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EFFECT OF PHYSICAL PARAMETERS ON THE REACTION OF GRAPHITE WITH SILICA IN VACUUM

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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By L. A. Haas and S. E. Khalafalla

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UNITED STATES DEPARTMENT OF THE INTERIOR
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EFFECT OF PHYSICAL PARAMETERS ON THE REACTION OF GRAPHITE WITH SILICA IN VACUUM

by

L. A. Haas[1] and S. E. Khalafalla[2]

ABSTRACT

The degree of reduction of various silica-graphite mixtures was studied in a batch reactor to determine optimum physical conditions for maximizing the carbothermic reduction of silica. The extent of interaction was determined for reactant mixtures in loose powder and briquet forms at pressures less than 0.01 torr and temperatures up to 1,445° C. Molar ratios were varied from 0.05 to 6.5 with maximum reaction at a ratio of about 1.5. The solid-solid reaction did not appear to involve gaseous intermediates. The extent of reaction better correlated with the number of interparticle contacts than with the true surface area of the reactants. Carbonized dextrose was a better reductant than graphite.

INTRODUCTION

The increased use of vacuum in metallurgical processes and the possibility of extraterrestrial applications of such processes in the foreseeable future have created a need for thorough understanding of the behavior of materials in vacuum at high temperatures. This Bureau of Mines study of the carbothermic reduction of silica attempts to determine the optimum physical conditions for maximizing the interaction of silica with graphite.

Carbothermic reduction of metal oxides was first attempted in 1884 by Puttner (11).[3] Little use of this technique has been made since then, despite the increasing importance of the direct production of pure metals from oxides. Only limited work has been done on the direct reduction of solid silicon dioxide, particularly because of the multiplicity of possible products, ranging from SiO to Si and SiC. Also, because of the stability of silica, extremely high temperatures or vacuum are necessary for reaction.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

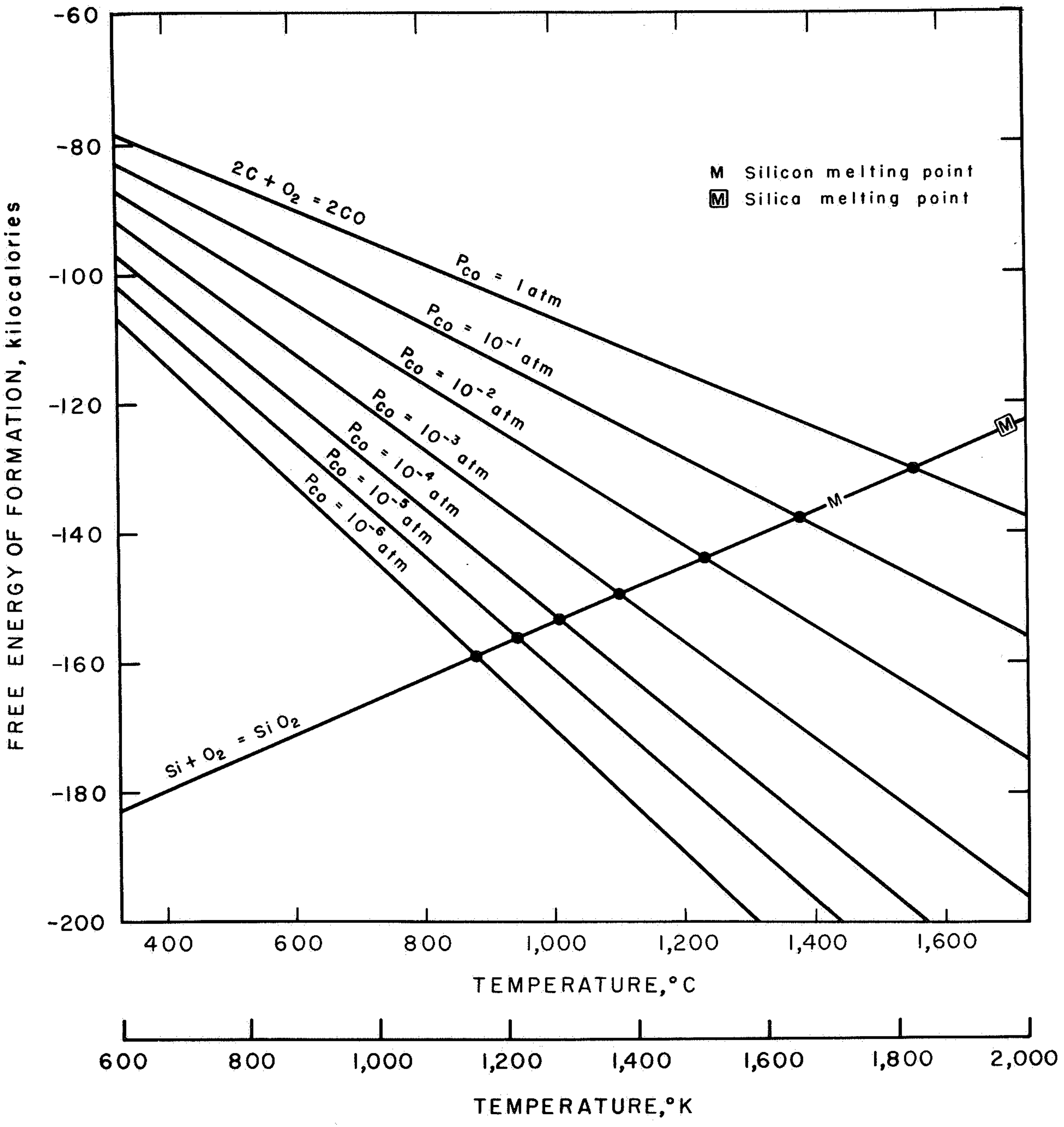

FIGURE 1. - Ellingham Diagram for the Carbon and Silica Reaction.

Thermodynamically, as can be seen from the Ellingham diagram of figure 1,[4] the reaction can proceed above 1,600° C at a carbon monoxide pressure of 1 atm absolute. However, the reaction temperature can be progressively lowered by decreasing the pressure; for example, at 10^{-4} atm the reaction may take place at about 1,000° C.

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[4] Free energy data required to construct figure 1 were taken from the tables of Wicks and Block (14).

In view of the feasibility of the vacuum carbothermal reduction of silica, the Bureau of Mines is attempting to define the various parameters of the reaction and to determine their effect on the extent of silica reduction. The data obtained from vacuum reduction of silica may be useful in metallurgical processes at atmospheric pressure since in blast furnace operations the rate of silica reduction both determines the amount of silicon in the pig iron and influences the transfer of sulfur from the metal to the slag (6).

In these studies the Bureau of Mines is cooperating with the National Aeronautics and Space Administration (NASA)[5] in developing processing technology for possible utilization of lunar materials as resources for oxygen and water. If the oxygen needed to sustain life and for rocket fuel oxidant can be extracted from silica on the moon, space capsules will be able to transport a larger payload. This study constitutes one phase of a multidisciplinary effort to extract oxygen via carbon monoxide from possible lunar oxides.

RAW MATERIALS

The silica samples, analyses of which are given in table 1, were obtained from two sources; the silica used in studies of large particle sizes was from Wausau, Wis., and technical-grade Fisher[6] silica was used in all other experiments. Three forms of carbon were used, as follows: "Low-density graphite" was finely divided form, obtained from Ultra-Carbon Corp.; "high-density graphite" was obtained from crushed electrode rods; and "carbonized dextrose" was obtained by the dehydration of dextrose. The ash content of these graphites was less than 30 ppm.

TABLE 1. - Chemical analyses of silica samples

Chemical constituents	Chemical analysis, percent	
	Fisher silica	Wausau silica
SiO_2	99.1	97.4
CaO	.35	.30
Al_2O_3	<.05	1.4
MgO	.09	<.05
Fe_2O_3	.05	.11
TiO_2	<.05	<.05
C	<.1	<.1
L.O.I.[1]	<.1	.23

[1] Loss on ignition at 950° C in 4 hours.

The particle size of the reactants was determined by microscopic examination and found to correspond approximately to the mean diameter of the screen openings. Polyester resin particle mounts containing silica and graphite particles were made, and the cross section of the particles was exposed by grinding and polishing the mount. The silica was approximately spherical, while the graphite particles were very irregular. The crystal structure of the silica was quartz.

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[5] This work was supported by NASA Contract R-09-040-001.

[6] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

APPARATUS

The furnace used in this research (fig. 2) was described in a previous publication (7). Small modifications included a quartz lens in the furnace top to permit optical temperature measurements, and a Leeds and Northrup disappearing-filament pyrometer, which was used to check the thermocouple temperature. The thermocouple was calibrated with the melting point of a bridge of gold wire (12-mm length by 0.25-mm diameter) between two 0.25-mm-diameter platinum wires. The gold bridge was inserted in the quartz beaker

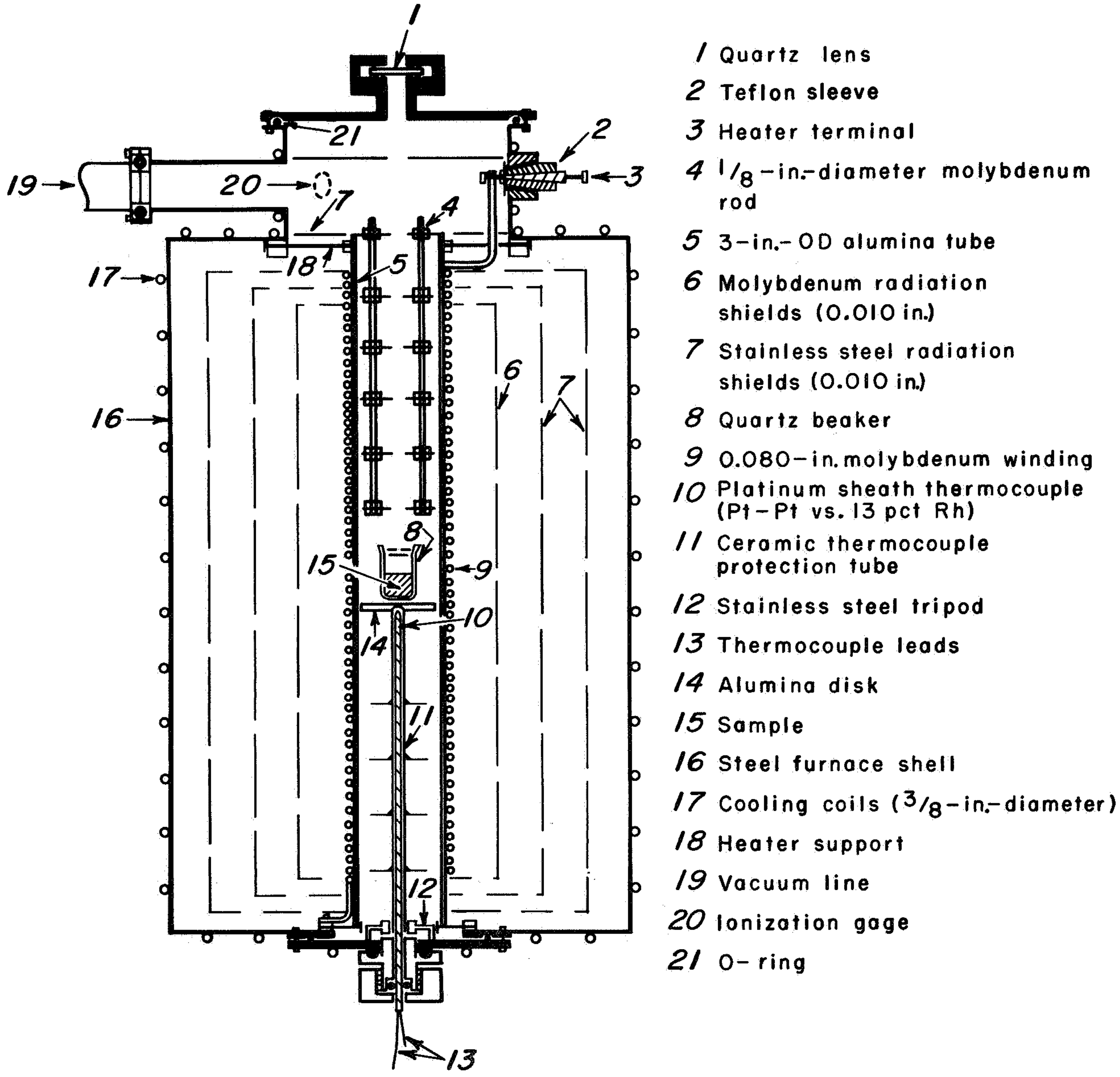

FIGURE 2. - Cross Section of the Vacuum Furnace Assembly.

As the melting point was approached, the heating rate was maintained at 0.1° C per minute. An open circuit occurred when the gold bridge melted, and the temperature of the thermocouple was noted. Temperature variation of the furnace was maintained within 5° C with a Leeds and Northrup series 60 set-point control system.

The ultimate vacuum achieved by the cold furnace without a sample was $<10^{-5}$ torr. The leak rate was less than 1 micron-liter per minute. In all the tests discussed in this report, the pressure at the highest furnace temperature was held below 0.01 torr, which is at least two orders of magnitude less than the equilibrium pressure at temperatures above 1,200° C (fig. 1). High vacuum lowered the equilibrium reaction temperature and facilitated quick removal of CO, thereby decreasing the possibility of interaction between the gaseous products and reactants.

PROCEDURE

After dried sample constituents were weighed individually and mixed in a Pitchford blender for 10 minutes, the sample was placed in a weighed, fused-silica beaker (35-mm diameter by 75-mm height). When dried at 110° C to constant weight, the loaded beaker was covered with a molybdenum baffle and inserted in the furnace. Before heating, the chamber was slowly evacuated to less than 0.1 torr, backfilled with high-purity helium, and reevacuated to reduce the possibility that residual oxygen remaining in the furnace would oxidize the graphite. Samples were degassed overnight at 900° C in a vacuum of less than 10^{-5} torr. To reduce the amount of heat-up reaction, the furnace was rapidly heated from 900° C to the desired operating temperature. This level was held for 5 hours and then rapidly reduced to room temperature. The cold sample was removed, weighed, and analyzed for silica and carbon. Blank runs to test the extent of reaction during the transient heat-up and cool-down periods were made by heating samples to the highest operating temperature and immediately cooling. For all practical purposes, the amount reacted was negligible and well within the limits of experimental error.

The initial and final chemical analyses and the observed weight loss were used to calculate the extent of reaction. The weight loss from discharge analysis was also calculated. Fair agreement with the observed weight loss was obtained by assuming that the only gaseous products were silicon and carbon monoxide. The hypothesis was confirmed by mass spectroscopic examination of the reaction products, in which a major peak was indicated at mass number 28. The vapor pressure of silicon is high enough at the operating conditions for some sublimation to occur, and a considerable amount of condensate was observed on the radiation shields. To calculate the amount of oxygen extracted, it was assumed that carbon reacted with silica and was lost as carbon monoxide, since nearly equal numbers of moles of carbon and oxygen were removed.

RESULTS AND DISCUSSION

General Comments

Since temperature, particle size of reactants, and reactant proportions are the principal factors influencing a solid-state reaction, their effects were investigated by varying one factor at a time. To reduce the number of experiments to a practical level, a common temperature, molar ratio, reaction period, and particle size were selected for most determinations. To simplify the discussion only typical data are reported.

Temperature Dependence

An understanding of the reactions required measuring the degree of reactivity at various temperatures under controlled conditions. Experiments were first performed on the individual raw materials. After 5 hours at 1,400° C, the weight loss of the 15-gram silica blank was 0.6 percent (table 2), and that of the 10-gram graphite blank was 0.7 percent. The 16-percent greater weight loss for graphite indicates greater gas adsorption, or possibly a slight oxidation with residual oxygen in the furnace chamber.

TABLE 2. - Experimental data for the temperature effect on the carbothermic reduction of silica

Test	Temp., ° C	Residue analysis, percent		5-hour weight-loss, percent		Total oxygen removed, percent
		Σ Si as SiO_2	Carbon	Calculated	Observed	
SILICA BLANK						
1..........	1,400	99	<0.1	-	0.6	-
GRAPHITE BLANK						
2..........	1,400	<0.003	99.9	-	0.7	-
EQUIMOLAR MIXTURES OF SILICA AND GRAPHITE						
3..........	25	83.0	16.7	-	0.0	-
4..........	975	82.0	16.7	0.3	.1	-
5..........	1,170	82.2	16.0	1.6	.6	-
6..........	1,350	83.1	15.8	3.8	2.8	1.5
7..........	1,375	84.2	15.3	5.4	4.2	2.5
8..........	1,395	86.6	14.9	8.1	7.5	7.0
9..........	1,405	87.3	14.6	8.2	7.2	7.0
10..........	1,410	88.9	14.4	9.1	9.0	10.0
11..........	1,425	92.3	12.8	13.3	13.7	14.5
12..........	1,445	100.7	10.1	22.2	21.7	25.0

Mixtures of 0.2 mole each of graphite (0.11-mm diameter), and silica (0.15-mm diameter) were then made. The top and bottom portions of the mixed sample were analyzed separately, and no sign of segregation was noted. Similar mixtures were then heated in the furnace for 5 hours at various temperatures (table 2 and fig. 3). No appreciable reaction occurred below 975° C. Elyutin (5) discovered a correlation between the melting point of an oxide, T_m, and the temperature at which carbon begins to reduce the metal oxide, T_r. The six oxides he investigated obeyed the following empirical relationship:

$$T_r = 0.46\ T_m + 250.$$

Substituting the melting point of silica in the above equation, a reaction temperature of 1,040° C is obtained. This value agrees reasonably with the results of tests 4 and 5 in table 2. Above 1,445° C, the carbon monoxide formation and evolution was so vigorous that it was difficult to prevent sample blowout.

The results in table 2 indicated that fair agreement was obtained between the calculated and observed weight loss. The calculated weight loss was determined from the change in chemical composition, on the assumption that the only gaseous products of the reaction were carbon monoxide and silicon. The percent of the total oxygen removed was obtained indirectly by silicon and carbon material balances. The weight loss was roughly proportional to the percent oxygen removed. In the remaining experimental results, only the observed weight-loss data will be presented.

Effect of Particle Size

The dependence of the degree of reaction on particle size was determined at 1,400° C with a reactant molar ratio of one. Tests 13 to 16 listed in table 3 were performed with 0.15-mm silica mixed with various sizes of low-density graphite. The variation of the extent of reaction with the graphite particle diameter is illustrated in table 3 and in figure 4, curve a. The maximum amount of reaction or weight loss occurred with 0.07-mm graphite particles; smaller or larger graphite particles significantly lowered the reduction rate. Similar results were observed by varying the silica particle size while maintaining the graphite size at about 0.11 mm. As shown in table 3,

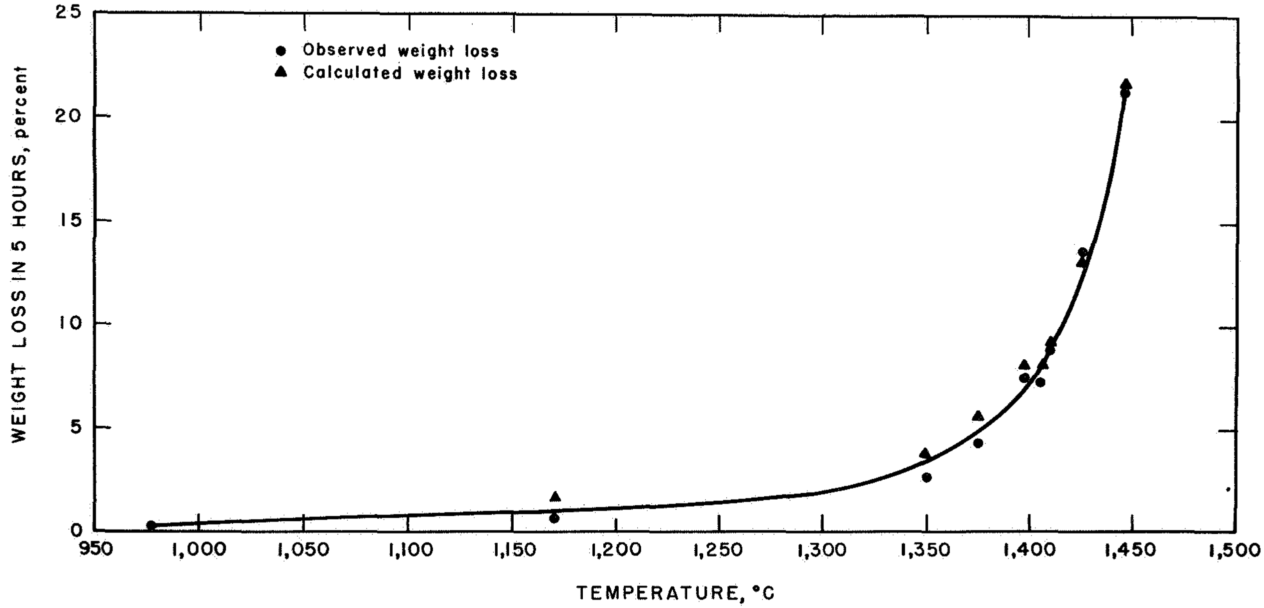

FIGURE 3. - Temperature Dependence of the Carbothermic Reduction of Silica in Vacuum ($<10^{-2}$ torr).

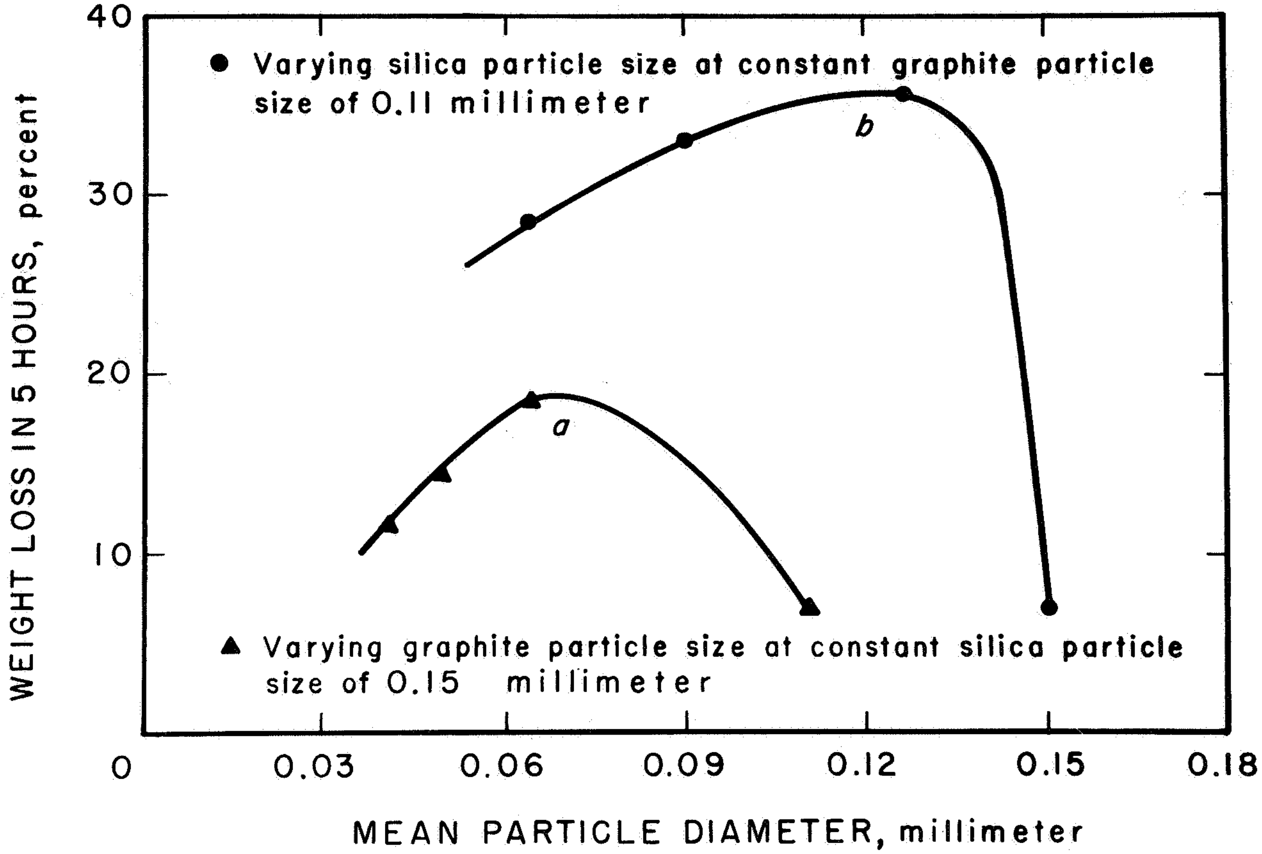

FIGURE 4. - Effect of Reactant Particle Size on the Degree of Reaction of Equimolar Quantities of Low-Density Graphite and Silica.

maximum reaction occurred with about 0.13-mm silica, indicated by tests 13 and 17 through 19. Results of these experiments are shown in figure 4, curve <u>b</u>.

TABLE 3. - Experimental results for the effect of particle size on the reaction of low-density graphite with silica

Test	Mean particle size of reactants, mm		Crucible diameter, cm	5-hour weight-loss, percent
	Silica	Graphite		
13	0.15	0.11	4.3	7.2
14	.15	.06	4.3	18.7
15	.15	.05	4.3	14.1
16	.15	.04	4.3	11.9
17	.13	.11	4.3	35.6
18	.09	.11	4.3	33.0
19	.06	.11	4.3	28.5
20	.06	.11	6.4	83.9

One might expect the degree of reaction to increase with increasing fineness of the reactants, owing to the larger surface area and the greater number of silica-graphite particle contacts. However, chemical analysis of the charge residue showed a concentration difference between the top and bottom portions of the samples, suggesting that carbon monoxide removal from the bottom portions of the bed was inadequate. The phenomenon probably resulted from low gas permeability of charge with finely divided particles. That gaseous products must be removed for the reaction to continue can be evidenced from the descending left-side branches of curves a and b in figure 4. Test 19 was conducted with an equal amount of sample spread 2 cm deep in a crucible four times larger than that in test 20. The amount of reaction increased threefold. Results of these studies indicated that, with a sample depth of 2 cm, the reactant mean particle diameter must be larger than 0.1 mm to prevent the gas-removal rate from controlling the overall process. Similar results were reported by Craven (3) for the uranium dioxide-graphite system, in which the upward diffusion through the body of charge was rate-controlling when the bed was of low permeability. An experiment was also performed with the reactants compressed into a dense briquet. An equimolar mixture of 0.11-mm graphite and 0.15-mm silica was compressed at 130 tons per square centimeter into a cylinder, 1.9 cm in both diameter and height. The briquet had 19 percent porosity, but the extent of reaction was only one-tenth as much as with loose powders, reemphasizing the important role played by gas permeability of the charge.

To eliminate the gas permeability problem, further tests were performed with particles larger than 0.10 mm. Because Fisher silica was not available in the larger sizes, silica obtained from Wausau, Wis., was used. The less than 1 percent porosity of this silica, as measured with a Beckman air pycnometer, was verified by the extremely low true surface area (BET). Only the surface area of the very fine silica could be determined with the modified Perkin-Elmer sorptometer (2). The geometric surface area was calculated for each silica sample, and for the finer samples was found to be approximately half as much as the BET surface area (table 4). Assuming the tetragonal close packing of nonporous spherical particles (10), the number of particles per gram was calculated from the mean diameter and the bulk density. The validity of the calculations was justified by the fair agreement between the experimental and the calculated number of particles.

Figure 5 shows the variation with silica particle size of the silica reduction (curve a), the number of particles per gram (curve b), and the geometric surface area (curve c). Curves a and b decrease nearly hyperbolically with increasing particle diameter and in a parallel manner, but curve c, which describes the surface area variation with particle subdivision, decreases at a lesser rate. Since the number of particles should vary as the reciprocal cube of the diameter, a plot of the extent of reaction (fig. 6, curve a) and number of particles (fig. 6, curve b) was made against the cube of the reciprocal particle diameter. Although these plots were linear, a plot of the variation of geometric surface area on the same graph was not. On the other hand, when the amount of reaction and geometric surface area were plotted against the reciprocal of particle diameter, the function exhibited a linear variation (fig. 7, curve b). In figure 7, curve a, weight loss (and also the number of particles per gram) exhibited a cubic power

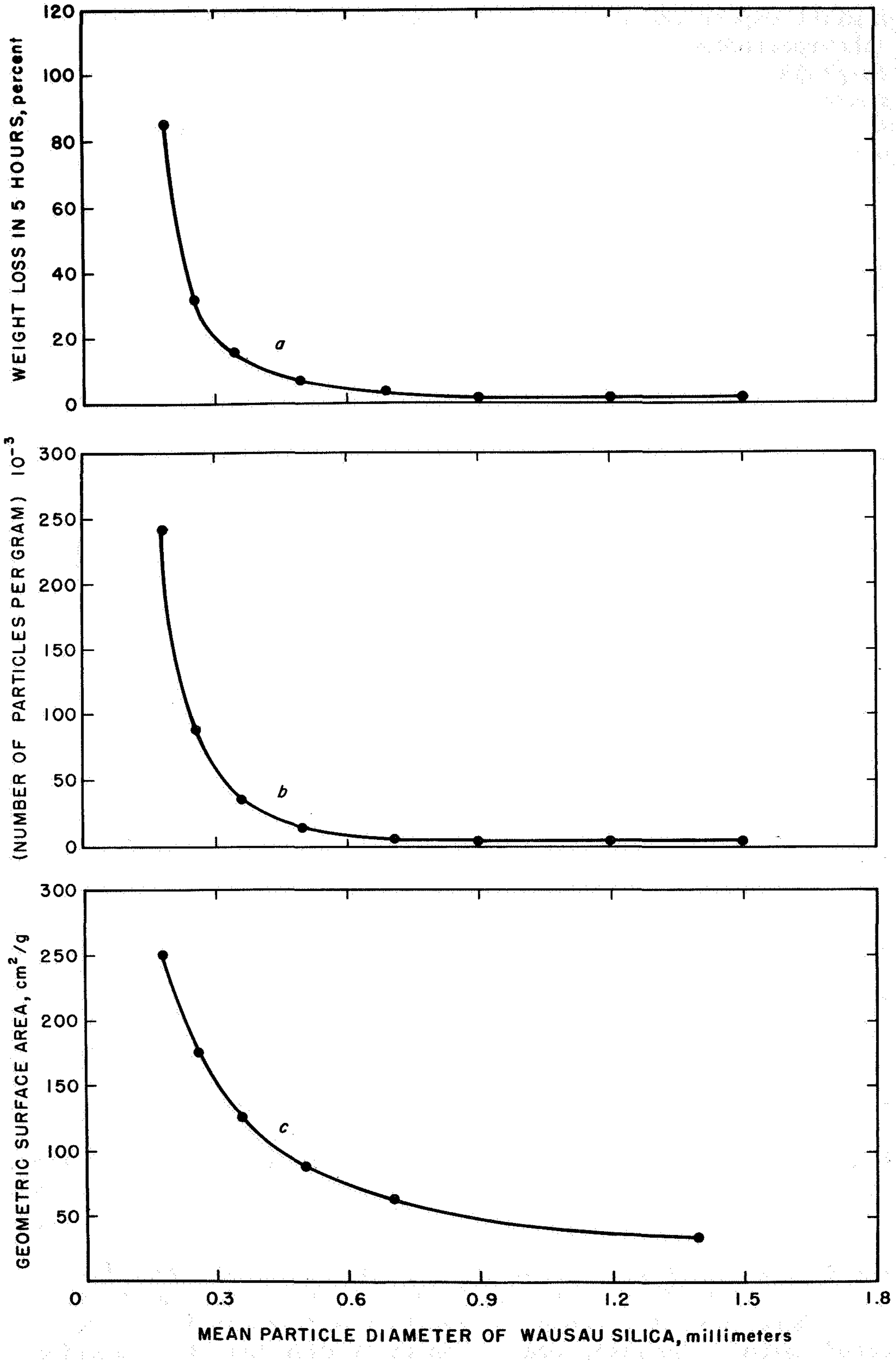

FIGURE 5. - Effect of Silica Particle Diameter on Amount of Reaction, Number of Particles per Gram, and Geometric Surface Area.

functional variation. It appears, therefore, that a better correlation of the degree of reaction was obtained with the number of silica particles per gram than with their geometric surface area. Table 4 shows that more than 80 percent of the total oxygen can be extracted in 5 hours with 0.18-mm-diameter Wasau silica and 0.11-mm graphite.

TABLE 4. - Carbothermic reduction data with Wausau silica

Test	Mean silica particle diameter, mm	Number of particles per gram	Surface area, cm^2/g		5-hour weight-loss, percent	Total oxygen removed, percent
			Geometric	BET		
21.......	1.41	500	31.4	-	1.92	3.0
22.......	.71	3,940	62.5	-	3.45	7.0
23.......	.50	11,120	88.5	-	6.35	7.5
24.......	.36	31,350	125	-	14.5	18.5
25.......	.25	88,300	175	-	32.7	35.0
26.......	.18	250,000	245	-	81.8	83.5
27.......	.09	2,010,000	500	990	70.6	65.9

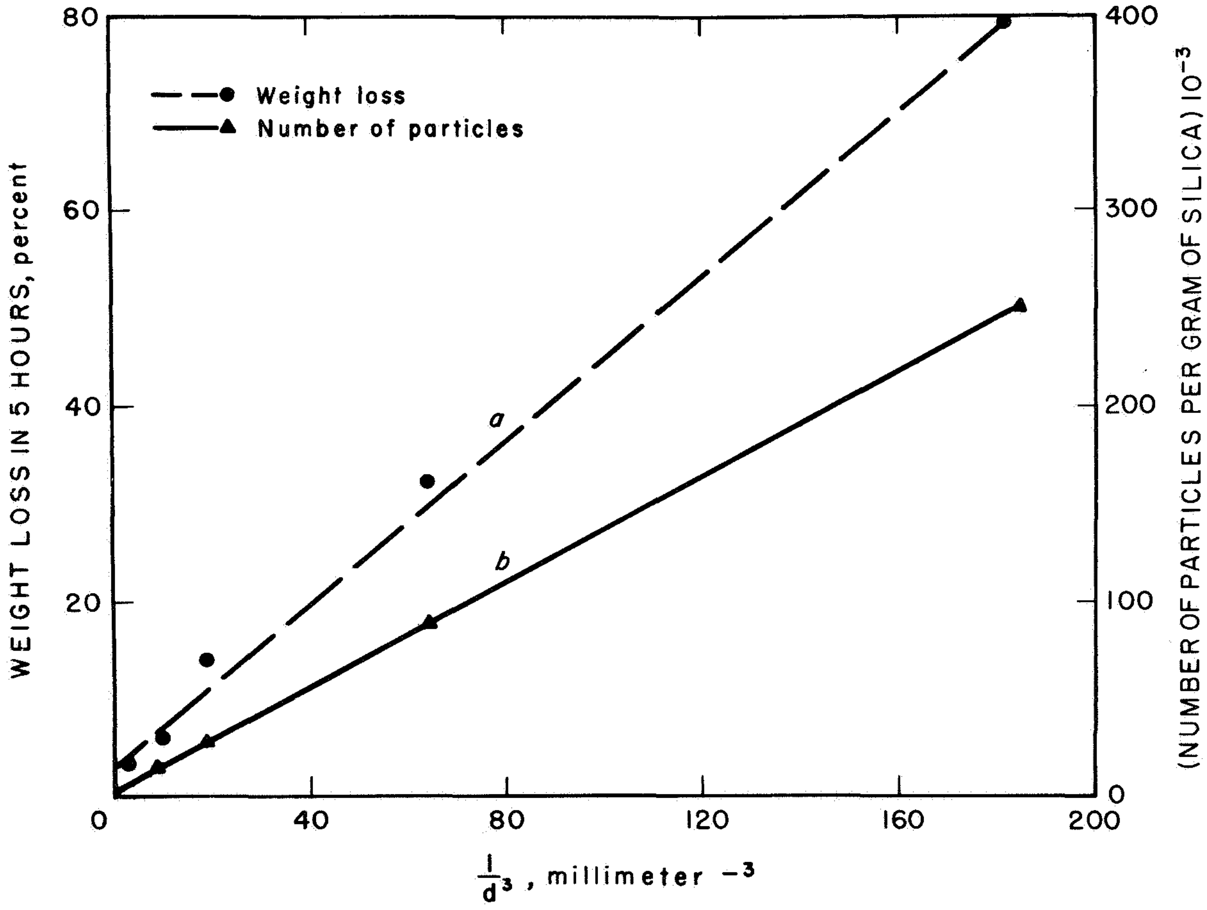

FIGURE 6. - Comparison of the Degree of Reaction and the Number of Particles With the Reciprocal Cube of the Particle Diameter.

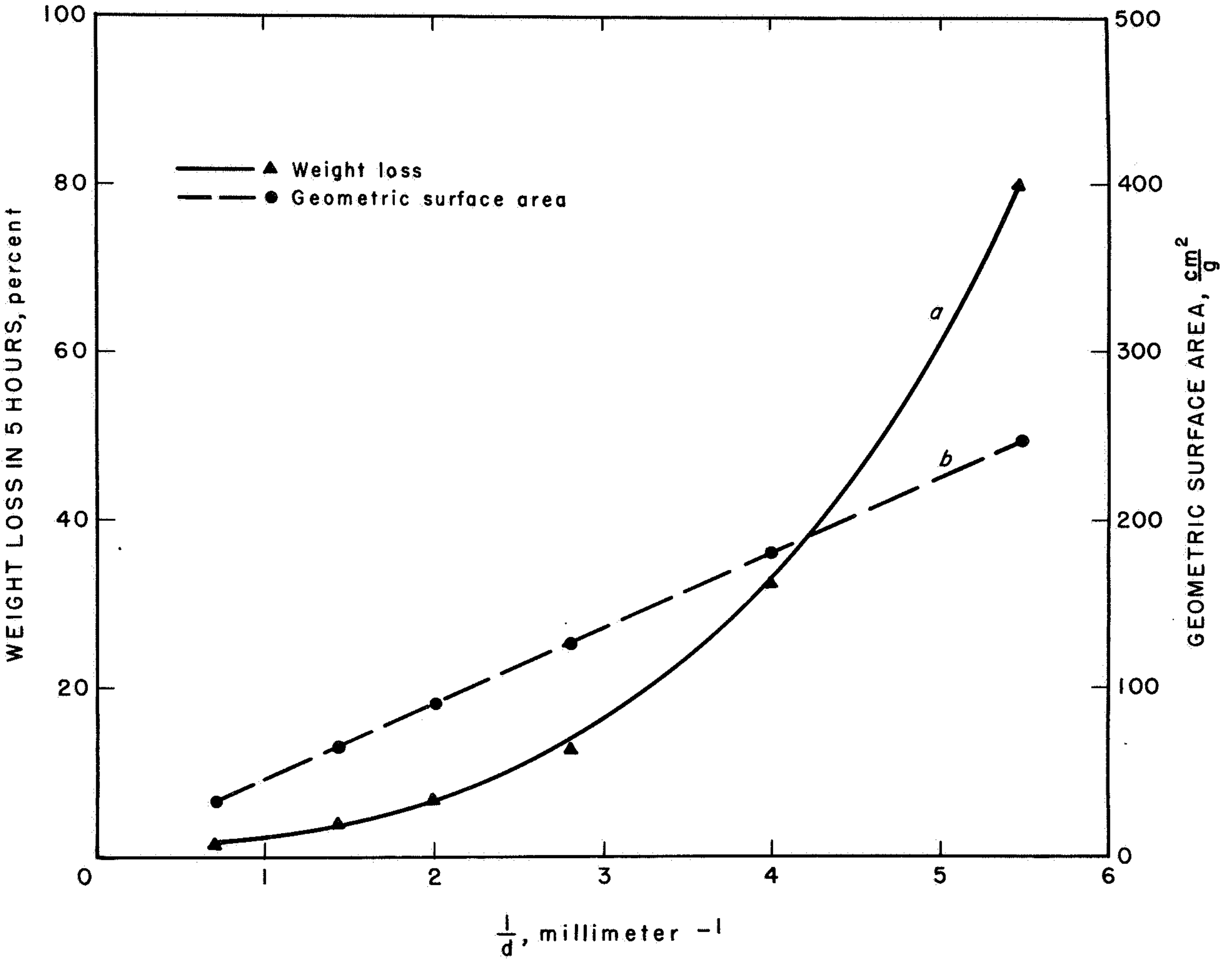

FIGURE 7. - Comparison of the Degree of Reaction and the Geometric Surface Area With the Reciprocal of the Particle Diameter.

Large-particle-size experiments were also performed on the graphite reactant to determine whether the degree of reaction would decrease proportionally with fewer contacts. Since large graphite particles were not available, graphite rods were comminuted and the different screen fractions were used. The experimental results given in table 5 indicate that the amount of reaction increases with decreasing graphite particle size in the range investigated. The true change in a surface area with particle subdivision was actually small compared with the change in the number of graphite particles or the maximum number of graphite-silica contacts. The graphite BET surface areas were 30 to 70 times larger than the geometric surface area calculated by assuming nonporous spherical particles. The experimental results shown in figure 8 indicated that the reaction rate decreased hyperbolically with increasing graphite particle diameter. In figure 9, the rate was also plotted versus the number of graphite particles. The linear plot indicated that the reaction was dependent on the number of silica-graphite contacts. It can be assumed therefore that with particles larger than about 0.11 mm the rate varied proportionally with the number of silica or graphite particles per gram.

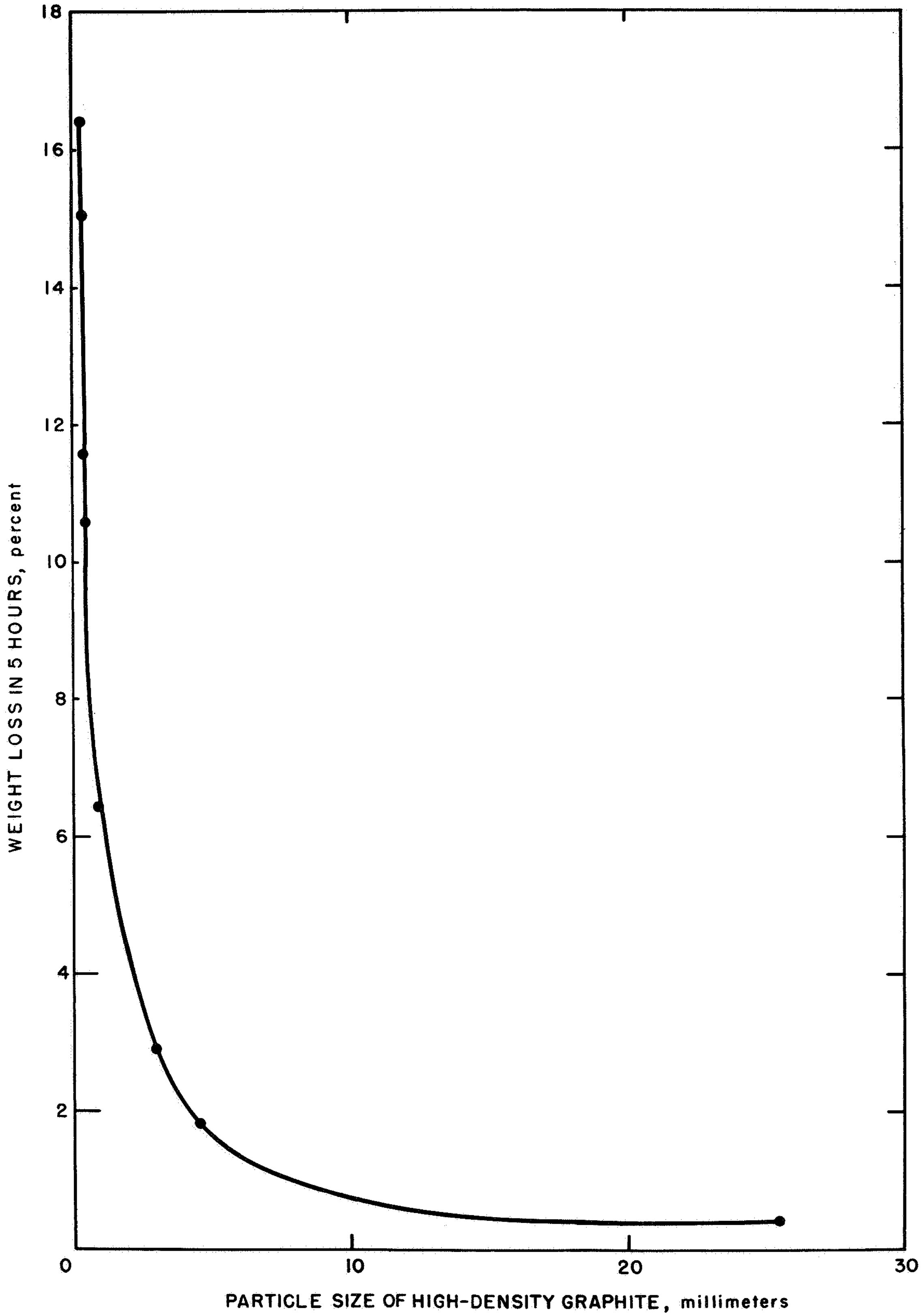

FIGURE 8. - Variation of Amount of Reaction With Graphite Particle Size.

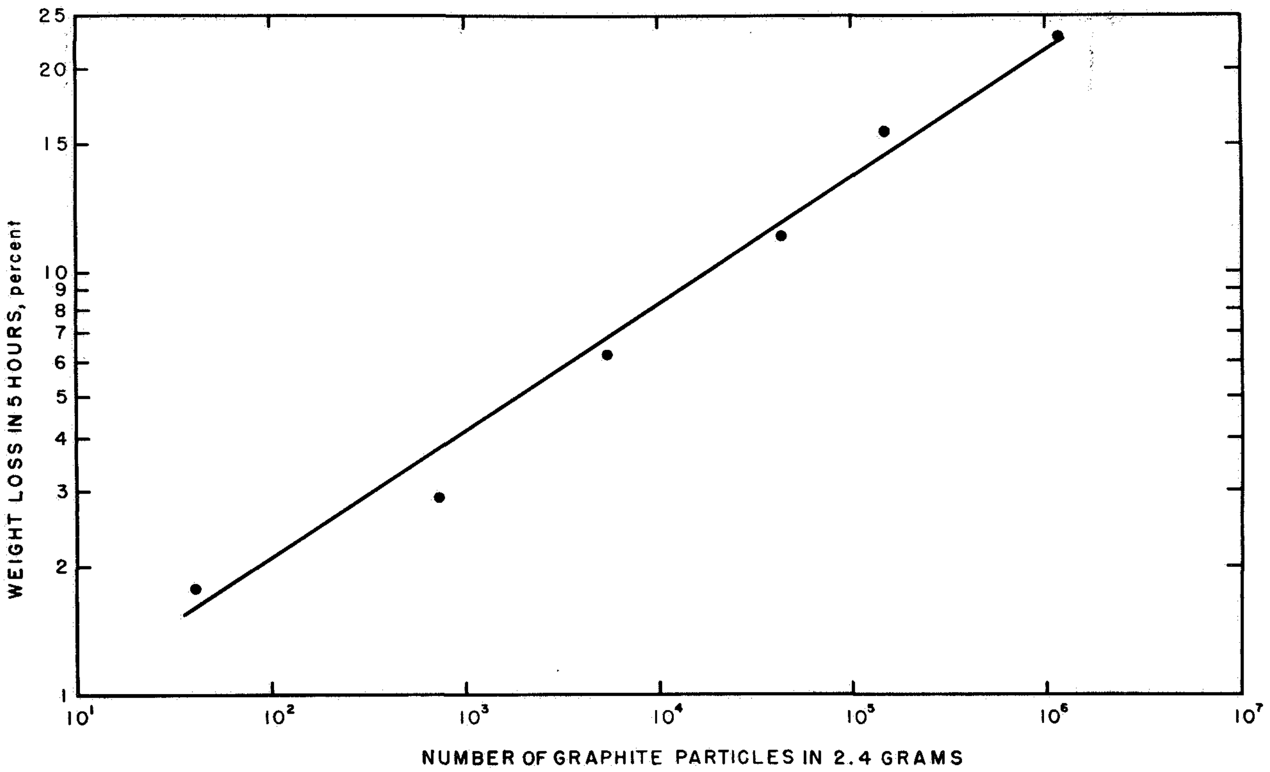

FIGURE 9. - Dependence of the Degree of Reaction on the Number of Graphite Particles.

TABLE 5. - Experimental results for the reaction of high-density graphite with 0.15-mm Fisher silica

Test	Physical properties of graphite				5-hour weight-loss, percent
	Mean diameter, mm	Number of particles in 2.4 gram	Surface area, cm^2/g		
			Geometric	BET	
28..............	0.11	-	754	21,200	16.5
29..............	.18	1,108,800	467	-	22.0
30..............	.25	142,857	332	-	15.1
31..............	.36	43,636	242	11,450	11.6
32..............	.72	5,584	121.9	9,070	6.4
33..............	1.78	727	45.1	-	2.9
34..............	4.60	41	10.3	-	1.8
35..............	25.40	1	2.0	-	.4

A detailed mechanism has not been proposed, although certain features of the reaction can be ascertained. The reaction between silica and graphite can occur either by direct contact between the solid phases, or by vaporization and/or decomposition of silica followed by the attack of the gaseous species formed on graphite. The following reactions are possible, either consecutively or concurrently:

$$SiO_{2(s)} \longrightarrow SiO_{(g)} + \tfrac{1}{2}\,O_{2(g)} \tag{1}$$

$$C_{(s)} + \tfrac{1}{2}\,O_{2(g)} \longrightarrow CO_{(g)} \tag{2}$$

$$SiO_{2(s)} + 2C_{(s)} \longrightarrow Si_{(s)} + 2\,CO_{(g)}. \tag{3}$$

Klinger (8) proposed that the reaction occurs by steps (1) and (2). Such a gas-solid reaction, dependent on the true surface area of graphite, is obviously not supported by the results of the present investigation. An additional experiment in which no weight change was observed when a single disk of graphite was placed just above (but not in contact with) the silica powder, further eliminated the possibility of silica decomposition as a step in the reaction mechanism. It is concluded, therefore, that silica does not decompose unless it is in direct contact with graphite. These results suggest a topochemical type of reaction which is proportional to the interfacial contact area between the two solid phases.

Effect of Reactant Proportions

The dependence of the amount of reaction on the quantity of each reactant was determined by fixing the charge weight at 14.4 grams and varying the amount of silica and graphite. High-density graphite, 0.18 mm in diameter, and Fisher silica, 0.15 mm in diameter, were used. The results shown in table 6 and figure 10 indicated that the amount of reaction increases as the amount of reductant decreases or the amount of silica increases. Contrary to the carbon reduction of other oxides such as Fe_2O_3 and Co_2O_3 (9, 15), which apparently proceed indirectly via carbon monoxide formed from interaction of the dioxide with carbon, the carbothermal reduction of silica appears to be a direct process. Other investigators (1, 4) have found the silica reduction rate to be more dependent on the amount of oxidant than on the amount of reductant.

TABLE 6. - Experimental results for the effect of reactant proportions on the reaction weight loss

Test	Charge composition				Reactant molar ratio, SiO_2/C	5-hour weight-loss, percent
	Silica		Graphite			
	Percent	Mole	Percent	Mole		
36	20.0	0.048	80.0	0.960	0.05	1.5
37	40.0	.096	60.0	.720	.13	8.1
38	60.0	.144	40.0	.480	.30	12.1
39	60.0	.144	40.0	.480	.30	12.5
40	83.3	.200	16.7	.200	1.00	21.4
41	90.0	.216	10.0	.120	1.80	22.9
42	95.0	.228	5.0	.060	3.80	17.4
43	97.0	.233	3.0	.036	6.47	11.2

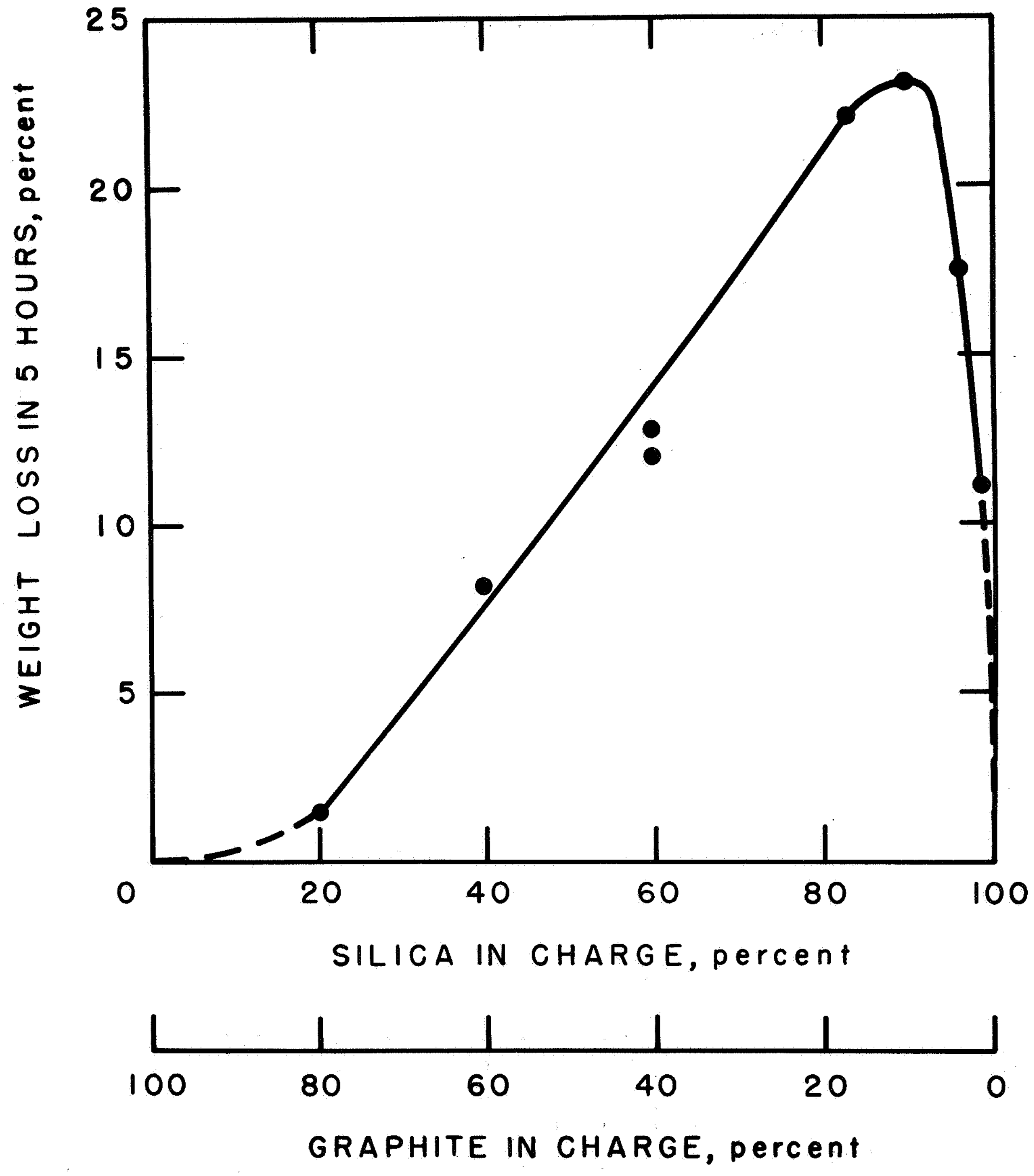

FIGURE 10. - Weight-Loss Variation With the Amount of Silica and Graphite in the Charge.

The data shown in figure 10 were replotted using the molar ratio as the abscissa instead of the silica percent. From the results shown in figure 11, it appears that the maximum reaction occurs at a molar ratio of about 1.5.

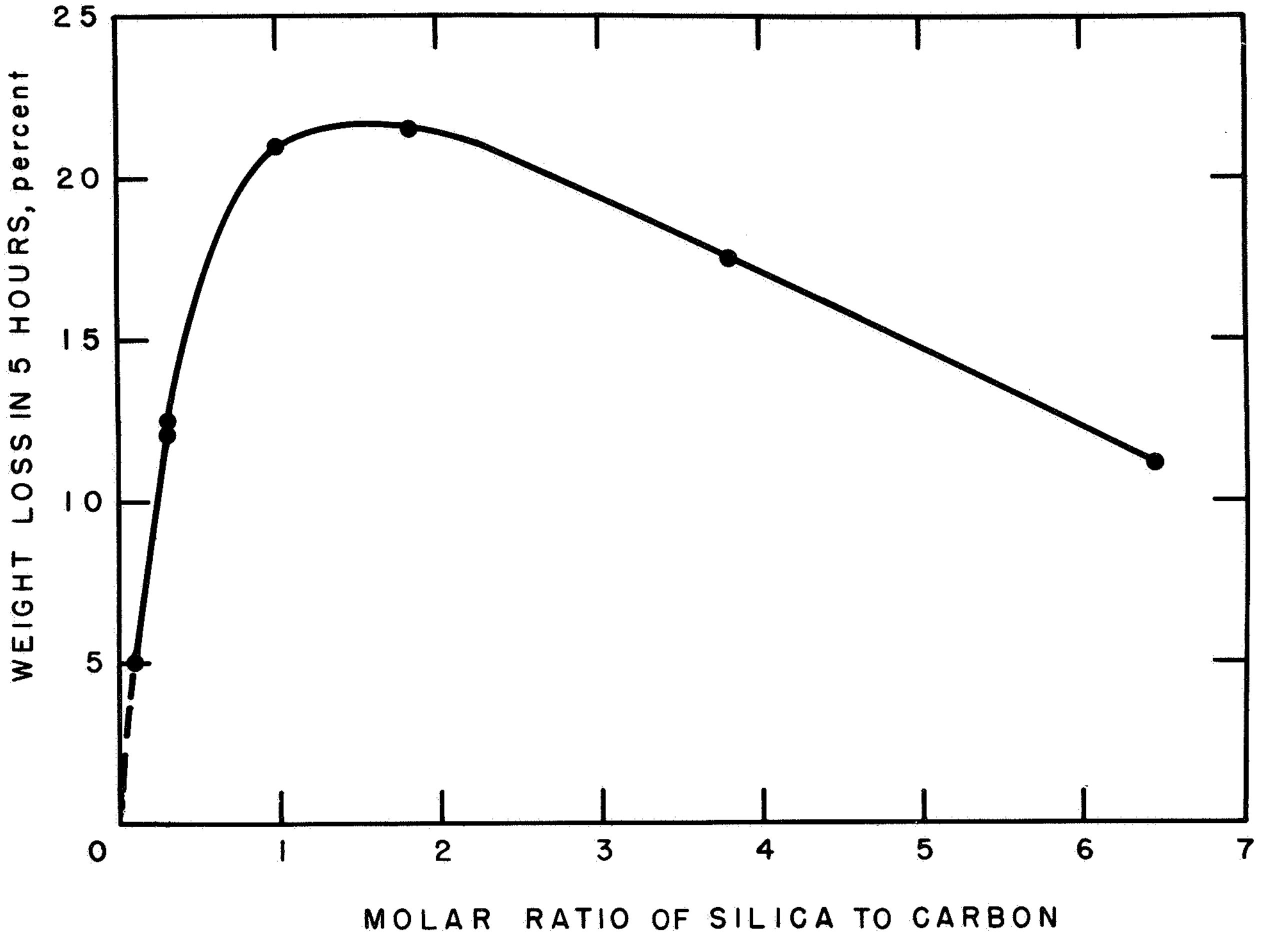

FIGURE 11. - Weight-Loss Variation With the Silica-to-Graphite Molar Ratio.

Carbonized Dextrose as Reductant

The results of studies on particle size indicated that the extent of reaction was strongly dependent on the total contact area between the reactants as well as on the overall porosity of the bed. Finely divided reactants yielded less reaction because entrapped gaseous products built pressures well above that of the ambient chamber. Attempts were made, therefore, to increase the bed porosity by agglomerating the powder reactants into pellets with a binder that would volatilize when heated, leaving a porous pellet. Dextrose, which thermally decomposes to yield carbon and water, was used. The carbon served as a reductant in addition to its role as a binder.

The thermal properties of reagent-grade dextrose in a helium atmosphere were first determined at 150° C, at which temperature a foaming, syrupy mass was obtained. On further heating, it became a porous, voluminous charred sinter. The escaping water caused foaming and considerable swelling. After 4 hours at 600° C, constant weight was obtained.

Since thermally decomposed dextrose may have different reducing properties than graphite, vacuum reduction tests were carried out with various proportions of both reductants. The charge consisted of 0.15-mm Fisher silica and 0.11-mm low-density graphite or granulated dextrose. The granulated dextrose samples were pelletized and heated in a helium atmosphere at 600° C until constant weight was obtained. Half of the pellets were reacted in the vacuum furnace and the unreacted portion was analyzed.

Vacuum furnace results (table 7) show that carbonized dextrose is a better reductant than graphite. The result is undoubtedly attributed to the intimate contact of carbonized dextrose with silica, since dextrose when heated will liquefy and coat silica particles. Such a hypothesis agrees with the results of Vertman (13) who reported that various forms of carbon have different reducing activities. He showed that soot reduced chromium oxide almost twice as fast as graphite. Saltsbury and coworkers (12) stated that charcoal has a higher activity than graphite and that the increase in activity probably results from adsorbed hydrogen. Figure 12 shows the plot of the observed weight loss against the initial percent reductant in the charge. When reduction was carried out with carbonized dextrose, curve *a* was obtained, while curve *b* represents the reduction data with low-density graphite. It is interesting to note that the maximum reaction can be achieved with 3.5 to 4 percent graphite, whereas maximization of the reaction with carbonized dextrose was not achieved in the range investigated. Pellets with greater than 19 percent dextrose (corresponding to 6 percent charred carbon) were difficult to prepare.

TABLE 7. - Data for carbothermal reduction of silica with carbonized dextrose or graphite

Test	Charge			Discharge			Weight-loss, pct/hr
	Analysis, percent		Weight, grams	Analysis, percent		Weight, grams	
	Carbon	Silica		Carbon	Silica		
CARBONIZED DEXTROSE REDUCTANT, 1-HOUR TEST							
44...........	1.1	96.7	13.940	<0.01	98.0	12.935	7.2
45...........	1.7	95.9	12.551	.23	97.5	11.585	7.7
46...........	2.8	94.5	11.928	.83	96.6	10.728	10.1
47...........	2.8	94.5	13.341	.80	97.2	11.769	11.8
48...........	4.7	93.8	10.019	3.06	95.9	8.483	15.3
49...........	5.7	92.2	12.657	3.82	93.6	10.731	15.2
GRAPHITE REDUCTANT, 5-HOUR TEST							
50...........	1.4	98.6	12.295	0.15	96.7	11.509	2.9
51...........	3.8	96.2	11.734	.26	97.6	9.177	4.4
52...........	4.8	95.2	12.596	1.92	99.3	11.129	2.3
53...........	7.0	93.0	12.897	4.43	97.4	11.905	1.5
54...........	9.1	90.9	13.142	6.57	95.3	12.134	1.5
55...........	16.7	83.3	14.373	14.6	87.3	13.318	1.4
56...........	16.7	83.3	14.379	14.8	85.7	13.457	1.3
57...........	28.6	71.4	16.765	27.5	72.5	15.964	1.0
58...........	28.6	71.4	16.792	27.5	72.5	15.988	.9

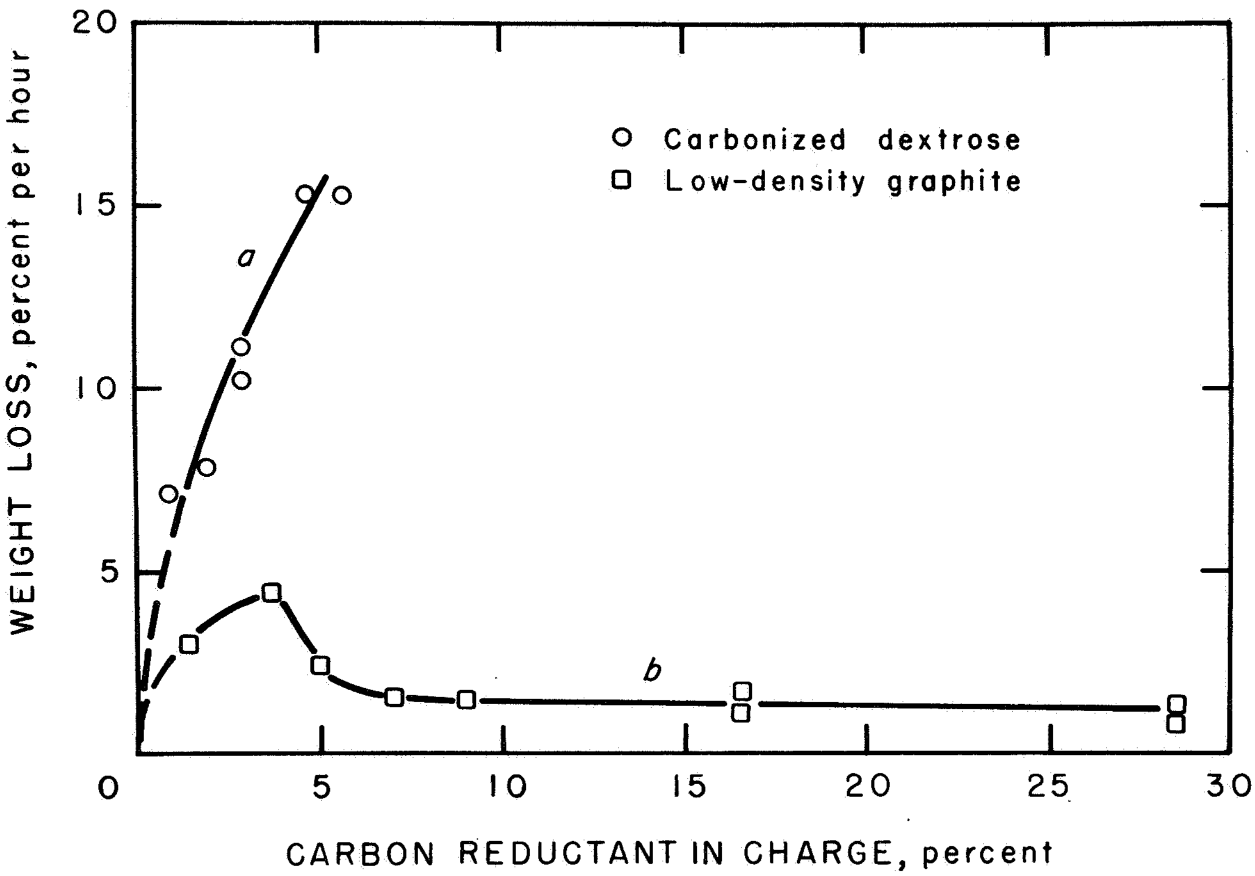

FIGURE 12. - Variation of Weight Loss per Hour With Percent Carbon in the Charge.

CONCLUSIONS

The carbothermal reduction of silica in vacuum did not occur appreciably below 1,300° C. Above 1,445° C, carbon monoxide formed so rapidly that it was difficult to retain unreacted sample in the crucible. Maximum interaction was obtained at a silica-to-graphite molar ratio of about 1.5, and with reactant particle diameters of 0.06 to 0.13 mm. With finer reactants, the gas permeability of the charge was too low to permit free liberation of the gaseous products. For particle sizes larger than 0.13 mm, the amount of reaction better correlated with the number of particles than with the surface area of the reactants.

At 1,400° C for 5 hours, over 80 percent of the total oxygen was extracted from an equimolar powdered mixture containing Wausau silica and graphite particles of approximately 0.15-mm diameter. Carbonized dextrose provided a better reductant than graphite.

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