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OTTAWA

*MEASUREMENT OF THE REACTIVITY OF  
CARBONS FOR METALLURGICAL PROCESSES*

*PART I - THEORETICAL CONSIDERATIONS*

by

D. A. REEVE

*PART II - REACTIVITY OF CRUSHED COKE*

by

D. A. REEVE, N. J. RAMEY AND K. H. HAMPEL

METALS REDUCTION AND ENERGY CENTRE

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MEASUREMENT OF THE REACTIVITY OF CARBONS FOR METALLURGICAL PROCESSES

Part I - Theoretical Considerations

by

D.A. Reeve\*

Part II - Reactivity of Crushed Coke

by

D.A. Reeve\*, N.J. Ramey\*\* and K.H. Hampel \*\*\*

ABSTRACT

In Part I of this report, the importance of the reactivity of carbons to such metallurgical processes as the blast furnace and the SL/RN Direct Reduction Process is examined and the chemistry of the Boudouard Reaction is discussed.

In Part II, three test methods for measuring the reactivity of cokes to carbon dioxide are compared, a loss-in-weight method, a gas-analysis method with constant CO<sub>2</sub> flow rate, and a gas-analysis method with a variable CO<sub>2</sub> flow rate but constant amount of conversion of CO<sub>2</sub> to CO. Test results from the three methods on a series of eight cokes made from North American coking coals showed that any of the three methods would give acceptable relative reactivity values. A correlation between coke reactivity and blast furnace performance does not appear to have been established.

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LA MESURE DE LA RÉACTIVITÉ DES CARBONES POUR LES  
PROCÉDÉS MÉTALLURGIQUES

1<sup>ere</sup> PARTIE - LES CONSIDÉRATIONS THÉORIQUES

par

D. A. Reeve\*

2<sup>e</sup> PARTIE - LA RÉACTIVITÉ DU COKE CONCASSÉ

par

D. A. Reeve\*, N. J. Ramey\*\* et K. H. Hampel\*\*\*

RÉSUMÉ

Dans la 1<sup>ere</sup> Partie de ce rapport, l'auteur examine l'importance de la réactivité des carbones dans les procédés métallurgiques tels que le haut fourneau et le Procédé SL/RN de Réduction Directe. De plus, on discute de la chimie de la Réaction Boudouard.

Dans la 2<sup>e</sup> Partie, les auteurs comparent trois méthodes d'essai pour mesurer la réactivité des cokes au gaz carbonique: une méthode de chute de poids, une méthode d'analyse de gaz avec un débit constant de CO<sub>2</sub>, et une méthode d'analyse de gaz avec un débit variable de CO<sub>2</sub> mais une quantité constante de conversion de CO<sub>2</sub> à CO. Les résultats d'essai des trois méthodes sur une série de huit cokes faits des charbons cokéfiantes du Nord Amérique ont montré que n'importe lesquelles des trois méthodes donneraient des valeurs de réactivité relativement acceptables. Une corrélation entre la réactivité du coke et la performance du haut fourneau ne paraît pas avoir été établie.

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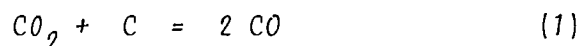
Part I - Theoretical Considerations

by

D.A. Reeve

INTRODUCTION

Measurement of the ability of coke to react with carbon dioxide (its reactivity) has been a continuing subject of debate and unsatisfactory conclusions. The stoichiometry (although not the mechanism) of the reaction between carbon dioxide and carbon is represented by the equation:



Dissension on the value of coke reactivity testing has arisen from both the complexity of the reaction mechanism, represented stoichiometrically in equation (1), and the relation of coke reactivity to blast furnace performance (for metallurgical cokes). Indeed, because of the established adsorption of the carbon monoxide reaction product on the surface of the reacting coke, the absolute reactivity of the sample being tested can be considered to be a function of time throughout the test. Because of this, the International Standards Association Technical Committee 27 (Solid Mineral Fuels) is no longer recommending an International Standard test for coke reactivity<sup>(1)</sup>. The precise role of coke reactivity in blast furnace operation does not appear to have been established. Miyazu and co-workers<sup>(2)</sup>, from observations of factors which influence blast furnace coke rate (the number of pounds of coke required to produce one ton of hot metal) taken over a two-year period at the Keihin Works of Nippon Kokan Kabushiki Kaisha, Kawasaki, Japan, have concluded that coke

reactivity does have an effect on coke rate. However, this conclusion was based on the entire period, whereas no correlation was found during some four-month parts of the two-year period; therefore the conclusions were not considered to be completely valid. Schenck and Wenzel<sup>(3)</sup> have used an apparatus for measuring carbon dioxide reduction by coke under conditions representing such blast furnace parameters as temperature gradient, variation in gas analysis, increase in gas pressure, and increase of mechanical pressure on coke in the blast furnace stack. Test results indicated that the  $CO_2$  reduction reaction in the blast furnace proceeds along different lines from in standardized laboratory reductions.

It would be perhaps relevant at this stage to discuss briefly the part played by coke in the reduction zone of the blast furnace. The reduction of the iron ore proceeds by an indirect method in that the iron oxide is reduced by carbon monoxide, and the carbon dioxide thus produced reacts with coke to regenerate carbon monoxide. The thermochemistry of the reduction zone of the blast furnace depends to a large extent on the relative rates of the reaction of  $CO$  with iron oxide and of  $CO_2$  with coke. From a thermodynamic-equilibrium view point, for temperatures above about  $800^{\circ}C$ , the equilibrium  $CO/CO_2$  ratio for reaction (1), the Boudouard reaction, is always higher than that for the indirect reduction of iron oxide. Therefore blast furnace stack gas produced by the carbon equilibrium has a sufficiently high  $CO/CO_2$  ratio to cause the reaction between iron oxide and carbon monoxide to go from left to right. It is desirable to have a coke showing minimum reactivity to  $CO_2$  in the upper part of the blast furnace to minimize loss of carbon as  $CO$  by the Boudouard reaction. Also, of course, metallurgical coke must possess the quality of good combustibility at the tuyères to provide the energy requirements for the reduction process.

Various methods of modelling the shaft of the blast furnace have been proposed for describing the chemical performance of this gas-solids counter-flow reactor. One such model, developed by Rist<sup>(4)</sup> (Figure 1), depicts graphically the exchange of oxygen between the downward moving solid charge and the upward moving gases. Co-ordinates are chosen to represent both phases such that the oxygen transfer relation between carbon and iron can be described linearly. These co-ordinates are the  $O/Fe$  and  $O/C$  ratios of the iron oxide and reducing gas, respectively, at various levels in the blast furnace. The abscissa shows the degree of oxidation of carbon in mole  $O$ /mole  $C$  (also equivalent to  $CO_2/CO+CO_2$ ), while the ordinate shows the degree of oxidation of iron in mole  $O$ /mole  $Fe$ .

The course of the reduction process in the blast furnace is followed by the "operating line" EA, with a slope equal to  $C/Fe$ , the carbon or gas consumption per unit of  $Fe$  produced. The shaded area shows the equilibrium restrictions on the system at about  $1000^{\circ}C$ .

Gaseous reduction, represented by AB in Figure 1, is most efficient when gas is in equilibrium with wüstite at point W. The temperature corresponding to point W (defining the "reserve zone" temperature) is the highest at which carbon dioxide will just not react with coke under blast furnace conditions. Thus the reactivity of the coke should directly influence the blast furnace shaft conditions. For ideal counter-flow conditions, the operating line passes close to the point W but, if the coke is more reactive, W moves to the right (discontinuous line in Figure 1) and the blast furnace top gas will become richer in carbon dioxide.

The reactivity of carbon can influence the performance of such solid-state direct reduction iron making processes as the SL/RN Process as well as the blast furnace process. In the SL/RN Process, as much carbon monoxide as possible is required in the bottom part of the rotating kiln, but



the upper temperature limit of operation is to a certain extent constrained by the ash fusion point of the reductant; above this temperature unacceptable clinker formation may occur. Therefore, to maintain satisfactory reduction of iron ore by carbon monoxide from the gasification of the reductant, carbon reactivity has to be balanced against ash fusion temperature. Also, in this type of process as well as in the blast furnace, carbon reactivity may go hand in hand with iron ore reducibility. Correlations between them may become apparent from experiments using either isothermal loss-in-weight techniques or complex non-isothermal methods such as the Rist Apparatus<sup>(4)</sup>.

#### CHEMISTRY OF THE GASIFICATION REACTION

The reactivity of a particular coke, as well as being dependent on the properties of the parent coal, is to a large extent governed by such factors as final temperature of carbonization, carbonization rate, and moisture content of the coal. Reactivity is often measured by reacting coke with carbon dioxide at high temperatures. However, this reaction has long been recognized as being very complex and this section will attempt to summarize some of the more recent conclusions on the kinetics of the gasification reaction.

In 1958, Blayden<sup>(5)</sup> reviewed current knowledge on the reactivity of cokes and chars and pointed out the importance of surface oxide complexes and active reaction sites in the gasification reaction. He also noted that the relative contributions of chemical reactions at the coke surface and of mass transfer effects, arising from diffusion at the reaction interface, vary with reaction conditions. In a series of publications<sup>(6, 11)</sup>, Turkdogan et al have studied the rate of oxidation of graphite, charcoal, and metallurgical coke in carbon dioxide-carbon monoxide mixtures. This definitive work has, to a large

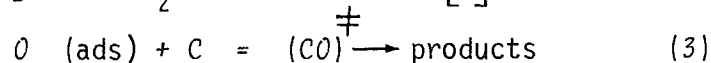
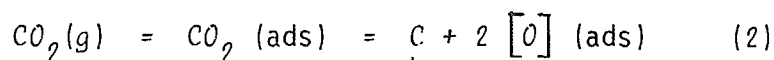
extent, put into a perspective the effects of mass transfer and chemical contributions to the gasification reaction and has also studied the effects of particle size, temperature, pressure, and porosity on the reaction kinetics.

In pure carbon dioxide, there are three limiting cases of rate-controlling processes:

- (i) complete internal burning of minus one-cm particles below 900°C, the diffusion in and out of pores being essentially complete and the rate of internal burning being controlled by the chemical reaction rate of gas and carbon;
- (ii) partial internal burning between 1000 to 1300°C in which the rate is controlled both by the chemical reaction and incomplete pore diffusion of gaseous reactants and products; and
- (iii) external burning (at higher temperatures, depending on particle size, pressure, and gas composition) in which oxidation rate is controlled by a gas-film diffusion process

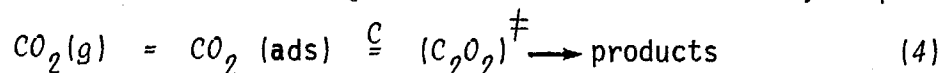
At the temperature and the particle size used in this investigation (1000°C and -20 +35 mesh, respectively), the reaction rate seems to be controlled by a mechanism in the transition region between the first two rate-limiting cases. In fact, Turkdogan<sup>(6)</sup> gives a critical maximum sphere diameter of 0.3 cm for complete pore diffusion at 1000°C and one atmosphere CO<sub>2</sub> and, for larger particle sizes, it is the lack of complete pore diffusion in the carbon particles which leads to an apparent complex pressure dependence of the reaction rates at temperatures above 1000°C.

As postulated previously by other workers<sup>(12, 13)</sup>, the rate controlling reaction for the oxidation of carbon by carbon dioxide in the absence of carbon monoxide is considered to be the formation of carbon monoxide in the chemi-sorbed layer via an activated complex:



On the other hand, in the presence of CO (more than 10 percent), a second mechanism that is in series with the first and involves CO<sub>2</sub> dissociation on the

carbon surface, with a rate very much faster than the first, is postulated:



This control of oxidation rate by two reactions in series, the second being much faster than the first for very low CO concentrations, to some extent negates the argument that reactivity tests such as the loss-in-weight method are not valid because of poisoning of the coke surface by adsorbed reaction product. Consequently, the argument has been applied that a method in which the amount of CO<sub>2</sub> to CO conversion is controlled (third method of the present study) should be used to minimize errors caused by CO reaction inhibition.

In spite of the above argument, under the conditions used in the present study, incomplete internal burning of coke will be controlled both by chemical reaction on pore walls and by counter-diffusion of CO<sub>2</sub> and CO in the pores. Therefore within the pores themselves, CO adsorption must play some part in reaction rate control even though pure CO<sub>2</sub> is used as the reaction gas, although the retarding effect of the CO adsorption will diminish with increasing temperature.

Very recently, Turkdogan and Vinters<sup>(14)</sup> have studied the catalytic oxidation of carbons by impregnating electrode graphite granules with silver, copper, chromium, zinc, nickel, cobalt, and iron. When the graphite was impregnated with iron, nickel, or cobalt, the oxidation rate in CO<sub>2</sub>/CO mixtures increased by several orders of magnitude but silver, copper, zinc, and chromium had virtually no effect on the rate of oxidation of graphite in CO<sub>2</sub>. Therefore, it may be inferred that the presence of sodium in lignite chars, used for the SL/RN Process, may affect their reactivities as well as the ash fusion temperature.

## Part II - Reactivity of Crushed Coke

by

D.A. Reeve, N.J. Ramey and K.H. Hampel

### INTRODUCTION

In the laboratory, various methods have been used for establishing reactivity indices of coke, for example, weight loss, and gas analysis methods. Indirect assessments of reactivity such as measurement of electrical conductivity<sup>(15)</sup> also have been used. In this investigation, the three methods used were:

1. loss-in-weight method, reactivity being reported as the percentage loss in weight of the coke;
2. gas analysis method, reactivity being reported as the value of the  $CO_2/CO + CO_2$  ratio of exit gas with a constant inlet flow rate of  $CO_2$ ; and
3. gas analysis method, reactivity being reported as the  $CO_2$  flow rate necessary to produce 20 per cent by volume of  $CO$  in the exit gas.

#### Loss-in-Weight Method

The experimental technique for the loss-in-weight method was similar to that used by Thompson, Mantione, and Aikman<sup>(16)</sup>, except that the sample weight was less (5 g instead of 50) and the sample was loose in an alumina boat in the furnace reaction tube instead of as a plug. Thompson et al had found that a reaction temperature of approximately 1000°C gave the best separation of reactivity values for high and low-reactivity cokes and, consequently, this temperature was used for all the test methods described in the

present report.

The apparatus is shown in Figure 2. Carbon dioxide from a cylinder was dried in a tower of magnesium perchlorate, passed through the reaction tube at a flow rate of 50 cc/min, and monitored by a capillary flowmeter using dibutyl phthalate as the manometric fluid. Flow was kept constant by means of a constant-head bubbler tube containing vacuum-pump oil. The alumina boat in the reaction tube ( 1 inch in diameter) contained 5 g of 20 to 35-mesh coke and the sample temperature was monitored by a thermocouple whose tip dipped into the sample.

The test sample was preheated to 1000<sup>0</sup>C in a flow of nitrogen, and oxidation of the coke by carbon dioxide was allowed to proceed for two hours. Reactivity of the coke to carbon dioxide was reported as the loss in weight, with a correction for ash content, expressed as a percentage of the original sample weight.

#### Gas Analysis Method, with Uncontrolled Conversion of $CO_2$ to $CO$

The apparatus used for this method of testing coke reactivity was the same as shown in Figure 2. Again, 5 g of 20 to 35-mesh coke was contained in an alumina boat. However, reactivity was expressed as the  $CO_2/(CO + CO_2)$  ratio of the product gases after 90 minutes reaction time (when this ratio had become approximately constant), for a carbon dioxide inlet flow rate of 50 cc/min. Gas analysis was done with a Fisher Partitioner gas chromatograph coupled to an Infotronics automatic digital integrator. The chromatograph was calibrated before each test with a standard mixture of 15 per cent  $CO_2$ , 10 per cent  $CO$  and 75 per cent nitrogen.

This gas analysis method is similar to the Japanese Industrial Standard Method (JIS K2151, Section 7) except that a plug sample was not used.

Gas Analysis Method, with Controlled Conversion of  $CO_2$  to  $CO$

The third test method used for the reactivity of coke was based on a Norwegian proposal<sup>(17)</sup> to the International Standards Organization Technical Committee 27 (Solid Mineral Fuels) and attempts to take into account the possible inhibiting effect of carbon monoxide on the reaction rate.

The apparatus is shown in Figure 3. A fixed volume (10 cc) of 20 to 35-mesh coke, rather than a fixed weight, was held in the hot zone of a vertical furnace on a sintered quartz frit in a quartz tube. A thin layer of small, loose pieces of silica was placed between the frit and the sample. A fixed volume of sample, rather than a fixed weight as in the first two methods, was used in an effort to achieve the same sample geometric surface area for each test. The flow of carbon dioxide from a cylinder was controlled with a needle valve and rotameter-type flow meter. A mercury manometer was included in the system to allow  $CO_2$  flows to be corrected to S.T.P. ( $0^{\circ}C$  and 760 mm Hg). After drying in a tower of magnesium perchlorate, the  $CO_2$  was preheated as it passed down a narrow tube in the furnace before entering the bottom of the reaction vessel. Temperature of the coke sample was monitored by a sheathed thermocouple penetrating the sample. A flow of nitrogen was passed through the system until the test temperature of  $1000^{\circ}C$  had been attained. Any volatile matter was expelled from the sample by heating to  $1000^{\circ}C$  under nitrogen in a separate furnace; this procedure helped to prolong the life of the silica reaction vessel.

This test was done by adjusting the carbon dioxide flow to give a reaction rate resulting in 20 per cent by volume carbon monoxide in the product gases after 90 minutes had elapsed from the start of the test. Gas analysis was done with the gas chromatograph, but future analysis will be done with an infra-red analyzer to achieve continuous measurement of the  $CO_2$

in the exit gas. If no gas analysis equipment were available, it would still be possible to do the test by monitoring the flow of exit gas with a meter calibrated with a 20:80 (volume)  $CO:CO_2$  mixture, assuming that, for 20 per cent conversion of the original  $CO_2$  stream, one molecule of  $CO_2$  will yield 1.2 molecules of  $CO$  (Equation 1).

The reactivity ( $R$ ) of the coke was expressed by the equation:

$$R = \frac{V}{G-a} \quad (5)$$

where

{	$R$ is expressed in cc $CO_2$ /(min g fixed carbon) at S.T.P.
	$V$ is $CO_2$ flow in cc/minute
	$G$ is sample weight in grams
	$a$ is ash content of sample in grams

Thus, this method minimizes those factors which may affect the reaction mechanism for the oxidation of carbon by carbon dioxide by: - (a) providing a constant surface for reaction, (b) standardizing the product gas composition, and (c) preheating the carbon dioxide to minimize effects of sample-bed temperature distribution between samples of different reactivity. Differences in sample-bed temperature distribution could be further minimized by using a reaction tube made from a material such as stainless steel that has a higher thermal conductivity than quartz.

## RESULTS AND DISCUSSION

Reactivity measurements, using the three test methods and made on eight different coke samples, covered a wide range of reactivities. Results are given in Table 1; in most cases, the reactivity listed is the average from three tests.

Table 1: Coke Reactivity Results from the Three Test Methods

Sample	Method 1 percentage weight loss	Method 2 $CO_2 / (CO + CO_2)$ after 90 minutes	Method 3 cc $CO_2$ at S.T.P./ (minute g fixed carbon)
A	20.8	0.537	0.605
B	16.2	0.620	0.572
C	12.7	0.639	0.525
D	12.1	0.652	0.351
E	11.0	0.686	0.327
F	10.6	0.728	0.270
G	10.3	0.737	0.261
H	7.3	0.797	0.259

The coke samples A to H had been prepared by carbonization of coals of different compositions in the Mines Branch movable-wall test ovens. In accord with the findings of Thompson et al <sup>(16)</sup>, there was no correlation between reactivity and composition of the parent coal. This lack of correlation is illustrated in Figure 4 in which reactivity\* determined by Method 1 is plotted against percentage of volatile matter in the parent coals.

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\*Data for Figure 4 were obtained from coke samples different from those included in Table 1.



For the second test method, the change in the  $CO_2/(CO+CO_2)$  ratio of the product gases with time is shown in Figure 5. The  $CO_2/(CO+CO_2)$  ratio was constant within 90 minutes after which the reactivity was reported. There was some doubt as to whether a constant value had been obtained after 60 minutes of reaction time (time specified in the Japanese Industrial Standard Test, JIS K2151, Section 7). Based on Figure 5, a test time of 90 minutes was chosen for Test Method No. 3 (gas analysis with controlled conversion of  $CO_2$  to  $CO$ ).

Correlations between the three methods are shown in Figures 6, 7, and 8 with the respective statistically calculated correlation coefficients. All three correlation coefficients lie within the 0.001 probability level; such excellent correlations indicate that, for the coke samples studied, any of the three methods gave satisfactory results for the relative reactivities of the samples.

#### SUMMARY AND CONCLUSIONS

Three test methods for the measurement of the reactivity of coke to carbon dioxide have been compared. The first was a loss-in-weight method, whereas the second and third were gas analysis methods. A brief survey on the chemistry of the gasification reaction indicated that the reaction mechanism at the test temperature ( $1000^{\circ}C$ ) will be controlled by both chemical reaction on pore walls and counter-diffusion of  $CO$  and  $CO_2$  within pores, the latter factor raising the possibility of inhibition of the reaction by adsorbed carbon monoxide. The third reactivity test method attempted to take these factors into account by reporting reactivity after a  $CO:CO_2$  volume ratio of 20:80 had been established in the product gas.

Correlations between test results, however, indicated that any of the three methods could be used for reporting the relative reactivities of the eight coke samples selected for the investigation. Such correlations may not necessarily be obtained for all carbons and, based on the theoretical considerations, the third method is suggested as the preferred one.

The measurement of the reactivity of coke to carbon dioxide may be a useful test for monitoring both the uniformity of coke and the uniformity of coke plant operation<sup>(16)</sup>. However, a definite correlation between coke reactivity and blast furnace performance has yet to be established and relative reactivities as measured by the techniques described in this report may not relate to relative reactivities in the blast furnace.

A second report<sup>(18)</sup> will describe reactivity test methods applicable to large samples (formed coke and lumps of oven coke).

#### ACKNOWLEDGEMENTS

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REFERENCES

1. Thibault, Ch. Gh., Association Technique de la Sidérurgie, Paris, France, Private Communication.
2. Miyazu, T., Fukuyama, T., and Koizumi, T., "Effect of Coke Properties on Blast Furnace Operation", Nippon Kokan Technical Report - Overseas, December 1970, Nippon Kokan Kabushiki Kaisha, Japan.
3. Schenck, H., and Wenzel, W., "Prüfung der Reaktionsfähigkeit von Koks unter Hockofenbedingungen" (Testing the Reactivity of Coke under Blast Furnace Conditions), Proc. Int. Cong. Coke in Iron and Steel Industry, Charleroi, 1966 (C.N.R.M. and INICHAR, Liège, 1967), 299-303.
4. Rist, A., and Meysson, N., "A Dual Graphic Representation of the Blast Furnace Mass and Heat Balances", J. Metals, 19, 50, (1967).
5. Blayden, H.E., "Reactivity of Cokes and Chars: A Review", Proc. Conf. Science in the Use of Coal, Sheffield, 1958, Inst. Fuel, London (1958), E-1-6.
6. Turkdogan, E.T., Koump, V., Vinters, J.V., and Perzak, T.F., "Rate of Oxidation of Graphite in Carbon Dioxide", Carbon, 6, 467-484, (1968).
7. Turkdogan, E.T., and Vinters, J.V., "Kinetics of Oxidation of Graphite and Charcoal in Carbon Dioxide", Carbon, 7, 101-117, (1969).
8. Turkdogan, E.T., and Vinters, J.V., "Effect of Carbon Monoxide on the Rate of Oxidation of Charcoal, Graphite and Coke in Carbon Dioxide", Carbon, 8, 39-53, (1970).
9. Turkdogan, E.T., Olsson, R.G., and Vinters, J.V., "Pore Characteristics of Carbons", Carbon, 8, 545-564, (1970).
10. Turkdogan, E.T., and Tien, R.H., "Incomplete Pore Diffusion Effect on Internal Burning of Carbon", Carbon, 8, 607-621, (1970).
11. Turkdogan, E.T., "Effects of Temperature, Pressure, Gas Composition, Particle Size and Nature of Carbon on the Rate of Oxidation of Carbons in CO<sub>2</sub>-CO Gas Mixtures", Ninth Biennial Conf. on Carbon, Chestnut Hill, Mass., June 16-20, (1969).
12. Mentser, M., and Ergun, S., "Kinetics of the Oxygen Exchange Between CO<sub>2</sub> and CO on Carbon", Eighth Biennial Conf. on Carbon, S.U.N.Y. Buffalo, Buffalo, N.Y., 19-23 June, (1967).
13. St. Clair, H.W., "Mathematical Simulation of a Gas-Solid Reaction in a Packed Bed - Reaction of CO<sub>2</sub> with Coke", U.S. Dept. of the Interior, Bureau of Mines Report of Investigations R.I. 7476, (1971).

14. Turkdogan, E.T., and Vinters, J.V., "Catalytic Oxidation of Carbon", Carbon, 10, 97-111, (1972).
15. Botham, J.C., "Electrical Resistivity of Coke with Special Reference to Foundry Coke", Mines Branch Internal Report FMP 67/12-CG, Department of Energy, Mines and Resources, Ottawa, Canada.
16. Thompson, R.R., Mantione, A.F., and Aikman, R.P., "Improvement of Coke Uniformity through Measurement of Coke Reactivity", Blast Furnace and Steel Plant, 59, 161-177, (1971).
17. International Organization for Standardization, Technical Committee 27 (Solid Mineral Fuels), Document ISO/TC 27/WG8 (Norway-3) 179, November, 1971, "Norwegian Comments and Report on the Measurement of the Reactivity of Coke".
18. Rawson, R.N., and Reeve, D.A., "Measurement of the Reactivity of Carbons for Metallurgical Processes, Part III - Formed Coke", Technical Bulletin, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada, in preparation.

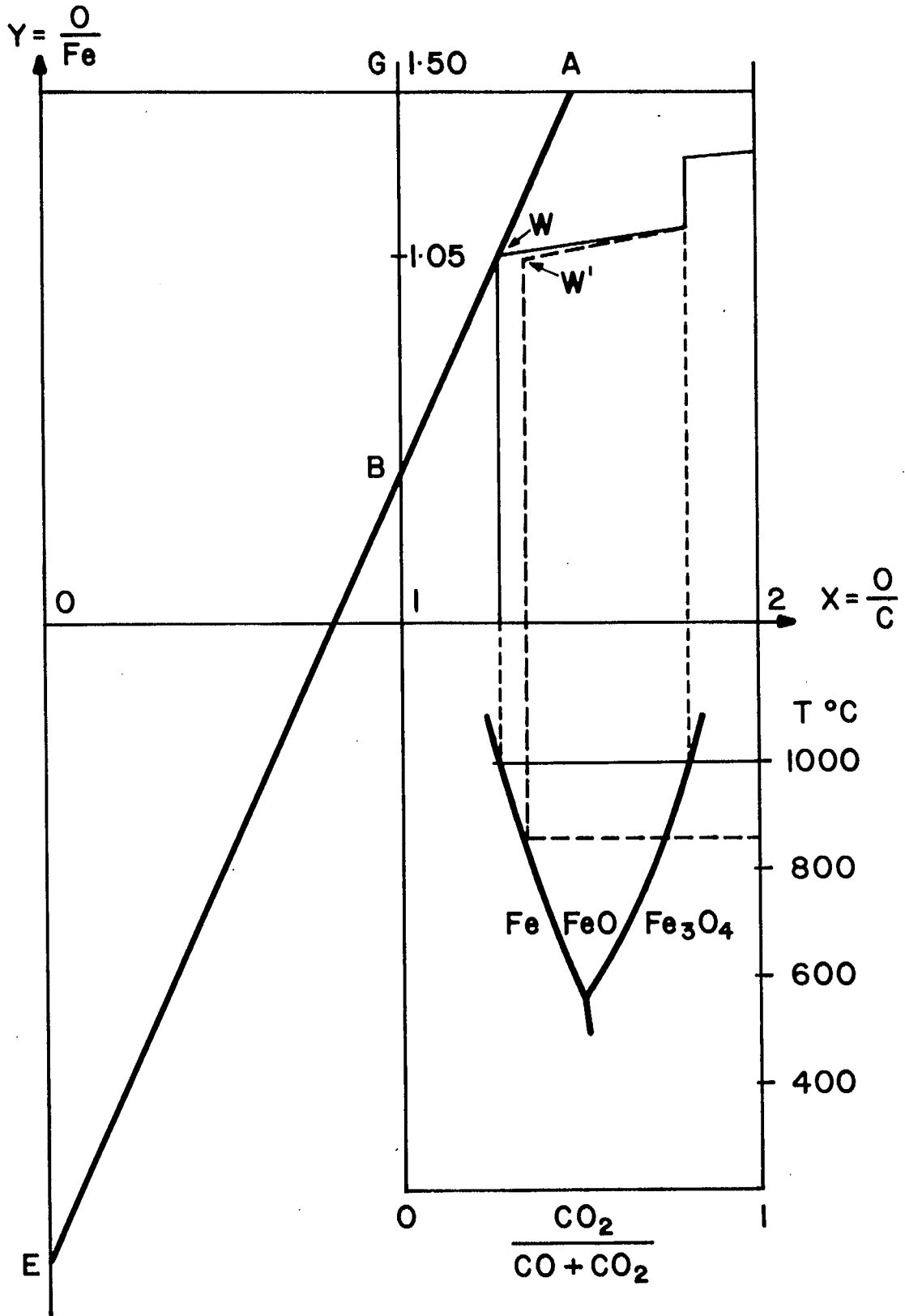


FIGURE 1. Effect of Coke Reactivity on the Operating Line of the Rist Diagram

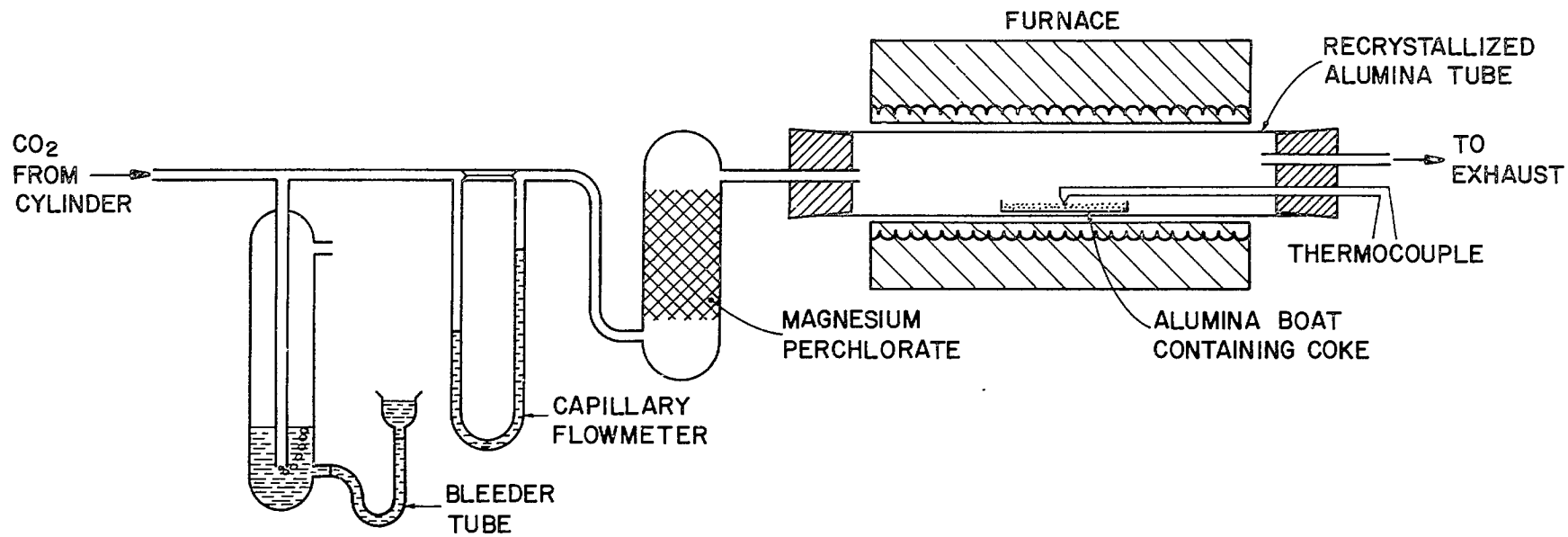


FIGURE 2. Loss-in-Weight Reactivity Test Apparatus

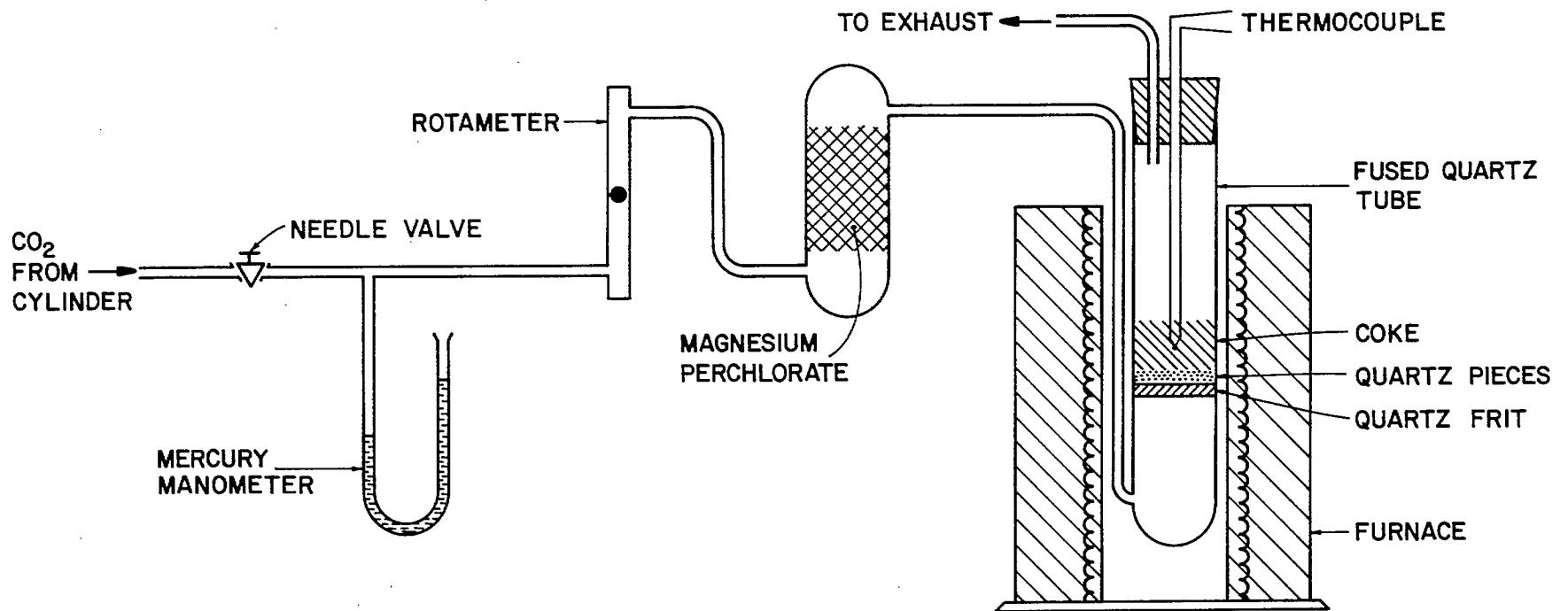


FIGURE 3. Gas Analysis Reactivity Test Apparatus (Controlled Amount of Conversion of CO<sub>2</sub> to CO)

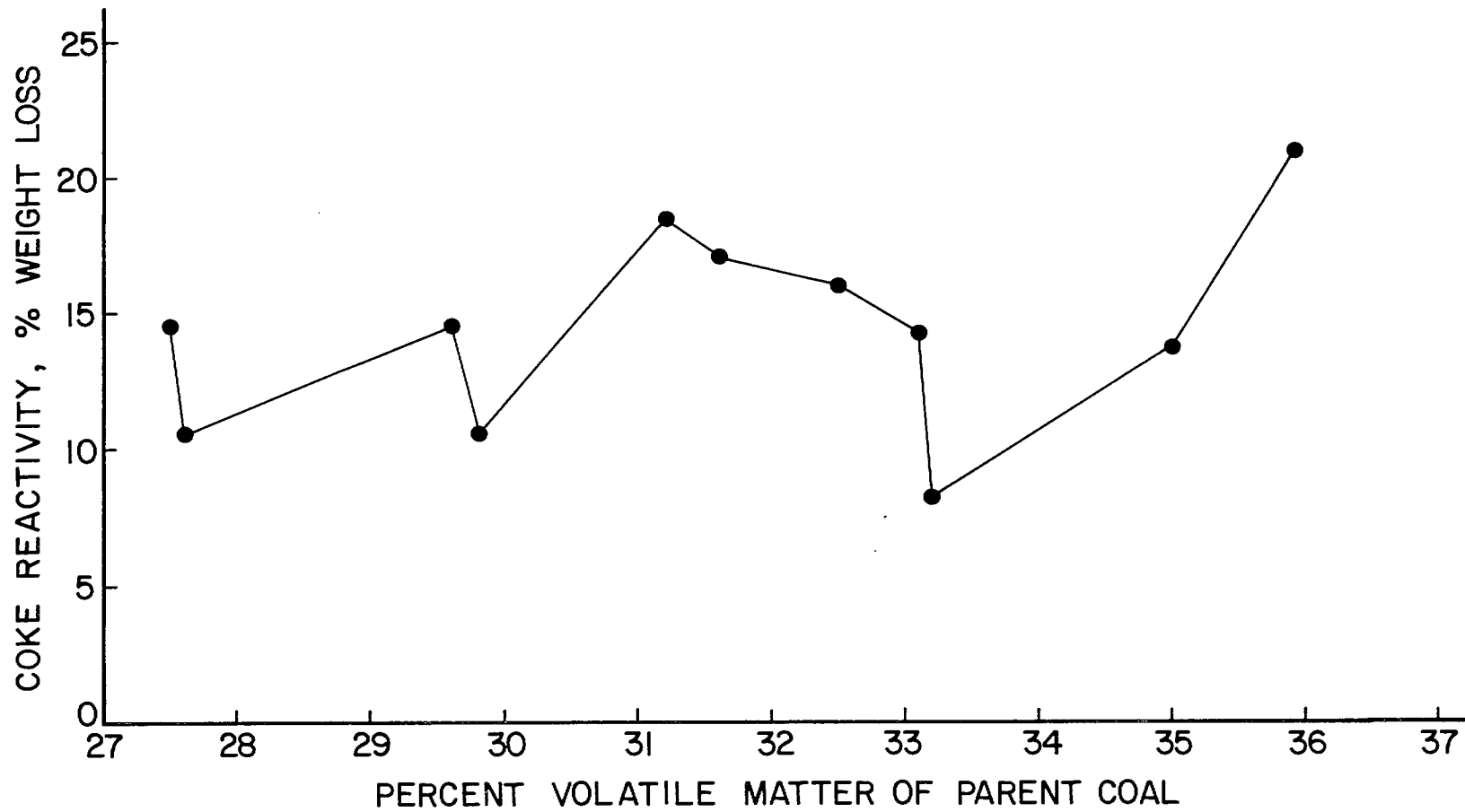


FIGURE 4. Influence of Coal Volatiles on Coke Reactivity



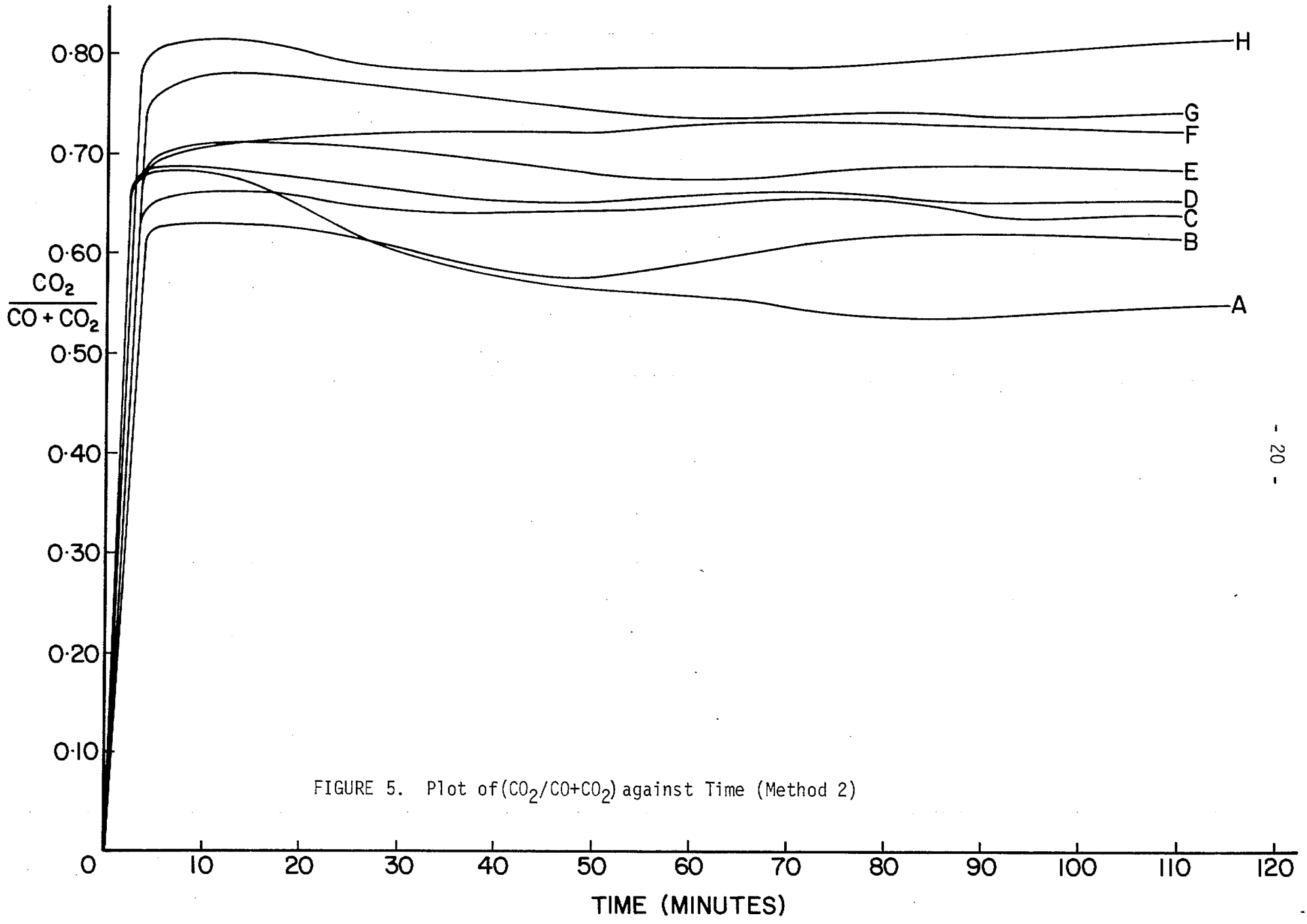


FIGURE 5. Plot of  $(CO_2/CO+CO_2)$  against Time (Method 2)

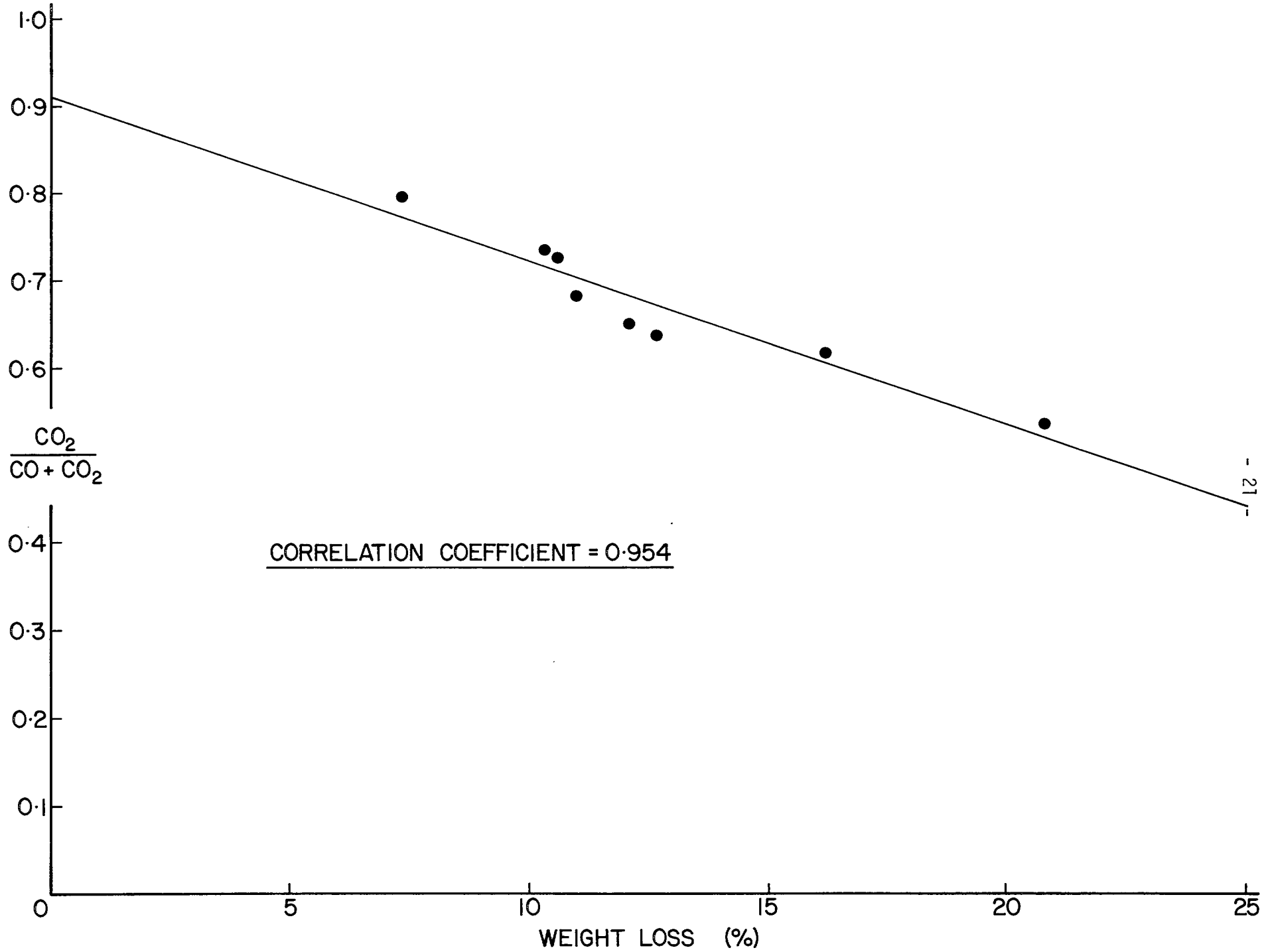


FIGURE 6. Correlation between Reactivity Measurements from Test Methods 1 and 2

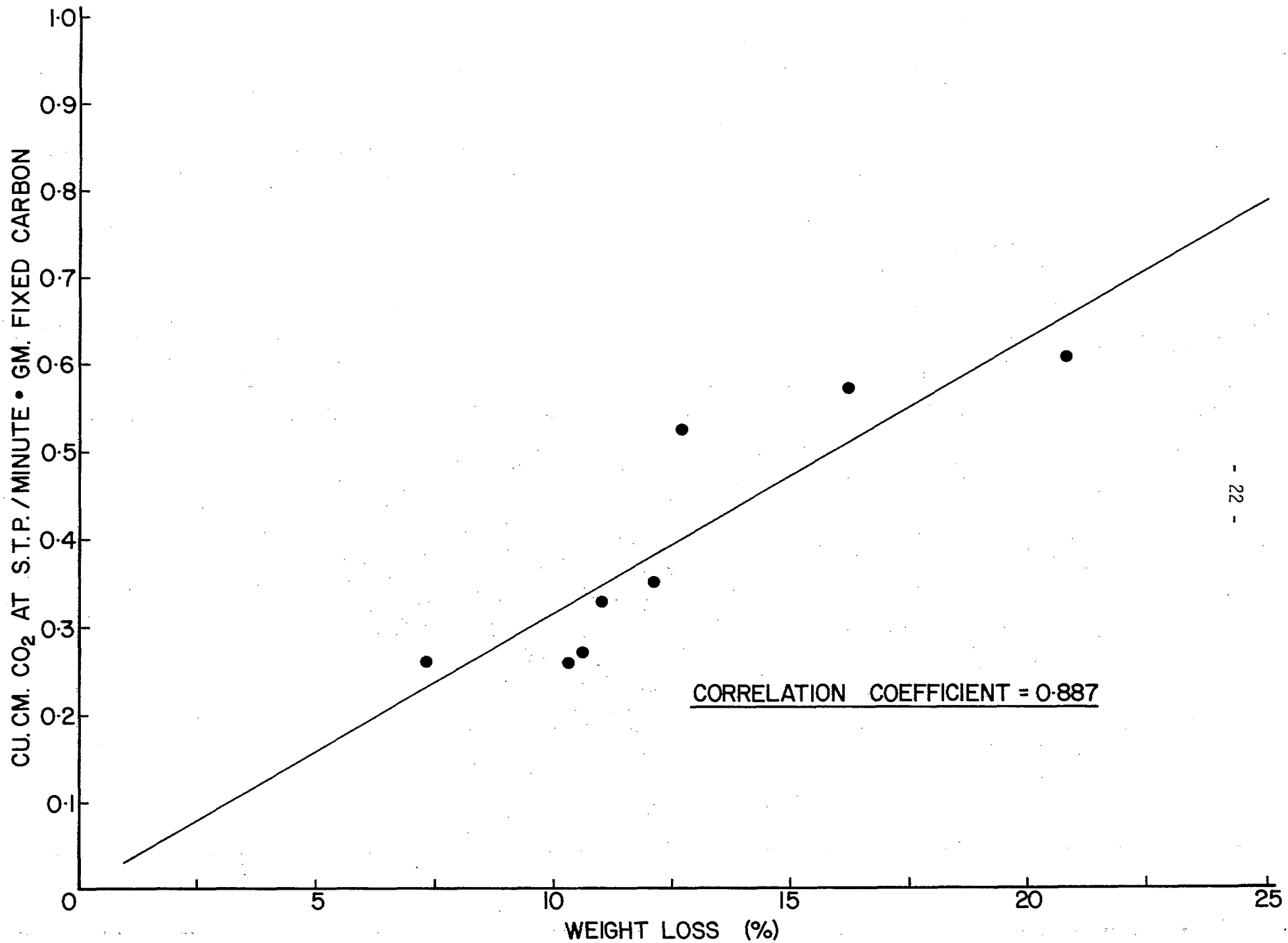


FIGURE 7. Correlation between Reactivity Measurements from Test Methods 1 and 3

