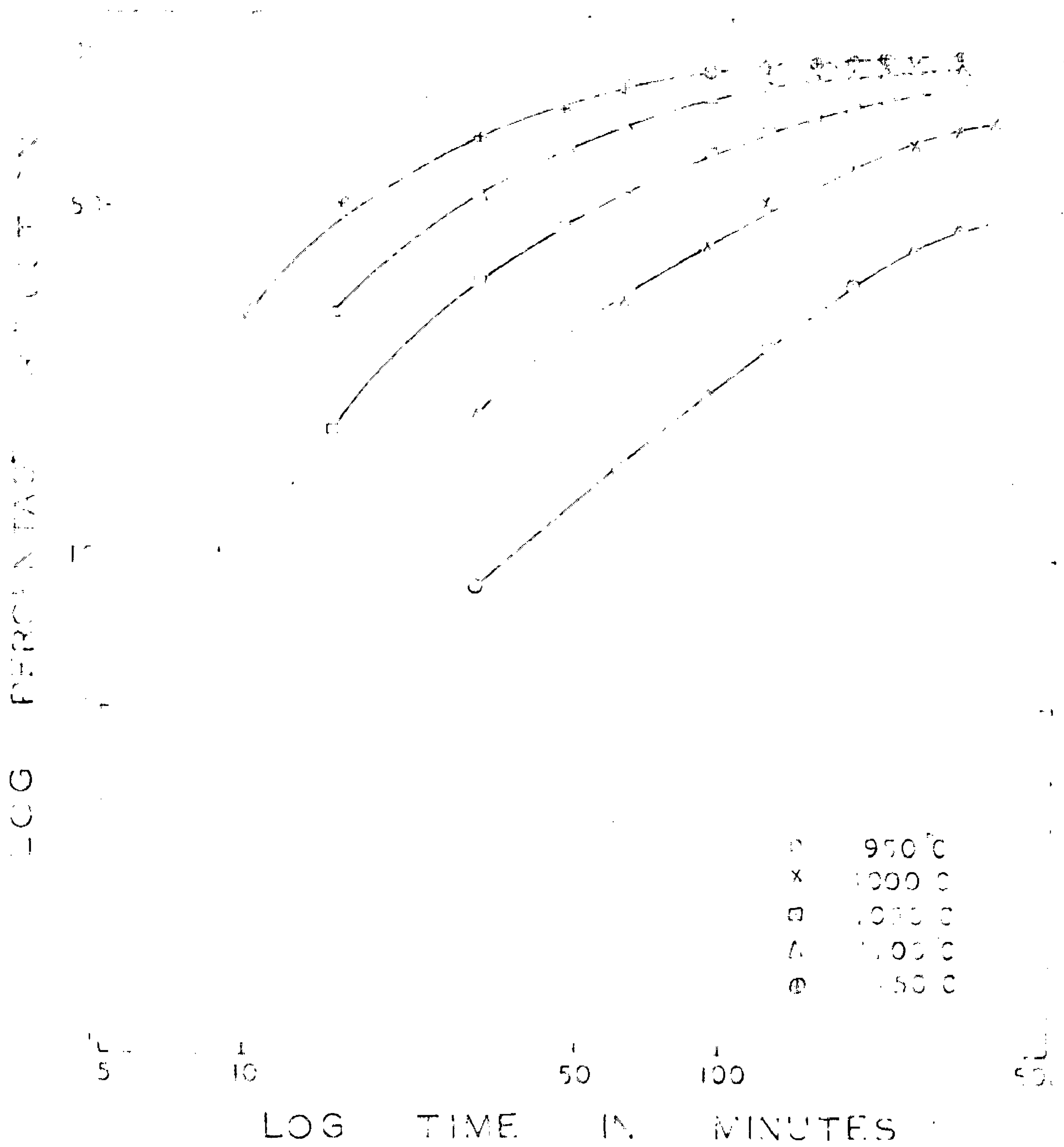


FIG.3.9 _ PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1mm OF Hg)

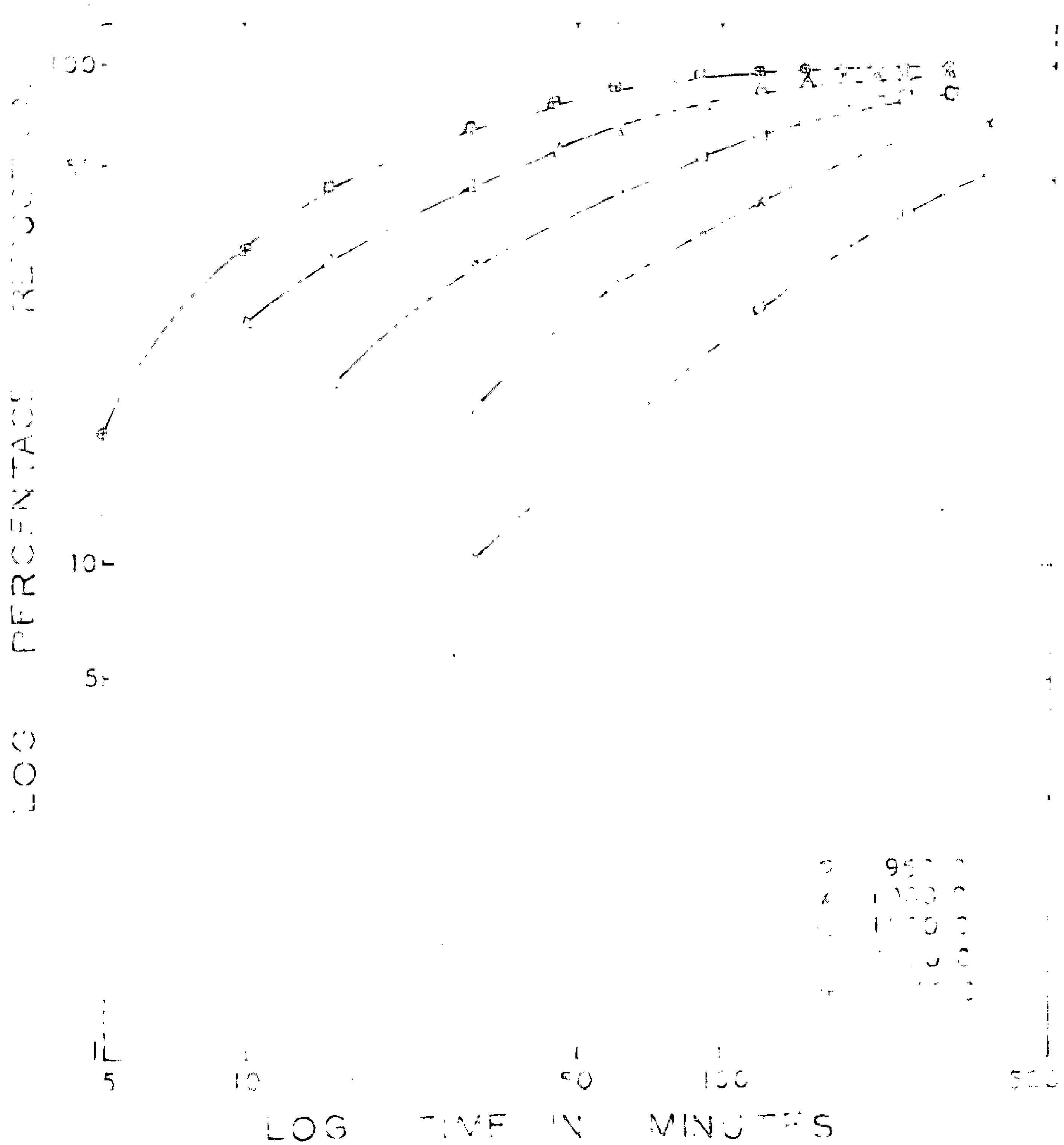


FIG.3.10a PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1 mm OF Hg)

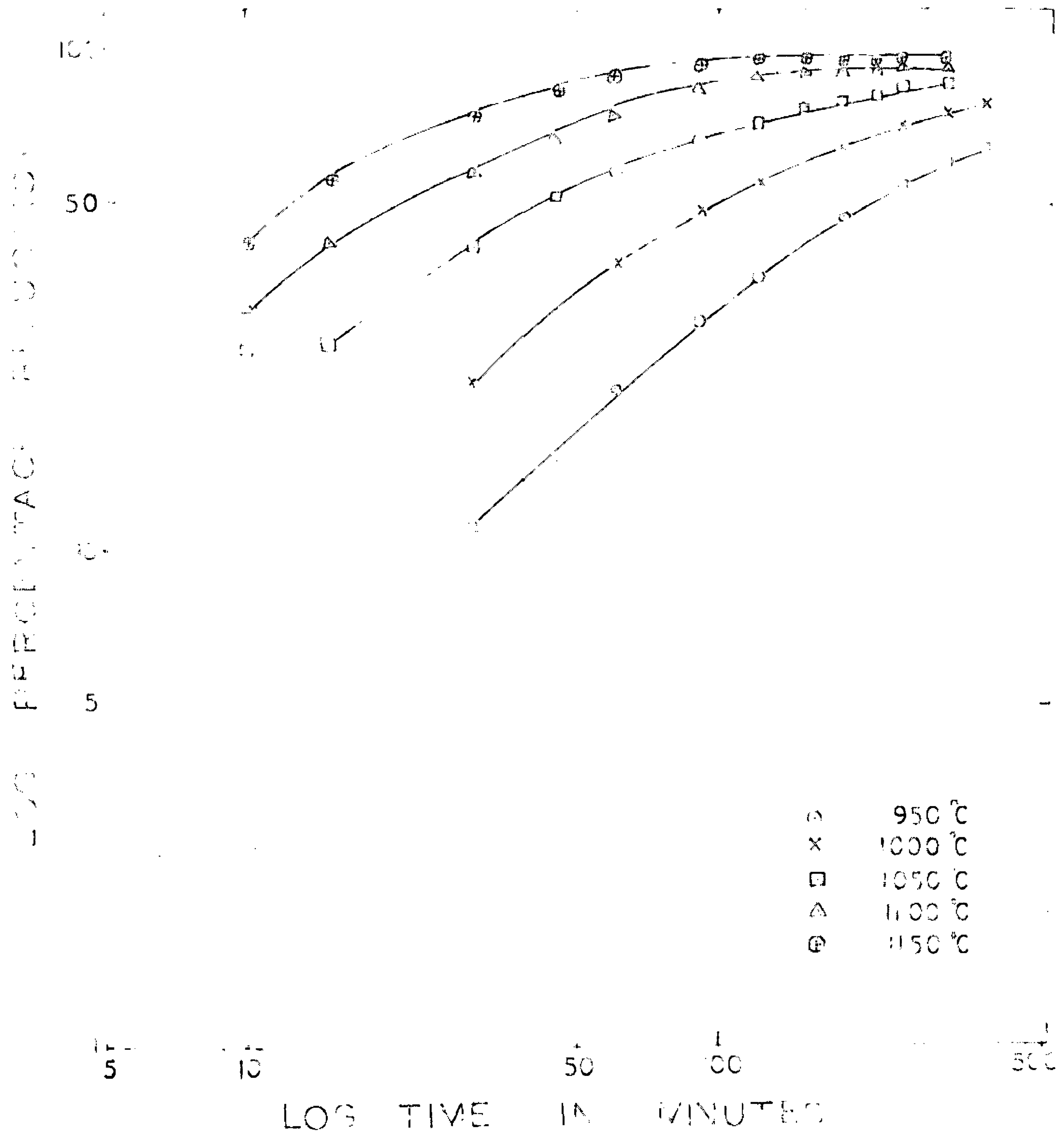


FIG.3 11 _ PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 3 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1 mm OF Hg)

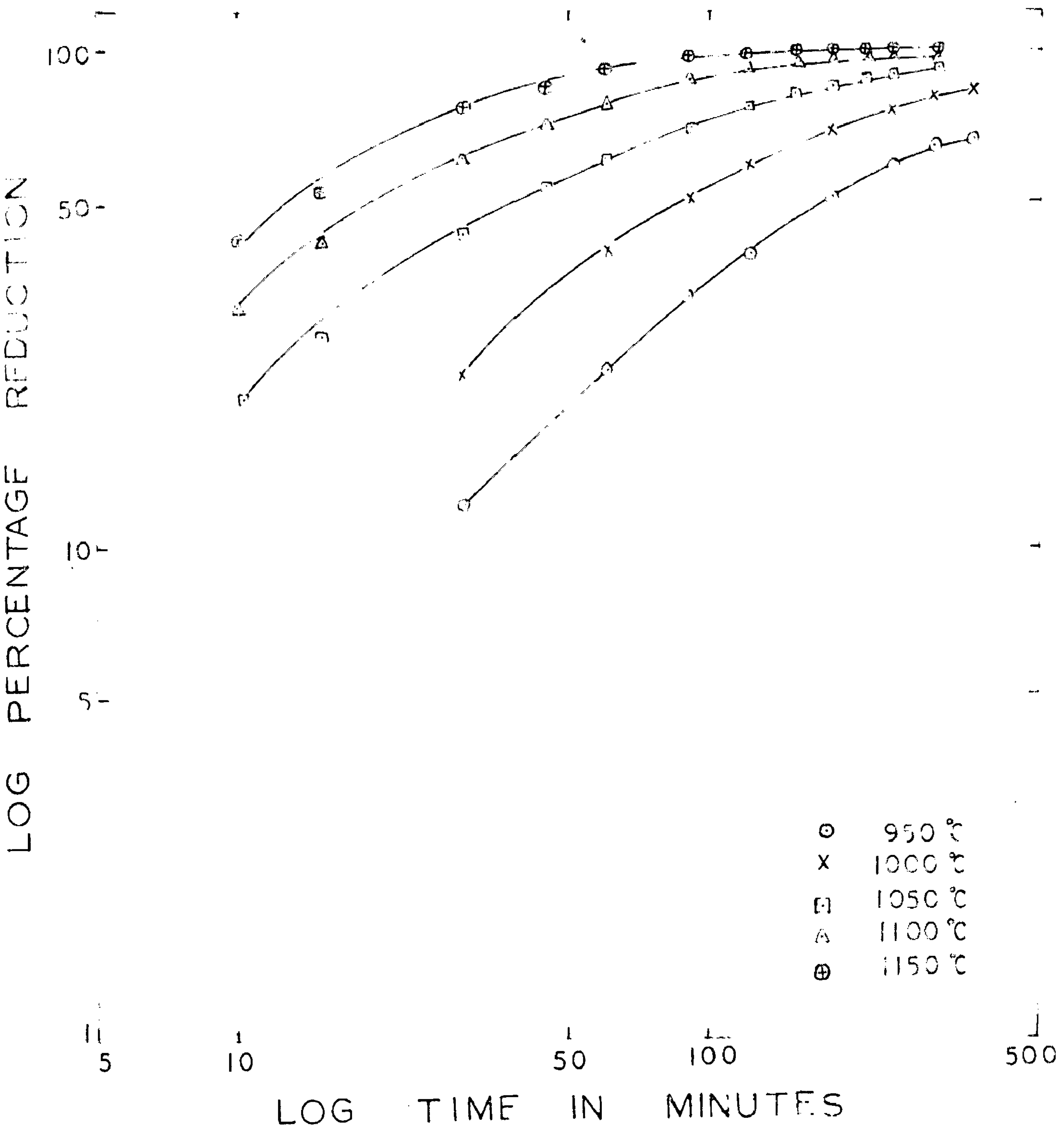


FIG.3·12_PLOT OF LOG PERCENTAGE REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0·1mm OF Hg)

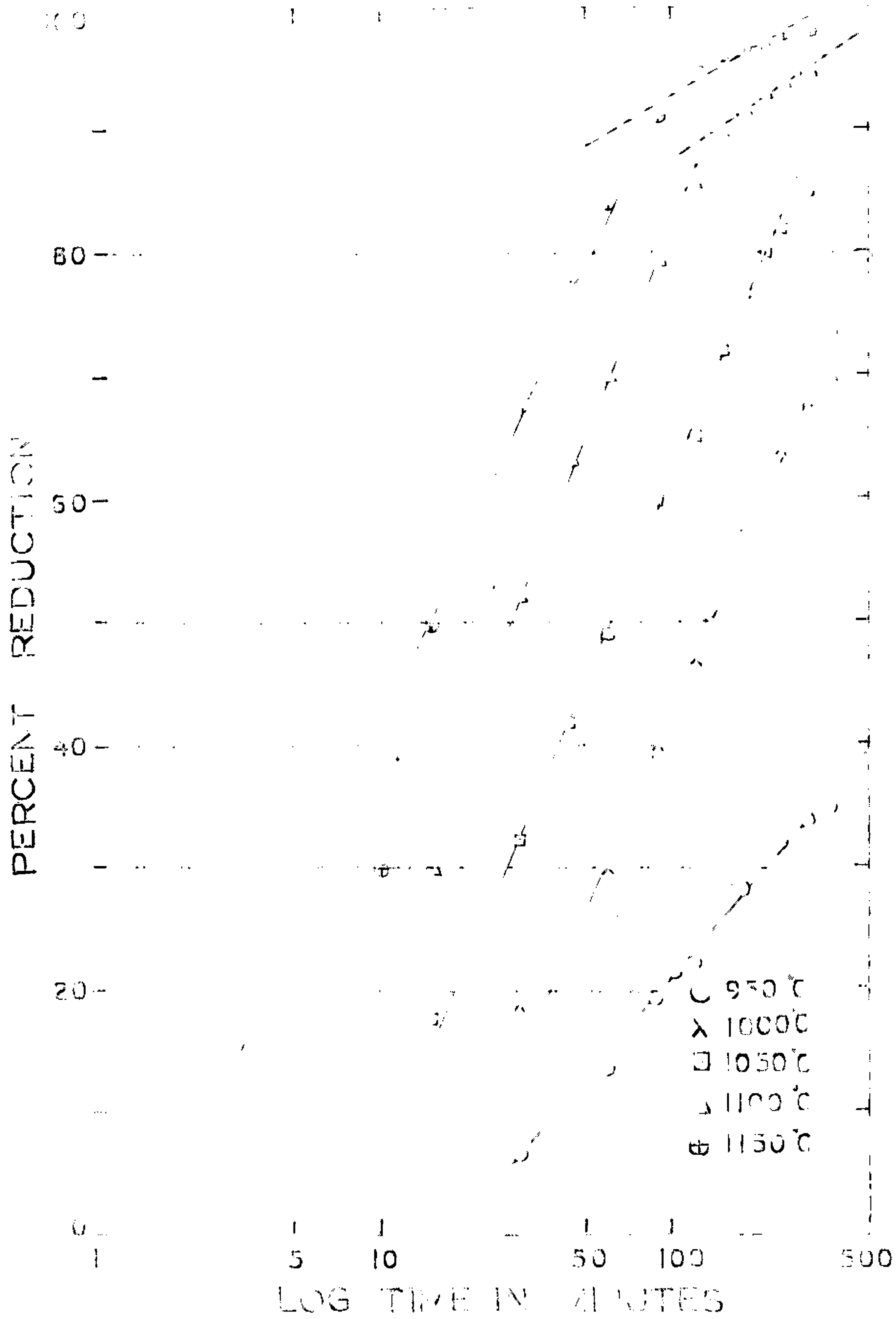


FIG.3.13_PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1mm OF Hg)

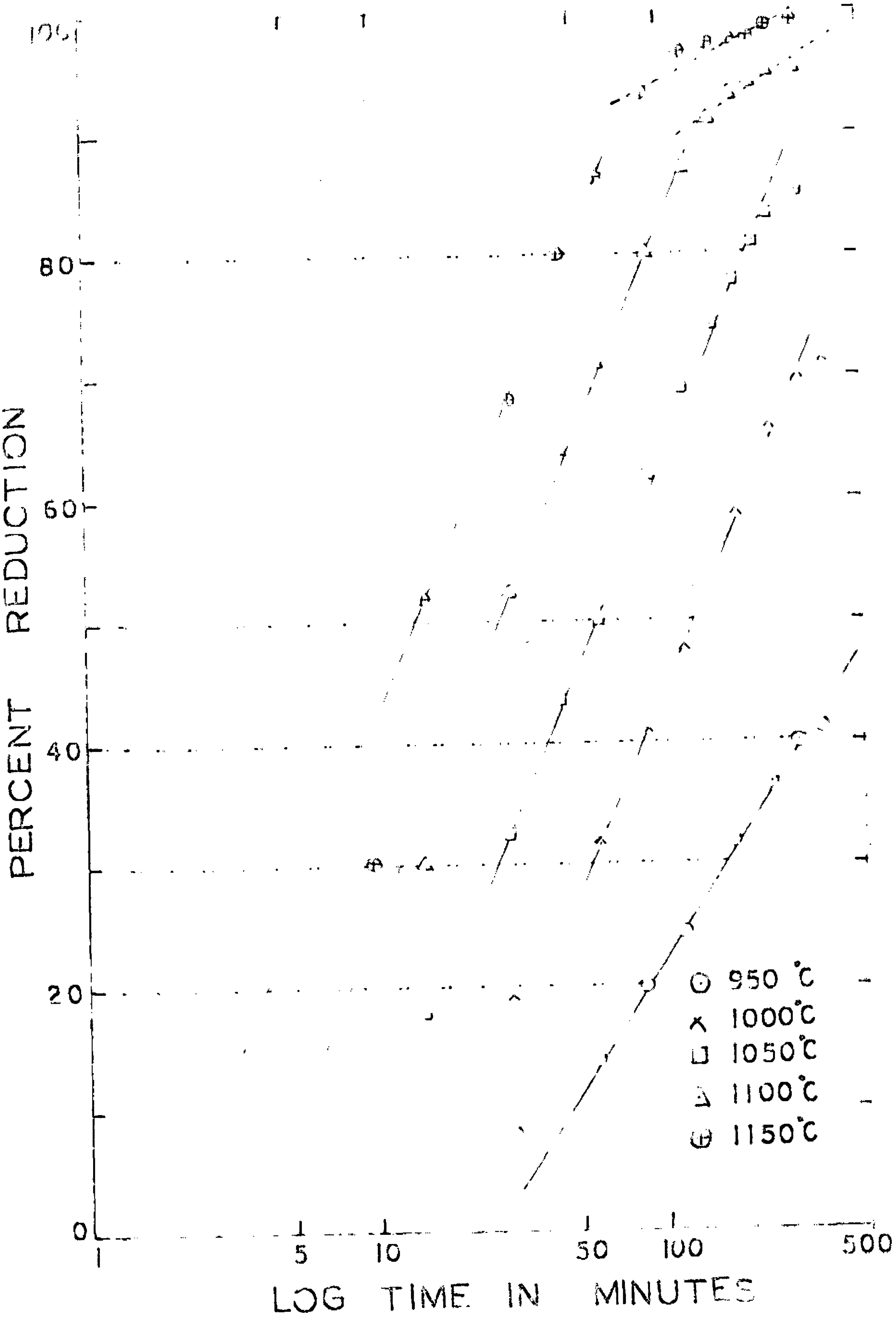


FIG.3.14_PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1mm OF Hg)

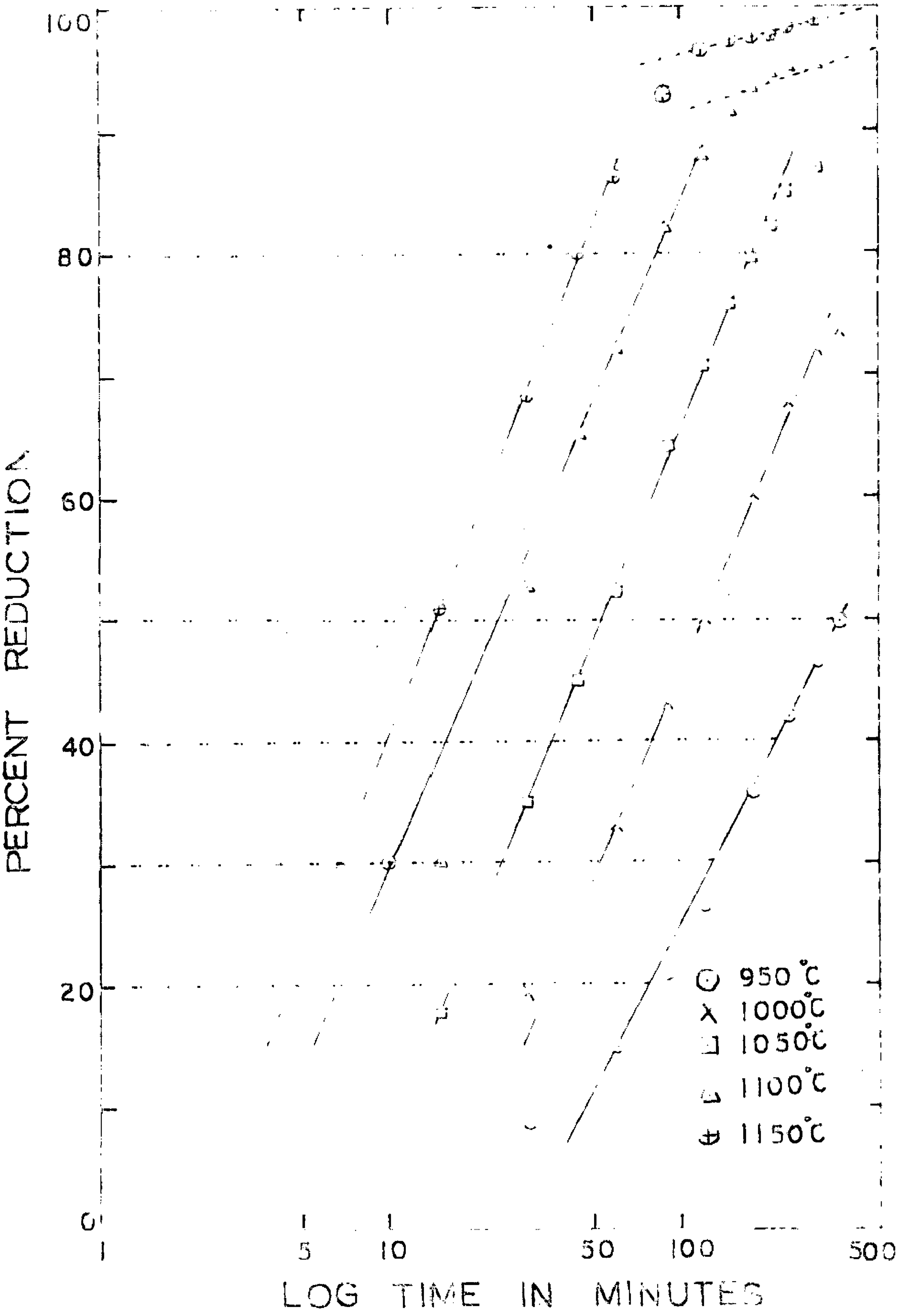


FIG. 3.15 _PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 5% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1mm OF Hg)

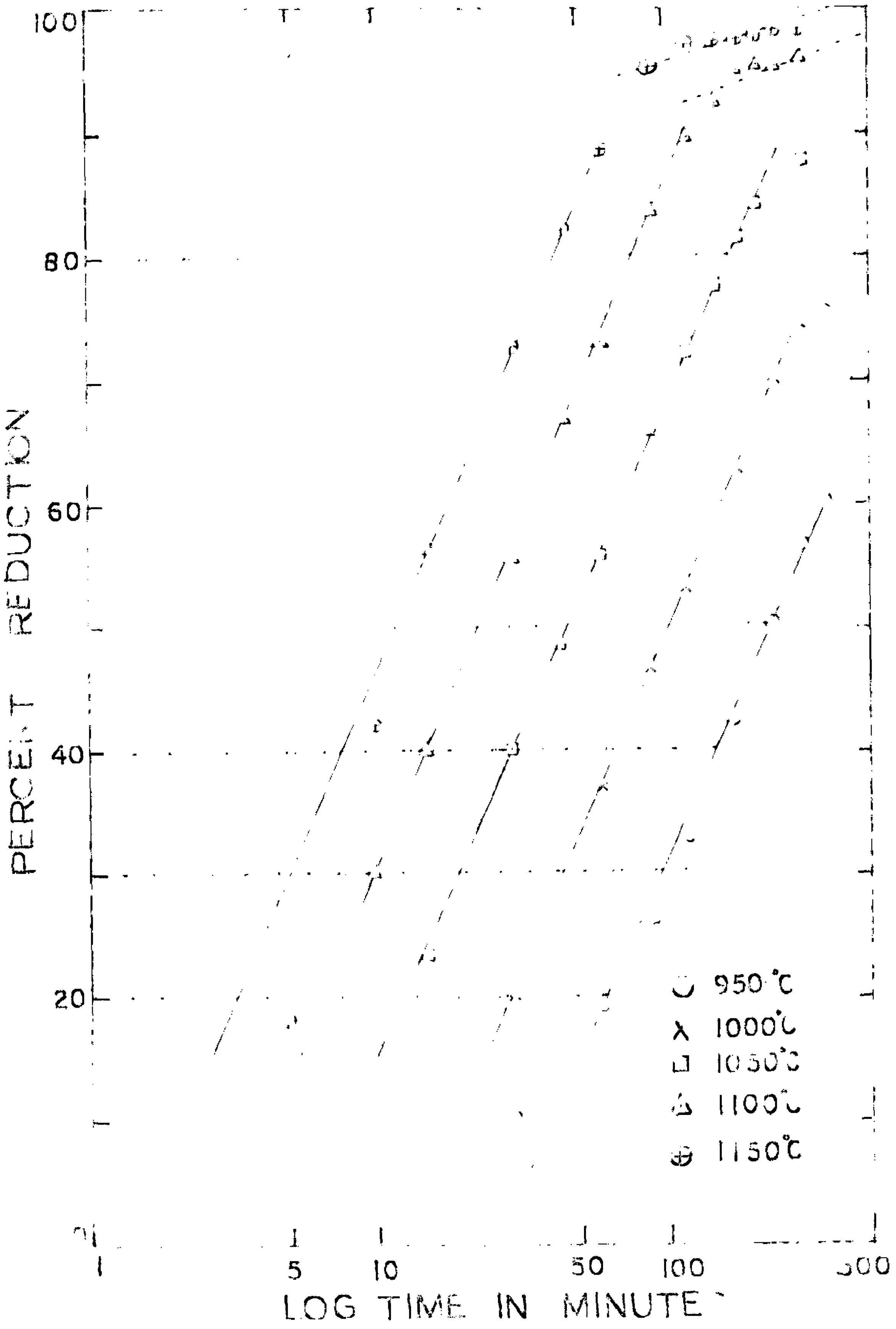


FIG.3.16_PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1mm OF Hg)

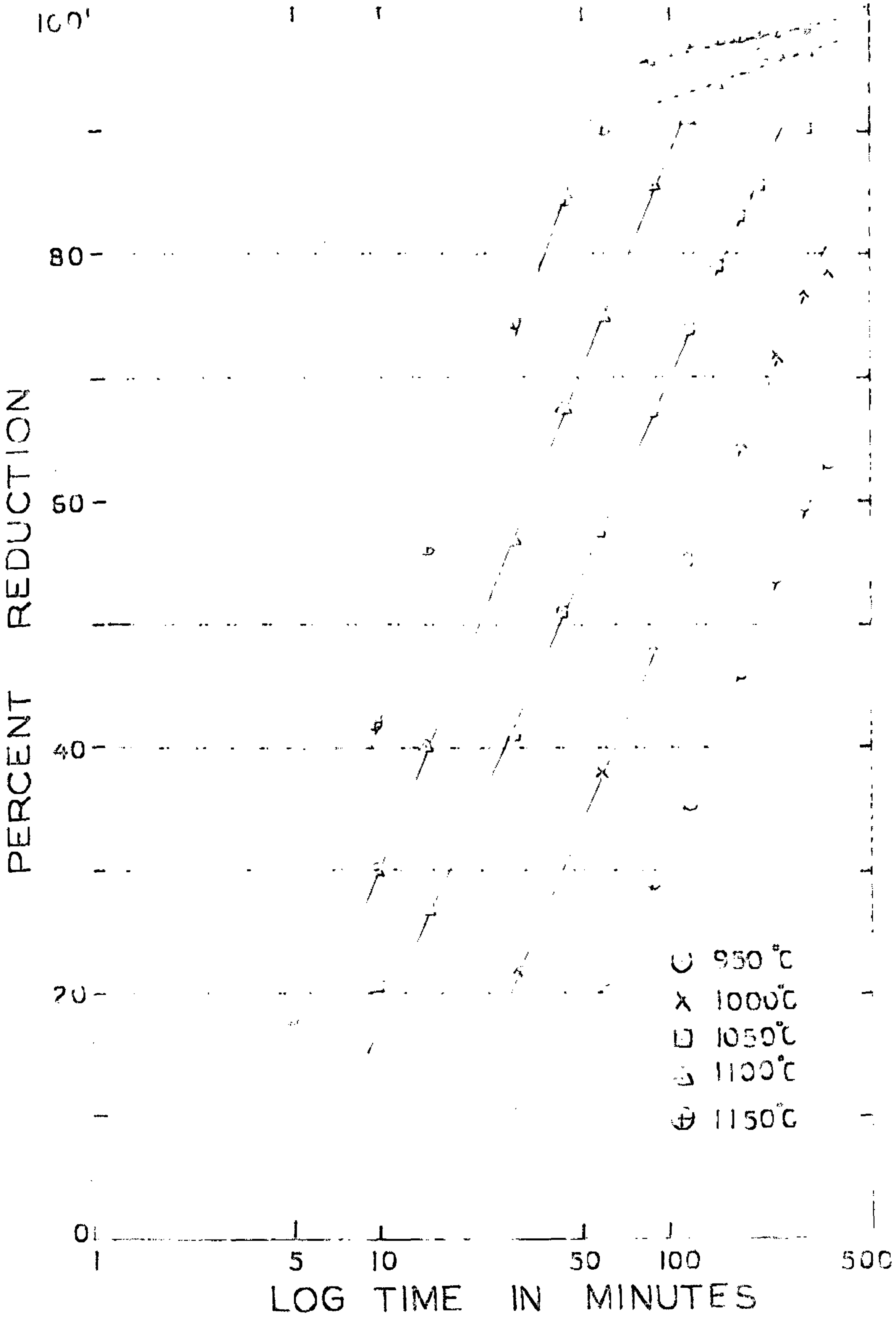


FIG.3.17_ PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0·1mm OF Hg)

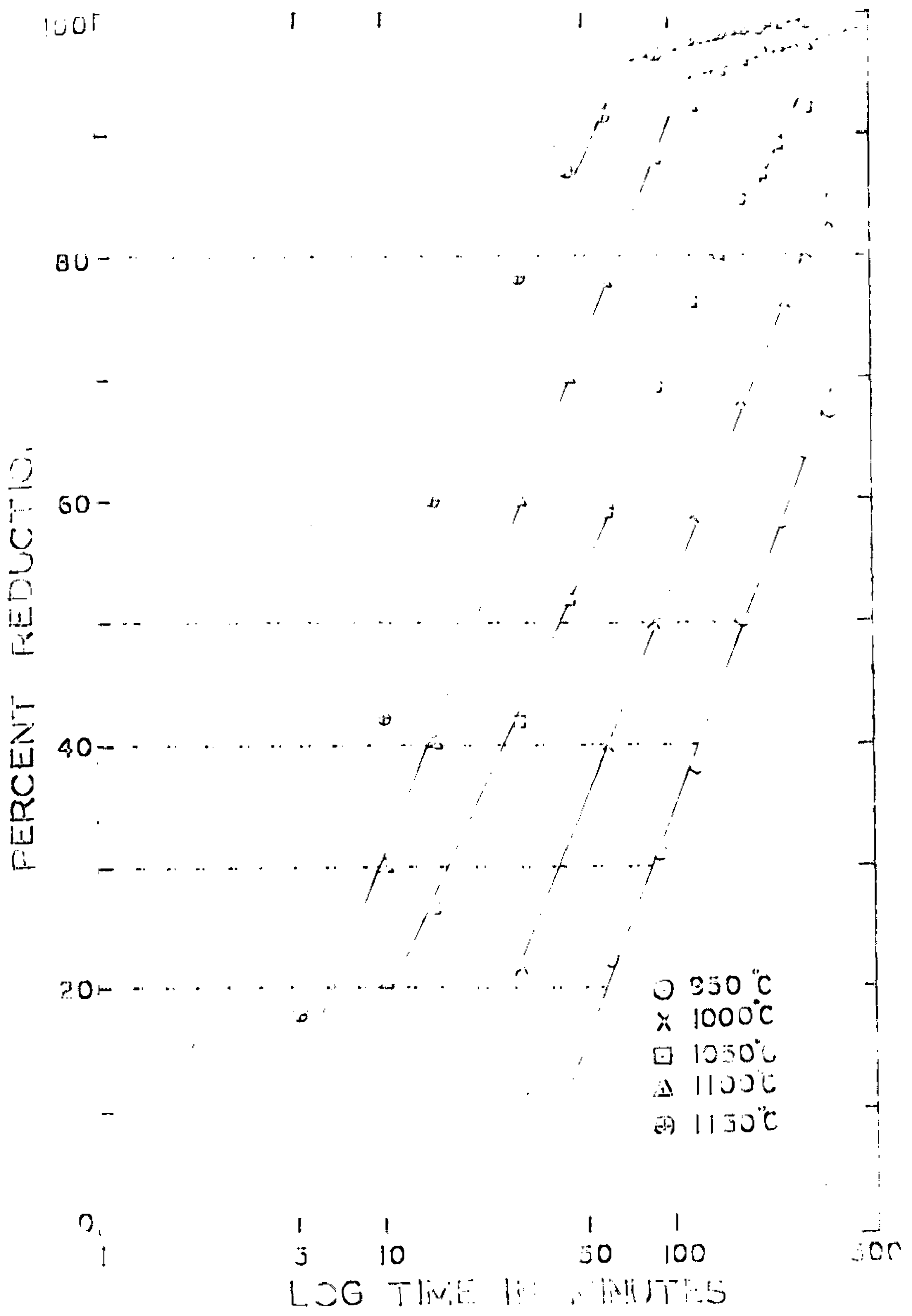


FIG.3.10_ PLOT OF PERCENT REDUCTION VS LOG TIME FOR BRIQUETTES REDUCED WITH 5% EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0·1mm OF Hg)

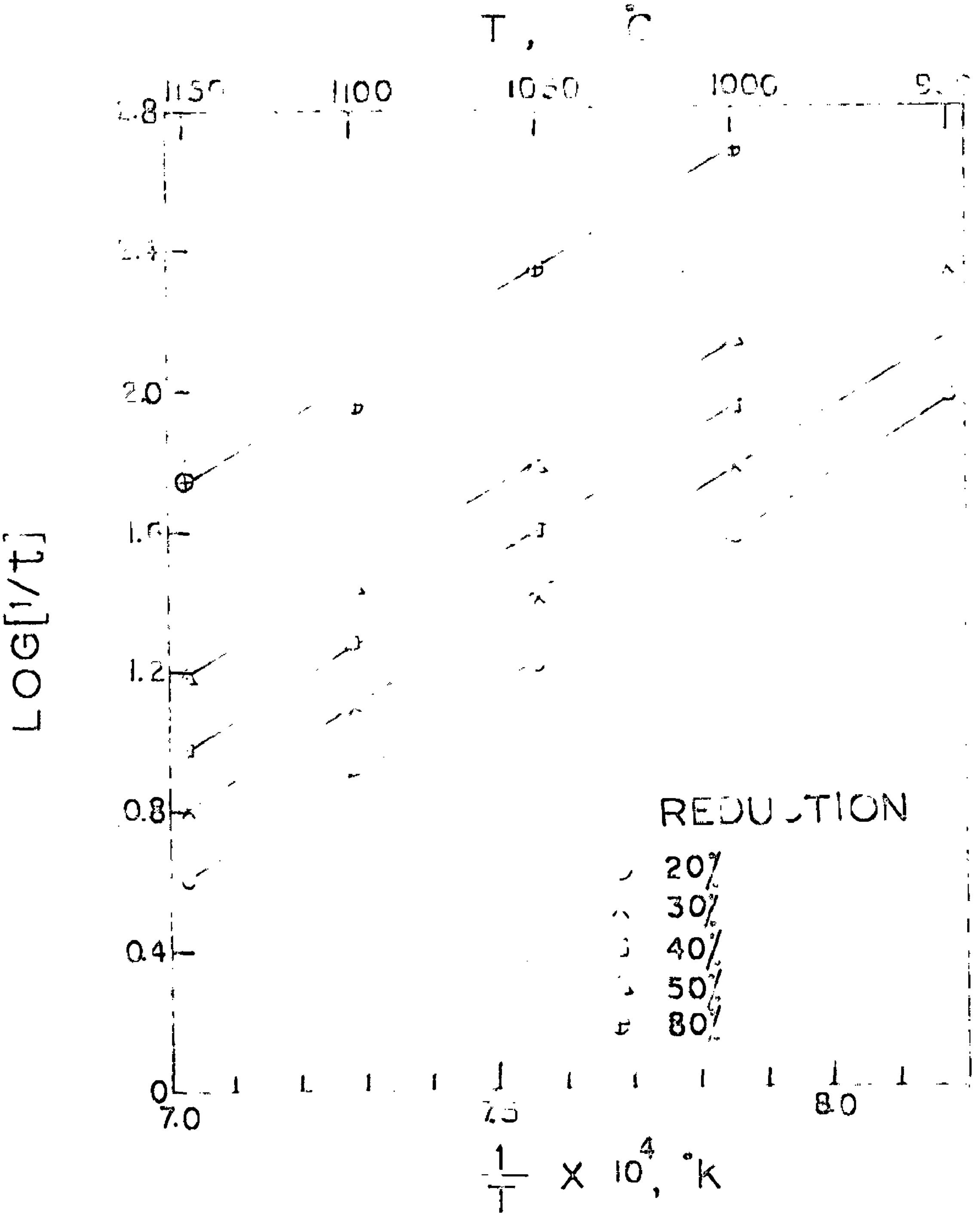


FIG.3.19 _ PLOT OF LOG(1/t)VS1/T×10$^4$°K FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1mm OF Hg)

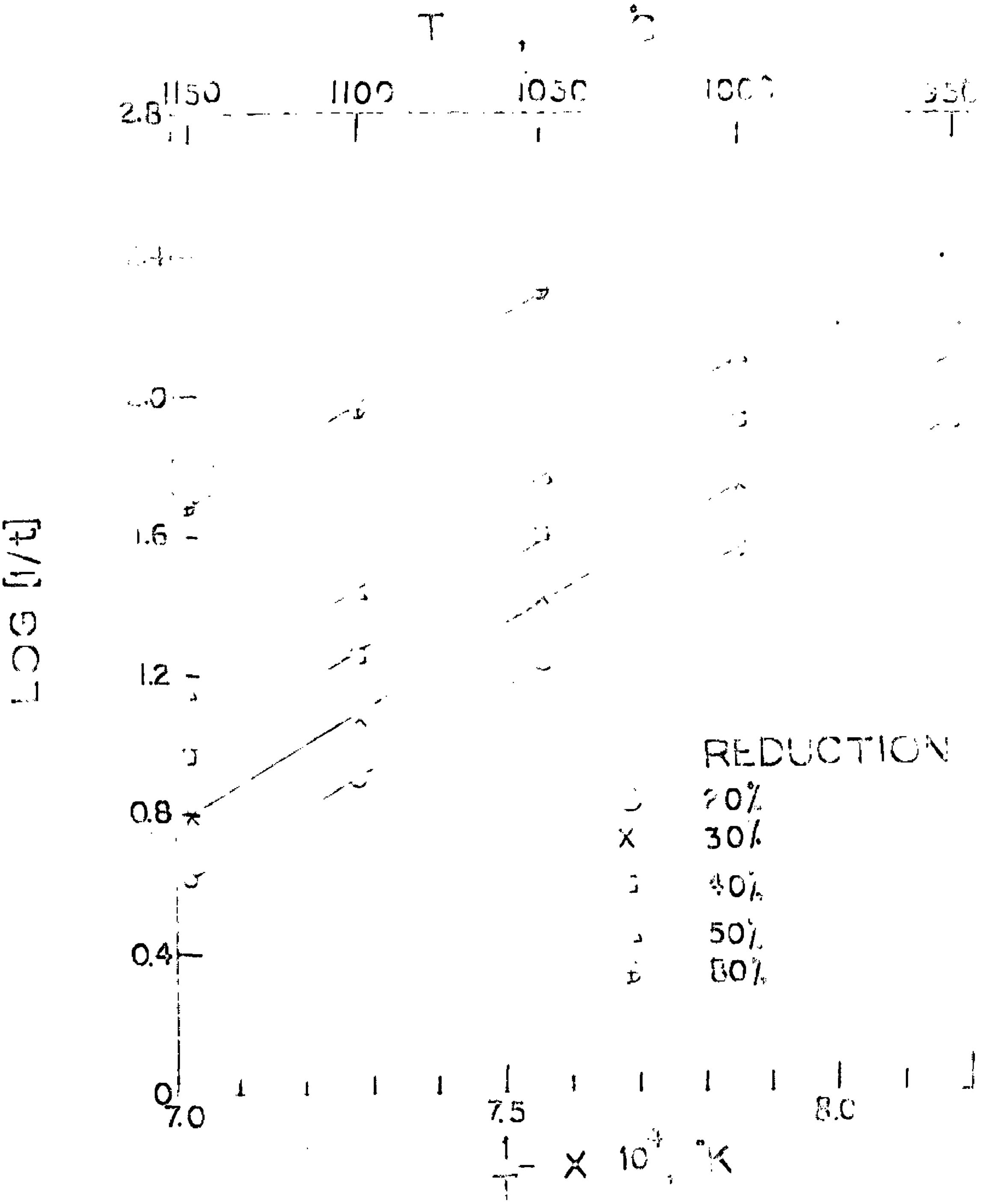


FIG 3.20_ PLOT OF LOG(1/t)VS 1/T×10$^{4}$°K FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1mm OF Hg)

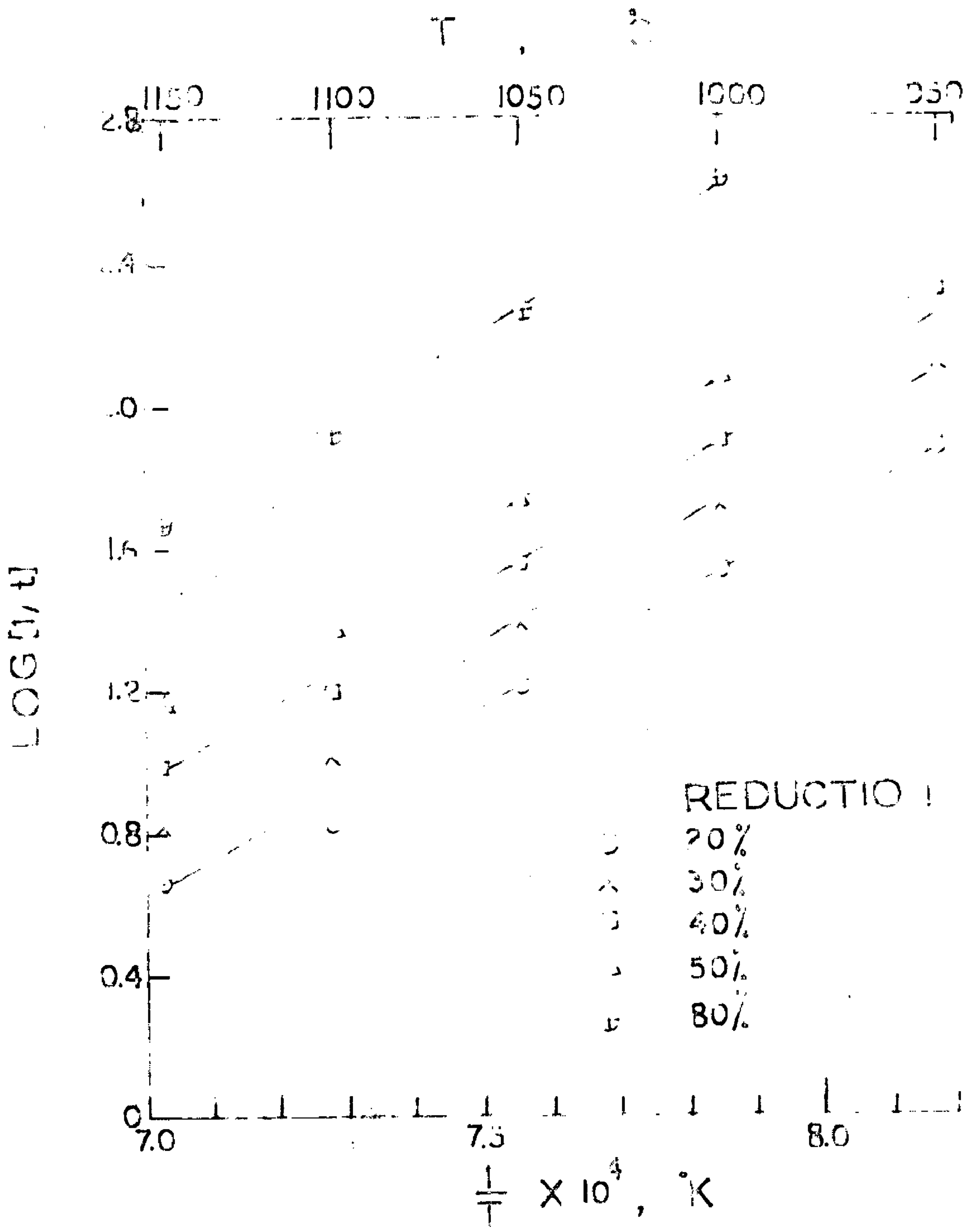


FIG. 3.21 _ PLOT OF LOG(1/t) VS 1/T $\times 10^4$ °K FOR BRIQUETTES REDUCED WITH 5% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1mm OF Hg)

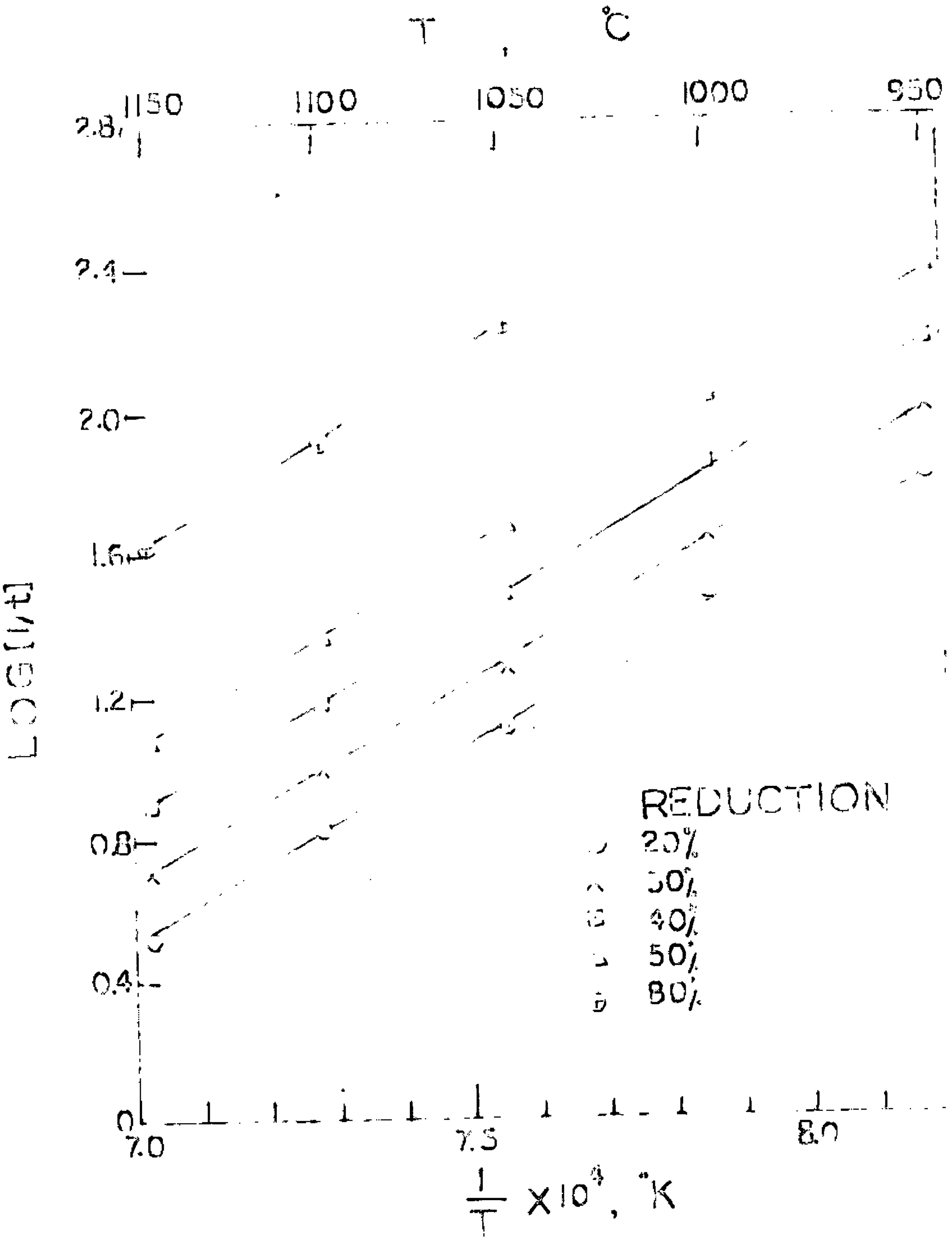


FIG. 3.22_PLOT OF LOG(1/t) VS 1/T × $10^4$ °K FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1mm OF Hg)

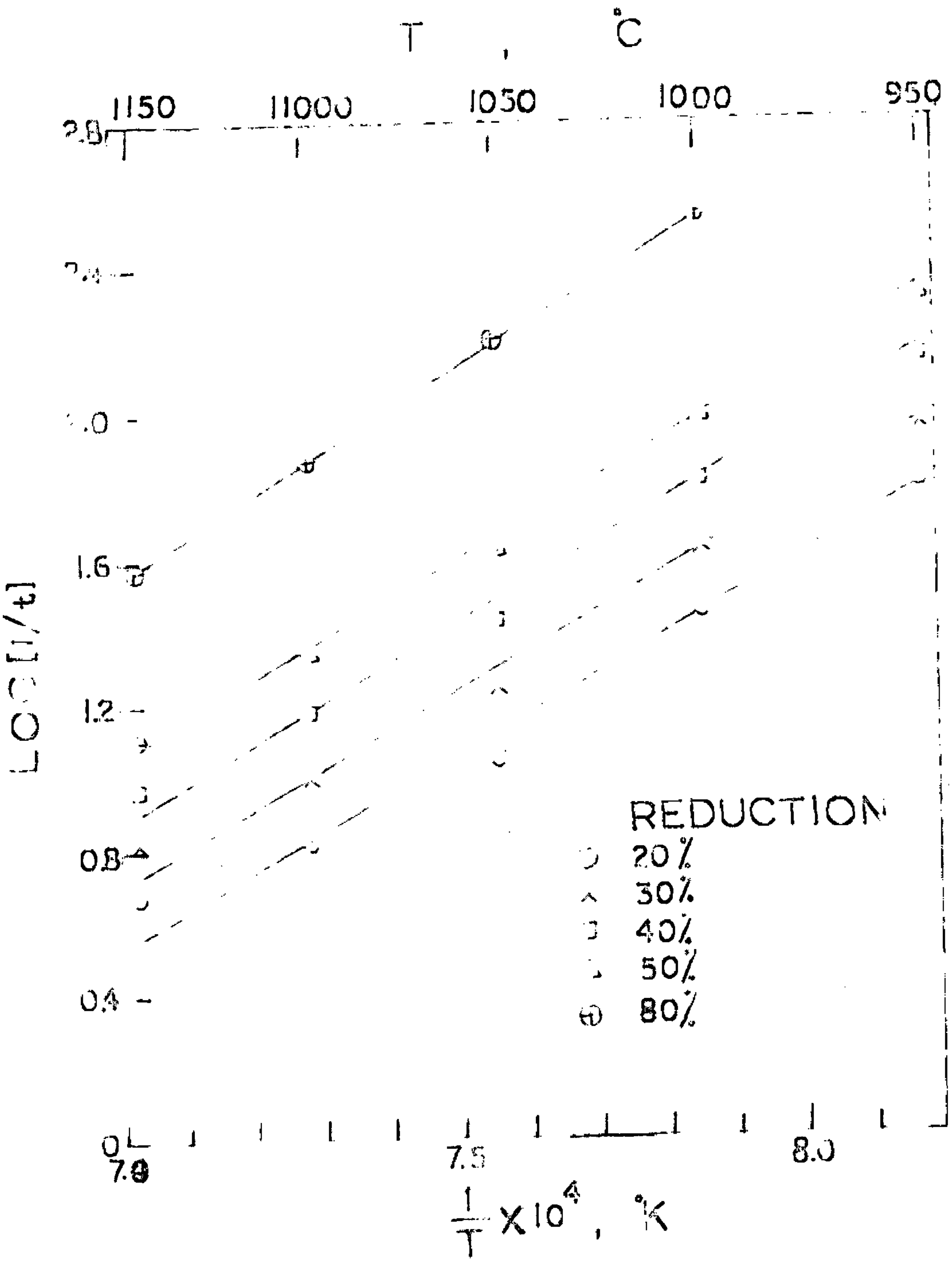


FIG. 3.23 - PLOT OF LOG (1/t) VS 1/T × $10^4$ °K FOR BRIQUETTES REDUCED WITH 3% EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1 mm OF Hg)

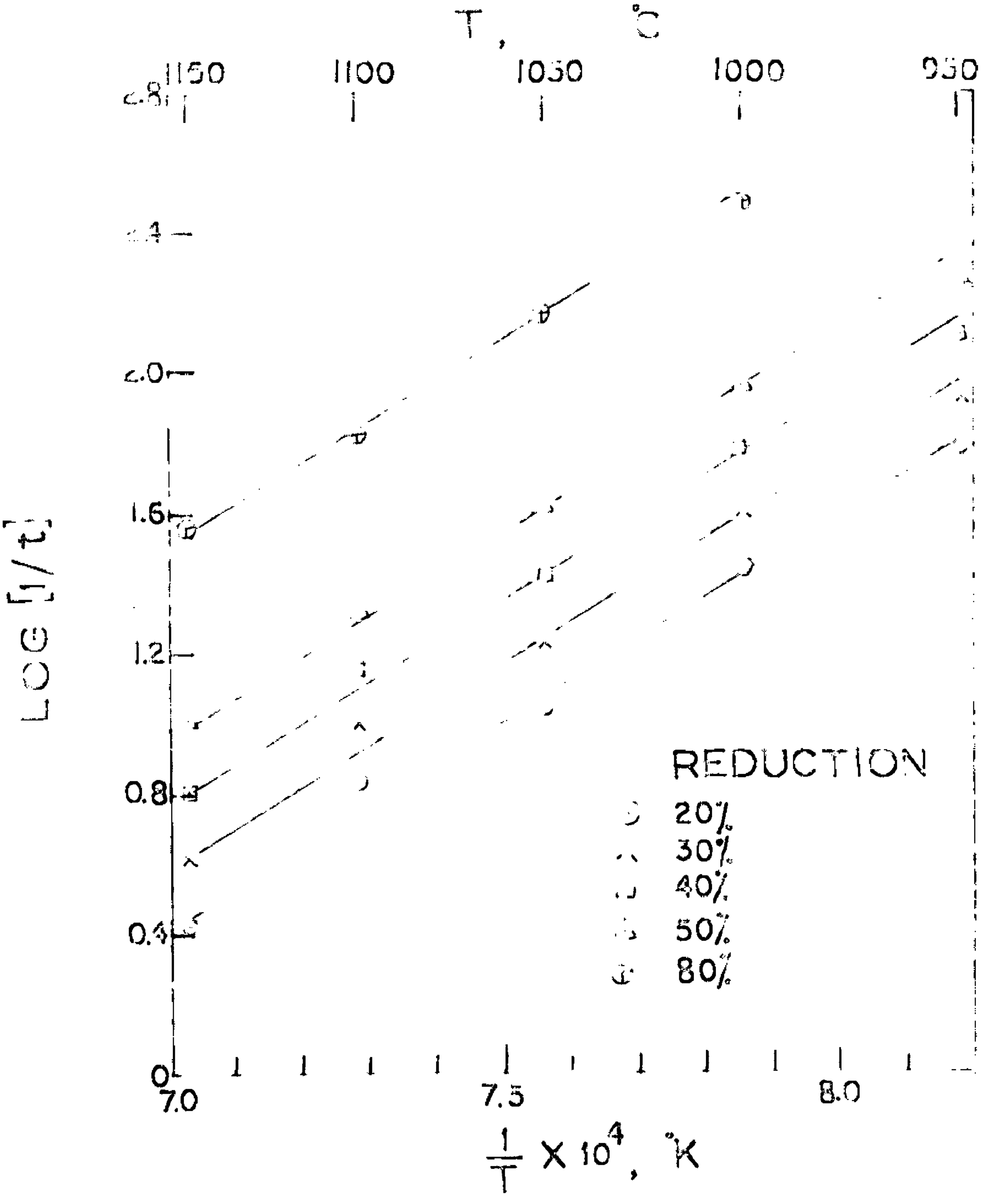


FIG. 3.24_PLOT OF LOG (1/t) VS 1/T $\times 10^4$ °K FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1mm OF Hg)

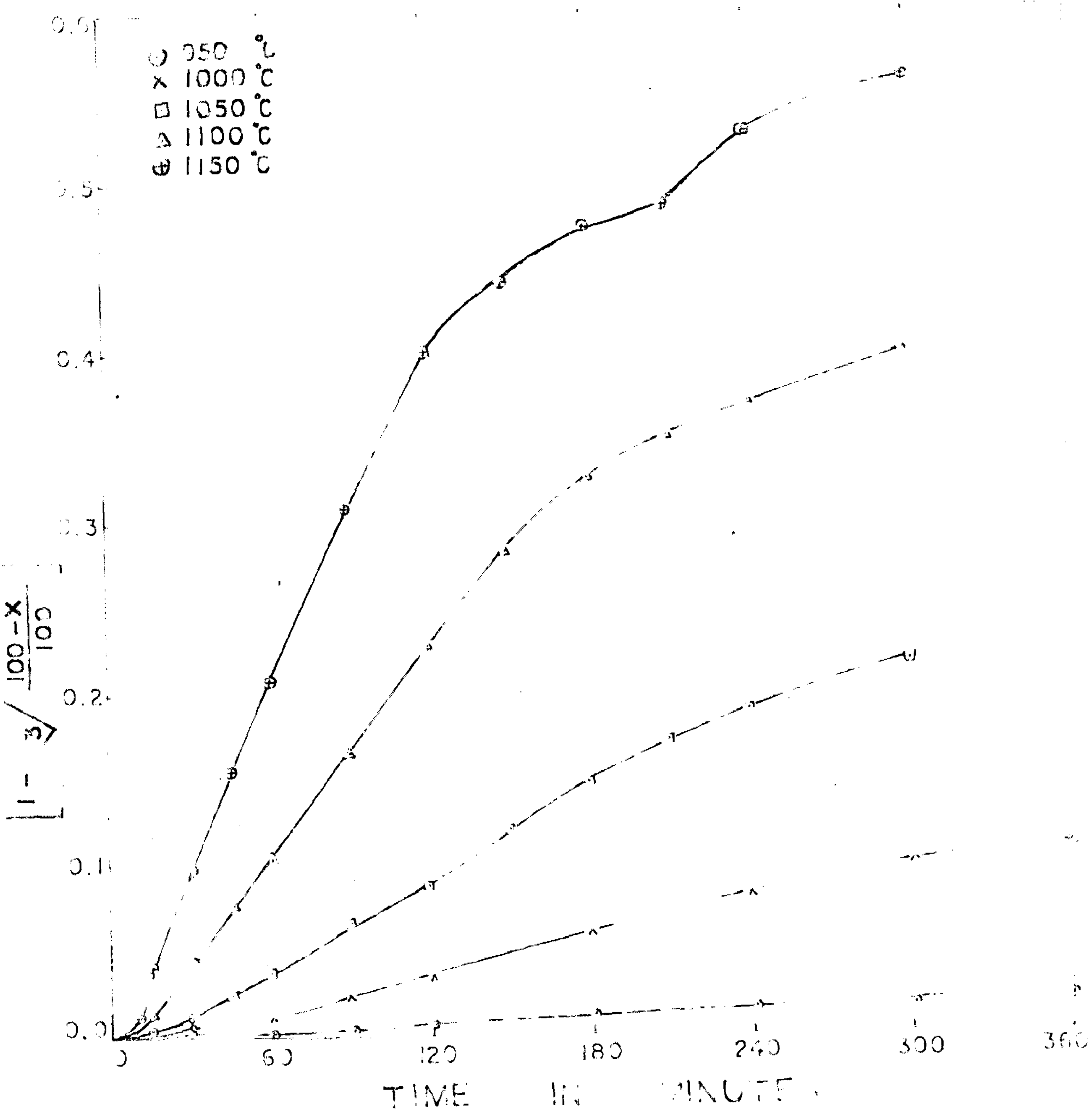


FIG.3.25 _ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1mm OF Hg)

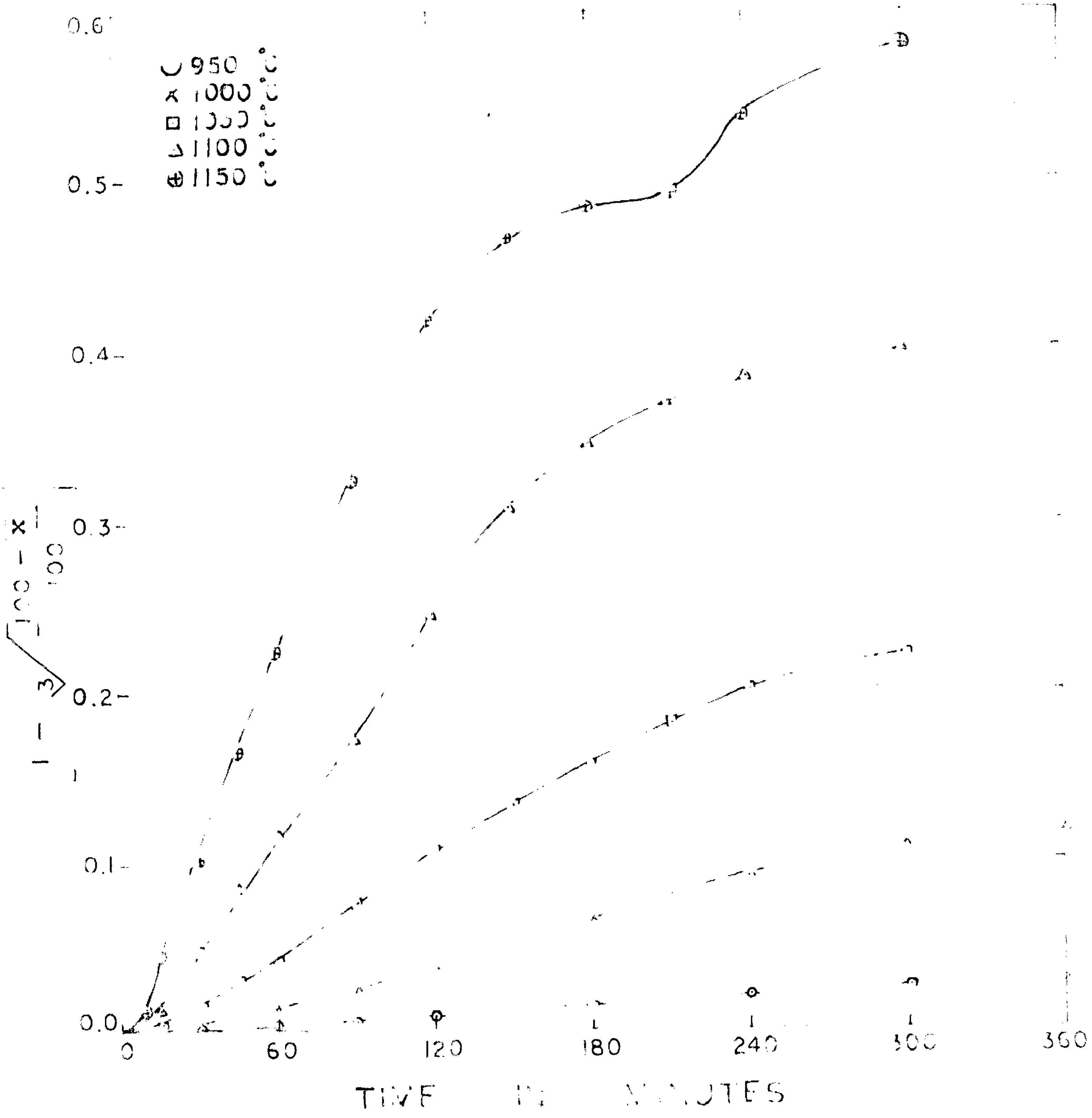


FIG.3.26_ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH 3 % EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0·1mm OF Hg)

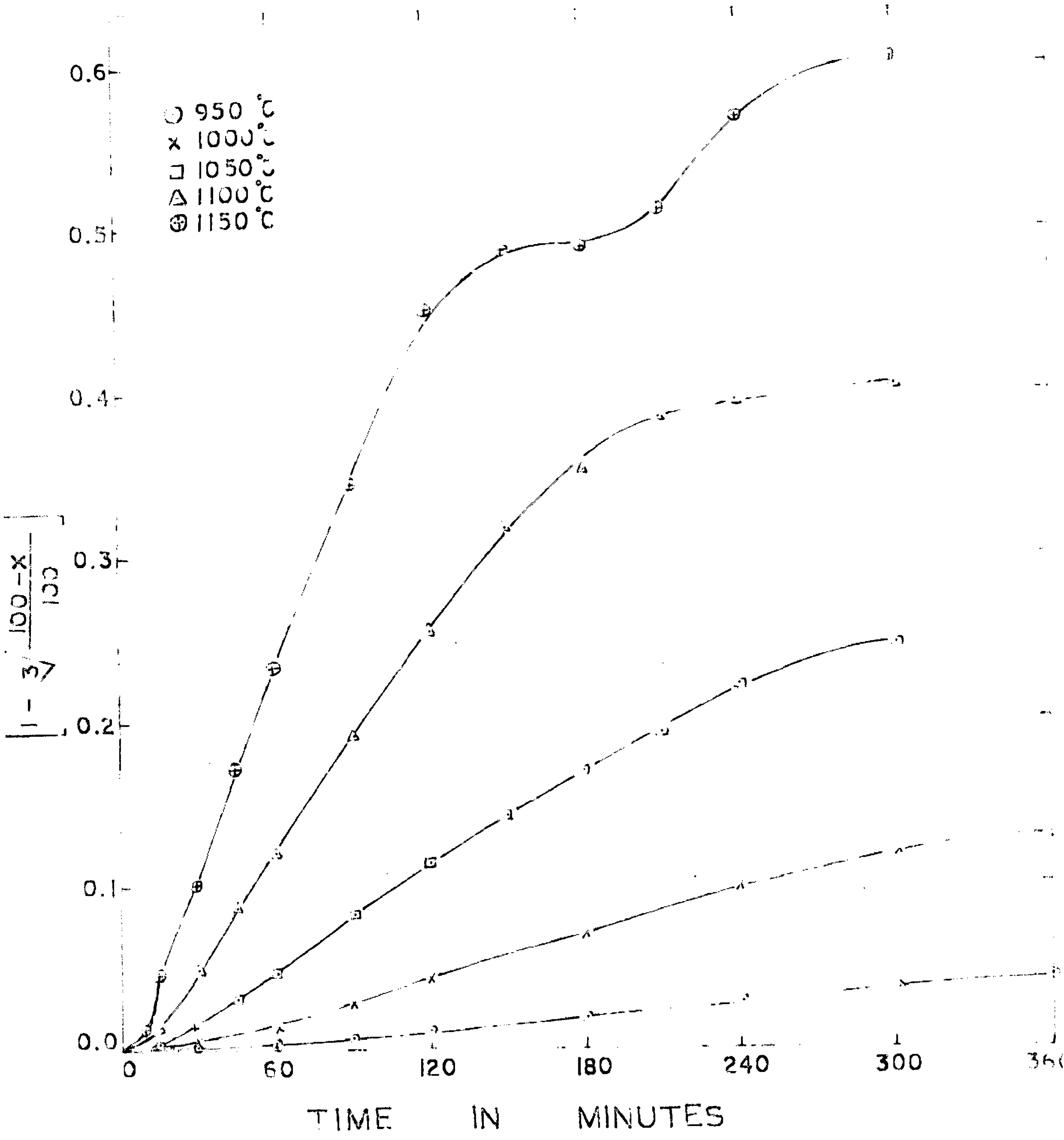


FIG.3.27_ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH 5% EXCESS THAN STOICHIOMETRIC AMOUNT OF LOW GRADE COKE UNDER REDUCED PRESSURE (0.1mm OF Hg)

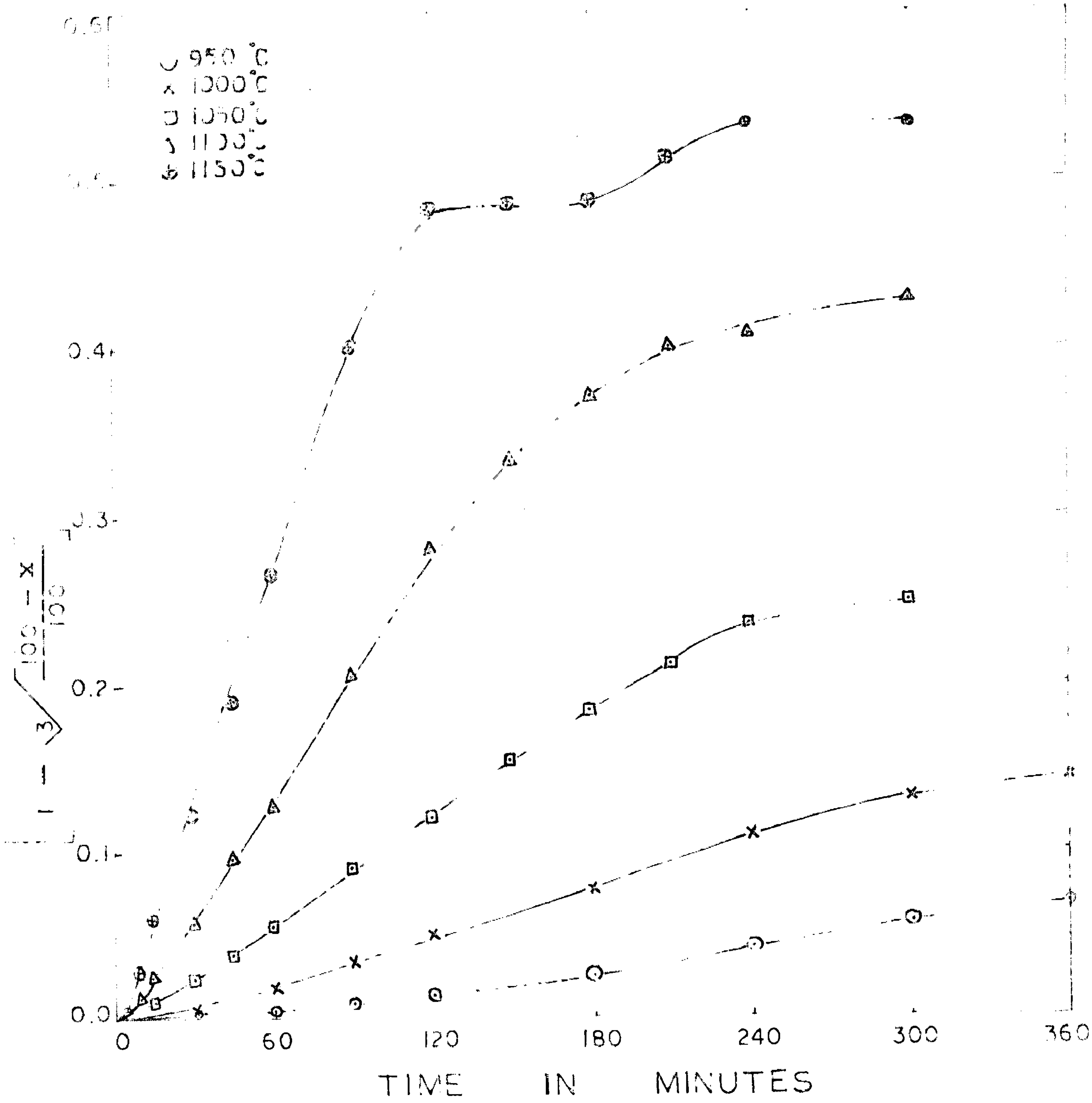


FIG.3·28_ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0·1mm OF Hg)

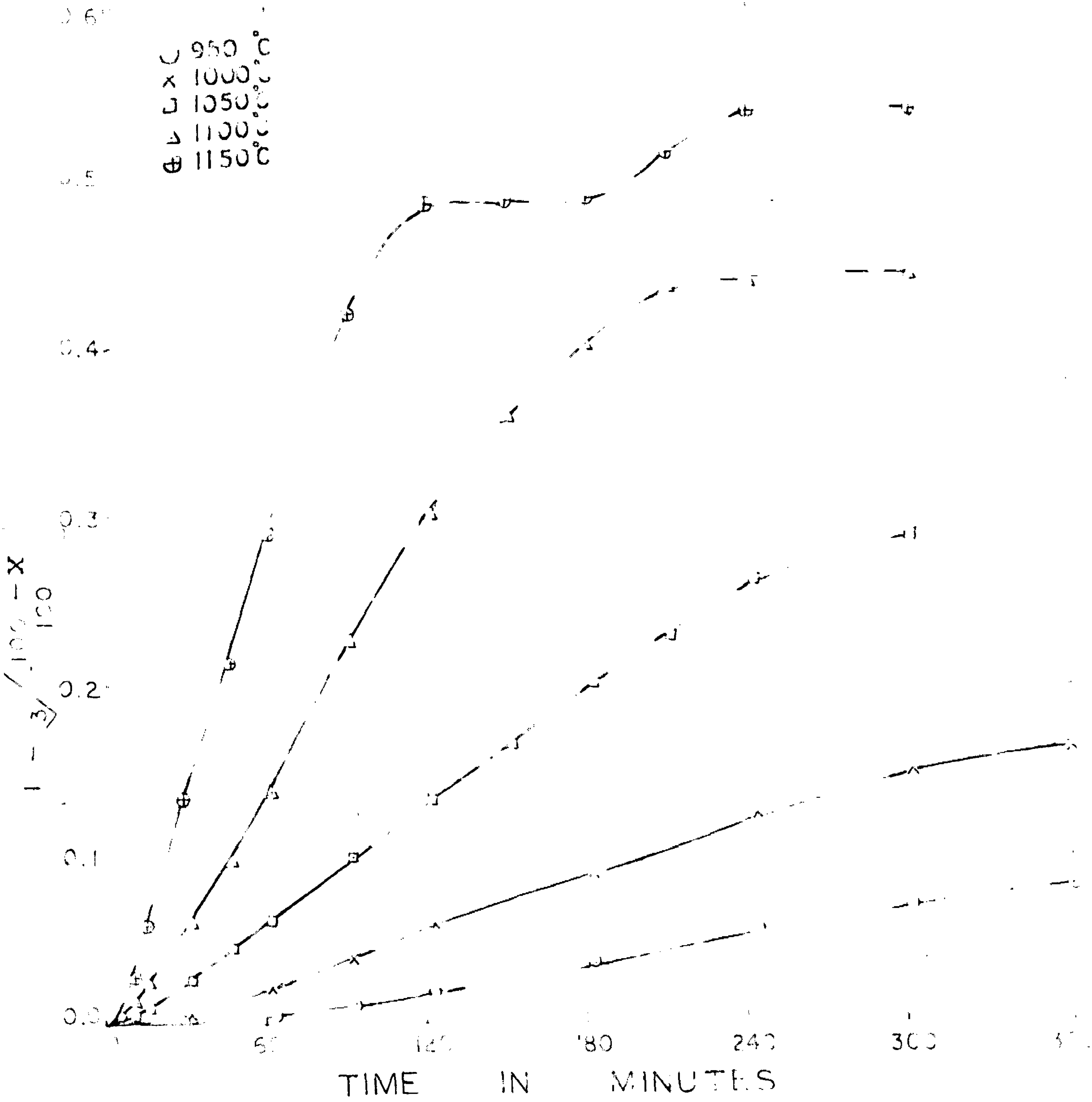


FIG.3.29_ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH 3 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0.1mm OF Hg)

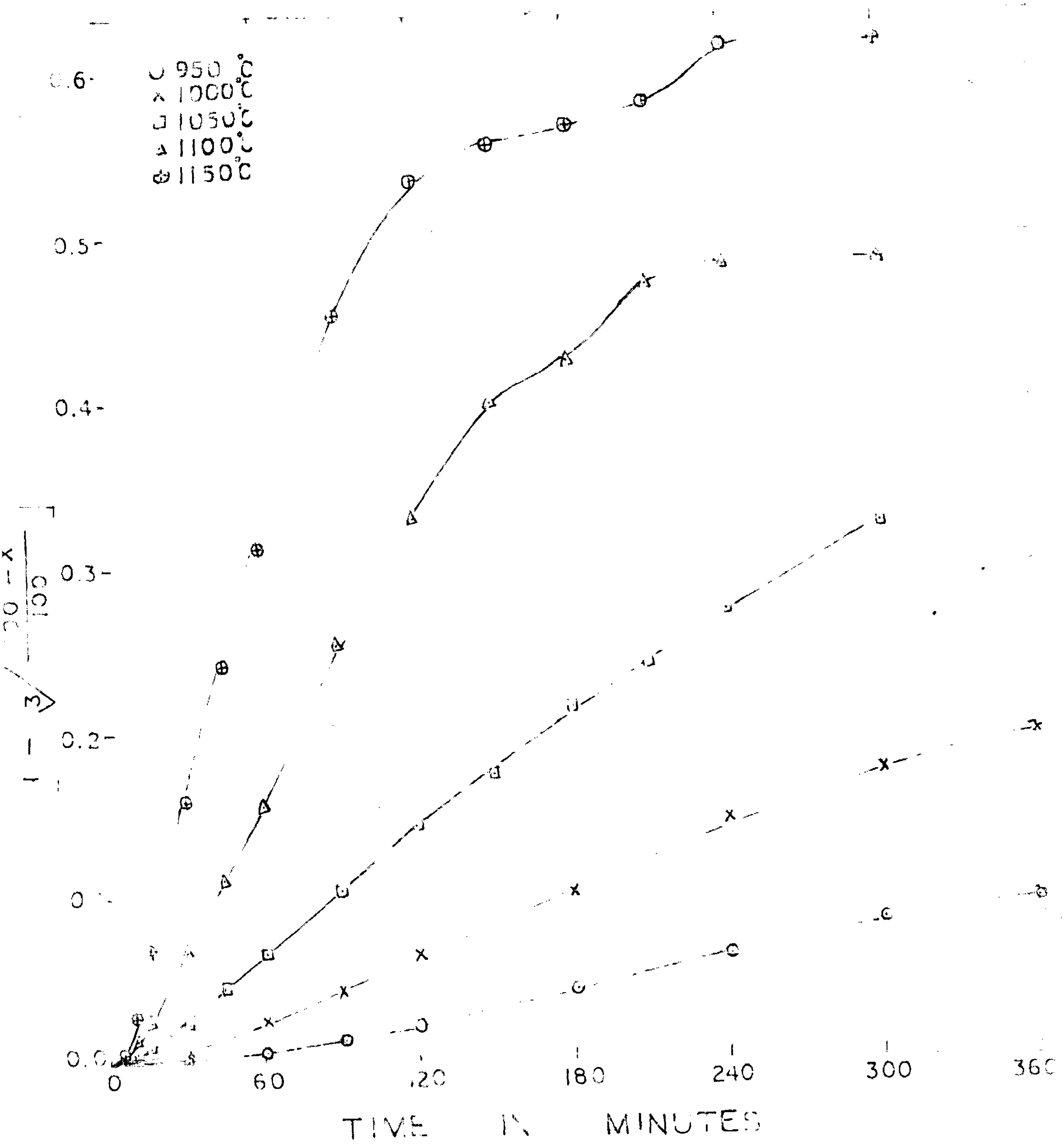


FIG.3.30 _ PLOT OF $\left(1-\sqrt[3]{\frac{100-X}{100}}\right)^2$ VS TIME FOR BRIQUETTES REDUCED WITH 5 % EXCESS THAN STOICHIOMETRIC AMOUNT OF WOOD CHARCOAL UNDER REDUCED PRESSURE (0·1mm OF Hg)

## 3.2 DISCUSSIONS OF THE RESULTS

From the results, reported above, it is seen that during initial stages of reduction, the reaction rate is relatively very high. This may be due to the surface reaction between the reactants. After sometime, when appreciable reduction (about 30% ) due to surface reaction has taken place, the results obey the semi-logarithmic rate law relationship as given in Eq.(i). The validity of semilogarithmic rate equation in the present investigation suggests that the chemical reactions at the interfaces ($Fe_3O_4/Fe_2O_3$, $FeO/Fe_3O_4$ and Fe/FeO) do not control the rate of reduction of iron oxide. Hence, after 30% reduction and below 85% reduction the following steps can be considered to elucidate the exact mechanism of iron oxide reduction.

(a) Diffusion of carbon through iron to Fe/FeO interface.

(b) Diffusion of iron through FeO to $FeO/Fe_3O_4$ and subsequently through $Fe_3O_4$ to $Fe_3O_4/Fe_2O_3$ interface.

(c) Diffusion of oxygen through iron to Fe/C interface and subsequently reacting with carbon.

If the rate of carbon diffusion controls the overall reaction velocity, then as suggested by Jander[19], there should be linear relationship between $(1-\sqrt[3]{\frac{100-X}{100}})^2$ and time, where X being percentage of reduction. However, no linear relationship is obtained with both types of reductants (low grade coke and wood charcoal) in the temperature range

960 to $1150^{\circ}$C for different amounts of reductants in the present investigation as shown in figures 3.25 to 3.30. This indicates that carbon diffusion through iron to Fe/FeO and subsequent diffusion to FeO/$Fe_3O_4$ interfaces does not control the rate of reduction.

Now one is left with steps (B) and (c), which are likely to control the rate of reduction. It has been shown by Brichenell[26] and co-workers that diffusion of iron through iron oxide is faster than that of oxygen in iron. This observation is also supported by the larger ionic radius of oxygen ions ($O^{2-}$ = 1.32 Å) as compared with that of $Fe^{2+}$ and $Fe^{3+}$ ions (0.87 Å and 0.67 Å). Thus it can be said that diffusion of iron through FeO or $Fe_3O_4$ controls the rate of reduction. The activation energy values found in the present investigation for the briquettes reduced with stoichiometric, 3% excess and 5% excess than stoichiometric amounts of low grade coke and wood charcoal are given in table X and found to be in close agreement with the reported value (55 Kcal/gm mole), for diffusion of iron through $Fe_3O_4$. Hence, diffusion of iron through $Fe_3O_4$ is the most probable rate determining step.

The semi-logarithmic rate law as shown by Eq.(1) is found to hold good even above 85% reduction. But the slope of the lines considerably changes after

85% reduction which is a suggestive of the change in mechanism of iron oxide reduction. Due to lack of experimental data,the exact mechanism above 85% reduction could not be suggested.

# CHAPTER - IV

# APPLICATIONS OF PRE-REDUCED BRIQUETTES

## 4.1. INTRODUCTION

The pre-reduced briquettes with sufficient degree of metallization can provide an attractive substitute for conventional scrap used in electric arc and LD. Steel making converters. They can also provide a ready means of increasing hot metal production from blast furnace when demand is high. Pre-reduced agglomerates in the form of iron powders after subjecting to crushing and magnetic separation treatment can also be injected through tuyeres in the blast furnaces. This iron powder can also be used as a coolant material in the steel making processes.

## 4.2 QUALITY REQUIREMENTS OF PRE-REDUCED BRIQUETTES FOR BLAST FURNACE CHARGE

The blast furnace is a kind of counterflow reactor in which the descending burden reacts with the ascending reducing gases. Thus, the pre-reduced briquettes charged in the furnace are under severe conditions of pressure and temperature. So the pre-reduced agglomerates must possess certain following properties[3] otherwise, their disintegration occurs which causes deterioration of the furnace performance resulting, consequently, in the decrease of blast furnace efficiency.

### (A) Physical Properties

The pre-reduced briquettes should have sufficient physical strength to withstand mechanical handling at the time of charging in the blast furnace and subsequently to withstand heavy loads under which the charge comprising of pre-reduced briquettes is put in the furnace. Moreover, beside having physical strength, briquettes should also have a proper size distribution i.e. neither excessive amount of fines nor lumps, as they lower down the smelting efficiency of the furnace.

(B) Behaviour at high temperature

Pre-reduced agglomerates, when charged into the furnace, are firstly heated by upstreaming hot gases and then reduced by carbon. Melting takes place in the lower parts of the furnace. In this course of treatment, the pre-reduced agglomerates should neither swell nor generate fines as they impair the smooth operation(27) of the furnace.

(C) Chemical Properties

The pre-reduction, whether carried out at mine or steelworks, pre-reduced agglomerates must have sufficient resistance to reoxidation against atmospheric oxygen and humidity.

The presence of alkali elements such as Zn, Pb and like others are harmful as they accelerate the wear of the lining. Some of the detrimental elements like Cu, Ni etc. can not be separated from iron in blast furnace or in steel making processes, pre-reduced materials should not contain those elements as far as possible.

The presence of slag forming constituents such as $SiO_2$, $Al_2O_3$ etc. in pre-reduced agglomerates are not desirable. Their presence increases thermal load on the furnace, slag volume, lime consumption and thus productivity is affected.

(D) Degree of Reduction

The advantages of using pre-reduced briquettes viz. decrease in coke rate and increase in production depend largely on degree of reduction[28]. This can be better realized when we consider that pre-reduction of hematite to wustite, where degree of reduction is only 33%. , is meaningless as much of the oxygen is still to be removed. Marked improvement in productivity can only be expected when pre-reduced materials contain large amount of metallic iron, in other words by achieving high degree of reduction. The best results are obtained with 100% pre-reduction. But this much reduction from practical point of view, can only be obtained at the expense of strength of pre-reduced briquettes as to achieve 100% reduction, excess amount of solid fuel would be needed which would decrease the strength of pre-reduced briquettes. Therefore, the degree of reduction, generally reached, is in between 70 to 90% .

## 6.3 APPLICATIONS OF PRE-REDUCED MATERIALS IN IRON AND STEEL MAKING

The applications of pre-reduced agglomerates in iron and steelmaking can be classified and discussed in the following way.

(A) Pre-reduced agglomerates in iron making,

(B) Pre-reduced agglomerates in steel making,

  (i) Oxygen steel making,

  (ii) Electric arc steelmaking

  (iii) Continuous steelmaking.

### 4.3.1 PRE-REDUCED AGGLOMERATES IN IRON MAKING

Blast furnaces on account of their excellent productivity and economics occupy a unique position in the field of iron making. However, its supremacy has been threatened all over the world by the growing shortage of metallurgical grade coking coal. The scientists and technologists are actively carrying out researches with a view to increase the productivity and decrease the coke rates in the blast furnace. Utilization of pre-reduced burden is one such step in the way of achieving [29] these objectives.

Pre-reduced materials in the blast furnace decrease the coke rate and increase production. Their use have been realised in two ways.

(i) Injection of pre-reduced materials in the form of iron powder through tuyeres in an experimental blast furnace.

(ii) Charging of pre-reduced agglomerates in experimental blast furnace.

The experimental results thus obtained, agree well with the theoretical calculations and can be expressed in terms of increase in production and decrease in coke rate.

Steel company of Canada[4] has achieved 23% increase in productivity and 20% decrease in coke rate by charging pre-reduced pellets (88.7% Fe and 90.6% metallization) which comprises of 30% of the total charge. At Hegachide plant, Yawata (Japan), 18.4% increase in production and 18% decrease in coke rate have been obtained [4] by charging sponge iron (69% Fe and 56% metallization) comprising of 40% of the total charge. On average, it can be said that each percent of pre-reduction increases productivity and decreases coke rate by approximately 1% and 1/2% respectively. The injection of pre-reduced materials in the form of iron powder through tuyeres in the blast furnace have also been reported to be economical.

The most favourable conditions [30] for the application of pre-reduced agglomerates in iron making occur, when

(i) the existing blast furnaces can not cope up with country's requirement for iron and steel.

(ii) the cost of coke delivered to the blast furnace is high.

The use of highly metallized burden in the blast furnace is still open to question as pointed out by Astier [30]. Since, already a higher percentage of oxygen is removed during pre-reduction, a high shaft of existing blast furnace seems more or less useless as now it has to perform only melting and refining functions.

However, use of metallized agglomerates in electric smelting furnace seem to be justified [31] because of the following reasons,

(i) There is no pre-reduction inside the furnace

(ii) Large decrease in electrical energy requirements and building up of high voltage transformers lead to erection of electrical smelting units in the range of 1200-2000 metric tons of hot metal/day.

### 4.3.2 PRE-REDUCED AGGLOMERATES IN STEEL MAKING

The pre-reduced agglomerates can be used as a coolant material or as a substitute for scrap in L.D. steelmaking process. But very little work has been reported[31] in the literature as far as the use of metallized materials in L.D. converter is concerned. It has been established[31] that the semi-continuous feeding of metallized ore of high iron content to L.D. converter during the fourth and eighth minutes of the blowing period produces very satisfactory results.

Tests carried out on 35 ton experimental converter with metallized agglomerates have shown that conversion to steel can take place without ejection and semi-continuous charging during the blow can give rise to favourable cooling. Japanese steelmakers have also indicated the favourable advantage of using metallized materials in L.D. steelmaking. The following few advantages of using metallized materials have been mentioned.

(i) Uniformity in size and chemical composition,

(ii) Ease of handling and weighing,

(iii) Increased control over final composition of steel.

(iv) Rapid melting, with a consequent reduction in tap to tap interval time.

## (B) Electric Steelmaking

Before the World War II, due to high cost and low production, electric arc furnaces were mainly used for the production of alloys and special steels. In the early 1950's,[32,33] as cost of power and scrap reduced, the arc furnaces were used also for production of mild steels and flat products. Many economic and technological improvements e.g. improved furnace design, ultra high power concept, adaptibility to continuous casting and/or pressure pouring etc. have brought the arc furnaces into prominent position all over the world.

Pre-reduced briquettes with high degree of metallization have been shown to be an excellent feed for electric arc furnaces. It has been anticipated[34] that the mixture of pre-reduced iron ore and scrap reduces the power consumption by 10 to 25% and heat timings by 12 to 35%. Rates of electrode wear and refractory lining are improved and the air pollution problem is decreased to minimum. Sibakin and his colleagues[35] have reported that the heat times for melts with sponge iron assuming 5%. acid gangue would be considerably less, at any sponge percentage, than the heat times of all scrap heats. Miller(34) has commented over this and suggested that gangue and unreduced FeO in metallized agglomerates will raise the power consumption and melt time, as the metallized ore proportion increases beyond 60% . However, it can be assumed that pre-reduced ore and scrap [36] are ideal electric furnace steelmaking feeds.

It is worthwhile to mention the results of the trials carried out at steel Company of Canada[31] on an experimental scale and at Luken Steel Company U.S.A.(37) on commercial scale. Steel Company of Canada could achieve 45% increase in productivity in experimental electric furnaces by employing continuous charging methods. A substantial reduction in the overall heat time and refractory consumption has been reported[31], by the virtual elimination of the normal refining period associated with all scrap heats. Commercial scale tests carried out by Luken Steel Company, U.S.A. reported that in the large furnace tests, electric energy and refractory consumption is higher than for conventional all scrap melts. These tests reveal that metallized agglomerates in electric furnace increase the productivity and result in clean operation and easy adjustment of the final composition of steel.

It is established that the method of continuous charging[31,37] of pre-reduced materials in electric furnace will further increase the productivity, decrease the thermal and electric load and cost of production. The cost savings will be due to the elimination of the following operations

i) Material handling,

ii) Reduced demands on the furnace emission control system.

iii) Reduction in the number of missed heats because of better process control.

iv) Increased potential of closed loop computer control.

### (c) Continuous Steel making

If pre-reduced agglomerates with more than 90% metallization of constant physical and chemical quality be made available, then these can be used effectively[31] in the continuous steelmaking processes. In BISRA 'Spray refining' and IRSID processes the continuous feeding of pre-reduced material in the powder or granular form may be quite important and better operational control could be achieved. British steel industry will be using metallized charges as a coolant material for 'spray refining' process.

## SUGGESTIONS FOR FURTHER WORK

Further work can be suggested for studying the following aspects,

1. Study of the kinetics of reduction of iron oxide with charcoal and coke beyond 85% reduction.
2. Pilot plant studies to produce pre-reduced and metallized briquettes from charcoal and coke from economic point of view.

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# APPENDIX 'A'

The percentage reduction has been calculated on oxygen basis. Weight loss obtained after reduction is due to carbon, oxygen and removable ingradients (volatile matter in the reductant and ignition loss of iron ore fines) removed from the bricuette. Thus the oxygen removed during reduction is calculated by subtracting the sum of weight of carbon removed and removable ingradients from the weight loss data obtained. Then using the following formula

$$\frac{\text{oxygen removed}}{\text{theoretical removable oxygen}} \times 100$$

the percentage reduction is found out.

# TABLE -I

## Analysis of Iron Ore Fines

### (A) Sieve Analysis

Weight of Sample = 500 gms

| S.No. | Sieve Size | Weight retained (gms.) | % Weight retained |
|---|---|---|---|
| 1. | 120 | 212.50 | 42.50 |
| 2. | 150 | 288.50 | 57.50 |

### (B) Chemical Analysis

| S.No. | Ingradients | Weight percent |
|---|---|---|
| 1. | Moisture | 0.48 |
| 2. | Ignition loss | 0.78 |
| 3. | Total iron | 59.37 |

# TABLE -II

## Analysis of Solid Reductants

(Wood charcoal and low grade coke)

### (A) Sieve Analysis

Weight of Sample = 500 gms

| Sl. No. | Sieve Size | LOW GRADE COKE |  | WOOD CHARCOAL |  |
|---|---|---|---|---|---|
|  |  | Weight retained (gms.) | % Weight retained | Weight retained (gms) | % Weight retained |
| 1. | 120 | 186.60 | 37.32 | 108.45 | 21.69 |
| 2. | 150 | 313.40 | 62.68 | 391.55 | 78.31 |

### (B) Proximate Analysis

| Sl. No. | Ingradients | Proximate Analysis of Low grade coke | Proximate Analysis of Wood Charcoal |  |
|---|---|---|---|---|
|  |  |  | Before Volatile matter removal | After Volatile matter removal |
| 1. | Moisture | 0.92 wt.% | 6.45 wt% | 2.07 wt % |
| 2. | Ash | 29.47 wt % | 5.53 wt% | 8.25 wt % |
| 3. | Volatile Matter | 4.68 wt % | 25.87 wt% | 6.49 wt % |
| 4. | Fixed Carbon | 64.93 wt.% | 62.15 wt% | 83.19 wt % |

TABLE III- Percentage used with different amounts of (0.1 mm of Hg)

| Time of reduction (minutes) | Composition of the Briquette<br>Iron ore = 77.09%<br>Low grade coke = 22.91%<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 72.77%<br>Low grade coke = 27.23%<br>(5% excess than stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 11 | 950 | 1000 | 1050 | 1100 | 1150 |
| 10 | - | - | - | - | 20. | - | - | - | - | 22.02 |
| 15 | - | - | 16.01 | 21.22 | 25. | - | - | 17.41 | 22.41 | 26.42 |
| 30 | 13.01 | 16.15 | 22.04 | 26.65 | 29. | 14.38 | 18.12 | 23.26 | 28.39 | 31.17 |
| 45 | - | | 25.61 | 30.29 | 33. | | | 26.80 | 31.07 | 34.18 |
| 60 | 16.52 | 20.99 | 28.10 | 32.45 | 35. | 18.15 | 21.89 | 29.48 | 33.18 | 35.89 |
| 90 | 18.23 | 23.68 | 30.42 | 35.08 | 37. | 20.02 | 24.30 | 31.78 | 35.81 | 38.45 |
| 20 | 19.25 | 25.66 | 31.56 | 36.59 | 38. | 21.11 | 26.41 | 33.00 | 37.22 | 39.29 |
| 50 | | | 33.13 | 37.40 | 38. | | | 34.46 | 38.24 | 39.47 |
| 80 | 20.06 | 28.01 | 34.12 | 37.89 | 39. | 22.77 | 28.52 | 35.58 | 38.66 | 39.49 |
| 10 | | | 34.80 | 38.06 | 39. | | | 36.09 | 38.90 | 39.53 |
| 40 | 21.58 | 29.61 | 35.21 | 38.23 | 39. | 23.98 | 30.20 | 36.59 | 38.96 | 39.72 |
| 00 | 21.86 | 30.73 | 35.82 | 38.42 | 39. | 24.38 | 30.98 | 36.93 | 39.01 | 39.92 |
| 60 | 22.44 | 31.21 | | | | 25.82 | 31.63 | | | |

TABLE III- Percentage weight loss of iron ore briquettes reduced with different amounts of Low Grade Coke under reduced pressure (0.1 mm of Hg)

| Time of reduction (minutes) | Composition of the Briquette<br>Iron ore = 77.09%<br>Low grade coke = 22.91%<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 74.43%<br>Low grade coke = 25.57 %<br>(3% Excess than stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 72.77%<br>Low grade coke = 27.23%<br>(5% excess than stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 10 | - | - | - | - | 20.02 | - | - | - | - | 21.01 | - | - | - | - | 22.02 |
| 15 | - | - | 16.01 | 21.22 | 25.26 | - | - | 16.72 | 22.01 | 26.01 | - | - | 17.41 | 22.41 | 26.42 |
| 30 | 13.01 | 16.15 | 22.04 | 26.65 | 29.87 | 13.62 | 17.66 | 23.20 | 28.00 | 31.13 | 14.38 | 18.12 | 23.26 | 28.39 | 31.17 |
| 45 | - | | 25.61 | 30.29 | 33.31 | | | 26.10 | 30.80 | 33.68 | | | 26.80 | 31.07 | 34.18 |
| 60 | 16.52 | 20.99 | 28.10 | 32.45 | 35.29 | 17.41 | 21.54 | 28.06 | 32.64 | 35.64 | 18.15 | 21.89 | 29.48 | 33.18 | 35.89 |
| 90 | 18.23 | 23.68 | 30.42 | 35.08 | 37.80 | 19.25 | 24.13 | 30.50 | 35.45 | 37.89 | 20.02 | 24.30 | 31.78 | 35.81 | 38.45 |
| 120 | 19.25 | 25.66 | 31.56 | 36.59 | 38.74 | 20.32 | 26.14 | 32.90 | 36.92 | 38.99 | 21.11 | 26.41 | 33.00 | 37.22 | 39.29 |
| 150 | | | 33.13 | 37.40 | 38.99 | | | 34.00 | 37.85 | 39.00 | | | 34.46 | 38.24 | 39.47 |
| 180 | 20.86 | 28.01 | 34.12 | 37.89 | 39.15 | 21.46 | 28.25 | 34.70 | 38.25 | 39.32 | 22.77 | 28.52 | 35.58 | 38.66 | 39.49 |
| 210 | | | 34.80 | 38.06 | 39.18 | | | 35.78 | 38.46 | 39.36 | | | 36.09 | 38.90 | 39.53 |
| 240 | 21.58 | 29.61 | 35.21 | 38.23 | 39.37 | 23.41 | 29.88 | 35.96 | 38.57 | 39.51 | 23.98 | 30.20 | 36.59 | 38.96 | 39.72 |
| 300 | 21.85 | 30.73 | 35.82 | 38.42 | 39.45 | 24.12 | 30.88 | 36.31 | 38.67 | 39.62 | 24.38 | 30.98 | 36.93 | 39.01 | 39.92 |
| 360 | 22.44 | 31.21 | | | | 24.41 | 31.24 | | | | 25.82 | 31.63 | | | |

TABLE IV - Percentage weight loss of iron ore briquettes reduced with different amount of wood charcoal under reduced pressure (0.1 mm of Hg)

| Time of reduction (mts) | Composition of the Briquette<br>Iron ore = 81.19%<br>Wood charcoal = 18.81 %<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore =78.87%<br>Wood charcoal =21.13%<br>(3% excess than stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 77.41%<br>Wood charcoal = 22.59%<br>(5% excess than stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 5 | | | | | 18.32 | | | | | 18.81 | | | | | 19.02 |
| 10 | | | | 21.64 | 23.53 | | | 19.59 | 22.31 | 25.51 | | | 20.20 | 22.87 | 26.88 |
| 15 | | | 21.88 | 24.77 | 28.21 | | | 22.61 | 25.30 | 28.20 | | | 23.32 | 26.21 | 30.51 |
| 30 | 16.33 | 20.11 | 25.29 | 29.27 | 32.22 | 16.98 | 21.40 | 26.21 | 29.78 | 33.24 | 17.44 | 21.43 | 26.85 | 30.40 | 34.08 |
| 45 | | | 27.80 | 31.76 | 35.80 | | | 28.59 | 32.21 | 36.58 | | | 29.18 | 32.94 | 37.18 |
| 60 | 19.42 | 23.78 | 29.93 | 33.43 | 38.08 | 19.88 | 24.31 | 30.39 | 34.32 | 38.81 | 20.50 | 24.92 | 31.02 | 34.81 | 39.22 |
| 90 | 21.81 | 26.25 | 33.13 | 36.86 | 40.53 | 22.21 | 26.64 | 33.60 | 37.31 | 41.27 | 22.79 | 27.01 | 34.21 | 37.72 | 41.51 |
| 120 | 23.26 | 27.82 | 35.48 | 38.97 | 41.57 | 24.04 | 28.50 | 35.87 | 39.27 | 41.91 | 24.55 | 28.98 | 36.38 | 39.62 | 42.20 |
| 150 | | | 36.79 | 40.19 | 42.05 | | | 37.22 | 40.13 | 42.31 | | | 37.64 | 40.68 | 42.56 |
| 180 | 25.36 | 29.84 | 37.76 | 40.57 | 42.15 | 26.26 | 30.71 | 38.05 | 40.80 | 42.38 | 26.78 | 31.00 | 38.62 | 40.96 | 42.66 |
| 210 | | | 38.20 | 40.81 | 42.28 | | | 38.62 | 41.01 | 42.52 | | | 39.21 | 41.26 | 42.75 |
| 240 | 27.02 | 31.42 | 38.76 | 40.88 | 42.35 | 27.86 | 32.28 | 39.14 | 41.20 | 42.60 | 28.25 | 32.66 | 39.68 | 41.41 | 42.81 |
| 300 | 28.55 | 32.84 | 39.01 | 41.02 | 42.37 | 29.12 | 33.45 | 39.56 | 41.53 | 42.61 | 29.42 | 33.82 | 40.22 | 41.61 | 42.83 |
| 360 | 29.38 | 33.85 | | | | 29.93 | 34.40 | | | | 30.36 | 34.82 | | | |

TABLE V- Percentage carbon left in the iron ore briquettes after reduction with different Low Grade Coke under reduced pressure (0.1 mm of Hg)

| Time of reduction (mts) | Composition of the Briquette<br>Iron ore = 77.09%<br>Low grade coke = 22.91%<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 74.43%<br>Low grade coke = 25.57%<br>(3% excess than stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 72.77%<br>Low grade coke = 27.23%<br>(5% excess than stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 10 | | | | | 6.37 | | | | | 9.15 | | | | | 10.03 |
| 15 | | | 7.92 | 5.15 | 5.10 | | | 9.35 | 7.14 | 7.03 | | | 12.50 | 9.62 | 9.36 |
| 30 | 8.73 | 7.03 | 7.01 | 4.10 | 4.00 | 11.35 | 9.49 | 6.41 | 5.27 | 5.10 | 13.97 | 12.03 | 9.62 | 7.50 | 7.45 |
| 45 | | | 3.17 | 2.65 | 2.59 | - | | 6.01 | 4.64 | 4.52 | - | - | 7.79 | 6.99 | 6.46 |
| 60 | 6.59 | 5.54 | 2.05 | 1.85 | 1.80 | 10.73 | 7.98 | 4.80 | 3.76 | 3.71 | 11.28 | 10.64 | 6.37 | 6.08 | 5.81 |
| 90 | 6.03 | 4.69 | 1.91 | 1.11 | 0.72 | 8.05 | 7.08 | 3.60 | 2.98 | 2.74 | 10.46 | 9.93 | 6.14 | 5.19 | 4.40 |
| 120 | 5.59 | 4.08 | 1.79 | 0.89 | 0.52 | 7.81 | 6.37 | 3.50 | 2.75 | 2.31 | 10.30 | 9.08 | 6.04 | 4.75 | 4.17 |
| 150 | | | 1.62 | 0.87 | 0.51 | | | 3.36 | 2.63 | 2.30 | | | 5.44 | 4.38 | 4.15 |
| 180 | 5.50 | 3.87 | 1.51 | 0.85 | 0.50 | 7.08 | 6.31 | 3.30 | 2.57 | 2.29 | 10.24 | 8.70 | 4.98 | 4.26 | 4.14 |
| 210 | | | 1.49 | 0.84 | 0.49 | | | 3.10 | 2.55 | 2.28 | | | 4.95 | 4.24 | 4.13 |
| 240 | 5.41 | 3.52 | 1.47 | 0.83 | 0.48 | 6.98 | 5.97 | 3.07 | 2.54 | 2.26 | 10.11 | 8.34 | 4.94 | 4.23 | 4.12 |
| 300 | 5.31 | 3.21 | 1.46 | 0.82 | 0.47 | 6.91 | 5.67 | 3.05 | 2.53 | 2.24 | 9.98 | 8.28 | 4.93 | 4.22 | 4.11 |
| 360 | 4.94 | 3.12 | | | | 6.82 | 5.56 | | | | 9.63 | 7.87 | | | |

TABLE VI- Percentage carbon left in the iron ore briquettes after reduction with different amounts of Wood charcoal under reduced pressure (0.1 mm of Hg)

| Time of reduction (mts) | Composition of the Briquette<br>Iron ore = 81.19%<br>Wood charcoal = 18.81%<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 78.87%<br>Wood charcoal = 21.13%<br>(3% excess than stoichiometric amount of reductant | | | | | Composition of the Briquette<br>Iron ore = 77.41%<br>Wood charcoal = 22.59%<br>5% Excess than stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 5 | | | | | 8.35 | | | | | 11.32 | | | | | 14.65 |
| 10 | | | | 8.53 | 8.17 | | | 10.98 | 10.19 | 9.37 | | | 13.94 | 13.02 | 11.26 |
| 15 | | | 6.51 | 6.49 | 6.44 | | | 9.22 | 9.18 | 9.10 | | | 11.95 | 11.05 | 10.97 |
| 30 | 8.67 | 6.98 | 5.94 | 5.86 | 5.79 | 11.79 | 10.85 | 8.57 | 8.06 | 8.02 | 14.99 | 12.96 | 11.27 | 11.08 | 9.78 |
| 45 | | | 5.24 | 5.12 | 4.19 | | | 8.06 | 7.67 | 6.65 | | | 10.79 | 10.39 | 9.27 |
| 60 | 7.50 | 6.85 | 4.93 | 4.75 | 3.22 | 10.83 | 9.76 | 7.54 | 7.06 | 5.54 | 13.97 | 12.83 | 10.27 | 9.96 | 8.08 |
| 90 | 6.63 | 6.25 | 3.54 | 3.46 | 2.22 | 10.50 | 9.46 | 6.32 | 6.15 | 4.18 | 13.34 | 12.62 | 8.98 | 8.91 | 6.73 |
| 120 | 6.53 | 6.17 | 2.55 | 2.53 | 1.58 | 9.54 | 9.13 | 5.31 | 5.23 | 3.84 | 12.86 | 12.21 | 8.06 | 7.86 | 6.33 |
| 150 | - | - | 2.29 | 2.01 | 1.11 | | | 4.96 | 4.89 | 3.45 | | | 7.56 | 7.31 | 6.03 |
| 180 | 6.42 | 6.13 | 2.25 | 1.96 | 1.05 | 9.38 | 8.72 | 4.92 | 4.55 | 3.39 | 12.83 | 12.01 | 7.42 | 7.16 | 5.96 |
| 210 | - | - | 2.18 | 1.92 | 1.02 | | | 4.83 | 4.52 | 3.35 | | | 7.22 | 7.10 | 5.92 |
| 240 | 6.35 | 6.10 | 216 | 1.91 | 1.01 | 9.32 | 8.53 | 4.81 | 4.34 | 3.33 | 12.81 | 11.80 | 7.21 | 6.96 | 5.91 |
| 300 | 6.11 | 5.57 | 2.15 | 1.89 | 0.99 | 9.25 | 8.30 | 4.79 | 4.32 | 3.32 | 12.79 | 11.37 | 7.20 | 6.78 | 5.89 |
| 360 | 6.07 | 4.93 | | | | 9.13 | 7.71 | | | | 12.45 | 10.85 | | | |

TABLE VII– Percentage reduction[∆] of iron ore briquettes reduced with different amounts of Low Grade Coke under reduced pressure (0.1 mm of Hg)

| Time of reduction (mts.) | Composition of the Briquette<br>Iron ore = 77.09%<br>Low grade coke = 22.91%<br>(Stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron ore = 74.43%<br>Low grade coke = 25.5 %<br>(3% excess than stoichiometric amount of reductant) | | | | | Composition of the Briquette<br>Iron Ore = 72.77%<br>Low grade coke = 27.23%<br>(Excess than Stoichiometric amount of reductant) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in °C | | | | | in °C | | | | | in °C | | | | |
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 10 | | | | | 30.10 | | | | | 30.17 | | | | | 30.19 |
| 15 | | | 17.72 | 30.01 | 50.15 | | | 17.76 | 30.04 | 51.01 | | | 17.81 | 30.12 | 51.80 |
| 30 | 6.70 | 19.01 | 32.40 | 52.12 | 67.88 | 7.90 | 19.25 | 32.44 | 52.24 | 68.21 | 8.75 | 19.50 | 35.02 | 52.50 | 68.32 |
| 45 | | | 42.01 | 63.21 | 78.06 | | | 43.51 | 64.08 | 78.90 | | | 44.38 | 65.11 | 79.89 |
| 60 | 13.61 | 30.08 | 49.10 | 70.02 | 84.18 | 13.81 | 32.00 | 50.04 | 70.90 | 85.06 | 15.01 | 32.98 | 52.28 | 72.01 | 86.22 |
| 90 | 19.40 | 40.10 | 60.03 | 79.50 | 91.30 | 20.01 | 41.13 | 62.01 | 80.04 | 91.99 | 21.10 | 42.88 | 64.12 | 82.11 | 92.97 |
| 120 | 22.30 | 47.03 | 65.28 | 86.02 | 95.07 | 24.52 | 46.14 | 69.13 | 87.13 | 95.61 | 26.48 | 50.02 | 70.70 | 87.79 | 96.43 |
| 150 | | | 72.34 | 90.02 | 96.24 | | | 74.28 | 91.10 | 96.80 | | | 75.78 | 91.55 | 97.22 |
| 180 | 28.20 | 57.72 | 76.81 | 92.40 | 97.00 | 32.19 | 59.10 | 77.79 | 93.00 | 97.21 | 35.78 | 60.09 | 79.62 | 93.25 | 97.30 |
| 210 | | | 80.05 | 93.26 | 97.18 | | | 81.02 | 94.01 | 97.20 | | | 82.26 | 94.50 | 97.68 |
| 240 | 32.11 | 64.16 | 82.11 | 94.10 | 98.01 | 36.72 | 66.11 | 83.20 | 94.51 | 98.11 | 42.03 | 67.71 | 85.01 | 94.82 | 98.53 |
| 300 | 34.01 | 68.10 | 85.02 | 94.96 | 98.42 | 40.02 | 70.08 | 85.07 | 95.03 | 98.64 | 46.51 | 72.11 | 87.10 | 95.13 | 98.89 |
| 360 | 35.12 | 70.09 | | | | 41.20 | 71.32 | | | | 49.89 | 73.40 | | | |

[∆] The calculations for percentage reduction is shown in Appendix A.

TABLE VIII- Percentage reduction[Δ] of iron ore briquettes reduced with different amounts of Wood charcoal under reduced pressure (0.1 mm of Hg)

| Time of reduction (mts) | Composition of the Briquette<br>Iron ore = 81.19%<br>Wood charcoal = 18.81%<br>(Stoichiometric amount of reductant)<br>in °C | | | | | Composition of the Briquette<br>Iron ore = 78.87%<br>Wood charcoal = 21.13%<br>(3% Excess than Stoichiometric amount of reductant)<br>in °C | | | | | Composition of the Briquette<br>Iron ore = 77.41%<br>Wood charcoal = 22.59 %<br>(5% Excess than Stoichiometric amount of reductant)<br>in °C | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 | 950 | 1000 | 1050 | 1100 | 1150 |
| 5 | | | | | 18.04 | | | | | 18.11 | | | | | 18.15 |
| 10 | | | | 30.02 | 42.13 | | | 20.63 | 30.10 | 42.18 | | | 20.70 | 30.12 | 42.81 |
| 15 | | | 26.31 | 40.05 | 56.29 | | | 26.74 | 40.15 | 56.32 | | | 26.80 | 40.18 | 60.02 |
| 30 | 10.05 | 20.04 | 39.86 | 55.86 | 72.43 | 11.20 | 21.81 | 41.13 | 57.10 | 74.46 | 12.02 | 22.04 | 42.01 | 60.07 | 78.25 |
| 45 | | | 48.55 | 66.91 | 81.89 | | | 51.17 | 67.50 | 84.38 | | | 52.00 | 70.08 | 86.80 |
| 60 | 19.25 | 37.00 | 55.75 | 73.18 | 88.56 | 21.04 | 38.02 | 57.50 | 75.00 | 90.02 | 22.50 | 40.10 | 59.11 | 77.75 | 91.40 |
| 90 | 26.50 | 46.46 | 65.83 | 83.48 | 95.01 | 28.94 | 48.28 | 67.61 | 85.54 | 95.61 | 31.36 | 50.19 | 69.28 | 87.76 | 96.48 |
| 120 | 33.04 | 53.13 | 72.00 | 89.52 | 97.13 | 35.54 | 56.05 | 74.01 | 90.82 | 97.15 | 38.25 | 58.50 | 76.01 | 92.30 | 98.03 |
| 150 | | | 77.46 | 92.39 | 97.17 | | | 79.08 | 93.49 | 97.20 | | | 80.09 | 95.02 | 98.35 |
| 180 | 42.51 | 62.52 | 81.32 | 94.00 | 97.23 | 46.00 | 65.06 | 83.10 | 95.04 | 97.24 | 50.01 | 68.31 | 84.60 | 95.80 | 98.50 |
| 210 | | | 84.12 | 95.03 | 97.68 | | | 85.59 | 96.00 | 97.71 | | | 86.70 | 97.01 | 98.65 |
| 240 | 50.11 | 70.08 | 86 36 | 95.24 | 98.00 | 53.78 | 72.11 | 88.09 | 96.10 | 98.10 | 57.86 | 76.10 | 89.13 | 97.15 | 99.00 |
| 300 | 56.48 | 74.25 | 87.42 | 95.88 | 98.01 | 59.86 | 76.90 | 90.04 | 96.20 | 98.11 | 64.10 | 80.06 | 92.01 | 97.20 | 99.01 |
| 360 | 60.02 | 76.00 | | | | 63.31 | 78.69 | | | | 67.21 | 82.58 | | | |

[Δ] The calculations for percentage reduction is shown in Appendix A

# TABLE -IX

Value of slopes of the plots of percent reduction vs log time for iron ore briquettes reduced at various temperatures with different amounts of low grade coke and wood charcoal under reduced pressure(0.1 mm of Hg)

| | Temperature of reduction | Slopes of the plots of percent reduction vs log time ($sec^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Low grade coke | | | Wood charcoal | | |
| | | Stoichiometric amount | 3% excess than stoichiometric amount | 5% excess than stoichiometric amount | Stoichiometric amount | 3% excess than stoichiometric amount | 5% excess than stoichiometric amount |
| Before 85% reduction | 950°C | 27.50 | 36.75 | 44.00 | 52.50 | 58.05 | 60.75 |
| | 1000°C | 54.50 | 54.25 | 55.50 | 54.75 | 55.50 | 58.50 |
| | 1050°C | 53.75 | 55.75 | 56.00 | 54.00 | 53.25 | 52.50 |
| | 1100°C | 60.00 | 56.75 | 54.25 | 56.00 | 58.00 | 60.00 |
| | 1150°C | 53.50 | 55.25 | 60.00 | 54.25 | 66.50 | 52.50 |
| After 85% reduction | 1100°C | 16.50 | 15.00 | 8.75 | 10.00 | 8.25 | 7.50 |
| | 1150°C | 15.00 | 12.50 | 7.25 | 8.25 | 5.75 | 7.25 |

## TABLE -X

Value of Activation energies obtained below 85% reduction for iron ore briquettes reduced with different amounts of low grade coke and wood charcoal under reduced pressure (0.1 mm of Hg)

| Reductants | Activation energy (Kcals/gm.mole) | | |
|---|---|---|---|
| | Stoichiometric amount | 3% excess than stoichiometric amount | 5% Excess Stoichiometric amount |
| Low grade coke | 50.2± 2.7 | 51.4 ± 1.1 | 50.2 ±1.2 |
| Wood Charcoal | 52.5± 1.1 | 50.2 ± 0.8 | 52.5 ±1.4 |