BM-RI--591

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report of investigations 5911

PRODUCTION OF SYNTHESIS GAS AND HYDROGEN BY THE STEAM-IRON PROCESS:

Pilot Plant Study of Fluidized and Free-Falling Beds

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UNITED STATES DEPARTMENT OF THE INTERIOR

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MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Gasior, Stanley J

Production of synthesis gas and hydrogen by the steam-iron process: pilot plant study of fluidized and free-falling beds, by S. J. Gasior [and others. Washington] U. S. Dept. of the Interior, Bureau of Mines [1961]

iv, 49 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report of investigations, 5911)

Bibliographical footnotes.

1. Synthesis gas. 2. Hydrogen. I. Title: Steam-iron process. II. Title: Fluidized and free-falling beds. (Series)

TN23.U7 no. 5911 622.06173

U. S. Dept. of the Int. Library

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PRODUCTION OF SYNTHESIS GAS AND HYDROGEN BY THE STEAM-IRON PROCESS:

Pilot Plant Study of Fluidized and Free-Falling Beds[1]

by

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Daniel Bienstock,[2] and H. E. Benson[4]

SUMMARY

Pilot plant studies showed the technical feasibility of fluidized-bed operation for producing hydrogen and synthesis gas by the steam-iron process. A mixture of iron and iron oxide from 20- to 100-mesh was partially reduced with a simulated producer gas and then oxidized with steam and/or carbon dioxide.

Results of tests show the effects of pressure, temperature, bed height, gas-to-solids ratio, type of iron oxide, and composition of gas on the gas and solids conversions during reduction and oxidation.

A baffled free-fall solids system was also found operable. The short residence time of about 5 seconds limited conversion of the solids.

INTRODUCTION

Hydrogen has been produced commercially on a small scale for many years by the Messerschmitt[5] and Lane[6] processes. In both processes, a fixed bed of granular iron oxide is treated with a reducing gas such as producer gas and is then oxidized with steam to produce hydrogen. Because of the inefficiency of the cyclic operation and the low reaction rate resulting from the necessary use of large granules of iron oxide in the fixed bed, the cost of producing hydrogen by this method is relatively high. Use of fluidized beds for the

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[5] Messerschmitt, A., Process of Producing Hydrogen: U.S. Patent 971,206, Sept. 27, 1910.

[6] Lane, H., Process for the Production of Hydrogen: U.S. Patent 1,078,686, Nov. 18, 1913.

steam-iron process has been proposed by many investigators[7-10] to improve the gas-solids contact and to provide for continuous operation by movement of the solids between the oxidation and reduction zones. Because small particles with high specific surface areas are used in fluidized operation, a faster reaction rate was anticipated than that for fixed-bed operations.

The Bureau of Mines constructed a pilot plant to study the continuous steam-iron process as a possible means of producing synthesis gas or hydrogen more economically than by oxygen-steam coal-gasification processes. As production of synthesis gas containing carbon monoxide and hydrogen is of interest to the Bureau, several experiments were made with carbon dioxide and steam to oxidize the reduced iron and thus produce synthesis gas rather than hydrogen. The supposed advantage of producing hydrogen and synthesis gas by this method lies in the elimination of investment and operating cost of the oxygen plant required for modern gasification processes.

Both fluidized and free-falling solids systems have been investigated. In free-fall, the solids are dropped through the reaction zone countercurrent to the rising gas. The solids are impeded only by a spiral rod arrangement in the reactor, which serves to disperse the solids and thus minimize gas or solids channeling.

Operation of the steam-iron system using either the fluidized bed or free-fall of solids involves a continuous flow of an iron and iron oxide mixture through a reduction unit where it is partially reduced with producer gas. The flow of solids continues through an oxidizer where the solids are oxidized with steam or steam and carbon dioxide to produce hydrogen or synthesis gas. The iron and iron oxide mixture is then returned to the reduction unit to repeat the process. To approach countercurrent operation the solids are fed at the top of the reaction zone and the gas at the bottom. The object of the experimental program was to determine the operability of the process and the maximum gas utilization and solids conversion obtainable in each step. From equilibrium and economic considerations, the most suitable operating range for the oxidation and reduction is between 700° and 900° C. and at pressures up to 300 p.s.i. Therefore, the following goals were established for the operation of the process:

1. Utilization of approximately 65 percent of the hydrogen and carbon monoxide in producer gas while reducing iron oxide from 5 to 35 percent at about 750° C. This would result in producer gas consumption of about 6.6 cubic feet per pound of solids.

2. Utilization of about 55 percent of the steam or steam and carbon dioxide during oxidation of the solids from 35 to 5 percent reduced at about 750° C.

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[7] Barr, Frank T., High-Pressure Hydrogen: U.S. Patent 2,449,635, Sept. 21, 1948.

[8] Marshall, W. H. Jr., Hydrogen: U.S. Patent 2,198,560, Apr. 23, 1940.

[9] Reed, H. C., and Berg, C. H., Hydrogen: U.S. Patent 2,635,947, Apr. 21, 1953.

[10] Johnson, W. B., Synthesis of Methane: U.S. Patent 2,686,819, Aug. 17, 1954.

These gas conversions are about 5 percent less than those defined by equilibrium at 750° C.

Thermodynamic Equilibrium Considerations

The equilibrium relationships obtained from the literature[11] for the systems Fe_3O_4-H_2-FeO-H_2O and FeO-H_2-Fe-H_2O for temperatures of 500° to 900° C. are shown in figure 1 and table 1. Figure 2 and table 1 show the equilibrium relationships for the systems Fe_3O_4-CO-FeO-CO_2 from 700° to 900° C.[12] Equilibrium relationships were calculated to include the 500° to 700° C. range.

TABLE 1. - Thermodynamic data for steam-iron process

Temperature, ° C.	Phase	Equilibrium ratio, CO_2/CO	Oxidation of CO, percent	Equilibrium ratio, H_2O/H_2	Oxidation of H_2, percent
500................	Fe_3O_4/Fe	1.06	51	0.214	18
550................	Fe_3O_4/Fe	1.00	50	.283	22
600................	Fe_3O_4/FeO FeO/Fe	1.05 .91	51 48	.461 .334	32 25
700................	Fe_3O_4/FeO FeO/Fe	1.68 .678	63 40	1.12 .420	53 30
800................	Fe_3O_4/FeO FeO/Fe	2.40 .552	71 36	2.35 .501	70 33
900................	Fe_3O_4/FeO FeO/Fe	3.24 .466	76 32	- .580	- 37

The equilibrium data established the theoretical limiting conversions for reduction and oxidation. For example, hydrogen can reduce Fe_3O_4 to iron at 500° C. until the H_2O/H_2 ratio reaches 0.21/1 or about 18 percent of the hydrogen is converted to water. Beyond about 560° C., FeO is formed first in the reduction of Fe_3O_4. Thus at temperatures above 560° C., the limiting conversions for both changes in solid phases must be considered. For example, at 800° C., Fe_3O_4 is reduced to FeO on reaction with hydrogen until the H_2O/H_2 ratio reaches 2.35/1 or 70 percent of the hydrogen is converted to water vapor. However, for the reduction of FeO to iron at 800° C., the equilibrium H_2O/H_2 ratio is 0.51/1, and only 33 percent of the hydrogen can be converted to water vapor. This shows that the Fe_3O_4 phase must be present to yield high gas conversions in reduction; conversely, the iron phase must be present to yield

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[11] Emmett, P. H., and Shultz, J. F., The principle cause of discrepancies among equilibrium measurements of the systems Fe_3O_4-H_2-Fe-H_2O, Fe_3O_4-H_2-FeO-H_2O, and FeO-H_2-Fe-H_2O: Jour. Am. Chem. Soc., vol. 55, 1933, pp. 1376-1389.

[12] Eastman, E. D., and Evans, R. M., Equilibria Involving the Oxide of Iron: Jour. Am. Chem. Soc., vol. 46, 1924, pp. 888-903.

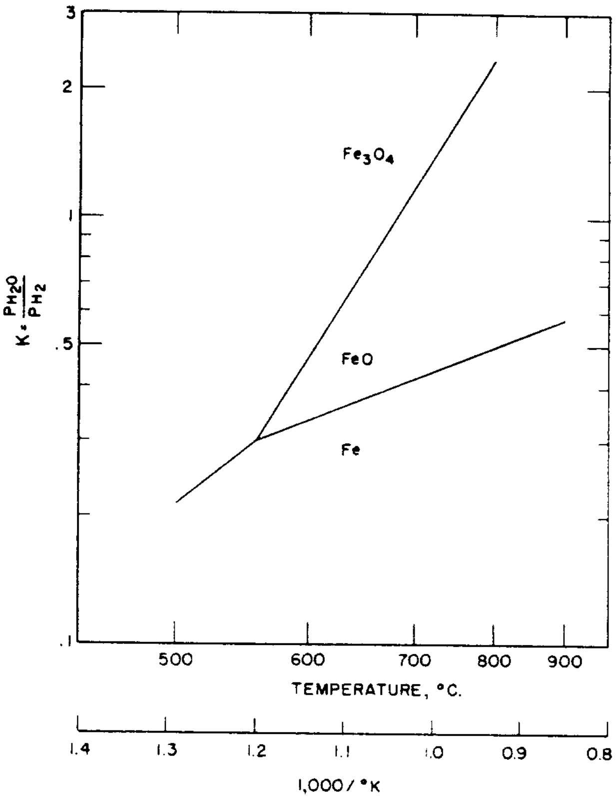

FIGURE 1. - Equilibrium Constants for Systems Fe_3O_4-H_2-FeO-H_2O and FeO-H_2-Fe-H_2O.

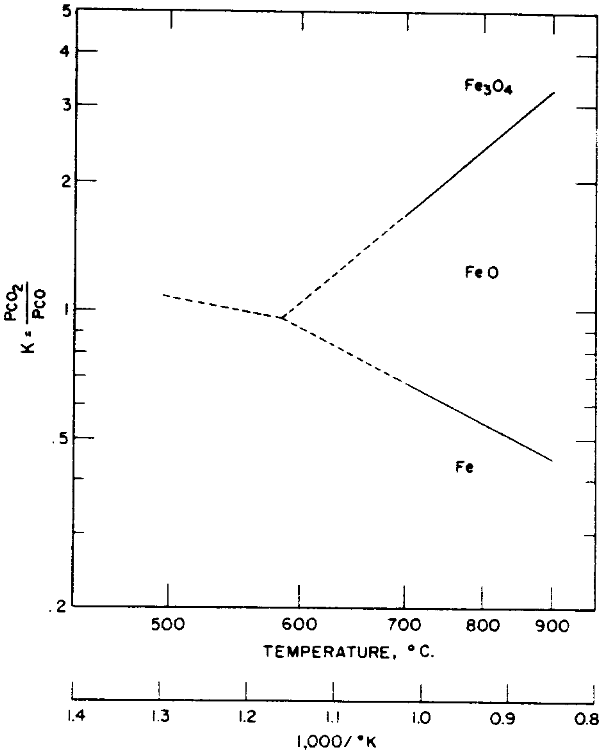

FIGURE 2. - Equilibrium Constants for Systems Fe_3O_4-CO-FeO-CO_2 and FeO-CO-Fe-CO_2.

high gas conversions during oxidation. The equilibrium relationship applies equally to the conversion of carbon dioxide to carbon monoxide or water to hydrogen when oxidizing iron or FeO. Conversions below theoretical are to be expected, particularly in the reduction of iron oxide with producer gas. The presence of moisture and carbon dioxide in the producer gas restricts the utilization of hydrogen and carbon monoxide.

Chemical and Free Energy Change Considerations

The steam-iron process involves the following chemical reactions:

$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O \qquad \text{(fig. 3)}$$

$$FeO + H_2 \rightleftharpoons Fe + H_2O \qquad \text{(fig. 4)}$$

$$FeO + CO \rightleftharpoons Fe + CO_2 \qquad \text{(fig. 5)}$$

$$Fe_3O_4 + H_2 \rightleftharpoons 3FeO + H_2O \qquad \text{(fig. 6)}$$

$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2 \qquad \text{(fig. 7)}$$

$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 \qquad \text{(fig. 8)}$$

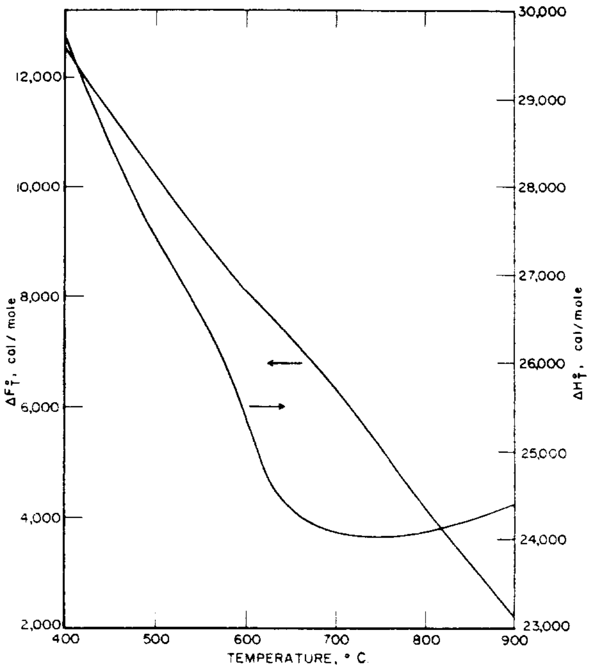

FIGURE 3. - Change in Enthalpy and Free Energy With Temperature for Reaction $Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O$.

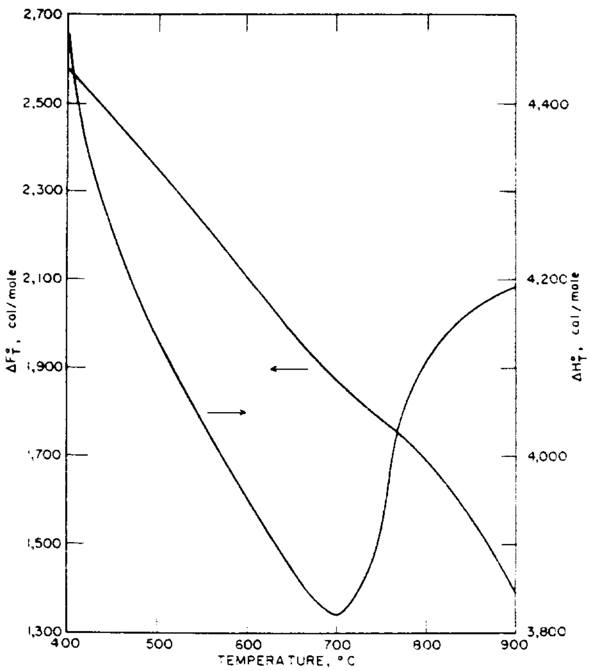

FIGURE 4. - Change in Enthalpy and Free Energy With Temperature for Reaction $FeO + H_2 \rightleftarrows Fe + H_2O$.

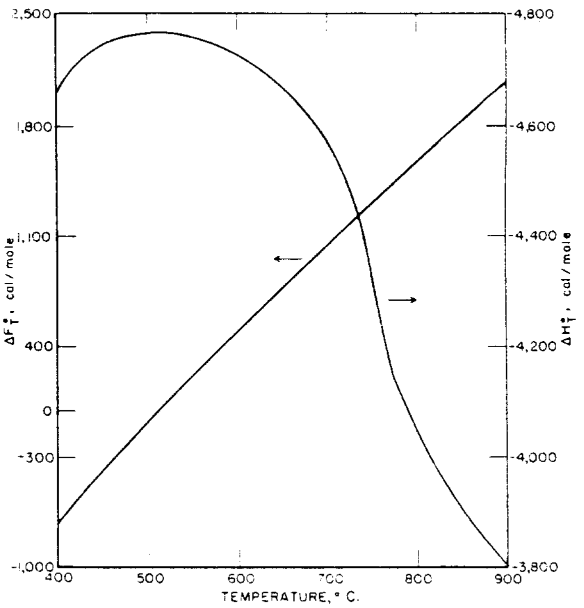

FIGURE 5. - Change in Enthalpy and Free Energy With Temperature for Reaction $FeO + CO \rightleftarrows Fe + CO_2$.

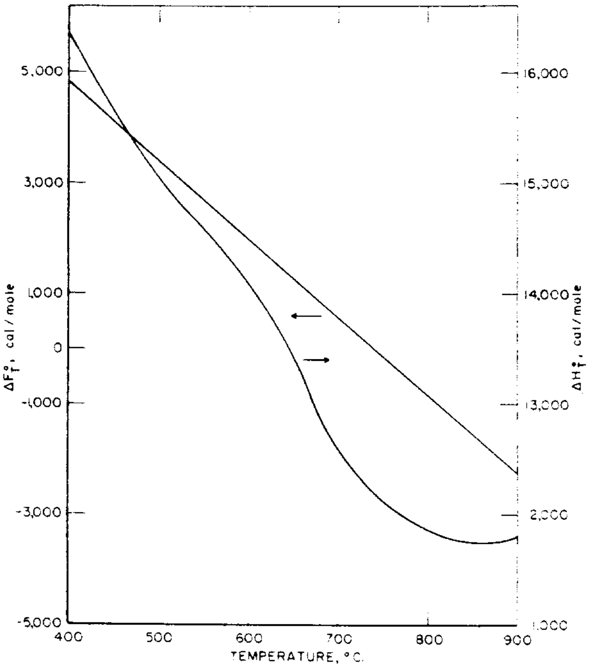

FIGURE 6. - Change in Enthalpy and Free Energy With Temperature for Reaction $Fe_3O_4 + H_2 \rightleftarrows 3FeO + H_2O$.

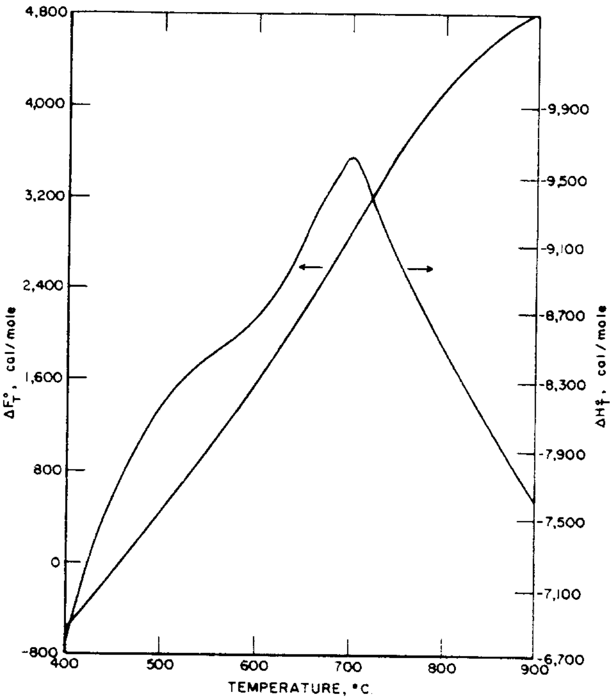

FIGURE 7. - Change in Enthalpy and Free Energy With Temperature for Reaction $Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$.

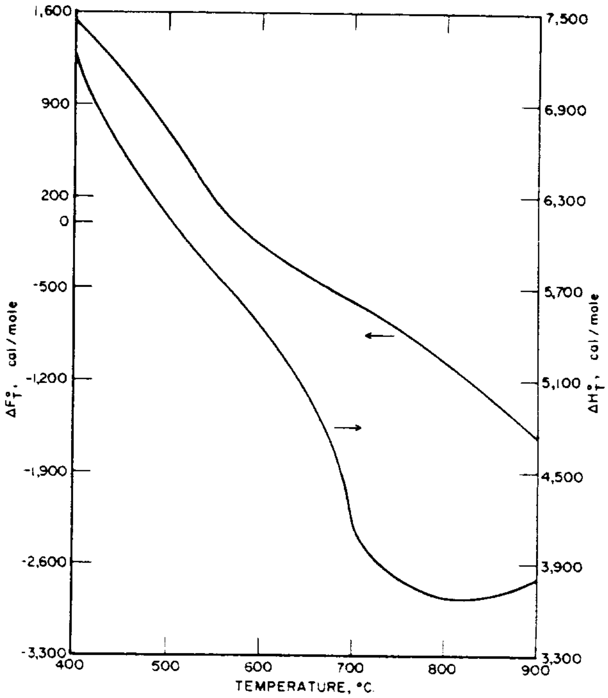

FIGURE 8. - Change in Enthalpy and Free Energy With Temperature for Reaction $Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$.

The effect of temperature on the free energy change (ΔF) and enthalpy (ΔH) for each of the above reactions is shown in the figure listed opposite the reaction. The temperature-versus-ΔF plot indicates whether or not the reaction can take place within the temperature limits specified. For example, the data in figure 3 show that the reaction $Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$ cannot be expected to proceed to the right at 400° C. owing to the high positive value of the free energy change for the system. Conversely, the reaction can be expected to proceed to the left spontaneously.

Calculations of the theoretical heat requirements for the steam-iron reactor are shown in the appendix.The choice of reaction temperatures was based upon equilibrium data, kinetics, and practical experience obtained from pilot plant studies. Because equilibrium data indicated that conversions increased with an increase in temperature during reduction and increased with a decrease in temperature during oxidation, conditions were chosen so that the solids-inlet and gas-outlet temperatures were 800° C. for reduction and 750° C. for oxidation. Theoretical gas conversions at these conditions are 70 percent for reduction and 60 percent for oxidation, accompanied by an incremental solids conversion of about 30 percent. As shown in the appendix. to sustain the endothermic reduction, the temperature of the producer gas to the reductor must be about 940° C. Because the oxidation reaction is exothermic, the temperature of the inlet steam is only 416 ° C.

EXPERIMENTAL PROCEDURE

Description of Apparatus: Reactor

The experimental work was conducted in the pilot plant shown in figure 9; the flowsheet for the system is shown in figure 10. One reactor is provided so that either reduction or oxidation is conducted at one time. The original reactor was made from a 10-foot length of 2-inch schedule 160, 347 stainless steel pipe. After about 10,000 hours of service at 600° to 900° C. and 15 to 300 p.s.i.g., considerable metal creep had occurred, and a new reactor, 20-feet long, fabricated from 2-inch schedule 160, 321 stainless steel pipe, was installed.

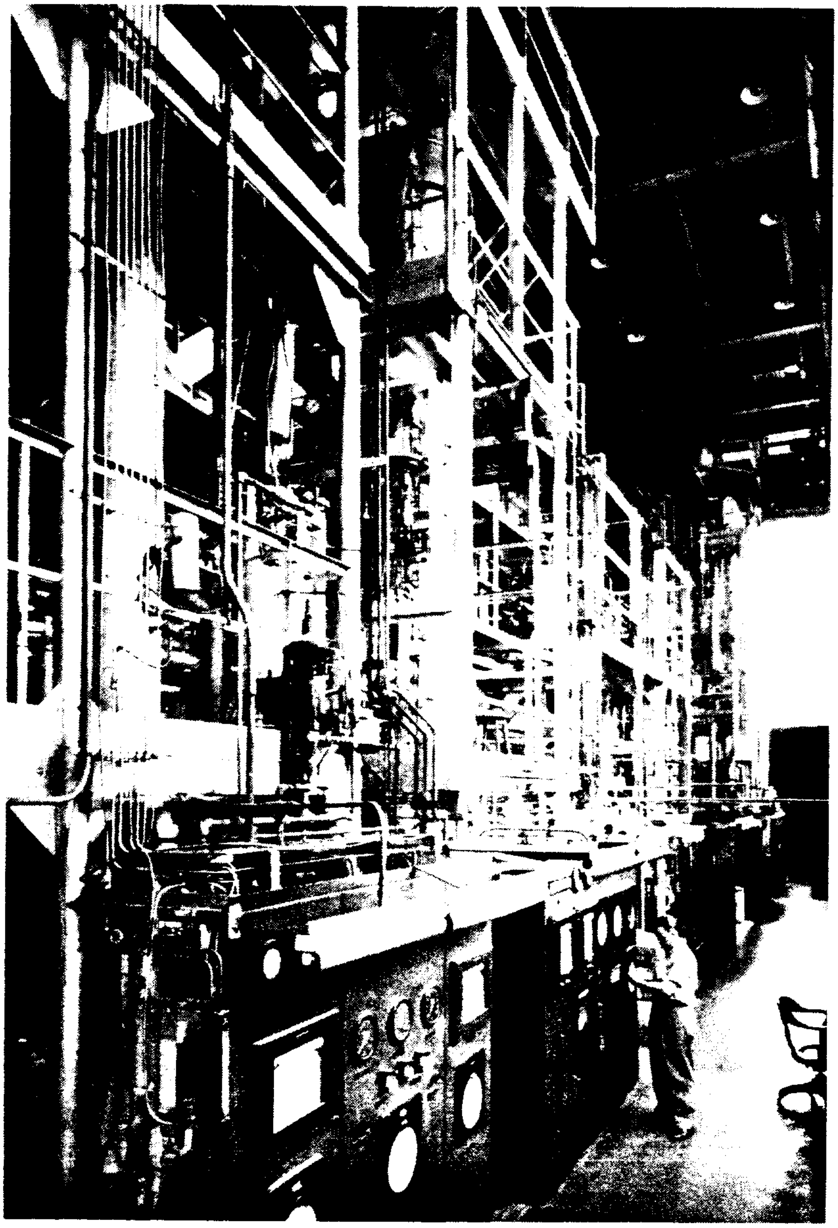

FIGURE 9. - Pilot Plant for the Preparation of Synthesis Gas or Hydrogen by the Steam-Iron Process.

Heat is supplied by individually controlled nickel-chromium alloy wire-wound heaters. The temperature is held within a ± 10° C. range up to 900° C. The solids are gravity-fed by a star feeder into the top of the reactor and are removed from the bottom through a level control-discharge valve. A spiral rod (see fig. 11) inserted into the reactor helps disperse the solids and reduce slugging.

The gases are metered into the bottom of the reactor and flow upward through the solids. The reacted gas passes from the top of the reactor and enters the tail gas system. It flows through a series of traps and filters where entrained solids and condensibles are collected. The gas then passes through a pressure

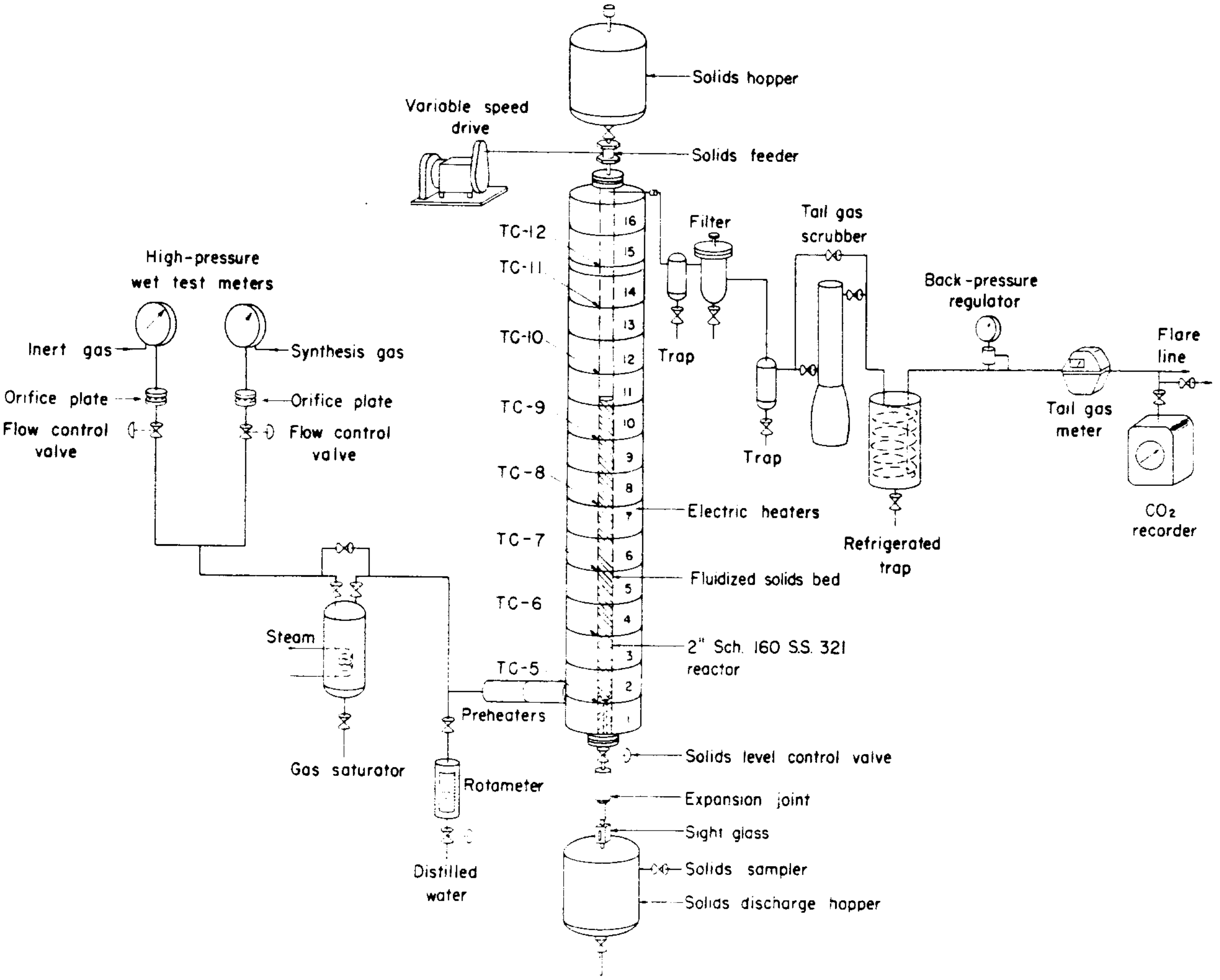

FIGURE 10. - Schematic Flowsheet of the Pilot Plant for the Preparation of Synthesis Gas or Hydrogen by the Steam-Iron Process.

letdown valve where the pressure is reduced to about 0.3 p.s.i.g. The product gas is metered at low pressure and vented. A recorder-analyzer continuously monitors the carbon dioxide content of the gas. A representative sample of the product gas is obtained from the exit-gas system for analysis by mass spectrometry. A gas saturator located in the feed-gas line permits the addition and control of the water vapor content of the simulated producer gas during reduction experiments.

The superficial linear velocity of the gas in the reactor is about 0.6 foot per second for proper solids fluidization. At higher velocities the solids tend to blow out of the reactor, and at lower velocities they tend to cake or agglomerate, depending upon the temperature and degree of reduction. The solids-bed height is maintained at the desired level by an air-actuated discharge valve. The valve is activated by the pressure drop across the fluidized bed. The rate of solids flow through the reactor depends upon

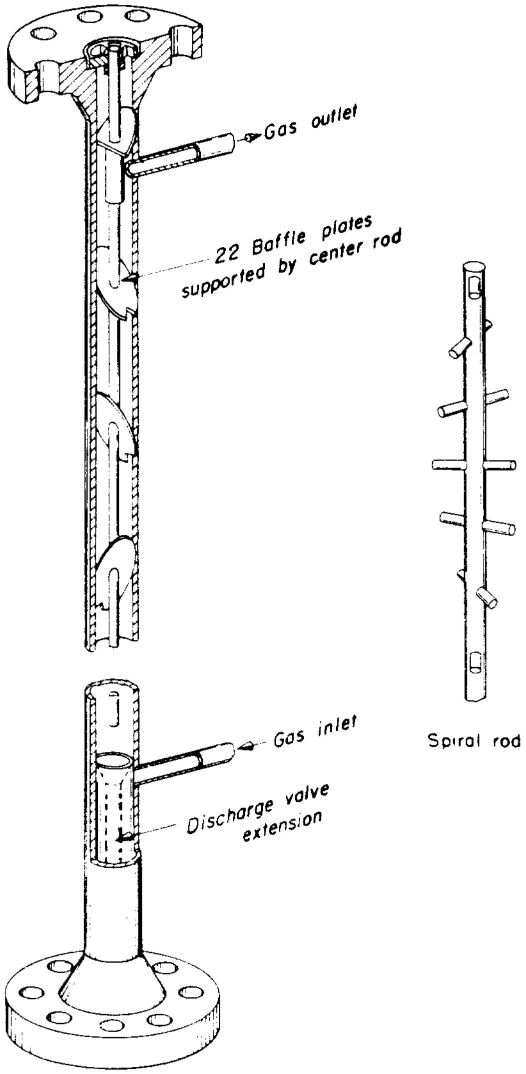

FIGURE 11. - Spiral Rod or Baffle Arrangement for the Steam-Iron Reactor.

the solids feed rate. Solids residence time is therefore dependent upon the feed rate and the bed height. The gas velocity during solids free-fall tests is limited to the terminal settling velocity of the solids. Velocities as high as 3 feet per second with steam were attained during oxidation, and as high as 5 feet per second with hydrogen during reduction, with very little solids carry-over. Solids measuring 20 to 100 U.S. Tyler mesh were used.

Oxidation is performed with steam or carbon dioxide or with mixtures of these gases in ratios of 3, 2, and 1. Steam is obtained in the desired quantities by metering distilled water into the gas preheater, which serves as a boiler. The preheater is a stainless steel pipe 1 inch in diameter and 36 inches long. A finned-type divider constructed of strips of steel is inserted into the pipe for better heat transfer. Heat is supplied to the preheater by strip heaters. The carbon dioxide is obtained from high-pressure cylinders.

Composition of Simulated Gas

Simulated producer gas is blended to the following composition and supplied to the steam-iron system for reduction:

Component:	Percent by volume	Component:	Percent by volume
CO_2....	5-6	H_2O....	0-3
CO.....	9-30	CH^4....	0-7
H_2.....	10-27	N_2.....	49-54

Composition of Commercial Producer Gas

The composition of the simulated producer gas is based on the composition of commercial producer gas.[13] Analyses of producer gases from the principal solid fuels are approximately as follows:

Fuel:	Gas composition, volume-percent				
	CO_2	CO	H_2	CH_4	N_2
Bituminous coal..................	4.7	25.0	14.5	3.1	52.7
Coke.............................	3.6	31.0	9.3	.7	44.3
Anthracite.......................	5.0	27.1	16.6	.9	50.4

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[13] Battelle Memorial Institute, Economics of Fuel Gas From Coal: McGraw-Hill Book Co., Inc., New York, N.Y., 1950, p. 14.

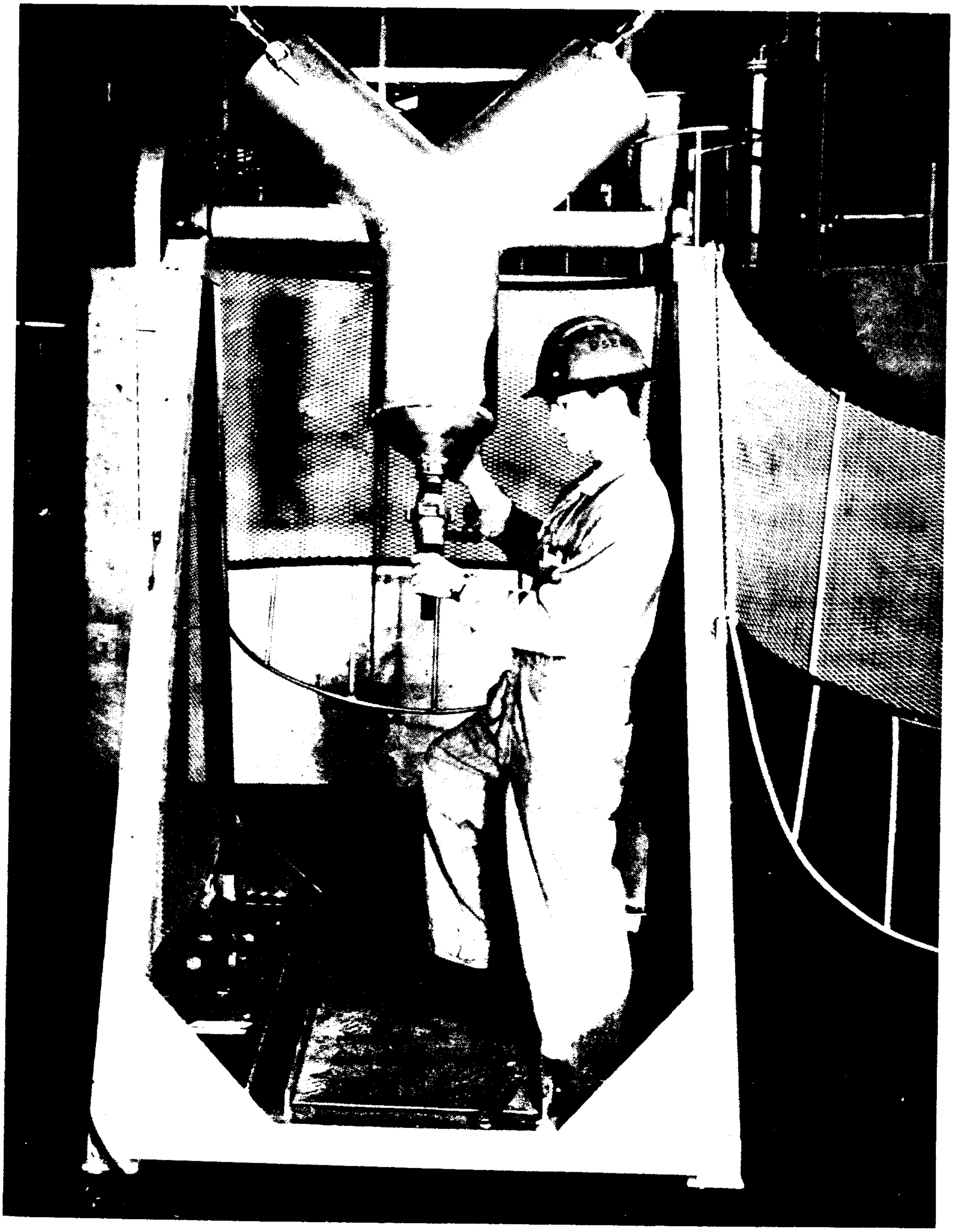

FIGURE 12. - Blender Used for Mixing Iron Oxide Solids for the Steam-Iron Process.

Sampling Procedure and Analysis

Solids Blender

At the completion of each experiment the solids are transferred from the bottom receiver hopper to the blender shown in figure 12. The solids are under an inert atmosphere during transfer. After blending for one-half hour a sample is taken.

FIGURE 13. - Apparatus for Analyzing Solids by Steam Oxidation for the Steam-Iron Process.

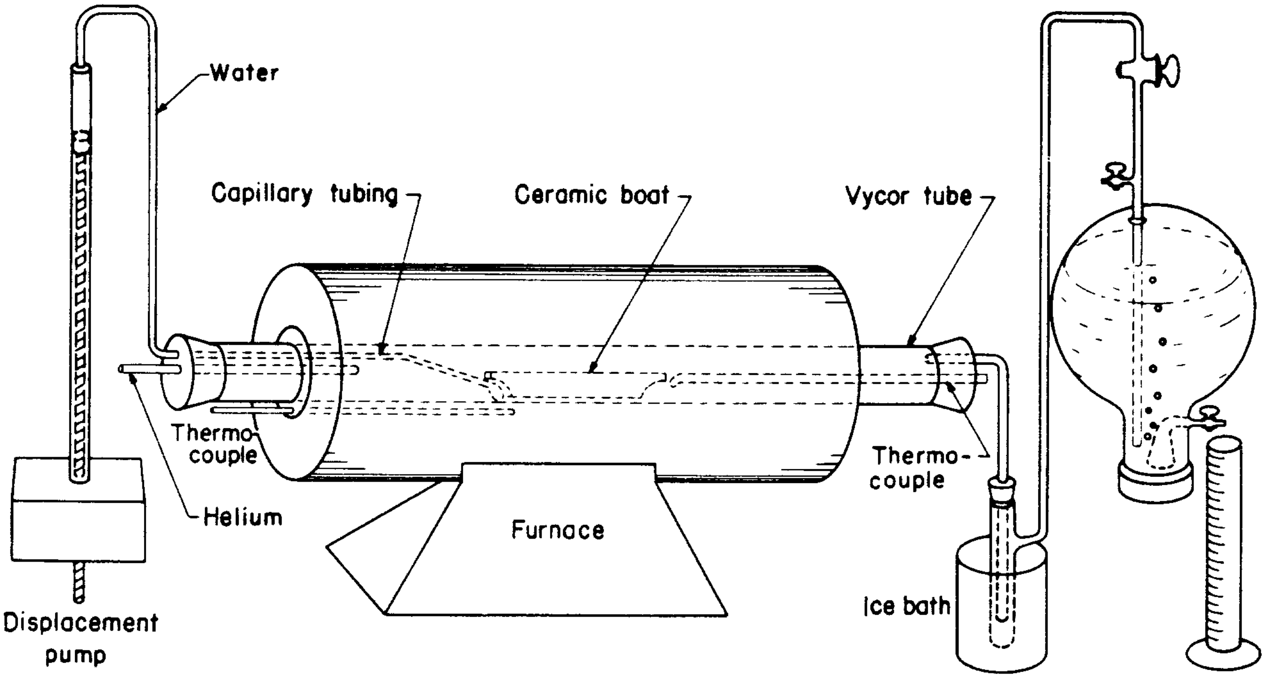

FIGURE 14. - Schematic of Apparatus for Analyzing Solids by Steam Oxidation for the Steam-Iron Process.

Solids Analyzer

Because of the many solids analyses required for control purposes, a procedure for the relatively rapid determination of the degree of reduction and carbon content of the solids was developed as follows: A 3-gram sample is charged to the oxidizer shown in figures 13 and 14. The sample is oxidized for 2 hours at 900° C. with steam flowing at about 0.3 cc. per minute. Gases evolved from the oxidation are collected in a 5-liter flask by displacement of a saturated sodium sulfate solution. At the completion of the oxidation, the entire system is purged with 500 cc. of helium. An Orsat analysis of the gas is made. From the volume and composition of the gas, the degree of reduction and the carbon content of the solids can be calculated as shown in the appendix.

Solids Sampler

A spot sample of the solids is obtained during each steady-state period using the solids sampling apparatus shown in figure 15. The spot sample is processed as described above, except for the blending.

Comparison of Chemical and Indirect Method of Analysis

As a check on the indirect or gas evolution method, chemical analyses of the solids are also made to determine the degree of reduction and the carbon content of the solids. The iron content of the solids is determined oxodimetrically with dichromate; the carbon content, gravimetrically by combustion. Usually the results from the two methods agree as follows: