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CANADIAN OBSERVATIONS ON THE PROPOSED ISO/TC 102/SC 3 METHOD FOR MEASURING THE RELATIVE REDUCIBILITY OF NATURAL AND PROCESSED IRON ORES

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by

D.A. Reeve* and J.H. Walsh**

FOREWORD

This Technical Bulletin presents results of a series of tests done to evaluate some of the parameters of the proposed ISO/TC 102/SC 3 (International Organization for Standardization, Technical Committee 102 - Iron Ores, Sub-Committee 3 - Physical Testing of Iron Ores) method for measuring the relative reducibility of natural and processed iron ores, and to make recommendations for possible consideration in drafting the next ISO proposal.

The present report (with the exception of Figure 1) was tabled at the first working group meeting of ISO/TC 102/SC 3 held in Düsseldorf, West Germany, October 4th - 7th, 1971, and was given the ISO Document Number (Canada-3) 187E.

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Direction des Mines Bulletin technique TB 144

Les Observations canadiennes sur la méthode proposée par la ISO/TC 102/SC 3 pour mesurer la réductibilité relative des minerais de fer naturels et traités

par

D.A. Reeve*, et J.H. Walsh**

Avant-propos

On présente dans ce bulletin technique les résultats d'une série d'essais faits pour évaluer quelques-uns des paramètres d'une méthode proposée par la ISO/TC 102/SC 3 (Organisation internationale de normalisation, Comité technique 102 - Minerais de fer, Sous-comité 3 - Essai physique des minerais de fer) pour mesurer la réductibilité relative des minerais de fer naturels et traités et pour présenter des recommandations pour une considération possible faite par écrit de la prochaine proposition de la ISO.

Le rapport actuel (à l'exception de figure 1) a été présenté à la première réunion du groupe de travail de la ISO/TC 102/SC 3 à Düsseldorf, Allemagne de l'Ouest, du 4 au 7 octobre 1971, et porte le numéro de document (Canada - 3) 187-E de la ISO.

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INTRODUCTION

At the Fifth International Meeting of ISO/TC 102/SC 3 held in Ottawa, September 21 - 25, 1970, the Second Draft ISO Proposal for a method for measuring the relative reducibility of natural and processed iron ores (Document 174E[1]) was agreed upon by the attending delegates. Following that meeting, the Canadian Advisory Committee to ISO/TC 102 decided that Canada should have a more active participation in development of the reducibility test than before. Consequently, in February 1971, assembly began of a reducibility test apparatus at the Metals Reduction and Energy Centre of the Mines Branch in Ottawa.

After construction and testing of the apparatus had been completed, a series of tests was carried out to investigate several of the parameters which might influence the behaviour of iron ores under high-temperature reducing conditions and which might affect the reproducibility of the test method. The tests were done with Carol Lake pellets which were split from the same head sample used to supply the standard samples to participating countries in 1968. These pellets were supplied by the Iron Ore Company of Canada Limited, Sept Iles, Quebec. A chemical analysis of the pellets is given in Table 1.

TABLE 1

Chemical Analysis of Carol Lake Pellets

	Fe	Fe^{++}	P	Mn	SiO_2	Al_2O_3
Percentage:	65.28	0.36	0.010	0.18	5.05	0.31

The present report summarizes the results of this series of tests and attempts to point out areas of the test method which may lead to ambiguous and unreliable reducibility data. It is felt that these areas are worthy of more clarification in the next draft ISO proposal for a method of measuring the relative reducibility of natural and processed iron ores.

APPARATUS

The test apparatus for the determination of the reducibility of natural and processed iron ores was essentially identical to that described in ISO Document 174E[1], and is shown schematically in Figure 1. The reduction tube was made from Type 310 stainless steel and was suspended below a two-pan balance (capacity 20 kg, sensitivity 1 g).

The 30-inch long by 7-inch I.D. heating unit (11 kVA) of the furnace was constructed from quarter-circular Kanthal heating elements. The heating unit was divided into three zones, two 12 inches and one 6 inches long, with the 6-inch zone located at the top of the furnace. A temperature controller, sensing a single thermocouple at the mid-point of the heating unit, regulated two silicon-controlled rectifiers, one controlling the central set of elements and the other controlling the upper and lower sets of elements. Bias controls on the silicon-controlled rectifiers allowed independent adjustment of zone temperature. The temperature, up to 6 inches from the thermocouple, could be controlled to within 5°C by this system, and the temperature over the 30-inch heating unit was controlled to within 7°C.

A gas chromatograph with molecular-sieve and chromosorb-W columns was used for analysis of the exit gases from the reduction tube for carbon monoxide, carbon dioxide, and nitrogen. Gas samples were taken by syringe through a sample port attached to an extension of the gas outlet pipe of the reduction tube.

RESULTS AND DISCUSSION

(i) Effect of Flow Rate of Reducing Gas on Reducibility

As well as at total reducing-gas flow rate of 50 litres/min as stipulated in the Second Draft ISO Proposal (Document 174E), the reducibility of 500-g samples of the Carol Lake pellets was determined at total flow rates of 40, 25, and 20 litres/min, respectively. The oxygen removal:time curves for these flow rates are shown in Figure 2 and are essentially the same as those given by previous workers (see ISO Documents 150E[2] and 166E[3]). The reducibilities at atomic ratios of O/Fe of 0.75 and 0.90 are given in Table 2.

TABLE 2

Reducibility Test Results at Different Flow Rates

Flow rate (litres/min)	O/Fe = 0.9 (% O_2 loss/min)	O/Fe = 0.75 (% O_2 loss/min)	No. of Particles	Surface Area* (cm^2)
20	0.305	0.250	180	695
25	0.345	0.283	171	661
40	0.402	0.329	174	673
50	0.458	0.376	181	702

*Based on a mean particle diameter of 11.10 mm

The effect of flow rate of the reducing gas on reducibility is reflected by the reduction curve for $1/Q \rightarrow 0$, where Q is the flow rate in litres/min; this is also shown in Figure 2. This curve was plotted from data obtained by extrapolating to a zero value of 1/Q the straight lines obtained at different percentages of reduction on a graph of reduction time against 1/Q. This extrapolation method was described in Japanese Contribution 166E[3] and the $1/Q \rightarrow 0$ curve in Figure 2 shows the predicted reduction curve for extremely high flow rates.

However, in deciding upon a total flow rate for the reducibility test, the main requirement is that the minimum rate, defined as the flow rate at which the reduction reaction is controlled by the amount of carbon monoxide available, must be exceeded. Figure 3 shows the utilization of carbon monoxide and the production of carbon dioxide with time, as found by gas chromatographic analysis for total flow rates of 50, 40, and 20 litres/min, respectively.

Figure 3 indicates that the minimum flow rate is exceeded in all cases and, since the test measures the relative reducibility of iron ores, a lower flow rate than 50 litres/min could be tolerated and would be acceptable from the point of view of gas cost. Also, the reducibility of certain ores such as the difficult-to-reduce, compact, magnetite ore, described in Document

166E, has been shown to be almost unaffected by changes in flow rate of the reducing gas.

(ii) Effect of Particle Size on Reducibility

For a gas-solid reaction, the reaction rate is a function of the total surface area available for reaction. Hence, in Document 174E it is required that the number of particles in the test sample be reported for calculation of surface area. After sieving the Carol Lake pellets to the required size fraction, an average of 180 pellets was required to constitute a 500-g sample. However, keeping all other parameters the same, significant variations in reduction time were noted with different amounts of pellets. The two extreme cases in which the largest and smallest pellets (136 and 224, respectively) from the size fraction were chosen are shown in Figure 4 and the reducibility data are given in Table 3.

This factor, alone, of the effect of total surface area of the sample on reducibility could cause significant differences in both in-lab. and between-lab. reproducibility of test results. A smaller size fraction could not be used to solve this problem nor could the number of particles per test be standardized, but a sampling procedure, for obtaining a 500-g sample from the stipulated size fraction, such as a quartering or splitting technique could be written into the ISO proposal to ensure a test sample with a normal size distribution of particles within the stated range.

TABLE 3

Reducibility Test Results for Different Particle Sizes

Flow rate (litres/min)	O/Fe = 0.9 (%O_2 loss/min)	O/Fe = 0.75 (%O_2 loss/min)	No. of Particles /500-g Sample
50	0.352	0.292	136 (max. size)
50	0.427	0.350	224 (min. size)

(iii) Effect of Temperature on Reducibility

The Second Draft ISO Proposal requires a test temperature of 950 ± 10°C. Reduction curves for Carol Lake pellets with the thermocouple in the centre of the charge reading 940, 950, and 960°C, respectively, are shown in Figure 5. The reducibility data are given in Table 4.

TABLE 4

Reducibility Test Results at Different Temperatures

Temperature °C	O/Fe = 0.9 (%O_2 loss/min)	O/Fe = 0.75 (%O_2 loss/min)	No. of Particles /500-g Sample	Surface Area* (cm^2)
940	0.407	0.333	170	657
950	0.458	0.376	181	702
960	0.465	0.381	173	668

*Based on a mean particle diameter of 11.10 mm

The differences between the three reduction curves in Figure 5 would indicate that a range of temperature narrower than 20°C is required. Present furnace temperature control equipment makes it possible to construct a suitable furnace with control to within 10°C, and an allowable temperature of 950 ± 5°C would be more acceptable. However, because of the heat of reaction of carbon monoxide with iron oxide, the whole of the bed would not be expected to remain within these temperature limits, especially during the reduction of hematite to magnetite early in the test.

(iv) Preheating of Test Sample with the Reducing Gas

It has been noted (U.S.A. comments in Document 162E[4]) that swelling of the test sample may occur during preheating when inert gas is used, affecting the apparent rate of reduction of the sample. This swelling may be minimized if the reducing gas is used during preheating.

In the present study, no appreciable swelling of the Carol Lake pellets was observed when nitrogen was used during the preheating of sample. Figure 6 is the temperature:time curve for a 500-g sample heated from room temperature to 950°C. The total weight loss was 73 g after 100 minutes. The carbon monoxide utilization and carbon dioxide production are also shown in Figure 6 and the chemical analysis for the sample after cooling in nitrogen from 950°C is given in Table 5.

TABLE 5

Chemical Analysis of Reduced Pellets from the Preheat Test

	Fe^{o}	Fe^{++}	Fe^{+++}
Percentage:	35	41.6	0.10

Carbon deposition was found after the preheat test on the inner surfaces of the reduction tube and may have occurred on the pellets themselves. From a practical point of view, this carbon deposition together with test furnaces in different laboratories having different heating rates would preclude the use of reducing gas during preheating.

(v) Selection of Particles from the Reduced Sample for Chemical Analysis

The standard chemical analysis procedure for total iron, Fe^{++} and Fe^{+++} used at the Mines Branch (dissolution in hydrochloric acid, reduction to the ferrous state with stannous chloride and phosphoric acid, and titration with potassium dichromate solution using sodium diphenylamine p-sulphonate as internal indicator) required a sample weight equivalent to only two pellets (about 180 pellets in each test charge).

Because it cannot be assumed that each pellet in the charge has been reduced to the same degree after an overall degree of reduction of 60 per cent, a procedure for sampling the reduced charge for chemical analysis should be included in the description of the test method.

The procedure adopted for the present series of tests was to quarter the reduced pellets until from 20 to 25 pellets were left. Four pellets were picked at random from these and two at random were sent for chemical analysis. Crushing and splitting a certain percentage of the total charge may also be tried.

SUMMARY

Based on the present series of tests done on Carol Lake pellets, the following recommendations are made for the next draft ISO proposal for a method of measuring the relative reducibility of natural and processed iron ores:

A total reducing-gas flow rate as high as 50 litres/minute may not be necessary and the high cost of carbon monoxide gas would favour a lower flow rate.

As well as reporting the number of particles used to constitute the 500-g sample, a standard procedure for selecting pellets from the -10+12.5 mm size fraction should be written in the test procedure.

The acceptable temperature range for the test of 950±10°C should be reduced, possibly to 950±5°C.

Do not preheat the sample with reducing gas.

Write a procedure into the test method for obtaining a representative sample for chemical analysis from the reduced charge.

REFERENCES

1. Document ISO/TC 102/SC 3 (Secretariat - 65) 174E, "Second Draft ISO Proposal, A Method for Measuring the Relative Reducibility of Natural and Processed Iron Ores", (1971).

2. Document ISO/TC 102/WG 1 (France - 6) 150E, "Reducibility Results of the Tests of the French Committee Member, Tests made on the Pellets of Carol Lake", M. Pichon, (1969).

3. Document ISO/TC 102/SC 3 (Japan - 26) 166E, "Summary of Joint Experiment on Reducibility Test by the Method of First Draft ISO Proposal with Special Reference to Effect of Flow Rate of Reducing Gas on Reducibility", (1970).

4. Document ISO/TC 102/SC 3 (USA - 11) 162E, "USA Comments on ISO/TC 102/WG 1 (SC 3) Document 135E, First Draft Proposal, Method for Measuring the Relative Reducibility of Natural and Processed Iron Ores", (1970).

ACKNOWLEDGEMENTS

The writers thank the members of the Canadian Advisory Committee to ISO/TC 102 for their support of this work, especially Mr. R.C. Zavitz, of Dominion Foundries and Steel Limited, who is chairman of Committee SC 3. They thank Mr. D.D. Cameron for construction and development of the test apparatus, Mr. D.W. Morgan (a student of Waterloo University) for doing the tests described in this report, Dr. W.R. Leeder for assistance with the gas-chromatographic analysis, and the Chemical Analysis Section of the Mineral Sciences Division, Mines Branch, for the chemical analyses.

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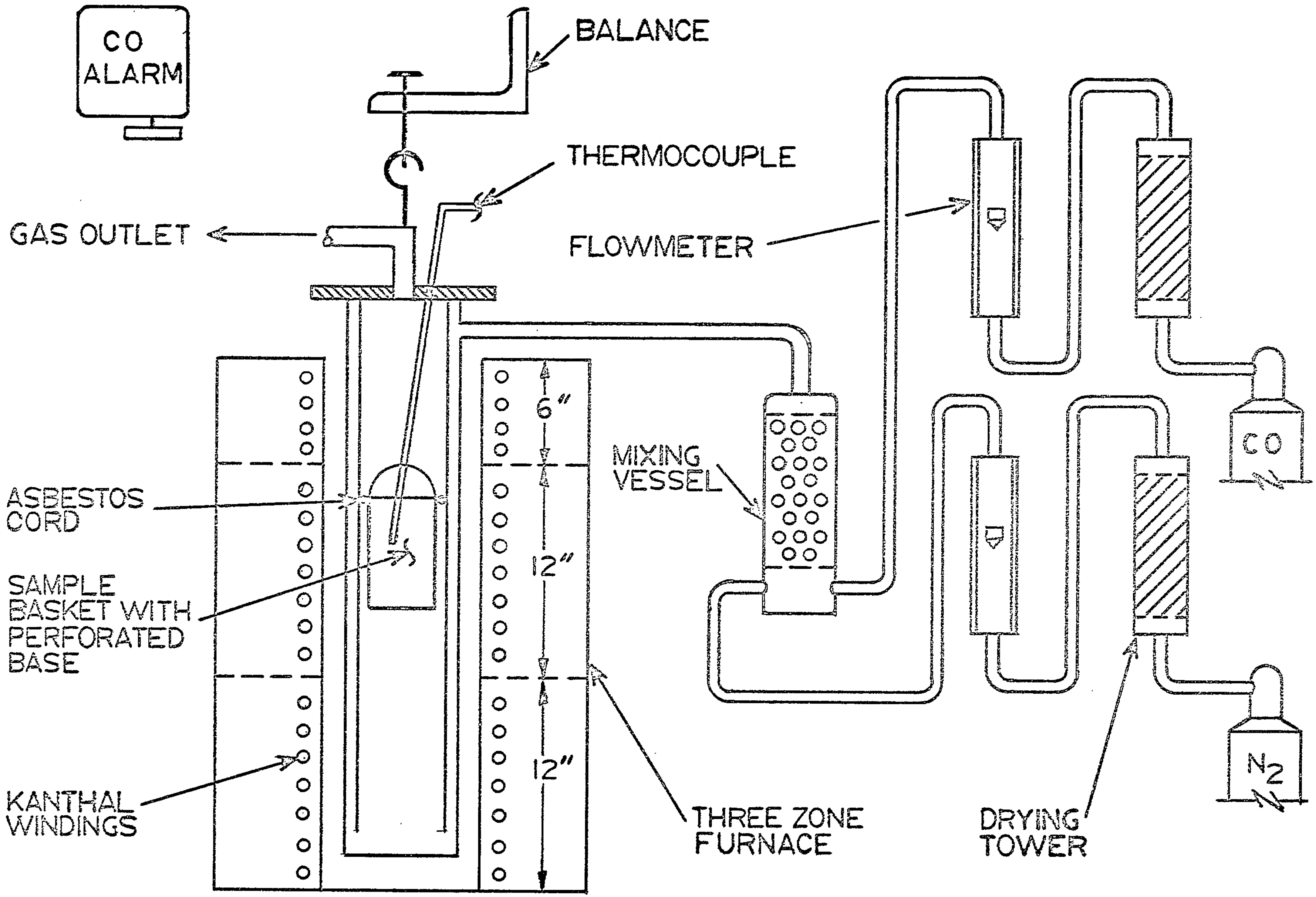

FIG. 1 - TEST APPARATUS FOR THE DETERMINATION OF THE REDUCIBILITY OF NATURAL AND PROCESSED IRON ORES

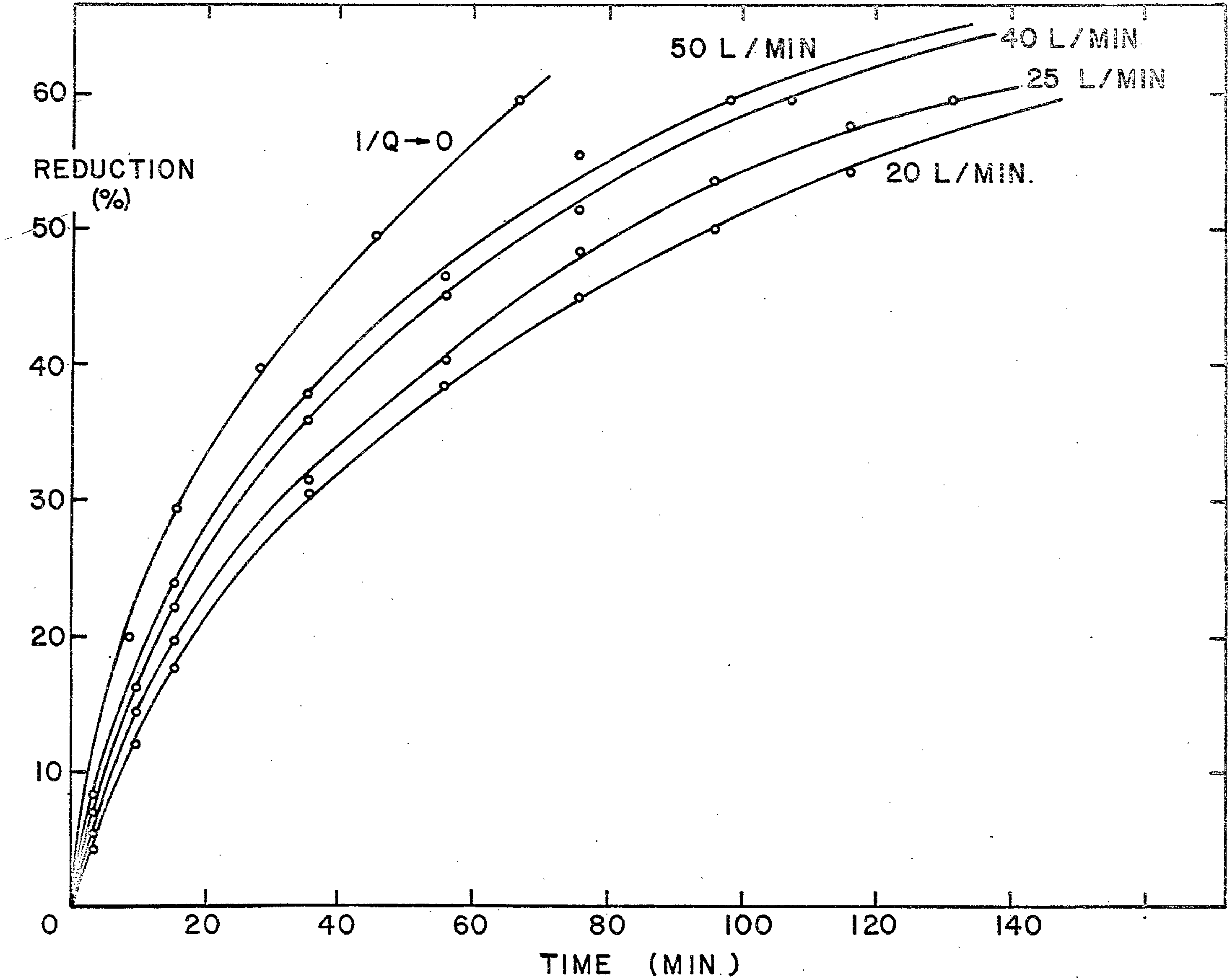

FIG. 2 - EFFECT OF FLOW RATE OF REDUCING GAS ON REDUCIBILITY

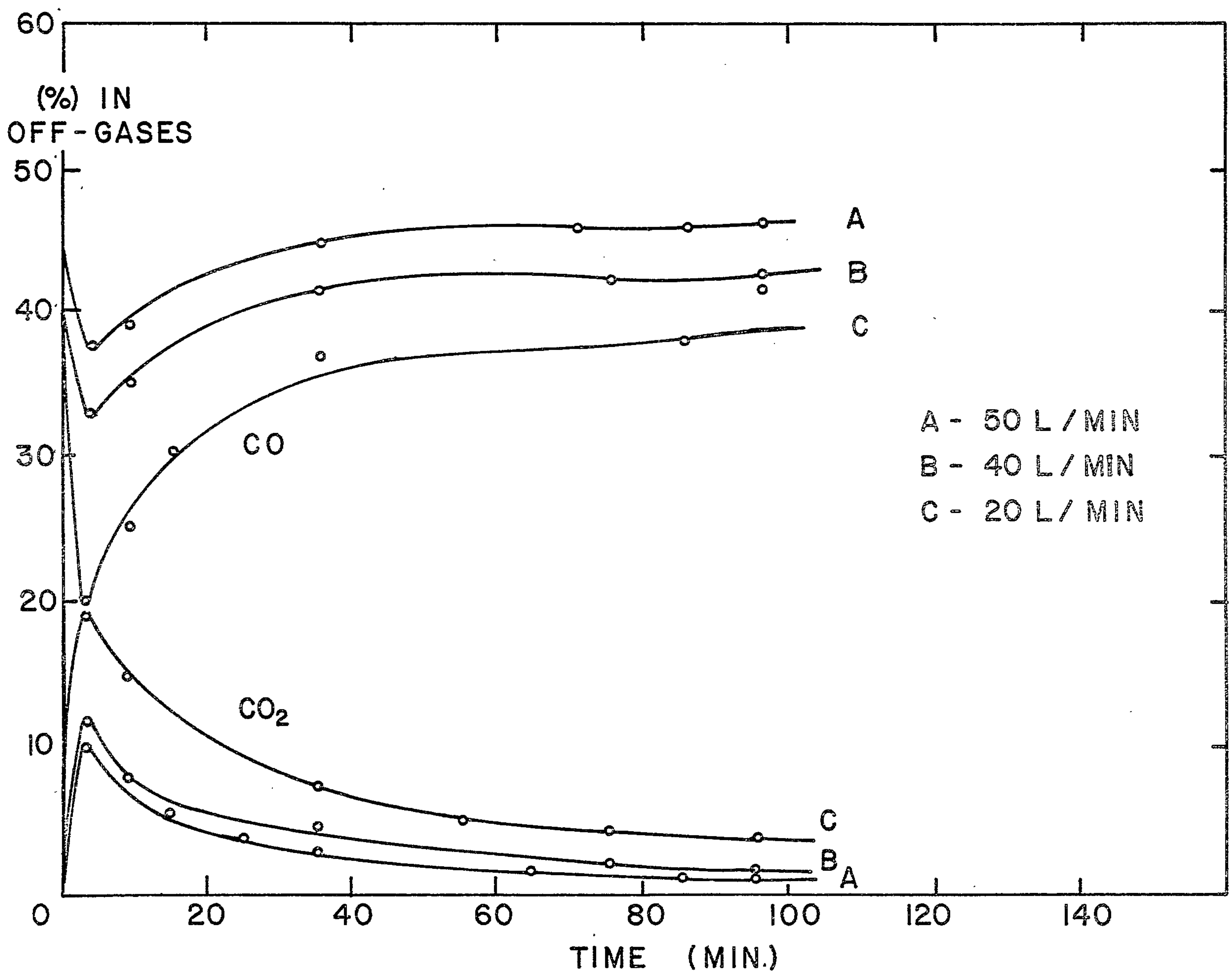

FIG. 3 - UTILIZATION OF CARBON MONOXIDE AND PRODUCTION OF CARBON DIOXIDE WITH TIME FOR DIFFERENT FLOW RATES

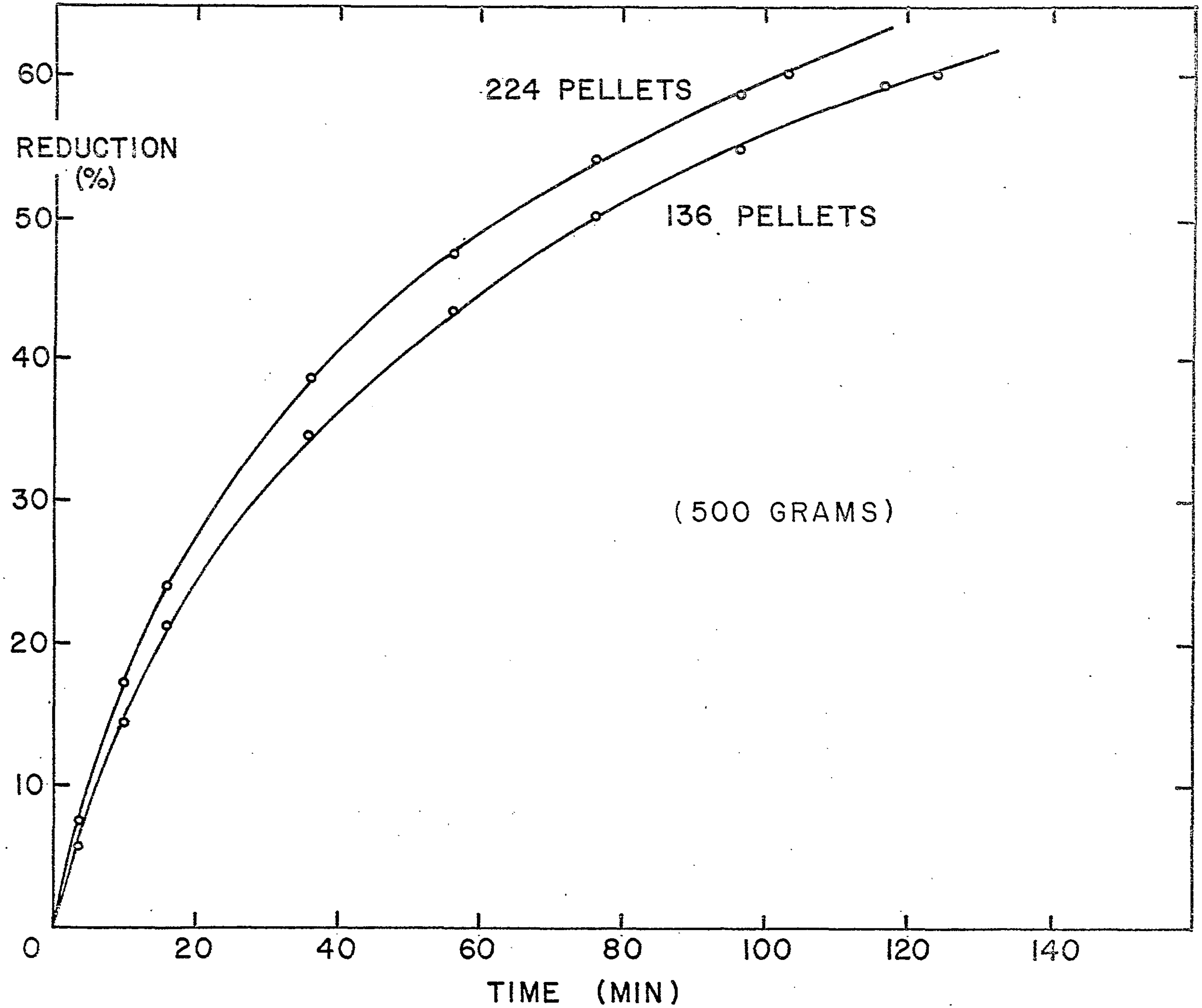

FIG.4. - EFFECT OF PARTICLE SIZE ON REDUCIBILITY

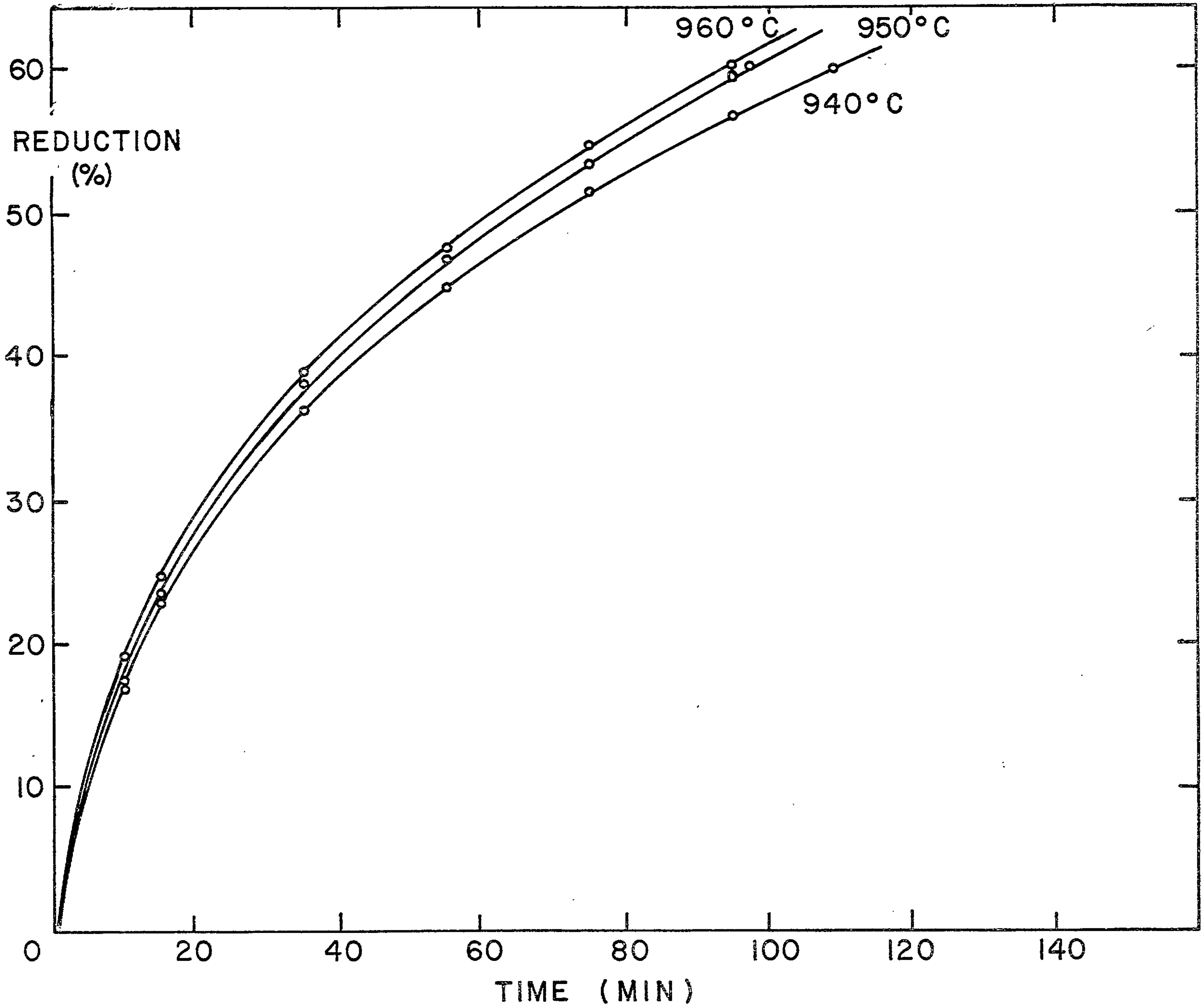

FIG.5.– EFFECT OF TEMPERATURE ON REDUCIBILITY

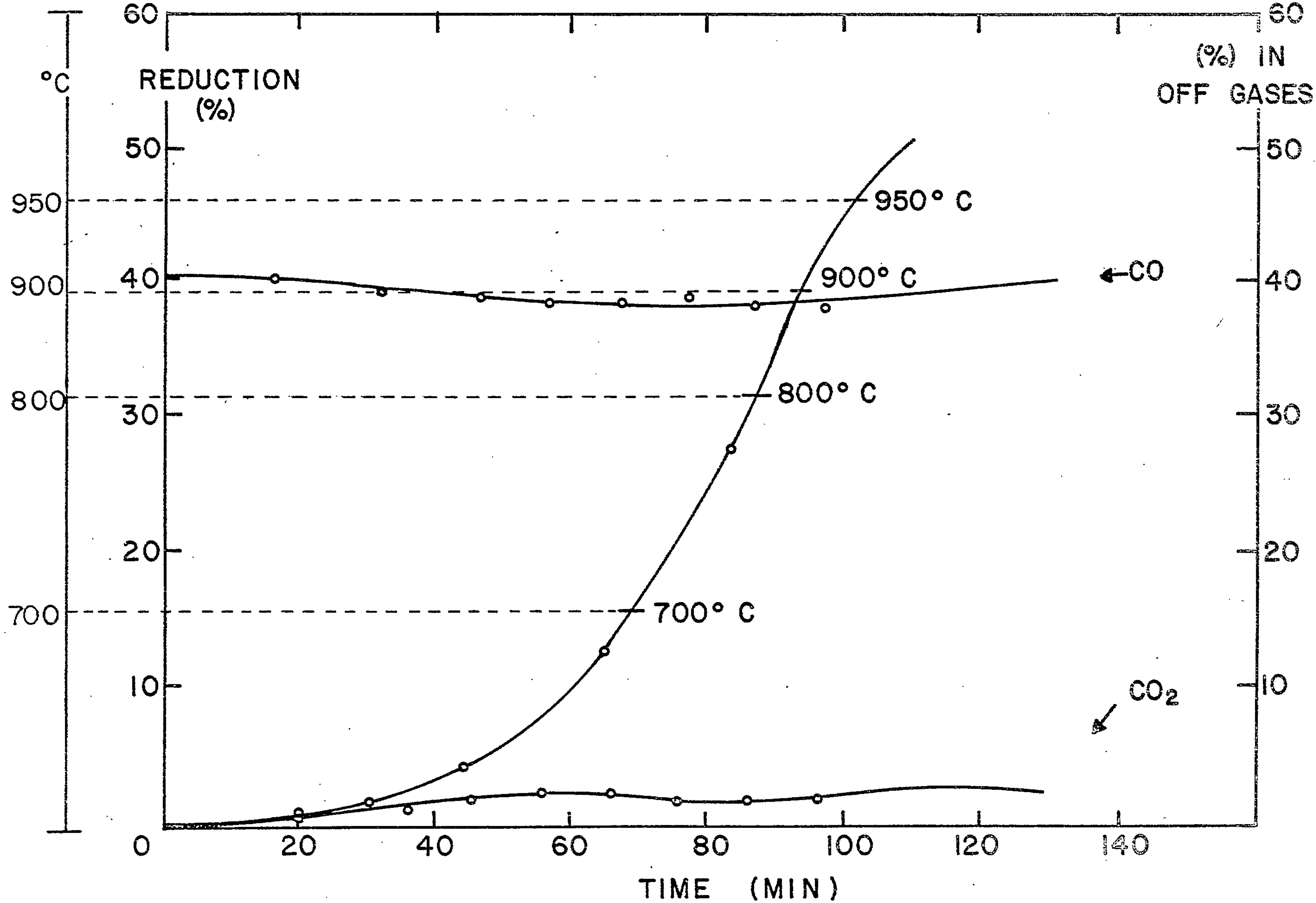

FIG. 6 – BEHAVIOUR OF CAROL LAKE PELLETS USING REDUCING GAS DURING PREHEATING