A LABORATORY METHOD FOR THE EVALUATION OF
IRON ORES FOR USE IN THE STEAM-IRON PROCESS
FOR THE PRODUCTION OF HYDROGEN

A Thesis
Presented to
the Faculty of the Graduate School
University of Missouri

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemical Engineering

by
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August 1949

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for the Production of Hydrogen

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CHAPTER I

INTRODUCTION

Hydrogen has long been an important industrial substance and several processes for its economical production have been used. One of the older processes utilizes the interaction of steam and iron at suitable temperatures to produce a very pure hydrogen. The iron used is ordinarily spathic iron ore, roasted to convert the iron carbonate to iron oxide.¹ It is charged into a reactor, reduced with water gas, and then oxidized with steam. The process is generally considered to be a result of the following chemical reactions:

A. for the oxidation cycle, with absorption of heat:

B. for the reduction cycle, with evolution of heat:

The first of the hydrogen produced is necessarily mixed

¹ R. M. Reed, "Present Day Hydrogen Manufacturing Processes," Trans. A. I. Ch. E., 42:379-401 (1946).

with some of the unreacted reducing gas and is discarded or burned to supply heat to the reactors. The rest of the hydrogen is of high purity and is useful in such processes as the hydrogenation of fats and oils.

The first commercial application of this process was made in 1903 by Howard Lane. Since that time, many modifications and improvements have been made in plant operation and technique. The construction of the retorts has been changed to more effectively utilize the thermal energy of the reducing gas and decrease the amount of additional fuel required, and the cycle of operation has been studied with regard to optimum length of purging, steaming, and reducing periods in an effort to produce the purest hydrogen at the lowest price.

Together with the above mentioned changes in plant operation and technique, there has been a continual search for a more efficient iron-bearing material. S. Hurst² writes thus:

"Many forms of iron have been used as contact mass with more or less success, ranging from crude iron ores to steel turnings. The ideal material for the purpose would contain sufficient iron to give capacity, with a suitable binder that would render the mass porous and at the same time maintain its shape for a reasonable time, disintegrating very slowly.

² S. Hurst, "Production of Hydrogen by the Steam-Iron Method," Oil and Soap, 16:29-35 (1939).

The binder should be very free from fluxing characteristics and as near as possible inert to the reaction gases. The hematite ores are not successful, and after many trial runs the low grade ores have been most satisfactory. Included in this class are some Virginia ores, Alabama brown ores, lump pyrites cinder, and some European ores of the iron carbonate group. Ores with small amounts of copper and/or manganese give evidence of greater activity and higher purity of gas made than those that are free from these elements. It is of course desirable that the mass be free or nearly so of sulfur which of course is not the case with pyrites cinder. This material is especially active as a contact mass but its initial sulfur content and subsequent affinity for sulfur, together with its lack of strength, make it the least desirable form of iron to use.

"Man-made briquettes have been tried with very little success and to date the natural ores are the most dependable materials to use. The early plants used heavy steel turnings packed into retorts, and satisfactory results were obtained. However, the water gas/hydrogen ratio was high and the need for a more efficient material led to the use of lump pyrites cinder. Natural ores came into use about 26 years ago and a large proportion of present-day plants continue to use them."

W. K. Hutchinson³ writes of recent developments in modern steam-iron plants producing hydrogen for England's barrage balloons. The ore used was a "calcined Staffordshire black band ore" containing up to 50 per cent carbonaceous material and sized from $3/4$ to $1\frac{1}{2}$ inches. He reports that an artificial contact material was successfully made and used, but that the extra expense of manufacture was not justified. A search for an alternative contact material

³ W. K. Hutchinson, "Theory and Practice of Hydrogen Production by the Steam-Iron Method," Gas World, 123:105-114 (1945).

based on the true spathic iron ore was also conducted. One such material was tested in an industrial plant after being selected from various ores from many deposits on the basis of desirable physical properties of the calcined material. The ore was calcined "in situ" and did not prove to be as porous as expected. The results were adequate, but the operation was not as efficient as when the standard ore was used.

The M. W. Kellogg Company has recently obtained⁴ two patents for processes utilizing the reaction of small iron particles (20 to 200 mesh) with steam and reducing gas. In the first, the reactions are accomplished in the gas phase, the particles being suspended in the reaction gases. In the second, the particles are contained within reaction vessels, hydrogen being formed by reaction with liquid water at 315 C and 1500 lb per sq in. The reduction is accomplished at 800 C with reducing gases made by the decomposition of methane.

Although the steam-iron process for hydrogen has long been a commercial process, it is apparent from the above considerations that a search for a more efficient contact mass is still being carried out. A survey of the

⁴ D. D. Howat, "Thermal Methods of Hydrogen Production. I Steam-Iron Process," Chemical Age (London) 51:539-43, 581-6, 561-5 (1944).

available literature reveals that no systematic investigation of possible contact materials has ever been made. It was the purpose of this experimental research to develop a laboratory method whereby the various contact masses may be tested and partially evaluated as to their possible use in the steam-iron process for the production of hydrogen.

CHAPTER II

METHOD OF INVESTIGATION

It was assumed that the comparative values of particular iron ores for use in the steam-iron process for the production of hydrogen could be estimated, in part, by determining the ease and degree of oxidation and reduction of the ore under controlled conditions simulating those of commercial operations. Although the results of these laboratory tests cannot guarantee the success of plant-scale operations, it should be possible to eliminate many unsuitable ores on this basis. Other characteristics of commercial importance, such as the ability of an ore to withstand repeated oxidation and reduction processes without crumbling, the sintering temperature, and the physical strength of the ore particles in deep beds, were not measured during this investigation.

It was further assumed that the ease and degree of oxidation and reduction of the ores could be determined by two controlled tests: starting with a "completely oxidized"¹ ore, the amount of water formed during a standardized reducing period would be an indication of its performance; starting with a "completely reduced"¹ ore, the amount of water formed during a standardized reducing period following a

¹ See page 19

standardized oxidation period would be another indication of its performance. It is necessary, of course, to completely specify the nature of the standardized periods. Having results of both kinds of tests on several different ores, it should be possible to rank the ores in these important respects as to their usefulness in the steam-iron process for the production of hydrogen.

Since it was the purpose of this investigation to develop a method for evaluation of the relative usefulness of the contact masses, it was desirable to choose one of the much-used spathic ores as the reference with which to compare the performance of the others. A program of tests was then devised which would produce the desired experimental data. To aid in the interpretation of the results, a number of operating variables were fixed at the start of the investigation.

The steam-iron process for the production of hydrogen is carried out commercially at temperatures between 1400 and 1900 F.² The lower temperature was selected since the reactor was made of 18-8 stainless steel which loses much of its chemical inertness at higher temperatures.

The rates of flow of the gases through the apparatus were also selected and held relatively constant. These

² R. M. Reed, "Present Day Hydrogen Manufacturing Processes," Trans. A. I. Ch. E. 42: 379-401 (1946).

rates were determined from experimental considerations and the size of the equipment. Nitrogen, for drying the equipment and providing an inert atmosphere, was used at a rate of 0.2 cubic feet per minute (measured at 70 F and 1 atmosphere). Hydrogen, used as the reducing gas, flowed at a rate of 0.15 cubic feet per minute (70 F and 1 atmosphere). Steam, used as the oxidizing agent, flowed at a rate of about 0.03 pounds per minute. These flow rates, based on the actual volume of the ore used in the reactor, are given below:

Volume of Gas per minute per Volume of Ore
(Calculated at 70 F, 1 atmosphere)

	Nitrogen	Hydrogen	Steam
Spathic Ore	10.1	7.60	33.5
Missouri Brown Ore	12.8	9.60	42.5
Iron Sinter	10.9	8.15	36.0

Another variable of importance is the size of the ore particles. Material passing a 0.525-inch screen and retained on a 0.371-inch screen was selected for the tests, although the largest size iron sinter available was that passing a 0.371-inch screen and retained on a 0.263-inch screen.

With these variables fixed, the following test procedures were adopted:

A. Controlled reduction of ores.

1. Oxidize the ore completely³ with an excess

³ See page 19

of steam.

2. Dry the equipment with nitrogen.
3. Reduce the oxidized ore with hydrogen flowing at 0.15 cubic feet per minute (70 F, 1 atmosphere) for (a) 6 minutes, (b) 20 minutes, and (c) 40 minutes, collecting the water formed during any one reducing period.
4. Dry the equipment with nitrogen.
5. Repeat the above steps until checks are obtained for the amount of water formed during each of the several reducing periods.
6. Compare the performance of the domestic ores with that of the spathic ore by noting the amount of water formed during reduction as a function of the volumes of hydrogen used per volume of ore.

B. Controlled oxidation of ores.

1. Reduce the ore completely⁴ with an excess of hydrogen.
2. Dry the equipment with nitrogen.
3. Oxidize the reduced ore with steam flowing at a rate of 0.03 pounds per minute for (a) 1 minute, (b) 2 minutes, (c) 3 minutes, and

⁴ See page 19.

(d) 4 minutes.

4. Dry the equipment with nitrogen.

5. Reduce the partially oxidized ore with hydrogen flowing at a rate of 0.15 cubic feet per minute for 40 minutes, collecting the water formed.

6. Dry the equipment with nitrogen.

7. Repeat the above steps for each of the several oxidizing periods until checks are obtained for the amount of water formed during the following reducing periods. (Steps 1 and 2 may not be necessary at all times).

8. Compare the performance of the domestic ores with that of the spathic ore by noting the amount of water collected during Step No. 5 as a function of the volumes of steam used per volume of ore.

The oxygen of the water collected in the above tests comes from two sources -- the ore and the reactor. The reactor blank, that water formed by the reduction of the oxidized surfaces of the reactor, was determined by the following test, conducted in the absence of the ore:

1. Completely oxidize⁵ the reactor surfaces with

⁵ See page 19.

an excess of steam.

2. Dry the equipment with nitrogen.

3. Reduce the reactor surfaces with hydrogen flowing at 0.15 cubic feet per minute for 6 minutes, collecting the water formed.

4. Dry the equipment with nitrogen.

Longer periods of reduction or shorter periods of oxidation had no appreciable effect on the magnitude of the reactor blank.

CHAPTER III

DESCRIPTION AND USE OF APPARATUS

The construction of the reactor is shown in Illustration I. The reactor was suspended vertically inside the furnace, with the lower part of the ore cartridge centered in the heating zone.

The furnace was manufactured by the Hevi Duty Electric Company, Milwaukee, Wisconsin. Its construction is indicated in Illustration II. The top of the furnace was closed with firebrick to eliminate convection currents between the heating element and the reactor. The two sections of the heating element were connected in parallel to the secondary of a modified Westinghouse Type C induction voltage regulator. Control of the furnace temperature was maintained by the use of a thermocouple placed between the reactor and the heating element and connected to a Brown temperature recording, indicating, and controlling potentiometer containing a mercury switch. This switch was connected to a magnetic switch which controlled the supply of current to the primary of the induction voltage regulator. With 24 volts on the heating element, the operating temperature range was 30 degrees at 1450 F, the voltage being turned on at 1420 F and off at 1450 F. This arrangement produced a temperature of 1420 ± 5 F in the thermocouple well of the

Illustration I. REACTOR CONSTRUCTION

Experimental Apparatus for Evaluation of Iron Ores
for Steam-Iron Hydrogen

Illustration II. TUBE FURNACE--4.5 KW, 30 V.

Experimental Apparatus for Evaluation of Iron Ores for
Steam-Iron Hydrogen

reactor. About two hours were required to bring the furnace up to temperature, and the use of a time clock which actuated the Brown potentiometer permitted this preheating period to be accomplished automatically.

Nitrogen and hydrogen were supplied from cylinders obtained from Puritan Compressed Gas Corporation, Kansas City, Missouri. The flow of these gases was measured at 70 F and 3 lb per sq in. gauge pressure by two calibrated orifices in the lines leading to the reactor. According to gas analyses reported by Puritan, the nitrogen contained a maximum of 5 per cent oxygen and the hydrogen was of 99.8 per cent purity.

The steam supply system is shown in Illustration III. The orifice was calibrated by diverting the steam from the reactor and condensing it, and then weighing the condensate in a tared flask. At the low rate of steam flow desired, the water tended to drip into the vaporizer, causing pressure variations which were reflected by the manometer fluid. This difficulty was overcome by installing, at the entrance to the vaporizer, a short length of 1/8-inch copper tubing, flattened at the end which touched the wall at the center of the vaporizer.

In addition to these considerations, it was also found that the orifice, which was a 1/8-inch needle valve, did not remain in exact calibration from day to day.

Therefore, before any of the controlled oxidation tests, the steam supply was determined accurately by direct weighing of the amount of condensate per unit time.

The water collection system is sketched in Illustration IV. The purpose of the particular design was two-fold: to permit condensation of the steam leaving the reactor so that it could be collected as a liquid, thus reducing the load on the drying bottles; and to permit evaporation and collection of all the water remaining in the system between the reactor and the drying bottles. The following procedure was used to accomplish these purposes:

A. During any oxidizing period:

Replace the liquid collecting bottle and the drying bottles with a liter flask. Conduct the oxidizing process while the interchanger is being cooled. Remove the flask and drain the interchanger. Then pass nitrogen through the system while the interchanger is being heated. This will rid the system of any and all water present from the oxidizing process.

B. During any reduction process:

Replace the liquid collecting bottle and the drying bottles. Conduct the reducing process while the

interchanger is being cooled. Steam leaving the reactor will condense and be collected as liquid, while the gases will be dried as they pass through the drying bottles. Drain the interchanger when the reduction has been accomplished. Then pass nitrogen through the system while the interchanger is being heated. This will remove the remainder of the water and permit its collection in the drying bottles. Weigh all three bottles to determine the amount of water collected.

The end point of the drying process was determined by noting the disappearance of the water droplets on the sides of the glass tubing in the apparatus between the interchanger and the drying bottles. Drying progressed from the first to the last part of this system, and was discontinued when the last part became dry.

A "complete oxidation" of an ore was considered to have been accomplished after an excess of 500 grams of steam had passed through the ore bed. A "complete reduction" of an ore was considered to have been accomplished when not more than one gram of water was collected during a 40-minute reduction with hydrogen. This measured reducing period usually followed a prolonged reduction of a variable length which depended on the previous treatment of the ore. In the absence of an ore, the "complete oxidation" of the

reactor was considered to have been accomplished when an excess of 200 grams of steam had passed through the reactor.

CHAPTER IV

SELECTION, TREATMENT, AND ANALYSES OF ORES

Because of time limitations, it was possible to test only three different ores: an imported English spathic ore, obtained from Durkee Famous Foods, Chicago, Illinois; a typical Missouri brown ore, obtained from the Missouri State Geologist, Rolla, Missouri; and a by-product pyrite sinter, obtained from The Tennessee Copper Company, Copperhill, Tennessee, and of the following reported analysis:

Iron	68.0%	Zinc	0.13%
Insolubles	2.5%	Phosphorus	0.005%
Silica	1.5%	Sulfur	0.05%
Copper	0.12%	Oxygen	balance

The ores were crushed and separated into the following screen sizes: 0.371 to 0.525 inches; 0.263 to 0.371 inches; and fines below 0.263 inches. There followed a two-hour calcination in an electric furnace at 1600 F and several preliminary oxidations and reductions in the reactor. The purpose of this treatment was to eliminate any sulfur in the ore and to leave it in a state approximating that while in actual use.

Analyses of these ores gave the following results:

(See Appendix C for analytical methods.)

	Spathic Ore	Brown Ore	Iron Sinter
Iron	46.88%	56.80%	69.92%
Manganese	2.53%	0.026%	0.048%
Silica	11.89%	4.47%	1.90%
Ignition loss	-4.18%(gain)	11.24%	-0.63%(gain)

It became evident during the testing of the ores that the spathic ore also contained sulfur. The persistent odor of H_2S in the gases leaving the reactor was unmistakable.

CHAPTER V

EXPERIMENTAL RESULTS

Details of the experiments conducted are contained in Appendices A and B. It will be noted that a quantity of calcined diaspore, obtained from the A. P. Green Firebrick Company, Mexico, Missouri, was present in the upper part of the reactor during the first several sets of experiments. This bed of diaspore was approximately 15 inches in length and served to preheat the gases.

Blank Tests 1, 2, and 3 were conducted with diaspore in the reactor. Blank Test 4 was conducted without the diaspore. The large amounts of water collected in these tests were attributed entirely to the reactor, since it was not obvious from Test 4 that the removal of the diaspore had any effect on the magnitude of the reactor blank.

In preliminary tests of the equipment the reactor had been heated to 2000 F for a short time. Examination of the reactor after Blank Test 4 showed surface scaling. To reduce the magnitude of the reactor blank, the 2-inch tube and the thermocouple well were replaced, and the inside of the 2-inch pipe, the tube, and the thermocouple well were polished. As shown in Blank Tests 5 through 10, the value of the reactor blank in the absence of the diaspore was decreased by these measures to less than 1.0 gram.

Fifty-two tests were then conducted on the assumption that the presence of the diaspora would have no effect on the value of the reactor blank. However the removal of the diaspora in Blank Tests 38 through 41 caused the value of the reactor blank to decrease to less than half of what it had been in Blank Tests 33 through 37, during which the diaspora was present. A new quantity of diaspora was used during Blank Tests 42 through 45 and 48 through 50. Blank Tests 46, 47, 51, and 52 were conducted without the diaspora. These tests proved conclusively that the large reactor blank values were due primarily to the presence of diaspora. Thereafter, all subsequent tests were conducted in the absence of the diaspora, and the average value of the reactor blank did not again deviate appreciably from 1 gram of water.

Some doubt now exists as to the actual value of the reactor blank in all tests conducted with the diaspora in the reactor. The value of the reactor blank was not constant during these tests: either the experimental technique was faulty, or the action of the diaspora was not constant. It is possible that water vapor was adsorbed on the diaspora, under which conditions the amount of water collected during the reduction and drying processes would be a function of previous treatment, and not necessarily constant.

Tables I, II, and III summarize the results of the controlled reduction tests. These data are plotted in Figure 1. Tables IV, V, and VI summarize the results of the controlled oxidation tests. These data are plotted in Figure 2.

TABLE I

CONTROLLED REDUCTION TESTS AT 1420 F ON SPATHIC ORE

Rate of Flow of hydrogen: 0.15 cu ft/min (70 F, 1 atm)

Excess steam for oxidation: 500 g in 30 min.

Ore: Weight: 1100 g Length of bed: 14 in.

Volume: 0.0198 cu ft Size: through 0.525 in. screen
retained on 0.371 in. screen

Number ^a of Test	Hydrogen for Reduction	Water Collected During Reduction	Presence of Diaspore	Reactor Blank	Corrected Water Formation
	$\frac{\text{Vol H}_2}{\text{Vol Ore}}$ ^b	Total cu ft	g	g	g
Blank	---	---	---	---	Unknown
3	152.	3.0	26.41	Yes	---
4	182.	3.6	24.64	Yes	---
5	182.	3.6	27.41	Yes	---
8	152.	3.0	26.73	Yes	---
Blank	---	---	---	Yes	2.5
Blank	---	---	---	No	1.0
9	45.6	0.9	10.13	No	---
10	45.6	0.9	9.66	No	---
11	304.	6.0	39.71	No	---
12	304.	6.0	41.14	No	---
Blank	---	---	---	No	0.9

^a See Appendix A^b Vol H₂/Vol Ore at 70 F, 1 atm.

TABLE II

27

CONTROLLED REDUCTION TESTS AT 1420 F ON BROWN ORE

Rate of flow of hydrogen: 0.15 cu ft/min (70 F, 1 atm)

Excess steam for oxidation: 500 g in 30 min.

Ore: Weight: 900 g Length of bed: 11 in.

Volume: 0.0156 cu ft. Size: through 0.525 in. screen
retained on 0.371 in. screen

Number of Test	^a Hydrogen for Reduction		Water Collected During Reduction	Presence of Diaspore	Reactor Blank	Corrected Water Formation
	^b $\frac{\text{Vol H}_2}{\text{Vol Ore}}$	Total cu ft	g		g	g
Blank	---	---	---	Yes	2.5	---
2	403.	6.3	66.51	Yes	---	63.7
3	403.	6.3	69.65	Yes	---	66.9
4	403.	6.3	68.51	Yes	---	65.7
Blank	---	---	---	Yes	3.1	---
Blank	---	---	---	Yes	2.0	---
5	57.6	0.9	14.54	Yes	---	12.0
6	57.6	0.9	15.86	Yes	---	13.4
7	192.	3.0	38.29	Yes	---	35.8
8	192.	3.0	40.6	Yes	---	38.1
Blank	---	---	---	Yes	3.0	---

^a See Appendix A^b Vol H₂/Vol Ore at 70 F, 1 atm.

TABLE III

28

CONTROLLED REDUCTION TESTS AT 1420 F ON IRON SINTER

Rate of flow of hydrogen: 0.15 cu ft/min (70 F, 1 atm)

Excess steam for oxidation: 500 g in 30 min.

Ore: Weight: 750 g Length of bed: 13 in.

Volume: 0.0184 cu ft Size: through 0.371 in. screen

retained on 0.263 in. screen

Number of Test	^a Hydrogen for Reduction		Water Collected During Reduction g	Presence of Diapore	Reactor Blank g	Corrected Water Formation g
	^b Vol H ₂ Vol Ore	Total cu ft				
Blank	---	---	---	Yes	3.1	---
1	326.	6.0	53.92	Yes	---	51.4
2	326.	6.0	56.93	Yes	---	54.4
3	367.	6.75	60.40	Yes	---	57.9
4	326.	6.0	52.14	Yes	---	49.6
5	326.	6.0	54.18	Yes	---	51.7
Blank	---	---	---	Yes	2.0	---
Blank	---	---	---	Yes	2.0	---
6	48.9	0.9	13.56	Yes	---	11.7
7	48.9	0.9	13.92	Yes	---	12.1
8	163.	3.0	34.12	Yes	---	32.2
9	163.	3.0	36.39	Yes	---	34.5
Blank	---	---	---	Yes	1.8	---

^a See Appendix A^b Vol H₂ / vol Ore at 70 F, 1 atm.

Figure 1. CONTROLLED REDUCTION TESTS AT 1420°F.

Ores initially oxidized with 500g excess steam.
Data from Tables I, II, and III.

CONTROLLED OXIDATION TESTS AT 1420 F ON SPATHIC ORE

Reduction period: 6 cu ft hydrogen (70 F, 1 atm) in 40 min.

(304 vol H_2 / vol. Ore in 40 min.)

No diasporic in reactor.

Ore: Weight: 1100 g Length of bed: 14 in.

Volume: 0.0198 cu ft Size: through 0.525 in. screen

retained on 0.371 in. screen

Number ^a of Test	Water Input Rate	Water Input	Water Collected During Reduction	Reactor Blank	Corrected Water Formation
	$\frac{lb}{min}$	$\frac{Vol H_2 O^b}{Vol Ore}$	g	g	g
Blank	---	---	---	---	0.9
19	0.0321	32.6	13.62	14.65	---
20	0.0286	32.6	13.62	13.75	---
21	0.033	32.7	13.65	13.92	---
22	0.033	71.8	30.0	22.07	---
25	0.0278	64.6	27.0	20.08	---
26	0.0326	74.0	30.9	24.38	---
27	0.0273	64.4	26.9	22.27	---
28	0.028	97.9	40.9	24.63	---
29	0.032	102	43.6	27.24	---
30	0.033	98.5	41.2	27.08	---
31	0.0321	131.	54.8	29.47	---
Blank	---	---	---	---	0.9

^a See Appendix B^b Vol $H_2 O$ / vol Ore at 70 F, 1 atm.

TABLE V

31

CONTROLLED OXIDATION TESTS AT 1420 F ON BROWN ORE

Reduction period: 6 cu ft hydrogen (70 F, 1 atm) in 40 min.

(384 vol H₂/ vol Ore in 40 min)

No diasporic in reactor.

Ore: Weight: 900 g Length of bed: 11 in.

Volume: 0.0156 cu ft Size: through 0.525 in. screen

retained on 0.371 in. screen

Number ^a of Test	Water Input Rate	Water Input Vol H ₂ O ^b Vol Ore	g	Water Collected During Reduction g	Reactor Blank g	Corrected Water Formation g
	$\frac{\text{lb}}{\text{min}}$					
Blank	----	---	---	---	0.9	---
17	0.0284	79.6	26.3	15.99	---	14.9
18	0.0284	83.0	27.4	20.81	---	19.8
19	0.0308	82.7	27.3	20.04	---	19.0
20	0.0268	78.8	26.0	19.73	---	18.7
22	0.0291	164.5	54.3	29.91	---	28.9
23	0.0286	165.5	54.6	32.35	---	31.3
24	0.0319	165.5	54.6	30.56	---	29.5
25	0.0308	165	54.4	32.73	---	31.7
Blank	---	---	---	---	1.2	---

^a See Appendix B^b Vol H₂O/ vol Ore at 70 F, 1 atm.

CONTROLLED OXIDATION TESTS AT 1420 F ON IRON SINTER

Reduction period: 6 cu ft hydrogen (70 F, 1 atm) in 40 min.

(326 vol H_2 / vol Ore in 40 min.)

No diasporic in reactor.

Ore: Weight: 750 g Length of bed: 13 in.

Volume: 0.0184 cu ft Size: through 0.371 in. screen

retained on 0.263 in. screen

Number ^a of Test	Water Input Rate	Water Input		Water Collected During Reduction	Reactor Blank	Corrected Water Formation
	$\frac{lb}{min}$	$\frac{Vol H_2O}{Vol Ore}$ ^b	g	g	g	g
Blank	----	---	---	---	1.2	---
13	0.0295	70	27.2	24.76	---	23.6
14	0.0326	69.7	27.1	21.55	---	20.4
15	0.0299	69.7	27.1	23.07	---	21.9
16	0.0309	69.7	27.1	23.28	---	22.1
18	0.0304	140.5	54.5	30.45	---	29.3
19	0.0309	140.5	54.5	30.7	---	29.5
20	0.03	140.5	54.5	30.76	---	29.6
Blank	---	---	---	---	1.2	---

^a See Appendix B^b Vol H_2O / vol Ore at 70 F, 1 atm.

CHAPTER VI

DISCUSSION OF RESULTS AND CONCLUSION

Several conclusions may be drawn from a consideration of Figures 1 and 2. It is demonstrated that controlled reduction and oxidation tests may be used in partial evaluation of the performance of an iron ore in the steam-iron process for the production of hydrogen. From Figure 1, it can be seen that the Missouri brown ore and the iron sinter are reduced to a greater extent than the spathic ore by any given amount of hydrogen. From Figure 2, it can be seen that the spathic ore and the iron sinter are oxidized to a greater extent than the Missouri brown ore by any given amount of steam. However, it appears that the Missouri brown ore may be oxidized and reduced to a greater extent than either the spathic ore or the iron sinter when very large amounts of oxidizing or reducing gases are used, but it is probable that the longer periods of time which are required for this greater reaction would never be used in a commercial operation.

The above conclusions must not be taken without reservations. The tests were conducted at only one temperature, and it is probable that each ore will react differently at another temperature. The gas velocities through the apparatus were also constant, and the rate of reaction should vary

with the rate of supply of oxidizing and reducing gases. Using material of different screen sizes may affect the fraction of the ore particles which reacts and thus would affect the rate of reaction also. The use of a reducing gas other than pure hydrogen may also affect the rate of reaction and possibly the attainment of equilibrium conditions.

One other variable should have been held constant during experimental work: The same volume of each of the ores should have been used in the reactor. Under these conditions, not only would the results of the tests have been reported for the same lengths of time for each of the several oxidizing and reducing periods, but the results would also have been reported at the same several values of volumes of oxidizing or reducing gases per unit volume of ore. Since there was some gas issuing from the reactor at all times, at least during the reducing periods, it is possible that the amount of reaction was somewhat affected by the length of the reaction period and not entirely a function of the volume of reactant per volume of ore. From the data in Tables I, II, and III, it can be seen that the volume of the spathic ore was greater than that of the iron sinter, and that the volume of the latter was greater than the volume of the brown ore. Thus the data of Figures 1 and 2 might also be plotted with water formation as a

function of the amount (volume) of hydrogen or steam. This would result in a relative lowering of the curves for the iron sinter and brown ore, with respect to the curve for the spathic ore, lowering the latter curve more than the former. The result of this relative shift of the curves would indicate that the brown ore could be reduced further than either of the other ores in a given time, and could be oxidized about as much as the spathic ore, although not as much as the iron sinter. Thus the ease and degree of oxidation and reduction of the several ores could still be distinguished by the controlled tests and the conclusions cited previously would still be valid. However, since it is the usual policy to report results of these kinds of tests as a function of the volume of ore, the graphs have been drawn in only this one manner.

As the investigation proceeded, several qualitative observations were made. The spathic ore apparently suffered no physical breakdown from continuous oxidation and reduction. No appreciable amount of fines was formed and the particles retained their hardness. Previous physical or chemical treatment of the spathic ore by Durkee Famous Foods, Inc., is unknown. The Missouri brown ore became brittle and some reduction in particle size occurred, although no great amount of dusting was noted. The brown ore could easily be broken with the fingers and

was not at any time as hard as the spathic ore. The iron sinter was also brittle, but did not produce more than a small amount of ore fines while in use. No evidence of sintering of the ores was detected, the ore particles separating freely when discharged from the reactor. The water collected during the reducing periods was accompanied by a very small amount of ore fines. No attempt was made to remove this solid material and the "weight of water collected" included the insignificant weight of the ore fines.

It is concluded that results of controlled oxidation and reduction tests of iron ores can distinguish between the performance of various ores in these tests. Thus a method has been developed whereby the various contact masses may be tested and partially evaluated as to their possible use in the steam-iron process for the production of hydrogen.

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APPENDIX A

Description of Test		Date	Temperature	Water Flow	
Ore	No. ¹		F	Excess	Time
				g	min
None	1	20 March (1947)	1450	50	2
None	2	24 "	1635	150	10
None	3	27 "	1510	80	5
None	4	28 "	1415	80	1
None	5	23 April	1450	50	5
None	6	23 "	1450	50	5
None	7	23 "	1450	80	6
None	8	23 "	1450	50	5
None	9	26 "	1450	80	6
None	10	26 "	1450	50	5
Durkee	1	28 May	1550	1000	75
Durkee	2	28 "	1550	1000	75
Durkee	3	29 "	1420	400	37
Durkee	4	31 "	1420	500	48
Durkee	5	31 "	1420	500	40
Durkee	6	7 June	1420	350	30
Durkee	7	7 "	1420	500	45
Durkee	8	7 "	1420	500	50
None	11	10 "	1420	150	12

EXPERIMENTAL DATA FROM CONTROLLED REDUCTION TESTS

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Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Diaspore Present	Notes
Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	g		
0.28	5	1.4	0.14	5	0.7	0.14	40	5.6	2.81	Yes	
0.28	5	1.4	0.24	3	0.72	0.28	10	2.8	2.55	Yes	
0.28	5	1.4	0.24	5	1.2	0.28	12	3.4	3.48	Yes	
0.28	6.5	1.82	0.24	5	1.2	0.28	10	2.8	2.42	No	
0.28	6	1.68	0.24	5	1.2	0.28	10	2.8	0.62	No	Reactor surfaces pol- ished before this test.
0.28	5	1.4	0.24	9	2.16	0.28	10	2.8	1.07	No	
0.28	7	1.96	0.24	5	1.2	0.28	10	2.8	0.97	No	
0.28	10	2.8	0.24	5	1.2	0.28	10	2.8	0.47	No	
0.28	10	2.8	0.24	5	1.2	0.28	10	2.8	0.55	No	
0.28	10	2.8	0.24	5	1.2	0.28	10	2.8	0.50	No	
0.20	20	4.0	0.15	20	3.0	0.20	20	4.0	31.59	Yes	Many preliminary treat- ments on this ore preceded these tests.
0.20	20	4.0	0.15	20	3.0	0.20	20	4.0	28.99	Yes	
0.20	29	5.8	0.15	20	3.0	0.20	20	4.0	26.41	Yes	
0.20	21	4.2	0.15	24	3.6	0.20	23	4.6	24.64	Yes	
0.20	18	3.6	0.15	24	3.6	0.20	20	4.0	27.41	Yes	
0.20	24	4.8	0.15	20	3.0	0.20	20	4.0	---	Yes	Faulty procedure
0.20	35	7.0	0.15	21	3.15	0.20	22	4.4	---	Yes	Faulty procedure
0.20	26	5.2	0.15	20	3.0	0.20	15	3.0	26.73	Yes	
0.20	15	3.0	0.15	5	0.75	0.20	15	1.0	---	Yes	Apparatus Failed

Description of Test		Date		Temperature	Water Flow	
Ore	No. ¹			F	Excess	Time
					g	min
None	12	10	June	1420	150	12
None	13	11	"	1420	200	15
None	14	11	"	1420	200	15
None	15	12	"	1420	200	15
None	16	12	"	1420	200	15
None	17	13	"	1410	200	14
None	18	13	"	1410	200	14
Mo. Brown	1 (9)	14	"	1410	500	34
Mo. Brown	2 (10)	14	"	1410	500	43
Mo. Brown	3 (11)	17	"	1410	500	36
Mo. Brown	4 (12)	17	"	1410	500	32
None	19	19	"	1420	200	14
None	20	19	"	1420	250	17
Iron Sinter	1 (13)	20	"	1420	550	55
Iron Sinter	2 (14)	20	"	1420	500	36
Iron Sinter	3 (15)	20	"	1420	500	45
Iron Sinter	4 (16)	21	"	1420	500	38
Iron Sinter	5 (17)	21	"	1420	500	38
None	21	24	"	1410	200	15

Description of Test		Date	Temperature	Water Flow	
Ore	No. ¹		F	Excess	Time
				g	min
None	22	24 June	1410	200	15
None	23	22 July	1410	200	10
None	24	22 "	1410	200	11
None	25	22 "	1410	230	13
None	26	29 "	1410	275	15
None	27	29 "	1420	220	10
None	28	1 Aug.	1420	200	11
None	29	1 "	1420	200	11
None	30	2 "	1420	200	8
Iron Sinter	6 (18)	5 "	1440	500	27
Iron Sinter	7 (19)	5 "	1440	500	24
Iron Sinter	8 (20)	11 "	1440	500	28
Iron Sinter	9 (21)	11 "	1440	500	24
None	31	12 "	1420	200	8
None	32	12 "	1420	200	9
Mo. Brown	5 (22)	14 "	1440	500	21
Mo. Brown	6 (23)	14 "	1440	500	21
Mo. Brown	7 (24)	15 "	1440	500	31
Mo. Brown	8 (25)	15 "	1440	500	24
None	33	16 "	1420	200	10
None	34	16 "	1420	200	11
None	35	16 "	1420	250	10

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Diaspore Present	Notes
Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	g		
0.20	14	2.8	0.15	7	1.05	0.20	14	2.8	2.81	Yes	
0.20	20	4.0	0.15	5	0.75	0.20	11	2.2	1.34	Yes	
0.20	19	3.8	0.15	5	0.75	0.20	15	3.0	5.86	Yes	
0.20	13	2.6	0.15	5	0.75	0.20	13	2.6	2.58	Yes	
0.20	18	3.6	0.15	5	0.75	0.20	12	2.4	2.61	Yes	
0.20	16	3.2	0.15	5	0.75	0.20	10	2.0	1.90	Yes	
0.20	15	3.0	0.15	5	0.75	0.20	13	2.6	2.77	Yes	
0.20	18	3.6	0.15	43	6.45	0.20	21	4.2	89.27	Yes	Previous treatment consisted of calcination at 1600 F for 2 hrs., and reduction with H ₂ for 2 hours. After initial reduction, ore was found to be pyrophoric.
0.20	25	5.0	0.15	42	6.3	0.20	20	4.0	66.51	Yes	
0.20	18	3.6	0.15	42	6.3	0.20	13	2.6	69.65	Yes	
0.20	25	5.0	0.15	42	6.3	0.20	15	3.0	68.51	Yes	
0.20	15	3.0	0.15	5	0.75	0.20	16	3.2	3.19	Yes	
0.20	22	4.4	0.15	5	0.75	0.20	17	3.4	3.06	Yes	
0.20	22	4.4	0.15	40	6.0	0.20	12	2.4	53.92	Yes	Previous treatment consisted of calcination at 1600 F for 2 hrs., and reduction with H ₂ for 2 hrs.
0.2	25	5.0	0.15	40	6.0	0.2	12	2.4	56.93	Yes	
0.2	17	3.4	0.15	45	6.75	0.2	13	2.6	60.40	Yes	
0.2	12	2.4	0.15	40	6.0	0.2	15	3.0	52.14	Yes	
0.2	19	3.8	0.15	40	6.0	0.2	12	2.4	54.18	Yes	
0.2	21	4.2	0.15	5	0.75	0.2	10	2.0	0.93	Yes	

Description of Test		Date	Temperature	Water Flow	
Ore	No. ¹		F	Excess	Time
				g	min
None	36	18 Aug.	1420	200	14
None	37	18 "	1420	230	14
None	38	19 "	1420	1000	--
None	39	21 "	1420	200	10
None	40	21 "	1420	200	11
None	41	21 "	1420	250	14
None	42	22 "	1420	230	11
None	43	22 "	1420	230	10
None	44	23 "	1420	200	10
None	45	23 "	1420	250	10
None	46	26 "	1420	200	9
None	47	26 "	1420	400	18
None	48	27 "	1420	200	12
None	49	11 Sept.	1420	200	12
None	50	11 "	1420	200	10
None	51	13 "	1420	280	12
None	52	13 "	1420	230	9
Durkee	9 (26)	15 "	1420	500	23
Durkee	10 (27)	15 "	1420	400	18
Durkee	11 (28)	15 "	1420	400	22
Durkee	12 (29)	15 "	1420	400	23

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Diaspore Present	Notes
<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	g		
0.2	12	2.4	0.15	5	0.75	0.2	?	?	---	Yes	N ₂ supply exhausted
0.2	13	2.6	0.15	5	0.75	0.2	16	3.2	2.89	Yes	
0.2	15	3.0	0.15	5	0.75	0.2	15	3.0	2.15	Yes	
0.2	22	4.4	0.15	5	0.75	0.2	15	3.0	2.70	Yes	
0.2	18	3.6	0.15	5	0.75	0.2	14	2.8	2.07	Yes	
0.2	19	3.8	0.15	5	0.75	0.2	16	3.2	1.57	Yes	
0.2	16	3.2	0.15	6	0.90	0.2	10	2.0	2.32	Yes	
0.2	18	3.6	0.15	6	0.90	0.2	12	2.4	2.08	Yes	
0.2	24	4.8	0.15	24	3.6	0.2	14	2.8	1.53	Yes	
0.2	16	3.2	0.15	6	0.9	0.2	15	3.0	13.56	Yes	
0.2	24	4.8	0.15	6	0.9	0.2	15	3.0	13.92	Yes	
0.2	18	3.6	0.15	20	3.0	0.2	15	3.0	34.12	Yes	
0.2	29	5.8	0.15	20	3.0	0.2	20	4.0	36.39	Yes	
0.2	18	3.6	0.15	6	0.9	0.2	12	2.4	1.41	Yes	
0.2	21	4.2	0.15	20	3.0	0.2	13	2.6	2.24	Yes	
0.2	22	4.4	0.15	6	0.9	0.2	15	3.0	14.54	Yes	
0.2	25	5.0	0.15	6	0.9	0.2	15	3.0	15.86	Yes	
0.2	23	4.6	0.15	20	3.0	0.2	18	3.6	38.29	Yes	
0.2	20	4.0	0.15	20	3.0	0.2	23	4.6	40.6	Yes	
0.2	15	3.0	0.15	20	3.0	0.2	16	3.2	5.26	Yes	
0.2	25	5.0	0.15	6	0.9	0.2	15	3.0	1.67	Yes	
0.2	17	3.4	0.15	20	3.0	0.2	15	3.0	3.85	Yes	

Description of Test		Date	Temperature	Water Flow	
Ore	No. ¹		F	Excess	Time
				g	min
None	53	16 Sept.	1420	240	9
None	54	16 "	1420	240	8
None	55	31 Dec.	1420	200	11

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Diaspore Present	Notes
<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> <u>min</u>	Time min	Quan- tity cu ft	g		
0.2	17	3.4	0.15	20	3.0	0.2	15	3.0	3.48	Yes	
0.2	17	3.4	0.15	7	1.05	0.2	29	5.8	2.24	Yes	
0.2	17	3.4	0.15	6	0.9	0.2	15	3.0	0.96	No	Reactor brushed out, filter installed.
0.2	16	3.2	0.15	6	0.9	0.2	15	3.0	0.95	No	
0.2	15	3.0	0.15	20	3.0	0.2	15	3.0	1.09	No	
0.2	15	3.0	0.15	20	3.0	0.2	19	3.8	1.1	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	2.1	Yes	New diaspore used.
0.2	20	4.0	0.15	6	0.9	0.2	20	4.0	5.03	Yes	
0.2	18	3.6	0.15	6	0.9	0.2	18	3.6	3.32	Yes	Reactor brushed out.
0.2	18	3.6	0.15	6	0.9	0.2	18	3.6	5.86	Yes	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	1.08	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	1.01	No	
0.2	16	3.2	0.15	6	0.9	0.2	15	3.0	5.36	Yes	
0.2	15	3.0	0.15	6	0.9	0.2	14	2.8	4.34	Yes	
0.2	15	3.0	0.15	6	0.9	0.2	14	2.8	3.98	Yes	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	1.06	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	0.84	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	10.13	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	9.66	No	
0.2	15	3.0	0.15	40	6.0	0.2	15	3.0	39.71	No	
0.2	15	3.0	0.15	40	6.0	0.2	15	3.0	41.14	No	

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Diaspore Present	Notes
<u>Rate</u> <u>cu ft</u> min	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> min	Time min	Quan- tity cu ft	<u>Rate</u> <u>cu ft</u> min	Time min	Quan- tity cu ft	g		
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	0.95	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	0.85	No	
0.2	15	3.0	0.15	6	0.9	0.2	15	3.0	0.84	No	

¹ Numbers in parentheses correspond to number of test in Laboratory Notebook containing pages 3151 to 3225

APPENDIX B

Description of Test		Date	Steam Flow			
Ore	No. ¹		Rate <u>lb</u> min	Time min	Quan- tity g	Excess g
Durkee	13(30)	1 Jan. (1948)	0.03	2	27.2	4
Durkee	14(31)	2 "	0.03	2	27.2	6
Durkee	15(32)	2 "	0.03	1	13.6	---
Durkee	16(33)	3 "	0.0325	1	14.75	---
Durkee	17(34)	3 "	0.032	1	14.7	---
Durkee	18(35)	3 "	0.0305	1	13.87	---
Durkee	19(36)	3 July	0.0321	0.933	13.62	---
Durkee	20(37)	3 "	0.0286	1.05	13.62	---
Durkee	21(38)	6 "	0.033	0.917	13.65	---
Durkee	22(39)	8 "	0.033	2.0	30.0	4
Durkee	23(40)	20 "	?	1.75	---	---
Durkee	24(41)	20 "	?	2.035	---	---
Durkee	25(42)	22 "	0.0278	2.14	27.0	4.5
Durkee	26(43)	22 "	0.0326	2.09	30.9	6
Durkee	27(44)	24 "	0.0273	2.17	26.9	4
Durkee	28(45)	24 "	0.028	3.22	40.9	8
Durkee	29(46)	30 "	0.032	3.00	43.6	6
Durkee	30(47)	30 "	0.033	2.75	41.2	6
Durkee	31(48)	30 "	0.0321	3.75	54.8	14.5
None	56	31 "	0.0321	14	202.	200.
Mo. Brown	9(26)	31 "	0.031	0.968	13.65	2.5

Description of Test			Date	Steam Flow			
Ore	No. ¹			Rate <u>lb</u> min	Time min	Quan- tity g	Excess g
Mo. Brown	10(27)	2	Aug.	0.0291	1.033	13.65	---
Mo. Brown	11(28)	2	"	0.0	0.0	0.0	0.0
Mo. Brown	12(29)	2	"	0.0	0.0	0.0	0.0
Mo. Brown	13(30)	2	"	0.0	0.0	0.0	0.0
Mo. Brown	14(31)	7	"	0.0	0.0	0.0	0.0
Mo. Brown	15(32)	7	"	0.0	0.0	0.0	0.0
Mo. Brown	16(33)	7	"	0.0	0.0	0.0	0.0
Mo. Brown	17(34)	9	"	0.0284	2.04	26.3	3.5
Mo. Brown	18(35)	9	"	0.0284	2.12	27.4	4.0
Mo. Brown	19(36)	9	"	0.0308	1.95	27.3	4.0
Mo. Brown	20(37)	9	"	0.0268	2.135	26.0	4.5
Mo. Brown	21(38)	10	"	0.0	0.0	0.0	0.0
Mo. Brown	22(39)	10	"	0.0291	4.12	54.3	10.5
Mo. Brown	23(40)	10	"	0.0286	4.21	54.6	13.5
Mo. Brown	24(41)	10	"	0.0319	3.77	54.6	14.
Mo. Brown	25(42)	11	"	0.0308	3.89	54.4	15.5
Mo. Brown	26(43)	11	"	0.0	0.0	0.0	0.0
Mo. Brown	27(44)	11	"	0.0	0.0	0.0	0.0
None	57	12	"	0.0368	12.	201.	200.
Iron Sinter	10(22)	13	"	0.0	0.0	0.0	0.0
Iron Sinter	11(23)	14	"	0.0	0.0	0.0	0.0
Iron Sinter	12(24)	18	"	0.0	0.0	0.0	0.0

Description of Test		Date	Steam Flow			
Ore	No. ¹		Rate <u>lb</u> min	Time min	Quan- tity g	Excess g
Iron Sinter	13(25)	23 Aug.	0.0295	2.03	27.2	3.5
Iron Sinter	14(26)	23 "	0.0326	1.83	27.1	3.
Iron Sinter	15(27)	23 "	0.0299	2.0	27.1	3.
Iron Sinter	16(28)	23 "	0.0309	1.93	27.1	3.
Iron Sinter	17(29)	24 "	0.0	0.0	0.0	0.0
Iron Sinter	18(30)	24 "	0.0304	3.95	54.5	10.
Iron Sinter	19(31)	24 "	0.0309	3.89	54.5	15.
Iron Sinter	20(32)	24 "	0.03	4.	54.5	19.
None	58	25 "	---	13.	---	200.

EXPERIMENTAL DATA FROM CONTROLLED OXIDATION TESTS

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Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Notes
Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	Rate cu ft min	Time min	Quan- tity cu ft	g	T = 1420 F No Diaspore Present
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	25.06	After 40-min. Reduction
0.2	18	3.6	0.15	40	6.0	0.20	15	3.0	25.1	
0.2	16	3.2	0.15	40	6.0	0.20	15	3.0	19.74	
0.2	15	3.0	0.15	40	6.0	0.20	20	4.0	16.92	
0.2	15	3.0	0.15	43	6.45	0.20	15	3.0	14.4	
0.2	16	3.2	0.15	40	6.0	0.20	15	3.0	11.76	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	14.65	After 40-min. reduction; water rates in previous tests of this group are considered to be inaccurate.
0.2	16	3.2	0.15	40	6.0	0.20	15	3.0	13.75	
0.2	15	3.0	0.15	44	6.6	0.20	15	3.0	13.92	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	22.07	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	---	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	---	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	20.8	
0.2	15	3.0	0.15	45	6.75	0.20	15	3.0	24.38	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	22.27	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	24.63	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	27.24	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	27.08	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	29.47	
0.20	15	3.0	0.15	6	0.9	0.20	15	3.0	0.89	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	33.9	After 40-min. Reduction

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Notes
<u>Rate</u> cu ft min	Time min	Quan- tity cu ft	<u>Rate</u> cu ft min	Time min	Quan- tity cu ft	<u>Rate</u> cu ft min	Time min	Quan- tity cu ft	g	
0.20	15	3.0	0.15	40	6.0	0.20	15	3.0	33.67	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	30.42	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	28.28	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	23.48	
0.2	8.	1.6	0.15	120	18.	0.20	15	3.0	31.45	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	1.92	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	1.49	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	15.99	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	20.81	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	20.04	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	19.73	
0.2	1.0	0.2	0.15	40	6.0	0.20	15	3.0	2.07	
0.20	15.	3.0	0.15	40	6.0	0.20	15	3.0	29.91	
0.20	15.	3.0	0.15	40	6.0	0.20	15	3.0	32.35	
0.20	15.	3.0	0.15	40	6.0	0.20	15	3.0	30.56	
0.20	15.	3.0	0.15	40	6.0	0.20	15	3.0	32.73	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	28.94	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	1.42	After 40-min reduction and 15-min drying.
0.20	15.	3.0	0.15	6	0.9	0.20	15	3.0	1.18	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	30.3	After 75-min reduction and 15-min drying.
0.0	0.0	0.0	0.15	18	2.7	0.20	15	3.0	11.28	After 40-min reduction and 15-min drying.
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	3.0	After 100-min reduction and 15-min drying.

Nitrogen Flow			Hydrogen Flow			Nitrogen Flow			Water Collected	Notes
<u>Rate</u> <u>cu ft</u> <u>min</u>	<u>Time</u> <u>min</u>	<u>Quan-</u> <u>tity</u> <u>cu ft</u>	<u>Rate</u> <u>cu ft</u> <u>min</u>	<u>Time</u> <u>min</u>	<u>Quan-</u> <u>tity</u> <u>cu ft</u>	<u>Rate</u> <u>cu ft</u> <u>min</u>	<u>Time</u> <u>min</u>	<u>Quan-</u> <u>tity</u> <u>cu ft</u>	g	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	24.76	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	21.55	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	23.07	
0.2	15	3.0	0.15	40	6.0	0.20	15	3.0	23.28	
0.0	0.0	0.0	0.15	40	6.0	0.20	15	3.0	1.39	After 40-min reduction and 15-min drying.
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	30.45	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	30.7	
0.2	15.	3.0	0.15	40	6.0	0.20	15	3.0	30.76	
0.2	15.	3.0	0.15	6	6.90	0.20	15	3.0	1.19	

¹ Numbers in parentheses correspond to number of test in Laboratory Notebook containing pages 3151 to 3225.

APPENDIX C

CHEMICAL ANALYSES OF ORES

Samples of approximately 25 g of each ore were powdered in a mortar, placed in an oven at 105 C, and dried over night.

Method for determination of ignition loss: Weigh out a 0.5 g sample of the ore in a tared crucible and heat for one hour at 1500 F.

Results of ignition loss determination:

	Spathic Ore	Brown Ore	Iron Sinter
Weight of crucible			
and ore	18.4488g	19.6900g	19.5295g
Weight of crucible	13.7342g	14.7850g	14.1270g
Weight of ore	4.7146g	4.9050g	5.4025g
Weight of crucible and			
ore after igniting	18.6458g	19.1380g	19.5634g
Per cent loss in			
weight	-4.18%	11.24%	-0.63%

Method for determination of silica: Weigh out a 2g sample of the ore into a 400 ml beaker and add 20 ml of concentrated hydrochloric acid. After digestion on a hot plate add 15 to 20 ml of perchloric acid and evaporate to fumes of HClO_4 . Cool and dilute to a volume of 200 ml. Filter

off the precipitate, ignite, and weigh.

Results of silica determination:

	Spathic Ore	Brown Ore	Iron Sinter
Weight of sample	2.1796g	2.1432g	2.2963g
Weight of crucible and precipitate	10.7195g	9.7212g	9.9646g
Weight of crucible	10.4604g	9.6255g	9.9210g
Weight of precipitate	0.2591g	0.0957g	0.0436g
Per cent silica	11.887%	4.465%	1.899%

Method for determination of iron: Place filtrate from silica determination in 500 ml volumetric flask. Take 50 ml sample, add 20 ml concentrated hydrochloric acid, and heat to boiling. Add stannous chloride solution until color of ferric ion disappears and then two drops more. Cool, dilute to 300 ml in volume, add 15 ml mercurous chloride solution, and 5 ml of concentrated sulfuric acid. After 15 minutes, add barium-diphenylamine-sulfonate indicator, and titrate with 0.1 N potassium dichromate solution.

Results of iron determination:

	Spathic Ore	Brown Ore	Iron Sinter
Aliquot part	0.10	0.10	0.10
0.1 N $K_2Cr_2O_7$	18.3 ml	21.8 ml	27.93ml
Weight of iron			
in sample	1.022g	1.2175g	1.560g
Per cent iron	46.88%	56.80%	67.92%

Method for determination of manganese: Take 100 ml sample of solution in volumetric flask, add 10 ml of 70 per cent perchloric acid, and heat on hot plate to fumes of $HClO_4$ for 10 minutes. Cool, add 12 ml of boiled, concentrated nitric acid, and dilute to 50 ml in volume. Add 2 g of sodium bismuthate and agitate for 1 minute. Dilute with an equal volume of cool water and filter through asbestos, washing with 3 per cent nitric acid solution. Titrate with 0.1 N ferrous ammonium sulfate solution.

Results of manganese determination:

	Spathic Ore	Brown Ore	Iron Sinter
Aliquot part	0.20	0.20	0.20
0.1 N $FeSO_4(NH_4)_2SO_4$	10.05 ml	0.10 ml	0.20ml
Weight of Manganese			
in sample	0.0552g	0.00055g	0.0011g
Per cent manganese	2.53%	0.026%	0.048%

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