

Report of Investigations 7461

PB196688



Batch Reduction of Iron Ore in Fluidized Bed

By John P. Hansen, J. E. Berryhill, and J. A. Aufman



UNITED STATES DEPARTMENT OF THE INTERIOR
Walter J. Hickel, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

REPRODUCED BY:
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161

NTIS

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

This publication has been cataloged as follows:

Hansen, John P

Batch reduction of iron ore in fluidized bed, by John P. Hansen, J. E. Berryhill, and J. A. Aufman. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1970]

25 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7461)

Based on work done in cooperation with the University of Alabama.

1. Iron ores. 2. Fluidization. I. Berryhill, J. E., jt. auth. II. Aufman, J. A., jt. auth. III. Title. (Series)

TN23.U7 no. 7461 622.06173

U.S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Experimental method.....	2
Apparatus.....	2
Raw materials.....	5
Procedure.....	6
Reaction rate.....	7
Results.....	8
Effect of temperature.....	8
Effect of gas composition.....	12
Effect of gas flow.....	20
Composition of exit gas.....	23
Conclusions.....	24

ILLUSTRATIONS

1. Fluidized bed.....	3
2. Schematic diagram of apparatus.....	4
3. Cross section of top-loading reactor.....	4
4. Shape of reduction curves for various rate-controlling steps.....	8
5. Effect of temperature on reduction of red ore using hydrogen.....	9
6. Effect of temperature on reduction of brown ore using hydrogen.....	10
7. Effect of temperature on reduction of red ore with carbon monoxide.....	11
8. Arrhenius plot of reduction rates.....	13
9. Reduction of red ore with various CO-H ₂ mixtures at 850° C.....	14
10. Reduction of red ore with various CO-H ₂ mixtures at 750° C.....	15
11. Reduction of brown ore with various CO-H ₂ mixtures at 900° C.....	16
12. Reduction of brown ore with various CO-H ₂ mixtures at 750° C.....	17
13. Reduction of brown ore with various H ₂ -N ₂ mixtures at 900° C.....	18
14. Reduction of brown ore with various CO-N ₂ mixtures at 900° C.....	19
15. Influence of nitrogen content on reduction rates of brown ore at 900° C.....	20
16. Influence of flow rate of hydrogen on reduction of red ore at 850° C.....	21
17. Influence of flow rate of carbon monoxide on reduction of red ore at 800° C.....	22
18. Influence of space velocity on reduction rate.....	23
19. Calculated composition of exit gas.....	24

TABLES

1. Chemical analysis of iron ores used for reduction tests.....	5
2. Screen analyses of iron ore samples.....	6
3. Calculated reduction rates of brown ore with various gas mixtures at 900° C.....	19
4. Calculated reduction rates of red ore with different superficial space velocities.....	22

BATCH REDUCTION OF IRON ORE IN FLUIDIZED BED

by

John P. Hansen,¹ J. E. Berryhill,² and J. A. Aufman³

ABSTRACT

Batches of red or brown iron ore concentrates, weighing 100 or 200 grams, were reduced with gaseous reductants in a laboratory-sized fluidized-bed reactor. Using a loss of weight technique, the rates of reduction were measured and the effects of temperature, gas consumption, and gas flow rates were determined.

Below about 725° C the rate of reduction was controlled by the chemical reaction at the reduction interface having an activation energy of about 10 kcal/g mole. Above about 725° C the rate of reduction appeared to be controlled by the flow of the gaseous reductant and therefore to be directly proportional to the flow rate.

Above 725° C, hydrogen reduced the iron ore much faster than carbon monoxide. In gas mixtures, carbon monoxide or nitrogen reduced the hydrogen partial pressure and lowered the reaction rate proportionally. When present in large concentrations, carbon monoxide had a serious inhibiting effect on the reduction rate, probably owing to carburization and sintering of the reduced iron. ()

INTRODUCTION

Fluidized beds have been used extensively since 1921, and have wide application in catalyzed gaseous reactions. The fluidized bed permits using solid particles of very fine sizes as catalysts, which provides tremendous active surface area without seriously restricting the flow of the gaseous reactants. Because of the turbulence in the fluid bed, temperature gradients are usually small and the entire unit is easily controlled at a constant, uniform temperature. Because of the constant, uniform bed temperature, thermal efficiency is

¹ Chief, Tuscaloosa Metallurgy Research Laboratory, Bureau of Mines, Tuscaloosa, Ala.

² Development engineer, Ethyl Corp., Baton Rouge, La., formerly with the Tuscaloosa Metallurgy Research Laboratory, Bureau of Mines, Tuscaloosa, Ala.

³ Metallurgist, Pratt & Whitney Aircraft, Hartford, Conn., formerly with the Tuscaloosa Metallurgy Research Laboratory, Bureau of Mines, Tuscaloosa, Ala.

poor unless several fluidized beds are operated concurrently to permit the countercurrent flow of the gases and solid particles.

More recently, fluidized beds have been investigated extensively for use in heterogeneous gas solid reactions, where the gas reacts with the solid particle. Of special interest has been the reduction of iron oxide to metal with hydrogen, carbon monoxide, or a mixture of the two from commercially available fuels such as coke oven gas, water gas, or reformed natural gas. The process is especially applicable to iron ore concentrates in which the iron oxide is present as a finely divided product. The fluidized bed does not require agglomeration of the fine particles, but on the contrary the large specific surface area of the concentrate and rapidly moving gas stream produces high rates of heat and mass transfer. The rapid reaction rate in the fluidized bed provides an efficient use of the reducing potential of the gas phase. The rapid heat transfer and turbulence of the bed provides a constant, uniform temperature within the bed.

The steel industry, reacting to high scrap iron prices during the 1950's, has shown avid interest in developing fluid bed processes to produce a highly metallized iron product for use as a scrap substitute. Many processes were developed using a fluidized bed. These differed in the composition of the reducing gas used, reaction temperature and pressure, the number of reduction steps, and the mechanical arrangement of the apparatus. The product was invariably a high metallic iron powder with varying carbon content which would be melted in an electric furnace or open hearth for steel production. The reduced metal powder, while basically a scrap substitute, has two principal advantages: (1) The concentration of residual tramp elements such as copper and nickel which are not removed during steelmaking is low, and (2) the metallized ore can be produced at a stable price in contrast to the fluctuating price of scrap iron.

With the sharp decrease in scrap prices and the advent of the basic oxygen converter with its lower scrap utilization and increased steel capacity, interest in reduced metal as a scrap substitute has waned and attention has been diverted to processes that would increase the productivity of the blast furnaces. As a result, the steel industry is presently developing processes for the production of high-quality blast furnace feed such as pellets, self-fluxing agglomerates, and prereduced or metallized blast furnace feed. While the end use of the reduced product is changed, the need for reduction to metallic iron or to some magnetic oxide still exists in the steel industry in the preparation of a high-quality blast furnace feed.

EXPERIMENTAL METHOD

Apparatus

A photograph of the laboratory-scale fluidized-bed reactor with the accessory equipment used in this investigation is shown in figure 1. A schematic diagram showing a bottom-fed reactor, with the principal components of the apparatus, is presented in figure 2. The initial reactor was constructed from a type 304 stainless steel pipe 1.75 inches inside diameter by

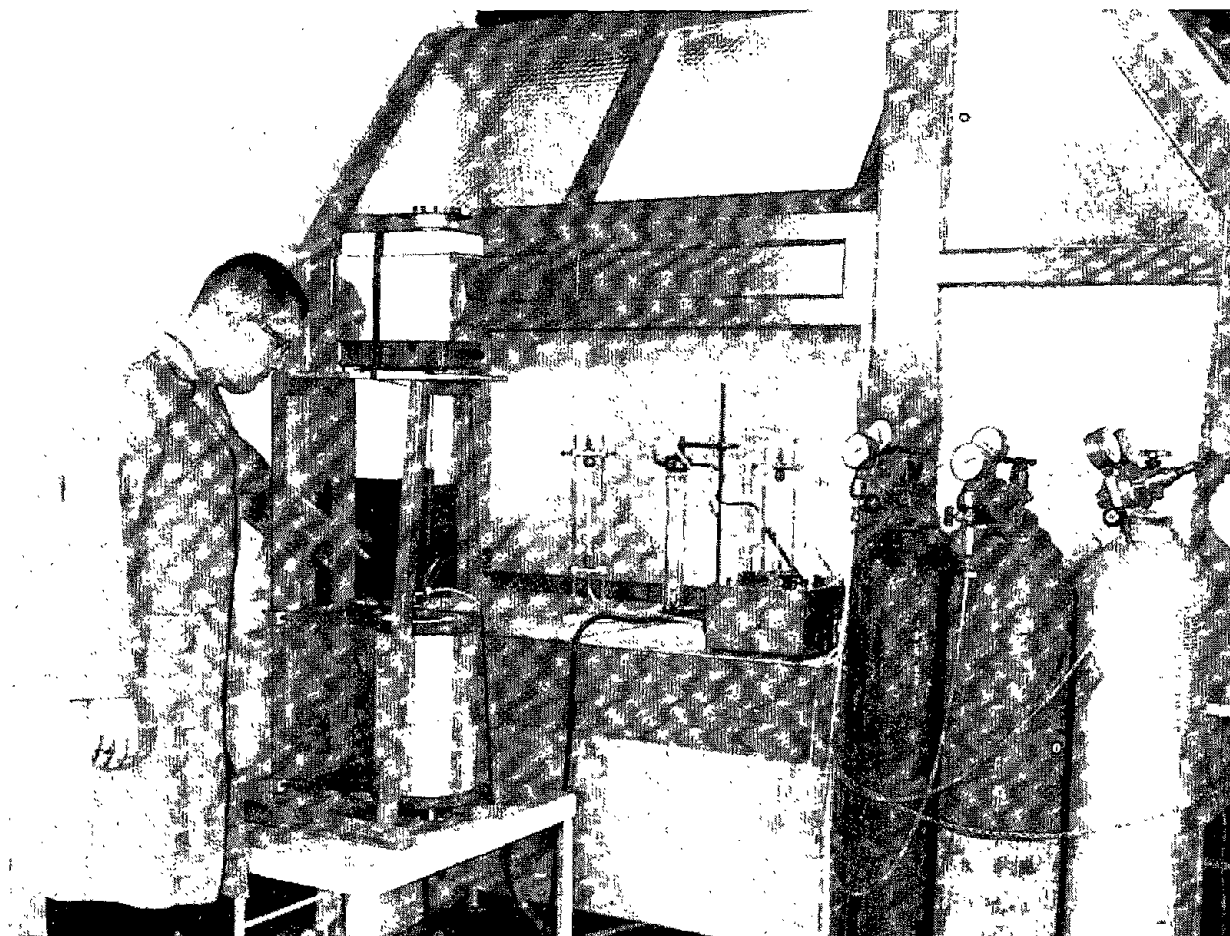


FIGURE 1. - Fluidized Bed.

11 inches long. The bottom was tapered to fit a 1/8-inch-inside-diameter stainless steel tube, which served as the gas inlet and preheat section. A 3/16-inch-diameter steel ball was used as a check valve, which prevented the ore from clogging the tube during loading and unloading. The top section, which contained the thermocouple well and gas exhaust port, was attached to the body by three machine screws. An asbestos gasket was used to seal the lid and prevent loss of reducing gas or ore particles during operation. A dust filter, consisting initially of a bent length of glass tubing packed with fiber glass, was used to minimize dust losses. The dust filter was later modified to use a stainless steel microfilter as a dust collector.

A top-loading reactor, which was also constructed and used in the investigation, is shown in figure 3. Several design changes were made to facilitate operation and use of the reactor. The gas inlet tube was incorporated in the lid and bent into a loop to suspend the reactor in the furnace. The gas entered the inlet tube which passed through the center of the reactor to pre-heat the gas. The dust was filtered from the exit gas stream by a stainless steel microfilter and passed out the exit tube. The top was fastened to the

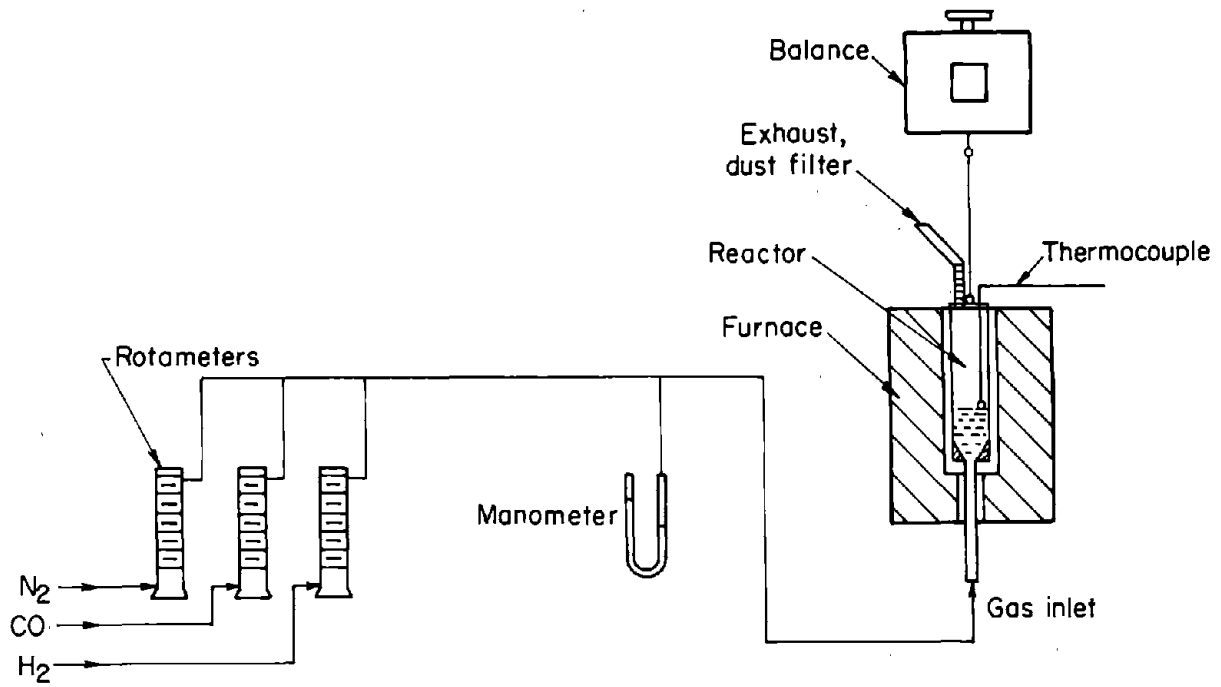


FIGURE 2. - Schematic Diagram of Apparatus.

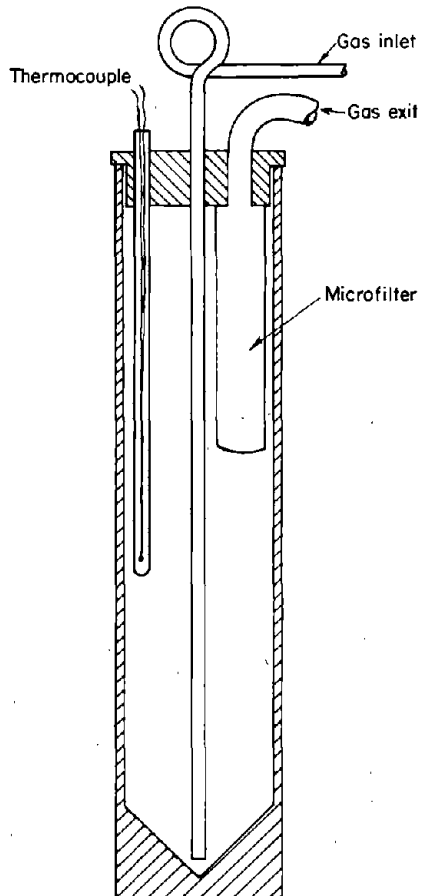


FIGURE 3. - Cross Section of Top-Loading Reactor.

body of the reactor by three thumb screws and sealed with high-temperature cement.

The reactor was heated externally by an electrical resistance tube furnace 2-1/2 inches in inside diameter by 12 inches in length. A second heating element, 7/8 inch in diameter and 2-1/2 inches long and placed concentric with and immediately below the first, heated the gas inlet tube which served as the gas preheater when the bottom-fed reactor was used. A variable-voltage transformer controlled the power input to the furnace, and temperature was controlled by an indicating off-on controller using a Chromel-Alumel⁴ thermocouple. The gas flow was measured with rotameters, and the pressure of the system was measured with a mercury-filled manometer.

The reactor assembly was suspended from a bottom-loading, 2,000-gram-capacity, direct-reading balance so that the weight losses could be determined periodically during the run. The rate of reduction was determined using the loss-of-weight technique.

Raw Materials

Two iron oxide concentrates were used during this investigation. The first was a table concentrate from a typical red iron ore from the Clinton Formation of the Birmingham district. The ore was obtained from a weathered outcrop of the Ida seam at the Ruffner mine operated by the United States Pipe and Foundry Co. Chemical analysis of the concentrate is shown in table 1. A screen analysis of the concentrate is given in table 2.

TABLE 1. - Chemical analysis of iron ores used
for reduction tests

Ingredient	Analysis, percent	
	Red ore	Brown ore
Fe.....	48.9	47.8
SiO ₂	19.7	11.5
Al ₂ O ₃	5.7	5.4
CaO.....	.6	-
MgO.....	.2	-
P.....	.1	.4
S.....	.1	-
Loss on ignition.....	-	13.4

The second material used for reduction tests was a composite of plus 1/8-inch concentrates produced in a cooperative drilling program made in Barbour, Butler, Crenshaw, and Pike Counties, Ala.⁵ The composite sample was crushed with a laboratory jaw crusher followed by a rolls crusher until the sample was virtually minus 20 mesh. The minus 20- plus 100-mesh size fraction was

⁴Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

⁵O'Neill, James F. Brown Iron Ore Resources: Barbour, Butler, Crenshaw, and Pike Counties, Ala. BuMines Inf. Circ. 8261, 1965, 59 pp.

screened from the crushed composite and used as the feed material for testing. The chemical analysis of this material is shown in table 1. The screen analysis of the brown ore composite is presented in table 2.

TABLE 2. - Screen analyses of iron ore samples

Screen (Tyler), mesh	Red ore		Brown ore	
	Wt retained, percent	Cumulative wt retained, percent	Wt retained, percent	Cumulative wt retained, percent
35.....	-	-	50.3	50.3
48.....	-	-	18.0	68.3
65.....	8.8	8.8	16.7	85.0
100.....	37.3	46.1	15.0	100.0
150.....	21.6	67.7	-	-
200.....	16.0	83.7	-	-
Pan.....	16.3	100.0	-	-
Total.....	100.0	100.0	100.0	100.0

Procedure

An ore charge of 100 grams of the brown ore composite, or 200 grams of the red ore, was weighed and placed in the reactor. The reactor lid, which also contained the dust filter and thermocouple well, was carefully fitted into place using an asbestos gasket. The lid was attached using three set screws which fit into conically shaped recesses in the reactor body and which pulled the lid down firmly against the gasket. The lid was sealed with a high-temperature cement.

The assembled reactor was suspended from the bottom-loading balance into the furnace, the gas and thermocouple connections were made, and the heat-up was started. A flow of nitrogen was passed through the furnace to provide an inert atmosphere and to sweep the ignition products from the reactor. When the furnace reached the operating temperature and the weight of the reactor became constant, the constant weight was recorded and the reducing gas was introduced at a predetermined flow rate. Periodically the weight was recorded and the loss of weight was determined.

At the conclusion of the test, nitrogen was introduced into the reactor to prevent further reduction or oxidation of the product while the charge cooled. The reduced product was analyzed for metallic iron using the mercuric chloride method, and for ferrous and total iron using the standard potassium dichromate methods. From the chemical analyses the degree of reduction was calculated and compared with that determined by the loss of weight.

The presence of fluidization was indicated during the run by oscillation of rotameter and manometer readings, and of the weight of the reactor. The absence of these oscillations indicated that the bed was no longer fluidized; this was usually due to caking of the ore or to gas leaks. These oscillations were known to indicate fluidization from earlier observations in a transparent reactor vessel.

Reaction Rate

The percent reduction during periodic time intervals was calculated from the loss-of-weight data obtained during reduction. It has been shown that the function $\left(1 - \left(1 - \frac{\text{percent reduction}}{100}\right)^{1/3}\right)$ represents the thickness of the reacted layer for particles of uniform shape and size.⁶ The fractional thickness of the reduced layer was plotted against time by using this function. These plots were useful in determining specific reaction rates for the reaction, and the rate-determining condition was indicated from the shape of the curve.⁷ If the percent reduction using the function $\left(1 - \left(1 - \frac{\text{percent reduction}}{100}\right)^{1/3}\right)$ is plotted against the reduced time

(time/time for complete reduction), as shown in figure 4, a straight line will be obtained if the reaction is controlled only by the chemical reaction at the interface. If either diffusion of the gas through the ambient layer or the flow rate of the gas is the only rate-controlling mechanism, the curve obtained will be concave. If diffusion through the reduced layer is the only rate-controlling mechanism, the curve will be sigmoidal. However, in the latter case the rate will be so much slower that the test will in most cases be stopped before final reduction is completed and will therefore appear to have negative curvature. Experimentally, of course, two or more mechanisms may contribute to control the reaction rate, and various shaped curves which may even change shape during the experiment will result.

Although the function is exact only for a single regularly shaped particle or particles of uniform shape and size, the function is useful for comparing test results for irregularly shaped particles of a given size distribution. It cannot be expected that linearity will persist until 100 percent reduction is attained; instead, the curve will usually flatten before reduction is completed. Because of the wide variation in particle size of the concentrates, the speed of the reaction interface was not calculated. Instead, the slope of the curve was used as the specific reaction rate, having units of reciprocal time. Because of differences in size distribution and weight of the charge, the reduction rates are not directly comparable between the two concentrates. That is, if either the weight or the size distribution of the sample is changed, the slope of the curve would change, even if all other test conditions remained constant.

⁶Hansen, John P., Gust Bitsianes, and T. L. Joseph. A Study of the Kinetics of Magnetic Roasting. Proc. Blast Furnace, Coke Oven, and Raw Mat. Conf., AIME, Chicago, Ill., v. 19, 1960, pp. 185-199.

Joseph, T. L., H. M. Beatty, and Gust Bitsianes. Calcination Rates and Sizing of Blast-Furnace Flux. AIME Tech. Pub. 1522, Cincinnati Meeting, April 1942, 14 pp.

⁷Yagi, S., and D. Kunii. Studies on Combustion of Carbon Particles in Flames and Fluidized Beds. 5th Symposium (International) on Combustion. Reinhold Pub. Co., New York, 1955, pp. 231-244, Chem. Eng. (Japan), v. 19, 1955, p. 500.

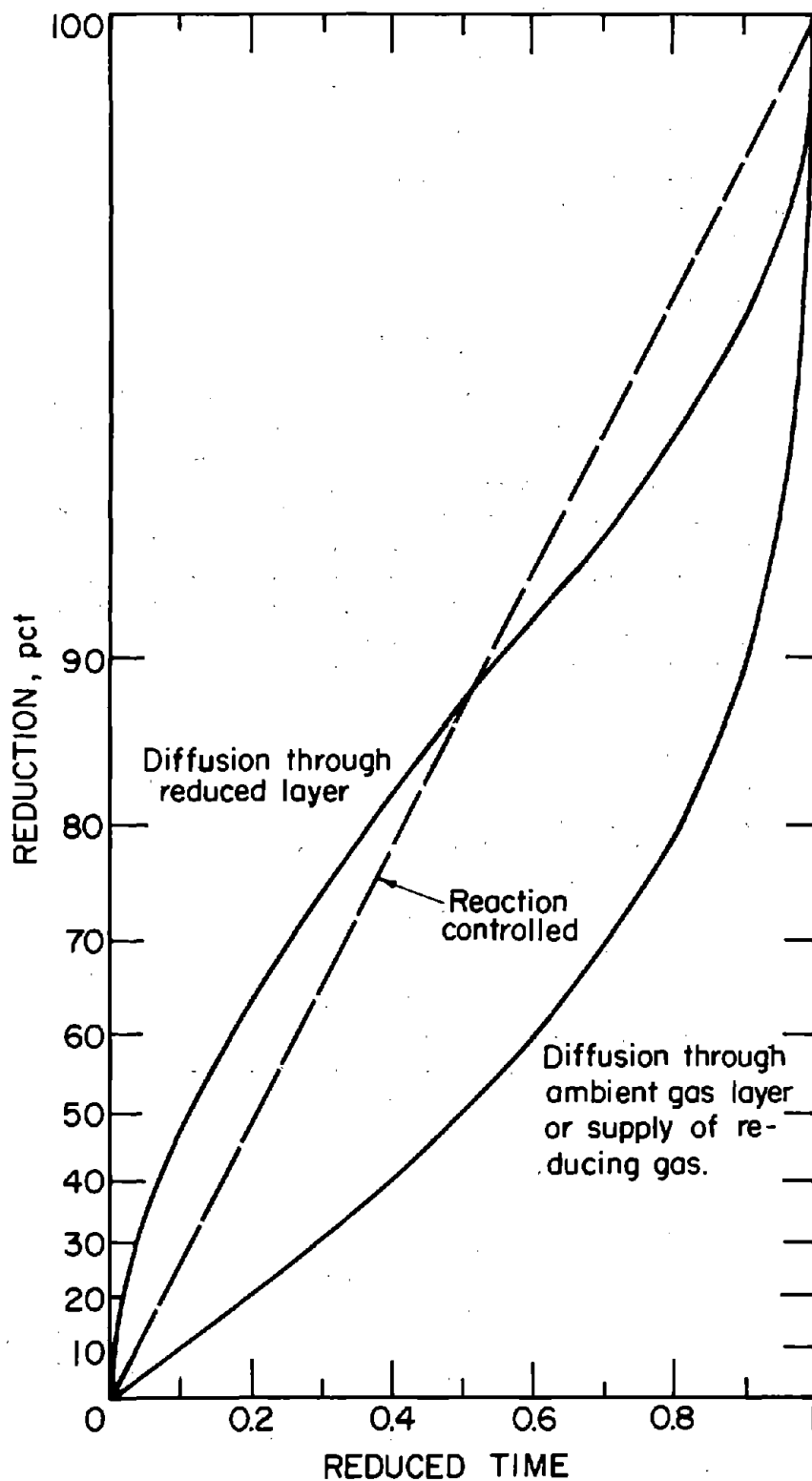


FIGURE 4. - Shape of Reduction Curves for Various Rate-Controlling Steps.

For tests using the red ore concentrate, 200 grams of iron ore concentrate were used. The flow of the reducing gases was adjusted to give a superficial space velocity of 0.30 foot per second, or 18.5 cubic feet of gas per hour, measured at the furnace pressure and at a temperature 50° C below the furnace temperature.

Using the brown ore concentrate, 100 grams of iron ore samples were used with a superficial space velocity of 0.32 foot per second, which amounted to 20.0 cubic feet of gas measured at the furnace temperature and pressure. Differences in temperature and gas flow rates for the two ore concentrates are the result of combining experimental data developed by two workers.

RESULTS

Effect of Temperature

Several experiments were run at various temperatures reducing the red ore concentrate with hydrogen. Typical results shown in figure 5 show that at temperatures of 500°, 650°, and 750° C straight lines are obtained from the reduction data. At

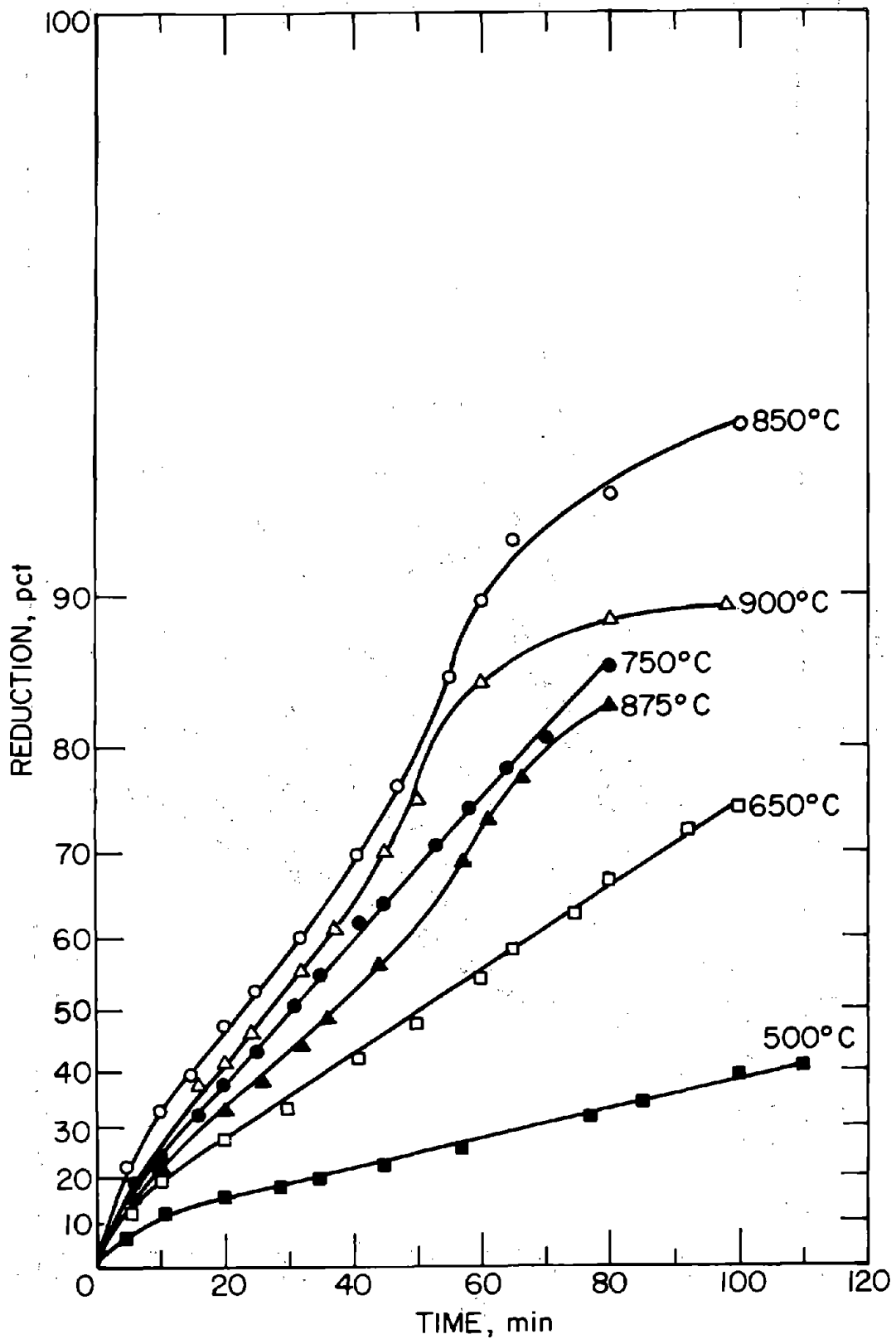


FIGURE 5. - Effect of Temperature on Reduction of Red Ore Using Hydrogen.

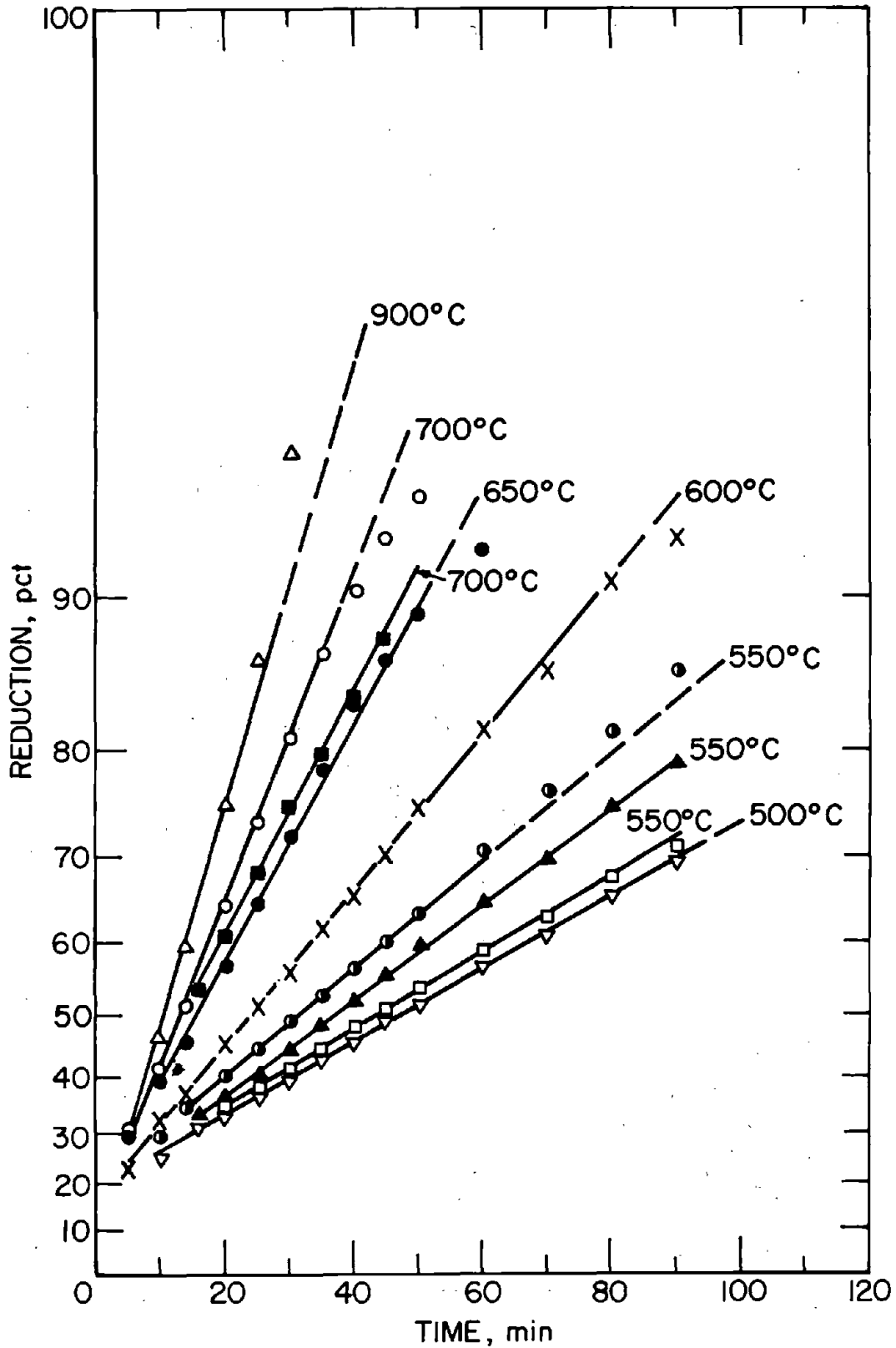


FIGURE 6. - Effect of Temperature on Reduction of Brown Ore Using Hydrogen.

temperatures above 750° C the curves have position curvature indicating that the reaction is being controlled either by diffusion through the ambient layer or by the flow rate of the gas. The rate of reduction becomes erratic but does not increase as the temperature is increased above 750° C.

The results of typical runs reducing the brown ore concentrate with hydrogen at various temperatures are shown in figure 6. Straight lines are obtained for all temperatures. The rate increases only slightly as the temperature increases above 725° C.

Several runs were made reducing red ore concentrate with carbon monoxide at varying temperatures. The use of carbon monoxide complicated the results because carbon precipitated, especially at low temperatures, from the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$. The precipitated carbon increased the weight of the reactor and introduced errors in reduction data. In normal operation the weight would decrease rapidly early in the run and then decrease more slowly; finally, the weight would increase. To determine the weight change due to reduction, the final percent reduction was determined from the chemical analysis. It was then assumed that any weight discrepancies resulted from carbon deposition and it was further assumed that the rate of carbon deposition was uniform throughout the run. By making these assumptions it was possible to determine the adjusted reduction rate. These results are shown in figure 7. A portion of

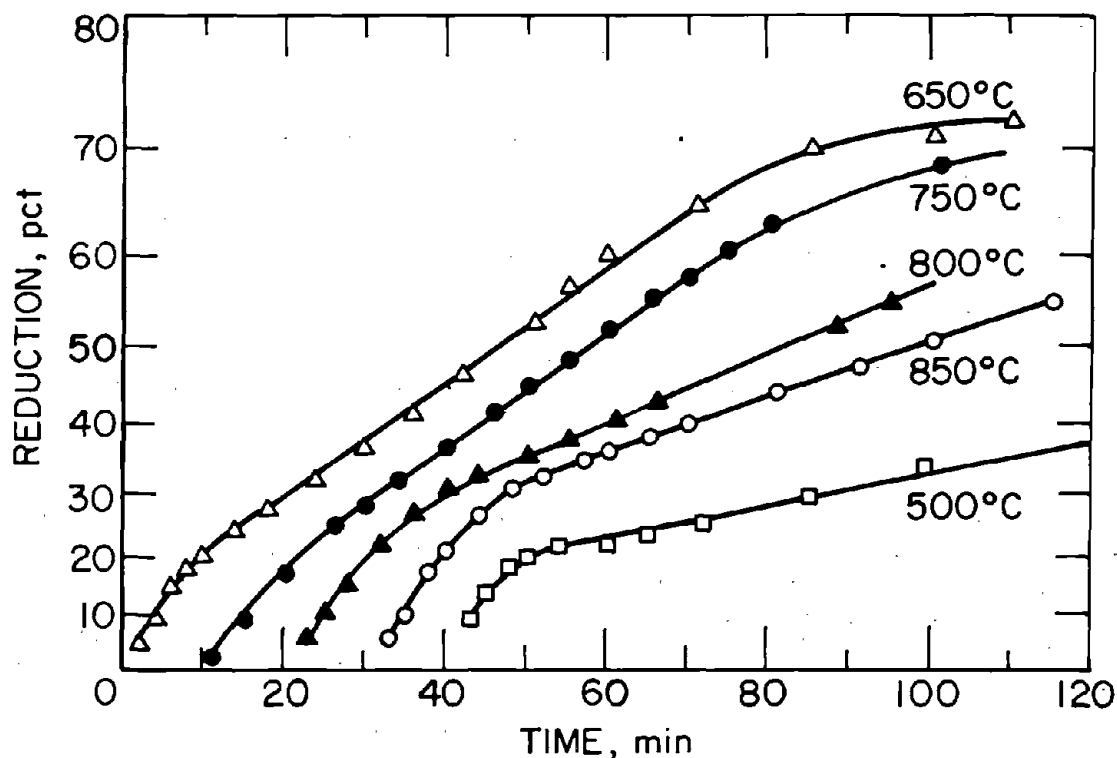


FIGURE 7. - Effect of Temperature on Reduction of Red Ore With Carbon Monoxide. (Data corrected for carbon deposition. Note: Succeeding test data offset 10 minutes to right to prevent curves from overlaying.)

the curves obtained is linear and the reduction rate increases rapidly as the temperature increases from 500° to 650° C. As the temperature is increased above 650° C, the rate of reduction decreases.

For any activated reaction the dependence of the reaction rate on temperature should be defined by Arrhenius' equation which states: $\text{rate} = A e^{-\frac{Q}{RT}}$, where Q is the activation energy. If the log of the rate is plotted against $\frac{1}{T}$ for an activated reaction, a straight line should be obtained. The slope of the line should be equal to $-\frac{Q}{2.3 R}$.

The log of the specific reduction rate plotted against the inverse absolute temperature, figure 8, gives linear relationships for temperatures between 500° and about 725° C. The activation energy calculated from these plots is as follows: 10,800 cal/g mole for reduction of red ore concentrate with hydrogen, 11,500 cal/g mole for reduction of the red ore concentrate with carbon monoxide, and 11,800 cal/g mole for reduction of the brown ore concentrate with hydrogen. The reaction rate in this temperature range is apparently controlled by the chemical reaction at the iron-wustite (Fe-FeO) interface for all three systems.

As the temperature is increased above 725° C, when hydrogen is used for reduction, the reaction rate becomes erratic, and only slight, if any, increase is noted. It appears that above about 725° C either gaseous diffusion or the flow rate of reducing gas becomes the rate-controlling mechanism. Although gaseous diffusion is not an activated reaction, the diffusion rate increases with the Nth power of temperature, where N is a constant between 1.5 and 2 depending on the gas under consideration. In such cases the log reduction rate should increase uniformly as $\frac{1}{T}$ decreases, yielding a "pseudo activation energy" of about 2T. Gaseous diffusion is therefore rejected as the rate-controlling mechanism, and it is concluded that for hydrogen the reaction is controlled by the chemical reaction at temperatures below about 725° C and by the flow rate of the reducing gas at the higher temperatures. The reducing potential of the gas is being either exhausted or reduced to the point of inefficiency as the gas passes through the bed.

For carbon monoxide the rate of reaction drops rapidly as the temperature increases above 750° C, probably due to some rate-inhibiting mechanism such as caking or sintering of the reduced iron layer. The sintering of the reduced iron layer would partially close the porosity and slow the reaction rate. The appearance of the rate-inhibiting mechanism at a lower temperature for carbon monoxide than for hydrogen is probably due to the carburization of the iron.

Effect of Gas Composition

To compare the relative effectiveness of carbon monoxide and hydrogen, several series of experiments were run in which the composition of the reducing gas was varied. Series of tests were run at various temperatures and using both the red and brown ore concentrate.

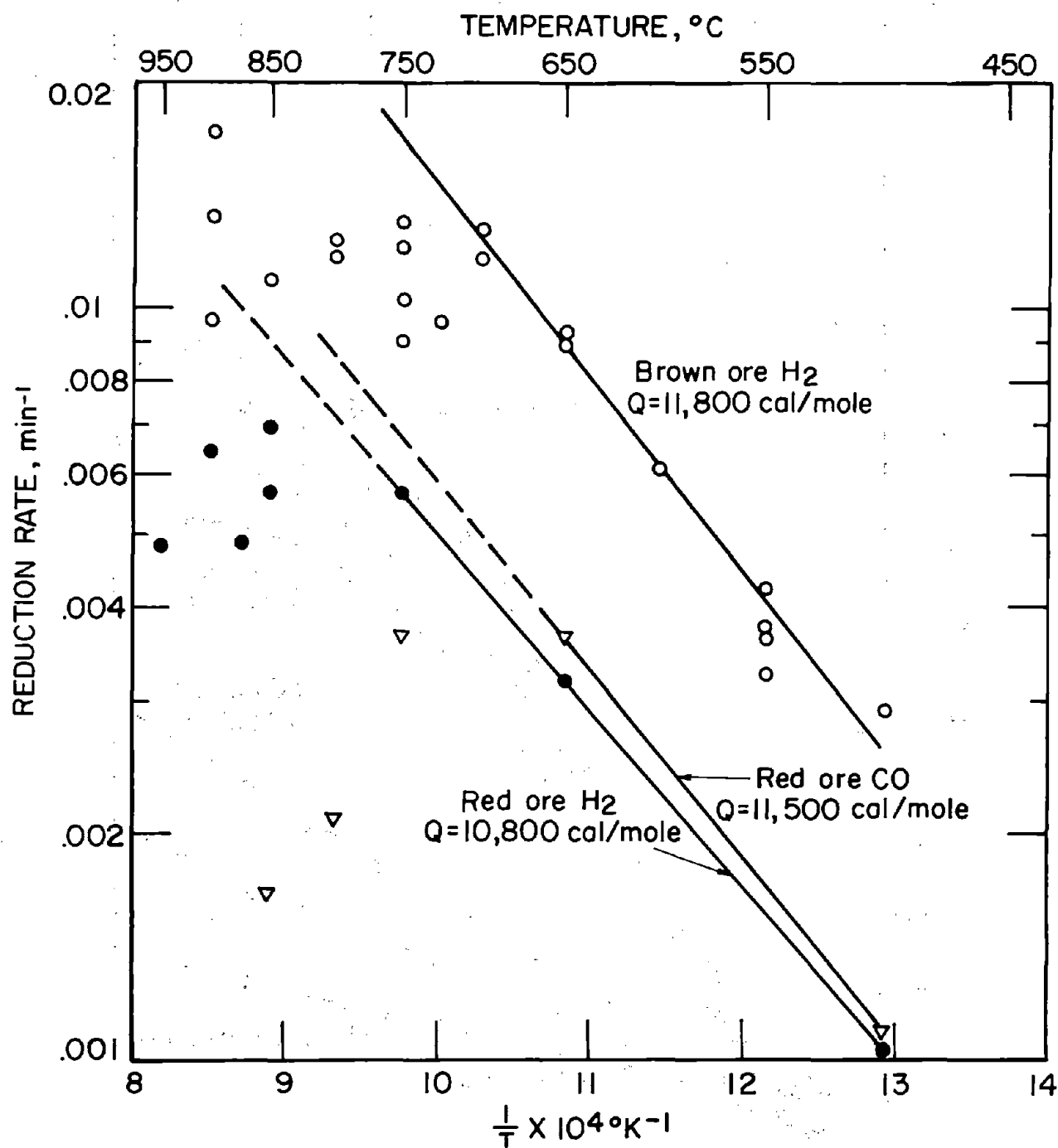


FIGURE 8. - Arrhenius Plot of Reduction Rates.

The results of the tests at 850°C using the red ore concentrate are shown in figure 9. The flow rate of the gas was constant. Hydrogen reduced the iron ore sample much more rapidly than carbon monoxide. The reduction rates for mixtures of the two gases were intermediate, and the reaction rate varied directly with the hydrogen content. When the carbon monoxide content

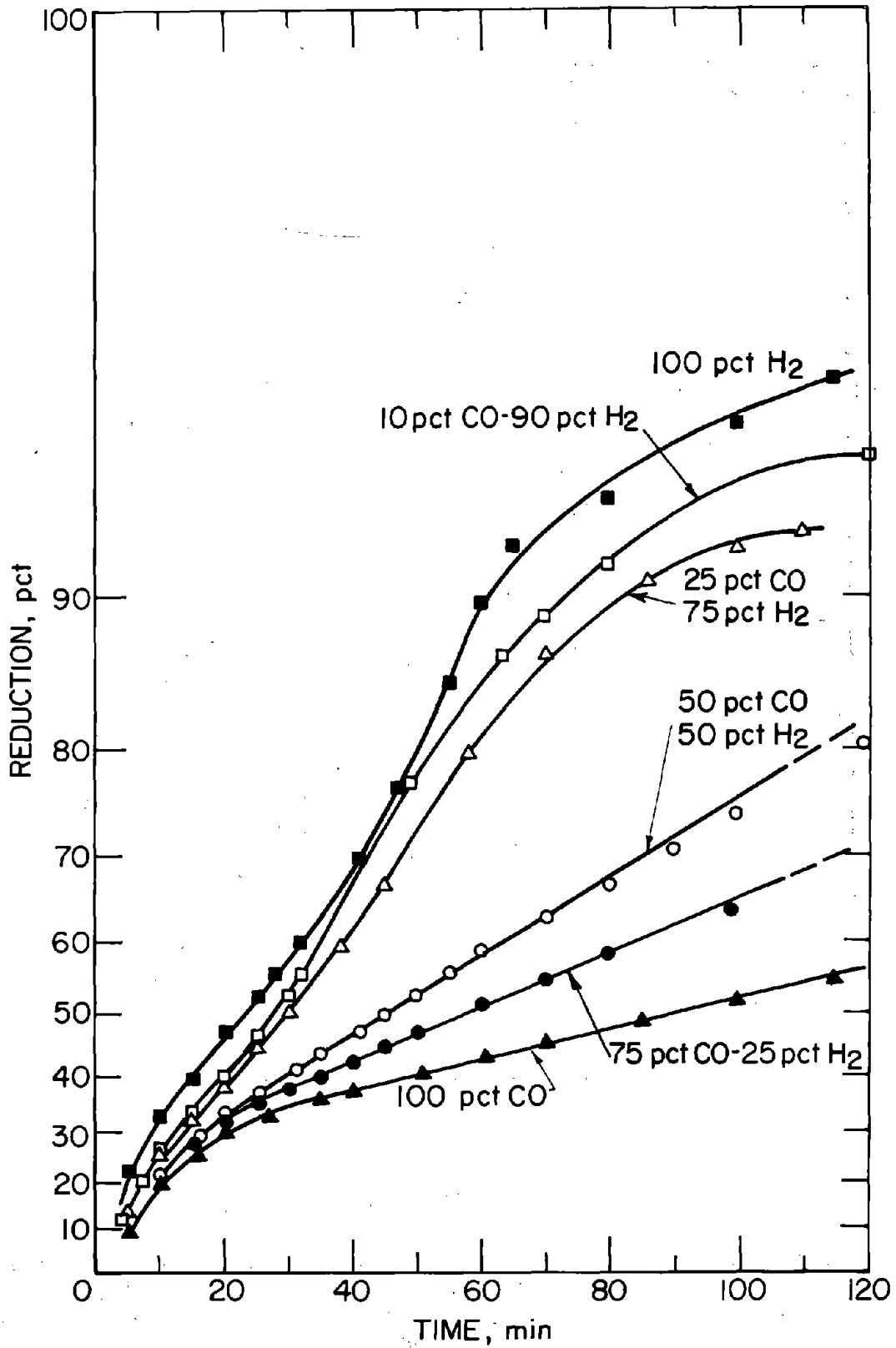


FIGURE 9: - Reduction of Red Ore With Various CO-H₂ Mixtures at 850° C.

was 50 percent or more, straight lines were obtained up to 70-percent reduction, indicating that some interface mechanism was rate controlling. As the hydrogen content increased above 50 percent, the curves appear to have positive curvature, indicating the gas flow rate was controlling the reaction rate.

The results for the test series at 750° C using the red ore concentrate are shown in figure 10. Again, the reduction rate with hydrogen is somewhat faster than that with carbon monoxide, and the reduction rates for the mixtures vary directly with the hydrogen content. Straight lines are obtained when the fractional thickness of the reduced layer is plotted against time, until about 60-percent reduction is obtained.

For the series run at 500° C using the red ore concentrate, the reduction rates for hydrogen, carbon monoxide, and mixtures of the two were so nearly identical that no significant differences were observed. Straight lines were obtained for all reduction runs.

Results of the series using brown iron ore concentrate at 900° C are shown in figure 11. Again, linear plots are obtained, and the reduction rate varies directly with the hydrogen content of the gas.

Results at 750° C using the brown iron ore are shown in figure 12.

Series of experiments were run on the brown ore at 900° C, in which the hydrogen or carbon monoxide was diluted with nitrogen. The results,

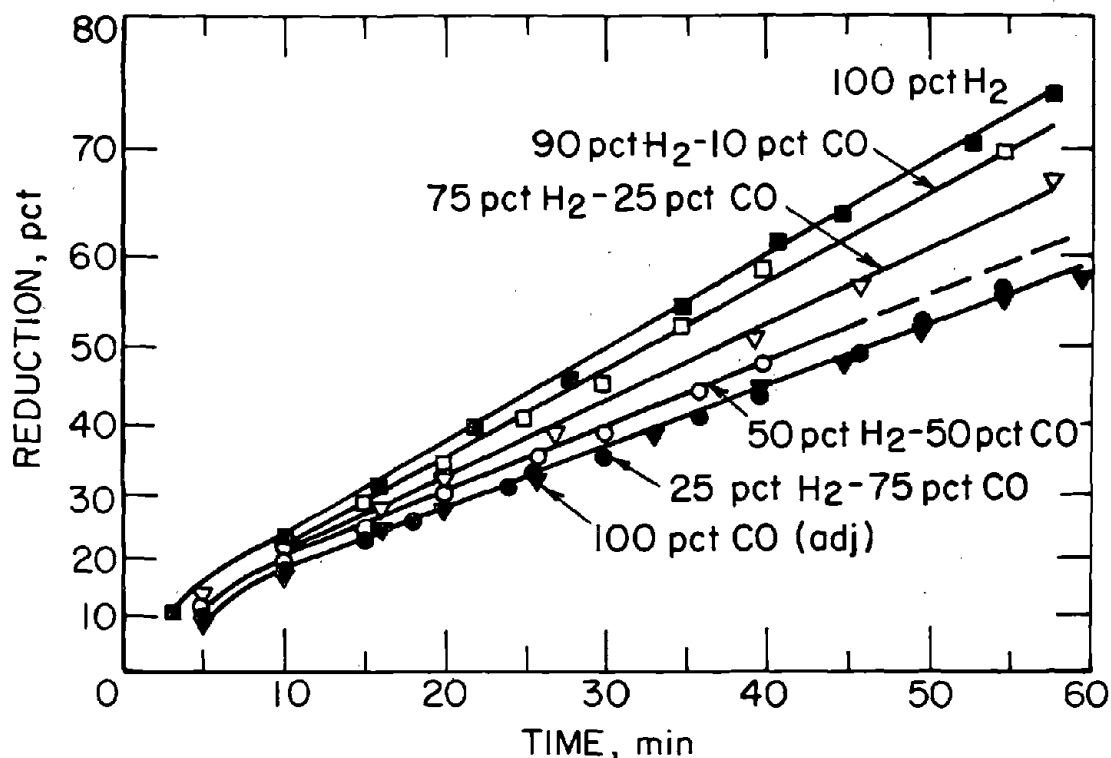


FIGURE 10. - Reduction of Red Ore With Various CO-H₂ Mixtures at 750° C.

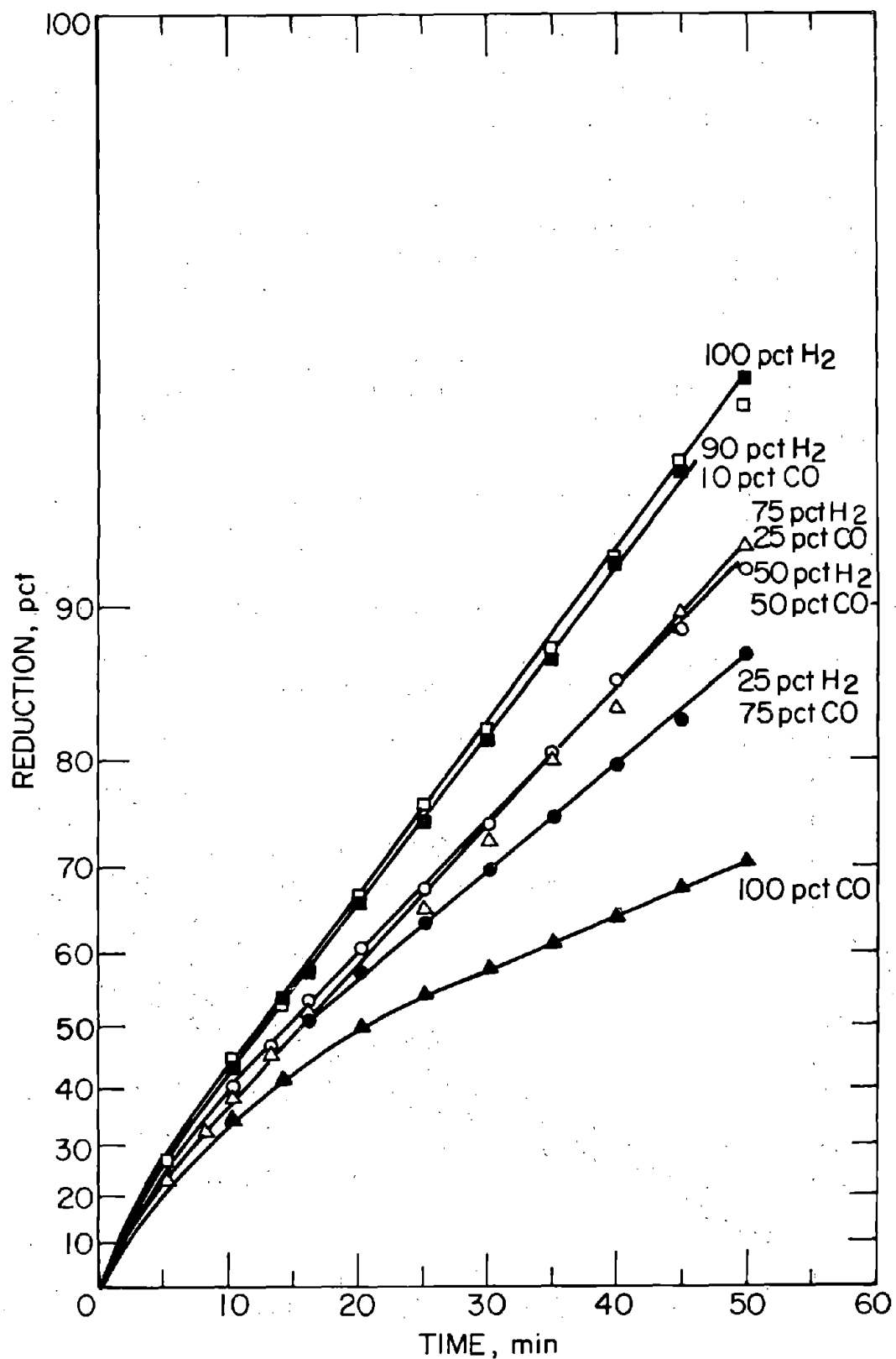


FIGURE 11. - Reduction of Brown Ore With Various CO-H₂ Mixtures at 900°C.

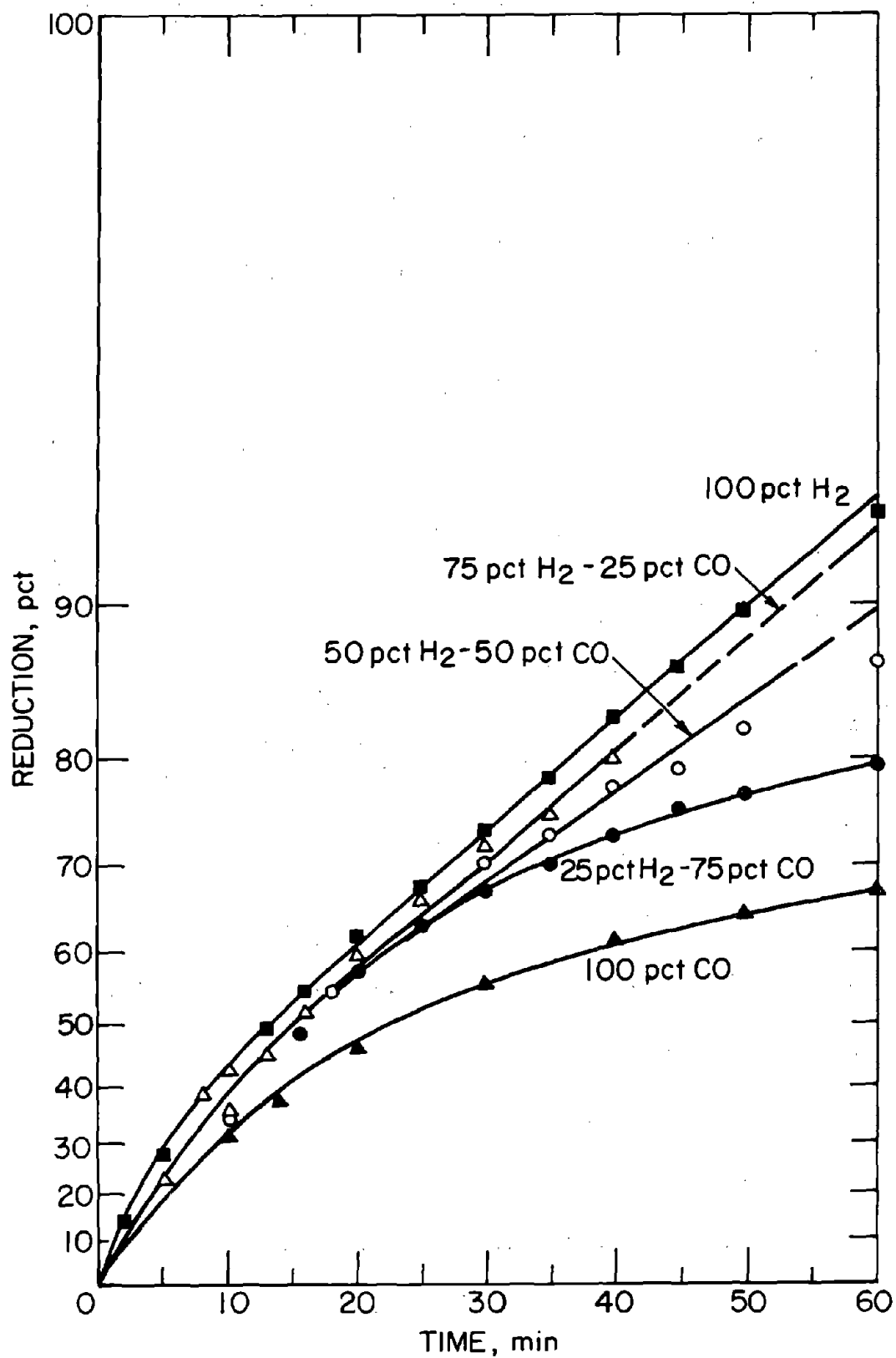


FIGURE 12. - Reduction of Brown Ore With Various CO-H₂ Mixtures at 750° C.

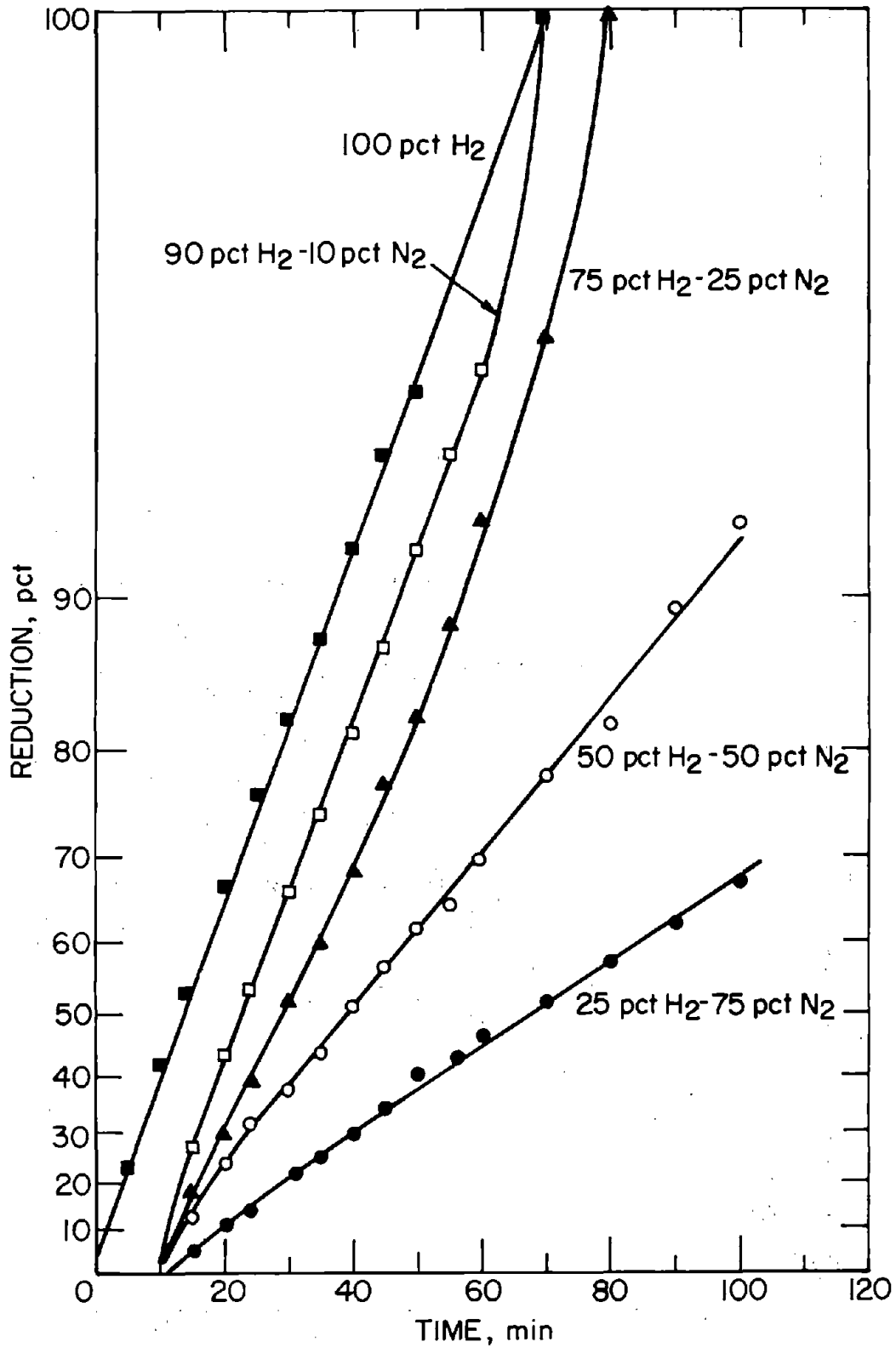


FIGURE 13. - Reduction of Brown Ore With Various H₂-N₂ Mixtures at 900° C. (Note that runs other than 100 pct hydrogen are offset 10 minutes to the right.)

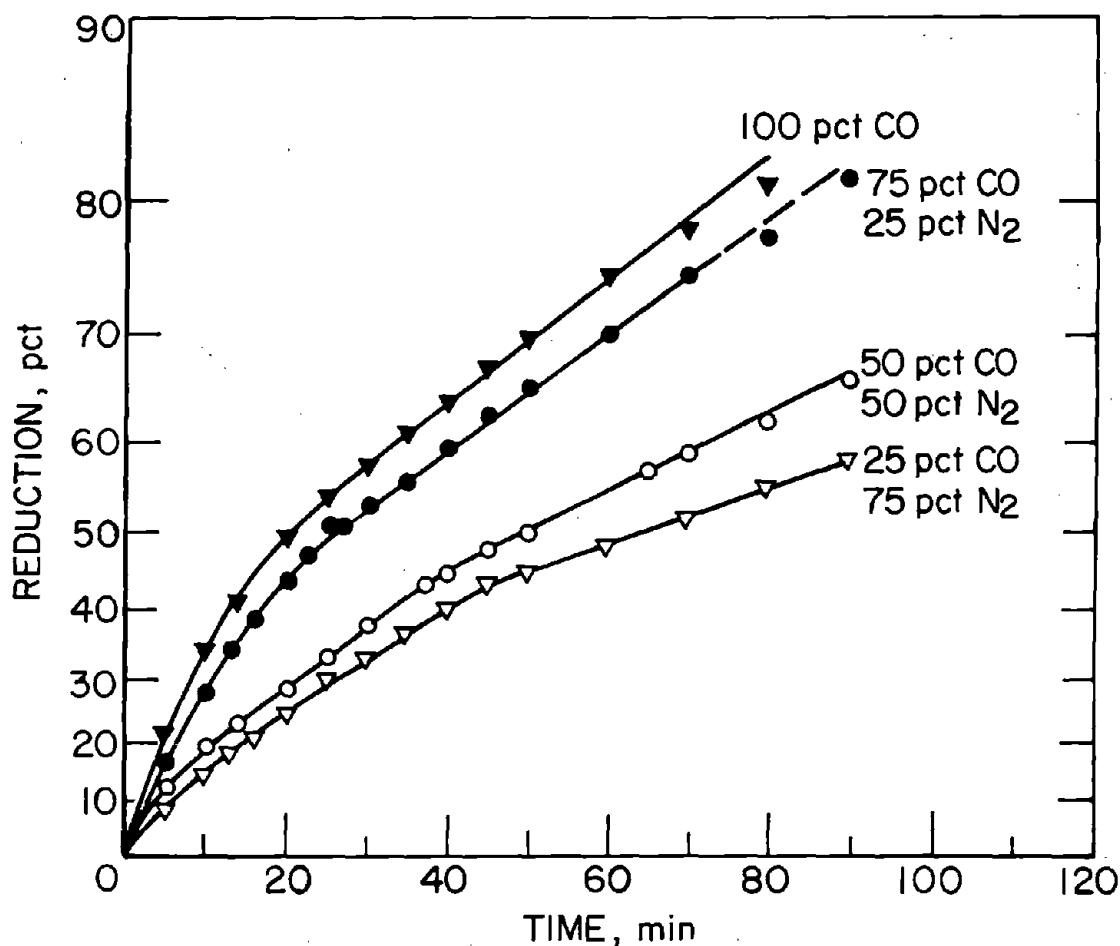


FIGURE 14. - Reduction of Brown Ore With Various CO-N₂ Mixtures at 900° C.

figures 13 and 14, show that the reduction rate is directly proportional to the pressure of the reducing gas. The addition of nitrogen dilutes the hydrogen and decreases its partial pressure, which in turn decreases the reduction rate proportionally.

The calculated reduction rates for the runs are shown in table 3. These data are shown graphically in figure 15.

TABLE 3. - Calculated reduction rates of brown ore with various gas mixtures at 900° C

Gas composition, pct		Hydrogen		Carbon monoxide	
Reductant	N ₂	Time, min	$\frac{1}{\text{Time}} \times 10^3$	Time, min	$\frac{1}{\text{Time}} \times 10^3$
25	75	270	3.70	560	1.79
50	50	166	6.02	394	2.54
75	25	100	10.0	268	3.73
100	0	74	13.5	101	5.53

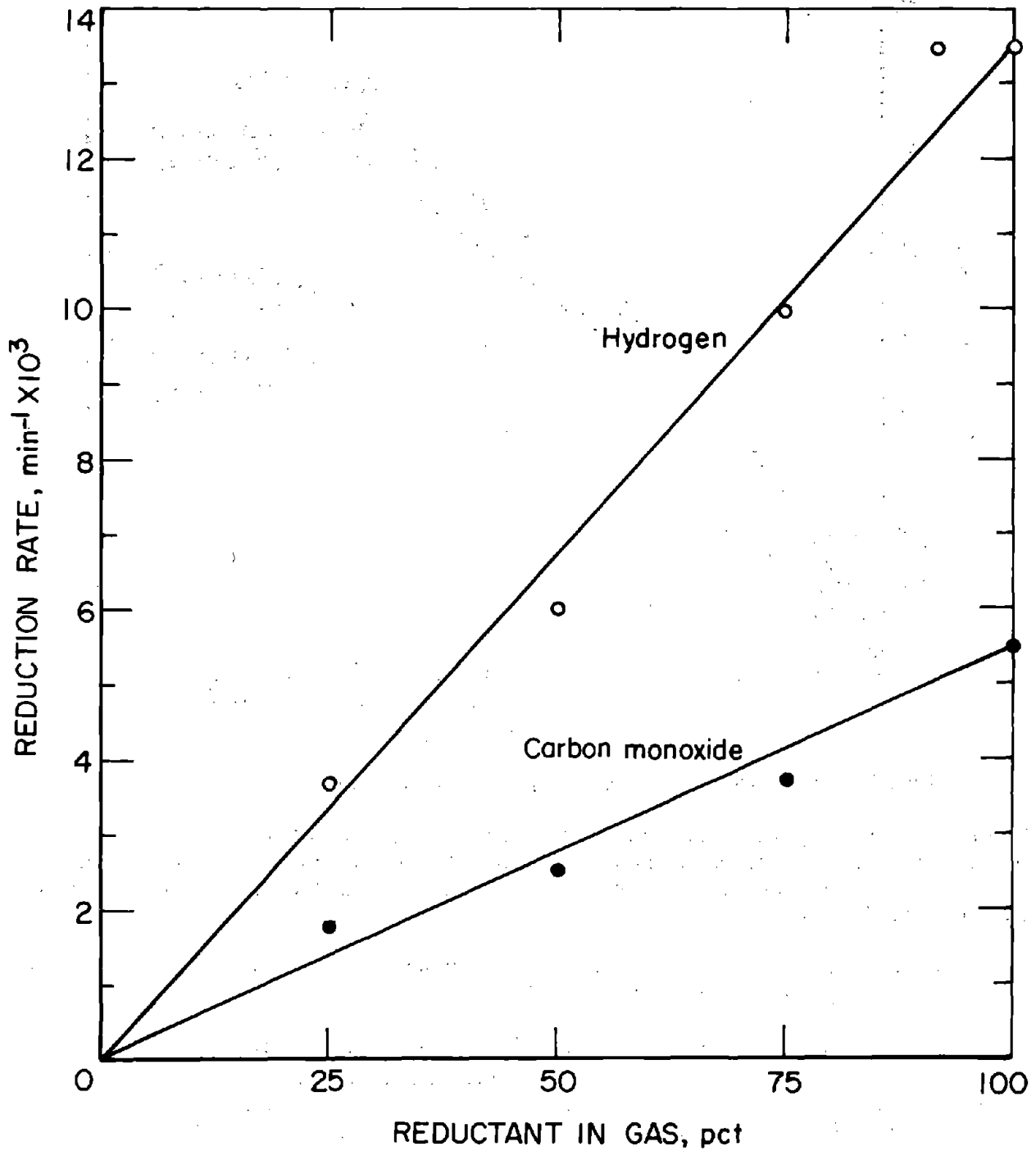


FIGURE 15. - Influence of Nitrogen Content on Reduction Rates of Brown Ore at 900° C.

Effect of Gas Flow

One of the conclusions from the study of the influence of temperature on the reduction rate was that at temperatures above about 725° C the reaction

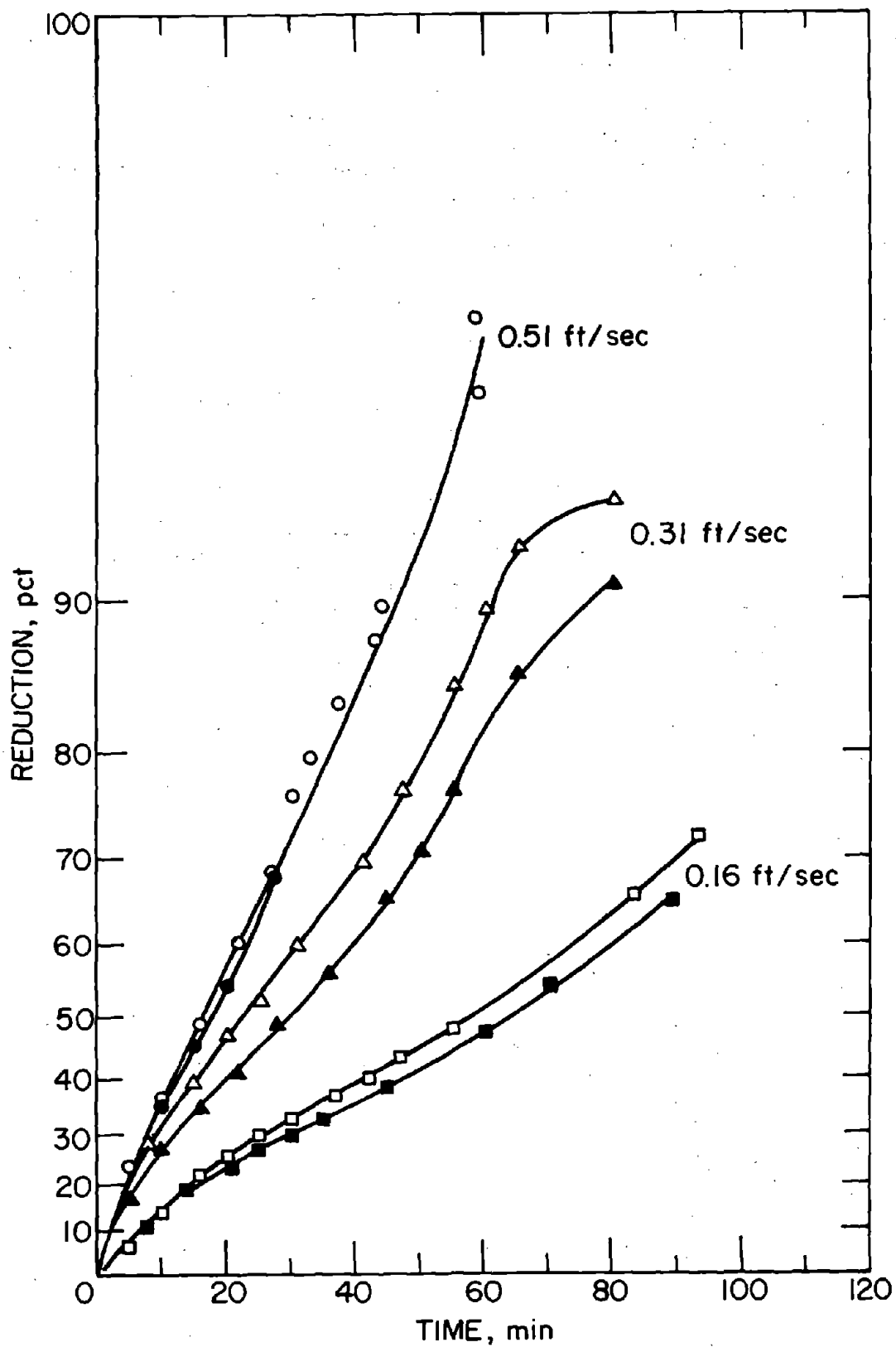


FIGURE 16. - Influence of Flow Rate of Hydrogen on Reduction of Red Ore at 850° C.

rate was controlled by the gas flow. To verify this conclusion, two series of experiments were run using the red ore concentrate. Experiments using hydrogen were run at 850° C; those using carbon monoxide were run at 800° C. Superficial space velocities of 0.16, 0.31, and 0.51 foot per second were used, which amounted to bulk flow rates of 9.4, 18.6, and 30.7 cubic feet of gas per hour, measured at the temperature and pressure of the reactor. Results of these reduction experiments are shown in figures 16 and 17. For hydrogen, figure 16, the reduction curves have positive curvature for all space velocities, indicating that flow rate is controlling the reaction speed. The reaction rate increases sharply as the space velocity increases. For carbon monoxide, figure 17, the rate of reduction increases rapidly with the higher space velocities, but the reduction curves remain linear, indicating that the increased space velocity has a profound effect on the reduction rate but is not rate controlling. This is also verified by the speed of reduction with carbon monoxide, which is very slow compared with the equivalent flow rate of hydrogen, although the reducing potential of the gas stream is nearly equivalent. The calculated reduction rates are shown in table 4.

TABLE 4. - Calculated reduction rates of red ore with different superficial space velocities

Superficial space velocity, ft/sec	Carbon monoxide		Hydrogen	
	Time, min	$\frac{1}{\text{Time}} \times 10^3$	Time, min	$\frac{1}{\text{Time}} \times 10^3$
0.16	850	1.18	318	3.14
.31	535	1.87	153	6.54
.51	372	2.69	95	10.5

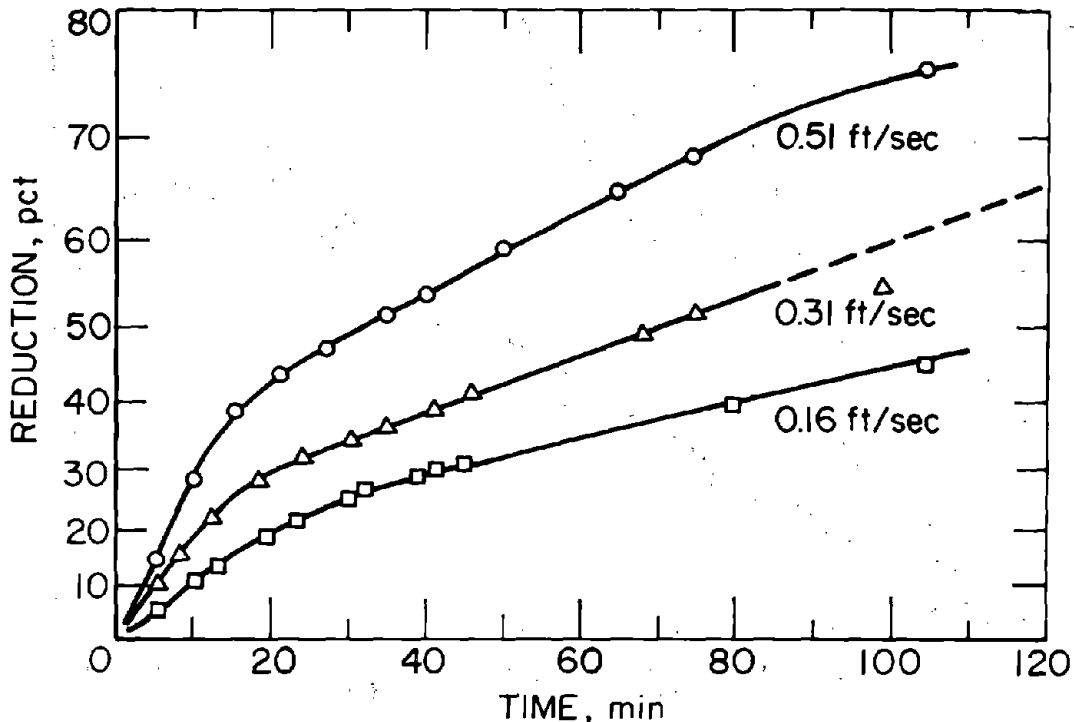


FIGURE 17. - Influence of Flow Rate of Carbon Monoxide on Reduction of Red Ore at 800° C.

Plotting these reaction rates against the superficial space velocity, figure 18, shows that the reaction rate is linear for hydrogen. For carbon monoxide the results are almost linear, but very much slower than similar results for hydrogen.

Composition of Exit Gas

Further evidence that above 700° C the hydrogen reaches equilibrium as it passes through the furnace and thereby controls the reaction rate can be obtained by calculating the composition of the exit gas. The amount of water

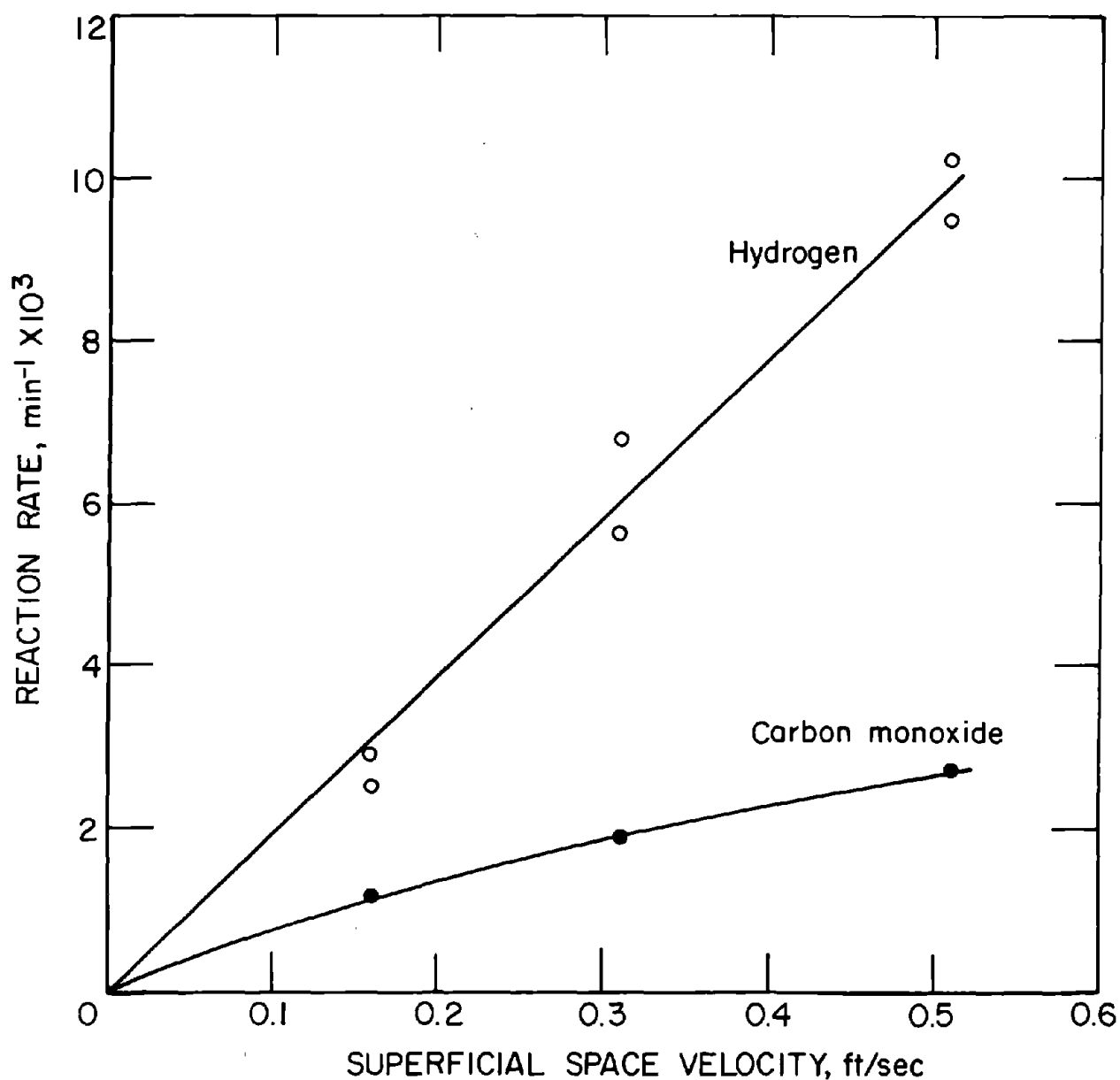


FIGURE 18. - Influence of Space Velocity on Reduction Rate.

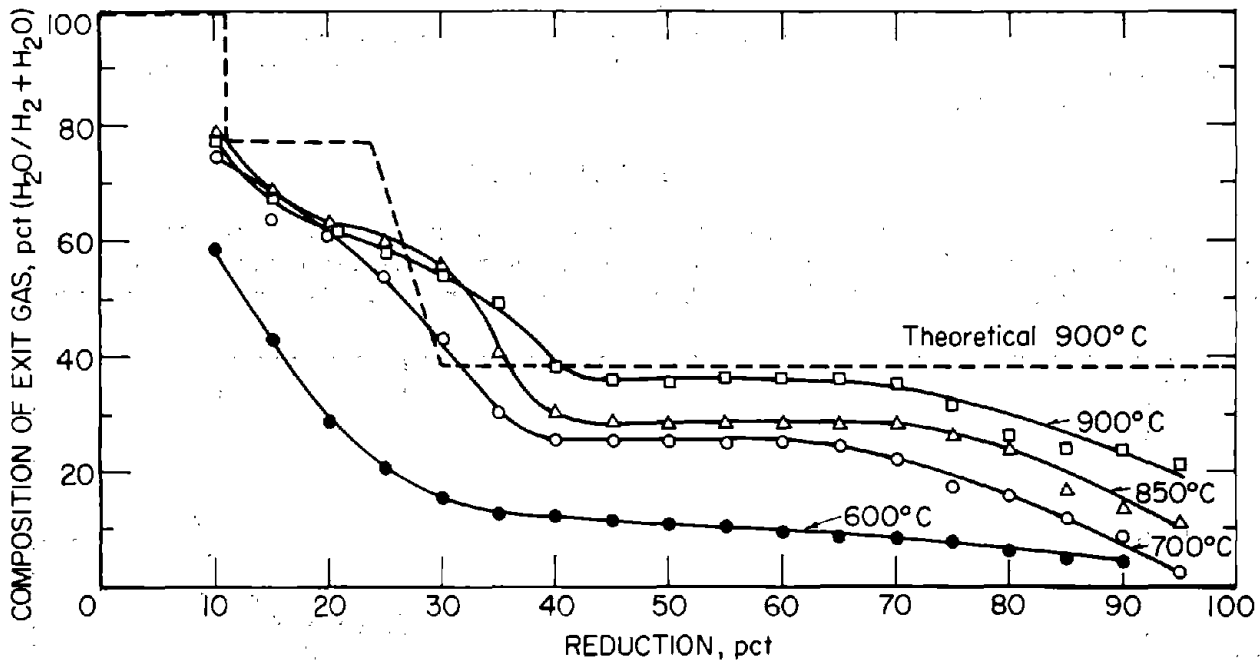


FIGURE 19. - Calculated Composition of Exit Gas.

formed and hydrogen oxidized per minute can be calculated from the loss of weight data, and from the amount of unreacted hydrogen obtained from the flow rate. The percentage $H_2O/H_2 + H_2O$ can be readily calculated during the run for various percent reductions. A plot of the composition of the exit gas against the percent reduction of the bed is shown in figure 19. The compositions of the gases in equilibrium with hematite-magnetite, magnetite-wustite, and wustite-iron are shown in the percent reduction range of 0-11, 11-33, and 33-100 percent, respectively, at $900^\circ C$. Variations and errors in the rate of gas flow will be reflected directly in the calculated water content of the exit gas, which explains why the exit gas for the $900^\circ C$ run, for example, has a higher water content than theoretically possible. While the percent water vapor in the exit gas is erratic until about 40 percent of the reduction is complete, the composition of the exit gas compares very well with the equilibrium composition between 40- and 70-percent reduction at temperatures above $700^\circ C$.

At $600^\circ C$ the composition of the exit gas is far below the equilibrium composition.

CONCLUSIONS

1. A fluidized-bed reactor is an effective method of reducing iron oxides with either carbon monoxide, hydrogen, or mixtures of the two.
2. At temperatures below about $725^\circ C$, depending on the gas composition and ore charged, the rate of reduction is controlled by the chemical reaction at the Fe-FeO interface. The activation energy for this reaction was between 10,800 and 11,800 cal/g mole.

3. The carbon monoxide reduced the red ore faster than did hydrogen at temperatures below 650° C. As the temperature was increased above 750° C, however, some inhibiting mechanism became active for the carbon monoxide reduction so the rate of reduction decreased rapidly on further increase in temperature. The $\left(1 - \left(1 - \frac{\text{percent reduction}}{100}\right)^{1/3}\right)$ curves were linear at the elevated temperature, indicating that the reduction rate was still being controlled by a reduction at the interface. The rate-inhibiting mechanism, which was present only with carbon monoxide reduction, is probably associated with the carburization and sintering of the reduced iron to effectively seal the reduction interface. It is noted that the eutectoid temperature for the iron-carbon is about 725° C, so that carburized iron would be austenitic above this temperature, while iron oxide reduced with hydrogen and not carburized would require temperatures above 900° C to become austenitic. Austenite would sinter more rapidly than ferrite at the same temperature because of its higher diffusion coefficient.

4. When reducing the iron ore concentrate with mixtures of pure CO and hydrogen, little difference is noted in the reaction rates at 500° C. As the temperature is increased to 750° C, the hydrogen gives more rapid reduction than carbon monoxide, and mixtures of the two give intermediate rates depending on the amount of hydrogen present. At 850° C hydrogen again reduces the ore much faster than carbon monoxide, and additions of carbon monoxide do not decrease the rate appreciably until the concentration exceeds 50 percent.

5. When hydrogen or carbon monoxide is diluted with nitrogen, the reduction rate is directly proportional to the partial pressure of the reducing constituent in the gas.

6. When reducing with hydrogen above 725° C, the rate of reduction was controlled by the flow rate of the reducing gas. The gas entering the reactor would react with the ore until its reducing potential was virtually depleted. The reduction rate, measured at 850° C, was directly proportional to the gas flow rate. Although the flow rate of carbon monoxide has a profound effect on the reducing rate at 800° C, it did not limit the reaction rate.

7. Optimum operating conditions for fluid bed reduction to obtain most effective use of the reducing potential of the gas are as follows:

- a. Temperature should be 725° C or higher. Only slight benefits are obtained by use of higher temperature.
- b. Highest reduction rates are obtained at these temperatures with hydrogen. Small additions of carbon monoxide have only slight inhibiting effects on the reduction rate. When the carbon monoxide exceeds 50 percent, the reduction rate is reduced sharply, probably owing to the carburization of the reduced iron.
- c. Since the reaction rate is controlled by the reducing potential of the gas, additions of water vapor, carbon dioxide, or oxygen would have a deleterious effect on the reduction rate.

