

FIGURE 27. - Effect of Pressure on Conversion During Oxidation at 750° C., Free-Fall, Constant Gas-to-Solids Feed, and Ratio of 7.5.

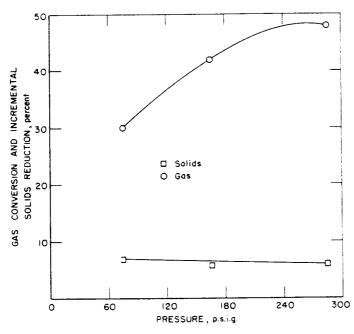


FIGURE 28. - Effect of Pressure on Conversion During Reduction at 750° C., Free-Fall, Constant Gas-Solids Feed, and Ratio of 2.5.

Highly reduced solids, 73percent reduced, were reacted in the oxidizer with steam. ally constant gas conversions, averaging about 45 percent, and solids conversions, averaging about 50 percent, were obtained in the oxidation throughout the range of pressures tested, as shown in figure 27. A constant incremental reduction of the solids of about 6 to 7 percent was obtained in experiment 24R-9 at pressures of 75, 165, and 285 pounds per square inch gage with simulated producer gas. However, increased conversion of the gas from 30 to 48 percent was obtained with the increased pressure. gas and solids conversions during reduction are plotted in figure The additional conversion occurred because high pressures favor the formation of elemental carbon and methane by the following reactions:

$$2CO \rightarrow C + CO_{2}$$

$$CO + 3H_{2} \rightarrow CH_{4} + H_{2}O.$$

Generally no change in reduction or oxidation of the solids was observed on changing the pressure at constant throughputs. Possibly an interaction existed because of change in gas velocity that occurred with the changing pressure in these tests. Additional tests would be required at different pressures and constant gas velocity and gas-to-solids ratio to eliminate this variable.

Results obtained from the pressure-effect studies in a solids free-fall system indicate differences from those obtained in the fluidized-bed tests. However, these differences can be attributed to the operational

variables. The results were obtained at the following tabulated operational conditions:

	Solids free-fall	Fluidized-bed	
Solids residence time	About 5 sec.	About 1 to 3 hrs.	
Gas velocity	Varying	Constant	
Throughputs	Constant	Varying	

Effect of Gas-to-Solids Ratio on Conversion

The gas-to-solids ratio was varied from 2.5 to 22.5 during oxidation experiment 24X-8 and from 1 to 38 during reduction experiment 24R-8 to determine how the gas and solids conversions were affected. Because the gas velocity is not limited in solids free-fall operation as it is in a fluidized bed system, the gas-to-solids ratios could be varied by changing either the gas or solids flow. Results from these tests are shown in table 14 and are summarized as follows:

Oxidation

- 1. An increase of gas flows from 30 to 90 std.c.f.-per hour at a constant solids rate of 4 pounds per hour resulted in a decrease of gas conversion of from 20 to 6 percent; at a solids rate of 12 pounds per hour the gas conversion decreased from 44 to 21 percent. Incremental solids conversion increased from 16 to 17 percent and from 12 to 17 percent, indicating a leveling-off of the solids conversion at 17 percent.
- 2. Conversely the decrease in solids flow at the constant gas rate resulted in a decrease of gas conversion from 44 to 20 and 21 to 6 percent, respectively, with an increase of 12 to 16 percent and then a leveling-off of the incremental solids conversion at 17 percent.
- 3. Changing the gas rate from 30 to 90 std.c.f. per hour and the solids rate from 12 to 4 pounds per hour decreased the gas conversion from 44 to 6 percent and increased solids conversion from 12 to 17 percent.

Reduction

The results obtained during reduction with hydrogen were essentially the same as obtained from the oxidation with steam, except that the maximum gas conversion obtained was 23 percent and that the incremental solids conversion increased from 5 to 42 percent with no apparent leveling-off. The conversions were obtained with a gas-to-solid ratio variation from 1 to 38.

The leveling-off effect of the solids conversion during oxidation can possibly be attributed to the following factors: Owing to the equilibrium limitations, oxidation is performed on solids that are approximately 65-percent oxidized. This means that theoretically the solids can be oxidized 35 incremental-percent. On the other hand, reduction is performed on solids that are about 5-percent reduced. This means that theoretically the solids can be reduced 95 incremental-percent. The closer the solids approach being completely oxidized or completely reduced, the greater is the difficulty of continuing reaction.

Probably once the surface of the solid particle is converted, a barrier is formed retarding conversion of the remaining solids. Further conversion proceeds at a comparatively slow rate by way of diffusion or migration.

TABLE 14. - Effect of gas-to-solids ratio on gas and solids conversion during oxidation and reduction at 750° C., 15 p.s.i.g., and a solids free-fall system

		Flows	S	Gas-to-	Conv	ersion,	F1c	x wo
		Gas,	Solids,	solids	рe	ercent	conve	ersion
Experiment	Condition	cu.ft./hr.	lb./hr.	ratios		Solids ¹		Solids
24 X- 8	Constant solids	30	4	7.5	20	16	6.0	0.64
	rates	90	4	22.5	6	17	5.4	1
		30	12	2.5	44	12	13.2	1.44
	:	90	12	7.5	21	17	18.9	2.04
	Constant gas	30	12	2.5	44	12	13.2	1.44
	rates	30	4	7.5	20	16	6.0	.64
		90	12	7.5	21	17	18.9	.04
		90	4	22.5	6	17	5.4	.68
	Varied gas and	30	12	2.5	44	12	13.2	1.44
	solids rates	60	8	7.5	19	15	11.4	1.20
		90	4	22.5	6	17	5.4	.68
24R-8	Constant solids	30	4	7.5	20	17	6.0	.68
	rates	150	4	38.0	3	42	4.5	1
		30	30	1.0	23	5	6.9	1.50
		75	30	2.5	17	12	12.7	3.6
	Constant gas	30	30	1	23	5	6.9	1.50
	rates	30	4	7.5	20	17	6.0	.68
	Varied gas and	30	30	1	23	5	6.9	1.50
	solids rates	60	8	7.5	21	18	12.6	1.44
		150	44	38	3	42	4.5	1.68

¹ Percent reduction of solids before and after tests given in table 12.

The solids rate was varied from 15 to 150 pounds per hour during oxidation experiment 24X-2 and from 6 to 60 pounds per hour during reduction experiment 25R-2, while the gas rate was held constant to determine how the gas and solids conversions were affected at the relatively high gas and solids throughputs. Natural magnetite was used for this set of tests as compared to synthetic magnetite for the previous tests. The solids for oxidation experiment 25X-2 were reduced to 63 percent to determine what effect highly reduced solids had on conversion during the solids free-fall test. Steam-to-hydrogen conversion of 9 to 38 percent was obtained with a consistent incremental solids conversion of 38 percent during variation of the gas-to-solids ratio variations of from 28.5 to 2.9, as shown in table 15. The gas rate was 428 std.c.f. per hour or equivalent to a gas velocity of 3 feet per second at the operating conditions. Irrespective of the tenfold change in gas-to-solids ratio, the

solids residence time apparently is the limiting factor in solids conversion of a highly reduced solid.

TABLE 15. - Effect of gas-to-solids ratio on gas and solids conversion during oxidation and reduction at 3 feet per second gas velocity, 135 p.s.i.g., and solids free-fall system

		Gas rate, cu.ft./hr. H ₂ +CO/ N ₂ +CO ₂ +H ₂ O H ₂ O				lids		active
Experiment	Temperature, ° C.			rate, lb./hr.		gas-to-soli ratio		
25X-2	800		-	428		15 30 90 150		28.5 14.3 4.8 2.9
25R-2	780	1172/268 -		1172/268 -		6 12 18 36 60		28.7 14.3 9.6 4.8 2.9
	Gas	Red	uction	of				
	conversion,		ids, pe					onversion
	percent	In	Out	Chang	e		Gas	Solids
25X-2	9	63	25	. 38			38.5	5.7
	21	63	25	38		•	39.9	11.4
	23	63	25	38		1	98.4	34.2
	38	63	25	38		16	62.6	57.0
25 R-2	² 11	6	12	6			8.9	.4
	14	6	12	6		2	24.1	.7
	14	6	15	9		1	24.1	1.6
	13	6	14	8		ì	22.4	3.6
	13	6	12	6		2	22.4	3.6

H₂ 19.5, CO 19.5, N₂ 52, CO₂ 6.0, and H₂O 3.0 volume percent.

²Hydrogen conversion.

Reduction experiment 25R-2, performed with a constant simulated producer-gas rate of 440 std.c.f. per hour and a varying gas-to-solid ratio varying from 73.3 to 7.3, produced an average hydrogen conversion of 13 percent accompanied by an average incremental solids conversion of 7 percent. No reaction of the carbon monoxide with the iron oxide was indicated. Because of the short residence time of the solids in the reactor, the time of contact may be insufficient for the carbon monoxide to react. Other investigators²³ have shown that the reduction of iron oxide proceeds at least twice as fast with hydrogen as with carbon monoxide. If the carbon monoxide cannot be consumed in a solids free-fall system owing to the limited residence time, then this system would not be applicable for reduction.

²³Williams, J. and Quade, G., Use of Fluid-Bed Process with Gases Containing Hydrogen and Carbon Monoxide for the Reduction of Iron Ores: Stahl u. Eisen, vol. 79, No. 15, 1959, pp. 1058-1064.

The relatively small hydrogen conversion with the small solids conversions can also be attributed to the limited solids residence time and, possibly, to a relatively small amount of hydrogen, about 20 percent, in the total gas volume.

CONCLUSIONS

The pilot plant studies have demonstrated the operability of the reduction and oxidation steps for producing hydrogen or synthesis gas by a continuous steam-iron system. As carbon dioxide reacts in the oxidation step at about the same degree as steam, carbon monoxide can also be produced.

Although the production of synthesis gas is technically feasible, it is less attractive economically than the production of hydrogen because of the need for supplying carbon dioxide. The economics of producing synthesis gas with the steam-iron process could be improved if the carbon dioxide requirements could be decreased. To achieve this a method must be devised for increasing the amount of reaction of steam with the iron carbide or free carbon that is produced in the reduction step.

A few process limitations were indicated from the pilot plant experiments. Beyond 800° C. there is increasing tendency of the particles to agglomerate with resulting difficulty in maintaining fluidization. This difficulty probably does not occur with free-falling solids flow, as the particles are present in a dilute phase and their residence time in the reactor is only a few seconds.

Carbon formation during the reduction can become excessive, especially during operation at elevated pressure. However, if the system temperature is maintained at 700° C. or higher, carbon laydown is minimized.

The investigations of the effect of height of the fluidized bed and gasto-solids ratio in both the fluidized and free-fall systems indicate that the solids become more difficult to reduce beyond about 30-percent reduction. At this stage, FeO is being reduced to iron, and undoubtedly this is more difficult than the reduction of $\operatorname{Fe_3O_4}$ to FeO. In the fluidized operation, back mixing of the solids prevented the desired countercurrent gas-to-solids flow that would provide contact between fresh reducing gas and FeO at the bottom of the reactor rather than with a mixture of $\operatorname{Fe_3O_4}$ and FeO. The factor limiting the conversion in the free-fall system is the short residence time of the solids of only a few seconds. Use of a taller reactor and an improved baffle arrangement might provide enough time for the desired solids conversion. If the free-fall system is feasible, considerably higher throughputs of solids and gas can be obtained than with a fluidized reactor.

About 25 incremental-percent solids conversion was achieved in the reduction and oxidation steps with fluidized operation at gas conversions close to equilibrium. To achieve the 30 incremental-percent solids conversions originally established as a goal, either a longer residence time for reduction might be provided than the 2 hours usually employed in our tests, or a staged-type of reduction made, whereby mixing of the oxidized and partially reduced solids would be avoided.

Based on the variable studies, the optimum conditions for producing hydrogen in a fluidized system are as follows:

Reduction:

Temperature - 750° to 800° C.

Pressure - Atmospheric or elevated

Space velocity of producer gas - 300 V/V-hr. (based on operation at 7 atmospheres)

Solids residence time - 2 to 3 hours

Incremental solids reduction - 25 to 30 percent

Conversion of H₂+CO in producer gas - 65 percent

Oxidation:

Temperature - 600 to 800° C.

Pressure - Up to 30 atmospheres

Space velocity of steam - 350 V/V-hr. (based on operation at 7 atmospheres)

Solids residence time - 30 minutes Incremental solids oxidation - 25 to 30 percent Conversion of steam - 50 to 60 percent

Purity of hydrogen - 91 to 98 percent without CO₂ removal or 95 to 99+ percent with CO₂ removal

The operating conditions for producing synthesis gas are similar, except that carbon dioxide plus steam is used for oxidation. The consumption of carbon dioxide is less than the amount of carbon monoxide produced because of reactions of steam with iron carbide and carbon formed in the reduction. Operation near the upper temperature range, 750° to 800° C., is preferred for the oxidation to produce synthesis gas.

Diagrams showing production of hydrogen from coal by the steam-iron process and conventional steam-oxygen gasification of coal are given in figures 29 and 30. The conventional process requires at least one and probably two stages of carbon monoxide conversion and carbon dioxide removal; these steps are eliminated in the steam-iron process. Both processes require removal of sulfur compounds. As shown in figure 30, the energy in the spent gas from the reduction unit is used for compression of air supplied to the gas producer. From a process standpoint, the steam-iron system utilizing the fluidized bed or solids free-fall technique is simpler than the conventional method, and should merit serious consideration when the use of coal for hydrogen production becomes economically feasible.

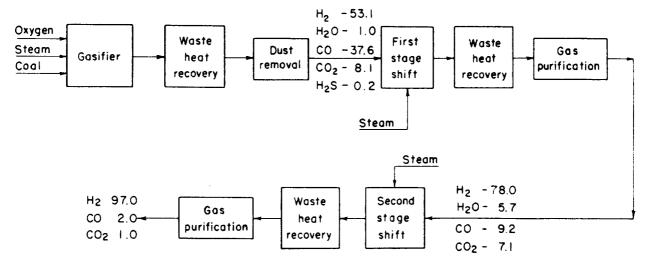


FIGURE 29. - Process Flowsheet: Hydrogen Production via Oxygen Coal Gasifier.

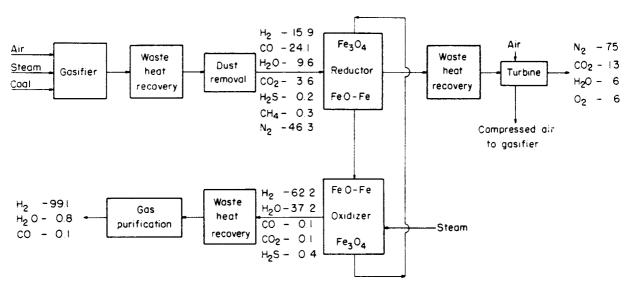


FIGURE 30. - Process Flowsheet: Hydrogen Production via Steam-Iron Process.

APPENDIX

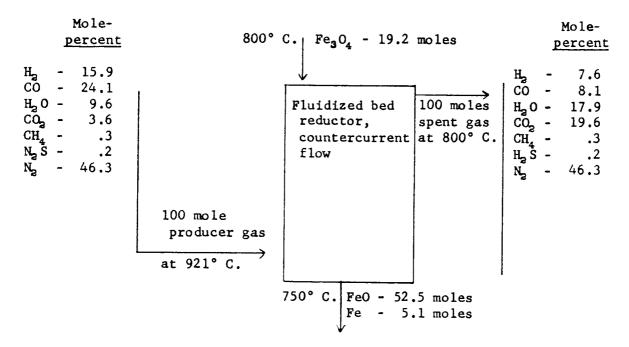
Calculations for the Theoretical Heat Requirement

Heat Balance Calculation for a Theoretical Reductor

Temperature of producer gas feed

Assumed conditions:

- 1. Temperature Fe_3O_4 in = 800° C.
- 2. Temperature of FeO + Fe = 750° C.
- 3. Temperature of the spent producer gas approaches the temperature of the incoming solids = 800° C.
- 4. Operation is adiabatic; heat losses are negligible.
- 5. The producer gas is obtained from a highly efficient gas producer.
- 6. Equilibrium ratios of $\rm H_2\,O/H_2$ and $\rm CO_2\,/CO$ are attained over Fe₃O₄-FeO phase.
- 7. No carbon deposition.
- 8. Gas flow upward countercurrent to downward moving bed of fluidized solids.



Determination of producer gas temperature required

Heat of reaction is calculated as follows:

	Gram-moles	Standard heat of formation ²⁴		
	(net)	cal./mole	Cal.	Cal.
	· · · · · · · · · · · · · · · · · · ·	Reactants		
Fe ₃ 0 ₄	19.2	267,800	5,141,700	-
CO	16.0	26,420	422,700	-
Total	-	-	-	5,564,400
		Products		
Fe0	52.5	63,800	3,349,500	
H ₂ 0	8.3	57,800	479,700	
CÕ ₂	16.0	94,050	1,504,800	
Z				5,334,000
Standard heat of	230,400			

Sensible heat OUT:

	Gram-mole	Cal./mole ²⁵	Cal.
Fe0	52.5	9,750	511,880
Fe	5.1	6,250	31,880
Н ₂	7.6	5,550	42,180
CÕ	8.1	5,800	46,980
Н ₂ О	17.9	6,980	124,940
CÕ ₂	19.6	8,970	175,810
CH ₄	.3	11,000	3,300
H ₂ Š	} 46.5	5,730	266,450
Total	-	-	1,203,420

(Sensible heat IN) \pm (Heat of reaction) = (Sensible heat OUT + (Heat loss)²⁶ For exothermic reaction, the heat of reaction is positive.

For endothermic reaction, the heat of reaction is negative.

Sensible heat required IN

	cal.
Total sensible heat OUT	1,203,420
Heat of reaction	230,400
Total	1,433,820

²⁴Coughlin, James P., Contributions to the Data on Theoretical Metallurgy: Bureau of Mines Bull. 542, 1954, 80 pp.

²⁶Assumed negligible.

²⁵Kelley, K. K., Contributions to the Data on Theoretical Metallurgy: Bureau of Mines Bull. 584, 1960, 232 pp.

Calculation for required temperature of IN gas

	cal.
Total heat out	1,433,820
Sensible heat in Fe_3O_4 - 19.2 gram moles x 38,400 cals.	737,280
Sensible heat required in gas	696,540

Heat content of producer gas feed at 900° and 1,000° C.

	Gas feed at 900° C.			Gas feed at 1,000° C.		
	Gram-					
	moles	Cal./mole	Cals.	Moles	Cal./mole	Cals.
H ₂	15.9	6,230	99,060	15.9	6,950	110,510
CÕ	24.1	6,600	159,060	24.1	7,400	178,340
Н ₂ 0	9.6	8,000	76,800	9.6	9,010	86,500
co ₂	3.6	10,280	37,010	3.6	11,620	41,830
CH4	.3	12,000	3,600	.3	14,180	4,250
H ₂ Š	} 46.5	6,540	304,110	46.5	7,310	339,920
Total		-	679,640	!	-	761,350

Required temperature = $900 + x^{\circ} C$.

$$\mathbf{x}^{\circ} = (1,000-900) \quad \frac{696,540-679,640}{761,350-679,640}$$

$$= (100) \quad \frac{16,900}{81,710}$$

$$\mathbf{T} = 900 + 21 = 921^{\circ} \text{ C.}$$

Check of gas temperature IN

Sensible heat of gas in

	gram-mole	cal./mole	Cal.	
H ₂	15.9	6,470	102,900	T -
CO	24.1	6,880	165,800	-
H ₂ 0	9.6	8,300	79,710	-
co ₂	3.6	10,630	38,300	_
CH ₄	.3	12,770	3,830	-
H ₂ Š	} 46.5	6,580	306,000	
Total			696,540	696,540

Sensible heat of Fe_3O_4 IN

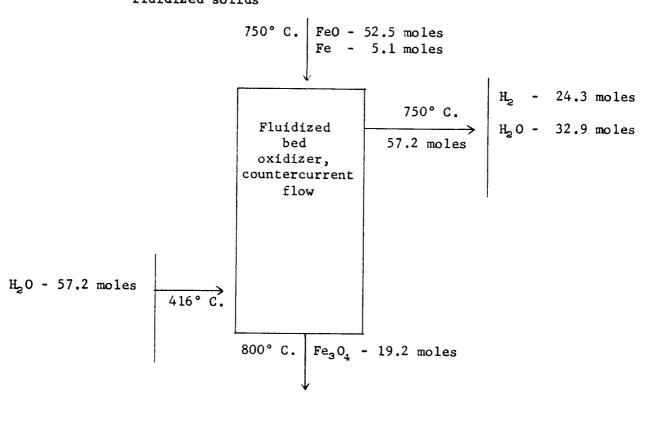
	gram-mole	cal./mole	Cal.	
Fe ₃ 0 ₄	19.2	38,400	737,280	737,280
Total sensible heat	IN	• • • • • • • • • • • • • •	• • • • • • • • • •	1,433,820
Total sensible heat	OUT plus rea	ction heat	• • • • • • • • •	1,433,820

Heat Balance Calculation for a Theoretical Oxidizer

Temperature of steam feed

Assumed conditions:

- 1. Temperature of FeO + Fe = 750° C.
- 2. Temperature of $Fe_3O_4 = 800^{\circ} C$.
- 3. Temperature of the spent steam approaches the temperature of the incoming solids = 750° C.
- 4. Operation is adiabatic; heat losses are negligible
- 5. Equilibrium ratios of $\rm H_2/H_2O$ are attained over the Fe-FeO phase
- Gas flow upward countercurrent to downward moving bed of fluidized solids



Heat of reaction is calculated as follows:

	gram-moles	Standard heat of formation, cal./mole	cal.
	Reactan	ts	
H ₂ OFeO	24.3 52.5	57,798 64,620	1,404,490 3,392,550
Total	-	-	4,797,040
	Product	s	
Fe ₃ 0 ₄	19.2	267,800	5,141,700
Standard heat of rea	ction (endothe	rmic)	344,660

Sensible heat OUT:

	gram-mole	cal./mole	cal.
Fe ₃ 0 ₄	19.2	38,400	737,280
H ₂		5,160	125,390
H ₂ 0		6,500	213,850
Total		-	1,076,520

Calculation for required temperature of steam IN

Sensible heat in solids in:

	gram-moles	cal./mole	cal.
Fe0	52.5	9,750	511,880
Fe	5.1	6,250	31,880
Total	-	-	543,760

188,100/57.2 = 3,288 cal./gram-mole.

From steam tables, 27 this is equivalent to a steam temperature of 416° C.

²⁷Work cited in footnote 25.

Calculations for the Determination of the Percent Reduction of the Solids and the Free Carbon Content of the Solids

Sample calculations for the determination of the degree of reduction of the solids and the free carbon content of the solids.

Basis:

$$3Fe + 4H20 \Longrightarrow Fe3O4 + 4H2$$

$$3FeO + H2O \Longrightarrow Fe3O4 + H2$$

$$C + 2H2O \Longrightarrow CO2 + 2H2$$

Sample calculation:

- 3.00 gram sample of the reduced solids are oxidized with steam at at 900° C. (complete oxidation).
- 1,495 cc. of gas is evolved, collected and measured at 30° C. and 730 mm. of mercury.

The gas collected includes helium to purge the system.

Orsat analysis:

Components	Volume-percent	Carbon-containing gases, volume-percent
CO ₂	9.5	9.5
0,	.4	-
H_2	37.1	-
co,	2.6	2.6
He	50.4	-
Total	100.0	12.1

Determination of carbon in sample:

$$(1,495)$$
 $\left(\frac{273}{303}\right)\left(\frac{730}{760}\right)$ (0.121) = 156 cc.

$$\frac{(156 \text{ cc.})(12.0 \text{ g. carbon/g.-mol.})}{(22,400 \text{ cc./g.-mol.})(3.00 \text{ g. sample})} \times 100 = 2.8 \text{ percent carbon}$$

Hydrogen evolved due to oxidation of carbon to CO and CO2:

$$2(9.5) + 2.6 = 21.6$$
 percent

Hydrogen evolved due to oxidation of iron:

$$37.1 - 21.6 = 15.5 percent$$

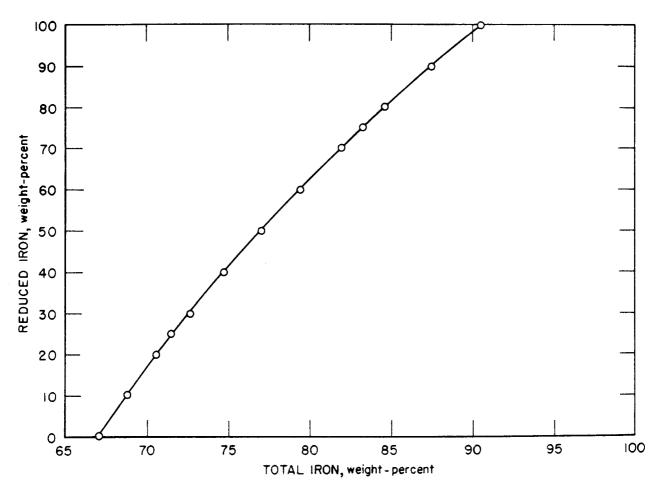


FIGURE 31. - Percent Reduction as a Function of Total Iron in Natural Magnetite.

Determination of reduced iron in the sample:

1,495 cc.
$$\left(\frac{273}{303}\right)\left(\frac{730}{760}\right)$$
 (0.155) = 200 cc.

Four moles H₂ reduces 1 mole Fe₃O₄ (3 moles Fe).

$$3/4 \times 55.85$$
 g. (mol. wt. of Fe) = 41.9 g. Fe per mole H₂

$$\frac{(200 \text{ cc.}) (41.9 \text{ g./g.-mole})}{(22,400 \text{ cc./g.-mole})} = 0.375 \text{ g. reduced iron.}$$

Figure 31, plotted from actual determinations of total and reduced iron, illustrates the percentage of reduced iron as a function of total iron for a natural iron ore. The percent reduction of the iron can be determined from the weight of reduced iron as calculated above by the following equation and use of figure 31, in which in both instances the same estimated fractional weight of iron is used,

$$\frac{A}{B \times C} \times 100 = D,$$

where A = weight of reduced iron in grams, determined as shown above,

B = weight of sample minus weight of carbon, grams determined as shown above,

C = total iron, fractional weight estimated by trial and error,

D = percent reduction of solids.

When the estimated percent of total iron in the sample gives the same percent reduction of the iron by use of the equation as by use of figure 31, this percentage is considered as the percent reduction of the solids.

Calculations for the Determination of Stoichiometric Gas and Solids Flow for Reduction and Oxidation

Sample calculations for the determination of stoichiometric solids and gas flow for 30-percent reduction:

Basis:

1.
$$1/3 \text{ Fe}_3 O_4 + 4/3 \text{ H}_2 = \text{Fe} + 4/3 \text{ H}_2 O$$
 or
 $1/3 \text{ Fe}_3 O_4 + 4/3 \text{ CO} = \text{Fe} + 4/3 \text{ CO}_2$

$$\frac{1 \text{ lb.}}{55.85 \text{ lb.}} \frac{4 \text{ lbs. mole}}{3} \frac{359 \text{ cu.ft}}{\text{lb. mole}} = 8.56 \text{ std. c.f.}^{28} \text{ of H}_2 \text{ or CO}$$
to produce 1 lb. of iron from Fe₃O₄.

- 2. Producer gas contains 40 percent $H_2 + C0$.
- 3. Fluidization velocity set at 0.6 ft./sec. or 128 std. c.f. per hour at 750° C. and 195 p.s.i.g. in a reactor with a cross-section area of 0.01556 sq. ft.
 - 4. Assume 95 percent oxidized solids that contain 67 percent iron.
 - 5. Assume 70 percent conversion of H2+C0 in producer gas.
 - 6. Assume 30 incremental percent solids reduction.
- A. 8.56 cu. ft. of H₂+CO to produce 1 lb. of iron from Fe₃O₄ (100 percent removal of oxygen) or
 - 2.57 cu. ft. of H₂+CO for a 30-percent removal or
 - 1.72 cu. ft. of H2+CO for 1 lb. of solids containing 67 percent iron.
- B. $\frac{128 \text{ cu. ft.}}{\text{hr.}}$ producer gas x 0.4 (40 percent H₂+CO) = 51.2 cu.ft./hr. H₂+CO,

²⁸ At 0° C. and 760 mm. of mercury.

51.2 cu.ft · x 0.7 (70-percent conversion) = 35.8 cu.ft./hr. H₂+CO converted, hr.

$$\frac{35.8 \text{ cu.ft.}}{1.72 \text{ cu.ft.-hr./1b}} = 20.8 \text{ lb./hr. solids}$$

will be reduced 30 incremental-percent by 128 cu.ft./hr. of producer gas. This is considered the stoichiometric gas-solids flow.

$$\frac{51.2 \text{ cu.ft. reactive gas } (\text{H}_2+\text{CO})}{20.8 \text{ lb. solids}}$$

or about 2.5 cu.ft. reactive gas/lb. solids is the stoichiometric ratio for 30 incremental-percent reduction that would make the solids going to the oxidizer 35 percent reduced.

Sample calculations for the determination of stoichiometric solids and gas flow for oxidation:

Basis:

1. Fe + 4/3
$$H_2O = 1/3$$
 $Fe_3O_4 + 4/3$ H_2 or

Fe + 4/3 $CO_2 = 1/3$ $Fe_3O_4 + 4/3$ CO

$$\frac{1 \text{ lb.}}{55.85} \times \frac{4 \text{ lb. mole}}{3} \times \frac{359 \text{ cu.ft}}{1 \text{ b. mole}} = 8.56 \text{ std. c.f.}^{29} \text{ of } H_2O \text{ or } CO_2 \text{ to oxidize 1 lb. of iron to } Fe_3O_4.$$

- 2. Fluidization velocity set at 0.6 ft./sec. or 128 std. c.f. per hour at 750° C. and 195 p.s.i.g. in a reactor with a cross-section area of 0.01556 sq. ft.
 - 3. The 35-percent reduced solids contain 74 percent iron.
 - 4. Assume 60-percent conversion of H₂O/CO₂.
 - 5. Assume 30 incremental-percent change of solids.
- A. 8.56 cu.ft. of H2O/CO2 to oxidize 1 lb. of iron 100 percent.
 - 2.57 cu.ft. for a 30 percent change.
 - 1.90 cu. ft. of H₂O/CO₂ for 1 lb. of solids containing 74 percent iron.

128 cu.ft./hr. x 0.6 (60 percent conversion) = 77 cu.ft./hr. converted.

$$\frac{77 \text{ cu.ft.}}{1.90 \text{ cu.ft.-hr./lb.}} = 40.5 \text{ lb./hr. of solids,}$$

will be oxidized 30 incremental-percent by 128 cu.ft./hr. of H2O/CO2.

²⁹ At 0° C. and 760 mm. of mercury.

This is considered the stoichiometric gas-solids flow. This means

 $\frac{128 \text{ cu.ft.}}{40.5 \text{ lb.}} = \frac{3.2 \text{ cu.ft.}}{1 \text{ lb.}}$ is the stoichiometric ratio for 30 incremental-

percent oxidation.

Calculations for Process Requirements

Results from the above calculations indicate that for reduction a reactive gas ($\rm H_2+C0$) to solids ratio of 2.5 std. c.f./lb. of solids, or for a producer-gas containing 40 percent reactive gas, a ratio of 6.3 std. c.f./lb. of solids was required. Also, for oxidation a ratio of reactive gas ($\rm H_2\,O+CO_2$) to solids ratio of 3.2 std. c.f./lb. of solids was required. Assume that 60 percent of the gases were converted. Therefore, 1.92 std. c.f. of $\rm H_2+CO/lb$. solids is produced from 6.3 std. c.f. of producer gas, or 6.3/1.9 = 3.3 std. c.f. of producer gas required to produce 1 std. c.f. $\rm H_2+CO$ or 3,300 per 1,000 std. c.f. $\rm H_2+CO$.

Solids usage:

As shown in calculating the produced gas requirement, 1.9 std. c.f. of $\rm H_2$ +CO is produced from 1 lb. of the reduced solids; therefore 1,000 cu.ft. of $\rm H_2$ +CO can be produced from 530 pounds of solids.