Experiment	Type of analysis	Reduction, percent	Carbon content, percent
23X-6B................	Chemical	8.6	0.7
	Indirect	8.8	.5
23R-10...............	Chemical	24	1.1
	Indirect	26	1.0

Gas analysis

The feed gas is periodically analyzed with the mass spectrometer. Occasional spot checks of the feed gas are performed by Orsat analysis. Duplicate product-gas samples are taken at least twice during steady-state periods. These samples are taken from the low-pressure (0.3 p.s.i.g.) section of the tail-gas system. The product-gas samples are analyzed by mass spectrometry.

Operational Limits of the Pilot Plant

Linear velocities of the gas are restricted to about 0.5 to 0.8 foot per second for fluidization, and 3 to 5 feet per second for free fall. Thus any change in reactor pressure requires a change in the quantity of feed gas. A change in the feed-gas rate usually necessitates a change in the solids rate, as a constant gas-to-solids ratio is usually maintained.

During fluidized-bed experiments a star feeder supplies the reactor with solids of 20- to 100-mesh size at a maximum rate of 35 and a minimum of 4 pounds per hour. The capacity of the solids hoppers limits the amount of
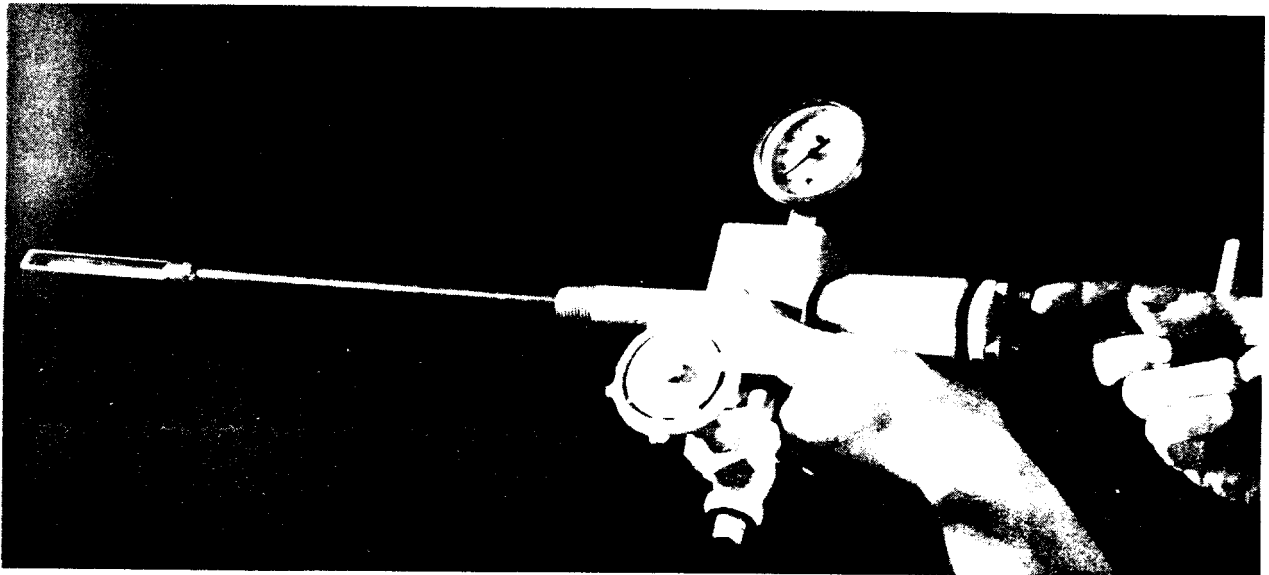

FIGURE 15. - Apparatus for Obtaining Solids Samples During Operation of the Steam-Iron Pilot Plant.

solids treated to about 200 pounds. Thus the duration of the tests is 5.7 hours at the maximum rate, and 50 hours at the minimum rate. For the solids free-fall tests an air-operated plug valve regulates the solids feed to the reactor at rates of 20 to 500 pounds per hour. Pressure limitations of the reactor are 320 p.s.i.g. at 810° C. and 1,400 p.s.i.g. at 490° C.

Operational Procedures and Variations

Preparation of Solids

Magnetite not previously used in the system is reduced with a simulated producer gas and oxidized with steam or steam and carbon dioxide at least twice before any experimental data is recorded for the particular solid. Owing to the inability to attain the required degree of reduction of solids at required gas conversions in one pass through the reactor, the solids were prereduced or preoxidized for subsequent experiments. The solids are prepared for reduction tests by oxidizing them to 95 percent (based on Fe_3O_4) or a degree of reduction of 5 percent; similarly, for oxidation tests the solids were reduced to a state of about 35 percent. Appreciable caking or agglomeration of the solids occurred when fresh magnetite was used at 700° to 800° C. and generally during reduction when the degree of reduction of the solids was about 20 percent or more.

Operational Variables During Fluidized Bed Tests

During all tests a continuous flow of solids and gas was maintained to and from the reactor. The solid particles were kept in motion in the fluidized bed and flowed in a steady downward direction as the solids were continuously removed at the bottom. This continuous motion was necessary to minimize caking or agglomeration. If operating conditions were to be changed during a test, the reactor would be emptied of all solids and the test resumed at the new conditions.

As previously mentioned, the superficial linear velocity of the gas through the reactor is limited to the fluidization of the solids or about 0.6 foot per second. As the optimum gas-to-solids ratio is defined by the desired conversions of solids and gas, the solids throughput is also dependent upon the fluidization velocity, as shown in the appendix. In many of the variable studies it was desirable to operate at the same solids throughput and reactive gas-solids ratio in both reduction and oxidation. To do so, the reduction had to be operated at a higher pressure because the producer gas used in reduction contains about 40 percent reducing gases. A greater quantity of total gas is required in reduction to maintain the quantity of reactive gases constant in both steps, and thus the pressure during reduction was increased correspondingly to the increased flow in order to keep the gas velocity at about 0.6 foot per second.

Operational Variables During Free-Fall Tests

During all solids free-fall tests the spiral rod assembly shown in figure 11 was inserted into the reactor. The rod minimizes the possibility of gas or

solids channeling, helps disperse the solids for better gas-solids contact, and increases the residence time of the solids. The residence time in the reactor is increased from about 1 second with the empty reactor to about 5 seconds with the spiral rod. The linear velocity of the gas is limited only by the terminal settling velocity of the solids. Gas velocities up to 5 feet per second were attained during free-fall reduction with no apparent solids carryover.

Since the solids and gas remain in the reactor only a few seconds during free-fall tests, steady conditions are obtained rapidly. Many operating changes can be made and the results observed within a short time. The tendency of the solids to agglomerate during fluidized-bed reduction was not evident during the free-fall tests.

<div align="center">DISCUSSION OF RESULTS</div>

<div align="center">Fluidized-Bed Experiments</div>

A study was made of the variables affecting the oxidation and reduction of the solids. Reduction tests are designated by the letter R inserted into the experiment number; oxidation tests are designated by the letter X. Unless otherwise noted the height of the fluidized bed of solids was 16 feet.
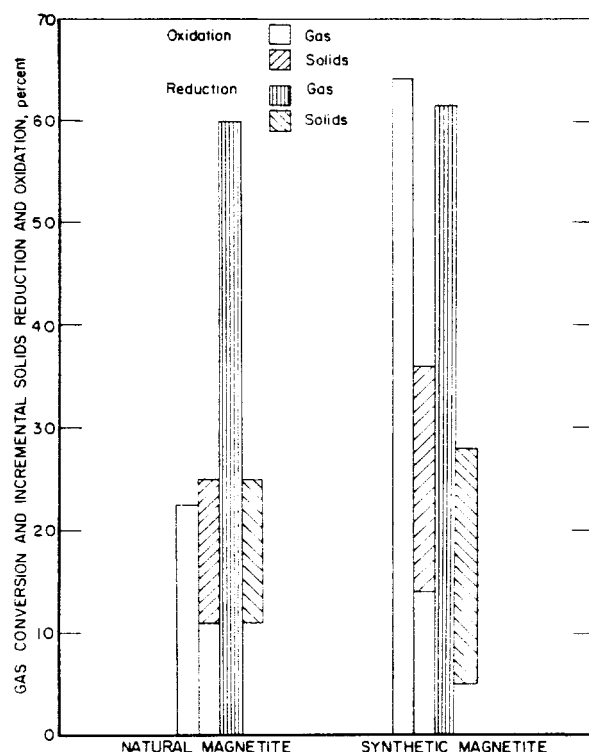
Effect of Composition of Magnetite on Conversion

When alkali-promoted fused iron oxides, synthetic magnetites, were used, gas conversions of 64 and 62 percent accompanied by incremental solids conversions of 22 and 23 percent were obtained during oxidation and reduction, respectively. Gas conversions of 23 and 60 percent accompanied by solids conversions of 14 percent were obtained, respectively, during oxidation and reduction using natural magnetite at comparable operating conditions such as temperature, bed height, and gas-to-solids ratio as shown in table 2 and figure 16. Composition of the magnetites, shown in table 3, indicates that the major difference between the natural and synthetic magnetites was in the silica, magnesia, and potassium oxide concentrations. The low potassium oxide content and/or high silica concentrations, coupled with the physical interspersion of the silica in natural magnetite, may have some retarding effect on the reaction of the iron oxide. Differences in porosity and specific surface area are also possible contributing factors to the difference in reactivity.

FIGURE 16. - Effect of Magnetite Composition on Conversion During Oxidation and Reduction at 750°C. and 12-Foot Bed.

TABLE 2. - Effect of magnetite composition on gas and solids conversion in reduction and oxidation at 750° C.

Experiment	Reactor pressure, p.s.i.g.	Gas rate, cu.ft./hr.		Solids rate, lb./hr.	Bed height, ft.	Residence time	
		H_2+CO/ CO_2+N_2	H_2O/CO_2			Solids, min.	Gas, sec.
2OR-3[1]	100	[2]28/42	-	11	12	129	24
23R-5[3]	130	[4]32/48	-	15	12	130	21
2OX-4[1]	100	-	35/35	20	12	71	10
23X-6[3]	90	-	26/26	15	12	93	21

	Gas conversion, percent	Reduction of solids, percent			Free carbon content of solids, weight-percent		
		In	Out	Change	In	Out	Change
2OR-3[1]	60	11	25	14	2.9	3.8	0.9
23R-5[3]	62	5	28	23	.1	.3	.2
2OX-4[1]	23	25	11	14	3.8	3.2	.6
23X-6[3]	64	36	14	22	1.0	.9	.1

[1] Natural magnetite.
[2] H_2 16.4, CO 23.6, N_2 52.8, and 7.2 volume-percent.
[3] Synthetic magnetite.
[4] H_2 20.1, CO 20.1, N_2 52.6, and CO_2 7.1 volume-percent.

TABLE 3. - Composition of magnetites used in the steam-iron process, percent

Constituent	Synthetic magnetite	Natural magnetite
Total iron	66.78	67.0
Al_2O_3	0	.73
MgO	4.62	.09
Cr_2O_3	0.75	0
Mn_3O_4	.03	.05
K_2O	.61	.08
SiO_2	.62	4.88

Effect of Bed Height on Conversion

Gas conversions of 56, 62, 66, and 71 percent accompanied by incremental solids conversions of 19, 21, 23, and 25 percent were obtained for bed heights of 4, 8, 12, and 16 feet, respectively, during reduction at 800° C. and 200 p.s.i.g. During oxidation at equivalent bed heights, gas conversions of 61, 64, 69, and 69 percent accompanied by incremental solids conversions of 18, 19, 20, and 23 percent, respectively, were obtained at 800° C. and 60 p.s.i.g. as shown in table 4 and figures 17 and 18.

TABLE 4. - Effect of bed height on gas and solids conversion
during oxidation and reduction at 800° C.

Experiment	Reactor pressure, p.s.i.g.	Gas rate, cu.ft./hr. H_2 +CO CO_2 +N_2	Gas rate, cu.ft./hr. H_2O/CO_2	Solids rate, lb./hr.	Bed height, ft.	Residence time Solids, min.	Residence time Gas, sec.
23R-4..........	200	[1]35/52	-	15	4	31	6
					8	62	12
					12	93	19
					16	124	26
23X-4..........	60	-	20/20	15	4	31	6
					8	62	11
					12	93	17
					16	124	22

	Gas conversion, percent	Reduction of solids, percent In	Reduction of solids, percent Out	Reduction of solids, percent Change	Free carbon content of solids, weight-percent In	Free carbon content of solids, weight-percent Out	Free carbon content of solids, weight-percent Change
23R-4..........	56	5	24	19	0.1	0.6	0.5
	62	5	26	21	.1	.6	.5
	66	5	28	23	.1	.6	.5
	71	5	30	25	.1	.5	.4
23X-4..........	61	33	15	18	.9	.2	.7
	64	33	14	19	.9	.1	.8
	69	33	13	20	.9	.3	.6
	69	33	10	23	.9	.1	.8

[1]H_2 17.5, CO 17.5, N_2 52.6, and CO_2 7.2 volume-percent.

Constant gas and solids rates were maintained throughout the respective
experiments; thus the residence time of the solids in the reaction zone
increased proportionately to the bed height. Relatively high gas conversions
were obtained in both oxidation and reduction at the 16-foot level, but the
accompanying solids conversions were about 5 incremental-percent less than
calculated from the gas conversions. A possible explanation for the relatively
small incremental increase on solids conversion with bed height is that back
mixing of the solids may be occurring. Thus in reduction, the reduced solids,
FeO and iron, are not isolated from the highly oxidized feed, principally
Fe_3O_4. Consequently, true countercurrent gas-to-solids contact is not
achieved, and part of the advantage of increasing the height of the bed is
lost. High gas conversion was achieved; however, once the gas becomes highly
converted due to reduction of Fe_3O_4 to FeO, it is no longer effective for
reducing FeO. Thus if the converted gas contacts FeO near the top of the
bed, it cannot reduce it. Also, if Fe_3O_4 is present (owing to back-mixing)
near the bottom of the bed, fresh gas is being used to reduce Fe_3O_4. This gas
could be used more advantageously for reducing FeO. This effect can be seen
by referring to the equilibrium gas conversions in table 1. The conversions
achieved thus far are indicative of equilibrium conditions with the Fe_3O_4-to-
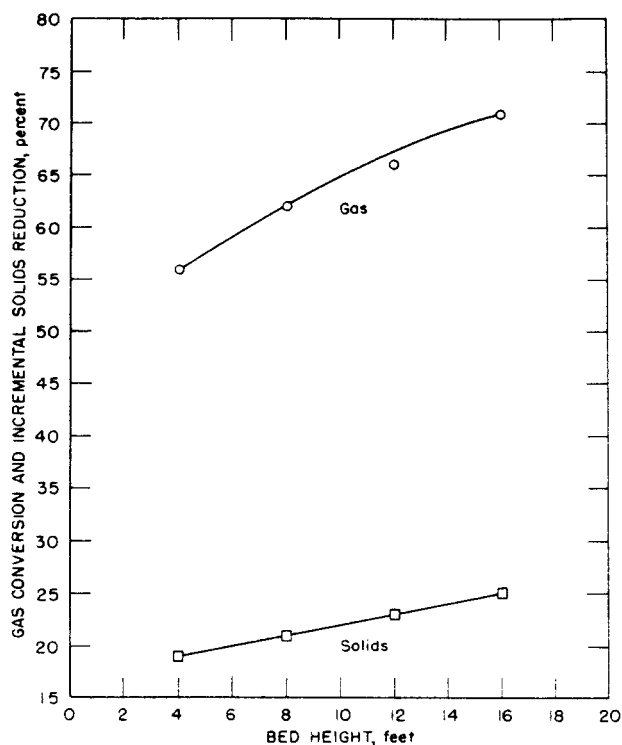FeO reduction.

FIGURE 17. - Effect of Bed Height on Gas and Solids Conversions During Reduction at 800° C.
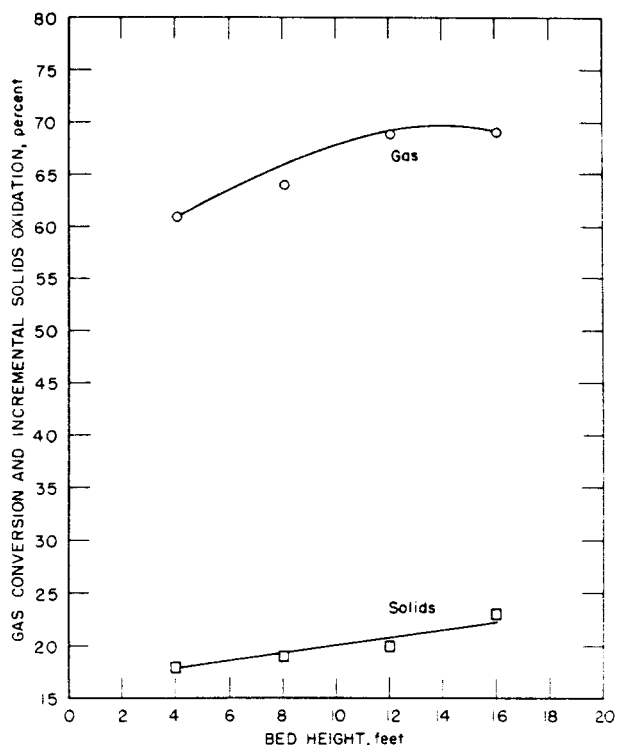
FIGURE 18. - Effect of Bed Height on Gas and Solids Conversions During Oxidation at 800° C.

The probability that back-mixing is occurring in the reactor is supported by results from a study using a 2-inch-diameter glass column. The tests were performed at ambient temperatures and at near atmospheric pressures with a solids bed height of 4 to 6 feet. A spiral rod similar to the one shown in figure 3 was inserted into the glass column. The column was filled with about 2 feet of the gray-black Fe_3O_4 to which was added about 2 inches of the reddish-brown Fe_2O_3 and then another 2 feet of Fe_3O_4. In all cases the reddish-brown Fe_2O_3 was dispersed throughout the entire length of the bed in a matter of minutes. The tests were performed at a superficial linear gas velocity of 0.4 to 0.6 foot per second. A gas velocity of 0.4 foot per second is slightly above that required to expand the bed. Back mixing appeared to be the direct result of the slugging effect of gas pockets forming and collapsing in the solids bed. A recent study of the steam-carbon reaction in a fluidized bed[14] appears to corroborate back-mixing of solids. The investigators concluded that the fluid bed acted like a perfectly mixed bed despite use of a reactor of the large length-to-diameter ratio of about 20.

Baffles similar to the one shown in figure 11 installed in the glass column and subsequently in the reactor system minimized the back-mixing considerably; in the reactor, however, operating difficulties were encountered that far outweighed the advantages and precluded their use. Plugging was

[14]May, W. G., Mueller, R. H., and Sweetser, S. B., Carbon-Steam Reaction Kinetics from Pilot-Plant Data: Ind. Eng. Chem., vol. 50, 1958, pp. 1289-1296.

caused by solids agglomeration, which was probably due to retention of the solids at the baffles.

Effect of Temperature on Conversion

Oxidation and reduction were investigated at 600°, 675°, 700°, 750°, and 800° C. as shown in table 5. The conversion of gases and solids increased with increasing temperature up to about 750° C. During reduction, average gas conversions of 64 percent accompanied by average incremental solids conversions of 20 percent were obtained at 750° C.; at 800° C. conversions of 61 and 18 percent, respectively, were obtained. Similarly during oxidation, average gas conversions of 46 percent accompanied by average incremental solids conversions of 19 percent were obtained at 750° C., compared to values of 38 and 14 percent, respectively, at 800° C.

High temperatures favor higher conversion of the reducing gas. Oxidation with carbon dioxide also is favored at high temperatures, but the equilibrium regarding conversion of steam to hydrogen for the system $FeO-H_2-Fe-H_2O$ decreases slightly with increased temperature.

The lower conversions at 800° C. can be attributed possibly to a physical change occurring in the iron-iron oxide particle at the higher temperatures or to the fact that reduced iron becomes sticky at these temperatures. This characteristic of reduced iron has been reported by several investigators.[15-17] The tendency to stick has resulted in observed solids-agglomeration problems at high temperatures in a fluidized bed. Agglomeration of solid particles results in lower surface area, which decreases their reactivity and results in lower conversion.

Effect of Pressure on Conversion

The effect of pressure upon reduction and oxidation was investigated in experiments 24R-1 and 23X-17. In both tests a constant gas-to-solids flow was maintained, as shown in table 6. This meant that at 55 p.s.i.g. the gas flow was 32 cubic feet per hour (13 cubic feet H_2 +CO and 19 cubic feet N_2 +CO_2), and the solids flow was 7.5 pounds per hour; at 125 p.s.i.g. the gas flow was 64 cubic feet per hour (26 cubic feet H_2 +CO and 38 cubic feet N_2 +CO_2), and the solids flow was 15 pounds per hour.

[15] Stelling, O., Carbon Monoxide Reduction of Iron Ore: Jour. Metals, vol. 10, 1958, pp. 290-295.

[16] Stelling, O., Treatment of Pulverulent Iron Oxides: British Patent 747,584, Nov. 6, 1953.

[17] Meyer, H. H., The Rate of Reduction of Iron Ores in a Gas Stream: Mitt. Kaiser Wilhelm-Inst. Eisenforsch., vol. 10, 1938, pp. 107-116.

TABLE 5. - Effect of temperature on gas and solids conversion
during oxidation and reduction in a 16-foot
fluidized bed

Experiment	Pressure, p.s.i.g.	Gas rate, cu.ft./hr.		Solids, rate, lb./hr.	Residence time,		Temperature, ° C.
		H_2+CO/N_2+CO_2	H_2O/CO_2		Solids, min.	Gas, sec.	
23R-7.........	195	[1]35/52	-	15	124	26	675
							750
23R-11........	200	[3]35/50	-	15	124	26	750
							800
23X-11........	150	-	60/0	18	104	15	750
							800
23X-12........	60	-	11/11	10	187	41	700
							750
							800
24R-10........	165	[5]32/48	-	15	124	28	600
							700
							800
24X-10........	90	-	40/0	15	124	22	600
							700
							800

Experiment	Gas conversion, percent	Reduction of solids, percent			Free carbon content of solids, weight-percent		
		In	Out	Change	In	Out	Change
23R-7.........	[2]49	8	17	9	0.5	1.6	1.1
	65	8	25	17	.5	1.5	1.0
23R-11........	[2]62	7	30	23	.5	1.2	.7
	50	7	27	20	.5	.7	.2
23X-11........	[4]42	28	4	24	1.1	.2	.9
	36	28	5	23	1.1	.3	.8
23X-12........	[4]39	27	11	16	.9	.5	.4
	49	27	13	14	.9	.2	.7
	47	27	13	14	.9	.2	.7
24R-10........	[2]42	4	17	13	.3	.9	.6
	63	4	19	15	.3	.6	.3
	72	4	19	15	.3	.3	.0
24X-10........	[2]33	17	8	9	.6	.3	.3
	31	17	8	9	.6	.4	.2
	32	17	13	4	.6	.3	.3

[1]H_2 20, CO 20, N_2 53, and CO_2 7 volume-percent.
[2]Conversion of H_2+CO.
[3]H_2 20.6, CO 20.6, N_2 51.8, and CO_2 7.0 volume-percent.
[4]Conversion of H_2O or H_2O+CO_2.
[5]H_2 20, CO 20, N_2 53, and CO_2 7 volume-percent.

TABLE 6. - <u>Effect of pressure on gas and solids conversion</u>
<u>during oxidation and reduction at 750° C. in</u>
<u>a 16-foot fluidized bed</u>

Experiment	Reactor pressure, p.s.i.g.	Gas rate, cu.ft./hr.		Solids rate, lb./hr.	Reactive gas/solids ratio, cu.ft./lb.	Gas conversion, percent
		CO_2+N_2	H_2O/CO_2			
23X-17.........	55	-	16/16	15	2.1/1.0	40
	125	-	32/32	30	2.1/1.0	39
24R-1.........	55	[1]13/19	-	7.5	1.7/1.0	54
	125	26/38	-	15.0	1.7/1.0	59

Experiment	Gas conversion rate[2] percent/min.	Reduction of solids, percent			Solids conversion rate, percent/min.	Free carbon content of solids, percent		
		In	Out	Change		In	Out	Change
23X-17.........	0.32	26	12	14	0.11	0.6	0.2	0.4
	.62	26	10	16	.26	.6	.2	.4
24R-1.........	.22	14	27	13	.05	.2	1.3	1.1
	.48	14	28	14	.11	.2	1.2	1.0

[1]H_2 20.3, CO 20.3, N_2 52.2, and CO_2 7.2 volume-percent.
[2]Based on solids residence time.

A first-order effect of pressure on the reaction rate was indicated, as the incremental conversion of solids and conversion of gas in both the oxidation and reduction were the same at both pressures, whereas the throughputs were twice as large at the higher pressure. This meant that the reaction rate was doubled by doubling the pressure. Although the rate of reaction appeared to be a direct function of pressure, the overall gas and solids conversion seemed to be independent of pressure in spite of the fact that the solids residence time in the reactor was about 124 minutes at the lower pressure and 62 minutes at the higher pressure. The apparent inability to affect a change in gas and solids conversions at a longer residence time is indicated from observations made by Gamburg.[18] He reports that "the residence time of the iron in the oxidizing furnace should not be more than 4 minutes."

Effect of Gas-to-Solids Ratio on Conversion

The effect of varying the solids throughput at a constant gas flow in reduction and oxidation was investigated. The stoichiometric flow of solids was used as a base case for comparison, and the solids rate was varied above and below this value. The stoichiometric flow for reduction is defined as the flow of solids at which 70-percent conversion of the hydrogen plus carbon

[18]Gamburg, D. Yu., and Sarychev, B. L., Study of the Kinetics of Oxidation of Reduced Iron Catalysts and Ores by Steam for the Purpose of Obtaining Hydrogen: Khimiia i Tekhnologiia, Topliva i Masel 3, No. 10, 1958, pp. 16-24.

monoxide in the reducing gas can be obtained with a 30-percent incremental change in the reduction of the solids. For oxidation, 60-percent conversion of the steam and carbon dioxide and the same 30-percent change in the solids is used in defining the stoichiometric solids flow. Sample calculations are shown in appendix II to illustrate the stoichiometric determination for reduction and for oxidation. However, since the experimental data indicated that the solids conversions as defined in the stoichiometric calculations were not being attained, the gas or solids rate was adjusted to reflect actual conversions. This meant that the actual gas and solids rates varied slightly from the calculated stoichiometric rates.

The results on the effect of gas-to-solids variation are shown in figures 19 and 20 and given in detail in table 7. The stoichiometric gas-to-solids ratios were 2.9 and 3.2 for experiments 22R-3 and 22X-3, respectively.

TABLE 7. - Effect of reactive gas-to-solids ratio on gas and solids conversion during oxidation and reduction at 750° C.

Experiment	Reactor pressure, p.s.i.g.	Gas rate, cu.ft./hr.		Solids rate, lb./hr.	Reactive gas/solids ratio, cu.ft./lb.
		H_2 +CO/ CO_2 +N_2	H_2O/CO_2		
22X-3............	105	-	32/32	30	2.1/1
				20	3.2/1
				10	6.4/1
22R-3...........	120	[1]35/50	-	14	2.5/1
				12	2.9/1
				10	3.5/1

Experiment	Adjusted stoichiometric gas-solids ratio	Gas conversion, percent	Reduction of solids, percent			Free carbon content of solids, percent		
			In	Out	Change	In	Out	Change
22X-3............	3.2	62	34	17	17	1.4	0.7	0.7
	3.2	57	34	13	21	1.4	.5	.9
	3.2	34	34	8	26	1.4	.2	1.2
22R-3...........	2.9	69	4	20	16	.1	.7	.6
	2.9	62	4	25	21	.1	.8	.7
	2.9	57	4	27	23	.1	.8	.7

[1]H_2 20.6, CO 20.6, N_2 51.8, and CO_2 7.0 volume-percent.

Gas-to-solids ratio below the stoichiometric values, obtained by increasing the solids flow at constants gas flow, resulted in near theoretical gas conversion with low solids conversion. Increasing the gas-to-solids ratio above stoichiometric values effected an increase in the solids conversion with lower gas conversions. Gas-to-solids ratios at stoichiometric rates produced gas conversions at near theoretical values accompanied by incremental solids conversions about 5 percent less than was calculated. The back mixing of the solids in the fluidized bed apparently limited the solids conversion to about 21 percent.
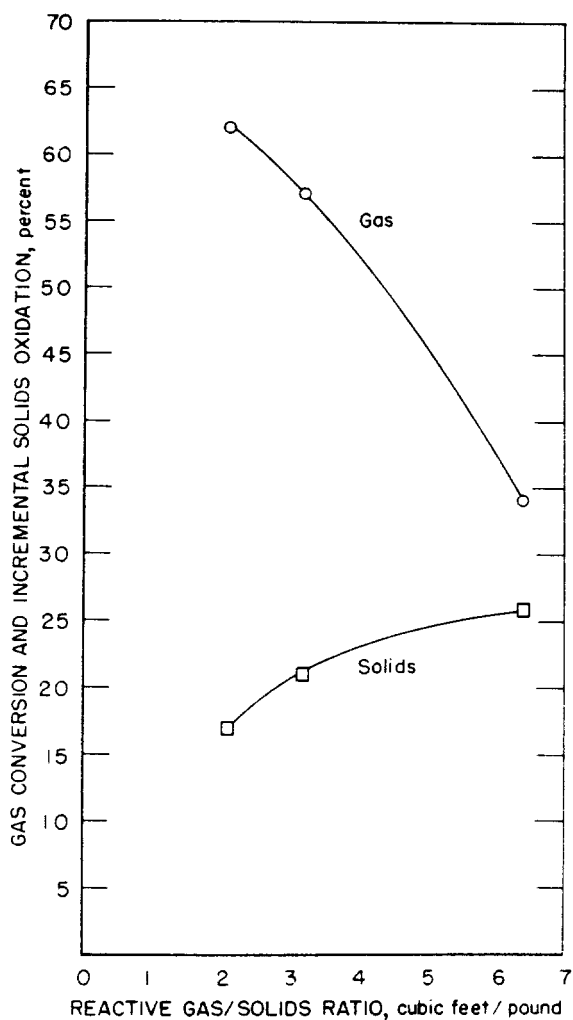
FIGURE 19. - Effect of Reactive Gas-to-
Solids Ratio on Gas and
Solids Conversions During
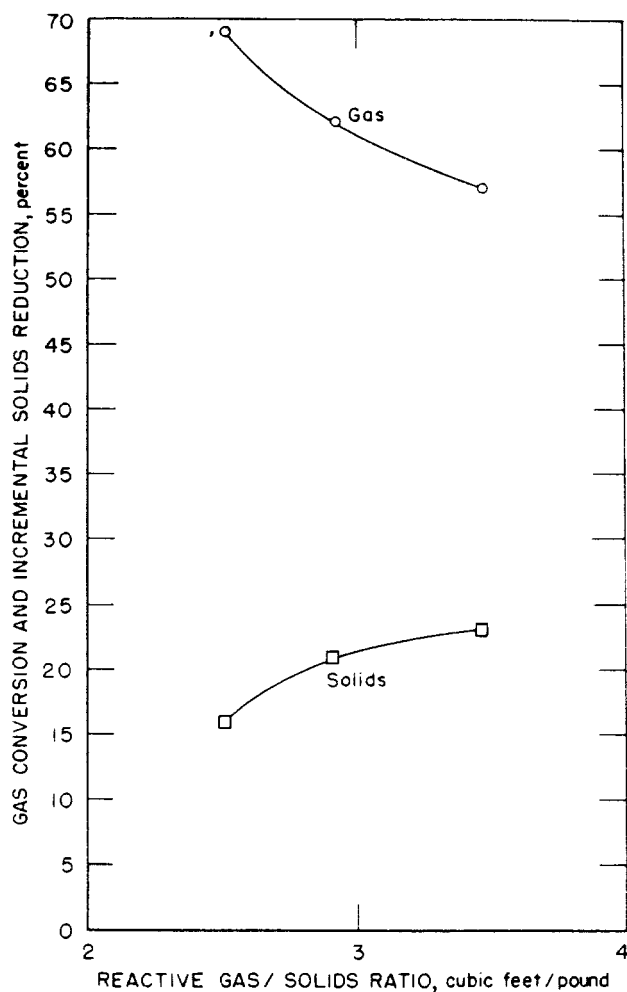Oxidation at 750°C., Ex-
periment 22X-3.

FIGURE 20. - Effect of Reactive Gas-to-
Solids Ratio on Gas and
Solids Conversions During
Reduction at 750°C., Ex-
periment 22R-3.

Utilization of Methane during Reduction

Reduction experiments were performed to determine whether methane, which
is generally found in low concentrations of 1 to 4 percent in producer gas,
could be utilized in the reduction of iron oxide. Gallusser[19] describes a
process in which iron ore is reduced by natural gas. On the other hand,
Maier[20] found that natural gas was a poor reducing agent. A simulated pro-
ducer gas containing about 7 percent methane and 3 percent water vapor was

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[19]Gallusser, H., The Use of Natural Gas in theReduction of Iron Ores: Blast
Furnace and Steel Plant, December 1958, pp. 1301-1302.
[20]Maier, C. G., and Thomas, S. B., Reduction of Iron and Steel from Ore:
Bureau of Mines Rept. of Investigations 3229, 1934, pp. 33-49.

used in the reduction experiments. To permit more accurate measurements, a higher concentration of methane was used than is normally found in producer gas.

The reaction of methane and water should proceed readily at 750° C. from an equilibrium standpoint (log K = -1.6) to form hydrogen and carbon monoxide according to the reaction:

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO.$$
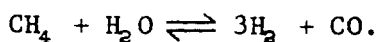
However, the low methane content, the presence of hydrogen and carbon monoxide in the simulated producer gas, and the operation at elevated pressure are all unfavorable for the conversion of methane. Results from experiments performed at 750° to 800° C. and 170 p.s.i.g. indicated that only a relatively small quantity (about 5 percent) of the methane present reacted and that the reduction of the iron oxide was not significantly affected, as shown in table 8 and figure 21.

TABLE 8. - Utilization of methane during reduction at 170 p.s.i.g.

Experiment	Temperature, ° C.	Feed gas rate, cu.ft./hr. H_2 +CO/CO_2 +N_2 +CH_4 +H_2O	Solids rate, lb./hr.	Reactive gas/solids ratio, cu.ft./lb.	Residence time, Solids, min.	Gas, sec.
23R-9.........	800	[1]35/59	15	2.3/1.0	124	26
23R-10........	750	[2]35/61	20	1.8/1.0	94	26
23R-11........	800	[1]35/59	15	2.3/1.0	124	26

Experiment	Gas conversion, percent		Reduction of solids, percent			Free carbon content of solids, weight-percent		
	H_2 +CO	CH_4	In	Out	Change	In	Out	Change
23R-9.........	69	7	4	28	24	0.6	1.1	0.5
23R-10........	58	3	6	26	20	.5	1.0	.5
23R-11........	58	6	7	28	21	.5	1.1	.6

[1]H_2 18.6, CO 18.6, N_2 46.9, CO_2 6.4, CH_4 7.4, and H_2O 2.1 volume-percent.
[2]H_2 18.2, CO 18.2, N_2 45.9, CO_2 6.3, CH_4 8.3, and H_2O 3.1 volume percent.

Effect of Reducing Gas on Conversion

Variation in the hydrogen-to-carbon monoxide ratios from 0.5/1 to 3/1 in a simulated producer feed gas had a negligible effect on gas and solids conversions during reduction at 750° C., 110 p.s.i.g., and a ratio of reactive gas (H_2 +CO) to solids of 1.7. These results are shown in table 9 and figure 22. The formation of free carbon was greater at the lower hydrogen-to-carbon monoxide ratios. Meyer[21] reports that carbon formation was greater when the feed gas contained a higher hydrogen-to-carbon monoxide ratio. His contentions were that with a higher proportion of hydrogen, the carbon dioxide decreased according to

[21]Work cited in footnote 17, p. 21.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O,$$
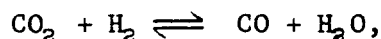
and that with a decrease in carbon dioxide, carbon deposition increased according to

$$2CO \rightleftharpoons CO_2 + C.$$
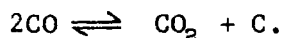
The difference in findings may be attributed to either temperature or mode of operation. His investigation was performed at 500° to 600° C., fixed bed, and no apparent pressure; ours was at 750° C., fluidized bed, and at 110 p.s.i.g.

TABLE 9. - Effect of reducing gas ratio on gas and solids conversion in reduction at 750° C., 110 p.s.i.g., and a 16-foot fluidized bed

Experiment	Reactor pressure, p.s.i.g.	Gas rate, cu.ft./hr. H_2+CO/CO_2+N_2	Solids rate, lb./hr.	Reactive gas/solids ratio	Ratio in feed gas, H_2/CO
23R-12.........	110	[1]26/38	15	1.7/1.0	0.5
	110	[2]26/38	15	1.7/1.0	1.0
	110	[3]26/38	15	1.7/1.0	3.0

Experiment	Gas conversion, percent	Reduction of solids, percent			Free carbon content in solids, weight-percent		
		In	Out	Change	In	Out	Change
23R-12.........	74	5	24	19	0.3	1.1	0.8
	67	5	24	19	.3	.8	.5
	68	5	24	22	.3	.7	.4

[1]H_2 13.5, CO 27.1, N_2 52.2, and CO_2 7.2 volume-percent.
[2]H_2 20.3, CO 20.3, N_2 52.2, and CO_2 7.2 volume-percent.
[3]H_2 30.5, CO 10.1, N_2 52.2, and CO_2 7.2 volume-percent.

Effect of Oxidizing Gases on Conversion

Oxidation experiments were performed to determine the relative reactivity of steam and carbon dioxide with 85- and 25-percent-reduced magnetite at 600° and 750° C., respectively.

Results from oxidation of the 85-percent-reduced magnetite at 90 p.s.i.g., 600° C., and a gas-to-solids ratio of 4.3 resulted in a carbon dioxide conversion of 61 percent accompanied by an incremental solids conversion of 62 percent, compared to conversions with steam of 79 and 64 percent for gas and solids, respectively.

Oxidation of the 25-percent-reduced magnetite at 750° C., 45 p.s.i.g., and a gas-to-solids ratio of 2.2 resulted in gas conversion of 43 percent accompanied by incremental solids conversions of 16 percent for both steam and carbon dioxide oxidation, as shown in table 10. The results indicate that steam and carbon dioxide are equally reactive at conditions considered typical for the steam-iron process as outlined in this report. The carbon content of the solids was increased from 1.0 to 5.3 percent by weight. The
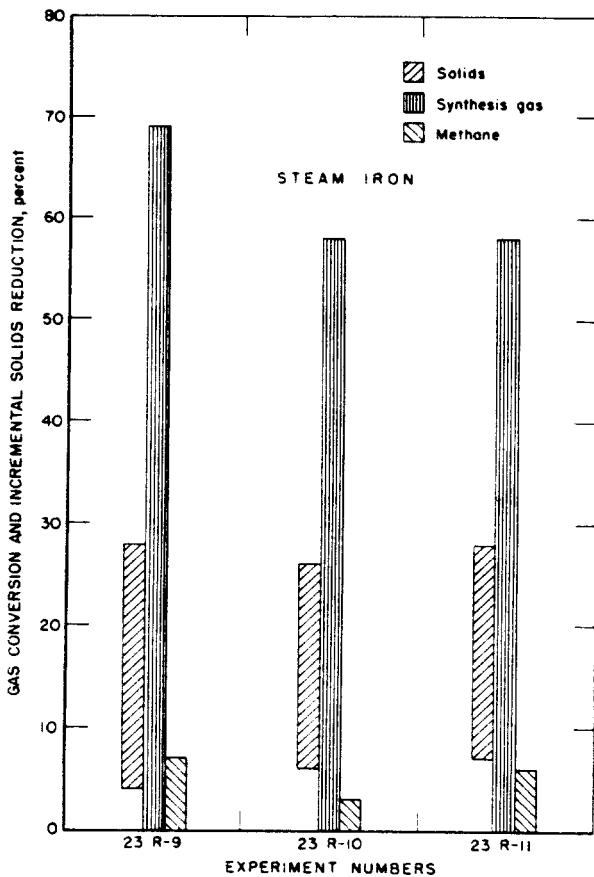
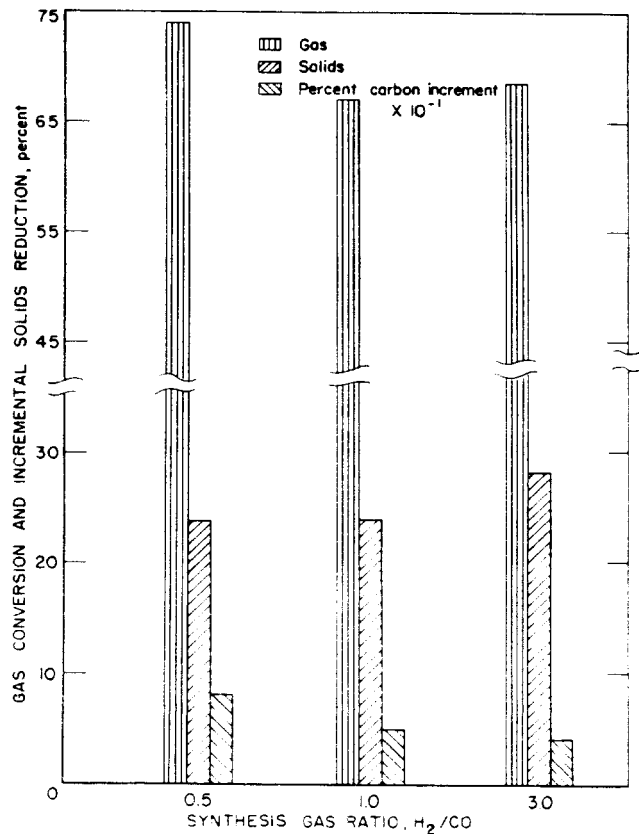FIGURE 21. - Utilization of Methane During Reduction at 170 p.s.i.g.

FIGURE 22. - Effect of Reducing-Gas Ratio on Gas and Solids Conversions During Reduction at 750° C., 110 p.s.i.g., and 16-Foot Bed, Experiment 23R-12.

presence of this large amount of carbon could hinder contact between the carbon dioxide and Fe and FeO, resulting in decreased reaction. Carbon could be formed under the prevailing conditions as follows: Carbon dioxide is first reduced to carbon monoxide; the carbon monoxide then reacts in the presence of iron or iron oxide to form carbon dioxide and carbon as shown in the following reactions:

$$Fe + CO_2 \rightleftharpoons FeO + CO$$

$$3FeO + CO_2 \rightleftharpoons Fe_3O_4 + CO$$
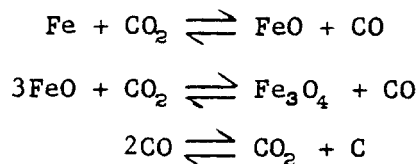
$$2CO \rightleftharpoons CO_2 + C$$

According to the free energy change, reaction $2CO \rightleftharpoons CO_2 + C$ is also favored at 600° C. This could have contributed to the apparent lower conversion of carbon dioxide at 600° C. as compared to the steam conversion.

TABLE 10. - Effect of oxidizing gases on reduced synthetic
magnetite in a 16-foot bed

Experiment	Temperature, ° C.	Pressure, p.s.i.g.	Gas-to-solids ratio, cu.ft./lb.	Solids rate, lb./hr.	Gas rate, cu.ft./hr. $H_2O + CO_2$
23X-7..........	600	90	4.3	15	0+65
	600	90	4.3	15	32.5+32.5
	600	90	4.3	15	65+0
23X-14.........	750	45	2.2	10	22+0
	750	45	2.2	10	0+22

Experiment	Gas conversion, percent	Reduction of solids, percent			Free carbon content in solids, weight-percent		
		In	Out	Change	In	Out	Change
23X-7..........	61	85	23	62	1.0	5.3	4.3
	59	85	23	62	1.0	2.7	1.7
	79	85	21	64	1.0	1.0	0
23X-14.........	43	25	9	16	.2	.1	.1
	43	25	9	16	.2	.1	.1

Effect of Temperature on Hydrogen Purity

Oxidation tests using steam were made to determine the yield and purity
of the hydrogen at 600° and 750° C. A fluidized bed of reduced iron oxide
oxidized with steam at 600° C. produced a gas containing 97 percent hydrogen
on a dry basis. Near equilibrium conversion of 53 percent of the steam was
attained accompanied by an incremental change in the solids of 24 percent.
The other constituents of the product gas were carbon monoxide, carbon dioxide,
and a trace of methane. Oxidation performed at 750° C. produced a gas contain-
ing 91 percent hydrogen. A steam-to-hydrogen conversion of 64 percent was
obtained with an incremental change in solids of 22 percent. About equal quan-
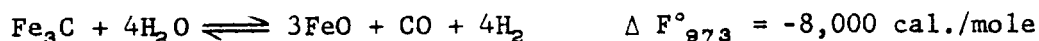tities of carbon monoxide and carbon dioxide and a small amount of methane was
produced.

Operating conditions during these tests are given in table 11. The pro-
duction of carbon-containing gases is low at 600° C., and the concentration
of carbon in the solids before and after reduction is about the same. At
higher temperatures a less pure hydrogen product gas is formed owing to reac-
tion of steam with carbon or carbon with iron oxide. The carbon had been
formed during the reduction of iron oxide with producer gas. About 90 percent
of the carbon was reacted. The residence time of the solids in these tests
was 124 minutes. Probably the purity of the hydrogen could be improved by
operating at a shorter solids residence time, as the reactions involving
carbon are slower than those of iron at 600° to 800° C. For producing hydro-
gen of high purity, low temperatures of 500° to 600° C. should be avoided in
the reduction, as the formation of carbidic and free carbon is favored in
this range. Iron carbide reacts readily even considerably below 600° C. to
form the carbon-containing gases.

TABLE 11. - Effect of temperature on purity of hydrogen produced in oxidation of reduced iron containing free carbon in a 16-foot bed

Experiment	Pressure, p.s.i.g.	Gas (H_2O) rate, cu.ft./hr.	Solids rate, lb./hr.	Reactive gas/solids ratio, cu.ft./lb.	Residence time	
					Solids, min.	Gas, sec.
23X-5..........	60	44	15	2.9	124	20
23X-6..........	90	48	15	3.2	124	19

Experiment	Temperature, °C.	Gas conversion, percent	Composition of tail gas, percent	Reduction of solids, percent			Free carbon content of solids, weight-percent		
				In	Out	Change	In	Out	Change
23X-5..........	600	53	H_2 - 97.3 CO - 0.9 CO_2 - 1.7 CH_4 - 0.1	39	15	24	1.7	1.6	0.1
23X-6..........	750	64	H_2 - 90.9 CO - 4.5 CO_2 - 4.1 CH_4 - 0.5	36	14	22	1.0	.1	.9

Carburization

To improve the economy of producing synthesis gas by the steam-iron process, it was believed necessary to introduce carbon into the solids during reduction. If the carbon reacted in the oxidation, less carbon dioxide would be required. According to the free energy change involved in the following reactions,

$$Fe_3C + 4H_2O \rightleftharpoons 3FeO + CO + 4H_2 \qquad \Delta F°_{973} = -8,000 \text{ cal./mole}$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad \Delta F°_{973} = -1,000 \text{ cal./mole}$$

the oxidation of iron carbide with steam proceeds more readily than the steam oxidation of carbon. Thus carburization of iron was considered a likely route for the carbon requirements according to the following reaction:

$$3Fe + 2CO \rightarrow Fe_3C + CO_2 .$$
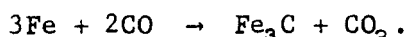
Tests were made at 15 p.s.i.g. pressure with producer gas containing 10 percent hydrogen and 39 percent carbon monoxide to determine the optimum temperature for producing carbidic carbon. Elemental carbon was produced simultaneously with the iron carbide and at a higher rate, as shown in figure 23. The formation of free carbon was maximum at about 500° C., whereas the formation of cementite reached a peak about 100° C. higher. After passing through
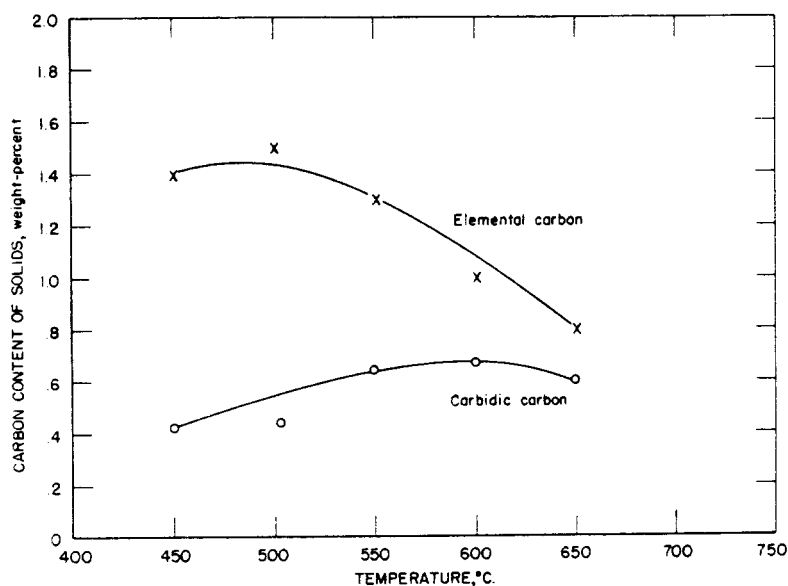
FIGURE 23. - Effect of Temperature on Carbon Formation at 15 p.s.i.g., 45-Inch Bed, and 46-Percent Reduction of Solids, Experiment 11R.

the maximum, the production of free carbon decreased rapidly with increasing temperature.

The maximum amount of iron carbide produced at 600° C. with an iron oxide reduced 46 percent was about 0.7 percent of the total weight of the solids. This percentage of iron carbide would permit only a slight decrease in the carbon dioxide requirement for producing synthesis gas of $1H_2+1CO$ composition. Some carbon dioxide requirement is obtained by reaction of free carbon with steam, especially at 750° C. and higher.

The steam oxidation tests discussed previously showed that most of the free carbon reacted at 750° C. and that an appreciable amount of carbon monoxide and carbon dioxide was formed. Possibly synthesis gas of suitable H_2-to-$CO+CO_2$ content can be produced without the need for providing carbon dioxide to the oxidizer.
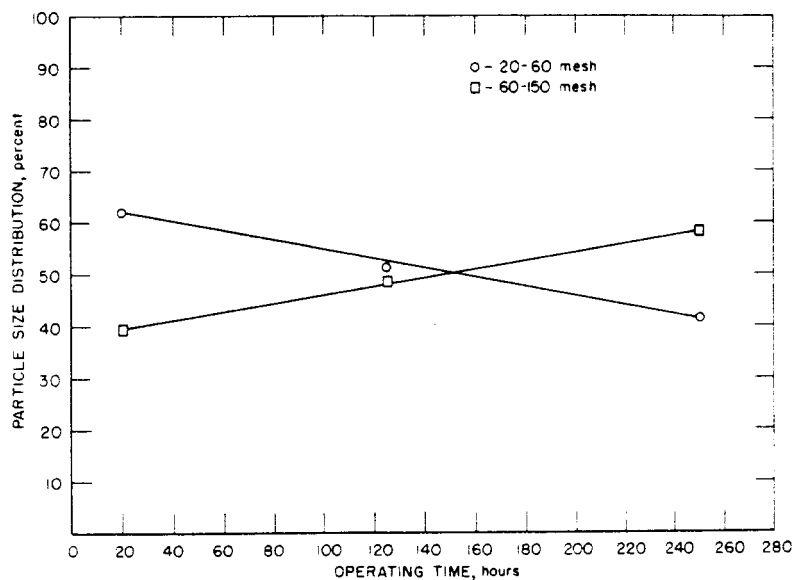
Attrition of Solids

A study of the particle size of the solids before and after operation indicated that attrition occurs in the fluidized-bed steam-iron reaction; however, owing to the noncontinuous type of operation characteristic of the pilot plant, handling losses preclude precise results. The decrease in the quantity of 20- to 60-mesh particles and the increase in the amount of smaller 60- to 150-mesh particles with time of operation, plotted in figure 24, show a qualitative trend of particle degradation. The solids were subjected to 250

FIGURE 24. - Solids Attrition as a Function of Hours of Operation.

hours of operation at average temperatures of 750° C. and average pressures of 100 p.s.i.g. During this time seven oxidations and eight reductions were performed alternately. In the absence of quantitative data, replacement of iron oxide can be estimated from pilot plant results given for removal of hydrogen sulfide from gases in a fluidized bed or iron oxide[22] at 350° to 400° C. This iron oxide alternately goes through the absorption step and air regeneration at 600° to 800° C. to oxidize iron sulfide to oxide. Losses computed on the basis of these published results would amount to about 1 pound of ore per 5,000 cubic feet of hydrogen produced for the steam-iron system.

Process Requirements

Based on a 70-percent conversion of the hydrogen and carbon monoxide contained in producer gas and considering that 40 percent of the producer gas is hydrogen and carbon monoxide, about 3,300 cubic feet of producer gas is required to produce 1,000 cubic feet of hydrogen or synthesis gas. This also assumes that during oxidation 60 percent of the steam and/or carbon dioxide is converted. About 530 pounds of 35-percent-reduced solids are required to produce 1,000 cubic feet of hydrogen or synthesis gas. (See appendix for calculations.)

Solids Free-Fall Experiments

Effect of Gas Velocity on Conversion

Results of free-fall experiments showing the effect of gas velocity upon the conversion of gas and solids at constant gas-to-solids ratio are given in table 12 and figures 25 and 26. The tests were made in reduction experiments 24R-8 and oxidation experiment 24X-8 at 15 p.s.i.g., 750° C., and a gas-to-solids ratio of 7.5 cubic feet per pound. Hydrogen was used for the reduction and steam for the oxidation to avoid carbon deposition, which complicates analysis of the data. The gas velocity was increased in increments of 1 foot per second from 1 to 4 feet per second in the reduction and from 1 to 3 feet per second in the oxidation. To maintain the constant gas-to-solids ratio, the solids flow was increased proportionally to the increased gas flow.

Despite the fourfold increase in throughput during reduction and three-fold increase during oxidation, the conversion of gas and solids remained constant, as shown in figures 25 and 26. Maintenance of the conversion at the higher flows in this countercurrent free-fall system probably results from the increased hold-up of the solids, and thus their residence time in the reactor, with increasing gas velocity. As the residence time of the solids is only a few seconds, a relatively small change is sufficient to affect the conversion.

Effect of Pressure on Conversion

Variation of the pressure from 25 to 285 p.s.i.g. was investigated in oxidation experiment 24X-9 and from 75 to 285 p.s.i.g. in reduction experiment

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[22]Reeve, L., Desulfurization of Coke-Oven Gas at Appleby-Frodingham: Jour. Inst. Fuel, July 1958, pp. 319-324.

24R-9 using a reactor temperature of 750° C. The gas and solids flows were constant with the gas-to-solids ratios of 7.5 and 2.5 cubic feet per pound in the oxidation and reduction, respectively. Results of these tests are given in table 13.

TABLE 12. - Effect of gas velocity on gas and solids conversion during reduction and oxidation at 750° C. and 15 p.s.i.g. in a solids free-fall system

Experiment	Gas flow, cu.ft./hr.		Solids rate, lb./hr.	Gas-to-solids ratio, cu.ft./lb.	Gas velocity, ft./sec.
	H_2	H_2O			
24X-8..........		30	4	7.5	1
		60	8	7.5	2
		90	12	7.5	3
		30	12	2.5	1
		90	4	22.5	3
24R-8..........	30		4	7.5	1
	60		8	7.5	2
	90		12	7.5	3
	120		16	7.5	4
	150		4	38	5
	75		30	2.5	2.5
	30		30	1.0	1.0

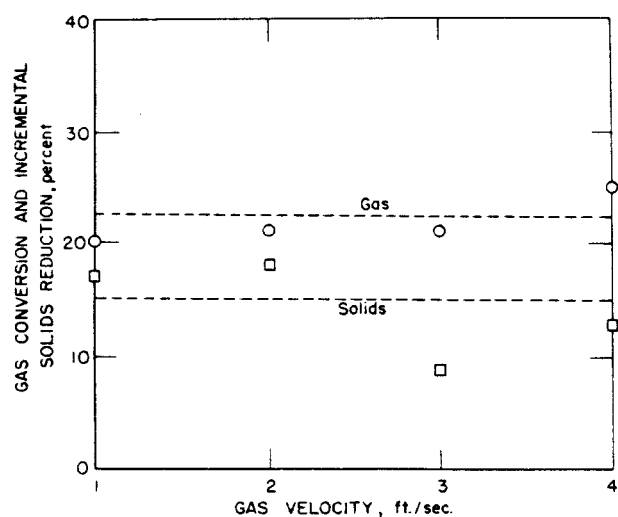| Experiment	Gas conversion percent	Reduction of solids, percent			Free carbon content of solids, weight-percent		
		In	Out	Change	In	Out	Change
24X-8..........	20	37	21	16	0.2	0.1	0.1
	19	37	22	15	.2	.1	.1
	21	37	20	17	.2	.1	.1
	44	37	25	12	.2	.1	.1
	6	37	20	17	.2	.1	.1
24R-8..........	20	2	19	17	.1	.1	0
	21	2	20	18	.1	.1	0
	21	2	11	9	.1	.1	0
	25	2	15	13	.1	.1	0
	3	2	55	42	.1	.1	0
	17	2	14	12	.1	.1	0
	23	2	7	5	.1	.1	0

FIGURE 25. - Effect of Gas Velocity on Conversion During Reduction at 750°C., Free-Fall, 15 p.s.i.g., and Gas-to-Solids Ratio of 7.5.
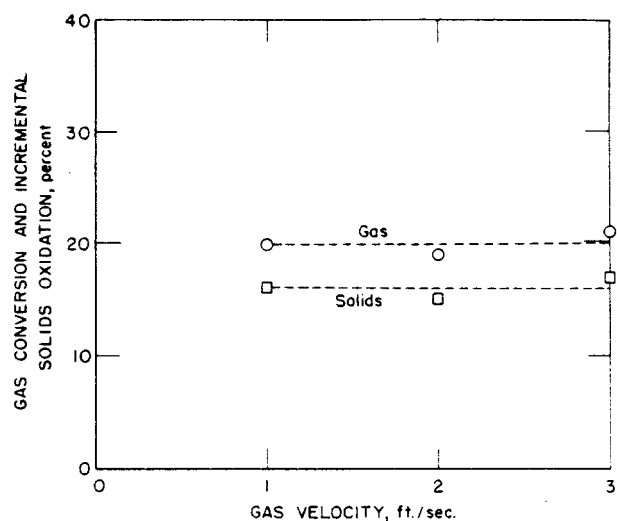
FIGURE 26. - Effect of Gas Velocity on Conversion During Oxidation at 750°C., Free-Fall, 15 p.s.i.g., and Gas-to-Solids Ratio of 7.5.

TABLE 13. - Effect of pressure on gas and solids conversion during oxidation and reduction at 750° C. and in a solids free-fall system

Experiment	Gas rate, cu.ft./hr.		Solids rate, lb./hr.	Reactive gas-to-solids ratio, cu.ft./lb.	Pressure, p.s.i.g.
	H_2 +CO/ N_2 +CO_2	$H_2$0			
24X-9..........		120	16	7.5	25
					75
					165
					285
24R-9..........	[1]16/24		6.4	2.5	75
					165
					285

Experiment	Gas conversion, percent	Reduction of solids, percent			Free carbon content of solids, weight-percent		
		In	Out	Change	In	Out	Change
24X-9..........	45	73	19	54	0.1	0.1	0
	42	73	24	49	.1	.1	0
	49	73	30	43	.1	.1	0
	45	73	19	54	.1	.1	0
24R-9..........	30	3	10	7	.1	.3	.2
	42	3	9	6	.1	.6	.5
	48	3	9	6	.1	2.1	2.0

[1]H_2 20, CO 20, CO_2 7, and N_2 53 volume-percent.