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SPONGE IRON AND DIRECT-IRON PROCESSES

By Edward P. Barrett

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SPONGE IRON AND DIRECT-IRON PROCESSES [1]

By

Edward P. Barrett [2]

Introduction

SPONGE IRON has been defined as the metallic product formed by the reduction (removal of combined oxygen) of iron ore or other iron oxides at temperatures below the fusion point of iron. This product probably derived the name "sponge iron" from its porous nature.

When the reduction proceeds at slightly higher temperatures and the particles of metal weld together or finally even melt to yield pellets or balls that lack the porosity and low-density characteristic of sponge iron, the product might more correctly be called "direct iron."

This bulletin presents a general description of methods that have been proposed or tried for the production of sponge iron and direct iron.

The extensive literature on these subjects has been abstracted and quoted freely. Publications containing more detailed information on the different methods are cited in the footnotes and in the bibliography.

The history of sponge iron has been so discouraging that many men in the iron and steel industry are violently opposed to giving it any further consideration. Costs usually have been high and quality low. Some monumental failures on record tend to restrain capital. Under present conditions no one has the temerity to view any proposed kind of sponge iron as a general replacement for the standard metallury of iron. There are some, however, who still believe that a sponge-iron process may prove useful in certain localities as a supplement to the existing industry; this bulletin should therefore interest those courageous individuals. Those areas in this country and in the world where coking coal is not available must look to sponge iron and other forms of direct iron as the basis for at least small economical production of iron and steel products. Also, in time of war the cost of adding more coke ovens and blast furnaces to be used only temporarily invites attention to the possibility of producing a usable melting stock more quickly and with less expenditure of capital. War activity slows down the building industry, and the brick and cement industries suffer. If their plants can be diverted in part to producing such a melting stock, which will supplement the short supplies of scrap, even at a higher cost, the over-all national economy will benefit.

There are as many grades of sponge iron as there are iron ores. Usually the grade of a sponge iron is of no better quality than the ore from which it can be made. Sponge iron in powdered form may be of high chemical quality, but it melts slowly. When used in a melting furnace, it must be in compacted masses, pigs, or briquets low in sulfur and preferably low in phosphorus. Acutal control of its sulfur content was made possible through the work of the Bureau of Mines during World War II and shortly thereafter. Reappraisal of its utility in view of these improvements is now in order.

ACKNOWLEDGMENTS

This bulletin is one of many covering the various aspects of the Bureau of Mines program directed toward the more effective utilization of our mineral resources. The work reported herein fell within the scope of the former Metallurgical Branch, whose activities embraced the separation of difficultly beneficiated ores, the production of pure metals from domestic deposits, the exploitation of marginal-ore reserves, the recovery of secondary metals, and the improvement of present industrial metallurgical practice.

This bulletin was prepared under the general supervision of Oliver C. Ralston, chief metallurgist, Bureau of Mines, Washington, D. C. The Bureau of Mines is grateful to the American Institute of Mining and Metallurgical Engineers for permission to use material appearing in the bibliography and to P. E. Cavanagh, Ontario Research Foundation, for permission to use abstracts of an unpublished manuscript on the Wiberg process. The author is also indebted to the many other persons who assisted in the preparation of this report.

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[1] Work on manuscript completed July 1951.

[2] Consulting engineer, Bureau of Mines.

REVIEW OF PROCESSES

This review must necessarily be limited to a general outline of the most important developments. Although many investigators in various countries have experimented with sponge iron, available records are very incomplete. Few attempts have been made to pool the knowledge and experience gained by different experimenters, partly because there was little incentive to record reasons for failure and partly because of the desire to keep trade secrets. Other processes for direct reduction of iron ore to metal, such as the Basset rotary-kiln process, which does not produce sponge, are mentioned only briefly or omitted.

PRIMITIVE SMELTING

The first iron weapons were hammered out of masses of meteoric iron. Later, probably before the period of authentic history, men discovered how to reduce iron from its ores with charcoal. Fires were built in rude pits in the ground, and from these a crude furnace was gradually developed by digging deeper pits lined with clay. Rude bellows made of hides forced air into the mixture of charcoal and ore in the pits. If the temperature was high enough, the reduced iron softened and tended to settle and gather at the bottom of the pit into a bloom that could be removed. Gradually, laborious hammering and reheating freed the bloom of slag and adhering charcoal, and it was formed into bars and other shapes.

This process, with modifications, was used widely. It had the advantage of producing iron direct from the ore in one operation and was simple in principle, although it required much hand labor and painstaking skill for successful operation. The process was crude and inefficient; it consumed a large quantity of charcoal (3,500 to 5,000 pounds per ton of blooms) and often required carefully hand-picked ore. The final temperature was so low that few of the impurities in the ore were reduced, and a very pure iron, except for a small proportion of occluded slag, resulted, but at the cost of a large loss of iron through imperfect reduction or by oxidation.

In certain districts of China the native method evolved the process still employed in one district of Shansi Province. Ore mixed with half its weight of coal is packed in cylindrical clay crucibles 4 feet long and 5 inches in diameter; 250 to 275 crucibles are placed upright in an enclosure about 12 feet long and 4 feet wide, and coal is packed around them. Air enters by natural draft at the bottom through interstices in the floor, which is made of old crucible butts. The charge is heated for about 3 days. Small blooms formed at the bottom of the crucibles, where the heat is most intense, are worked with infinite labor and care into many kinds of wrought-iron objects. In the upper part of the crucibles the iron forms in small pellets; these are often melted with more coal in a crucible furnace heated by a hand blower to make cast iron for small castings.

PROCESSES FOR PRODUCTION OF SPONGE IRON

The earliest recorded attempt to produce sponge iron is said to have been made in England in 1837, where the iron was used in processes for extracting copper.[3] In 1859 Bronac and Deberrypon used the same method for precipitating copper in the dry way, and Gossage introduced sponge iron as a precipitant of copper from leaching solutions. In this early work in England several types of furnaces were proposed, but the one most generally used was a coal-fired, airtight reverberatory heated bright red. The charge was 6 inches deep and consisted of coal and either pyrite cinder or iron ore; it was turned over two or three times during the reduction, and the reduced material was discharged into airtight sheet-iron boxes. Reduction required 9 to 12 hours for the part of the charge nearest the fire bridge, 18 hours for the next, and 24 hours for that farthest from the fire bridge.

Since this early attempt hundreds of methods have been patented, and many serious attempts have been made to develop a workable sponge-iron process. Most of the earlier processes are described briefly by Tiemann.[4] In some of them sponge iron for use in copper-extraction processes was sought, but in most of them a product for use in the manufacture of steel was the objective. Only experiments that have technical or historical importance can be reviewed here. They are grouped according to type of furnace and method of heating the charge.

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[3] Lunge, George, Manufacture of Sulfuric Acid and Alkali, with the Collateral Branches: New York, vol. 1, pt. 3, 1913, pp. 1506–1516.
Greenawalt, W. E., Hydrometallurgy of Copper: New York, 1912, pp. 273–277.
Wagner's Jahresbericht: 1862, p. 133; 1863, p. 153.

[4] Tiemann, H. P., Iron and Steel Handbook: McGraw-Hill Book Co., Inc., New York, 2d ed., 1919, pp. 134–148.

METHODS USING MULTIPLE-UNIT CHARGES [5]

Twynam Process.—Briquets of ore and carbonaceous matter were thrown into the bath of metal in a basic open-hearth furnace.

Rudolphs-Landin Process.—Briquets of fine ore, carbonaceous material, and fluxes were dried, the iron was reduced while passing through a long furnace, and the reduced briquets were melted in a reverberatory furnace.

Leckie Process.—Briquets of ore and coal or peat were heated and reduced in chambers connecting with an open-hearth furnace containing a bath of pig iron in which they were then melted.

Gerhardt Process.—Briquets of ore, flux, carbonaceous material, and tar were heated in a puddling furnace to produce blooms of reduced iron.

Larkins Process.—Magnetic concentrates were molded into bricks with carbonaceous matter and placed in D-shaped retorts, which were externally heated by gas. Reduced-iron powder was obtained after the retorts had been kept at a red heat for 24 hours.

Du Puy Process.—Charges of about 116 pounds each of ground iron ore mixed with carbonaceous matter and fluxes were packed in cylindrical sheet-iron canisters, which were about 13 inches high and 15 inches in diameter and weighed 6 pounds. The charges were heated to welding heat 5 to 10 hours on the coke-covered hearth of a common open reverberatory furnace. The reduced iron, still in its canister, was either melted in the same furnace with cast iron and then hammered to muck bars or was melted in the open hearth.

Lang Process.[6]—In 1920 Lang patented a similar process, which is said to have been used in the production of steel at Monterey, Calif. Powdered ore and coal were mixed and packed in cylindrical steel shells, which were heated in a reverberatory furnace, where they passed from the cool to the hot end while reduction of the ore took place. The product was dropped directly into an electric furnace, melted, and refined into steel.

Sieurin Process.—At Höganäs, Sweden, in 1909 Sieurin [7] developed a process that proved applicable to conditions in that country. By this process approximately 3,700 tons of metal was produced in 1911, 4,000 tons in 1912, 7,000 tons each year from 1913 to 1920, and 10,000 tons a year by 1930. The plant was still in operation in 1951.

Sieurin used a tunnel kiln [8] fired with gas from Swedish coal. The charge, consisting of ore, lime, and coal spread in layers, was placed in saggers and run on cars into the kiln for reduction exactly as brick is charged for burning.

VERTICAL RETORT FURNACES—PROCESSES

Many attempts have been made to use externally heated vertical retorts or shafts containing a charge of ore mixed with carbonaceous material. In the continuous process the charge is fed at the top of the retort and passes down through it; reduced iron, with residual carbon and gangue, is discharged at the bottom. The heat necessary for preheating the charge and for the reduction reactions is generated by burning gas, oil, or coal around the outside of the retort and is transmitted to the charge by conduction through the walls. Naturally, there is a large heat gradient from the outside walls of the retort to the center of the charge.

Chenot Process.[9]—High-grade ore mixed with a slight excess of charcoal (about 1.5 tons of calcined ore to 0.5 ton of charcoal) was charged into the top of vertical, rectangular retorts 28 to 33 feet high, 1½ feet wide, and 5 to 6½ feet long. The upper part of each retort was made of firebrick; it was surrounded and heated by a series of vertical flues, open at the top and connecting below with fireplaces. The bottom section was of sheet iron, water-jacketed to receive and keep the iron sponge out of contact with the air until cold. Operation was continuous, and the reduction stage in the upper section of the retort required about 3 days. The cooled sponge was melted in crucibles. Later, Chenot tried to heat and reduce the ore by passing a stream of hot producer gas through it instead of mixing it with carbon.

Blair Process .[10]—About 1870 Blair treated ore and charcoal in retorts about 4½ feet in diameter and 40 to 50 feet high; his process was similar to that of Chenot, with the cooling chamber at the bottom of the retort. The discharged sponge iron was cool and did not reoxidize. It was pressed into blooms or, when in lumps, used direct and charged in place of scrap into an open-hearth furnace for melting. Blair also tried hot producer gas for reducing the ore but without success.

Morse Process.—H. W. Morse tried to produce sponge iron in vertical retorts at Fitchburg, Mass., in October 1917 and reported the results in a manuscript dated March 1918. He conducted a series of tests with a continuous ver-

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[5] Tiemann, H. P., Work cited in footnote 4 for the first six processes described.

[6] Lang, Herbert, Another Direct Process for Steel Making: Iron Age, vol. 107, 1921, p. 1237.

[7] Sieurin, E., Höganäs Jarnsvamp: Pres. at meeting, Technical Institute of Ironworkers, Stockholm, Sweden, 1913. [The Manufacture of Sponge Iron. Historical and Statistical Handbook of Sweden]: Stockholm, 2d ed., pt. 2, 1914, pp. 285–286.

[8] Dressler, Philip, Adaptation of Tunnel and Car Kilns to Firing Refractories: Jour. Am. Ceram. Soc., vol. 8, 1925, pp. 43–54.

[9] Tiemann, H. P., Iron and Steel Handbook: New York, 2d ed., 1919, pp. 134–148.
Harbord, F. W., and Hall, J. W., Metallurgy of Iron and Steel: Philadelphia, 4th ed., 1911, pp. 291–295.

[10] See footnote 9.

tical fire-clay retort of the Fitchburg Gas & Electric Co., one of a battery of eight retorts of the Glover-West type made by the Didier-March Co. and ordinarily used for coking coal. The retorts are oval, measuring 18 by 32½ inches at the bottom, 10½ by 27 inches at the top, and 24 feet in height, with walls 3½ inches thick. They are surrounded by checkerwork flues into which gas and air are admitted. Gas is fed into the checkerwork 4 feet above the base, so that the upper 20 feet is heated. Cold air enters at the base, cools the lower 4 feet of the retort, and then meets the gas and burns in the upper 20 feet. A worm mechanism for discharging lies in the chamber on which the retort rests. In the tests on iron ore this discharging device held up the charge satisfactorily when the product was spongy but allowed the entire contents of the retort to discharge rapidly when the product was sandy.

After a few failures a fairly good sponge iron containing about 69 percent of metallic iron was made. Morse estimated that for economical operation the charge would pass through the retort so fast that the product would contain only about 40 percent of metallic iron. A temperature of at least 1,300° C. had to be maintained in the combustion flues around the retort. The exhaust gases from the flues left the bench above 1,000° C., causing a large waste-heat loss. Part of this loss probably could be recovered by using the gases to preheat the charge before it enters the top of the retort. The charge contained 100 parts of magnetite and 30 parts of coal. It was estimated that 15 to 24 hours was required to produce a fairly well reduced iron in the form of loose grains; to obtain iron of the same copper-precipitating value, but in the form of a coherent sponge, about 40 hours was necessary.

In general, the few tests made showed that the reduction required more time and heat input than had been anticipated and that the rate of heat transmission through the retort walls and charge was slower than expected. In consequence, the capacity tends to be low; this and the high first cost of the installation are serious disadvantages. Morse recommended that in future experiments the retorts should be made thinner and of silicon carbide instead of clay, thus giving better refractoriness, greater heat conductivity, and greater mechanical strength and resistance to abrasion. He also advised changing the dimensions of the retorts to about 6 by 36 inches at the top and 12 by 42 inches at the bottom.

Conclusions Regarding Externally Heated Retort Furnaces.—The following conclusions have been reached regarding externally heated retort furnaces:

1. The reduction reactions absorb so much heat that the output of sponge iron is limited by the rate of heat flow into the charge.
2. The charge conducts heat slowly. If the retort walls become too hot in an attempt to increase the flow of heat, the charge fuses and sticks to the walls.
3. When fine ore particles are showered through the reducing gases, the period of fall in retorts of reasonable height is too short to effect appreciable reduction.

(*a*) Insufficient gas is available to reduce a reasonable quantity of ore.

(*b*) Unless the velocity of the heated gas in the shaft is very slow, the ore particles will be carried over the top.

ROTARY-HEARTH FURNACE

DEVELOPMENT BY CHINO COPPER CO.

In 1920 Thornhill [11] and H. G. S. Anderson designed a very different type of furnace, which was brought to the point of commercial operation and may be regarded as the culmination of extended and careful experiments by the Chino Copper Co.

EXPERIMENTAL FURNACE

One of the first experimental furnaces was about 2 feet high; it had an arched top, a hearth about 2½ feet in diameter, and two 6-inch carborundum tubes above the hearth for heating. This furnace produced sponge iron at the rate of about 20 pounds an hour or 500 pounds a day. A larger furnace installed later was successful. According to reports, its maximum capacity was about 7 tons of sponge iron a day. The furnace was enclosed in firebrick rigidly contained in heavy structural steel, was 12 feet in inside diameter, and had seven carborundum tubes for heating. Each tube was 8 inches in inside diameter, with a 1-inch wall, and was made of five 30-inch lengths fitted together like tile pipe. The clean, high-grade sponge iron produced by this process proved an excellent precipitant for copper. The muffled type of heating was efficient in the use of fuel as reducing agent but inefficient in its use for heating. Plant costs and maintenance charges were high. A plant designed to produce 100 tons of iron daily failed in Kuji, Japan, in 1927.

ROTARY-KILN FURNACE

Many attempts have been made to reduce iron ores in rotary kilns. The usual type of kiln is a horizontal or slightly inclined rotating

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[11] Thornhill, E. B., Apparatus for Production of Sponge Iron and Other Metallic Products: United States Patent 1,452,626, Apr. 24, 1923; Process for the Production of Sponge Iron and Other Metallic Products: United States Patent 1,452,627, Apr. 24, 1923.
Iron Age, Washington Prods Under Tombstones in Graveyard of Sponge-Iron Processes: July 23, 1942, pp. 81–83.

cylinder commonly made of steel and lined with firebrick or other refractory material. Such a furnace can be used to advantage for heating charges in either a batch or a continuous process. Ore or an ore-coal mixture is fed at the upper end. The charge, which ordinarily fills one-fifth to one-third of the volume of the cylinder, is heated with oil, gas, or pulverized-coal burners or with hot reducing gases introduced at the lower end. Rotation of the kiln thoroughly mixes the charge and exposes it to the heating or reducing gases present; the charge is also heated rapidly by continual contact of fresh portions with the hot walls of the kiln.

JONES PROCESS

J. T. Jones made extensive experiments with this process. Most of the work[12] seems to have been done from 1907 to 1912. Jones and his associates patented[13] several furnaces and many ideas for sponge-iron production, but the main idea is that of reducing iron ores in a rotary kiln and melting the reduced iron in an open-hearth furnace to form steel or balling it in a puddling furnace to obtain wrought iron.

In his earlier work Jones used a rotary kiln with a gas producer adjoining the lower end. Ore fed to the upper end of the kiln passed countercurrent to the flow of gas. After the gas had traveled about two-thirds of the length of the kiln air was introduced to burn it, thus maintaining an oxidizing and heating zone next to the feed end to preheat the ore and drive off the sulfur in the ore. In the lower two-thirds of the kiln, or reducing zone, the hot ore was reduced by the hot gas from the producer and then discharged into cars in a pit below the lower end of the furnace. Jones' patent also specified the optional introduction of a limited quantity of coal just below the oxidizing zone of the kiln. Later, because the temperature was not high enough or because the reducing action of the gas was not strong enough, the furnace seemingly was changed so that coal and ore were both charged together (500 pounds of coal to 2,000 pounds of ore) into the feed end of the kiln while producer gas was admitted at the discharge end with just enough air to generate the required heat and to keep the products of combustion somewhat reducing. Jones seems to have depended on the coal charged to reduce the ore and to have burned the producer gas partly to heat the charge and partly to maintain in the kiln an atmosphere reducing enough to prevent the reduced iron from reoxidizing before discharge.

Jones' later patents described a furnace that comprised two inclined kilns placed end to end, the second slightly lower than the first, which discharged into it. Oil or pulverized coal was to be burned in both sections, but the proportion of air was varied to maintain an oxidizing atmosphere in the first section and a reducing atmosphere in the second or discharge section. The ore feed was crushed to a fineness of ⅛ to 1 inch. The maximum temperature was given as about 940° C. During this investigation furnaces were operated at Iron Mountain and Republic, Mich. One kiln was 120 feet long and 8 feet in diameter. The work seems to have been done on an unnecessarily large scale, considering that it was experimental.

About 1912, having spent much money, Jones discontinued his work because it had not proved commercially successful.

BRUCKNER FURNACE

EXPERIMENTAL WORK

A Bruckner furnace (a short, horizontal rotary kiln) was made by lining a section of a White-Howell furnace with 4½ inches of firebrick and building a 30-inch brick wall in each end. A 12-inch opening was made in one end for an oil burner and an 18-inch opening in the other end for connection to the stack. In one side, midway between the ends, was a 6-inch charging and discharging door. The furnace was 4½ feet in inside diameter and 7 feet long, had a capacity of 2,000 pounds, and was rotated at a rate of 1.28 r. p. m. The charge (1,400 pounds of calcine) was heated with a fuel-oil flame to 700° C. in 1¼ hours; about 600 pounds of coal was then added and the furnace rotated for three-fourths hour, during which time the hydrocarbons burned off. The oil flame was then started again, and in 1¾ to 2 hours the temperature reached 925° C. and reduction was complete. Twenty gallons of oil was consumed per ton of charge. The product had a copper-precipitating value of 1.5, or contained about 59 percent of metallic iron.

In August 1914 a larger Bruckner furnace was tried.[14] It was 7 feet in diameter and 17 feet long within, and its operating capacity was 13,000 pounds of charge consisting of 100 parts of calcine and 40 parts of coal. The furnace revolved at the rate of 2.25 r. p. m. and was heated from one end by burning oil. Burning off the hydrocarbons in the coal required 3 to 4

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[12] Iron Age, The Jones Process for Metallizing Ore: Vol. 88, pt. 2, 1911, p. 1305.

Iron Trade Review, The New Step Process Furnace at Iron Mountain, Mich., for Smelting Ores: Vol. 43, 1908, pp. 771–772; Making Steel Direct From Ores: Vol. 68, 1921, pp. 1375–1376.

[13] Jones, J. T., Method of Reducing Ores: United States Patent 880,799, Mar. 3, 1908. Method of Treating Iron Ores: United States Patent 890,234, June 9, 1908; United States Patent 930,764, Aug. 10, 1909. Method of Treating Ore: United States Patents 891,704 and 891,705, June 23, 1908; United States Patent 899,405, Sept. 22, 1908. Method of Reducing Iron Ore: United States Patent 981,280, Jan. 10, 1911.

Jones, A. G., Metallizing Process: United States Patent 1,174,729, Mar. 7, 1916.

[14] Anaconda Copper Mining Co., Report of Research Department for 1912, 1913, and 1914: 1915. Frederick Laist and F. F. Frick were given credit for the development.

hours and completing the reduction, 4½ hours. The final temperature was 925° C. The reduced product was discharged into airtight boxes and cooled. Quenching in water proved unsatisfactory. From a long-continued test of this furnace cost estimates were made for a plant designed to have two Bruckner furnaces 10 feet in diameter and 23 feet long, lined with 9 inches of brick, and fired with powdered coal instead of oil. Apparently the experimental results were considered promising enough to warrant use of this process if the plant ever needed sponge iron for precipitating copper. The opportunity came in 1951, when a plan for working the upper levels of the Butte (Mont.) area by the Anaconda Copper Mining Co. was approved, and the sponge iron for precipitation of copper in a flotation pulp was included in the plans for a large concentrator.

TESTS AT AJO, ARIZ.

In 1918 or 1919 the New Cornelia Copper Co. made further tests on the production of sponge iron, using a Bruckner oil-fired furnace. The tests paralleled the work of Laist and Frick. A charge consisted of 3,250 pounds (37.5 parts) of coal and 8,610 pounds (100 parts) of pyrite calcines containing 3.2 percent Cu, 52 percent Fe, and 10 percent S. Temperatures were maintained at 760° to 815° C. during the first heat and at 925° to 980° C. during the second. The total time of heating was about 6½ hours, and the consumption of oil was 76 gallons per heat or 17.6 gallons per ton of calcine. The product contained only 27.8 percent metallic iron. A reduction of 72.4 percent of the available iron (that not present as FeS) was obtained. These data represent the average of 25 separate runs. The poor reduction obtained was attributed to the high sulfur content of the calcine; this explanation may be questioned, as the author's work shows that the quantity of coal in the charge was undoubtedly too small for complete reduction.

PROCESSES USING MULTIPLE-HEARTH FURNACE

In 1912 at the plant of the New Cornelia Copper Co., Ajo, Ariz., Croasdale [15] attempted to prepare sponge iron from calcine obtained by roasting iron pyrite in a Wedge double-function furnace. This furnace delivered hot calcine directly to the reducing zone; its three upper hearths were of the ordinary type for roasting sulfide ore, and the three lower ones were muffle hearths heated with oil from outside fireboxes. Both sets were sealed from each other by automatic cast-iron valves, so every effort was made to keep the furnace airtight. Each hearth was connected with the flue. A screw feeder attached to the side of the furnace delivered pulverized coal to the first muffle hearth. The experiment failed, as the temperature of the reducing zone was too low (500° to 700° C.) and could not be increased without warping the clay tiles and burning out the muffle.

TESTS AT ANACONDA, MONT.

In 1913 at the plant of the Anaconda Copper Co. Laist and Frick [16] attempted to prepare sponge iron from iron pyrite containing copper. The pyrite was roasted in a six-hearth McDougall furnace; the calcine contained 14 percent insoluble, 3.4 percent sulfur (S), 56 percent iron (Fe), and 8 percent copper (Cu). Small-scale crucible tests with bituminous coal as the reducing agent gave good results.

A six-hearth McDougall furnace was set up, and hot, partly roasted calcine from another furnace was fed to the first hearth. Roasting was completed and the calcine preheated to 925° C. by oil burners on the third hearth. The three lower hearths had oil-fired muffle floors. Fine coal was fed on the fourth hearth. The muffles failed under the intense heat required to maintain a reducing temperature. They were heated by both oil and coal.

Reduction was incomplete because transfer of heat to the charge was poor and air leaked into the hearth.

PROCESSES INVOLVING REDUCTION BY GASES IN ABSENCE OF SOLID CARBON

Most of the methods described above depend on the reduction of iron ore by solid carbonaceous material mixed and heated in direct contact with the ore. Both carbon monoxide and hydrogen reduce iron oxides, and many attempts have been made to develop a process that employs gases alone for reduction. A practical solution of the problems involved presents many difficulties, such as the generation of reducing gases and the design of furnaces that will use the reducing power of these gases efficiently and yet give a large output of metallic iron.

The proposed methods employ two general types of reduction furnaces—the horizontal revolving kiln and the vertical shaft. As in all methods of producing sponge iron, the main problem is to maintain simultaneously high enough temperatures and strong enough reducing conditions in large masses of ore charge. There is also the problem of generating large volumes of strongly reducing gases cheaply. The reduction reactions between the gas and the iron oxides are not instantaneous; they re-

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[15] Croasdale, Stuart, Leaching Experiments on Ajo Ores: Trans. Am. Inst. Min. Eng., vol. 49, 1914, pp. 648–653.

[16] Laist, F., and Frick, F. F., Precipitation of Copper from Solution at Anaconda: Trans. Am. Inst. Min. Eng., vol. 49, 1914, pp. 694–700.

quire some time, even when temperatures are comparatively high and the ore particles are small. Contact between the gas and the ore charge should be uniform and intimate. A relatively large volume of reducing gas is necessary to reduce a given volume of ore; if the gas passes through the furnace slowly, the capacity of the furnace to produce completely reduced sponge iron becomes small.

Several investigators mentioned have attempted to reduce iron ore with gases. Bourcoud's process involves the treatment of preheated ore in an inclined rotary kiln with hot producer gas having a high content of CO. In his earlier tests with long rotary kilns Jones tried to reduce the hot ore by passing producer gas alone over the charge; apparently the reducing action was not efficient, and he soon began to mix coal with the ore. In his later furnaces Jones seems to have depended almost entirely on coal for reduction and to have used the producer gas, burned incompletely, to maintain the temperature required in the furnace and charge. His experiments indicate that reduction by gases alone could not be accomplished in this type of furnace.

BOURCOUD PROCESS

In 1918 Bourcoud[17] presented the details of his so-called open-cycle process for making reduced iron. Gas made from powdered coal in a special producer is passed over iron ore in a rotating kiln. The reduced iron is pressed into cakes and fed into an electric furnace for melting and refining into steel.

The gas producer[18] was designed to operate on the theoretical principle that at a high enough temperature coal can be burned to produce only the reducing gases carbon monoxide (CO) and hydrogen (H_2). The producer may be a horizontal or a vertical combustion chamber. In the former all of the fuel is burned rapidly, but combustion is incomplete. At the high temperature required the carbon dioxide (CO_2) and water (H_2O) combine with the carbon (C) left to form carbon monoxide (CO) and hydrogen (H_2). In the vertical chamber enough air for complete combustion is introduced with the first powdered coal injected; farther along in the generator chamber enough additional coal is injected to convert the CO_2 and H_2O to CO and H_2. The temperature of the gases at the center of the combustion chamber—probably the point at which reduction to CO takes place—is 1,300° C. As the fuel is finely powdered, the reaction can be rapid. Air going to the producer is preheated on the recuperative principle to 400° C. when the producer is working continuously or to 800° C. when it is working intermittently.

If the reactions are to be completed rapidly enough in such a CO generator, the temperature maintained in the reaction chamber must be high. Dependence on the carbon in the coal to burn to CO to maintain the required temperature of the gases and the furnace chamber leaves a rather small margin of available heat for conduction and other losses. Either auxiliary heating, perhaps by electric resistance coils, or very heavy insulation would probably be necessary in working out the generator design.

The reduction furnace is a horizontal, cylindrical rotating shell lined with refractory tiles shaped to form a helical interior and thus insure that the ore moves forward continuously to meet the gas stream entering from the opposite direction. Most of the waste gas is fed back to the producer. The ore is preheated in a horizontal, cylindrical rotating furnace heated by part of the gas from the reduction furnace. Construction and maintenance of the helical reduction chamber probably would be difficult. Efficient utilization of the reducing power of the CO gas in such a furnace presents another difficulty. Bourcoud's gas producer has been seriously criticized as impracticable; the whole process needs practical demonstration, but his outline of the process contains an interesting and suggestive theoretical discussion. On the whole, however, his process cannot be given much weight until it has been actually tested. F. T. Snyder[19] suggested a similar process.

REDUCTION BY GASES IN SHAFT FURNACE—PROCESSES

In a vertical shaft filled with a slowly descending bed of properly prepared ore the conditions for efficient use of the reducing gas, with reasonably large furnace capacity, should be more favorable. Several investigators have obtained promising experimental results with such furnaces. Chenot used producer gas for reduction in some of his experiments with externally heated vertical retorts.

Tiemann[20] mentions several other so-called direct processes in which gas was to be used to reduce a column of heated ore in vertical shaft furnaces of various designs. Hot producer gas or incompletely burned natural gas was to be passed up the shaft to reduce the ore, with or without auxiliary heating around

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[17] Bourcoud, A. E., Direct Process for Steel Manufacture: Proc. 20th Meeting Am. Iron and Steel Inst., Nov. 18, 1921; Method of and Apparatus for Reducing Metallic Oxides: United States Patent 1,344,977, June 29, 1920.

[18] Bourcoud, A. E., Gasification of Powdered Coal: Chem. and Met. Eng., vol. 24, 1921, p. 600.

[19] Stansfield, Alfred, Commercial Feasibility of the Electric Smelting of Iron Ores in British Columbia: British Columbia Dept. of Mines Bull. 2, 1919, 85 pp.

[20] Tiemann, H. P., Iron and Steel Handbook: McGraw-Hill Book Co., Inc., New York, 2d ed., 1919, pp. 134–148.

TABLE 1.—*Selected list of processes using heated reducing gases*

Date	Inventor	Apparatus	Reducing gas	Temperature, °C.
1876	Lyttle	Shaft furnace	CO and N_2	(1)
1882	Tourangin	do	$CO+H_2+N_2$	620- 780
1920	Bourcoud	Rotary kiln	$CO+H_2$	1,000-1,100
1921	Wiberg	Shaft furnace	CO	900-1,000
1926	Pehrson	Rotary kiln, 2-diameter	Gas	
1926	Parsons and Peacock	Multiple-hearth	$CO+H_2$	800-1,000
1927	Percy	Shaft furnace	H_2+CO	(1)
1928	Bror	Tunnel kiln	CO	900-1,100
1929	do	Tunnel kiln, 3-zone	$CO+H_2$	850-1,200
1931	Percy	Shaft	$CO+H_2$	
1931	Pardee	Endless conveyor	CO	850-1,150
1931	Berry	Shaft furnace	$CO+H_2$	
1932	Gustafsson	Rotary kiln, 3 in series	$CO+H_2$	850-1,000
1934	Stälhane and Stälhane	Rotary kiln	Gas	
1934	Kalling	do	do	
1934	Stälhane and Stälhane	Rotary kiln, 2 in series	$CO+H_2$	1,000-1,200
1934	Brown	2-kiln and shaft	$CO+H_2$	[2] 1,090
1935	Christensen	Multiple chambers, ore in suspension	CO	550-1,050
1935	Thomas	Rotary kiln	$CO+H_2$	1,000
1938	Schmalfeldt	do	CO	750- 900
1939	Avery	Shaft furnace	$CO+H_2$	700-1,100
1939	Clark	Shaft, heated by induction	$CO+H_2$	925-1,040
1941	Foerster	Shaft, externally heated, ore in suspension	$CO+H_2$	
1941	Hardy	Perforated shaking table	CO or H_2	650-1,000
1941	Madaras	Metal retorts, pulsating gas	$CO+H_2$	
1942	Hodson and Hirsch	Shaft, ore in suspension	$CO+H_2$	
1942	Brassert	Hearth, porous ore fluidized	$CO+H_2$	900
1942	Clark	Vertical tube, 100 feet long, heated by induction.	$CO+H_2$	850
1943	Dill	Alloy retort, externally heated, fluidized ore	$CO+H_2$	650-1,100
1943	Payne	Perforated shaking table	$CO+H_2$	900
1943	Brassert and Hartley	Alloy retort, externally heated, porous hearth, fluidized ore.	$CO+H_2$	
1943	Burruss and Drapeau	Stationary hearth, with rabbles	$CO+H_2$	760-1,000
1944	Lewis	Shaft, ore in suspension	CO or H_2	700
1944	Hodson and Hirsch	do	CO	700- 800
1945	Brassert	Movable grate	$CO+H_2$	
1945	Silvasy	Retort, externally heated, ore in suspension	$CO+H_2$	800-1,050
1945	Brassert and Ramseyer	Multiple bubble hearth, ore in suspension	H_2	585- 815
1946	Caldwell	Tubes, externally heated, ore in suspension	CO or H_2	700- 925
1946	Newkirk and Ensign	Kiln, 3 sections, oscillating	H_2	
1946	Brassert	Multiple-hearth, slotted, fluidized ore	H_2	585- 815
1946	Firth	Shaft furnace	$CO+H_2$	950
1947	Riveroll	Shaft, externally heated	Gas	650- 900
1947	Griswold and Cape	Multiple-hearth, porous lower hearth	do	

[1] Highly heated.
[2] Maximum.

the shaft. Few data from actual trials of these proposed methods are available.

Selected List of Processes Using Heated Reducing Gases.—Table 1 lists processes that employ heated reducing gases.

Riveroll Process.—Riveroll [21] proposed to reduce iron ore in a high vertical retort surrounded by a heating chamber in which oil was burned to complete combustion. The hot gases passed into the central chamber, which contained the ore, just below the upper third of its height and thus preheated the ore in an oxidizing atmosphere. The preheated ore moved downward into the reducing zone kept hot by conduction through the walls separating it from the heating chamber. Here the ore was reduced by natural gas or oil vapor admitted near the bottom of the retort. Beneath the heated zone was a cooling zone from which the cool, reduced material was discharged into closed containers or directly into an electric melting furnace.

Much experimental work was done in a furnace of this type at Wilmington, Calif., in 1920. The retort was 40 feet high, 18 inches wide, and 10 feet long and held 35 tons of ore. The temperatures in the charge were said to be 750° to 785° C. The ore passed through the retort in 7 days, and the consumption of natural gas was 10,000 cubic feet per ton of sponge iron

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[21] Riveroll, Elfego, Method of and Apparatus for the Production of Iron and Steel: United States Patent 1,370,915, Mar. 8, 1921. Process for Recovery of Iron from Ore: United States Patent 2,417,949, Mar. 25, 1947.

produced. A sample of the product contained about 45 percent metallic iron, 30 percent unreduced iron oxide, and only a trace of carbon.

E. Mill later remodeled the furnace, placing several large copper rods horizontally across the bottom of the retort. Heat generated by the passage of electricity through these bars was carried upward by the reducing gases. Both Mill and Riveroll claimed that once the temperature of the charge was raised to that of rapid reduction the heat of reaction sufficed to maintain it. Samples of the sponge iron made by Mill were incompletely reduced, doubtless owing to the difficulty of heating such a large mass of ore to 800° or 900° C. by the method employed.

DIRECT-IRON PROCESSES

KRUPP-RENN PROCESS

The Krupp-Renn [22] process is a continuous reduction method for treating low-grade siliceous iron ores in long rotary kilns.

Ore, limestone, and solid fuel, 0.2 to 0.3 inch in size, are mixed with an intermediate product from the slag-crushing process and fed continuously into a long rotary kiln countercurrent to the flow of hot gases. The preheating zone of the kiln is about 20 percent of the total length. The charge becomes heated to about 600° C. by the time it enters the reducing zone, where the continuous evolution of carbon monoxide from the mass protects it from contact with the kiln gases. The temperature increases steadily, and reduction of the iron oxides is complete when the charge enters the lumping or blooming zone at approximately 1,100° C. This last zone comprises about 20 percent of the total length of the kiln and is heated by a powdered-coal burner. Some of the sponge iron oxidizes and forms a slag with the gangue of the ore. The heat of combustion of the iron and the heat of formation of the slag raise the temperature to 1,200° to 1,400 C. The half-soft slag liquates from the skeletons of unburned sponge iron, which then weld together into metal granules coated with stiff slag. In the interior of the charge the FeO is reduced to metal again. The alternate oxidation of the iron on the surface of the charge and its reduction in the interior of the charge continue during the passage through the final zone until the slag is virtually iron-free; much of it is pasted onto the exterior of the roughly spherical lumps of iron that continue to grow in diameter by picking up more small granules that weld to them when pressed through the slag coating. This coating hinders reoxidation of iron in the lower end of the kiln.

The viscous, glassy slag containing the iron granules and excess coke flows from the lower end of the kiln, where it is cooled with water sprays, crushed, and treated on a magnetic separator to recover the iron granules; these usually are 0.06 to 2.0 inches in size. The larger granules are relatively high grade but the smaller ones, finer than 20-mesh, carry so much adhering slag that they are passed through the kiln again.

The time for passage through the kiln is about 7 hours.

Slag Composition.—A CaO/SiO_2 ratio of about 0.09 is desired. Higher ratios increase fuel consumption and above 0.16 cause rings to form about 65 feet from the burner end of the kiln where slag first begins to form.

Slag Volume.—The reaction in the lumping zone requires 1,300 to 1,800 pounds of slag for each ton of lumps.

Average Fuel Consumption.—For reducing iron oxides 1,800 to 1,900 pounds of coke breeze is required per net ton of product. For heating the charge about 580 pounds of pulverized coal is required per net ton of product.

Advantages of Krupp-Renn Process.—The process can be used to recover about 92 percent of the iron in high-silica, low-grade iron ores.

Nickel and copper in the ores will be recovered in the product; chromium remains in the slag.

Any kind of solid carbonaceous fuel can be used.

Disadvantages of Krupp-Renn Process.—Unless low-sulfur fuel is used for reduction, the product contains so much sulfur that it can be charged only to a blast furnace for refining.

The hot zone requires frequent relining.

COMMERCIAL PLANTS

During World War II the Krupp-Renn process was used in Germany and Japan to increase the production of much-needed iron and steel. In 1939, 18 Krupp-Renn furnaces were either in use or under construction in Germany; 2 of them had been operating continuously for 4 years.[23] There were 3 small and 16 large rotary kilns in 8 plants in Japan and 6 rotary kilns each in Korea and Manchuria. All of the plants in Japan used anthracite for reducing the ore and subbituminous coal for firing the kilns. Table 2 gives the name and location of these 31 plants, together with the kind of ores used, size and capacity of the kilns, type of product, and a

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[22] Iron Age, Smelting Low-Grade Ores by the Krupp-Renn Process: Vol. 157, 1946, pp. 70-75.

[23] Johannsen, Friedrich, [The Present Status of the Krupp-Renn Extraction Process]: Stahl u. Eisen, vol. 59, No. 37, 1939, pp. 1041-1046. [The Use of Krupp-Renn Bloom Process in the Far East]: Stahl u. Eisen, vol. 60, 1940, pp. 910-912.

TABLE 2.—*Rotary-kiln plants, Japan, Korea, and Manchuria*

Name of plant and location	Ore used	Kilns, number and size	Rated capacity, ore per 24 hours, metric tons	Type of product	Typical analysis of product, percent
Iwaki Cement Co., Ltd., Nanoa-shi, Ishikawa-ken.	Limonite	1 (3.45 by 88 m.) 2 (3.45 by 73 m.)	212	Ni and Cr luppe	Fe, 94.6; C, 1.13; Si, 0.065; P, 0.097; S, 022; Ni, 1.9; Cr, 1.58.
Kawasaki Heavy Ind. Co., Ltd., Kuji Town, Iwato-ken.	Sandy limonite	2 (3.6 by 60 m.) 1 (1.0 by 8 m.)	152	Luppe	C, 1.5; Si, 0.2; P, 0.24; S, 0.1; Mn, 0.1; Ti, trace.
Nippon Metallurgical Ind. Co., Ltd., Iwataki, Kyoto-ken.	Limonite	4 (3.6 by 70 m.)	288	Nickel luppe	Fe, 93.47; C, 0.80; Si, 0.32; P, 0.113; S, 0.124; Ni, 2.53; Cr, 1.18; Co, 0.10.
Nippon Nickel Co., Ltd., Onishi, Cumma-ken.	Serpentine limonite.	1 (2.8 by 50 m.)	60	do	C, 0.8; Si, 1.8; P, 0.2; S, 0.22; Ni, 1.3; Cr, 0.6; Mn, 0.45.
Nippon Iron Sand Steel Ind. Co., Ltd., Hachinohe.	Leached iron sands.	2 (2.8 by 50 m.)	120	Sponge iron	No data.
Nippon Iron Sand Co., Ltd., Takasago, Hyogo-ken.	do	2 (1.83 by 27 m.) 1 (1.25 by 17 m.)	72	do	Do.
Riken Industrial Corp., Hirai, Tokyo	Limonite, domestic and imported.	2 (2.3 by 38.0 m.)	72	Ni and Cr luppe	Fe, 92.13; C, ?; Si, 1.20; P, 0.05; S, 0.20; Ni, 1.70; Cr, 2.01.
Toa Jyukogyo-sha, Tsukiji. Fukuoka-ken.	Mill scale	1 (1.8 by 30 m.)	36	Sponge iron	Fe, 93.0; C, 0.52; Si, 0.38; P, 0.03; S, 0.18; Mn, 0.32.
Japan total		19	1,012		
Mitsubishi Co., Seishin, Korea	Mosan magnetite	6 (3.6 by 70 m.)	432	Luppe	Fe, 95.0; C, 1.0; SiO_2, 3.5; S, 0.15; P, 0.15.
Manchurian Iron & Steel Co.:					
Anshan, Manchuria	Hematite and magnetite.	4 (3.0 by 60 m.)	240	do	Fe, 97.0; C, 0.7; S, 0.35; P, 0.12; Si, 0.6.
Fushun, Manchuria	Magnetite	2 (3.0 by 60 m.)	120	do	No data.
Grand total		31	1,804		

typical analysis of the product. Johnston[24] reports that these 31 kilns produced 646,385 metric tons of luppe (lumps) during the period 1939–45.

Operation in Czechoslovakia.—During German occupation of Czechoslovakia a Krupp-Renn furnace was built at Kraluv Dvur. The kiln was 197 feet long and 11 feet 10 inches in external diameter. The upper part was lined with ordinary firebrick and the lower part with a special aluminosilicate brick.

The normal burden consisted of a mixture of low-grade Czech ores—Krusna Hora and Zdice—flue dust from two Kraluv Dvur blast furnaces, and coke breeze. Analyses of the burden materials, slag, and metal produced are given in table 3.

Coal, containing about 30 percent ash and 7 percent water, used for firing the kiln amounted to about 10 percent of the weight of the ore, and the coke breeze, containing about 14 percent each ash and water, used for reduction amounted to about 26 percent of the weight of the ore.

A record of five campaigns (February 1946 to November 1948) shows that an average of 72 metric tons of reduced iron containing 92 percent Fe was obtained from 270 tons of 28-percent Fe ore charged daily. The ratio of campaign days in operation to total days gives a kiln availability of 71.4 percent, which is much better than was obtained in either Germany or Japan.

The optimum slag composition for smooth operation on Czech ores is shown in table 3. In normal operation on these ores any rings that formed were easily removed by increasing the quantity of coke breeze and lengthening the pulverized-coal flame. An ore containing a gangue that tends to soften and fuse too far up in the kiln is likely to form rings that cannot be melted down. Apparently, less ringing will occur when the gangue is refractory, with a short fusion range, and melts only after almost all of the iron in the ore has been reduced.

BASSET PROCESS

In France Basset[25] claimed to have perfected a process that seems to be similar to the Jones "step process" except that the reduced metal was melted in the same rotary-kiln furnace in which reduction took place and was poured continuously, as either pig iron or steel, into ingot molds. One furnace operated by Basset was 150 feet long and 8 feet in diameter. Ore and coal, charged at one end of the furnace, were pushed toward the hot end, where there was an enlarged section to collect the molten metal and slag formed. Pulverized coal was used for fuel. The air for combustion was preheated to about 1,000° C. by a regenerative

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[24] Johnston, Theo L., Sponge Iron in Japan: Bureau of Mines Inf. Circ. 7440, 1948, 12 pp.

[25] Cram, P. H. (American consul, Nancy, France), Metallurgical Notes: Cons. Rept., April 1921.

Miltoun, F., Will Exploit New Steel-Making Process: Iron Trade Rev., vol. 67, 1920, p. 1335.

Wüst, F., [The Basset Process of Direct-Iron Production]: Stahl u. Eisen, vol. 41, 1921, pp. 1841–1848.

Whitfield, R., The Production of Iron and Steel Direct from Ores: Iron and Coal Trades Rev., vol. 105, 1922, p. 84.

Iron Trade Review, Making Steel Direct from Ore: Vol. 68, 1921, pp. 1375–1376.

Basset, L. P., Process for the Direct Manufacture of Iron and Steel: United States Patent 1,435,686, Nov. 14, 1922.

TABLE 3.—*Analyses of burden materials and metal produced in Czechoslovakia, dry basis*[1]

	Krusna Hora crude, percent	Roasted Zdice, percent	Slag, percent	Metal, percent
Fe	30.0	26.0	-----	-----
P	.5	1.0	-----	1.4–1.6
Mn	.1	.1	-----	.1
SiO_2	25–26	24.0	60.0	-----
Al_2O_3	10.0	10.0	20–25	-----
CaO	2.0	2.4	6–7	-----
MgO	1.5	1.6	5–6	-----
S	.3	.5	-----	.5–1.0
C	-----	-----	-----	.5–0.8
Si	-----	-----	-----	.1

[1] Data from unpublished manuscript by P. E. Henry, C. F. Ramseyer, and J. R. Miller (Ramseyer & Miller, Inc., New York).

system similar to that employed in open-hearth practice. The exit gases contained 44 percent carbon monoxide, which could have been utilized elsewhere in the plant. This process was widely heralded and severely criticized but so far as is known has never passed the experimental stage.

Basset seems to have operated such a kiln to produce balls 1 to 10 inches in diameter, composed of partly reduced iron (the reduction was 60 to 70 percent) and a little carbon fused together and coated with a large quantity of high-lime slag. Such balls can be melted down in the open hearth to form steel. The kiln sloped 5 percent from feed to discharge end and rotated at a rate of 1 to 2 r. p. m. The charge consisted of 2,000 kg. of iron ore (50 percent Fe) to 860 kg. of lime and 400 kg. of anthracite. The product was heated enough to ball and become coated with slag; it was then discharged and cooled in air. The slag coating hindered reoxidation. In this process the incoming air for burning the powdered coal was preheated only to 100° to 200° C., and the coal was burned incompletely. Ordinarily much iron was lost in melting the product.

DISADVANTAGES OF PROCESS

These rotary-kiln furnaces failed chiefly because trouble with the lining and the sticking and fusion of the charge made continuous operation impossible; there were also other disadvantages. As would be expected, the difficulties were similar to those experienced by Jones in Michigan. In forming a balled product the charge tended to fuse and build up on the lining in large rings at the point where the heating flame struck the lining, about 3.5 meters from the discharge end. With higher furnace temperatures and with fusion of the charge, the abrasion and corrosion of the lining at the hot end were severe.

Operation of the kilns could never be continued longer than a few days without a shutdown. Linings of silica, carborundum, chrome, magnesia bricks, and petroleum coke were tried with similar unsatisfactory results.

RECENT IMPROVEMENTS

More recently, the Basset process has been modified to produce molten cast iron and cement clinker. This modification requires ores whose gangue can be so changed by additions that it issues as cement clinker at the same temperature that high-carbon cast iron forms and melts. The process is said to be in use in Denmark. Inasmuch as it makes molten iron directly and is not a sponge-iron process in any sense of the word, further discussion is not germane.

MODIFIED SMELTING PROCESS WITH ELECTRIC FURNACE

Use of a rotary kiln for preheating and reducing the ore-coal charge before being charged to an electric smelting furnace has been suggested, as the hot reduced or partly reduced charge containing carbonized coal is in excellent condition for efficient conversion to iron in the electric furnace. In 1920 T. S. Curtis, of the Vitrefrax Co., Los Angeles, Calif., attempted to reduce ore mixed with coal or coke in a rotary kiln heated by the gases from a Rennerfelt steel furnace in which the product of the kiln was melted. The experiment was discontinued before satisfactory results were obtained.

Early in 1923 Driscoll,[26] of Oakland, Calif., tested the production of pig iron by virtually the same method. He used a 50-kw. experimental electric furnace to smelt a mixture of ore and lignite. A constricted opening in the roof of the furnace connected directly with a rotary kiln, slightly inclined to the horizontal, in which the furnace charge was preheated and supposedly reduced in part. Driscoll claimed to be able to extract valuable byproducts from the volatile matter distilled from the lignite in the rotary kiln. The maximum temperature attained at the lower end of the preheating kiln, just before the charge entered the electric furnace, was about 820° C.—too low for any appreciable reduction of the ore to metallic iron at this stage. The electric furnace produced white iron.

The whole idea is essentially a modification of the Swedish shaft-type electric furnace; the vertical shaft, however, is turned on its side and used as a rotary preheating kiln. The furnace also may be regarded as an open-pit type of electric smelting furnace supplemented by a preheating kiln, the addition of which necessitates decreasing the roof opening of the open-top furnace. This latter change

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[26] Driscoll, R. A., Electric Furnace: United States Patent 1,421,185, June 27, 1922.

tends to introduce serious difficulties through overheating the roof. Although Driscoll's furnace design does not seem to be workable, the general idea offers two possible advantages: (1) Saving much of the heat now wasted in the ordinary open-top electric furnace—that in the unburned CO and the sensible heat of waste gases—and (2) using lower grade fuels for reducing the ore instead of the charcoal or coke now used in standard electric smelting furnaces. At best, however, the rotary kiln would probably do little more than preheat the charge, thus throwing most of the burden of reduction on the electric furnace and making difficult the production of anything but white iron. This furnace, even if it could be made workable, presents most of the disadvantages of the electric shaft furnace.

REDUCTION OF OXIDES OF IRON

FUNDAMENTAL THEORY AND DATA

The fundamental physical and chemical properties of the oxides of iron and the available reducing agents are important factors in the development of new methods for treating these oxides commercially. Experimental development is possible without such knowledge, but usually there is loss of efficiency and the chances for success are poorer. In a study of the reduction of iron oxides on a commercial scale the basic material data are: (1) Physical and chemical properties of the oxides and important reducing agents available, (2) equilibrium conditions, (3) reaction velocities, and (4) quantities of heat involved.

GASES FOR REDUCING IRON OXIDES

CARBON MONOXIDE

The most important common reducing agent for oxides of iron is carbon monoxide, ordinarily derived from the incomplete combustion of carbon. It reacts with all oxides of iron to form CO_2 and a lower oxide of iron or metallic iron. Carbon and oxygen unite to form two oxides, CO and CO_2, mixtures of which under certain conditions will reduce iron oxide and under other conditions may oxidize metallic iron or ferrous oxide; thus, certain ratios of CO to CO_2 are reducing or oxidizing. Too frequently gas mixtures free of oxygen but containing CO_2 and CO are termed "reducing" or "nonoxidizing." A high CO_2 content may make them oxidizing.

Important results of numerous investigations have been reviewed by Williams, Barrett, and Larsen,[27] Eastman,[28] and Ralston.[29]

HYDROGEN

Hydrogen ranks second to CO in practical importance in the reduction of oxides of iron. The reactions are similar to those in which CO is an active agent.

Eastman and Evans[30] summarized the results of investigations on equilibria of iron oxide systems involving mixtures of hydrogen and water vapor. Their choice of the best data is reported by Ralston.[31]

OTHER GASES

Specht and Zapffe[32] made an exhaustive examination of all work on low-temperature gaseous reduction. They classify gaseous media used in reduction processes as three types:

1. Hydrogen.
2. Carbon monoxide often mixed with hydrogen.
3. Other mixed gases such as: (*a*) Coal gas, (*b*) bosh gas, (*c*) fuel gas, (*d*) illuminating gas, (*e*) methane (not a mixture), (*f*) natural gas, (*g*) oil gas, (*h*) producer gas, and (*i*) water gas.

They conclude that reduction with nearly all commonly used gaseous media utilizes hydrogen and carbon monoxide as the active agents.

Maier and Thomas[33] made a thorough and critical study of the theoretical and practical aspects of the direct use of methane or natural gas for producing sponge iron. They state:

> While it was possible to produce a very satisfactory grade of iron by direct reduction, the rate of reduction at all temperatures below the sintering point of the reduced iron was so slow as to be prohibitive (a treatment time of some 50 hours was required to reduce pyrite cinder). Methane, in the absence of catalysts, decomposes slowly under conditions where it is thermodynamically almost completely unstable.

Meyer and Eilender[34] concluded that "methane does not react as a reducing agent, the reduction being accomplished by its decomposition products."

EQUILIBRIUM DATA

Equilibrium data on the reduction of iron oxides with hydrogen and carbon monoxide are shown in figures 1 and 2. The equilibrium constants K_1 and K_2 (fig. 1) for the reversible reactions

$$FeO + CO = Fe + CO_2, \tag{1}$$

$$FeO + H_2 = Fe + H_2O \tag{2}$$

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[27] Williams, C. E., Barrett, E. P., and Larsen, B. M., Production of Sponge Iron: Bureau of Mines Bull. 270, 1927, 175 pp.

[28] Eastman, E. D., Equilibria in the Systems Fe–C–O and Fe–H–O and the Free Energies of the Oxides of Iron: Jour. Am. Chem. Soc., vol. 44, 1922, pp. 975–998.

[29] Ralston, Oliver C., Iron Oxide Reduction Equilibria. A Critique from the Standpoint of the Phase Rule and Thermodynamics: Bureau of Mines Bull. 296, 1929, 326 pp.

[30] Eastman, E. D., and Evans, R. M., Equilibria Involving Oxides of Iron: Jour. Am. Chem. Soc., vol. 46, 1924, pp. 888–903.

[31] See footnote 29.

[32] Specht, O. Geo., Jr., and Zapffe, Carl A., Gaseous Reduction of Magnetite Ore to Sponge Iron: Trans. Am. Inst. Min. and Met. Eng., Iron and Steel Div., vol. 167, 1946, pp. 237–271; bibliography, pp. 271–277; discussion, pp. 277–280. (Used by permission of the American Institute of Mining and Metallurgical Engineers.)

[33] Maier, C. G., and Thomas, S. B., Reduction of Iron Ore by Natural Gas. 4. Studies in Direct Production of Iron and Steel from Ore: Bureau of Mines Rept. of Investigations 3229, 1934, pp. 39–49.

[34] Meyer, Oscar, and Eilender, Walter, [The Reduction of Magnetite and Limonite with Methane]: Arch. Eisenhüttenw., vol. 4, 1931, pp. 357–360.

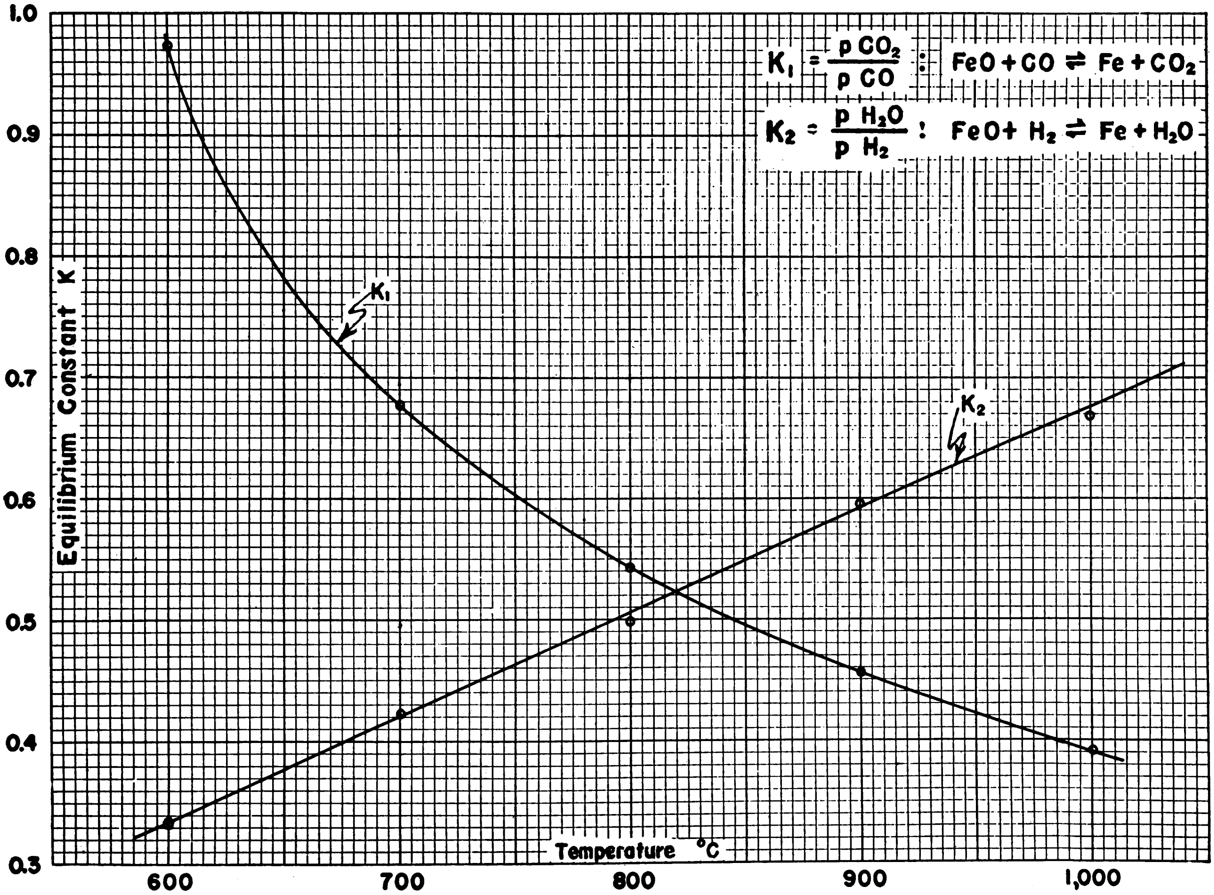

FIGURE 1.—EQUILIBRIUM DIAGRAM, REDUCTION OF FeO BY H_2 AND CO.

are derived from the data of Eastman[35] and Emmett and Shultz.[36]

Figure 2 shows the equilibrium constants for the reactions

$$Fe_3O_4 + CO = 3FeO + CO_2, \quad (3)$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O. \quad (4)$$

Values of K_1 and K_2 are derived from the data of Matsubara[37] and Emmett and Shultz,[38] respectively.

Ralston[39] prepared a discussion, referring to figure 108 in Bureau of Mines Bulletin 296, of two important papers on iron oxide reduction which were cited in Chemical Abstracts. An excerpt from his discussion follows:

> Wiberg presented a review of the equilibrium conditions in the reduction of iron oxides with CO, H_2, and CH_4. The approximate relation between the oxygen content of the wüstite area and the gas composition at equilibrium with the wüstite was calculated. Figure 3 shows the major lines in the Ralston diagram (fig. 108, Bull. 296) taken from the original but not including the dotted lines of equal oxygen content. Wüstite is ferrous oxide containing dissolved iron or magnetite, the amount depending on the proximity of the point of interest to the metallic iron side of the area or of the magnetite side of the area; the other phases are held in solid solution. Through certain temperature ranges wüstite can exist in equilibrium with oxyferrite (pure iron containing dissolved FeO), and at higher temperatures it can exist in equilibrium with oxyaustenite (pure iron containing solid solutions of both cementite, Fe_3C, and ferrous oxide). At the lower temperatures magnetite can pass directly into Fe_3C by reduction with CO gas.
>
> In (adiabatic) reduction of ferrous oxide to metallic form by pure CO the temperature of the system (presumably at about 1,000° C.) increases 100° to 150°, whereas with pure hydrogen it drops about 350° C. No change of temperature is noted when a gas mixture with 64 percent CO and 36 percent H_2 is used. However, if the ore is reduced with CH_4 or coke-oven gas, which usually contains a large proportion of methane, so much

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[35] Eastman, E. D., Equilibrium in the Systems, Iron-Carbon-Oxygen and Iron-Hydrogen-Oxygen, and the Free Energies of the Oxides of Iron: Jour. Am. Chem. Soc., vol. 44, 1922, pp. 975–998.

[36] Emmett, P. H., and Shultz, J. F., Equilibria in the Fe–H–O System. Indirect Calculation of the Water-Gas Equilibrium Constant: Jour. Am. Chem. Soc., vol. 52, 1930, pp. 4268–4285.

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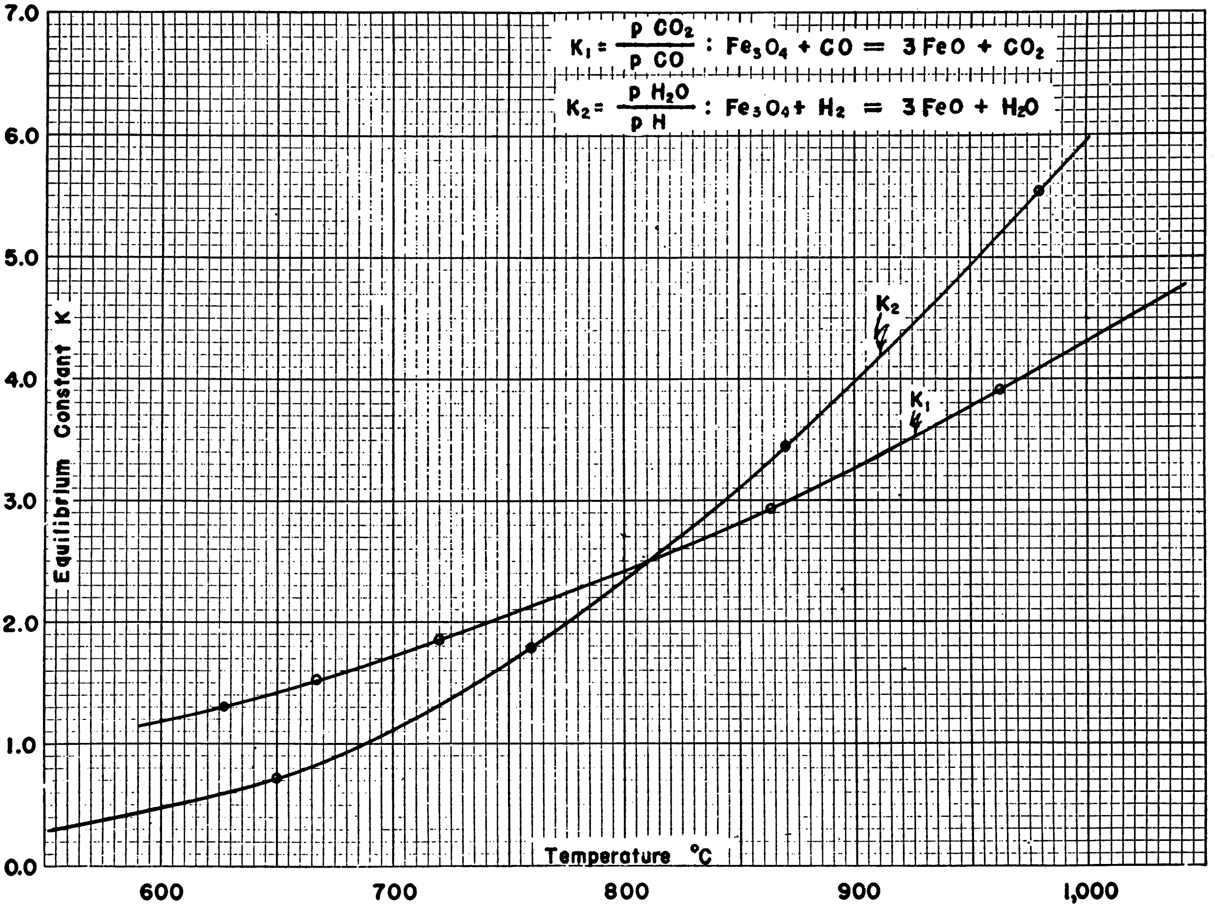

FIGURE 2.—EQUILIBRIUM DIAGRAM, REDUCTION OF Fe_3O_4 BY H_2 AND CO.

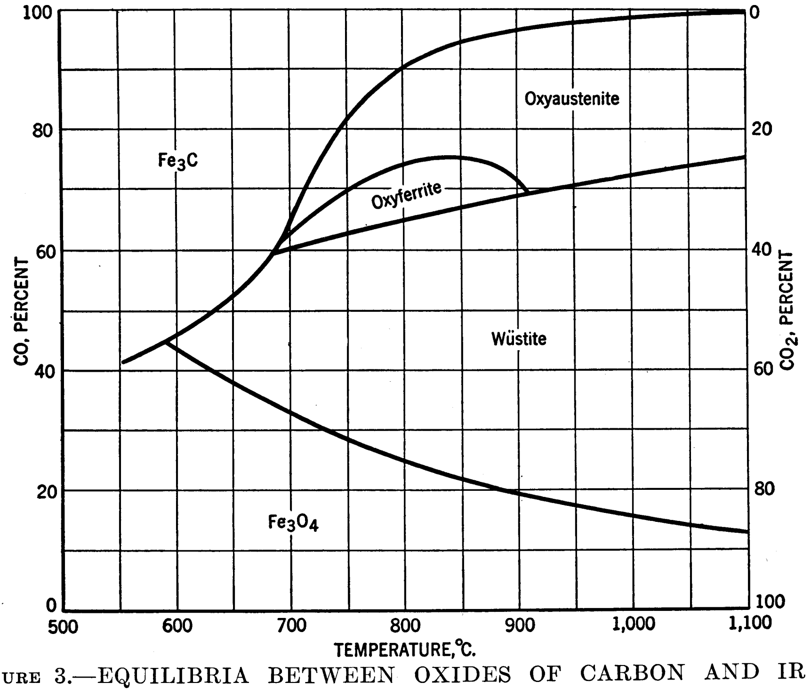

FIGURE 3.—EQUILIBRIA BETWEEN OXIDES OF CARBON AND IRON.

heat must be added that the reduction of iron ore can be carried out only in a retort or other furnace with special provision for supplying heat. Consequently, it is wiser to convert CH_4 to CO–H_2 mixture (called re-forming) by oxidation with O_2, H_2O, or CO_2.

Because of its higher rate of diffusion, hydrogen reduces ore more vigorously at 1,000° C. than does CO until about 75 percent of the oxygen of the iron ore has been removed. Beyond this point the reduction rate with hydrogen drops much more rapidly than that with CO. Reduction is accomplished in the shortest time with a mixture of CO and H_2. It will be noted that 74-percent deoxidation of Fe_2O_3 leaves a mixture of FeO and Fe in which the FeO phase is saturated with Fe in solid solution and the Fe phase contains FeO in solid solution. A slow-down in rate of reduction by either reducing gas would therefore be expected. However, Wiberg studied the reduction products under the microscope and observed that the high rate of reduction by CO toward the end is probably favored by its carbonizing action on metallic iron. In this instance the metallic iron is reduced from wüstite, forming a skin of reduced iron around each granule, and this iron contains Fe_3C in solid solution (oxyaustenite). Wiberg states that the reaction between the C of the austenite and the O of the wüstite produces gas under high pressure in the boundary region; this ruptures the iron scale and thus permits further coating of CO on the wüstite nuclei. He apparently does not acknowledge the existence of oxywüstite in which the Fe_3C and FeO can interact to develop CO; the equilibrium ratio of CO_2 corresponds to the ratio of these two solutes in the iron scale. Microscopic observation of the rupture can be taken as a fact, no matter which explanation is accepted. In reduction with H_2 a similar condition may develop except that only H_2 and not H_2O vapor can diffuse rapidly through the metallic-iron scale, and the pressure developed should be less. In the hydrogen system the oxyferrite area is probably much larger, and it is doubtful if the diagram could show any area of the hydrogen analog of oxyaustenite.

In the reduction of iron oxides with CO the diagram indicates that the iron ultimately can be carbonized completely to cementite (Fe_3C), but Wiberg says that it does not show the constant composition of the formula Fe_3C because this carbide possesses solvent power for both Fe and C, giving a more or less homogeneous region in the phase diagram where the composition can be variable. Metallic iron is also known to be a catalyst that causes splitting of CO into $C+CO_2$; this reaction, taking place within a zone of cementite, can disintegrate it so that a heavy coating of carbon can form on the iron or the cementite. This action was noted in using methane to reduce iron oxides to metal; iron also is a good catalyst for decomposition of methane. The resulting hydrogen is used to reduce the iron oxides to metal in the reduction column above the point where carbon deposition takes place.

Wiberg made a clever blank experiment, using a pure magnetite crystal for reduction by CO at 1,000° C. He noted that three layers were formed, a nucleus of unreduced Fe_3O_4, an intermediate layer of wüstite, and a surface layer of pure Fe (?). This shows that the oxygen passes through the wüstite layer by diffusion in a solid solution (as FeO). No porosity develops in the wüstite layer—only large fissures.

In sponge-iron processes employing a mixture of iron ore and carbon, CO is regenerated continuously by the action of CO_2 on carbon. The iron oxides are nearby for further immediate action of the CO.

Reduction of Fe_2O_3 with hydrogen begins around 325° C. and continues until pure iron is left without intermediate formation of FeO. Above 570° C. FeO is stable and is formed as an intermediate product between magnetite and metallic iron. For an oxide simply dried at 300° C. reduction by hydrogen begins at 240°, but for an oxide calcined at 1,300° C. reduction begins above 400° C., owing to the dense, well-crystallized condition. In the first instance Fe_3O_4 is formed by the reduction at 300° C., but in the second no Fe_3O_4 is formed. (This latter observation is difficult to understand as it does not confirm conditions predicted from the equilibrium diagram.)

The decomposition of CO in the presence of different iron compounds was studied to determine catalytic reactions, if any. No decomposition of CO takes place with gases containing less than 45 percent CO. For concentrations greater than 55 percent CO catalysis is very pronounced. Fe_2O_3, Fe_3O_4, and cementite have no catalytic effect on decomposition of CO. No FeO is produced by CO reduction (decomposition ?). (This assertion is true at temperatures below 570° C., according to the equilibrium diagrams, but is not understandable for the higher temperatures.)

Catalysis of CO decomposition was studied with about 20 metals and oxides. Cu, Pb, and Sn oxides are reduced quantitatively and oxides of W and Mo incompletely, even at 1,000° C., while Al_2O_3 and Cr_2O_3 are unaffected. Only oxides of Fe, Co, and Ni show a pronounced drop in pressure ($2CO=C+CO_2$) and a heavy carbon deposit; they are the only ones that can be called decomposition catalysts. Experiments were conducted to show the relation between catalytic decomposition properties and magnetism of the metals. The catalytic effect is believed to be due to surface adsorption, which depends on the radius of curvature of the catalyst particles. The rate of catalysis by Fe increases up to 580° C. It appears that the reduced iron is in a very fine state of subdivision, and at 580° C. these particles agglomerate and thus increase the radius of curvature. Dilution of the powdered iron with an inert substance prevents agglomeration and preserves catalytic activity independent of temperature (Chem. Abs., vol. 36, p. 6931).

The most practical conclusions from these papers are:

1. Intimate association of impurities is generally not desirable; it causes difficulties in reduction by either hydrogen or CO gas and hence, also, by solid fuels, which form CO as an intermediary reducing agent.
2. Prior heating of iron oxides or iron ores, except for removing sulfur by sintering and for combining "paint rock" into particles that can be more easily handled, is likely to convert the iron oxides to a much more inactive form and slow down the rate of reduction.
3. Both the FeO formed and the iron metal produced are contaminated by each other in solid solution, resulting in slower reduction after all Fe_2O_3 and Fe_3O_4 have disappeared. The little oxygen that remains in sponge iron, consisting of FeO dissolved in metallic solid iron, is almost beyond practical reach of gaseous reducing agents—even hydrogen—and should not be attempted commercially.
4. At practical operating temperatures (1,000° C.) carbon monoxide reacts exothermically while hydrogen reacts endothermically, and adiabatic conditions are reached with a mixture of 64 percent CO and 36 percent H_2. A mixture of the two gases has been shown to effect the most rapid reduction.
5. At low temperatures CO is an ineffective reducing agent, probably on account of its greater tendency to split into C and CO_2, but hydrogen is efficient on all but precalcined materials at temperatures as low as 300° C. At high temperatures the dissociation of water vapor into hydrogen and oxygen contributes to the ineffectiveness of hydrogen in practical operating ranges.
6. At high operating temperatures hydrogen can penetrate reaction products more effectively, but the iron produced by CO reduction cracks and scales off, thus providing freer access of CO and making it the best all-round reducing agent.
7. Carbonization of iron by CO permits preparation of a sponge-iron product containing oxygen and enough

carbon to effect its removal when the metal is melted. This result is not possible with hydrogen.

HEAT QUANTITIES INVOLVED IN REDUCTION REACTIONS

The amount of heat involved in the reactions that take place in an iron-ore reduction process is an important factor in the proper understanding of the requirements and difficulties involved in developing a suitable furnace. The best values for the heats of formation at 25° C. of the six oxides appearing in the several reduction reactions listed below are those given by Rossini:[40]

	Calories per gram-mole		*Calories per gram-mole*
Fe_2O_3	198, 500	CO	26, 416
Fe_3O_4	266, 900	CO_2	94, 052
FeO	64, 620	H_2O (gas)	57, 798

By suitable combinations of the heats of formation listed above the heat of any of the reduction reactions taking place in the ternary systems Fe–C–O and Fe–H–O at room temperature (25° C.) can be determined readily.

In the several processes developed to reduce iron ore either by solid carbon or by the reducing gases CO and H_2 one or more of the following reactions take place:

	Calories per gram-mole
1. $3Fe_2O_3+CO=2Fe_3O_4+CO_2$	−5, 936
2. $3Fe_2O_3+H_2=2Fe_3O_4+H_2O$	3, 902
3. $Fe_3O_4+CO=3FeO+CO_2$	5, 404
4. $Fe_3O_4+H_2=3FeO+H_2O$	15, 242
5. $FeO+CO=Fe+CO_2$	−3, 016
6. $FeO+H_2=Fe+H_2O$	6, 822
7. $Fe_3O_4+4CO=3Fe+4CO_2$	−3, 644
8. $Fe_3O_4+4H_2=3Fe+4H_2O$	35, 708
9. $FeO+C=Fe+CO$	38, 204

In practice, of course, none of the above reactions takes place at room temperature. To determine the reaction heat at an elevated temperature (t° C.), however, it is necessary only to add to the reaction heat at 25° C. (considered positive when endothermic and negative when exothermic) the heat required to raise the temperature of the products of reaction from 25° C. to t° C. and subtract the heat required to heat the reactants through the same temperature interval. The sensible heat of each reactant and each product of reaction appearing in the nine equations listed here has been given, at 100° C. intervals, up to 827° C. (1,100° K.).[41] At 1,100° K. the sensible heats of these elements and oxides are:

	Calories per mole		*Calories per mole*
Fe_2O_3	27, 290	CO	5, 992
Fe_3O_4	39, 900	CO_2	9, 308
FeO	10, 740	H_2	5, 673
Fe	7, 160	H_2O	7, 215
C	3, 320		

Many of the direct-reduction and sponge-iron processes that have been proposed operate at approximately 1,100° K. (1,521° F.). For convenient reference the heats of the reactions considered here at 1,521° F. (827° C.) have been computed and are given in table 4 in (1) calories per mole, (2) calories per gram of iron, and (3) B. t. u. per net ton of iron:

TABLE 4.—*Heats of reactions involved in the reduction of iron ore at 827° C.*

Reaction	Calories per mole	Calories per gram of iron	B. t. u. per ton of iron
1	−4, 690	−14. 0	−50, 400
2	3, 374	10. 1	36, 400
3	1, 040	6. 2	22, 300
4	9, 104	54. 4	195, 800
5	−3, 280	−58. 7	−211, 300
6	4, 784	85. 6	308, 100
7	−8, 800	−52. 5	−189, 000
8	23, 456	140. 0	504, 000
9	37, 296	667. 8	2, 404, 000

Reactions 1 and 2 represent the operations involved in the "magnetic roasting" of iron ore by means of CO and H_2, respectively. Although the conversion of hematite into magnetite by CO is exothermic and by H_2 endothermic, both reaction heats are low, and the difference in thermal requirements between CO and H_2 as reducing agents for the first step in the deoxidation of Fe_2O_3 has little practical significance.

Reactions 3 and 4 correspond to the second step in the conversion of Fe_2O_3 into metallic iron. In this step the conversion of Fe_3O_4 into FeO is endothermic for both CO and H_2. Reactions 5 and 6 represent the final removal of oxygen from iron ore and the conversion of FeO into metallic Fe. In this step reduction by CO (fig. 1) is significantly exothermic (giving out more than 200,000 B. t. u. per ton), whereas the reduction by H_2 (fig. 2) is strongly endothermic (absorbing more than 300,000 B. t. u. per ton).

When the iron is reduced below 1,050° F., FeO does not appear, being thermodynamically unstable below this temperature (fig. 3), and magnetite is reduced directly to metallic iron. Reaction 7 or 8 takes place when either CO or H_2 is used to produce metallic iron from Fe_3O_4 at temperatures below 1,050° F.

Reaction 9 is the basis of processes for producing metallic iron by "direct reduction by carbon." It is strongly endothermic, absorbing more than 2 million B. t. u. per ton of iron, a thermal requirement far in excess of that involved even in the strongly endothermic reduction of iron ore by hydrogen.

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[40] Perry, John H. (Editor), Chemical Engineers Handbook: New York, 3d ed., sec. 3, 1950, pp. 237–239.

[41] Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. X. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds: Bureau of Mines Bull. 476, 1949, 241 pp.

In the so-called Haber water-gas reaction,

$$CO_2+H_2=CO+H_2O,$$

the endothermic reaction heat at 25° C. is 9,838 calories per mole. At 827° C. the reaction heat is slightly less endothermic (8,064 calories per mole). The difference between the heats of reaction in reactions 1 and 2 is equal to the water-gas reaction heat, inasmuch as the iron oxides Fe_2O_3 and Fe_3O_4 cancel when reaction 2 is subtracted from reaction 1. The same is true when reaction 4 is subtracted from reaction 3 and when reaction 6 is subtracted from reaction 5. The difference between the reaction heats in reactions 7 and 8 must, of course, be divided by 4 to equal the water-gas reaction heat.

MEASURE OF REDUCIBILITY

Numerous methods have been employed to measure the reducibility of iron oxides in reducing gases. Most of these studies have been made in combustion tube furnaces. Hydrogen was passed over small samples of iron oxides in combustion boats heated to some specific temperature in the tube. The water vapor was absorbed and weighed at intervals.

LOSS-IN-WEIGHT METHOD

The Bureau of Mines at Minneapolis developed the loss-in-weight method [42] for measuring rates of deoxidation of iron oxides in reducing gases. As the volume of oxygen removed is weighed directly, no absorption apparatus is needed. Any reducing gas or mixtures of reducing gases may be used. Much larger quantities of material are used than in other methods; the results obtained are therefore more accurate, and the samples more nearly represent the ore tested. Excellent gas-solid contact is obtained as the reducing gas passes through a column of broken solids.

Two sizes of the apparatus have been used at Minneapolis:

1. Small laboratory apparatus for treating 227 grams of minus-0.742-inch pieces.
2. Larger apparatus for treating 50 pounds of minus-2½-inch pieces.

The small loss-in-weight apparatus was a 20-gage alloy-steel tube 2 inches in diameter and 12 inches in length, with the lower end closed, suspended from a balance into a heating chamber.

Figure 4 is a schematic drawing of the apparatus; figure 5 shows the retort, hydrogen inlet, and the connection to balance.

Preparation of Ores for Deoxidation Test.—It is essential that the material used in each test be representative of the ore being tested.

About 100 pounds of ore is sized on a 0.525-inch screen. The oversize material is crushed to pass this screen and is then added to the minus-0.525-inch portion. The entire lot is put through a Jones-type sampler to obtain about 10 pounds of representative sample. The 10-pound sample is wet-screened on 20-

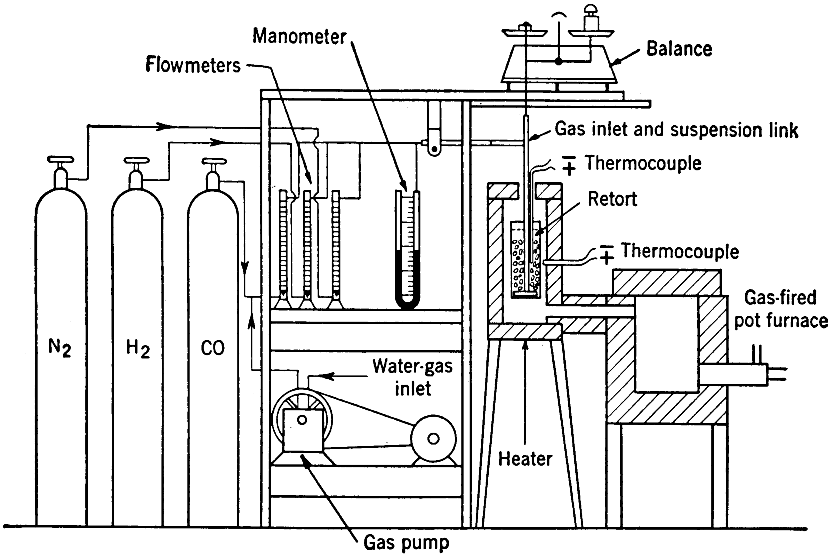

Figure 4.—SCHEMATIC DRAWING OF APPARATUS FOR STUDYING THE DEOXIDATION OF IRON OXIDES BY VARIOUS GAS MIXTURES.

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[42] Barrett, E. P., and Wood, C. E., Loss-in-Weight Method for Determining Rates of Deoxidation of Iron Oxides: Ind. Eng. Chem., anal. ed., vol. 18, May 1946, pp. 285, 286.

mesh. The plus-20-mesh material is dried at 105° C. and screened to give four sizes:

1. Minus-0.525-inch, plus-3-mesh.
2. Minus-3-, plus-6-mesh.
3. Minus-6-, plus-10-mesh.
4. Minus-10-, plus-20-mesh.

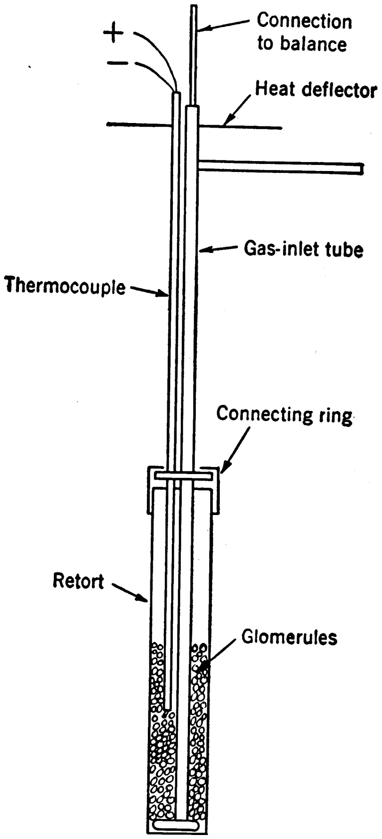

FIGURE 5.—SCHEMATIC SKETCH OF RETORT FOR LOSS-IN-WEIGHT APPARATUS.

Composite samples (227 grams each) are prepared from the four screen sizes. One composite is crushed, ground, and analyzed for ferric iron and ferrous iron. The total oxygen in the sample is computed from the analyses. Other composite samples are treated in the loss-in-weight apparatus to determine reducibility at specific temperatures and rates of flow of hydrogen, carbon monoxide, or mixtures of hydrogen and carbon monoxide. Definite volumes of nitrogen, water vapor, or carbon dioxide may be mixed with the reducing gases.

Test Procedure.—The gas-inlet tube is inserted in the retort, and 227 grams of the iron oxide material is placed on top of the gas distributor at the bottom. The connecting ring is attached to the top of the retort by two alloy-steel pins inserted through holes in the ring and in the top section of the retort. The assembled retort is placed in the heater and connected to the balance above the heater. The thermocouple is connected to the pyrometer, and the gas-inlet tube is connected to the rotameter used to measure the flow of reducing gas to the retort.

The burner on the pot furnace is lighted, and nitrogen is passed through the retort at the rate of 0.23 c. f. m. until constant weight is attained at the temperature desired. Reducing gas is substituted for nitrogen, the temperature is maintained, and the loss in weight is recorded at regular intervals until constant weight is attained or the loss for each time interval is very small. Nitrogen is substituted for hydrogen, and the product in the retort is cooled without oxidation.

Table 5 is the log of a test in the small loss-in-weight apparatus.

Effect of Composition of Reducing Gas.—Tests were made in the small loss-in-weight apparatus on 227-gram samples, using different reducing gases at identical temperatures and rates of flow of the reducing gases (table 6).

Analysis of the product obtained by deoxidation in water gas showed that carburization had occurred.

	Carbon, percent		
	Total	Combined	Uncombined
Glomerules reduced in water gas	0. 80	0. 73	0. 07

Effect of Rate of Flow of Reducing Gas on Rate of Deoxidation.—Results of tests in the loss-in-weight apparatus show that rate of flow of the reducing gas greatly affects the rate of deoxidation of the iron oxide material being deoxidized.

A summary of the data obtained from tests in which 227 grams of minus-6-, plus-10-mesh ore was deoxidized at 900° C. in hydrogen flowing at 0.06, 0.12, 0.23, and 0.46 c. f. m. is shown in table 7.

These data indicate that in order to obtain a reasonable rate of deoxidation without sacrificing too much efficiency in the reaction of hydrogen with iron oxide, the rate of hydrogen flow should not be greater than 0.23 c. f. m. for each half pound of oxide material being deoxidized. Efficiencies are slightly higher at lower rates of flow over longer periods of time.

TABLE 5.—*Log of test in small loss-in-weight apparatus*

[Deoxidation of 227 grams of glomerules [1] made from Alan Wood magnetite concentrate in hydrogen (0.23 c. f. m.) at 800° C.]

Time, minutes	Temperature, °C. in—		Weight, grams		Deoxidation, percent	Remarks
	Heater	Charge	Retort	Loss		
0	795	810	1, 598. 2	0. 0	0. 0	Stopped N_2 flow; started H_2 flow.
10	790	780	1, 577. 0	21. 2	31. 3	
20	795	820	1, 563. 3	34. 9	51. 6	
30	785	800	1, 554. 6	43. 6	64. 4	
40	780	805	1, 545. 5	52. 7	77. 8	
50	785	805	1, 539. 4	58. 8	86. 9	
60	780	805	1, 535. 7	62. 5	92. 3	
70	775	795	1, 533. 0	65. 2	96. 3	
80	780	790	1, 532. 0	66. 2	97. 8	
90	780	800	1, 531. 6	66. 6	98. 4	
100	780	800	1, 531. 3	66. 9	98. 8	
110	785	795	1, 531. 2	67. 0	99. 0	
120	790	805	1, 531. 1	67. 1	99. 1	Stopped H_2 flow; cooled in N_2.

[1] Total Fe, 69.69 percent; ferrous Fe, 0.94 percent.

TABLE 6.—*Percentage deoxidation of 227 grams of minus-0.742-, plus-0.371-inch glomerules at 800° C.*

Minutes after gas entered retort	Deoxidation, percent—	
	In hydrogen	In water gas
10	31. 3	27. 2
20	51. 6	41. 9
30	64. 4	55. 2
40	77. 8	65. 7
50	86. 9	75. 5
60	92. 3	82. 3
70	96. 3	87. 1
80	97. 8	90. 3
90	98. 4	91. 9
100	98. 8	92. 6
110	99. 0	93. 5
120	99. 1	94. 2

TABLE 7.—*Summary of deoxidation tests*

	Rate of flow of hydrogen, c. f. m.			
	0. 06	0. 12	0. 23	0. 46
Deoxidation percent	99. 8	99. 6	99. 8	99. 5
Utilization of H_2 do	32. 4	35. 5	30. 8	23. 4
Time minutes	165	75	45	30

INVESTIGATIONS BY THE BUREAU OF MINES

REDUCTION BY CRUDE OIL

The Bureau of Mines has studied at length the various aspects of the problem of iron-ore reduction. In 1911 and 1912 D. A. Lyon and J. F. Cullen [43] investigated the reduction of iron ore by use of crude oil. They surveyed in detail available theoretical data on the subject and in 1913 prepared a preliminary report, entitled "Conditions Governing Reduction by Oil"; they compared reduction by carbon and by oil and oil vapors and indicated some of the difficulties probable in smelting iron ore by crude oil on any noteworthy scale. The proposed process used oil both for reducing and for heating the ore charge and burning it in the reaction chamber. Experiments were continued at the Harvard metallurgical laboratories to June 1, 1912, when the work was transferred to the Pittsburgh Experiment Station. The small-scale tests showed fairly good results, but those on a somewhat larger scale presented difficulties that finally caused the problem to be abandoned as giving too little promise of ultimate success.

REDUCTION IN EXTERNALLY HEATED ROTATING TUBES

In 1918 work on the production of sponge iron for precipitating copper was begun at the Southwest Experiment Station of the Bureau of Mines at Tucson, Ariz. The reduction furnace was a rotating metal tube heated externally by oil or gas. Pyrite calcine was fed into the tube, and oil gas was used as the reducing agent; later other fuel gases were tried, and finally coal was substituted for gas. The sponge iron was wanted as a precipitant for copper in leaching solutions.

This work ultimately was developed on a fairly large scale. A furnace of semicommercial size was tried at the Tintic Milling Co., Silver City, Utah, in 1922; it was a rotating thermalloy tube heated externally. The charge of crushed coal and ore passed through the hot tube at a temperature of about 950° C. A small furnace of this type gave promising results, but when larger sizes were tried the capacity decreased rapidly, and difficulties in operation and design became so great that work was finally abandoned.

TWO-DIAMETER INTERNALLY FIRED ROTARY KILN

Work on the production of sponge iron was begun at Seattle in the spring of 1920. Extensive experiments were carried on continuously until November 1924; these were confined to the reduction of iron ores by heating them in direct contact with various forms of solid carbon, which method seemed to be simpler technically than the reduction of iron ores by gases. It was felt that there was definite need for a simple process that would be applicable to the production of sponge iron on a fairly large scale and that the most promising course would be to develop the simpler phase of the problem to the point of industrial application before extending the experiments into the more difficult field of reducing iron ore by gases.

The work began with small tests in crucibles and was gradually amplified to production on a larger scale; 10- to 12-pound charges were treated in assay muffles, then 150-pound charges were reduced in an electrically heated muffle furnace. The results of these preliminary experiments and a survey of past attempts in sponge-iron production indicated that the direct-fired rotary kiln offered most promise for industrial application to the problem.

PRODUCTION OF SPONGE IRON IN SMALL, DIRECT-FIRED ROTARY KILN

Experiments demonstrated that rapid heating of the charge was necessary for economical production of sponge iron. A direct-fired rotary kiln seemed to satisfy this requirement better than any other simple type of furnace. The question as to whether the hot oxidizing gases of combustion would affect reduction adversely could be answered only by experiment.

The furnace was operated intermittently

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[43] Holmes, Joseph A., Second Annual Report of the Director of the Bureau of Mines to the Secretary of the Interior, for the Fiscal Year Ended June 30, 1912: 1912, pp. 69–70.

TABLE 8.—*Analyses of materials used in tests with direct-fired furnace, percent*

Product	Iron	Insoluble	Sulfur
Vancouver magnetite from Texada Island	54. 5	19. 1	0. 20
Magnetite from Dean Channel, British Columbia	45. 5	35. 5	. 02
Magnetite concentrate from Fierro, N. Mex	64. 5	6. 5	. 60
Bog-iron ore from Arlington, Wash	40–47. 0	3. 5	. 08
Roasted pyrite from Miami, Ariz	48. 0	12. 0	3. 84

Product	Volatile matter	Fixed carbon	Moisture	Sulfur	Ash
Bituminous coal	41. 46	41. 07	3. 65	0. 43	13. 83
Local gas coke	5. 50	68. 07	2. 33	. 47	24. 10
Carbocoal	13. 20	60. 20	1. 40	. 33	25. 20
Do	17. 58	35. 38	. 68	. 42	46. 36

with batch charges of 80 pounds each. Three methods of heating the furnace and charge were tried: (1) Heating the furnace to the desired temperature and then charging the ore and coal, (2) charging the ore and coal into the cold furnace and then heating, and (3) charging the ore into the cold furnace and heating to the desired temperature before adding the coal. The first method was finally adopted; the furnace was heated to 1,000° C., the dust chamber was moved aside, and the ore and coal were shoveled in through the end pipe. Temperatures, samples of gas, and grab samples of the charge were taken at regular intervals during the tests. At the end of a test the product was discharged into closed sheet-iron containers and allowed to cool.

In the first tests noncoking bituminous coal was mixed with the ore and charged to the heated kiln. Experiments showed that no reduction took place while the moisture and low-temperature volatile matter were being driven off. Because these reactions absorb heat and require time, in all later tests the coal was partly carbonized before being used as the reducing agent. The same furnace was also used for producing this low-temperature carbonized coal, hereafter called carbocoal. The crushed coal was charged into the hot furnace and kept at dull-red heat until no more dense black smoke was evolved. Then the product was discharged and cooled rapidly to below its ignition point. The use of carbocoal materially reduced the time required for making a test.

Table 8 gives analyses of the ores and reducing agents used in the tests in this furnace. Some carbocoal was made from Washington bituminous coal and some from a local lignitic coal of high ash content.

CONCLUSIONS AS TO DIRECT-FIRED ROTARY FURNACE

The results of this series of 34 tests in the direct-fired rotary furnace showed: [44]

1. When charges of iron ore and coal are heated in a direct-fired rotary furnace, a highly reducing atmosphere is maintained beneath the surface of the charge, although the atmosphere above the charge may be oxidizing to metallic iron.
2. The rate of reduction is slow at 850° C. but increases rapidly as the temperature increases. Best results are obtained at about 950° C. Temperatures above 1,025° C. cause the charge to sinter or the ore to stick to the lining.
3. There is only a slight difference in the rates of reduction of magnetite, hematite, and limonite ores in sizes finer than 4-mesh.
4. A slow speed of rotation of the furnace stirs the charge enough for rapid absorption of heat and consequently rapid reduction.
5. For best results the coal and ore particles should be about the same size and finer than 4-mesh.
6. Sixty parts of coal to 100 parts of ore was used successfully in the tests. High-ash lignite can be used as the reducing agent. Carbocoal formed by partial carbonization of noncoking subbituminous coal at a low temperature is the most satisfactory solid reducing agent. Tailings from the magnetic separation of metallic iron from the furnace product can be used as the reducing agent in a new charge.
7. Virtually complete reduction of the iron in the charge can be obtained in 45 to 50 minutes by heating the mixtures of iron ore and carbocoal at 950° C. in the rotary furnace.

CONTINUOUS OPERATION IN LARGER KILN AT SEATTLE

CONSTRUCTION OF KILN

The preliminary experiments indicated that the continuous kiln could probably be adapted successfully to large-scale production of sponge

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[44] Williams, C. E., Barrett, E. P., and Larsen, B. M., Production of Sponge Iron: Bureau of Mines Bull. 270, 1927, p. 124.

iron, but more work of a fundamental nature on a somewhat larger scale would have to be done before a plant of such size could be built and operated successfully.

The kiln (fig. 6) was built of the materials most readily available at the time. The capacity was 1,400 pounds of metallic iron in 24 hours.

EXPERIMENTAL OPERATION

To obtain experimental data, the kiln shown in figure 6 was used for separate short tests. In each test the actual conditions of continuous production were maintained for 2 or 3 hours, and then the kiln was shut down and cooled. All products were weighed and analyzed, and weight balances were calculated for some tests.

Description of a typical test will show the methods used more clearly. Tables 9, 10, and 11 give complete data of a run. Table 9 shows the data taken during operation of the kiln. The charge was subbituminous coal and iron ore in the ratio of 1.25 parts of coal to 1 part of ore (625 pounds of coal to 500 pounds of ore). The ore was calcined pyrite cinder that had been leached with sulfuric acid to extract its soluble copper. Both coal and ore were ground to minus-8-mesh before they were mixed. The calcine used contained about 62 percent iron, chiefly as Fe_3O_4; 13 percent gangue, chiefly SiO_2; and 1.5 percent sulfur. Before it was charged the furnace was heated by the oil burner to 1,020° C.; then the enlarged section was filled with 225 pounds of the charge. At first the kiln was rotated with the discharge pipe closed, and this starting charge was heated to more than 900° C. The furnace was then charged at the rate of 300 pounds an hour.

The ore-coal mixture first entered the narrow preheating section of the kiln and passed through it rapidly in a thin bed 1 or 2 inches deep. The time of passage through this section was 10 or 12 minutes; because of its exposure in a thin rolling layer to the stream of hot gases, the charge was heated quickly and entered the enlarged section at about 800° C. During this preheating period the moisture was driven out of the charge, and most of the volatile matter was distilled from the coal; very little reduction to metallic iron took place, although part of the reduction from Fe_2O_3 to Fe_3O_4 and from Fe_3O_4 to FeO undoubtedly was completed. From the narrow section the preheated material passed into the enlarged part of the kiln, where as a nearly level, slowly moving, but rolling bed 6 to 9 inches deep it was directly exposed along its upper surface to the hot flame from the oil burner. The charge remained in this section for 60 minutes, most of the time at the reduction temperature (875° to 975° C.). By the time it had reached the end wall it was completely reduced and was discharged through the pipe passing obliquely through the wall. During about a third of each revolution the inner open end of this pipe passed through the charge (see dotted line showing charge level in details of end, fig. 6), and each time a few pounds of product fell into a sheet-iron hopper, which was kept nearly full of discharged product. From the hopper the product passed into sheet-iron boxes, where it remained until cold.

TABLE 9.—*Log of kiln operation*

Time	Temperature, °C.	Oil, gallons	Pan	Feed, pounds	Remarks
9:00	----------	15	----------	----------	Burner started.
12:20	1,020	12	----------	225	Enlarged section charged.
1:15	910	----------	----------	----------	Feed started.
1:30	----------	----------	----------	----------	Discharge pipe opened; enlarged end level full.
1:40	----------	----------	----------	150	Charge fed into upper end.
2:00	950	12	----------	----------	
2:10	----------	----------	----------	300	Do.
2:25	940	----------	----------	----------	
2:30	----------	----------	1	----------	Pans changed.
2:40	----------	----------	----------	450	Charge fed into upper end.
3:00	940	----------	----------	----------	
3:10	----------	----------	----------	600	Do.
3:25	955	----------	----------	----------	
3:30	----------	----------	2	----------	Pans changed.
3:40	----------	----------	----------	750	Charge fed into upper end.
4:15	----------	----------	----------	900	Do
4:30	1,055	----------	3	----------	Pan changed; product in enlarged section discharged into can; some of the charge balled up slightly just before the last of the product was removed from the furnace; no indication of fusion when the first of the product was removed.

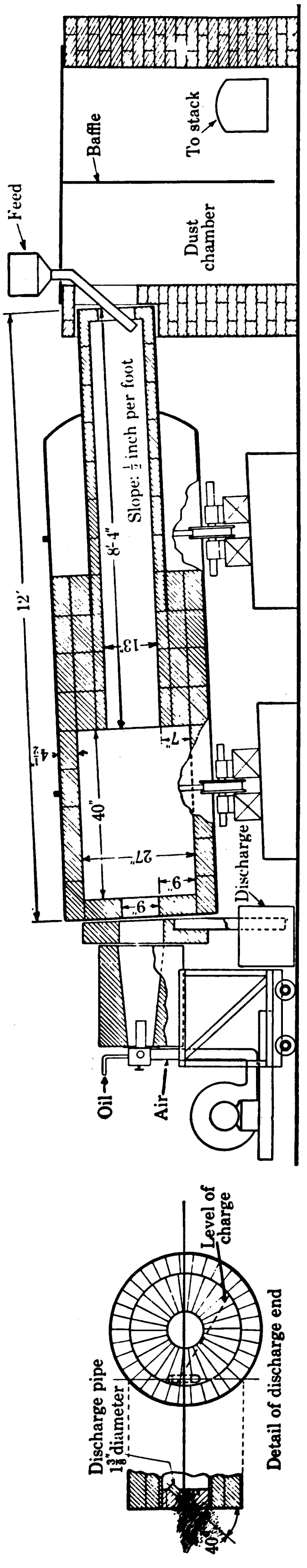

FIGURE 6.—SECTION OF LARGE KILN TESTED AT SEATTLE.

TABLE 10.—*Analyses of charge and products, Seattle, percent*

Sample	Total Fe	Metallic Fe	Reduction	Sulfur	Copper	Zinc	Carbon
Coal (subbituminous)	----------	----------	----------	0. 54	----------	----------	38. 00
Ore (sintered calcine)	61. 1	----------	----------	. 18	0. 31	0. 75	. 69
Discharge:							
Pan 1	52. 8	47. 0	89. 0	. 35	. 27	. 20	15. 90
Pan 2	51. 1	46. 6	91. 1	. 34	. 27	. 23	15. 90
Pan 3	53. 3	49. 2	92. 3	. 34	. 29	. 19	15. 20
Can 1	53. 3	49. 9	93. 6	. 31	. 30	. 18	12. 50
Incrustation on lining	51. 8	6. 0	----------	. 43	. 28	. 35	. 22
Residue in dust chamber	34. 5	----------	----------	. 32	. 17	. 70	11. 70
Residue in stack	28. 0	----------	----------	. 73	. 06	. 57	29. 50
Concentrate	71. 4	70. 2	98. 2	. 24	. 41	. 20	1. 64
Tailing	6. 6	2. 8	----------	. 65	. 002	. 18	38. 60

TABLE 11.—*Charge balance, feed, and products*

Material	Total weight, pounds	Iron		Sulfur			Copper		Zinc		Carbon	
		Pounds	Percent	Weight, pounds	Based on S in ore, percent	Based on S in charge, percent	Pounds	Percent	Pounds	Percent	Pounds	Percent
Coal (subbituminous)	625	--------	--------	3. 38	--------	79. 0	--------	--------	--------	--------	238. 0	98. 5
Ore (sintered calcine)	500	305. 0	100. 0	. 90	100. 0	21. 0	1. 55	100. 0	3. 75	100. 0	3. 4	1. 5
Total charge	1, 125	305. 0	100. 0	4. 28	100. 0	100. 0	1. 55	100. 0	3. 75	100. 0	242. 0	100. 0
Discharge:												
Pan 1	142	75. 0	24. 6	. 50	55. 6	11. 7	. 38	24. 5	. 28	7. 5	22. 6	9. 4
Pan 2	139	64. 9	21. 3	. 47	52. 3	11. 0	38	24. 5	. 32	8. 5	22. 1	9. 1
Pan 3	115	61. 4	20. 2	. 39	43. 3	9. 1	. 33	21. 3	. 22	5. 9	17. 5	7. 2
Can 1	114	60. 7	19. 9	. 35	38. 9	8. 2	. 34	22. 0	. 20	5. 3	14. 3	5. 9
Total furnace discharge	510	262. 0	86. 0	1. 71	190. 1	40. 0	1. 43	92. 3	1. 02	27. 1	76. 5	31. 6
Concentrate	360	258. 0	84. 3	. 85	94. 5	19. 9	1. 46	94. 2	. 72	19. 2	5. 9	2. 4
Tailing	146	9. 7	3. 2	. 95	105. 4	22. 2	--------	--------	. 27	7. 2	56. 5	23. 1
Overflow	10	3. 4	1. 1	--------	--------	--------	--------	--------	--------	--------	--------	--------
Incrustation on lining	40	20. 7	6. 8	. 08	8. 9	1. 8	. 11	7. 1	. 14	3. 7	--------	--------
Residue in dust chamber	20	6. 9	2. 3	. 06	6. 7	1. 4	. 03	1. 9	. 14	3. 7	2. 3	1. 0
Residue in stack	15	4. 2	1. 4	. 11	12. 2	2. 6	. 01	. 7	. 09	2. 4	4. 4	1. 8
Total waste products	85	35. 2	11. 6	. 25	27. 8	5. 8	. 15	9. 7	. 37	9. 8	6. 7	2. 8
Total accounted for	595	297. 2	97. 6	1. 96	217. 0	45. 8	1. 58	102. 0	1. 39	37. 0	75. 8	31. 1

REDUCTION OF VARIOUS ORES

Results of many tests indicated that nearly all types of iron ores may be treated equally well in a rotary kiln. The experimental work included runs on iron ores of the following types: A dense hematite containing a coarse silica gangue; a soft, porous bog ore, low in impurities; an artificial hematite, soft and porous, from the roasting of iron pyrite; an artificial magnetite, made by sintering this roasted-pyrite residue in a blast roaster with 15 percent of coal; several dense, hard, natural magnetites; a powdery, nearly pure iron oxide obtained as a sludge from a chemical reduction process employing scrap iron; and a copper-converter slag containing more than 50 percent of iron, mostly as Fe_3O_4.

Virtually all of these ores were reduced at about the same rate in the rotary kiln. The natural magnetites were reduced somewhat more slowly than the other ores tried. Artificial magnetites, such as high-iron converter slag and those produced by sintering processes, are easily reduced. Differences of physical structure seemed to have little effect on the rate of reduction of ores ground to 8-mesh. The only ore tested that gave trouble in the kiln was a very finely powdered magnetite, 75 percent of which was finer than 200-mesh. A completely reduced, high-grade sponge-iron concentrate could be made from it, but the loss by dusting was excessive; 15 to 20 percent of the iron in the charge was carried out of the stack as fine dust that would not settle in the dust chambers. Moreover, this ore persistently gave trouble by sticking to the kiln lining.

REDUCING AGENTS

Numerous tests showed definitely that strongly coking coals could not be used in the kiln charges. The whole charge when heated to the point at which the coal fused caked into a solid mass that revolved with the kiln and prevented further operation. Coals with only slight coking tendencies were used successfully, and the strongly coking coals were used by first carbonizing them enough to avoid coking in the kiln. Fortunately, the cheapest and most abundant reducing agent, low-grade, subbituminous, noncoking coal, was found to be the best suited to the process. The moisture and part of the volatile matter were quickly removed from this coal in the preheating zone of the kiln, giving a porous mass of soft carbon which, upon entering the reducing section of the kiln, reacted rapidly with CO_2 and maintained a highly reducing atmosphere in the charge, even at a temperature as low as 880° C.

Charcoal was an equally active reducing agent but was so light that an excessive amount was blown out of the kiln in the current of gases. Denser forms of carbon gave poorer results. At 900° C. anthracite gave noticeably slower reduction speeds than bituminous coal, and at 1,000° C. the reduction progressed rapidly until about 80 to 85 percent of the iron was reduced and then slowed down greatly.

When a hard, dense retort carbon was used, the iron was reduced very slowly in a charge held at 900° to 950° C. All tests pointed to the conclusion that the denser forms of carbon, such as anthracite, retort carbon, and hard coke, required higher temperatures to give the reduction speeds obtained with the more porous bituminous, subbituminous, and lignitic coals or charcoal at temperatures around 900° C.

FURNACE ATMOSPHERE, COAL RATIOS IN CHARGE, AND KILN DESIGN

Perhaps the greatest disadvantage of the direct-fired rotary-kiln process for the production of sponge iron is the large excess of coal required in the charge to maintain proper reducing conditions. Even where comparatively cheap low-grade coals are used, this excess will form an important item in the total cost of production. Use of the minimum ratio of coal to ore in the charge is therefore highly important. In the first successful experiments made with the kiln described in this section complete reduction of the iron seemed to require a coal-ore ratio of 1.25 : 1. In later tests, however, the quantity of coal was decreased first to 100 and then to 75 parts per 100 parts of ore. The quantity required seemed to be affected chiefly by the depth of charge and the atmosphere in the kiln.

Experiments indicate that by increasing the depth of charge in the reduction chamber, keeping out excess air, and operating the oil burner with a smoky flame the ratio can be reduced to 60 or 65 parts of coal per 100 parts of ore. Whether satisfactory reduction can be obtained below this ratio can be ascertained only by experiments on a larger scale than was possible in the work under discussion.

OPERATION OF 2½-TON FURNACE

Early in 1923 a kiln was built at the plant of the Tintic Milling Co., Silver City, Utah, to produce sponge iron for precipitating lead and silver from chloride-leaching solutions. The furnace ran successfully for several months and produced daily 2½ tons of sponge-iron concentrates containing 75 to 80 percent of iron. Work was suspended in September 1923, when the entire plant was shut down on account of shortage of ore.

CONSTRUCTION AND OPERATION OF KILN

The kiln was built from materials available at the plant and as a result was not of the desired dimensions or of best construction. For example, the small-diameter section was too long. The two shells of different diameters were tied together and lined with 12-inch fire-clay cupola blocks. The completed kiln was 27 feet long; 22 feet of its length was 32 inches in diameter (inside) and 5 feet was 48 inches. The maximum depth of charge in the enlarged section was 16 inches and in the smaller section 3 to 4 inches. The product was discharged through a thermalloy pipe 3 inches in diameter placed obliquely through the end wall of the enlarged section.

The charge—equal parts of hematite ore and bituminous coal, both crushed so that 80 percent passed an 8-mesh screen—was mixed and shoveled into the bin from which an inclined pipe fed it continuously into the kiln. The rate of charging was 780 pounds an hour and that of discharging, 480 pounds an hour. The charge remained in the small bore 20 minutes and in the enlarged end 1 hour; the speed of the furnace was 2 r. p. m. At this rate of feed the daily output of the furnace was 2⅓ tons of sponge-iron concentrate containing 80 percent of metallic iron or 1.8 tons of metallic iron. The average daily output of sponge-iron concentrate, however, was 2½ tons. One man per shift attended the furnace, as the ore and coal were crushed and put into the feed bin by the regular working force at the mill.

MAGNETIC CONCENTRATION

The cooled furnace product was fed continuously to the magnetic concentrator, which separated the sponge iron from the carbon and gangue particles and discharged the concentrate and the tailing into separate bins. This operation required no attention and gave no trouble; consequently, it entailed virtually no operating cost.

QUANTITY OF COAL USED FOR REDUCTION

A minimum of 80 parts of coal to 100 parts of ore was required. Insufficient coal in the charge was immediately manifested by sticking of the charge to the lining and by a falling off in the percentage of reduction obtained. No attempt was made to reduce the coal-ore ratio below 80:100. However, tests showed that part of the tailing, which contained about 60 percent carbon and 40 percent ash, could be substituted for coal in the charge, but if too much tailing was used the ash content of the reducing agent gradually increased until it caused the charge in the kiln to sinter.

Other tests have shown that the coal-ore ratio can probably be reduced to 60 or 65 parts of coal to 100 parts of ore in a properly designed large kiln.

OPERATING DIFFICULTIES

Use of Coking Coal.—The coal used was slightly coking, and as a result the charge became cemented together during the first few feet of its descent into the kiln and revolved as a solid mass that completely covered the kiln lining. This difficulty was readily corrected by inserting a ¾-inch steel rod through the charging pipe and allowing it to press against the inside of the kiln at the point where fusing of the charge was worst. The bar loosened the mass of charge which, in moving down the kiln, was completely broken into particles of the original size by the time it reached the junction of the two kiln sections.

Temperature Control.—Previous work had shown that the proper temperature range was 875° to 1,025° C., but operation of the kiln at Silver City showed that if the temperature remained above 950° C. the charge built up on the kiln lining much more rapidly than at a lower temperature.

Temperatures were taken by inserting into the charge a base-metal insulated thermocouple, whose end had been preheated nearly to the temperature of the charge, and holding it there until the meter reading became virtually constant.

Building up of Charge on Lining.—The most serious operating difficulty in the continuous production of sponge iron in the direct-fired kiln is the tendency of the charge to build up on the lining. This building up occurs mainly at the junction of the two kiln sections and also, but to a lesser extent, on the lining of the enlarged end; a steel bar was allowed to ride in the charge at the zone in the kiln where the building up took place and was held there by an attachment at the upper end of the kiln.

The exit gases were used to heat the lead solution as it passed to the precipitation tanks. Although these gases were combustible, they had to be ignited with a flame from an oil burner in the dust chamber.

Table 12 gives analyses of samples of the ore and coal used and of the sponge iron produced:

TABLE 12.—*Analyses of charge and products, Silver City, percent*

IRON ORE

	Weight	Insoluble	Iron	Sulfur
	100.0	12.4	49.3	0.53
Plus-4-mesh	4.0	10.1	52.4	------------
Minus-4-, plus-6-mesh	7.0	11.1	52.5	------------
Minus-6-, plus-8-mesh	7.0	10.4	51.6	------------
Minus-8-mesh	82.0	13.5	48.2	------------

COAL

Moisture	1.7
Volatile matter	30.8
Fixed carbon	56.8
Ash	10.7
Sulfur	93

SPONGE IRON

	Total iron	Metallic iron	Reduction	Sulfur	Carbon
Furnace product	71.2	29.9	96.0	0.78	41.5
Concentrate	39.7	77.4	97.0	.76	.2
Tailing	6.7	4.4	65.8	.71	67.8

CONTROL OF SULFUR IN SPONGE IRON PRODUCED IN ROTARY KILNS [45]

PURPOSE OF INVESTIGATION

At the beginning of World War II it appeared that a critical shortage of scrap suitable for use in the production of steel for armament and materiel would develop. Consequently, it would be advantageous to the country if methods for producing a scrap substitute could be developed and put into production rapidly with existing equipment constructed for other purposes and idle because of the war. Congress appropriated funds for an investigation of gaseous and solid-fuel reduction of iron ores, and the work was initiated by the Bureau of Mines in 1942 under the supervision of R. S. Dean, assistant director of the Bureau at that time. Much of it was a continuation of research undertaken earlier by the Bureau. The principal objectives of these investigations were to establish methods for the production of sponge iron low in sulfur and suitable for use as a scrap substitute and to utilize, wherever possible, equipment that was idle because of the war.

The rotary-kiln method appeared particularly attractive as a means of producing an emergency scrap substitute, because the process can be operated with a small number of workmen. Little new equipment would be required, as the cement plants in the United States had approximately 730 rotary kilns when the war began, and many of these plants, especially those in the eastern part of the country, were either idle or operating below capacity. Many of them were so constructed that they could have been converted rapidly to the production of sponge iron at small cost for new equipment.

In many regions the rotary-kiln method for the reduction of iron ore has the advantage over the blast furnace of not requiring coking coals, as most solid fuels can be used to reduce the ore, and coal, gas, or oil can be employed to supply the heat required by the rotary-kiln process.

Another consideration was that by the erection of a rotary-kiln plant near a mine it might be possible to utilize economically deposits of iron ore too small to warrant the construction of a blast furnace and the auxiliary equipment upon which its operation depends.

PRELIMINARY EXPERIMENTS

Tests proved that disks of well-reduced, low-sulfur sponge iron could be produced by heating, in covered crucibles, alternate layers of ore and reducing agent mixed with the correct proportion of lime or limestone. Reductions of more than 99 percent and sulfur contents of 0.008 to 0.03 percent were obtained. The next step in the process was to find a means of producing low-sulfur sponge iron from a mixture of granular ore, reducing agent, and desulfurizing material, as such a mixture would be employed in the production of sponge iron in the rotary kiln.

It was decided to use an externally heated rotary retort as a reasonable approach to conditions in a large rotary kiln. Tests in this equipment duplicated conditions in the large kiln satisfactorily; that is, results obtained from the laboratory tests in the rotating pipe furnace could be used to predict the ease of reduction obtainable with various combinations of ore and coal, the amount of sticking or balling to be expected, and the sulfur content of the sponge iron produced.

Figure 7 is a photograph of the rotary retort employed, and figure 8 is a drawing of the retort. The first retorts were made of low-carbon iron. These lasted for about six heats at a temperature of 1,900° F. but were inexpensive and easy to construct. Later, retorts of a heat-resistant alloy containing approximately 28 percent chromium and 6 percent nickel were obtained. The alloy retorts worked well and gave no trouble from oxidation even after 40 heats at 1,950° F. Some difficulty was experienced from warping of these alloy retorts, and they had to be straightened occasionally to make a good seal at the gasket, which is essential if reoxidation during cooling is to be eliminated.

The gaskets were made of two turns of ⅛-inch-diameter asbestos rope placed side by side. A new gasket was used for every test. This arrangement worked well, provided the pins compressing the gasket did not become loose. It was found necessary to hold each pin in place by passing a piece of oxidation-resistant wire through a hole in the pin.

These retorts were heated in a gas-fired furnace. The furnace sides were made of one layer of insulating firebrick on the inside surrounded by 4 inches of Sil-o-cell brick. The roof slabs were cast from a mixture of crushed insulating firebrick and lumnite cement. This furnace was heated with two gas burners of the type used for residential heating; each was 12 inches long and 3 inches wide and contained 140 holes approximately 5/64 inch in diameter.

The charge, usually consisting of 2 kg. of ore, 1.5 kg. of reductant, and a sulfur-control agent, was poured into the retort, which was then closed with the cover plate. The retort was placed in the furnace, and the cap was removed from the ⅛-inch gas outlet pipe to permit the escape of gases from the retort. Rotation was started, and the burners were lighted. Temperature was measured by means of a thermo-

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[45] Buehl, R. C., Shoub, E. P., and Riott, J. P., Control of Sulfur Content of Sponge Iron Produced in Rotary Kilns: Bureau of Mines Rept. of Investigations 4057, 1947, 102 pp.

couple projecting into the center of the retort and controlled manually by adjusting the quantity of gas to the burners. About 1 hour was required for the retort to reach the reduction temperature, which was usually 1,900° or 1,950° F. The test was then run at a constant temperature for the desired reduction period, or until the flame at the end of the ⅛-inch pipe outlet had decreased in length to less than 2 inches, indicating that the reaction was near completion. The burners were shut off, and a cap was placed on the ⅛-inch pipe as soon as gas ceased to issue from it. When the iron retorts were used, they were removed from the furnace and rotated on a stand adjacent to the furnace, as shown in figure 8. The retorts were then sprayed with water, so that they would cool in about 15 minutes. However, the high-chrome-alloy retorts tended to warp badly even when cooled in the air, so they were cooled in the furnace with the top removed. Air was blown into the furnace after the retorts had cooled below a red heat to increase the rate of cooling. When the retorts were cold enough to be handled with bare hands, the cover plate was removed, and the charge was inspected for balling and sticking to the retort. If the sponge iron stuck, the retort was cleaned by scraping before the next test was begun.

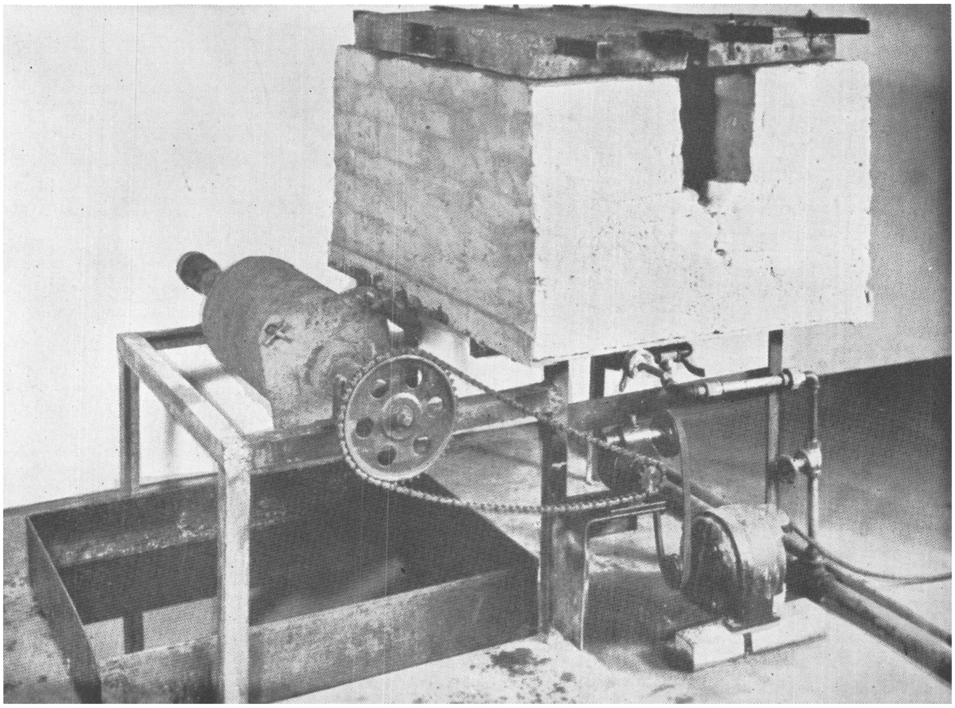

Figure 7.—EXTERNALLY HEATED ROTARY PIPE FURNACE, SHOWING RETORT REMOVED FROM THE FURNACE FOR COOLING.

COOPERATIVE AGREEMENT

Laboratory tests to develop a method of producing low-sulfur sponge iron that would be a desirable melting stock were begun at the Central Experiment Station, Bureau of Mines, Pittsburgh, Pa., in February 1943. The initial laboratory work indicated that low-sulfur sponge iron probably could be produced in a rotary kiln, and it was evident that large-scale pilot-plant tests were necessary to prove this point. There was neither equipment nor space for such tests at the Central Experiment Station, and results would have to be obtained rapidly if they were to be of value during the war. Consequently, it was decided to ren equipment that was in operating condition, if possible, rather than to construct such equipment and the necessary building under war conditions. Such equipment was available at the plant of the National Radiator Co., Johnstown, Pa., and under a series of agreements the use of the plant, equipment, and operating personnel was rented from that company on a pay-when-used basis. Pilot-plant tests were begun at Johnstown in July 1943.

Internally Fired 4- by 2- by 21-Foot Rotary Kiln.—Two kilns were used for this investigation. Minor alterations were made in the

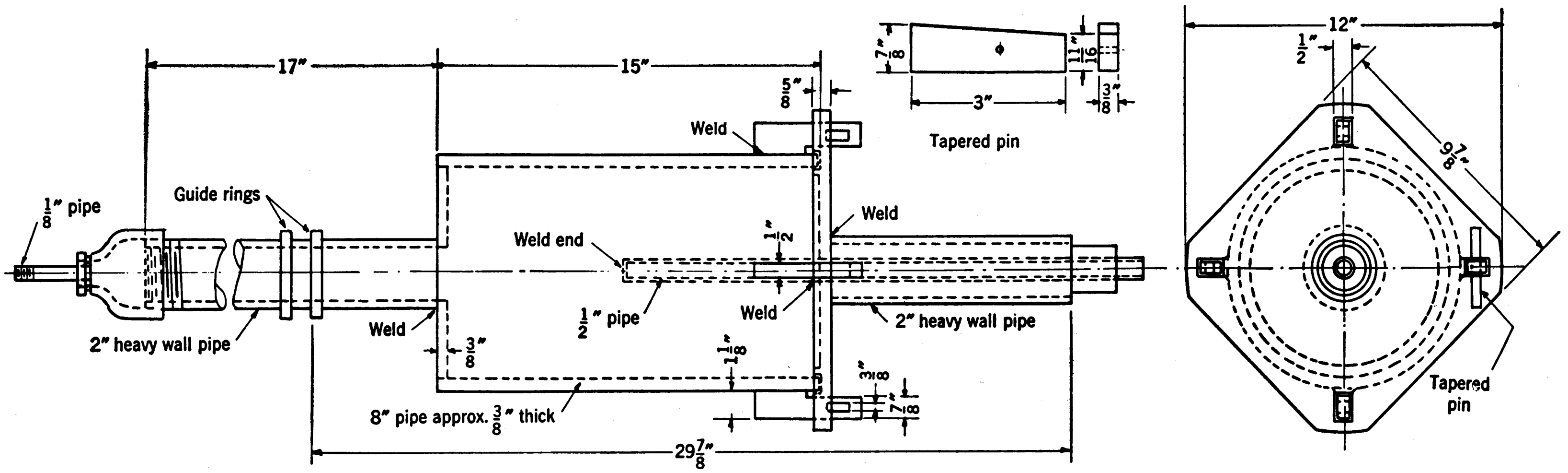

FIGURE 8.—HIGH-TEMPERATURE ROTARY RETORT USED FOR LABORATORY EXPERIMENTS.

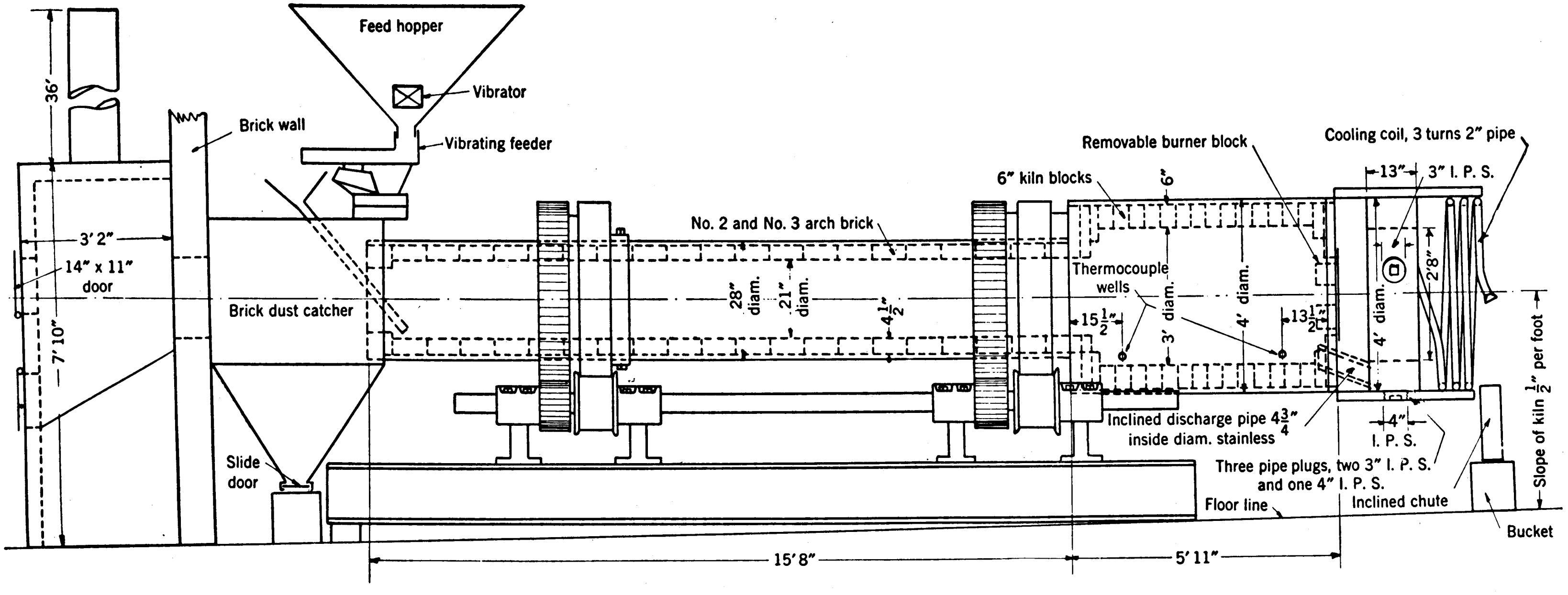

FIGURE 9.—INTERNALLY FIRED 4- BY 2- BY 21-FOOT ROTARY KILN, INCLUDING STACK, FEEDERS, AND COOLING SYSTEM.

smaller kiln by the Bureau of Mines, but no changes were made in the larger kiln.

Figure 9 is a drawing of this kiln, showing the important dimensions. The preheating or small-diameter section with a shell diameter of 28 inches and length of 15 feet 8 inches was standard equipment and contained the bull wheels and driving gear.

To this equipment the company added the enlarged section, which was 4 feet in diameter and 5 feet 7 inches long, in order to make a two-diameter kiln similar to that recommended in Bureau of Mines Bulletin 270.[46] The small-diameter section was lined with a 4½-inch layer of fire-clay arch brick and the large-diameter section with 6-inch kiln blocks of the same material. Following customary practice, this kiln is designated by the diameters of the two sections and its total length (4 by 2 by 21 feet). The pinion of the driving gear was attached to one of the shafts, which supported the trunnions, and this shaft was driven by a 2-hp. electric motor coupled to a gear reducer connected to the shaft by means of a chain drive. A metal drum and helical pipe coil were attached to the large-diameter section for cooling the sponge iron.

Cooling Drum and Coil.—A new feature [47] of this installation was the method of cooling the reduced sponge iron. Sponge iron is subject to rapid oxidation by air, steam, or carbon dioxide during cooling and consequently must be protected from these gases.

Sponge iron discharged from the large-diameter or reducing section of the kiln through a 4¾-inch i. d. stainless-steel pipe into the cooling drum. This alloy pipe passed through the brick at the discharge end of the kiln at an angle to the axis of the kiln, so that it scooped up sponge iron during each revolution. After the cooling drum was partly filled, the sponge iron entered the helical coil made from 2-inch pipe and discharged from this pipe through a chute into a bucket. The cool sponge iron in the pipe coil acted as a seal that prevented the entrance of air into the drum. The rate of discharge was controlled by a plug inserted in the free end of the helical pipe coil. With this method for controlling the discharge, the drum was about half full of sponge iron and coke during normal operation; because of the rotation of the kiln, hot sponge iron came in contact with the water-cooled metal surface of the drum so that cooling was much more rapid than it would have been in a stationary container. The sponge iron was in the cooling system abour 1 hour and was below 200° F. when discharged.

Sponge iron produced by reduction with solid reducing agents at temperatures above 1,800° F. will not reoxidize appreciably after it has been cooled to a temperature below 350° F. This statement does not necessarily hold for all sponge iron, as that reduced by gases at lower temperatures often is pyrophoric even when cooled in a protective atmosphere to room temperature.

Oil Burner.—The kiln was heated by a residential type of oil burner, which fired axially through the discharge end of the kiln into the reducing chamber. The shape of the flame is very important, as it must heat the large-diameter section of the kiln uniformly. Sponge iron will stick to any part of the kiln that is appreciably hotter than the desired reduction temperature. Because of the short length of the large-diameter section compared to its diameter, the flame must be short and wide.

Temperature Measurement.—Temperature measurements were made with a thermocouple connected to a manually operated potentiometer box. Two thermocouple wells passed through the brick side walls of the large-diameter section 13½ inches from the discharge end and 15½ inches from the junction of the two sections and projected about 4 inches into the inside of the brick lining of the furnace. Temperature was measured every half hour by stopping the kiln so that the thermocouple wells were within the charge, inserting the thermocouple, and setting the temperature after the reading became constant, which required about 1 minute in each well. The thermocouple wells were made of black iron pipe. When they became oxidized or coated with sponge iron after several days of use, they were driven into the kiln, and a new well was inserted from the outside; this change required about 5 minutes.

Internally Fired 6- by 5- by 60-Foot Rotary Kiln.—Figure 10 is a photograph of this kiln. The shell consisted of a 6-foot-diameter section of ½-inch steel plate 22½ feet long, a tapered section of 7/16-inch steel plate diminishing from 6 to 5 feet in diameter and 7½ feet long, and a 5-foot-diameter section of 7/16-inch plate 30 feet long, making a total length of 60 feet. The slope of the kiln was ½ inch a foot. Two tires 7 inches wide, each supported on four trunnions, were used. The kiln was driven by a 15-hp. motor through a variable-speed drive, on which was mounted the pinion of the main drive gear, which surrounded the 5-foot-diameter section. The entire lining of fire-clay kiln blocks was 6 inches thick.

Cooling Drum and Coil.—The cooling system was similar in design to that of the small kiln, except that the drum and coil surrounded the kiln. The cooling drum of ⅜-inch plate

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[46] Williams, C. E., Barrett, E. P., and Larsen, B. M., Production of Sponge Iron: Bureau of Mines Bull. 270, 1927, 175 pp.

[47] Buehl, R. C., Rotary Kiln: United States Patent 2,363,390, 1943.

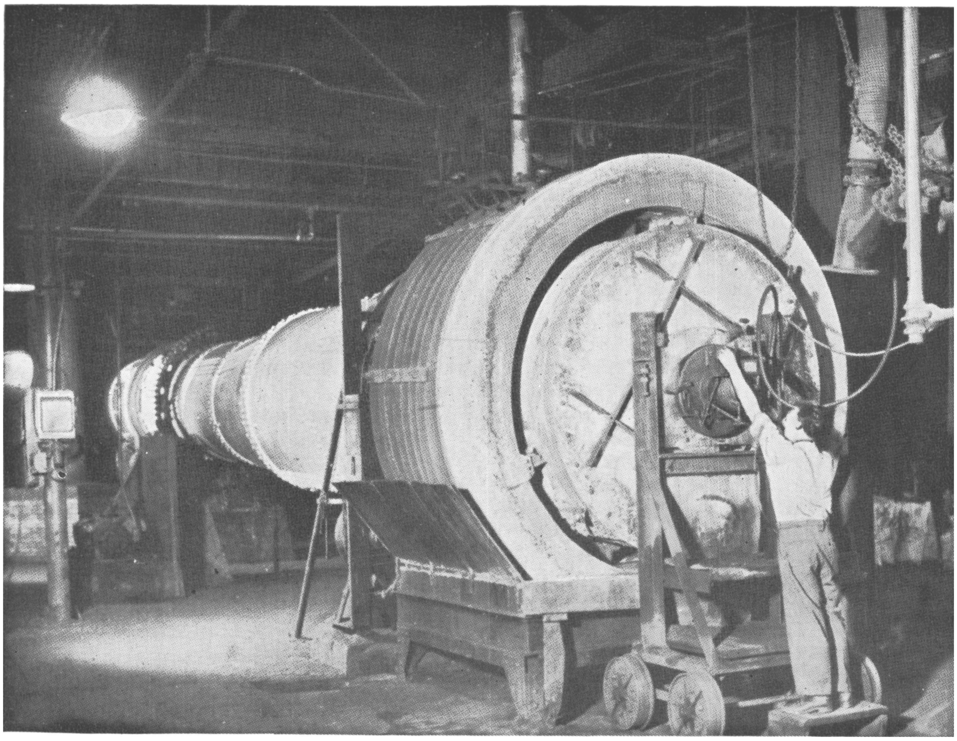

FIGURE 10.—INTERNALLY FIRED 6- BY 5- BY 60-FOOT KILN PHOTOGRAPHED FROM DISCHARGE END.

was welded; it was 7 feet in diameter inside, 8 feet 11 inches in diameter outside, and 16 inches in width. The cooling coil consisted of 8 turns of 4-inch pipe, with a median diameter of 8 feet 4 inches. A 4-inch-square stainless-steel pipe, containing a stainless-steel butterfly valve, connected the drum to the inside of the furnace. A flap valve mounted on the discharge end of the pipe coil was held in the closed position by a spring and opened with striking pins that could be set either to prevent discharge or to control the quantity of material discharged each revolution. The drum and coil were cooled by rotating in a pan filled with water and by water sprays.

Oil Burner.—A wide-angle industrial oil burner was employed.

Auxiliary Equipment.—Three hoppers with individual variable-speed screw feeders were mounted above the feed end of the kiln. A conveyor system was provided for filling these hoppers; it consisted of a bucket elevator and several screw feeders so arranged that the charge could be fed through a hammer mill for crushing if desired.

The pipe coils of the cooler discharged onto an inclined screen with ¼-inch openings. The material that passed through the screen was conveyed by a screw feeder and bucket elevator to a magnetic separator.

SULFUR-CONTROL REAGENTS

Several methods for controlling the sulfur content of the sponge iron were investigated. When no sulfur-control agent was employed, the sulfur content of the sponge iron produced from minus-⅛-inch ore was 0.10 to 0.16 percent, and from minus-½-inch ore it was 0.06 to 0.10 percent. Use of the coarser ore had no adverse effect upon the degree of reduction or the capacities obtained.

Limestone.—The addition of minus-20-mesh lime to the feed had the beneficial effect of reducing the sulfur content of the sponge iron to 0.05 to 0.06 percent; similarly, the addition of ground limestone yielded sponge iron containing 0.06 to 0.08 percent sulfur. A sized limestone (minus-8-, plus-20-mesh) from which the fine particles had been removed gave much less sulfur (0.04 to 0.05 percent). Coarser ore screened to minus-½-, plus-⅛-inch and minus-20-mesh lime were used in one test. The sponge iron produced contained 0.04 to 0.08 percent sulfur, which was about the same as in a test in which minus-⅛-inch ore and minus-20-mesh lime were used. However, the screened ore was coated with very fine particles, which adhered during the screening operation. In another test the screened ore was washed free of this fine material and then reduced in the presence of minus-20-mesh lime. The sulfur content of the sponge iron was definitely low (0.03 to 0.045 percent).

The sulfur-control methods tried with these raw materials indicated that sized limestone was the most satisfactory, considering the small cost of this method. It appeared advantageous to utilize minus-½-inch ore rather than grind the ore to a finer size.

Dolomite.—The encouraging results obtained by using a coke containing limestone (added before coking) as the reducing agent in the production of low-sulfur sponge iron spurred efforts to find a process that would be less expensive, would permit the use of any reducing agent, and would yield a sponge iron of lower sulfur content. The lime particles containing calcium sulfide are rejected with coke and other nonmagnetics during magnetic cleaning.

Earlier tests in which limestone had been used as the sulfur-control agent had demonstrated that the sulfur contained in the coal reacted with the limestone in preference to the iron under strongly reducing conditions, that high sulfur contents (above 0.1 percent) were obtained only when lime adhered to the sponge iron, and that the use of sized limestone (minus-8-, plus-20-mesh) resulted in less sulfur than when powdered lime or limestone was used. These results indicated that the main problem was to prevent the adhesion of the sulfur-control agent to the sponge iron and suggested that basic materials other than limestone be tried.

Sponge-iron tests of the sagger type were conducted independently of this investigation by G. B. Dalrymple [48] at the Bureau of Mines experiment station at College Park, Md. These tests indicated that raw dolomite was an effective sulfur-control agent.

Three tests were run in the alloy rotary retort previously described, with a charge of 2 kg. of Chateaugay ore and 1.5 kg. of dolomite coke. The results of tests made with this dolomite coke are given in table 13. In test R–67 ball-milled dolomite was used in the production of the coke, and the sulfur content of the sponge iron was about the same as had been obtained when an equal quantity of powdered limestone had been used in the manufacture of the coke. However, when minus-60-mesh dolomite was employed (tests R–66 and R–68), the sulfur content of the sponge iron was appreciably lower than generally had been obtained when limed coke was used. These tests showed the importance of controlling the particle size of the dolomite in dolomite coke to obtain a minimum sulfur content in the sponge iron.

In view of the encouraging results obtained in tests R–66 and R–68, it was decided to try anthracite fines as the reducing agent and include sized dolomite directly in the charge. The results of a series of such tests are shown in table 14. A ratio of 0.3 kg. of dolomite to 1.5 kg. of coal was chosen for the initial test because of the low sulfur content of the anthracite (0.7 percent). With this ratio, the sulfur content of the sponge iron was low in all the tests except R–72, in which the dolomite was used "as received" and contained about 40 percent by weight of minus-100-mesh particles. The variation of sulfur content (0.015 to 0.033 percent) in the remainder of these tests is not considered significant, as other results not herein reported have indicated that such variations occasionally are due to other factors.

The next step was to establish the minimum concentration of dolomite necessary to obtain a low-sulfur sponge iron. Tests R–88 and R–93 indicated that 0.1 kg. of minus-8-, plus-100-mesh dolomite to 1.5 kg. of anthracite gives a low-sulfur sponge iron, whereas lower percentages of dol-

TABLE 13.—*Use of low-temperature coke containing dolomite as the reducing agent in the production of low-sulfur sponge iron in rotary pipe furnace*

Ore: 2 kg. Chateaugay ore from New York, reconcentrated on d.-c. magnetic separator.
Reducing agent: 1.5 kg. low-temperature coke made from 4 parts minus-8-mesh Warden coal mixed with 1 part dolomite and coked in plumbago crucibles at 1,100°–1,200° F.
Temperature: 1,900° F. until reduction appeared complete.

Test	Size of dolomite	Analysis, percent			
		Evolution of sulfur	Total iron	Metallic iron	Reduction
R–67	Ball-milled to powder	0.046	89.2	79.8	84.5
R–66	Minus-60-mesh	.036	92.8	86.0	92.8
R–68	do	.021	92.9	87.4	94.1

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[48] Smith, Kenneth M., and Burton, S. E., Manufacture of Sponge Iron in Periodic Brick Kilns: Bureau of Mines Rept. of Investigations 3841, 1945, 38 pp.

TABLE 14.—*Effect of the addition of sized dolomite to the charge on the sulfur content of sponge iron produced in rotary pipe furnace*

Ore: 2 kg. Chateaugay ore from New York, reconcentrated on d.-c. magnetic separator.
Reducing agent: 1.5 kg. anthracite fines from Philadelphia & Reading Coal & Iron Co. St. Nicholas Central Breaker.
Addition agent: Sized dolomite.
Temperature: 1,900° F. until reduction appeared complete.

Test	Weight of dolomite, kg.	Size of dolomite	Analysis, percent			
			Evolution of sulfur	Total iron	Metallic iron	Reduction
R-85	0. 3	Minus-½-, plus-¼-inch	0. 024	94. 1	89. 6	95. 2
R-83	. 3	Minus-¼-inch, plus-8-mesh	. 033	94. 0	90. 6	96. 4
R-70	. 3	Minus-8-, plus-20-mesh	. 015	95. 1	92. 3	97. 1
R-73	. 3	Minus-8-, plus-100-mesh	. 021	95. 2	91. 5	95. 2
R-72	. 3	Minus-8-mesh [1]	. 097			
R-86	. 2	Minus-8-, plus-100-mesh	. 033	93. 7	84. 9	90. 8
R-88	. 1	do	. 024	95. 0	89. 1	93. 8
R-93	. 1	Minus-8-mesh [2]	. 020	94. 8	91. 8	96. 9
R-89	. 05	Minus-8-, plus-100-mesh	. 039	95. 4	92. 6	97. 1
R-91	. 025	do	. 10	95. 2	91. 8	96. 5
R-90	. 1	Minus-½-, plus-¼-inch	. 158	94. 1	91. 4	97. 1
R-99	[3] . 3	Minus-8-, plus-100-mesh	. 048	95. 4	93. 9	98. 4

[1] Sample containing all the fines resulting from grinding, approximately 40 percent minus-100-mesh (normal distribution).
[2] Sized dolomite as received from the J. E. Baker Co., York, Pa.
[3] Commercial burnt dolomite of type used for furnace refractory.

omite cause a sharp increase in sulfur, as can be seen from tests R-89 and R-91. Commercial-size minus-8-mesh dolomite resulted in very effective desulfurization, as recorded in test R-93, even though the dolomite contained about 1.5 percent of minus-100-mesh particles. The use of 0.1 kg. of dolomite, such as minus-½-, plus-¼-inch particles, did not yield a low-sulfur sponge iron, as shown in test R-90. It was therefore desirable to use a finer dolomite. As the dolomite was to be used in conjunction with magnetite ground to 8-mesh or finer, it was decided to use minus-8-mesh dolomite in order to decrease segregation in the kiln and increase the flow of material through the magnetic separator. In most of the tests minus-8-, plus-100-mesh dolomite was the desulfurizing agent, although it was realized that a closer sizing, such as minus-8-, plus-20-mesh might give less sulfur but would involve the rejection of a larger quantity of dolomite by the sizing operations.

Dolomite particles retain their size and shape better than limestone particles and are not reduced to fine dust as easily. With their burden of absorbed sulfur, they are more easily discarded in the magnetic separator.

Calcium and Magnesium Compounds.—Table 15 shows the desulfurizing power of several

TABLE 15.—*Effect of the addition of various control agents to the charge on the sulfur content of sponge iron produced in rotary pipe furnace*

Ore: 2 kg. Chateaugay ore from New York, reconcentrated on d.-c. magnetic separator.
Reducing agent: 1.5 kg. anthracite fines from Philadelphia & Reading Coal & Iron Co. St. Nicholas Central Breaker.
Addition agent: 0.1 kg. various materials sized to minus-8-, plus-100-mesh.
Temperature: 1,900° F. until reaction appeared complete.

Test	Weight of desulfurizer, kg.	Analysis, percent			
		Evolution of sulfur	Total iron	Metallic iron	Reduction
R-88	0.1 dolomite	0. 024	95. 0	89. 1	93. 8
R-98	.1 limestone	. 030	93. 4	87. 4	93. 6
R-95	.1 magnesite	. 20	93. 3	92. 5	99. 3
R-97	0.05 limestone 0.05 magnesite	. 086	94. 7	91. 7	96. 9

calcium and magnesium compounds sized to minus-8-, plus-100-mesh. In these laboratory tests sized limestone was almost as effective as sized dolomite, as shown by comparison of tests R–98 and R–88. However, when the rotary-kiln pilot-plant equipment was used, sized limestone did not yield sponge iron of such low sulfur content. Sized raw magnesite (magnesium carbonate) is not an effective desulfurizing agent, as shown by test R–95. Analysis of the magnesite follows:

	Percent		*Percent*
$MgCO_3$	88. 2	Fe_2O_3	1. 2
SiO_2	3. 5	Al_2O_3	. 9
$CaCO_3$	4. 8		

A mixture of limestone and magnesite that approximated the composition of dolomite was not an effective sulfur-control agent (test R–97). Obviously, the double carbonate, dolomite, which retains its physical shape, functions mainly through its lime content to trap sulfur vapors.

Sized Dolomite and Various Ores and Coals.—The results obtained by using sized dolomite as the sulfur-control agent in the production of sponge iron from other ores and coals are shown in table 16. In tests R–152 and R–155 on Scrub Oak (New Jersey) ore, a lower sulfur content was obtained when the minus-65-mesh particles were removed from the ore. In test R–202 on agglomerated Scrub Oak ore prepared from the minus-65-mesh fraction the sulfur content was about the same as when fine ore was reduced. The sulfur content of sponge iron reduced with petroleum coke containing 0.9 percent sulfur was low (0.019 percent), as shown in test R–181. Low-sulfur sponge iron was also obtained when a subbituminous coal from the Monolith mine, Hanna Field, Wyoming, containing 0.4 percent sulfur was used as the reducing agent. However, a coke breeze with a relatively high sulfur content (1.5 percent) did not give a low-sulfur sponge iron, even when the quantity of dolomite was increased to 0.6 kg. When Shasta magnetite was reduced with subbituminous coal from Wyoming, the sulfur content (0.067 percent) was considerably higher than when Chateaugay or Scrub Oak ore was reduced, as can be seen by comparison of tests R–84 with R–79 and R–223. This ore had been washed, magnetically concentrated, and roasted to give 0.009 percent of sulfur but contained more CaO (0.6 percent) and MgO (0.32 percent) than the other ores used in this series of tests, which may account for the higher sulfur content.

Several tests run in the rotary pipe furnace to test a foundry coke available for large-scale tests at Johnstown revealed that the material was an active reducing agent. When sized dolomite was added to mixtures of foundry coke and Scrub Oak ore and the entire mixture was heated at 1,950° F. for 1 hour 20 minutes, the iron products contained 0.012 to 0.018 percent sulfur and were 86 to 98 percent reduced. Without the addition of dolomite, the sulfur content of the sponge iron was 0.184 percent.

A test was then run to determine whether the magnetic reject could be utilized as part of the reducing agent. The charge consisted of 2 kg. of Scrub Oak ore, 0.75 kg. of foundry

TABLE 16.—*Effect of the addition of sized dolomite to the charge on the sulfur content of sponge iron produced in rotary pipe furnace from various ores and reducing agents*

Test	2 kg. ore	1.5 kg. reducer	Dolomite		Reduction temperature, °F.	Time at temperature, minutes	Analysis, percent			
			Weight, kg.	Size			Evolution of S	Total iron	Metallic iron	Reduction
R–152	Scrub Oak superconcentrate, minus-20-mesh.	Anthracite [1]	0.1	Minus-8-mesh [2]	1,950	80	0.027	95.8	92.2	96.2
R–155	Scrub Oak superconcentrate, minus-20-, plus-65-mesh.	do [1]	.1	do [2]	1,950	80	.010	97.3	96.0	98.7
R–202	Scrub Oak superconcentrate, glomerules.	do [1]	.1	do [2]	1,900	80	.026	92.8	83.7	90.2
R–181	Scrub Oak superconcentrate, minus-20-, plus-65-mesh.	Petroleum coke [3]	.1	do [2]	1,950	60	.019	96.5	91.4	94.7
R–222	do	Subbituminous coal [4] from Wyoming.	None	None	1,950	70	.053	97.3	93.4	95.9
R–223	do	do [4]	.1	Minus-8-mesh [2]	1,950	80	.037	96.0	89.9	93.6
R–79	Chateaugay reconcentrate	do [4]	.3	Minus-8-, plus-100-mesh.	1,900		.023	96.2	92.1	95.7
R–80	do	Coke breeze (1.5 percent sulfur).	.3	do	1,900		.098	92.4	89.7	97.1
R–81	do	do	.6	do	1,900		.063	92.6	86.5	93.4
R–84	Shasta magnetite [5]	Subbituminous coal [3] from Wyoming.	.3	do	1,900		.067	92.6	88.2	95.3

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[1] Buckwheat No. 4 anthracite from St. Nicholas colliery of the Philadelphia & Reading Coal & Iron Co.
[2] Sized.
[3] Petroleum coke from the Cleves refinery of the Gulf Oil Corp., Cincinnati, Ohio, crushed to minus-¼-inch.
[4] Subbituminous coal from the Monolith mine, Wyoming, crushed to minus-8-mesh.
[5] Shasta magnetite from California ground to 20-mesh, washed, magnetically concentrated, and roasted. Final sulfur content, 0.009 percent.

coke, 0.825 kg. of the nonmagnetic portion of a previous test, and 0.1 kg. of dolomite. The total quantity of reducing agent was increased slightly over earlier tests to allow for the dolomite and ash in the re-used portion. The sponge iron produced contained 0.019 percent sulfur and was 89 percent reduced. It therefore appears probable that partly exhausted reducing agent can be re-used at least once as a part of the charge.

PILOT-PLANT TESTS

The laboratory tests showed that low-sulfur sponge iron could be produced by adding sized dolomite (minus-8-, plus-100-mesh) to the charge. A series of tests was then run in the smaller (4- by 2- by 21-foot) kiln with sized dolomite as the sulfur-control agent.

Data on a typical test in which sized dolomite was added to the charge are given in table 17. In this test (No. CXI) a highly concentrated magnetite ore from the Scrub Oak mine in New Jersey was reduced with foundry coke. Commercial 6/20-size dolomite added to the extent of 15 percent of the weight of the ore was the sulfur-control agent. This dolomite contained 1.5 percent minus-100-mesh particles and analyzed 54.2 percent $CaCO_3$, 41.8 percent $MgCO_3$, and 2.0 percent SiO_2.

COMPARISON OF LABORATORY AND PILOT-PLANT TESTS

A large number of tests with identical raw materials were made in the laboratory rotary pipe furnace and the smaller (4- by 2- by 21-foot) internally fired rotary kiln. In general, the sulfur content of the sponge iron produced in the laboratory was 0.01 to 0.02 percent lower than in the pilot-plant tests, although agreement of the relative values for different raw materials was excellent. Likewise, agreement between relative values for the degree of reduction obtained with various raw materials was good.

More time was required to obtain efficient reduction in the internally fired rotary kiln than in the laboratory pipe furnace. When the usual charge was employed, the large-diameter reducing section of the 4- by 2- by 21-foot kiln held about 350 pounds of ore plus reducing agent and desulfurizing material. With the highly concentrated magnetite ore used, this is equivalent to 250 pounds of iron, or about 265 pounds of concentrated sponge iron. In test CXI, for which the data are given in table 17, the rate of draw during the latter part of the test was about 110 pounds an hour, the sponge iron showing good reduction. This was about the maximum rate of production possible with this kiln if a high degree of reduction was desired. At this rate of discharge the sponge iron would be in the reducing section approximately 2 hours 24 minutes. In the laboratory tests 1 hour 20 minutes was enough to give efficient reduction at a reducing temperature of 1,950° F. The time required to reduce ore in the internally fired kiln is nearly twice as long as in the laboratory pipe furnace, However, when the laboratory tests are run at 1,900° F., only 85-percent reduction is obtained in 1 hour 20 minutes, and more than 2 hours probably would be required to obtain the same reduction at 1,900° F.

SULFUR ON SURFACE OF SPONGE-IRON PARTICLES

The lower sulfur content of sponge iron obtained when minus-8-, plus-20-mesh limestone was used as the sulfur-control agent, compared with the results of similar tests in which finely ground limestone was employed, indicated that the problem of producing low-sulfur sponge iron was not entirely one of chemical equilibrium but involved physical factors as well. An investigation was therefore undertaken to determine the nature of sulfur absorbed by the sponge iron.

TABLE 17.—*Summary of test CXI in 4- by 2- by 21-foot kiln in which highly concentrated Scrub Oak magnetite ore (New Jersey) was reduced with foundry coke; sized dolomite was added as the sulfur-control agent*

Purpose of test: To determine satisfactory operating conditions and temperatures for the charge materials employed.
Charge ratio: 100 pounds of minus-20-mesh, plus-60-mesh highly concentrated Scrub Oak magnetite ore, 80 pounds of foundry coke ground in a hammer mill and screened to minus-¼-inch, and 15 pounds of commercial 6/20-size dolomite.
Burner: Oil, 5½-gallon-per-hour nozzle at beginning of test, 4½-gallon-per-hour nozzle later.

Duration of test, hours	Average temperature of thermocouple, ° F.		Ore feed, pounds	Sponge iron in 53 draws,[1] pounds	Chemical analysis, percent						
	Discharge end	Feed end			Sulfur	Total iron	Metallic iron	Reduction	SiO_2	Insoluble	C
31	1,925	1,850	2,300	1,436	0.041	92.9	86.6	93.2	1.26	2.70	0.40

[1] A draw averaged 27.1 pounds.

Analysis of sieve fractions of high-sulfur sponge iron prepared in the presence of sulfur-control agents showed that fine particles contained much more sulfur than coarse particles.

Experimental evidence establishing the existence of such a surface layer is presented in a separate publication,[49] which contains photomicrographs of the layer, sulfur prints, and graphs of sulfur content plotted against particle size. These data indicate that the sulfur contained within the iron particles is quite low (below 0.03 percent).

Consequently, it appears that in the production of low-sulfur sponge iron it is important to avoid the formation of a basic layer on the surface of the particles by preventing fine particles of sulfur-control agent from coming in too intimate contact with the ore during reduction.

The iron surfaces and the lime surfaces compete for the sulfur vapors coming from the reducing agent. The lime absorbs the sulfur vapor with much greater avidity, but it cannot absorb all of it.

CONCLUSIONS

1. Sponge iron with a low sulfur content (below 0.06 percent) can be produced in an internally fired kiln. One effective means of sulfur control is the addition of minus-20-, plus-100-mesh dolomite to the charge to the extent of 5 to 15 percent of the weight of the ore. When coke is used as the reducing agent, sponge iron with a low sulfur content can also be produced by mixing limestone with the coal before coking.
2. Limestone or dolomite containing a high proportion of fine particles added to the charge does not result in a low-sulfur sponge iron. A layer that contains all the sulfur above about 0.02 percent forms on the surface of the particles. Calculation of the iron-iron sulfide-calcium oxide-calcium sulfide equilibrium indicates that the sulfur content of sponge iron should be low (0.006 percent), provided no sulfur-control agent adheres to the sponge iron. Some sieve fractions of sponge iron made with sized dolomite as the sulfur-control agent contained 0.009 percent sulfur.
3. Iron ore can be reduced almost completely (95-percent reduction) in 2½ hours in an internally fired kiln. Magnetite ores should be ground to 10-mesh or finer and reduced at temperatures of about 1,950° F. Other iron ores can be considerably coarser (minus-¼-inch) and do not require as high reduction temperatures (1,800°–1,900° F.). In a small, externally heated rotary pipe furnace iron ore can be reduced almost completely in 1 hour 20 minutes at 1,950° F. The time required for reduction increases rapidly with small decreases in the reduction temperature.
4. Reducing agents vary considerably in the rate at which they will reduce a given ore at a specified temperature. Often considerable difference in reactivity will be observed between samples of reducing agents of the same type and with approximately the same chemical analysis.
5. To obtain maximum production, a large portion of the kiln must be heated to a uniform temperature. The shape of the flame of the burner used to heat the kiln is very important.
6. The drum and coil arrangement used for cooling the sponge iron was very satisfactory.
7. The refractory kiln lining has a relatively long life at normal reduction temperatures (below 2,000° F.).
8. Sintered masses and accretions on the walls of the kiln tend to form and grow at an increasing rate when the reduction temperature is raised to obtain more rapid reduction. However, for most raw materials there is an optimum temperature range at which rapid reduction can be obtained but at which the formation of sintered masses and accretions is sufficiently slow so that they do not seriously interfere with the operation of the process.
9. Magnetite ore can be magnetically concentrated to the extent that sponge iron made from it should be a desirable melting stock, particularly for electric furnaces.
10. Magnetic concentration of granular sponge iron effectively removes unconsumed reducing agent, ash, and sulfur-control agent. A large proportion of the gangue in the ore is also removed by magnetic concentration of the sponge iron. Finely disseminated gangue is not eliminated by magnetic concentration of unground sponge iron. Partial grinding of sponge iron will disintegrate gangue particles in preference to iron particles, and finely disseminated gangue usually can then be eliminated by removal of the fine particles or by magnetic concentration.

LARAMIE SPONGE-IRON PILOT PLANT

The Bureau of Mines, acting under congressional authorization in 1942, constructed a pilot plant at Laramie, Wyo., to investigate solid-fuel reduction of iron ores in a rotary kiln.

TWO-DIAMETER ROTARY KILN

The rotary kiln was modeled after the two-diameter rotary kiln developed by Williams, Barrett, and Larsen.[50] It consists of two sections joined together; one section is 50 feet long and 6 feet in diameter and the other 30 feet long

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[49] Buehl, R. C., Shoub, E. P., and Riott, J. P., Production of Low-Sulfur Sponge Iron: Am. Inst. Min. and Met. Eng. Tech. Pub. 2093, Metals Technol., October 1946, 10 pp.

[50] Williams, C. E., Barrett, E. P., and Larsen, B. M., Production of Sponge Iron: Bureau of Mines Bull. 270, 1927, 175 pp.

and 9 feet in diameter—a total length of 80 feet. A section 3 feet 9 inches long and 6 feet in diameter was added to the discharge end to permit discharge of large pieces and to provide an air seal. The sizes of the two sections were not predetermined but were the only suitable kiln sections available at the time of construction. Both sections were obtained second-hand. Details of the kiln construction are shown in figure 11.

The 6-foot section is lined with a 6-inch layer of fire-clay blocks and the 9-foot section with an insulating layer of 4-inch firebrick covered with a layer of 6-inch fire-clay blocks. All bricks were laid dry and then cemented by flushing with a liquid mixture of latite.

At the discharge end of the large-diameter section of the kiln a brick grating was constructed, so that the charge passed through the grating to a spiral cooler [51] mounted on the outside and cooled by water sprays. The openings in the grating are 2 by 4 inches; any lumps or nodules larger than the openings are discharged through the end of the kiln into a hopper and do not pass through the spiral cooler. The discharge end of the kiln is covered with a stationary firebrick-lined hood with an expansion-permitting air seal to prevent air from entering. This hood is provided with three observation windows and a hole for the burner.

Because of simplicity of installation, the kiln originally was fired with natural gas by means of an inspiration-type burner. Later, a system for firing with granulated coal was installed, so arranged that either gas or coal could be used. Oil firing was not attempted.

PLANT OPERATION

While the plant was in operation, 40 separate tests, each of which lasted 3 to 10 days, were made in the rotary kiln. The purpose of these tests was to establish an operating procedure that would be commercially feasible rather than to accumulate a mass of empirical data. Each test was made to determine the influence of one or more of the many variables affecting the production of sponge iron, with the ultimate goal of developing a continuous process that would yield high-grade sponge iron. Between tests changes and improvements in the flow scheme and equipment were made. Some of the tests yielded good sponge iron, some a fair product, and others a worthless material, which was discarded; all contributed valuable information applicable to large-scale production of sponge iron in a rotary kiln.

The general procedure in each test was as follows: The kiln was gradually heated for 6 to 8 hours with a gas burner until the large-diameter section was at a red heat of approximately 700° C. Charging was then started, and the temperature was gradually increased for another 6 hours, until the temperature in the charge in the large-diameter section was approximately 950° C. From then on adjustments in temperature, draft, rate of feed, and composition of feed were made according to conditions within the reducing zone as the test progressed. When the test was completed, the kiln was emptied of charge and gradually cooled for 48 hours before it was stopped.

Tests on Sunrise Ore.—The first 22 tests were made on red hematite ore from Sunrise, Wyo. The ore was the undersize material (minus-½-inch) screened from the regular run-of-mine production; it analyzed 50.8 percent iron, 16.7 percent acid insoluble, 0.05 percent sulfur, and small quantities of phosphorus, manganese, lime, titanium, and copper. It was fairly hard and crystalline, with a greasy or talcy "feel" when ground fine. The gangue minerals in the ore comprised various silicates intimately associated with iron oxide. As received, one-third of the ore was plus-10-mesh, and two-thirds was minus-10-mesh. The ore contained 12 to 15 percent moisture; after drying and crushing in preparation for charging to the kiln, it contained 2 percent moisture and was sized as follows:

	Percent
Minus-⅛-inch, plus-10-mesh	27. 8
Minus-10-, plus 35-mesh	44. 0
Minus-35-, plus-100-mesh	14. 1
Minus-100-mesh	14. 1
	100. 0

Subbituminous slack coal from the Hanna, Wyo., coal fields was used as a reducing agent in a few tests. A typical analysis of this coal showed 44.0 percent volatile matter, 46.0 percent fixed carbon, 9.0 percent ash, and 0.4 percent sulfur; the heating value was 11,000 B. t. u. per pound. Although a solid fuel containing less volatile carbon would have been more desirable, this coal was available at low cost and could be obtained readily, whereas other coals and coke were difficult to obtain.

Preliminary small-scale tests and calculations indicated that 40 parts of fixed carbon was necessary to reduce 100 parts of Sunrise ore. With the kiln rotating at ¾ r. p. m., slope at ½ inch per foot, and a charge weighing 80 pounds per cubic foot, it was estimated that 2 tons of charge per hour could be treated when heated to approximately 1,000° C.

In using subbituminous coal as the reducing agent, only the fixed carbon was considered to be effective, but it was believed that the volatile carbon would burn in the preheating section of

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[51] The cooler was made and used with the permission of the Plastic Metals Co., of Johnstown, Pa., which is the inventor of the cooler and owner of the patent rights.

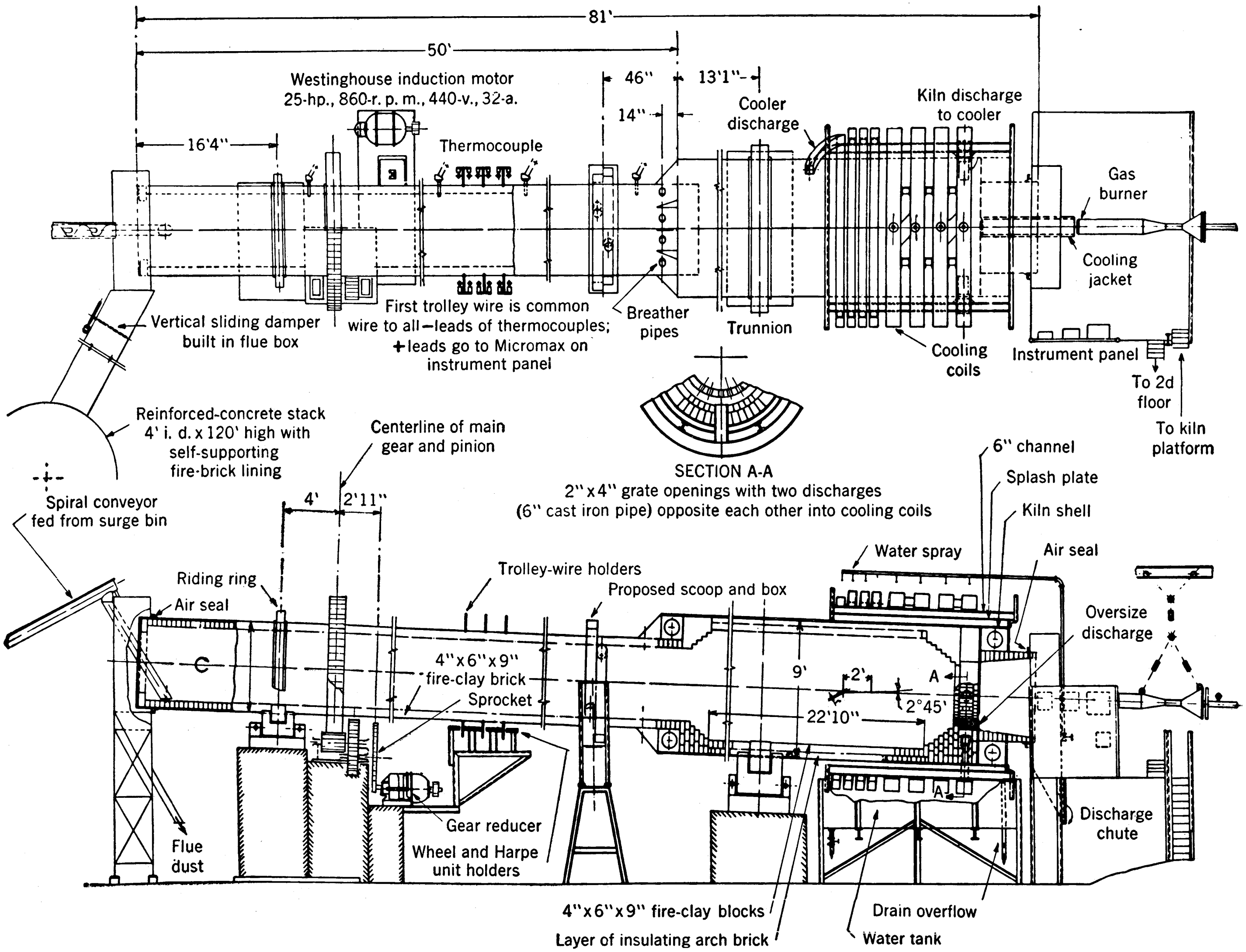

FIGURE 11.—DETAIL DRAWING OF TWO-DIAMETER ROTARY KILN.

the kiln and heat the iron ore to the temperature required for reduction. The method of utilizing this heat value and controlling the temperature attained was expected to prove a problem that would require considerable experimentation to solve. Coke breeze was mixed with coal in various proportions to lower the volatile carbon content of the charge, but its use was limited, owing to lack of a dependable supply, and its value, therefore, was not fully determined.

Control of volatile carbon depended upon control of air entering the kiln during volatilization. By wetting the incoming charge and excluding air the volatile carbon fumed off as a dense black smoke, and its heat value was wasted. By injecting air into the kiln the volatile carbon burned and resulted in higher temperatures than desired and often caused fusion of the charge in the preheating zone. Variation of conditions in the preheating zone was reflected in irregularities in the reducing zone and erratic products.

Because of its high-volatile carbon content, the use of Hanna (Wyo.) subbituminous coal introduced many problems. When made into char by a devolatilizing treatment, some of the difficulties were overcome, but such practice wasted almost half of the heating value of the coal.

Other methods of using this coal, whereby a fuller utilization of its heating value could be obtained, were studied and considered and were put into practice in tests 21 and 22. In these tests coal was introduced at the firing end of the kiln instead of the cold or feed end. Common practice in the cement industry for firing rotary kilns with pulverized coal is to blow the coal into the kiln with enough air so that the fine coal burns completely to gas while in suspension. For these tests the practice was varied slightly; the coal was ground to pass a ⅛-inch screen and therefore contained many granular pieces, screen tests showing 60 percent plus-35-mesh. When the granular coal was blown into the kiln, the fine particles as well as the volatile carbon of the coarse particles burned while in suspension, but the granular fixed carbon, or char, dropped out of the blown stream to the bed to act as the reducing agent.

The initial 11 tests showed that by first charring the subbituminous coal and then using char in the sponge-iron charge the volatile carbon content was less and conditions within the kiln could be controlled fairly well. However, conditions at the discharge end of the kiln were difficult to control because the hottest zone was at the discharge grates. The gas burner was in the hood 4 feet from the grates and cast a flame into the kiln in such a manner that the grates became overheated and often caused the discharging material to fuse at this point and clog the grates.

When the burner was moved farther into the kiln it became overheated; the gas would ignite and burn within the burner and become uncontrollable. Insulating or protecting the burner from overheating was tried but was not entirely effective. Other improvised burners, comprising an air-gas mixing chamber and straight pipes, were found unsatisfactory and were discarded. Finally, in test 17 a water jacket was made that permitted the burner to be placed 4 feet farther into the kiln. This solved the burner difficulties with gas burners as far as could be determined at this stage of operation.

The material discharged from the kiln in tests 1 to 22 was a mixture containing iron pellets and nodules, slag, semifused gangue minerals, coal ash, and char. Much of it consisted of semifused masses of iron and slag in which the iron was so interlocked that its recovery entailed more labor than it was worth, so most of it was discarded. Some of it was charged to a cupola furnace with coke and melted, yielding slag and white cast iron. Whenever possible, the larger nodules of iron were hand-picked from the discharged material, cleaned by tumbling in a ball mill, and stockpiled. Pockets of slag in the larger nodules could not be removed and accounted for the high insoluble content.

The small pieces that passed through the discharge grating and the cooler were separated magnetically into iron and nonmagnetic char and slag. The magnetic product was tumbled in a ball mill with low ball charge to clean the iron and was then screened on a ⅛-inch screen to separate the iron from slag. The nonmagnetic product was recycled if high in char; otherwise, it was discarded. The whole treatment was crude and laborious but was done, pending the development of a more suitable process. The finished products were separated into two stockpiles, one of nodules larger than ½ inch and the other of minus-½-, plus-⅛-inch pellets. Samples of each pile showed the analysis given in table 18.

Tests on Shasta Ore.—While tests were being made on Shasta magnetite ore (tests 23 to 39, inclusive), considerable work was done in testing various methods of separation and cleaning the iron after it was discharged from the kiln. Various machines were tried and, if satisfactory, were installed in a flow scheme that permitted a continuous flow from the kiln through the briquetting press. A magnetic pulley, crushing rolls, centrifugal polisher, Stearns magnetic separator, and briquetting press plus conveyors, elevators, and storage bins comprised the set-up. The treatment of the kiln product in this system was effective in removing an appreciable

TABLE 18.—*Results of tests on Sunrise ore*

Material	Tons	Analysis, percent						Percent reduction
		Metallic Fe	Total Fe	Insoluble	C	S	P	
Plus-½-inch nodules	23	84. 13	86. 6	8. 2	1. 32	0. 14	0. 08	97. 1
Minus-½-, plus-⅛-inch pellets	32	90. 56	91. 5	4. 5	2. 02	. 11	. 07	99. 0

amount of the impurities from the reduced iron. In test 39 iron ore and coal entered the plant at one end, and for the first time briquetted sponge iron was taken out at the other end in a continuous flow. There still remained considerable room for further development and improvement.

Experiment with Scoop Feeder on Kiln (Test 40).—A scoop feeder was installed in the small-diameter section of the kiln 6 feet from the junction of the two sections as a means of introducing part of the charge; the cold charge helped to prevent overheating of the junction where accretions always formed. Two scoops similar to ball-mill scoops were placed close together and attached to the outside of the kiln in such manner that material could be scooped up and discharged into the kiln twice each revolution of the kiln.

The test demonstrated that a scoop feeder provides additional means of controlling conditions within the kiln. Results showed that the method was practical and had possibilities for future development. After test 40 the plant was placed in a stand-by condition, and no further tests were made.

Plant Production.—The production from each of the various tests (23 to 40, inclusive) on Shasta ore was often set aside until the equipment for cleaning and briquetting could be operated. Many experiments in briquetting and changes in the flow scheme were made during the intervals between these tests; consequently, the production of briquets did not represent the production of individual tests. However, the production was separated into lots as made, and each lot was weighed, sampled, and stored until shipped. Some reoxidation took place from the time the sponge iron was produced to the time the briquets were sampled. Table 19 gives the data on the various lots.

The press could press cylindrical briquets 4 or 5 inches in diameter and 3 inches high at the rate of 14 a minute. Briquets made of granular sponge iron pressed at 12.5 tons per square inch weighed approximately 8 pounds and had a density of 4.7 to 5. These briquets were not durable enough to withstand rough handling, so various binders, such as asphalt, cement, kerosine, water, and acid, were tried. Best results were obtained when the cleaned, granular sponge iron was moistened with 3 percent of a 5-percent HCl solution just before briquetting. This acid caused some reoxidation but gave a durable briquet that became harder with age. The finished product of each test was briquetted, and the briquets were stockpiled until shipped.

In addition to the 55 tons of iron nodules and

TABLE 19.—*Results of tests on Shasta ore, Shasta, Calif.*

Lot No.	Tons	Analysis, percent							Percent reduction
		Metallic Fe	Total Fe	Insoluble	SiO_2	S	C	P	
1	19	80. 31	90. 02	3. 50	2. 36	0. 082	1. 01	0. 011	89. 21
2	15	81. 73	90. 50	3. 56	2. 48	. 052	1. 06	. 025	90. 31
3	26	70. 72	84. 78	4. 62	3. 76	. 106	. 62	Tr.	83. 42
4	14	76. 30	88. 12	3. 76	2. 56	. 047	. 95	Tr.	86. 59
5	14	76. 97	87. 68	3. 80	2. 40	. 066	1. 05	Tr.	87. 78
6	24	78. 08	86. 34	4. 96	3. 28	. 070	1. 21	Tr.	90. 43
7	5	76. 52	88. 12	3. 28	1. 96	. 052	1. 23	Tr.	86. 84
8	15	72. 06	85. 67	5. 00	3. 20	. 076	. 68	Tr.	84. 11
9	12	69. 38	86. 56	3. 28	2. 36	. 128	. 76	Tr.	80. 15
10	17	79. 87	88. 79	3. 80	2. 36	. 052	. 66	Tr.	89. 95
Total	161								

pellets shipped to a nearby steel plant, 3 carloads containing 160 tons of briquetted sponge iron were shipped to the Bureau of Mines alloy station at Redding, Calif., to be made into steel in an electric furnace. Small lots of granular sponge iron were shipped to copper companies and other interested parties for experimental work. The balance of the production, which was of inferior grade and of questionable value, was stockpiled near the plant for possible retreatment at some future date. Much of it was in the form of balls and nodules consisting of iron and char cemented together with slag and would require more effort to beneficiate than was warranted by the products that could be obtained.

OBSERVATIONS CONCERNING THE TESTS AT LARAMIE

The following conclusions were drawn from the tests at Laramie:

1. Coals containing large amounts of volatile matter should not be used as the reducing agent. They should be previously charred or carbonized to remove most of the volatile matter.
2. When the ore was fed into the cold end of the kiln and the fuel (minus-⅛-inch coal) was blown in at the hot end, the heat value of the coal was more effectively utilized. Blowing fuel and reducer into the kiln was tried with numerous combinations of coal and char, which at times gave good results but was never satisfactory enough to warrant its adoption as a regular procedure.
3. When the charge consisted of equal volumes of Sunrise hematite and char, particles of reduced iron welded together at temperatures of 1,000° C. or more into small pellets and irregularly shaped rounded nodules, often coated with slag.
4. There was little difference in the reduction of minus-⅛-inch Sunrise red hematite and of minus-⅛-inch Shasta dense magnetite in the rotary kiln.
5. Best results were obtained with Shasta magnetite when mixed with excess char and heated at 950° C. Pelletizing at higher temperatures was tried, but the product was an agglomerated mass of iron and slag, which did not respond to cleaning.
6. Generally, the slag-coated magnetic particles of sponge iron could be cleaned by passing them through a roll crusher and a centrifugal polishing machine (a hammer mill with rotor in vertical position), followed by a magnetic separator. This treatment removed the brittle slag and about 50 percent of the sulfur as brittle FeS in dust sizes.
7. An excess of reducing agent lessens the tendency of the particles to fuse together or to stick to the lining of the kiln.
8. Unburned char in the nonmagnetic product from the magnetic separator can be used as a part of the reducing agent in a new charge. This practice increases the gangue in the charge and if too much is used tends to increase ring formation.
9. In some tests the rate of heat transfer to the charge was very poor. Masses of cooler material sometimes formed in the interior of the charge and then disappeared for no apparent reason. (The speed of rotation was too slow to stir the material sufficiently to permit rapid heat transfer. There is a minimum peripheral speed required to cause a charge to "roll" in a rotary kiln. This action depends upon the kind of material, lining, depth of charge, temperature, and particle-size distribution in the material.)
10. The spiral cooler was very effective in cooling the hot discharged product from about 1,000° C. to about 100° C.
11. Durable briquets could be made from the cleaned granular sponge iron if it was moistened with 3 percent of a 5-percent HCl solution just before pressing at 12.5 tons per square inch. Briquets 4 or 5 inches in diameter and 3 inches in length could be made at the rate of 14 a minute. Each briquet weighed 8 pounds and had a density of 4.7 to 5.0.
12. The Krupp-Renn process was tried with some success but was abandoned in favor of making granular sponge iron at a lower temperature and briquetting the beneficiated sponge iron.
13. A definite operating procedure was not established.
14. One carload, 55 tons of nodules and pellets, and three carloads, 160 tons of briquets, were shipped for test work in steel making.
15. A high proportion of disseminated siliceous minerals in the iron ore is undesirable on account of excessive slag formation and formation of accretions and rings on the kiln lining, particularly at the junction between the small and large diameters of the kiln.
16. A boring bar like those often used in cement kilns would have advantages in removal of accretions and rings, particularly from the junction between the small- and large-diameter sections of the kiln where too frequently a run was stopped in the above work. A means of reducing the formation of rings and accretions would be to avoid a sharp change in diameter by substituting a long bevel in the masonry lining.

DESIGN OF ROTARY-KILN PLANT[52]

EQUIPMENT AND FACILITIES REQUIRED

A plant for the production of granular sponge iron should include the following equipment and facilities:

1. Railroad spur.
2. Unloading and materials-handling equipment.
3. Rotary drier (optional).
4. Grinding equipment.
5. Raw-materials storage.
6. Conveyor to feed charge into kiln.
7. Kiln, including suitable burner and arrangement for cooling the sponge iron.
8. Conveyor to magnetic separator.
9. Magnetic separator.
10. Conveyor equipment for finished material.
11. Storage for finished materials.
12. Shipping facilities.

MATERIALS-HANDLING EQUIPMENT

The raw materials, after grinding to the usual mesh size for the process, do not flow readily even when they are dry. A little moisture usually will cause the angle of repose to exceed 60°. As a result, material often will not flow out of storage hoppers, even though they have sloping bottoms and openings that may be as large as 6 inches square. Large vibrators on the sides of such hoppers tend to keep the material flowing. However, if the flow of material is interrupted while the vibrators are running, the vibrators may cause the material to pack very tightly.

The proper proportioning of the feed through the use of variable feeders is a difficult problem. Vibrating feeders were found to be very unsatisfactory for this purpose, as variations in the moisture content result in large variations in the rate of flow. Variable-speed screw feeders, on the other hand, performed acceptably well, provided the flow from the hoppers could be maintained. Any system of proportional feeding that does not involve weighing the charge should be checked and, if necessary, readjusted at definite intervals. It would therefore be well to install the feeders in an accessible place. Likewise they should be equipped with a mechanism that will give a signal or will start vibrators on the hoppers when they are receiving less than the normal quantity of material. Provision should also be made for cleaning the feeders and the bottoms of the hoppers readily if they jam with wet material. Nearly all of the difficulty can be avoided by partly drying the raw materials before storage; this probably could be done with waste heat from the kiln. Reduced granular sponge iron flows readily and does not present these difficulties in handling.

The inclined pipe through which the raw materials feed into the kiln has occasionally become jammed with the charge. Consequently, as large a pipe as feasible should be employed, and a clean path should be provided for the insertion of a cleaning rod down the pipe. This cleaning rod should be allowed to hang inside the feeding pipe during normal operation so that the pipe will not plug solid.

A ring of material often forms on the brick lining near the point where the charge enters the kiln, especially when the reducing agent has coking properties. The ring adheres loosely, and a scraper operating continuously should be provided to remove it as rapidly as it forms. As the kiln is relatively cool at the feed end, the scraper can be constructed of steel. The ring can also be removed by occasionally poking it with a rod, but this causes large pieces of charge to enter the kiln, and these may form balls; the rod therefore is not as satisfactory as the scraper.

ROTARY-KILN PROPORTIONS

The rotary-kiln process differs from calcining in that the material must be held at maximum temperatures for approximately 2 hours. The kiln design and proportions should therefore be different from those used for calcining operations, such as the production of cement. A relatively deep bed of material should be maintained at the discharge end of the kiln. The closed-end construction used in this investigation is satisfactory. If the usual type of firing hood is used at the discharge end in place of the closed-end construction, a refractory dam could be provided at the end of the kiln to maintain a definite depth of material in the furnace. For small kilns it is believed that the closed-end construction is preferable, but for large kilns the other arrangement might have some advantages. In the previous investigation the Bureau of Mines[53] proposed the use of a two-diameter kiln with the large-diameter section at the discharge end. This construction has proved to be satisfactory. The purpose of the two-diameter kiln is to permit rapid heating of the charge as a thin layer in the preheating section of the kiln, followed by reduction of the ore under strongly reducing conditions in a deep bed of material in the large-diameter section. With such a construction, it is important that the diameter of the preheating section should not be too small as compared to the diameter of the enlarged section. Too great a difference in diameter results in higher temperatures in the small-diameter section than in the large-diameter section, and material will adhere to

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[52] Buehl, R. C., Shoub, E. P., and Riott, J. P., Control of Sulfur Content of Sponge Iron Produced in Rotary Kilns: Bureau of Mines Rept. of Investigations 4057, 1947, 102 pp.

[53] Williams, C. E., Barrett, E. P., and Larsen, B. M., Production of Sponge Iron: Bureau of Mines Bull. 270, 1927, 175 pp.

the refractory of the small-diameter section near the junction of the two sections.

The use of two separate kilns independently fired and independently rotated and mounted, so that one will feed into the other, might be advantageous, especially if the ore has a high sulfur content. Ore could be preheated to the desired temperature in the higher kiln with an oxidizing flame to remove sulfur. The hot ore, plus reducing and desulfurizing agent, would then be fed into the lower kiln, which would be maintained at the optimum temperature for satisfactory reduction. Volatile matter from the coal and other combustible gases from the reducing kiln would be burned in the preheating kiln. This arrangement should permit separate control of the reduction and preheating operations, which would be especially desirable for experimental tests.

COOLING OF SPONGE IRON [54]

The cooling system employed was very satisfactory, provided there were no leaks in the drum. Most of the material discharged was of a light-gray color, which is a good indication that reoxidation was negligible. In general, a blue or reddish color indicates slight reoxidation, whereas a dark-brown or black material indicates excessive reoxidation. However, black material is often obtained from certain raw materials, for example, when subbituminous coal from Wyoming was used as a reducing agent, even though the reduction of sponge iron was very high and there was no indication of reoxidation. The variation in degree of reduction with particle size is an indication of reoxidation, as fine particles will reoxidize to a much greater extent than coarse particles.

Minute leaks in the cooling drum can cause considerable reoxidation of sponge iron, especially when the leaks permit cooling water to enter the drum. Consequently, an all-welded construction is preferable. For cleaning purposes at least two openings that can be sealed should be provided on the periphery of the cooling drum. They should be larger than the inside diameter of the pipe connecting the kiln and cooling drum and should be in a position that the pipe and cooling coil can be reached where they join the drum.

The pipe connecting the kiln with the cooling drum should be attached to the kiln as close to the end as possible. In a cooling system that extends from the end of the kiln this pipe should have a scooping action as the kiln revolves; that is, the pipe should come from the kiln at an angle, with the leading edge in the direction of rotation attached to the kiln. On the other hand, when a peripheral drum is employed, as in figure 9, a perpendicular drop from the kiln into the drum is satisfactory.

The pipe connecting the cooling drum with the furnace should be at least 4 inches in inside diameter; otherwise, the pipe may become jammed with sponge iron. If the pipe is large enough, such difficulty rarely occurs. A bar can be placed across the opening of this pipe to prevent the entrance of balls that are larger than the inside diameter of the cooling coil; with this construction, the cooling drum seldom needs to be opened except possibly at the beginning of operations. However, this arrangement leaves small balls of sponge iron in the kiln, which roll on top of the bed of charge and gradually increase in size until they are removed by some other method. Experience has indicated that it is desirable to permit balls to enter the drum and to modify the construction so that they can be removed occasionally by opening the drum with only short interruption of the continuous operation of the process. A valve in the pipe connecting the furnace and the cooling drum would serve this purpose. It could be used mainly to limit the discharge into the drum at the beginning of operations or while balls were being removed from the drum.

About an hour is required to cool the sponge iron, and the drum should be large enough to hold at least twice the hourly capacity of the kiln. The sponge iron would then cool sufficiently, even though the drum was only half full.

The main function of the cooling coil is to prevent air from entering the drum, although it serves also as an additional means of cooling the sponge iron. The coil must remain partly filled at all times; otherwise, air will enter the drum and cause reoxidation of the sponge iron. The coil must therefore be small enough in diameter that it will not drain the cooling drum, or it must be provided with a valve or orifice at the discharge end to limit the discharge and keep the pipe full of material.

BURNER

The composition and shape of the flame are important. To heat the reducing zone, it is necessary to employ a flame that widens out rapidly after leaving the burner. A narrow-angle flame will not give a sufficiently hot zone at the discharge end to prevent reoxidation. On the other hand, a short flame will decrease the effective length of the reducing zone. The flame must also be of such a nature as to avoid "hot spots" in the furnace. If any point becomes excessively hot, sintering, balling, and sticking to the walls will occur; moreover, slag will form and coat the particles of sponge iron.

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[54] Buehl, R. C., Shoub, E. P., and Riott, J. P., Control of Sulfur Content of Sponge Iron in Rotary Kilns: Bureau of Mines Rept. of Investigations 4057, 1947, 102 pp.

Such a slag coating usually contains much more sulfur than the iron and therefore raises the sulfur content of the final product.

It is difficult to maintain a flame of the proper shape and composition, as reducing gases from the charge and combustion of the reducing agent interfere with the heating flame. A temperature of ±20° F. can generally be maintained at a selected location, provided the rates of feed and discharge do not vary greatly. By adjusting the length of the burner flame two zones can be maintained at the same temperature if the distance between them is not too great. However, the problem is much more difficult in a long kiln, as the temperature in the reducing zone might vary considerably even when that in both ends is the same. To maintain the maximum depth of charge with the construction employed, the burner must fire through the center of the kiln and nearly tangential to the charge surface. It is therefore difficult to change the temperature distribution by tilting the burner or heating with multiple burners.

Another method of controlling distribution of temperature would be desirable. One method is to blow air into the preheating section of the kiln through pipes either inserted through the walls of the kiln or projecting into the kiln from the rear. This method would have the additional advantage of utilizing part of the volatile content of the reducing agent for preheating the charge.

KILN LINING

Ordinary fire-clay brick has been found satisfactory for lining the kiln. Reducing temperatures of 2,000° F. or less have very little effect upon this refractory. Higher temperatures tend to cause the formation of some slag, which attacks the lining. The bricks of the reducing zone require more frequent replacement than those in the remainder of the kiln. For example, when this experimental work was begun, the entire lining of the 4- by 2- by 21-foot kiln had been used for approximately 2 years. The reducing zone had several loose bricks, and it alone was relined after several tests had been performed in the kiln. The new lining remained in good condition until tests were made in which a slag was formed at approximately 2,250° F. When the high-temperature tests were completed, the reducing section was again relined, and this lining was in good condition at the end of the experimental work. The unreplaced section of the lining was still in excellent condition.

TEMPERATURE MEASUREMENTS

Thermocouples passing through the side of the kiln and extending into the charge have the advantage of permitting measurement of the temperature along the length of the kiln. Stopping the kiln for such measurements while the thermocouples are immersed in the charge, as was done in tests in the small kiln, interferes with continuous production and may reduce the capacity of the kiln to some extent. For continuous commercial production thermocouples attached to sliding contacts probably would be preferable, as readings of temperature would then be continuous. Measuring temperature with an optical pyrometer avoids the nuisance of changing thermocouples and wells but does not permit accurate determination of the temperature gradient along the length of the kiln; nor does it permit accurate readings, because the charge is not homogeneous in temperature and reflectivity.

SUGGESTIONS FOR OPERATION OF EQUIPMENT

RAW MATERIALS

The ore should be ground fine enough to give rapid reduction. However, too large a proportion of very fine particles is likely to cause excessive balling and sticking of the sponge iron to the walls of the kiln. In practice, it is possible to adjust these two factors satisfactorily. The rate at which reducing agents will reduce a given ore at a specified temperature varies considerably. At the higher reduction tempertures employed in later tests (1,900° to 1,950° F.), some samples from the following types of reducing agent were found to be active: High- and low-temperature coke, petroleum coke, anthracite, subbituminous coal, and char made from subbituminous coal. Surprisingly, other samples of petroleum coke and anthracite with analyses nearly identical to those of good reducing agents were inactive. It is very important that an active reducing agent be used.

PROCESS

The use of high reduction temperatures results in an increase in kiln capacity compared with operation at lower temperatures. However, high temperatures are likely to cause excessive balling and sticking, which must be offset to obtain the best operating temperatures. Under normal operation balling and sticking are related not only to operating temperature but also to raw materials and degree of reduction.

Certain raw materials permit a higher operating temperature than others. Consequently, comparison of the rates of reduction with different raw materials at a constant temperature rather than at the maximum temperature at which balling and sticking are not excessive is likely to be misleading. The use of a higher ratio of reducing agent to ore results in less balling and sticking of the sponge iron and may permit the use of somewhat higher operating temperatures. However, most of the volume of the kiln is occupied by the reducing agent, since it is less dense than ore, and an excessive amount is likely to cause a corresponding decrease in capacity. As most of the volatile content of coal is lost in the preheating section, it appears that the fixed-carbon content only is important; a ratio of the fixed-carbon content of the reducing agent to weight of ore of 0.35 to 0.60 appeared most satisfactory for the raw materials employed.

In starting a campaign the furnace should be moderately full before it reaches operating temperatures; otherwise, sticking to the walls of the kiln is likely to occur.

Whenever rotation of the kiln must be stopped for any reason, the feeders should be stopped and the burner turned off, if balling and sticking are to be kept at a minimum. Small balls apparently form in either of two ways: Several particles of granular material may sinter together on the surface of the charge, or pieces of accretions may fall off the walls. Small balls tend to rise to the surface of the charge, roll over the surface, and grow as does a snowball. Usually the balls contain only a small amount of coke, except near the center in some instances.

Accretions on the kiln walls usually contain considerable coke and are weak and adhere loosely at operating temperatures. They are easily removed by scraping with a rod. With the raw materials employed, accretions formed most readily at 2,000° to 2,100° F. Often, accretions formed in this temperature range were completely removed by heating to higher temperatures. Accretions usually can be removed by feeding only coke for a while and raising the temperature. It had been observed that sudden changes in temperature would cause accretions to fall off, even when the composition of the charge was normal.

Maximum production of a uniform grade of sponge iron was obtained with a uniform rate of discharge, constant operating temperatures, and as high a bed of charge as possible. To maintain a constant depth of bed with a constant volume of discharge, the rate of feed must be varied to offset changes in the iron content of the discharges and changes in the density of the furnace charge due to combustion of the reducing agent. Considerable time is required for the feed to pass through the preheating section, so that changes in the bed that require changes in the rate of feed must be anticipated. Successful operation of a kiln depends largely on the judgment of the operators. Unavoidable fluctuations in operating conditions cause variations in the rate of reduction, and the operator must determine the rate of discharge and whether a change in operating temperatures is desirable.

The magnetic properties of sponge iron vary with the degree of reduction. The quantity of sponge iron held by a magnet of suitable shape and strength increases with the degree of reduction. When operations are continued for a long time on the same ore, one can acquire considerable skill in estimating the degree of reduction from the quantity of material held by a particular magnet. Because of the time required for material to pass through the cooling drum and coil and the mixing of the contents of the drum, it is often advantageous to remove a small sample from the furnace for examination. Such a sample must be protected against reoxidation during cooling. A 7-foot length of 1½-inch iron pipe permanently capped at one end and loosely capped at the other can be used for sampling and cooling. One end of the pipe, with the cap removed, is inserted into the charge, and the other end is then lowered so that the sample will slide to the cooler end. This operation is repeated several times; then the pipe is removed from the furnace, and a cap is immediately placed on the open end. The sample should be allowed to cool in this pipe before the material is removed for examination.

FACTORS INVOLVED IN THE COST OF PRODUCING SPONGE IRON IN ROTARY KILNS

The conditions under which this project was operated were such that reliable data on the cost of producing sponge iron could not be determined. The smaller (4- by 2- by 21-foot) kiln obviously is too small for low-cost commercial production. The larger (6- by 5- by 60-foot) kiln was operated intermittently for a total of only 9 days. This short time of operation was not sufficient to establish good operating conditions or furnish reliable cost estimates.

A large part of the cost of sponge iron is represented by the raw materials, including freight and handling costs. The choice of raw materials and their cost are influenced greatly by the geographical location of the plant. Any cost estimate would therefore be valid only for the size of the plant and location exemplified. Consequently, instead of such a cost estimate, the important factors that determine the cost of sponge iron will be considered to aid anyone interested in the process to estimate the cost of producing sponge iron in a chosen location.

In considering the cost of a plant it should be remembered that, although the rotary kiln with its burner and cooling drum is the important part of the process, it represents only a small part of the cost of a complete plant. Consequently, an estimate of plant investment is beyond the scope of this investigation.

In estimating the capacity of a large kiln the most logical assumption probably would be that the capacity of the kiln is nearly proportional to the holding capacity of the reducing zone that can be maintained at uniform temperature. The maximum length of the reducing zone depends largely on the design and operation of the burner, as previously stated, and careful consideration would have to be given to these items.

About 1.4 tons of high-grade magnetite ore is required to produce a ton of sponge iron. For ores of lower iron content proportionately more ore would be required. A ratio of reducing agent to ore of 0.8 was found to be very satisfactory. This amounts to 1.15 tons of reducing agent per ton of sponge iron. However, unconsumed reducing agent recovered from the magnetic separator could be utilized again. By recirculation of the reducing agent operation with less than 0.6 ton of fresh reducing agent per ton of sponge iron should be possible. The dolomite required should be 150 to 450 pounds per ton of sponge iron, depending mainly on the sulfur content of the coal. The oil consumed for heating the small kiln was about 70 gallons per ton of sponge iron. For a large kiln the quantity of fuel required should be considerably less.

If suitable mechanization is provided for handling materials, one man per shift should be able to operate a large kiln, that is, control the temperature and the rate of feed and discharge, operate the magnetic separator, store the finished product, and dispose of the reject material. Several men per day would be required to supply the kiln operators with the raw material and ship the finished material, depending on the plant capacity and degree of mechanization. As the process is relatively simple, little technical supervision should be required. At least part of a chemist's time would be required for making chemical analyses.

Maintenance costs for the process should not be high. Aside from inspection and oiling, the equipment should require little maintenance over long periods of time. The hot end of the kiln would need to be rebricked periodically, perhaps once a year. The burner block probably would require more frequent replacement, and burner parts exposed to high temperatures would have to be replaced occasionally. If a belt-type magnetic separator is employed, the belt also would have to be replaced at intervals (probably every few months).

DETERMINATION OF METALLIC IRON AND OXYGEN IN SPONGE IRON[55]

In the investigation conducted by the Bureau of Mines concerning the production and utilization of sponge iron, it soon became evident that more information was needed regarding methods for determining the degree of reduction attained in manufacturing processes. Sponge irons made by different processes vary in physical characteristics and chemical composition, and a method of analysis that is suitable for one type is not necessarily applicable to all others. For example, the hydrogen-evolution method, which measures the volume of hydrogen evolved upon treating the sample with acid, accurately determines the oxygen content of some types of sponge iron. However, when the sponge iron contains combined carbon, hydrocarbon gases are also evolved, and large errors may result. Probably no single method will give accurate results in all instances, and for this reason it is desirable to have several reliable procedures available and to know the limitations of each.

For measuring the degree of reduction determination of either metallic iron or oxygen should suffice, although for practical application of sponge iron to the production of steel the oxygen content is more significant. After consideration of proposed methods of analysis in regard to their suitability for routine use and the probable influence of other substances four procedures were chosen for investigation:

1. Mercuric chloride method.
2. Copper sulfate method.
3. Hydrogen-reduction method.
4. Hydrogen-evolution methods.

The mercuric chloride and copper sulfate methods determine metallic iron; the hydrogen-reduction method determines oxygen; and the hydrogen-evolution methods give values for both. The term "oxygen," as used here, refers only to oxygen present as iron oxide. When carbon is present, iron combined with carbon is included in the metallic iron.

MERCURIC CHLORIDE METHOD

In this method the sample is treated with a hot solution of mercuric chloride, the metallic iron dissolving according to the following equations:

$$Fe+2HgCl_2=FeCl_2+Hg_2Cl_2, \qquad (1)$$

$$Fe+HgCl_2=FeCl_2+Hg. \qquad (2)$$

After filtration to remove mercurous chloride, mercury, and undissolved material the ferrous iron is titrated with a standard oxidizing solution. A number of investigators have accepted

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[55] Morris, J. P., Determination of Metallic Iron and Oxygen in Sponge Iron: Bureau of Mines Rept. of Investigations 3824, 1945, 31 pp.

this method as being the most accurate method for determining metallic iron in the presence of iron oxides. The procedure described in this report differs somewhat from those recommended by other investigators, especially in regard to the time allowed for decomposing the sample.

RECOMMENDED PROCEDURE

Transfer 0.25 gram of minus-65-mesh sponge iron to a dry 100-ml. volumetric flask in which the air has been displaced by CO_2. Add 3 grams of solid $HgCl_2$, stopper, and mix by shaking. Add 50 ml. of boiling water and swirl for 1 minute. (Carburized or badly reoxidized samples sometimes require boiling. For such samples heat quickly to boiling and boil for 1 minute.) Immediately fill the flask almost to the top with boiling water and stopper tightly with a rubber stopper. Place in lukewarm water for 1 or 2 minutes and then transfer to an ice bath. When cold, filter with suction through a 9-cm. No. 42 Whatman filter paper into a 500-ml. Erlemeyer flask. Wash flask and paper with about 100 ml. of cold water. Add 20 ml. of titrating solution and 5 or 6 drops of indicator and titrate with 0.1 N $K_2Cr_2O_7$.

Titrating solution required: To 500 ml. of water add 200 ml. of H_2SO_4. Cool and add 300 ml. of H_3PO_4 (85 percent).

Indicator: Dissolve 0.1 gram of barium diphenylamine sulfonate in 50 ml. of water.

CONCLUSION

The mercuric chloride method gives reasonable values for metallic iron in finely divided samples of sponge iron, with the following exceptions:

1. Oxide coatings on the iron particles may cause incomplete recovery of the metallic iron, especially with unground samples.
2. Low results for metallic iron are obtained in the presence of combined carbon or alkaline material.

COPPER SULFATE METHOD

In this method the sample is treated with a boiling solution of copper sulfate, the metallic iron dissolving according to the equation

$$Fe+CuSO_4=Cu+FeSO_4.$$

After insoluble material is removed by filtration and excess copper by precipitation with aluminum, the ferrous iron is titrated in the usual manner. The success of this method, as with others using neutral salt solutions, depends on complete dissolution of the metallic iron without appreciable attack on the iron oxides.

The results obtained on a number of test samples by using a 15-minute boiling period are shown in table 20 and figure 12. Obviously, the results of the copper sulfate method are much too high (see fig. 12), since the highest possible metallic iron content of each sample is given by the Fe_2O_3 curve. Evidently, the copper sulfate solution not only dissolved metallic iron but attacked iron oxide as well.

TABLE 20.—*Comparison of copper sulfate and mercuric chloride methods*

Sample	Oxygen, percent	Metallic iron, percent	
		$HgCl_2$ method	$CuSO_4$ method
A-12	0.00	100.0	99.4
B-3	.00	100.0	99.8
B-2	1.35	94.2	98.3
B-1	2.59	89.0	97.1
A-4	3.65	84.5	93.3
A-5	5.59	76.3	88.1
A-6	8.03	65.9	76.4
A-7	13.45	42.9	48.8

HYDROGEN-EVOLUTION METHODS

In these methods the hydrogen liberated upon treating the sample with acid is used as a measure of the metallic-iron content. Ferric iron in the oxides interferes by reacting with part of the metallic iron, but the error is small for well-reduced sponge iron and does not seriously impair the usefulness of the method for determining metallic iron. In fact, the reaction between ferric iron and metallic iron is an advantage because it permits accurate determinations of total iron and oxygen to be made simultaneously with the metallic iron. Determinations of total iron and oxygen are possible only when the iron oxides are easily soluble and enough metallic iron is present to insure complete reduction of the ferric iron, but these requirements are met by most sponge irons.

Relative to the determination of oxygen, the following reactions show that the volume of hydrogen evolved depends on the oxygen and total iron contents rather than on the metallic-iron content:

$$9Fe+3FeO+24H^{+}=12Fe^{++}+3H_2O+9H_2, \quad (1)$$

$$10Fe+Fe_2O_3+24H^{+}=12Fe^{++}+3H_2O+9H_2. \quad (2)$$

These two reactions, which involve the same amounts of oxygen and total iron but different amounts of metallic iron, give equal volumes of evolved hydrogen. Similarly, it can be shown that with any intermediate oxide composition the same volume of hydrogen is evolved as long

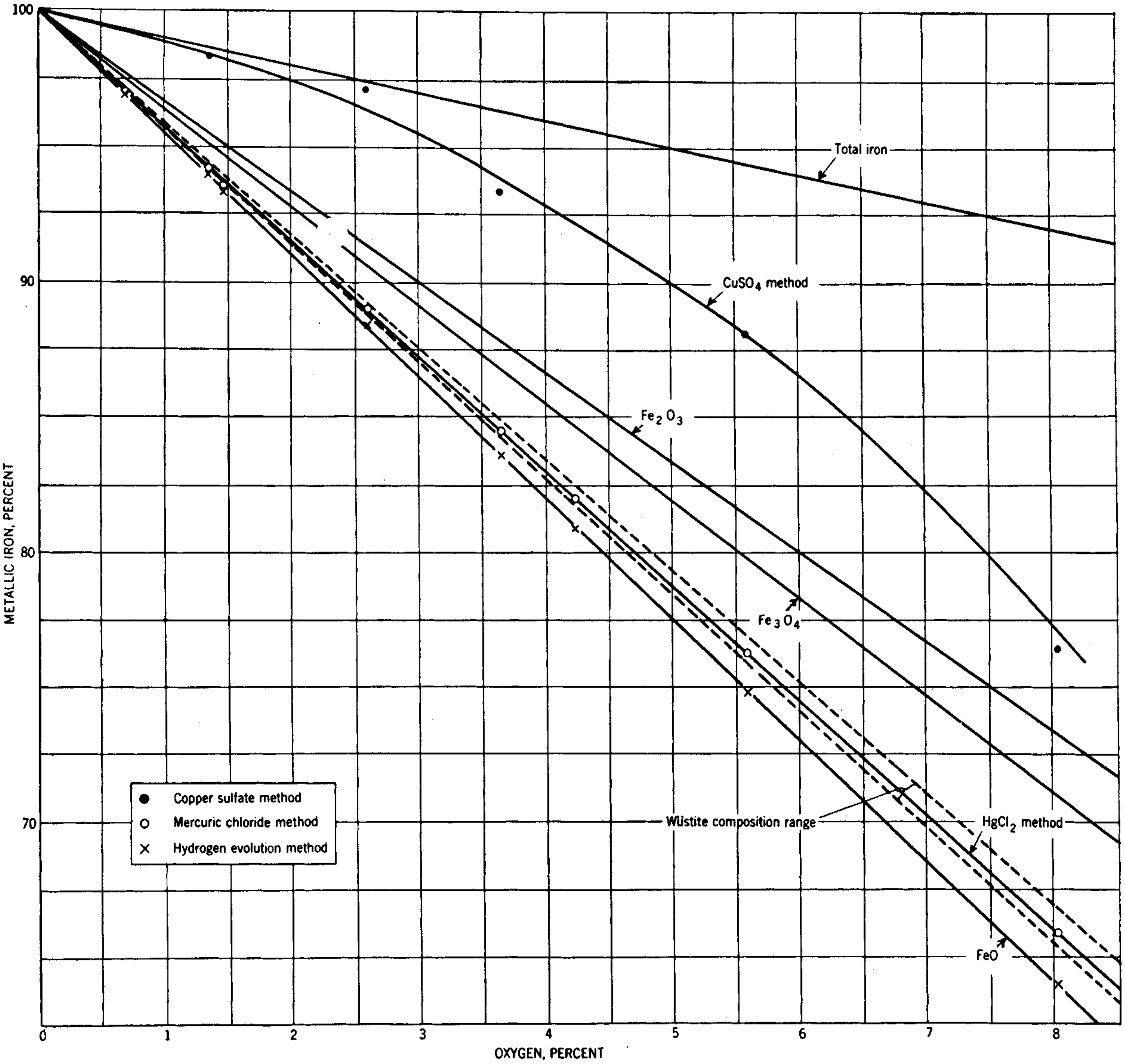

FIGURE 12.—COMPARISON OF RESULTS OF THE COPPER SULFATE, MERCURIC CHLORIDE, AND VOLUMETRIC HYDROGEN-EVOLUTION METHODS FOR METALLIC IRON IN UNOXIDIZED TEST SAMPLES.

as the oxygen and total-iron contents remain constant. Therefore, regardless of the actual reaction, reaction (1) can be used for calculating the oxygen content. From reaction (1) the following relation can be derived:

$$\text{Oxygen} = \frac{\text{Total iron} - \text{iron equivalent to evolved } H_2}{3.4900}.$$

Two procedures for measuring the volume of evolved hydrogen are described:

1. The "volumetric hydrogen-evolution method," in which the volume of the hydrogen is measured.
2. The "hydrogen-evolution-combustion method," in which the hydrogen is weighed as water, following combustion with copper oxide.

VOLUMETRIC HYDROGEN-EVOLUTION METHOD

A weighed sample of sponge iron is treated with dilute sulfuric acid in a closed system, and the increase in volume of the system caused by the evolution of hydrogen is measured.

The apparatus used is shown in figure 13 and is described as follows:

(*a*) 100-ml. reaction flask.
(*b*) Water bath; capacity, 4 liters.
(*c*) Movable support for water bath.
(*d*) Three-way stopcock.
(*e*) Opening to atmosphere.
(*f*) Calibrated 25-ml. burette.
(*g*) Water-cooled condenser.
(*h*) Calibrated gas burette, enlarged at top, lower part graduated from zero to 100 ml. in 0.2-ml. steps; total capacity, 275 ml.

(*i*) Zero mark of burette.
(*j*) Water jacket.
(*k*) Calibrated thermometer, graduated in tenths of a degree.
(*l*) Air inlet (for stirring water in jacket to equalize the temperature).
(*m*) 100-ml. bulb, which serves as a gas reservoir during boiling period.
(*n*) Leveling bulb; capacity, 500 ml.

Procedure.—Transfer 0.5 to 0.6 gram of sponge iron to a dry reaction flask. Fill burette *f* with 1–5 H_2SO_4 and adjust to the zero mark. Turn stopcock *d* to the atmosphere and remove acid in burette tip by blowing through *e*. Wash down sides of reaction flask with a little water, so that the gas in the flask will become saturated with water vapor, and attach to apparatus, first wetting the rubber stopper to insure a tight seal and to prevent the stopper from sticking to the glass. Raise leveling bulb *n* to remove the hydrogen from the previous run and adjust the level of water in the gas burette to zero mark *i*. Place water bath *b* in position, as shown in figure 13, and allow to stand for 10 minutes with stopcock *d* open to the atmosphere. Close stopcock *d* and record temperature (t_1) of the water bath.

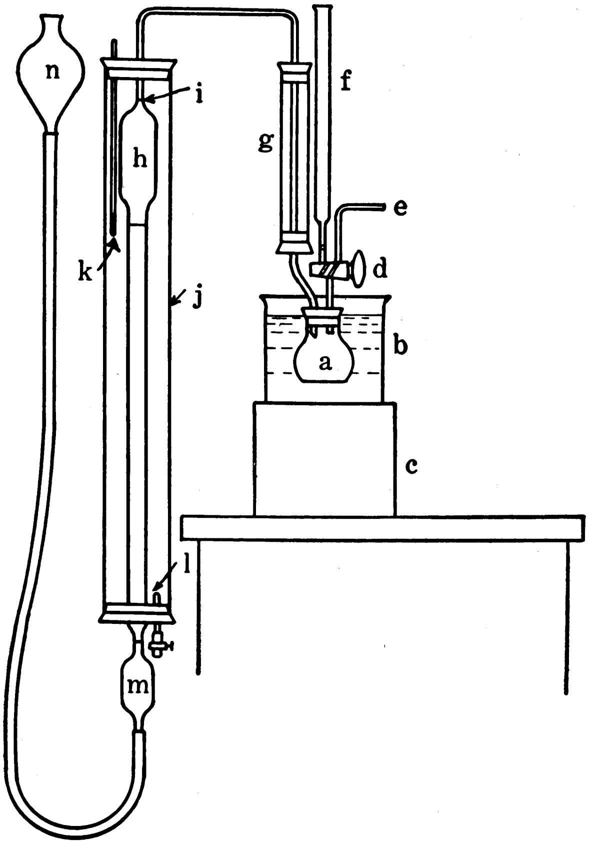

FIGURE 13.—VOLUMETRIC HYDROGEN-EVOLUTION APPARATUS.

Replace the water bath with a ring clamp and wire gauze and add exactly 25.0 ml. of acid to the reaction flask from burette *f*. Heat contents of the flask to boiling and boil until sample has dissolved, keeping the pressure inside the apparatus approximately constant by lowering the leveling bulb.

Remove flame and cool reaction flask by immersing in a beaker of cold tap water for 5 minutes. Replace the beaker with the water bath and allow to stand for 15 minutes. Adjust the level of the water in the leveling bulb to that in the burette and record the burette reading. Record the temperature of water bath *b* (t_2) and of water jacket *j* (t_3). Also record the barometer reading.

To determine total iron, remove the reaction flask, rinse stopper, and transfer the solution to a large beaker containing 250 ml. of cold water. Add 25 ml. of titrating solution and 8 or 9 drops of indicator and titrate with 0.2 N $K_2Cr_2O_7$. The end point can be detected easily in the presence of considerable carbon or other insoluble matter. The $K_2Cr_2O_7$ solution is best standardized by carrying samples of pure iron through all steps of the method.

Titrating solution required: To 500 ml. of water add 200 ml. of H_2SO_4. Cool and add 300 ml. of H_3PO_4 (85 percent).

Indicator: Dissolve 0.1 gram of barium diphenylamine sulfonate in 50 ml. of water.

Calculations.—The burette reading —25.0 ml. represents the volume of hydrogen liberated by the sample. Using temperature t_3 and the barometer reading corrected for the vapor pressure of water, convert this volume to standard temperature and pressure. Correct for a blank determined by carrying samples of pure iron through all steps of the method and calculate the metallic iron. One gram of pure iron liberates 401.8 ml. of hydrogen at 0° C. and a pressure of 760 mm. of Hg.[56]

For a more exact calculation any change in volume of gas in the apparatus at the beginning of the determination should be taken into account. For this purpose, two corrections must be applied to the burette reading before converting to standard conditions:

1. Upon the addition of acid to the reaction vessel, 25.0 ml. of gas at temperature t_1 was driven over into the gas burette and was included in the burette reading at temperature t_3. When t_3 differs from t_1, the burette reading must be corrected for the change in volume of this 25.0 ml. of gas in going from t_1 to t_3.

2. When the temperature of water bath *b* changes during a determination, it is necessary to correct the burette reading for the change in volume of approximately 100 ml. of gas (de-

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[56] Latimer, W. M., and Hildebrand, J. H., Reference Book of Inorganic Chemistry: MacMillan Co., New York, 1940, p. 6.

pending upon the size of the reaction vessel) in going from temperature t_1 to t_2.

Both of the above corrections are small, the sum of the two seldom exceeding 0.5 ml., and may be disregarded in routine analyses.

For calculating the oxygen content the following relation is used:

$$\text{Oxygen} = \frac{\text{Total iron} - \text{metallic iron}}{3.49}.$$

Conclusions.—The following conclusions were reached:

1. The volumetric hydrogen-evolution method always gives low results for metallic iron when iron oxide is present. The magnitude of the error depends upon the ferric iron content of the oxide and is small for well-reduced sponge iron.
2. The method accurately determines oxygen and total iron provided that the iron compounds are soluble and combined carbon is absent.
3. Combined carbon causes low results for metallic iron and high results for oxygen but does not affect the determination of total iron.
4. The method described is not applicable to samples containing appreciable amounts of sulfides, carbonates, or reduced metals other than iron.

HYDROGEN-EVOLUTION-COMBUSTION METHOD

The hydrogen-evolution-combustion method was designed primarily for the analysis of sponge iron containing combined carbon and is based upon the assumption that iron carbide liberates the same volume of hydrogen (including combined hydrogen) as an equivalent quantity of free iron. This is illustrated in the following equations:

$$3Fe + 6H^+ = 3Fe^{++} + 3H_2,$$

$$Fe_3C + 6H^+ = 3Fe^{++} + H_2 + CH_4.$$

The reaction shown for iron carbide is perhaps only one of a number of similar reactions that actually occur.

In this method the sample is treated with hydrochloric acid, and the evolved hydrogen and hydrocarbon gases are oxidized by hot copper oxide. The amounts of water and carbon dioxide formed determine, respectively, the metallic iron and combined carbon contents of the sample. As in the volumetric method, total iron may be determined by titration of the dissolved sample, and a simple calculation gives the oxygen content.

The essential features of the apparatus are shown in figure 14 and are described as follows:

(*a*) Nitrogen inlet.
(*b*) Rubber tube and screw clamp for regulating nitrogen flow through train.
(*c*) Bottle filled to shoulder with water.
(*d*) Sulfuric-acid bubble tube.
(*e*) Three-way stopcock.
(*f*) 25-ml. burette.
(*g*) Reaction vessel (100-ml. pyrex extraction flask).
(*h*) Water-cooled condenser.
(*i*) KOH solution bubble tube for removing HCl, H_2S, CO_2, and H_2O. Charge with 1–1 KOH solution through the stopcock at the bottom by applying suction at the end of combustion tube *m*. This bulb is recharged each day.
(*j*) Stetser-Norton bulb for removing last traces of HCl, H_2S, CO_2, and H_2O. Charge with 1 inch of ascarite in bottom and remainder of bulb with anhydrone. Recharge after 50 determinations.
(*k*) Oxygen inlet. Oxygen from a tank is first passed through a pressure regulator, a sulfuric-acid bubble tube, and a purifying jar containing ascarite and anhydrone, as shown for nitrogen at *b*, *c*, *d*, and *j*.
(*l*) Three-way stopcock.
(*m*) Fused-silica combustion tube. Length, 22 inches; inside diameter, ⅞ inch. Starting at the reduced end of tube, charge with: (1) Coarse silica chips (from a broken combustion tube) to 1 inch inside furnace; (2) thin plug of copper gauze; (3) 8 inches of copper oxide wire; (4) 3 inches of minus-16-mesh, plus-30-mesh alundum chips coated with copper oxide; (5) thin plug of copper gauze. Remainder of tube empty.
(*n*) Combustion furnace heated to 750° C.
(*o*) Stetser-Norton weighing bulb for the absorption of water. Charge with anhydrone.
(*p*) Stetser-Norton bulb for absorption of carbon dioxide. Charge with ¾ inch of anhydrone in bottom and with ascarite in remainder of bulb.
(*q*) Sulfuric-acid bubble tube.

At the beginning of a series of determinations the valve on the nitrogen tank is opened to give a somewhat greater flow of gas than is needed. Once adjusted, this valve requires no further attention, the rate of flow through the train being regulated by means of the screw clamp at *b* and the excess nitrogen bubbling out through *c* (fig. 14). A nitrogen flow of 100 ml. a minute through the train has proved satisfactory. In practice, this rate is maintained only approximately by noting the rate of bubbling in the various tubes.

Oxygen is used for a short time during sweeping to convert the reduced copper back into copper oxide. Alundum coated with copper oxide is placed in the front part of the combustion tube to react with most of the hydrogen, since the thin layers of copper formed on the alundum are easily reoxidized. When copper oxide wire is used alone, it reduces completely but oxidizes only on the surface. The alundum-copper oxide combination is prepared by saturating alundum chips with a strong solution of copper nitrate, followed by drying and igniting.

Weighing bulbs *o* and *p* should be shielded from the heat of the furnace. However, it is important that the exit end of the combustion tube and the connecting tube of bulb *o* be kept warm so that water condensing here will be

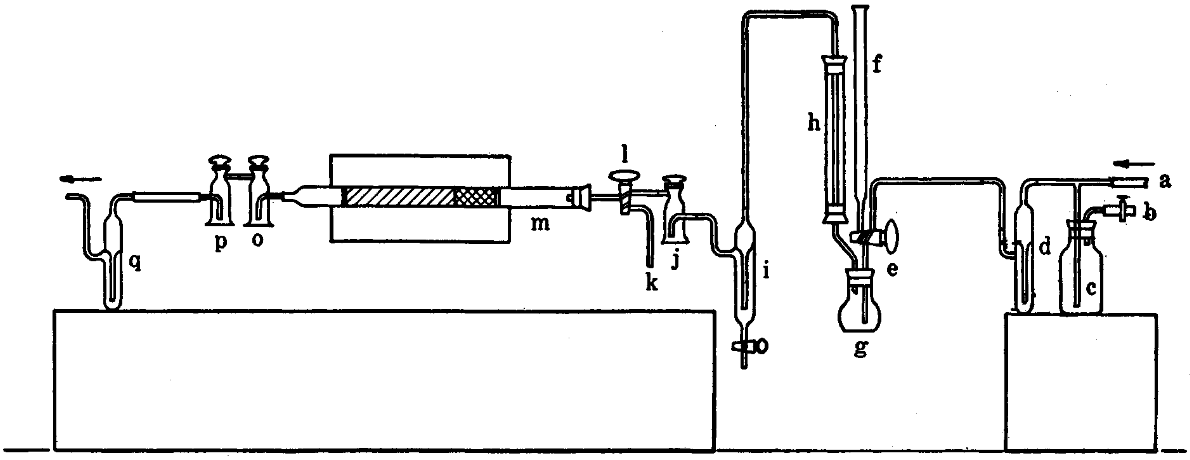

FIGURE 14.—HYDROGEN-EVOLUTION-COMBUSTION APPARATUS.

driven into the absorption bulb before the end of the determination. This can be accomplished by conducting heat to this point by means of a short piece of brass tubing fitted loosely over the end of the combustion tube.

Procedure.—Weigh out 0.5000 gram of sponge iron into a dry reaction flask, wet down the sample with a little water, and attach flask to apparatus after first wetting the stopper to insure a tight seal and to prevent the rubber from sticking to the glass. Attach weighing bulbs to train as shown in figure 14.

Open stopcock *e* to the nitrogen and adjust the rate of nitrogen flow to about 100 ml. a minute by means of screw clamp *b*. Add 25 ml. of 1–1 HCl from the burette and partly open stopcock *e* to admit nitrogen at about half the normal rate. Heat the reaction flask with a low flame until the reaction subsides somewhat; then heat to boiling and boil until sample dissolves. Remove flame and fully open stopcock *e* to the nitrogen. Sweep out the train with nitrogen for 15 minutes, switch to oxygen for 5 minutes by means of stopcock *l*, and finally sweep again with nitrogen for 15 minutes.

Remove absorption bulbs. Let stand beside balance for one-half hour and weigh.

Correct the weights of H_2O and CO_2 for blanks, determined by carrying samples of high-purity iron through all steps of the method, and calculate the metallic iron and combined carbon contents.

To determine total iron, detach reaction flask from apparatus and rinse rubber stopper and glass tubing. Add 1 drop of 10-percent stannous chloride solution, mix, wash down sides of flask, stopper, and cool. When cool, add 10 ml. of a saturated mercuric chloride solution, mix well, and wash down sides of flask. Allow to stand for 2 or 3 minutes and then transfer solution to a large beaker containing 200 ml. of cold water. Add 25 ml. of titration mixture and 8 or 9 drops of indicator and titrate with 0.2 N $K_2Cr_2O_7$. The solution of $K_2Cr_2O_7$ should be standardized by carrying samples of pure iron through all steps of the method.

The titration mixture and indicator required are the same as those described in the volumetric hydrogen-evolution procedure.

Calculations:

$$\text{Metallic iron, percent} = \frac{\text{Weight of } H_2O}{0.1613} \times 100.$$

$$\text{Combined carbon, percent} = \text{Weight of } CO_2 \times 0.5458 \times 100.$$

Conclusions.—The following conclusions were reached:

1. As in the volumetric procedure, the hydrogen-evolution-combustion method gives low results for metallic iron when iron oxide is present but accurately determines total iron and oxygen.
2. The combustion method is superior to the volumetric procedure when combined carbon is present because recovery of the evolved hydrogen is more complete. Moreover, the combustion method gives satisfactory results for combined carbon.
3. The method is not applicable to samples containing appreciable amounts of other reduced elements that liberate hydrogen.

HYDROGEN-REDUCTION METHOD

In this method the sample is reduced in a current of hydrogen at 1,000° C., and the loss in weight after correcting for loss of carbon and sulfur is assumed to equal the oxygen content. As an alternative procedure, the water formed may be collected and weighed, but careful attention must be given to blanks and little is gained in accuracy. Furthermore, some oxygen may be evolved as carbon monoxide, and the recovery of this oxygen complicates the latter procedure.

Apparatus.—The apparatus used comprised the following parts:

1. Combustion furnace with automatic temperature control.
2. Fused-silica combustion tube with one end reduced. Length, 30 inches; inside diameter, 1⅛ inches.
3. Rack for supporting the hot combustion tube when it is withdrawn from the furnace.
4. Hydrogen purifying train.
5. Alundum combustion boats. Length, 5 inches; width, ¾ inch; depth, ⅜ inch.
6. Combustion-boat shield—a thin-walled iron tube 7 inches long and 1 inch in diameter.

Hydrogen from a tank was purified by passing over metallic copper heated to 750° C. and then through concentrated sulfuric acid, ascarite, and finally anhydrone. The combustion tube was connected to the purifying train by 30 inches of rubber tubing so that the tube could be removed from the furnace and cooled, with the hydrogen flowing. Silica combustion boats proved unsatisfactory because of a tendency to flake.

Procedure.—Transfer 5 grams of sponge iron to a weighed alundum boat that previously has been reduced in hydrogen at 1,000° C. to constant weight. Place the boat inside the iron shield and slide into the combustion tube. Pass a current of hydrogen through the tube at a rate of 80 to 100 ml. a minute. When the air has been displaced, insert the combustion tube into the hot furnace. Treat for 6 hours or longer at 1,000° C. and then remove tube from the furnace and allow to cool while the hydrogen is flowing. Remove boat and weigh. Repeat, using 3-hour reduction periods, until the weight is constant. After the final weighing brush out the boat and reweigh the empty boat for the next run. Analyze the reduced sample for carbon and sulfur and deduct the carbon and sulfur losses from the total loss in weight. The remainder of the loss is assumed to be oxygen.

In applying the above procedure to the preparation of the test samples it was found that the alundum boats varied in weight except when the sample was completely reduced. Therefore, when preparing a test sample containing oxygen, the loss in weight was determined by weighing the reduced sample after it was carefully removed from the boat. The sample could be removed quite accurately since the original oxides were free from dust and the reduced material did not stick to the boat. As a further check, the empty boat was also weighed.

Discussion.—This method should give accurate results for oxygen in the presence of only metallic iron and iron oxides. Baxter and Hoover[57] used a similar procedure for determining the atomic weight of iron. With actual sponge iron, however, the accuracy of the method depends on the nature and amounts of the other constituents. In addition to the loss of oxygen from the iron oxides, loss in weight may also result from the presence of carbon, sulfur, volatile matter such as CO_2 or H_2O, and reducible oxides other than iron oxide. According to Cain and Pettijohn,[58] the more common metallic oxides react with hydrogen as follows: Oxides of Fe, Ni, and Cu are reduced completely; higher oxides of Mn, Ti, and V are reduced to MnO, Ti_2O_3, and V_2O_3, respectively; while SiO_2, Al_2O_3, and Cr_2O_3 are not affected. These reactions are for the free oxides only and do not apply necessarily when the oxides are combined with silica. For example, the ferric oxide of iron silicate is reduced to ferrous oxide but no further.

Since corrections are made for the loss of only carbon and sulfur, the method described probably gives somewhat high results for oxygen in most instances. Its most useful application is in the analysis of sponge irons containing coarse particles, since larger and more representative samples can be used than in the other procedures.

FERRIC CHLORIDE METHOD

In this method the metallic iron is removed from the sample of sponge iron by treating it with a 10-percent ferric chloride solution; a total-iron determination is then made on the residue. The method is especially suited to routine analyses of a number of samples. It has been used extensively over a period of years by the Bureau of Mines and the University of Minnesota Mines Experiment Station at Minneapolis, Minn.

Recommended Procedure.—Weigh a 0.25- to 0.50-gram sample into a 150-cc. beaker. Add 50 ml. of cool, freshly prepared 10-percent ferric chloride solution. Let beaker stand 3 to 4 hours in a cool place, stirring gently by rotating beaker every half hour, or stir gently with a mechanical stirrer for 1 hour. Filter through a good paper. Wash 10 times with cold water. Place filter and contents in a 50-cc. pyrex beaker. Dry on the hot plate. Ignite in muffle, with free circulation of air at not more than 650° C., and cool. Determine total iron in the residue and in another sample of the sponge iron. The difference between these percentages of total iron represents the metallic iron in the material. Run a blank determination under same conditions.

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[57] Baxter, G. P., and Hoover, C. R., A Revision of the Atomic Weight of Iron: Jour. Am. Chem. Soc., vol. 34, 1912, pp. 1657–1669.

[58] Cain, J. R., and Pettijohn, Earl, A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel: Nat. Bureau of Standards Technol. Paper 118, 1919, 33 pp.

SUMMARY AND CONCLUSIONS

Several methods for determining metallic iron and oxygen in sponge iron were studied; specially prepared test samples of known composition were used for this purpose. These samples were prepared from high-purity iron oxide and were similar to actual sponge iron in both physical and chemical constitution. The behavior of the analytical methods with actual sponge iron was shown to be similar to their behavior with the test samples. The following conclusions were reached:

1. In finely ground samples (minus-65-mesh) the mercuric chloride method gives accurate results for metallic iron in the presence of only metallic iron and iron oxides. The recovery of metallic iron is not always complete in samples of coarser particle size. Combined carbon and alkaline material such as free lime or magnesia cause low results, but with the small amounts of these substances ordinarily contained in sponge iron the errors seldom exceed 1 percent.
2. The copper sulfate method gives values for metallic iron that are much too high. These high values are probably the result of attack on the iron oxides by the copper sulfate solution.
3. The two hydrogen-evolution methods described give accurate results for oxygen and total iron but low values for metallic iron in samples containing only metallic iron and iron oxides. The error in the metallic-iron determination is the result of interference by ferric iron, which is always present in the oxide phase of the sample. Unlike the mercuric chloride method, the hydrogen-evolution methods are generally free from interference by alkaline material or coarse particle size, but in the presence of reduced elements (other than iron) that liberate hydrogen high results for metallic iron and low results for oxygen are obtained. When sponge iron contains combined carbon, part of the evolved hydrogen is in the form of hydrocarbon gases. Most of this hydrogen is recovered in the hydrogen - evolution - combustion method, but in the volumetric procedure low values for metallic iron and high values for oxygen result. In addition to oxygen, total iron, and metallic iron, the hydrogen-evolution-combustion method determines combined carbon directly.
4. The hydrogen-reduction method for determining oxygen is lengthy and not suited for routine work, except with easily reduced samples that are nearly free from carbon and sulfur, as, for example, iron powder produced from hydrogen-reduced sponge iron or from electrolytic iron. A useful application is in the analysis of sponge irons of coarse particle size, since large samples can be used. For samples of sponge iron containing volatile matter or reducible oxides other than iron oxide the method gives high results.

MAIER PROCESS

During 1931, 1932, and 1933 Maier and Thomas at the Bureau of Mines station in Berkeley, Calif., conducted an extensive series of laboratory investigations on utilization of natural gas for producing sponge iron from a large tonnage of pyrite cinders that had accumulated in the San Francisco Bay region.

DIRECT USE OF NATURAL GAS

A thorough and critical study was made of both the theoretical and practical aspects of the direct use of methane or natural gas for reducing iron oxides. In a typical test a treatment time of some 50 hours was required to satisfactorily reduce pyrite cinder. The slowness of the reduction is due not only to the chemical inertness of methane, which in the absence of catalysts decomposes slowly under conditions where it is thermodynamically almost completely unstable (900°), but also to the thermal requirements of direct reduction of iron oxides by methane.

Intensive study of the thermochemical requirements showed that nearly all of the necessary heat could be supplied if air at 1,000° C. was introduced with the gas. Portions of the charge near the air-gas inlets often fused. The atmosphere a short distance away from the inlet ports consisted of hydrogen and carbon monoxide, with the nitrogen from the air and a fair amount of unreacted methane. The hydrogen and carbon monoxide rapidly reduced the ore farther along, but conversion of the residual methane was negligible until a large part of the ore had been reduced.

IMPROVED METHOD OF UTILIZING NATURAL GAS

Results of the preliminary experiments showed that if the reactions in the initial stages of the reduction by preheated air-gas mixtures could be effected in a separate unit under accurate control, an improved yield of CO and H_2 and a superior method of reduction would result.

A converter using a nickel catalyst to react methane with CO_2 and H_2O was built upon a moderately large scale and operated continuously for many hundreds of hours without serious trouble, producing gas of the following percentage composition: N_2, 42.7; CH_4, 0.4; CO_2, 0.3; CO, 19.5; H_2, 36.4; H_2O, 0.7. It can be shown thermochemically that such a gas near 1,000° C., contacting iron oxide near 800° C., can thermally support reduction.

Of about a dozen reducing units tried, a radiant-heated rotary kiln of special design surpassed by far all other types in practicability and effectiveness for mechanical handling of hot sponge iron.

The capacity of the demonstration unit was 100 to 250 pounds of iron a day. When it produced 125 pounds a day, the iron oxide was 99+ percent reduced. The total consumption of natural gas for all purposes, including preheating the air, calcining the charge, etc., was about 30,000 cubic feet per ton of reduced iron.

1-TON ROTARY KILN

In cooperation with the Mountain Copper Co., Ltd., Martinez, Calif., a 1-ton kiln (capacity) of the same type that had been used at Berkeley was constructed. Figure 15 shows a section elevation of the 1-ton kiln and gas converter.

About 65 tons of Mococo tailings were treated in three campaigns lasting 11, 20, and 11 days, respectively. The average temperature in the kiln was 875° C. Average reduction to metal ranged from 84.2 to 91.2 percent (table 21).

Butane was used at Mococo, as natural gas was not available in the plant.

Maier [59] calculated that 28,000 cubic feet of natural gas would be used in producing 1 ton of iron. The exit gases from the kiln contained about two-thirds of the original CO and H_2 in unaltered form and combustible. This exit gas should be adequate to furnish all the heat required to reroast the high-sulfur calcines.

The addition of 3 to 5 percent of lime to the ore used in the rotary kiln eliminated sticking of the product at temperatures lower than 900° C. The lime content was indicated to be beneficial to subsequent melting for steel-making purposes.

Long periods of operation without serious trouble show that a moderately large scale catalytic converter can produce continuously a gas of the following percentage composition: N_2, 44.0; CH_4, 0.78; CO_2, 0.8; CO, 21.8; H_2, 30.7; H_2O, 2.0. Such a gas, near 1,000° C., contacting iron ore at 800° C., can constitute a thermally self-supporting reduction.

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[59] Maier, C. G., Sponge-Iron Experiments at Mococo: Bureau of Mines Bull. 396, 1936, 81 pp.

TABLE 21.—*Chemical analyses of ores used in test 3 at Mococo, Calif.*

Size	Percent					
	Fe	Insoluble	S	Cu	Zn	CaO
Minus-6-, plus-10-mesh	57.8	11.0	0.110	0.34	0.28	2.95
6-mesh	56.2	11.8	----	----	----	2.59
Minus-3-, plus-6-mesh	56.8	13.4	.102	.42	.37	1.91

SUMMARY OF TESTS

Test No.	Days operated	Ore charged, pounds per day	Average, percent		Average kiln temperature, °C.
			Reduction to metal	Gas utilization	
1	11	2,730	87.9	43.1	879
3	20	2,638	84.2	33.7	885
4	11	2,480	91.2	31.8	870

TYPICAL ANALYSES OF RE-FORMED BUTANE GAS

Test No.	Date	Butane, c. f. m.	Analysis of re-formed gas, percent					
			CH_4	CO_2	CO	H_2	N_2	H_2O
1	July 28–Aug. 9, 1934	4.30	0.70	0.8	21.8	30.4	44.5	1.9
2	Oct. 19–Nov. 24, 1934	4.33	.95	.8	21.9	30.6	43.7	2.0
3	Jan. 1–Jan. 29, 1935	4.33	.70	.7	21.8	31.0	43.8	2.0

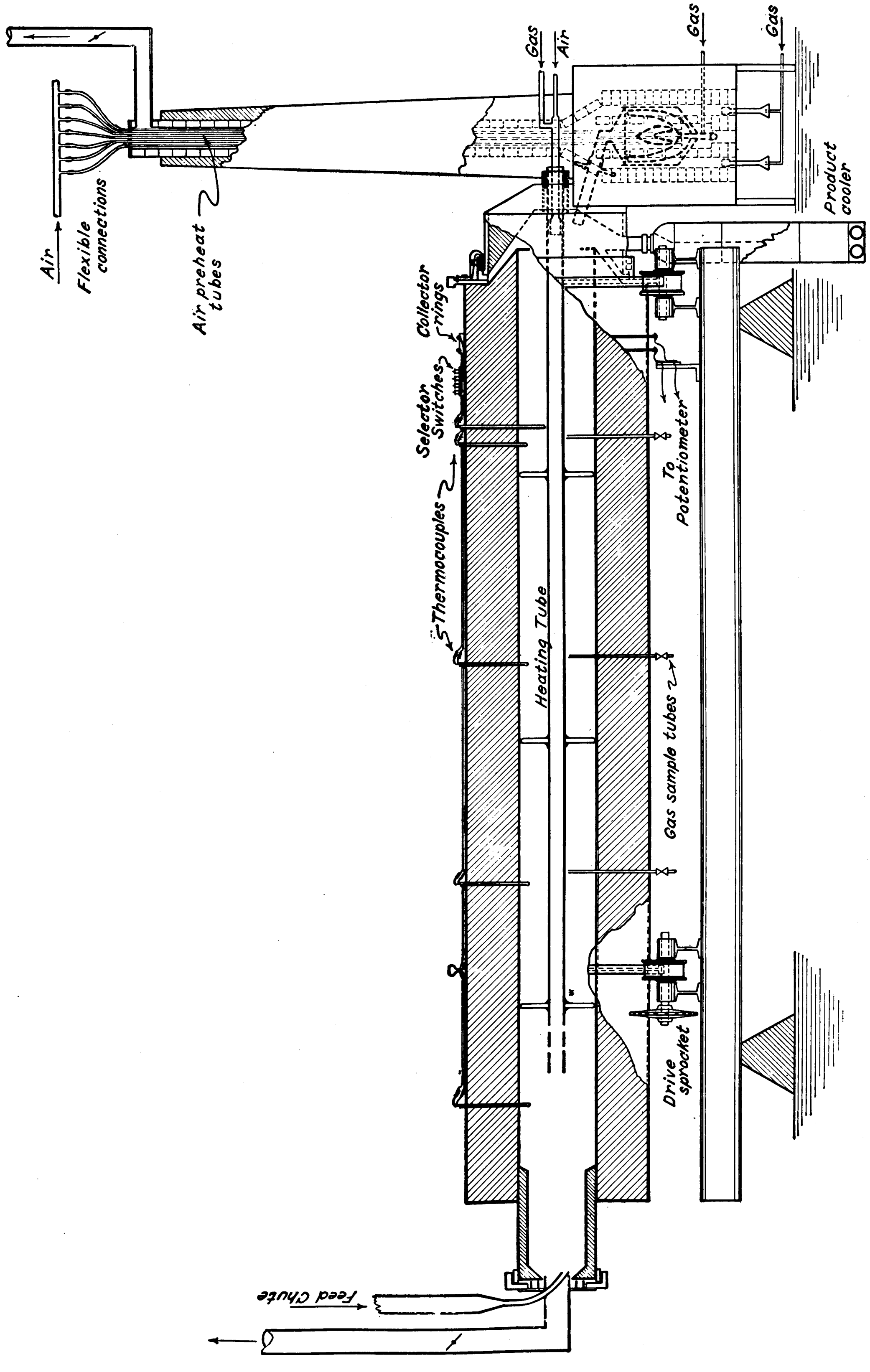

FIGURE 15.—SECTION ELEVATION OF MOCOCO KILN AND CONVERTER.

MADARAS PROCESS

The Madaras Steel Corp. built a semicommercial-scale sponge-iron plant at Longview, Tex., which was intended to be operated in conjunction with an electric steel foundry. After several attempts had been made to operate this plant, the Bureau of Mines leased the sponge-iron plant and conducted an extensive investigation of the Madaras process.[60] Several hundred tons of iron ore was treated, and a quantity of the sponge iron was converted into steel in an electric-arc furnace.

On completion of the Bureau of Mines investigation the process was modified and the plant redesigned. Several series of experiments were made.

In the Madaras process preheated ore is reduced in batches by hot hydrogen passed through the charge under pulsating pressures. In the modified process, part of which has been demonstrated experimentally, it is proposed to use:

1. Regenerative-type heaters for the thermal cracking of natural gas to hydrogen. Provision will be made to recover the carbon black, which will be carried out of the cracker by the hydrogen.
2. Unlined, noninsulated steel retorts 6 to 10 feet in diameter and 8 to 10 feet in height as reaction vessels. Ore charges containing about 15 tons of iron will be preheated and reduced in each retort.
3. Electric-arc furnaces for melting and refining the sponge iron.

A flow sheet of the proposed operation is shown in figure 16 and a photograph of the plant in figure 17.

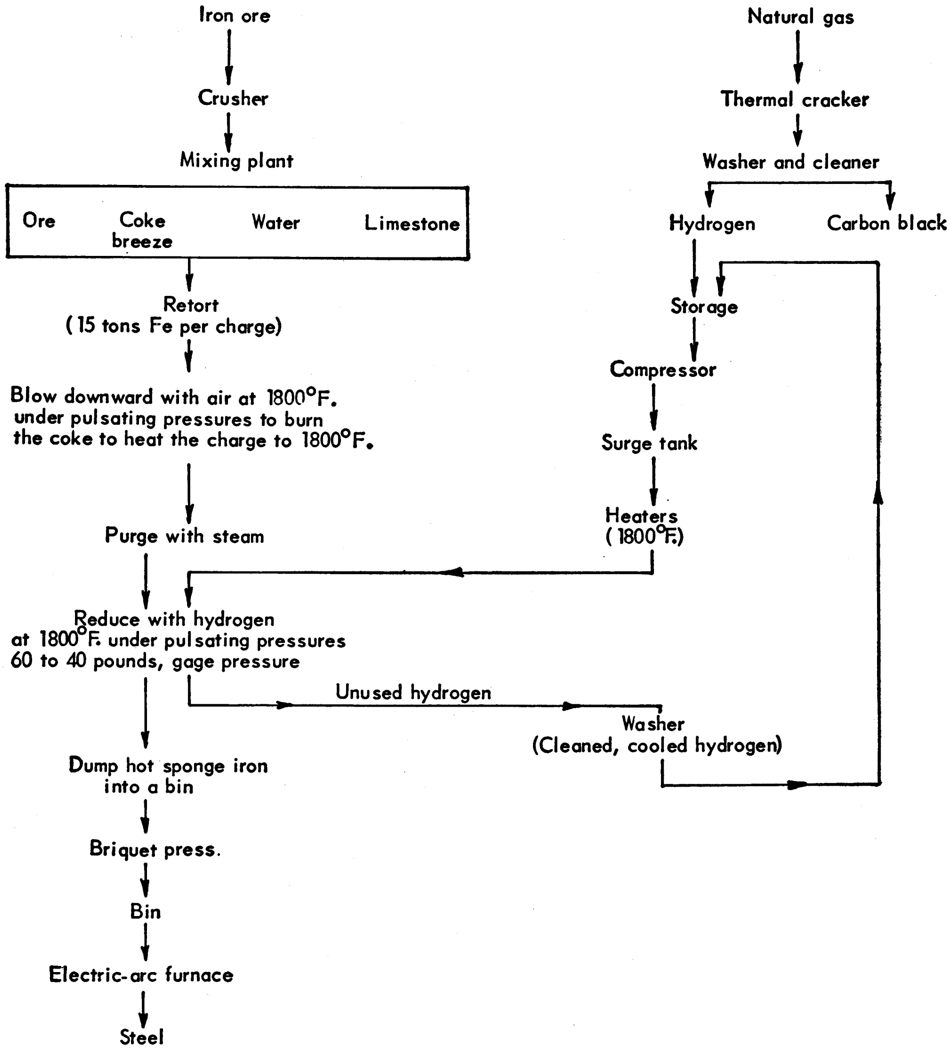

Figure 16.—FLOW SHEET OF MADARAS PROPOSED PROCESS.

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[60] Brown, Whitman E., Sponge-Iron Experiments at Longview, Tex.: Bureau of Mines Rept. of Investigations 3925, 1948, 58 pp.

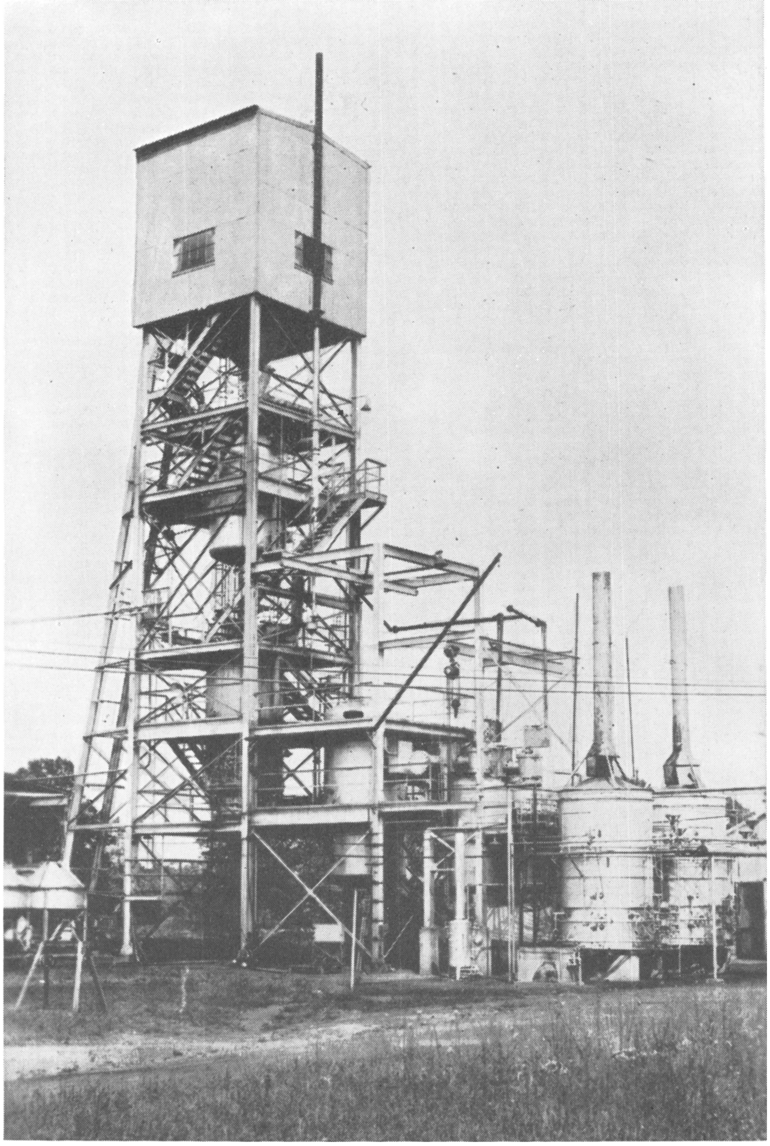

FIGURE 17.—MADARAS SPONGE-IRON PLANT, LONGVIEW, TEX.

PRODUCTION OF SPONGE IRON WITH PRODUCER GAS

The Bureau of Mines has done much work on pilot-plant[61] gaseous reduction of iron ores at the Boulder City, Nev., Experiment Station; its objective was the reduction of fine iron ore by means of producer gas. The use of producer gas was prompted by two considerations: (1) Possible utilization of large reserves of western noncoking bituminous coals and lignites contiguous to iron-ore deposits and (2) investigation of the results that might be achieved in the pilot-plant gaseous reduction of fine iron ores by means of a relatively low quality reducing gas. The results obtained, it was felt, would be valuable in indicating the direction that gaseous-reduction experimentation must take for the development of a commercially practicable and economic process for the production of sponge iron.

A Skinner multiple-hearth furnace was used for reducing the iron ore, primarily because the combustion gases could be isolated from the reducing gases and thereby prevent dilution of the reducing gas or introduction of oxidizing constituents.

The Skinner furnace contained 10 hearths. Figure 18 is a diagram showing the general

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[61] Torgeson, T. E., Evans, T. E., and Knickerbocker, R. G., Pilot-Plant Investigations—Production of Sponge Iron with Producer Gas: Bureau of Mines Rept. of Investigations 3994, December 1946, 42 pp.

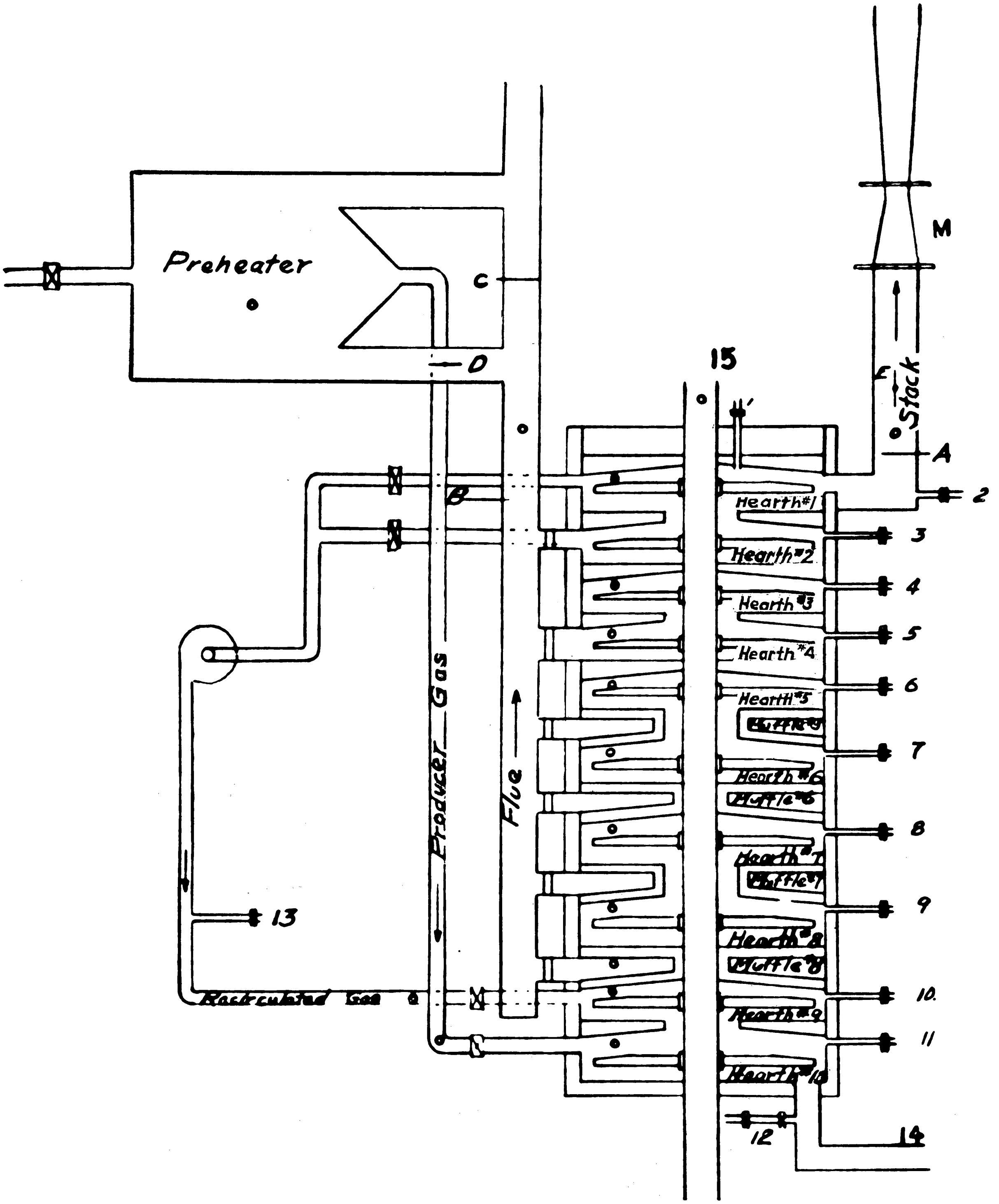

Figure 18.—SKINNER MULTIPLE-HEARTH FURNACE.

characteristics of the furnace construction. The furnace was 5 feet in diameter and 16 feet 6 inches high, inside dimensions. The total hearth area was about 195 square feet. The muffles above hearths 6, 7, 8, and 9, with the exception of the top one, were constructed of carborundum brick; the top hearth was made of a high-quality fire-clay brick. Each muffle was heated by means of two oil burners, one on each side of the furnace, set in the furnace wall.

The capacity of the Skinner furnace proved to be small, and considerable difficulty was experienced in attaining uninterrupted operation at high temperatures. The reduced ore tended to adhere to the walls around 900° C., greatly overloading the furnace column equipment. This trouble was aggravated by the fact that the semiplastic, partly metallized material was spread on the hearth floor by the rabble blades, building a dense, nearly solid, iron bed against the blades and producing a braking action that not only increased the power needed to move the column but also required the continual raising of the column by means of the bottom thrust bearing.

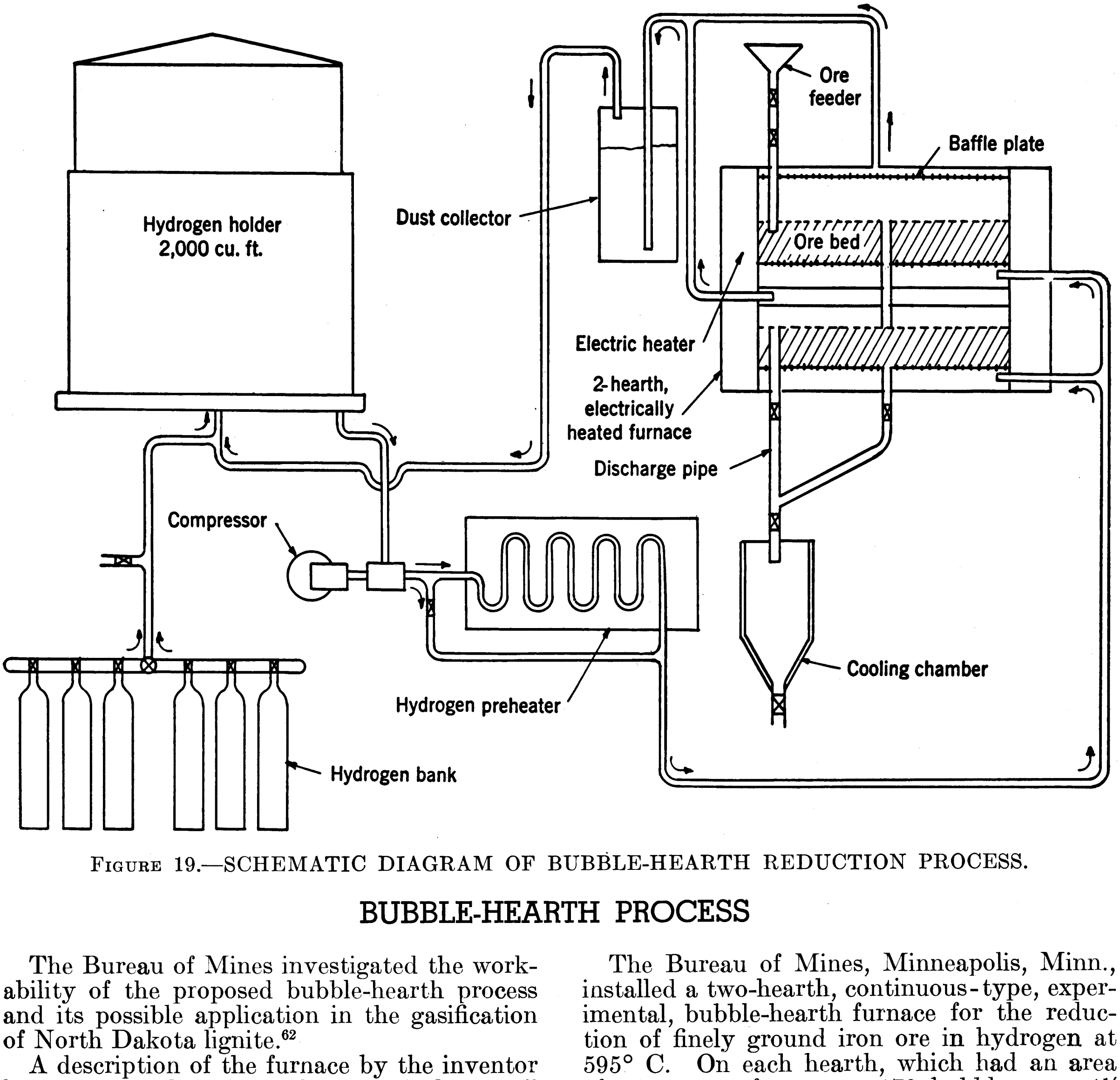

FIGURE 19.—SCHEMATIC DIAGRAM OF BUBBLE-HEARTH REDUCTION PROCESS.

BUBBLE-HEARTH PROCESS

The Bureau of Mines investigated the workability of the proposed bubble-hearth process and its possible application in the gasification of North Dakota lignite.[62]

A description of the furnace by the inventor has been published in the technical press.[63] It is similar to the bubble-cap column used in oil refining in which only liquids are used. The reducing gas is expected to fluidize the bed of small particles of iron ore on each hearth and to reduce the iron oxides to sponge iron.

The Bureau of Mines, Minneapolis, Minn., installed a two-hearth, continuous-type, experimental, bubble-hearth furnace for the reduction of finely ground iron ore in hydrogen at 595° C. On each hearth, which had an area of 3.7 square feet, were 170 bubble caps 1½ inches center to center. Each bubble cap had two openings or gas outlets, ⁵⁄₆₄ inch in diameter, parallel to the hearth. An alloy-steel strip 18 inches high was welded to each hearth to provide a spiral channel through which the ore moved from feed to discharge. A 2-inch pipe that extended 12 inches above each hearth permitted a charge 12 inches in depth on each hearth and provided passageways through

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[62] Barrett, E. P., Wood, C. E., Miller, V., Brown, W. E., Porath, P. R., and Prasky, C., Investigation of Bubble-Hearth Process for Production of Sponge Iron: Bureau of Mines Rept. of Investigations 4092, 1947, 15 pp.

[63] Ramseyer, C. F., Sponge Iron Furnace, Its Possibilities and Limitations: Iron and Steel Eng., July 1944, pp. 35–44, 72.

which the charge moved from the upper hearth to the lower hearth and from the lower hearth into the discharge cooler. The capacity of each hearth was 600 pounds of ore.

The alloy-steel reaction chamber was surrounded by a resistance-type electric furnace.

A schematic diagram of the experimental unit is shown in figure 19.

The data obtained during four tests, each of several days' duration, in the two-hearth, experimental, bubble-hearth furnace indicated that further laboratory investigation was necessary to establish the factors governing operation of the bubble-hearth process.

LABORATORY STUDY

A laboratory study of deoxidation of iron oxides fluidized in hydrogen at 585° C. was made in the loss-in-weight apparatus.[64] (See Measure of Reducibility, p. 18.)

As used in the fluidizing tests, it consisted of a 1.7-inch-diameter pyrex glass tube 12 inches long, closed at the bottom and suspended in a suitable gas-heated chamber. The tube containing the fine ore and a bed of granulated refractory for preheating the hydrogen was suspended from one pan of a torsion balance.

Figure 20 shows the pyrex reaction tube, the stainless-steel basket for supporting the pyrex tube, and the alloy tube that supports the reaction unit and through which the hydrogen passes to the bottom of the pyrex tube.

A window in the heating chamber and a suitable source of light permitted observation of the material in the pyrex tube while it was undergoing deoxidation. Temperatures at the center of the fluidized bed and in the space around the pyrex tube were measured with thermocouples and a portable potentiometer. The water vapor and unused hydrogen were discharged directly into the heating chamber, where the hydrogen burned. The degree of deoxidation at any time is determined by the loss in weight of the charge.

The oxide was fluidized easily, but as deoxidation increased a greater velocity of hydrogen was needed to fluidize the charge, until a condition was finally reached in which no amount of hydrogen would produce satisfactory fluidization. The maximum free velocity (velocity through hearth with no oxide present) obtainable in the bubble-hearth furnace was about 0.33 linear foot a second at 585° C., and in the laboratory apparatus the charge could be maintained in a fluidized condition with a hydrogen flow of 0.34 linear foot a second only until it had been deoxidized to the extent of about 54 percent. Deoxidation of the fluidized charge was continued by increasing the hydrogen flow until about 74-percent deoxidation was reached. However, when the hydrogen flow was increased to 0.62 foot a second, the finer particles of the charge were blown out of the tube at an excessive rate, and the loss in weight was no longer a measure of deoxidation.

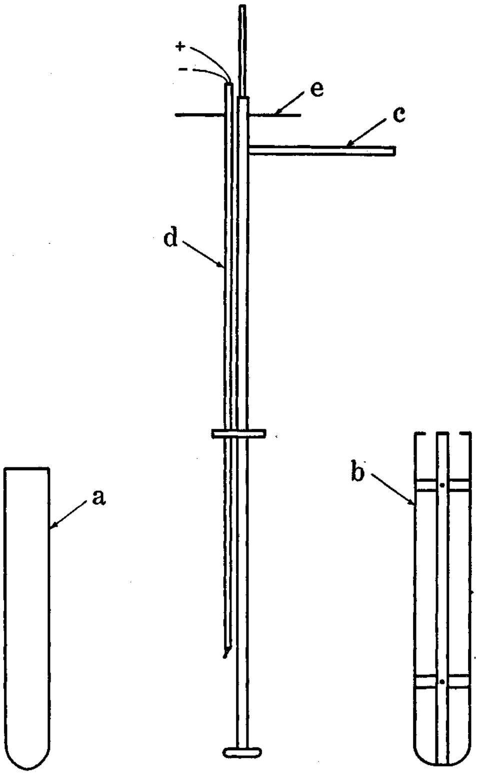

Figure 20.—PARTS OF LOSS-IN-WEIGHT APPARATUS: *a*, Pyrex Glass Tube; *b*, Stainless-Steel Basket; *c*, Hydrogen Inlet and Connection to the balance; *d*, Thermocouple; *e*, Heat Deflector.

Figure 21 shows graphically the relationship between the degree of deoxidation and the velocity of hydrogen necessary to keep the charge in a fluidized condition. This test shows clearly why the bubble-hearth furnace failed to operate as expected. As deoxidation approaches completion, a higher velocity of hydrogen is needed to produce fluidization, because the tendency of the iron particles to stick together increases as deoxidation increases. The crater at the top of the charge when fluidization ceased is shown in figure 22.

Inasmuch as movement of the ore through the bubble-hearth furnace depended on the ore being in a fluid state at all times, the results of the investigation show that this bubble-hearth process is not workable.

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[64] Barrett, E. P., and Wood, C. E., Loss-in-Weight Method for Determining Rates of Deoxidation of Iron Oxides: Ind. Eng. Chem., anal. ed., vol. 18, May 1946, pp. 285, 286.

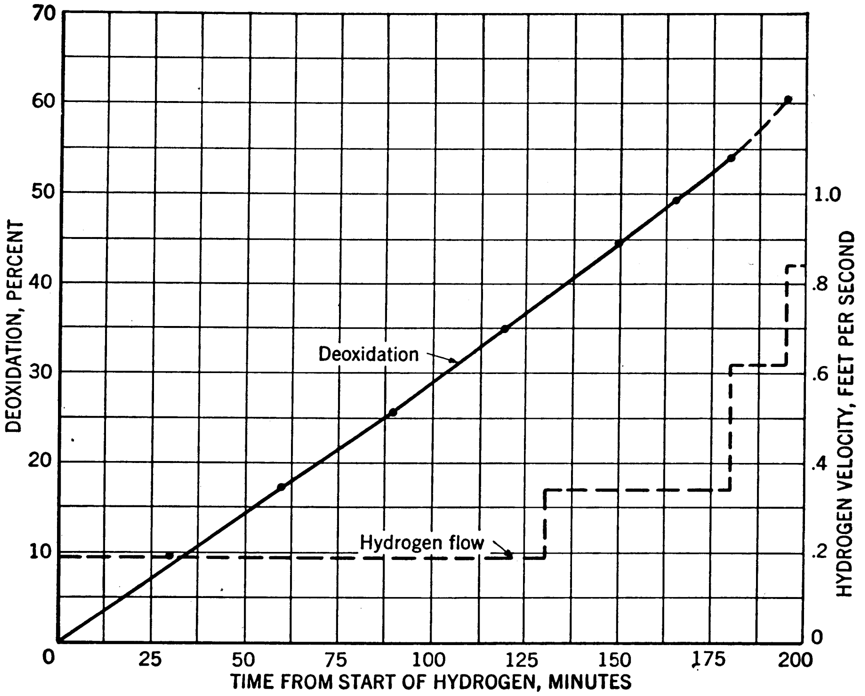

FIGURE 21.—RELATIONSHIP BETWEEN VELOCITY OF HYDROGEN NECESSARY TO MAINTAIN FLUIDIZATION AND THE DEGREE OF DEOXIDATION.

EXTERNALLY HEATED ALLOY-STEEL SHAFT FURNACE, MINNEAPOLIS

Results of tests in the small, externally heated, alloy-steel furnace indicated the feasibility of continuously reducing iron oxide glomerules in such a furnace by means of hot hydrogen or hot water gas.

A 1-ton unit (daily capacity) was constructed having facilities for purifying the gas that passed out of the top of the shaft and for recirculating it through the iron oxides in the shaft. A schematic drawing of the unit is shown in figure 23.

Description of Furnance.—The shaft furnace was fabricated from ⅛-inch 25–20 chrome-nickel steel. It was 6 inches in inside diameter at the top, 12 inches in inside diameter at the bottom, and 10 feet 4 inches in length. About 9 feet of the alloy shaft was enclosed in an insulating firebrick-lined cylindrical furnace 31 inches in inside diameter. Four air-gas burners firing tangentially into the furnace permitted uniform heating of the alloy shaft. Superimposed on the upper end of the shaft was a hopper and double-valve mechanism 4 feet long for feeding glomerules into the shaft.

A water-cooled section of ⅛-inch 18–8 alloy steel 12 inches in inside diameter at the top, 16 inches in inside diameter at the bottom, and 2 feet 6 inches in length was welded to the lower end of the alloy shaft. The water-cooled section was welded to the discharge hopper, in which a variable-speed mechanism continuously removed part of the cooled material from the bottom of the shaft.

Gas Heater.—The gas heater consisted of a cylinder 9 inches in outside diameter by 4 feet 3 inches in length, fabricated from ⅛-inch 18–8 alloy surrounded by 13 turns of 1¼-inch 18–8 alloy tubing wound in a spiral 12 inches in inside diameter. The cylinder was filled with ¾-inch pieces of fused alumina. The cylinder and coil were heated in an insulating firebrick-lined cylindrical pot furnace 31 inches in inside diameter by 6 feet 8 inches in length fired by two gas burners. The cold gas entered the top of the cylinder, passed into the coil near the bottom of the cylinder, and out of the coil near the top of the pot furnace.

Gas Holder.—This was a standard type of gas holder 22 feet in diameter by 18 feet in height. It was equipped with a steam coil to prevent the water from freezing in cold weather.

Hydrogen Manifold.—A standard type of manifold with one reducing valve and valve-controlled connections for six standard cylinders permitted filling the gas holder with hydrogen from cylinders.

Water-Gas Set.—This was a blow-run type for producing about 1,200 cubic feet an hour of blue water gas from coke.

Compressor.—The compressor was a single-stage hydrogen compressor, belt-driven by a 7½-hp. motor; it had a capacity of 50 cubic feet a minute at a pressure of 20 pounds a square inch.

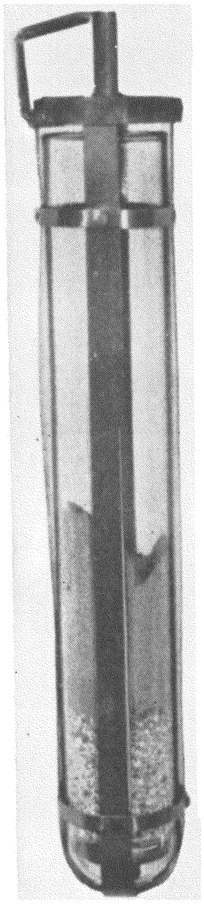

FIGURE 22.—CONDITION OF CHARGE IN PYREX BUBBLE HEARTH WHEN FLUIDIZATION CEASED.

Flowmeter.—A recording-type Foxboro flowmeter was installed in the gas line between the compressor and the heater.

Gas Washer.—The washer, which was a cylinder 18 inches in diameter by 8 feet in length made from ¼-inch steel sheet, was filled with refractory rings to within 2 feet of the top. Two gallons of water a minute was introduced through two spray nozzles just above the refractory column. Hot gases from the shaft furnace entered the washer at the bottom and passed through it into the gas holder.

Gas Scrubber.—The gas scrubber was a cylinder 18 inches in diameter by 12 feet in length, made from 5/16-inch steel sheet; it was filled to within 2½ feet of the top with minus-1½-inch, plus-¾-inch coke. About 6 inches above the top of the coke was a ¼-inch-diameter plate with 80 holes to distribute the caustic-soda solution over the surface of the coke charge; 3½ percent of caustic-soda solution was delivered to the top of the scrubber by a motor-driven centrifugal pump. The spent solution passed through a trap at the bottom of the scrubber into a drain.

When water gas was used to reduce the iron oxide glomerules, the gas from the holder was passed through this scrubber, where all but 1.0 percent of the CO_2 was removed before it was passed through the heater and the shaft filled with glomerules.

The scrubber was bypassed when hydrogen was used.

REDUCTION BY HYDROGEN

A number of runs were made to check the mechanical operation of the various parts of the apparatus. After a few minor changes were made a 5-day continuous test was run in which 10,300 pounds of minus-0.742-, plus-0.371-inch glomerules were charged to the furnace. The glomerules occasionally formed a bridge in the small-diameter top section. The deoxidized product was discharged regularly throughout the test. The operation of the test plant was very satisfactory, and the results show that the shaft furnace can be operated continuously on almost pure iron oxide glomerules.

To determine the effect of nitrogen in the reducing gas upon the sponge iron produced, a mixture of 75 parts of hydrogen and 25 parts of nitrogen was used.

Test 1.—The furnace was filled with glomerules, and the discharger was operated to loosen the charge and to cause the material to move freely in the shaft. Glomerules were charged at the top to keep the furnace filled.

Nitrogen was passed through the heater and the shaft to remove the air. The holder was filled to 30 inches with nitrogen and to 120 inches with hydrogen. The gas mixture was circulated through the heater and shaft immediately after the burners had been lighted. Data are given in table 22.

Test 2.—About 900 pounds of minus-0.742-, plus-0.371-inch glomerules made from iron oxide recovered from waste pickle liquor were available for reduction to sponge iron. As this quantity of glomerules was too small to treat in the 1-ton unit with continuous feed and discharge, it was reduced as a batch.

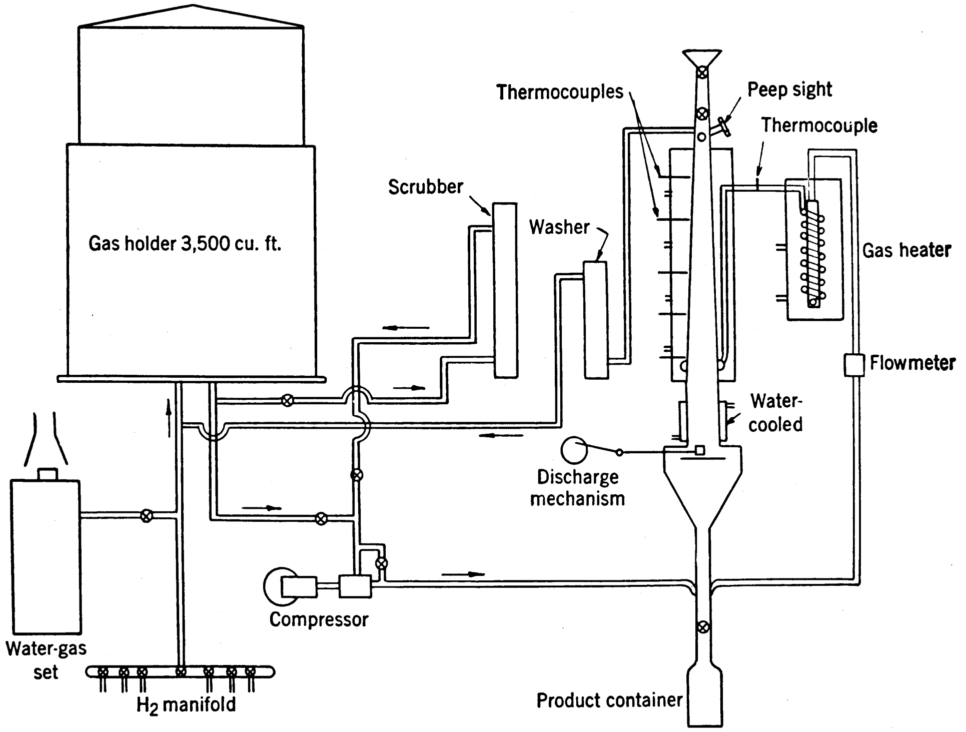

FIGURE 23.—SCHEMATIC SKETCH OF EXTERNALLY HEATED ALLOY-STEEL SHAFT FURNACE FOR REDUCING GLOMERULES; DAILY CAPACITY, 1 TON.

The lower section of the alloy shaft was filled with refractory balls, ¾ inch in diameter, to the level of the gas inlets. The space above the refractory balls was filled with 828 pounds of glomerules.

Gas (75 percent hydrogen, 25 percent nitrogen) from the gas holder was circulated through the glomerules in the shaft for 22½ hours. The temperature in the reducing zone and of the gas entering the shaft averaged about 800° C. for about 14 hours. The material in the furnace was cooled with the reducing gas passing through it for 5 hours.

The following day the reduced glomerules were removed by hand, as they were welded together too firmly to be broken by the discharger. Some oxidation occurred during cooling, and the product was classified according to color and sampled for analysis. The data are summarized in table 23.

Test 3.—This test was made to determine the effect of minus-0.371-inch, plus-4-mesh particles in the charge. The material used consisted of partly deoxidized glomerules from previous tests and broken glomerules, minus-0.371-inch size, that had been screened from glomerules as discharged from the baking furnace.

The test proceeded smoothly and demonstrated that much finer sizes of material could be used than had been anticipated.

The product discharged after balanced operation had been reached contained less than 0.50 percent oxygen, the maximum specified for iron powder. Data are given in table 24.

REDUCTION BY WATER GAS

Test 4.—Test 4 was made to determine the effect of using water gas instead of hydrogen in the deoxidation of iron oxide glomerules in the alloy-steel shaft furnace.

Results of tests in the loss-in-weight apparatus show that the rate of deoxidation in water gas is slower than in hydrogen; some carburization occurs, and less complete deoxidation is attained.

As the capacity of the water-gas set is about 1,200 cubic feet an hour and the shaft furnace needed about 3,000 cubic feet an hour, it was necessary to conserve the CO and H_2 in the gases leaving the top of the shaft. The hot gases passed from the shaft into a tower in which cold-water sprays condensed most of the water vapor and removed dust and some CO_2. The gases from the gas washer passed into the

TABLE 22.—*Summary of log, test 1, in 1-ton shaft furnace*

Time	Temperature, ° C.		Pounds		Remarks
	Shaft	Gas	Charged	Dis-charged	
Jan. 22, 1947:					
8:15 a. m.					Furnace filled with glomerules. 5 cylinders of N_2 put in holder. All N_2 in holder pumped through furnace. Holder filled to 30 inches with N_2 and to 120 inches with H_2.
1:00 p. m.					Gas circulation started.
1:15 p. m.					Burners and discharger started.
3:00 p. m.	700	690			
6:00 p. m. to 11:00 p. m.	765	750	600	460	
11:00 p. m. to 5:00 a. m.	790	800	564	426	
Jan. 23:					
5:00 a. m. to 11:00 a. m.	800	785	600	420	
11:00 a. m. to 5:00 p. m.	805	780	576	414	
5:00 p. m. to 11:00 p. m.	795	800	426	420	
11:00 p. m. to 5:00 a. m.	800	810	546	421	
Jan. 24:					
5:00 a. m. to 11:00 a. m.	790	795	558	420	
11:00 a. m. to 5:00 p. m.	805	800	552	426	
5:00 p. m. to 11:00 p. m	810	810	582	402	
11:00 p. m. to 5:00 a. m.	790	810	552	390	
Jan. 25:					
5:00 a. m. to 11:00 a. m.	800	810	582	421	
11:00 a. m. to 5:00 p. m.	790	815	600	444	
5:00 p. m. to 11:00 p. m.	800	810	462	426	
11:00 p. m. to 5:00 a. m.	810	805	372	437	
Jan. 26:					
5:00 a. m. to 11:00 a. m.				360	Burners turned off at 8:30 a. m. Discharger turned off and gas circulation stopped at 11:00 a. m.
11:00 a. m. to 8:30 a. m.					H_2 at 2 c. f. m. passed through shaft overnight.
Jan. 27:					
8:30 a. m. to 11:30 a. m.					Shaft emptied.

Total weight of glomerules charged	pounds	10,300
Average rate of feed	pounds/hour	92
Total weight of discharged product	pounds	8,483
Average rate of discharge	pounds/hour	70.7
Total weight of discharged product after balanced operation was reached	pounds	3,813
Average temperature in heater	° C	800
Average temperature in reduction zone	° C	800
Total volume of hydrogen used	cubic feet	307,080
Composition of reducing gas	percent	75 H_2, 25 N_2
Average rate of flow of gas	c. f. m.	56
Average rate of flow of hydrogen	c. f. m.	42

Burners were turned off and feed stopped at 7 a. m., Jan. 26.
Discharger was turned off at 3:00 p. m., Jan. 26.
Gas pump was turned off at 11:00 a. m., Jan. 27.

Sample	Analysis of product, percent	
	Total Fe	Oxygen
1	96.65	2.63
2	96.34	3.09
3	94.11	5.76
4	95.22	4.39
5	97.05	2.41
6	97.65	2.31
7	98.32	.73

TABLE 23.—*Summary of data, test 2*

Test was begun at 8:35 a. m., Jan 30, 1947.

Glomerules charged, minus-0.742-, plus-0.371-inch	pounds	828
Average temperature of glomerules	°C	800
Average temperature of reducing gas	°C	800
Average composition of reducing gas	percent	75 H_2, 25 N_2
Rate of flow of gas	c. f. m.	61
Total volume of hydrogen used	cubic feet	7,250

Test was completed at 7:00 a. m., Jan. 31.

Color	Pounds	Analysis of product, percent						
		Fe	O_2	N_2	S	SiO_2	Al_2O_3	Mn
Gray	421	97.75	0.24	0.0	0.003	0.26	0.05	0.47
Blue	109		.40					
Dark blue	10		.51					
Mixed	28		.47					

TABLE 24.—*Summary of log, test 3, in 1-ton shaft furnace*

Time	Temperature, ° C.		Remarks
	Furnace	Gas	
May 7, 1947			Furnace filled with 1,377 pounds of minus-0.742-inch, plus-4-mesh glomerules.
9:30 p. m.			Gas circulation started, 56 c. f. m. Burners started.
11:00 p. m.			Discharger started.
May 8:			
1:00 a. m.	715	800	Product recharged into top of shaft.
2:30 p. m.	795	795	Began to save product.
2:30 p. m. to 7:00 p. m.	800	805	Sample 1.
7:00 p. m. to 11:00 p. m.	805	800	Sample 2.
11:00 p. m. to 5:00 a. m.	800	800	Sample 3.
May 9:			
7:30 a. m.	785	795	Burners turned off.
5:00 a. m. to 11:00 a. m.			Sample 4.
11:10 a. m.		110	Gas circulation stopped. Small flow of N_2 into shaft.
11:00 a. m. to 3:00 p. m.		70	Sample 5. Test stopped.

Size of glomerules charged		Minus-0.742-inch, plus-4-mesh
Total weight of glomerules charged	pounds	3,441
Total weight of glomerules discharged	do	2,909
Discharged product after balanced operation had been reached	do	1,771
Average temperature in shaft	° C.	800
Average temperature of reducing gas entering shaft	° C.	800
Average composition of reducing gas	percent	75 H_2, 25 N_2
Average rate of flow of gas	c. f. m.	52
Average rate of flow of hydrogen	c. f. m.	39
Burners were turned off at 7:30 a. m., May 9.		
Final product was discharged at 3:00 p. m., May 9.		

Sample	Pounds	Analysis of product, percent	
		Total Fe	Oxygen
1	357	97.46	1.20
2	269	98.56	.29
3	383	98.45	.33
4	481	98.53	.23
5	281	98.53	.30

3,500-cubic foot gas holder. The gases from the holder passed through a scrubber in which nearly all of the CO_2 was removed by a 3.25-percent solution of caustic soda. The purified gas was heated to 800° C. and passed into the hot glomerules in the shaft. About 10-percent of the gas leaving the top of the shaft was wasted to prevent increase of nitrogen in the gas in the holder. Data for test 4 are given in table 25. The furnace and accessories are shown in figure 23 (p. 64).

Caustic-soda solution (3.25 percent NaOH) at 45° C. was pumped into the scrubber at the rate of 6 gallons a minute. This caused an appreciable quantity of water vapor to be carried in the purified gas and probably accounts for the use of more carbon monoxide than hydrogen in the reduction of the iron oxides in the shaft. The water vapor was introduced into the reducing gas to decrease carburization of the sponge iron by the carbon monoxide in the gas.

The mechanical operation of the furnace was almost identical with that when hydrogen was used.

CONCLUSION

Operation of the 1-ton shaft furnace demonstrated the feasibility of gaseous reduction of iron oxide glomerules in hydrogen and in water gas in a continuously operated, externally heated, alloy-steel shaft furnace.

TABLE 25.—*Summary of log, test 4, reduction by water gas*

Time	Temperature, °C.		Remarks
	Shaft	Gas	
Oct. 10, 1947			Gas holder filled. Water-gas set cleaned and refilled with coke. Shaft filled with glomerules.
5:00 p. m.			Gas circulation started.
6:00 p. m.			Burners started.
7:30 p. m.			Discharger started.
9:00 p. m.	790	805	
10:30 p. m.	790	790	Gas sample 1.
Oct. 11:			
8:00 a. m.	785	810	Gas samples 2 and 3.
10:00 a. m.	790	800	Gas samples 4 and 5.
10:00 a. m. to 2:30 p. m.	800	805	Gas samples 6 and 7. Product sample 1.
2:30 p. m. to 5:30 p. m.	805	820	Product sample 2.
5:30 p. m. to 10:30 p. m.	800	825	Product sample 3.
10:30 p. m. to 4:30 a. m.	785	820	Product sample 4.
Oct. 12:			
8:30 a. m.	790	810	Gas samples 8 and 9.
4:30 a. m. to 9:30 a. m.	790	810	Product sample 5.
9:30 a. m. to 2:30 p. m.	795	805	Product sample 6.
2:30 p. m. to 6:30 p. m.	805	800	Product sample 7.
6:30 p. m.			Burner turned off. Circulation of water gas stopped. H_2 at 2 c. f. m. passed through shaft furnace overnight.
Oct. 13			Furnace emptied. Product sample 8.

Size of glomerules charged	Minus-0.742-inch, plus-4-mesh
Total weight of glomerules charged pounds	6, 252
Total weight of glomerules discharged do	5, 291
Total weight of product saved do	3, 531
Average temperature in reducing zone °C	800
Average temperature of gas entering shaft °C	800
Average rate of flow of gas c. f. m.	50

Sample	Average composition of gas, percent			
	H_2	CO	CO_2	N_2
Leaving water-gas set	44. 1	47. 6	1. 7	5. 9
Entering shaft	46. 7	28. 5	1. 3	22. 8
Leaving washer	36. 5	19. 5	19. 9	23. 9

Sample	Pounds	Analysis of product, percent				
		Total Fe	Metallic Fe	Oxygen	Total C	S
1	511	90. 00	67. 18	5. 9	0. 20	0. 004
2	292	89. 10	62. 55	6. 5	. 28	. 007
3	382	93. 84	81. 95	2. 4	. 16	. 009
4	450	90. 87	66. 54	8. 2	. 14	. 009
5	382	88. 81	64. 24	5. 8	. 09	. 007
6	396	92. 06	77. 87	3. 5	. 11	. 007
7	298	92. 77	80. 23	3. 5	. 18	. 007
8	820	91. 96	77. 51	3. 7	. 21	. 009

PILOT-PLANT-SCALE INVESTIGATIONS

UNITED VERDE SHAFT FURNACE

The first industrial-scale research on the reduction of iron oxides by natural gas, re-formed by the Maier process developed by the Bureau of Mines at the Berkeley station, was undertaken in 1931 at Clarkdale, Ariz. This investigation was supervised by Oliver C. Ralston, then director of research for the United Verde Copper Co.

In the normal operation of the United Verde smelter about 1,000 tons of iron daily went into ferrous silicate slag. Ralston, Fowler, and Kuzell [65] describe a modified method of operating the converters, which produced ferrous oxide slag containing approximately 63.4 percent FeO, 15.4 percent SiO_2, 15.0 percent CaO, 2.0 percent Al_2O_3, and 0.5 percent Cu.

The ferrous oxide slag was granulated into spherical pellets 1 to 5 mm. in diameter by pouring it into a stream of water. The pellets were reduced with hot re-formed natural gas in a vertical-shaft furnace operating continu-

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[65] Ralston, O. C., Fowler, M. G., and Kuzell, G. R., Recovering Zinc from Copper Smelter Products: Eng. and Min. Jour., vol. 136, 1935, pp. 167–169.

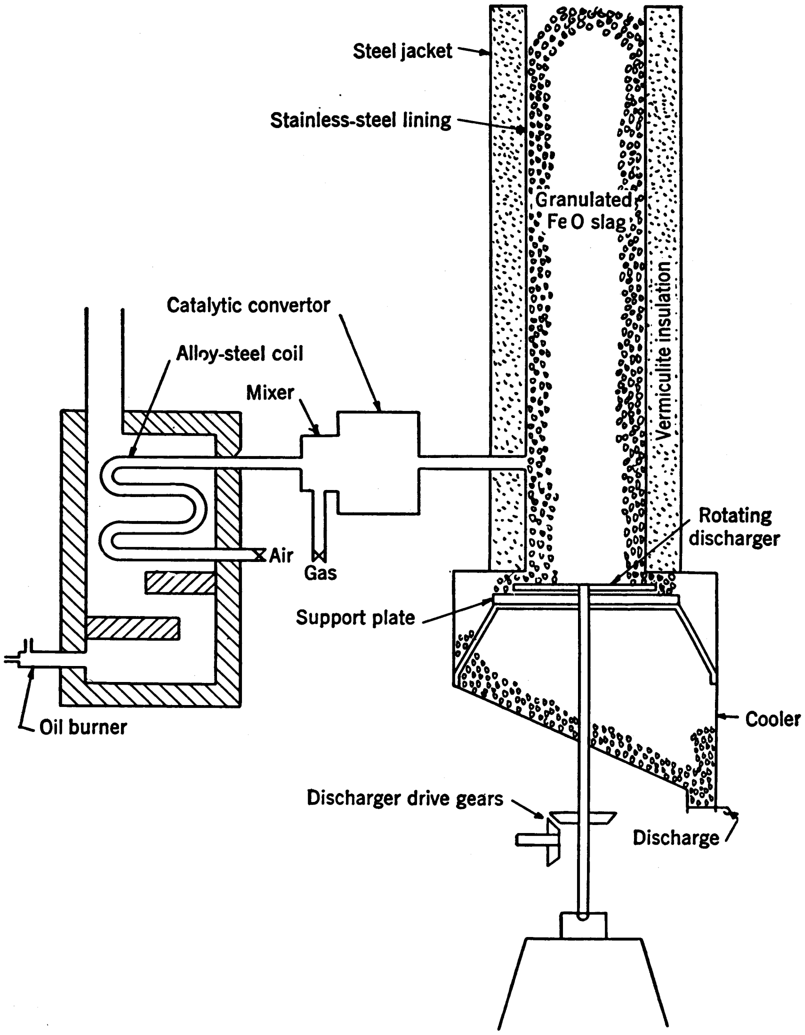

Figure 24.—SCHEMATIC SKETCH OF SHAFT FURNACE FOR REDUCING GRANULATED FERROUS OXIDE SLAG.

ously. A schematic sketch of the shaft furnace and catalytic converter is shown in figure 24.

The Maier process [66] of re-forming the natural gas functioned well after the proper design of catalyst chamber was evolved. (Some 30 designs were tried in this development.) The catalyst consisted of alundum granules saturated with nickel sulfate, which was soon converted to films of nickel over the alumina base.

The natural gas was mixed with air preheated to 800° C. in a proportion that would convert the carbon of the methane to CO and leave 2 volumes of H_2 per volume of CO. The composition of the re-formed gas was:

	Percent by volume
Unreacted CH_4	1.0 to 2.0
CO_2	1.0 to 2.0
Water vapor	1.0 to 2.0
Nitrogen	40
CO	18 to 19
H_2	36 to 38

The temperature of the pellets at the top of the column was about 500° C. In the reaction zone the temperature was 1,000° to 1,050° C.

The pellets were discharged continuously from the bottom of the shaft. They were about 95 percent reduced to metal and were melted easily in an electric furnace and cast into steel ingots. The steel contained 0.75 to 1.5 percent copper and low percentages of sulfur.

About 50 billets were forged during an in-

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[66] Maier, C. G., Sponge-Iron Experiments at Mococo: Bureau of Mines Bull. 396, 1936, 81 pp.

vestigation of their physical properties. Before the ingots could be forged or rolled satisfactorily, it was necessary to nickel-plate them by dipping into a bath of borax glass saturated with nickel oxide. About 50 cents worth of borax and nickel oxide was required for a ton of steel. Over 300 ingots were rolled into commercial shapes at Pittsburg, Calif.

CONCLUSIONS

1. Results obtained in this investigation show the feasibility of producing sponge iron from ferrous oxide slag by reduction in a shaft furnace in re-formed natural gas.

2. A catalytic converter can produce continuously a gas of the following average composition: 1.5 percent H_2O, 1.5 percent CO_2, 37.0 percent H_2, 18.5 percent CO, and 40.0 percent N_2.

3. Such a gas, near 1,000° C., contacting hot iron oxide, can thermally support reduction to metal. It reacted exothermically to raise the temperature of the solids in front of the gas inlet to 1,025° C.

MANUFACTURE OF SPONGE IRON IN CERAMIC KILNS

Sponge iron was first produced commercially in 1909 at Höganäs, Sweden, where Sieurin developed a process in which iron oxide was reduced to metal by packing the fine oxide in coke, coal, or charcoal in a container and heating it in a brickkiln at 1,900° to 2,150° F.; it was held at this temperature long enough to complete reduction and was then cooled to about 300° F. before being removed from the kiln.

The oxide may be mixed with the reducing mixture or may be placed in the sagger in layers with reducer between the layers. It may be pressed into bricks or extruded in shapes that can be placed in the sagger and surrounded with the reducer or reducer mixed with lime to trap sulfurous gases.

When the importation of Swedish sponge iron was interrupted by the war, the Bureau of Mines undertook a study of the Höganäs procedure for making sponge iron, with the idea of utilizing the many idle brickyards in the country to meet the threat of an impending shortage of the scrap essential in making the steel required for armaments.

The preliminary work on so-called brickyard sponge iron has been reported by Walker [67] and Ross,[68] while a report by Smith and Burton [69] gives the details of a successful campaign in using large, periodic brickkilns for making a good grade of sponge iron, at moderate cost, from iron ores and concentrates bought on the open market.

Walker records the results obtained in reducing 93 small (15- to 100-pound) lots of three iron ores in a gas-fired tunnel kiln at the ceramic plant of the United States Quarry Tile Co., at East Sparta, Ohio. Four commercially available fuels were tested as reducing agents, using three sizes of clay refractory saggers and two sizes of low-carbon steel containers. Five desulfurizing agents were tried.

The results show that reduction in saggers is more rapid when subbituminous coal is used in the reducer layers than when coke breeze is used as the reducer. Reduction at 1,750° F. requires about twice the time of heating as reduction at 1,950° F. Limestone is the most effective desulfurizer.

Ross conducted experiments in the shale-brick plant of the Binghamton Brick Co., at Binghamton, N. Y., to determine whether iron oxide could be reduced to sponge iron in the commercial brickkilns available, to measure the intensity of reduction and the temperatures required to effect reduction, and to determine the rate at which reduction takes place in the temperature ranges attainable in commercial kilns.

A small experimental downdraft kiln and a device for measuring temperatures and rates of reduction were constructed. Preliminary tests were made before using the standard commercial tunnel kilns.

IRON ORES

In the Binghampton experiments only commercial concentrates were used. The total iron ranged from 55.87 to 68.77 percent (86.8 to 95.0 percent magnetite), and the contained gangue material (SiO_2, Al_2O_3, CaO, and MgO) was not less than about 4.0 percent and exceeded 8.0 percent in some samples. The gangue material was retained unchanged in the final sponge iron, of which it constituted 5.3 to 10.6 percent on the basis of complete reduction of the magnetite (containing 37.6 percent oxygen).

Other iron ores are not, as a rule, as pure as magnetite concentrates. The iron ores listed in table 26 were reduced at Binghamton, N. Y., to permit comparison of the reducibility of hematites and limonites with magnetite. The Swedish hematites are the specular variety, not the earthy type as represented by red hematite, limonite, brown ore, and bog ores found in the United States.

The only pure iron oxide available was a synthetic rouge hematite donated by the Colum-

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[67] Walker, J. P., Reduction of Iron Ore in Clay and Steel Containers (Saggers): Bureau of Mines Rept. of Investigations 3819, 1945, 30 pp.

[68] Ross, Donald W., Production of Sponge Iron in a Shale-Brick Plant: Bureau of Mines Rept. of Investigations 3822, 1945, 27 pp.

[69] Smith, Kenneth M., and Burton, S. E., Manufacture of Sponge-Iron in Periodic Brickkilns: Bureau of Mines Rept. of Investigations 3841, 1945, 38 pp.

TABLE 26.—*Analyses of miscellaneous iron ores, percent*

Source	Sample No.	Total Fe	SiO_2	TiO_5	S	P	MnO_2	CaO	MgO	Al_2O_3	CO_2	Loss in ignition
Clinton (N. Y.) hematite	1	44.00	13.72	------	0.36	0.33	------	6.67	3.34	4.89	7.70	------
	2	42.2	14.1	0.6	.41	.51	------	6.34	2.5	4.70	7.30	------
Bennington (Vt.) limonite	14	53.52	6.35	------	------	------	------	------	------	------	.74	11.86
	171	54.02	5.87	.06	.00	.75	.97	.17	.49	4.28	.59	9.68
	172	54.48	4.36	.06	.02	.75	1.16	.40	.54	4.04	.33	10.19
	173	53.74	5.57	.08	.07	.75	1.04	.46	.52	4.37	.51	10.05
Scotia (Pa.) limonite	174	43.49	23.25	.16	.15	.069	.23	.22	.35	4.81	.56	[1] 6.20
Pennsylvania bog-iron ore	175	54.80	2.36	.00	.13	.43	.53	.30	.22	1.02	11.55	[1] 3.16
	[2] 175	73.8	------	------	------	------	------	------	------	------	------	.89
Hudson (N. Y.) siderite	------	29.28	25.07	.40	.58	.048	1.17	1.18	3.58	8.73	7.87	------
Soaking pit cinder from Central I. & S. Co	------	70.08	3.48	------	.04	.02	[3] .54	.54	.12	1.71	------	------

[1] Combined water.
[2] Calcined.
[3] This is calculated as Mn and not as MnO_2.

bian Carbon Co. Presumably, this was chemically pure hematite finely divided (minus-325-mesh). Although they yielded no usable sponge iron, the few experiments on reducing this rouge hematite disclosed important information on the conditions necessary for the successful manufacture of brickyard sponge iron.

REDUCING COAL

Swedish sponge iron was originally made by using charcoal as reducing fuel, but Swedish publications intimate that the Höganäs plant has found a way to use a local low-grade, high-ash, high-sulfur coal by mixing lime with it. At Binghamton several high-volatile bituminous coals, charcoal, anthracite, and mixtures of these materials with clay were tried. Most of the combinations served passably well as reducing agents.

Any substances that were particularly high in clay or claylike ash, on coming into contact with the ore during its early stages of reduction and before much metal appeared, tended to adhere to the sponge mass if pressed in solid contact with it.

Most of the carbonaceous materials tried lost weight, shrank, or otherwise deformed before a temperature was reached at which the ore mass became sufficiently bonded to be self-supporting. The high-volatile bituminous coals used lost their shape extensively, with resultant large cavities into which the unconsolidated ore flowed. When these bituminous coals were used as the surrounding carbon the sponge masses were very irregular in shape, and frequently all the sponge could not be recovered without inclusion of most or all of the surrounding spent coal. Charcoal and coke used as surrounding carbon served reasonably well, except when the charcoal was ground (graded in size for the purpose of producing a smooth surface on the sponge mass) the fines tended to burn out early in the operation, with resultant partial deformation of the ore mass.

Present-day anthracite retained much of its substance up to temperatures and reducing conditions that started self-bonding of the ore masses, and even from the containers the volume of the then largely spent anthracite was still sufficient to cover entirely the ore mass in the container. Because of its satisfactory performance, anthracite was employed, despite its sulfur content, as the surrounding carbon during the remainder of the project. Part of the tests used anthracite mixed with lime to capture the sulfur from the coal.

Exact analyses of the particular anthracite used for reduction were not made. Table 27 gives the composition supplied by the sales agencies.

TABLE 27.—*Anthracite analysis*

	A	B
Moisture ... percent	3.5	------
Volatile ... do	6.40– 6.50	6.25
Ash ... do	6.50– 6.90	9.5
Carbon ... do	83.10–83.60	82.75
Fusion temperature of ash ... °F	2,800	2,925
B. t. u. (dry)	13,700	13,200

The coal for firing was West Virginia low-grade, run-of-mine bituminous for the tunnel kiln. For the later work in periodic kilns the firing coal was West Virginia high-grade washed Nut coal. No analyses of either of the two grades of firing coal were obtained.

CONTAINERS

Virtually all saggers used for holding the charges heated in the brickkilns were produced in the plant of the Binghamton Brick Co. The company's common brick shale was tested in a quantity of several tons, as were Mount Jewett (Pa.) semi-fire-clay, Hanley Brick Co. semi-fire-clay, and Harbison-Walker

Refractories Co. zinc-retort clay mix from South Webster, Ohio. In addition, two zinc retorts were obtained from the New Jersey Zinc Co., Palmerton, Pa. The raw batch of these supposedly consisted of 35 percent Saint Louis Cheltenham clay and 65 percent silicon carbide. Two slip-cast retorts were obtained from the New Castle Refractories Co., New Castle, Pa. One of these contained silicon carbide and the other magnesia (talc). The experience with container clays on this project parallels common knowledge of clays used in this general type of metallurgy (glass-melting pots, zinc retorts); that is, few clays are eminently satisfactory.

The shale was hardly refractory enough to be satisfactory for containers even for low-temperature reduction. More thorough working of this clay in the wet state to develop its raw bonding power should give better results. It appears that if made from satisfactory clays having a long vitrification range, other conditions being optimum, containers could be charged without first being fired, at least in sizes up to 6½ inches in inside diameter. Of the four clays tested, the Harbison-Walker zinc-retort mix was the only one that proved eminently satisfactory for the purpose.

Preliminary experiments made in the tunnel kiln were run in the company's 6½- by 6½-inch (inside dimensions) rectangular containers (8¼ by 8¼ by 24 inches, outside dimensions) open at both ends. A flat fire-clay slab was used for bottom and top. Mount Jewett semi-fire-clay containers were used in the later experiments. In addition, 3-inch, 4-inch, 6-inch, and 8-inch (inside dimensions) round containers, all 12 inches long and open at both ends, were made in the company's plant from the company's shale with and without admixture of refractory clay. Little cracking was noticeable during drying, and the ware did not explode early in burning in the tunnel kiln. Cracks, apparently "making cracks," formed during later firing of these wares in the tunnel kiln. These defects were of a type that could be expected from extrusion machines and were perhaps normal. An irregular rip occurred from end to end of many of these wares during passage through the kiln. This kind of crack may have started during forming or drying. It appeared to be relief of strain in ware that is not well-bonded; where but one rip occurred per tile, the two sides of the rip frequently were some distance apart.

The experiments run in these tiles indicated that, with all conditions suitable, raw containers can be charged in sizes up to the 6½- by 6½-inch limit available. Furthermore, the necessity for nonleaking closure became forcibly evident at this time, as experiments run in these short 12-inch containers were entirely ruined unless the closures were substantially leak-free. This evidence on leaks substantiates that found in the test kiln.

Use of the containers that were made later is discussed under firing in downdraft kilns, where it is noted that of the three fire clays used on the project only the plastic Harbison-Walker clay proved eminently satisfactory for the purpose. In forming the containers on the extrusion machines of the company the shale probably gave the least total trouble from clay to fired ware, except that it did not compact and bond readily. The Hanley clay probably was next, followed closely by the Mount Jewett clay. The Harbison-Walker showed greater workability and greater raw bonding power than the other materials and was therefore proportionately more difficult to dry and, unless well-dried before being set in the tunnel kiln, tended to explode at the beginning of the fast-firing schedule of the tunnel kiln.

The two zinc retorts obtained from the New Jersey Zinc Co. and the two slip-cast containers obtained from the New Castle Refractories Co. were in prime condition at the conclusion of the project.

The choice of a suitable sagger for making brickyard sponge iron is a problem that will require much research and development. It is known that carbon monoxide has a disintegrating effect upon clay refractories, and this, in addition to the mechanical defects mentioned, shortens the life of saggers considerably. Tigerschiöld (Blad f. Bergshandteringens Vänner, vol. 20, 1932, pp. 219–289) estimates that the saggers at the Höganäs plant withstand 12 heating cycles and that 3 to 4 saggers (average) are consumed for each ton of sponge iron produced.

EXPERIMENTAL DOWNDRAFT TEST KILN

The experimental kiln was a downdraft type and was fired with oil and compressed air through burners having micrometer adjustment. The kiln hearth was approximately 30 inches wide and 48 inches long, and the distance from hearth to crown was approximately 42 inches. Checker bricks were set on the hearth so that the bottom of the kiln charge could be at any shorter distance from the crown. The kiln door was at one end of the hearth, and a series of pyrometer-tube holes through the crown was arranged along its median line. Firing was done into fire bags parallel to the length of the hearth.

The principal objectives of this test were to prove that iron oxide could be reduced to sponge in this type of kiln and to determine qualitatively the intensity of reduction, the temperatures required to effect reduction, and the rate of reduction in temperature ranges that could be covered by the commercial kilns at hand. The problem of obtaining the temperature and rate of reduction was attacked by means of the device shown diagrammatically in figure 25. This device consisted of a semi-fire-clay building-flue tile (inside dimensions, 11½ by 11½ by 24 inches; wall thickness, 1 inch) resting on a clay slab. The arrangement was supported at such elevation above the hearth that the porcelain thermocouple protection tubes, which passed through the multiple pyrometer-tube holes in the crown, protruded above the crown of the kiln and were there supported. They extended downward to the midheight of the ore mass, which was placed in the tile. In charging this container a clay slab that fitted the inside of the tile was laid on the supporting slab inside the tile and was luted around its edges. This served as a substantially airtight bottom joint throughout the reducing operation. Moreover, the tile was rather nonporous in structure. After filling, the top of the tile was sealed in the same manner and almost as tightly as the bottom, with the result that the excess of carbon introduced, surrounding the ore charge, still covered the charge with unburned coal at the end of the experiment. The tile was charged by placing 3 inches of minus-4-mesh anthracite and finer on the bottom; 81 pounds of a mixture of Tahawus magnetite concentrate containing 8 parts of anthracite to 100 parts of concentrate, molded into brick form by use of a paper-mill lignin-type binder, were next placed in the tile in the form of a hollow square built of these bricks laid on edge. A thin layer of anthracite was placed between these magnetite-concentrate bricks to insure that they would not adhere to one another. The outside of the square was thus approximately 1½ inches from the inside of the fine tile, and the wall of magnetite concentrate was approximately 2¼ inches thick. The space between tile and concentrate and the space within the hollow square of ore were filled with anthracite, as was the space from the top of the ore mass to the top of the tile. This ore mass, in the form of a hollow square pipe, was thus a forerunner of the cylindrical pipes (8½-inch diameter, 2¾-inch wall) produced in test 6 (p. 75) in the downdraft kiln.

For temperature-measuring purposes, a base-metal thermocouple in a porcelain protection tube was placed inside and at the approximate center of the square formed by the ore mass; another couple was placed on a line between this first couple and a third couple, which was outside the flue. The second couple was between the ore mass and the container wall. The third base-metal couple was placed so that its hot-junction end hung outside ½ to ¾ inch from the tile at the midwidth of one of the sides of the tile. The records obtained from these three couples are shown in figure 26. Temperature readings were taken every half hour. Each temperature reading of the couple outside the tile was checked by a Leeds & Northrup optical pyrometer that had been checked by its maker shortly before the test was started. The temperatures recorded are therefore reasonably accurate. (They check with the performance of pyrometric cones that were present in numerous parts of the kiln.) Relative to one another, correlation between couples was excellent, as can be seen from the chart. Toward the end of this burn the bare wires of couple 2 accidentally were moved into such a position outside the kiln that they were exposed to furnace gases, with the result that thereafter this couple deteriorated; beyond the forty-fifth hour its readings were no longer dependable. They did, however, continue to follow an intermediate course between couples 1 and 3 until they became very erratic.

The heating curves of figure 26 indicate clearly that a heat treatment equivalent to cone 3 (2,093° F., 1,145° C.) maintained for 24 hours is sufficient to reduce almost completely a thickness of 2¼ inches of Tahawus magnetite concentrate containing carbon if heated largely from one side.

It was noted that the temperature of the region outside but immediately adjoining a container in which a relatively large ore mass was being reduced tended, during reduction, to be slightly lower than the average temperature of the furnace atmosphere at a greater distance. Curve *3* indicates this phenomenon. As the temperature approached 2,000° F., the fires were steady, and the rate of advance was regular (curve *3*); then, rather promptly, as curves *1* and *2* began to fall farther behind, curve *3* faltered in its advance. As soon as this faltering was noted, however, the fires were adjusted downward to provide a soaking heat instead of an advancing temperature. The adjusting action may or may not have obliterated more prominent evidence of this behavior. Thus, apparently the heat absorption that was taking place inside the container was also minutely discernible at its outer surface. As evidenced by curves *1* and *3*, the reducing action was virtually completed before the burn was discontinued. The flat section of curve near the beginning of curve *1* possibly indicates the final evaporation of moisture that had collected at the center of the container by migration of water away from the surrounding rising (higher) temperature.

The ore mass contained carbon, and the

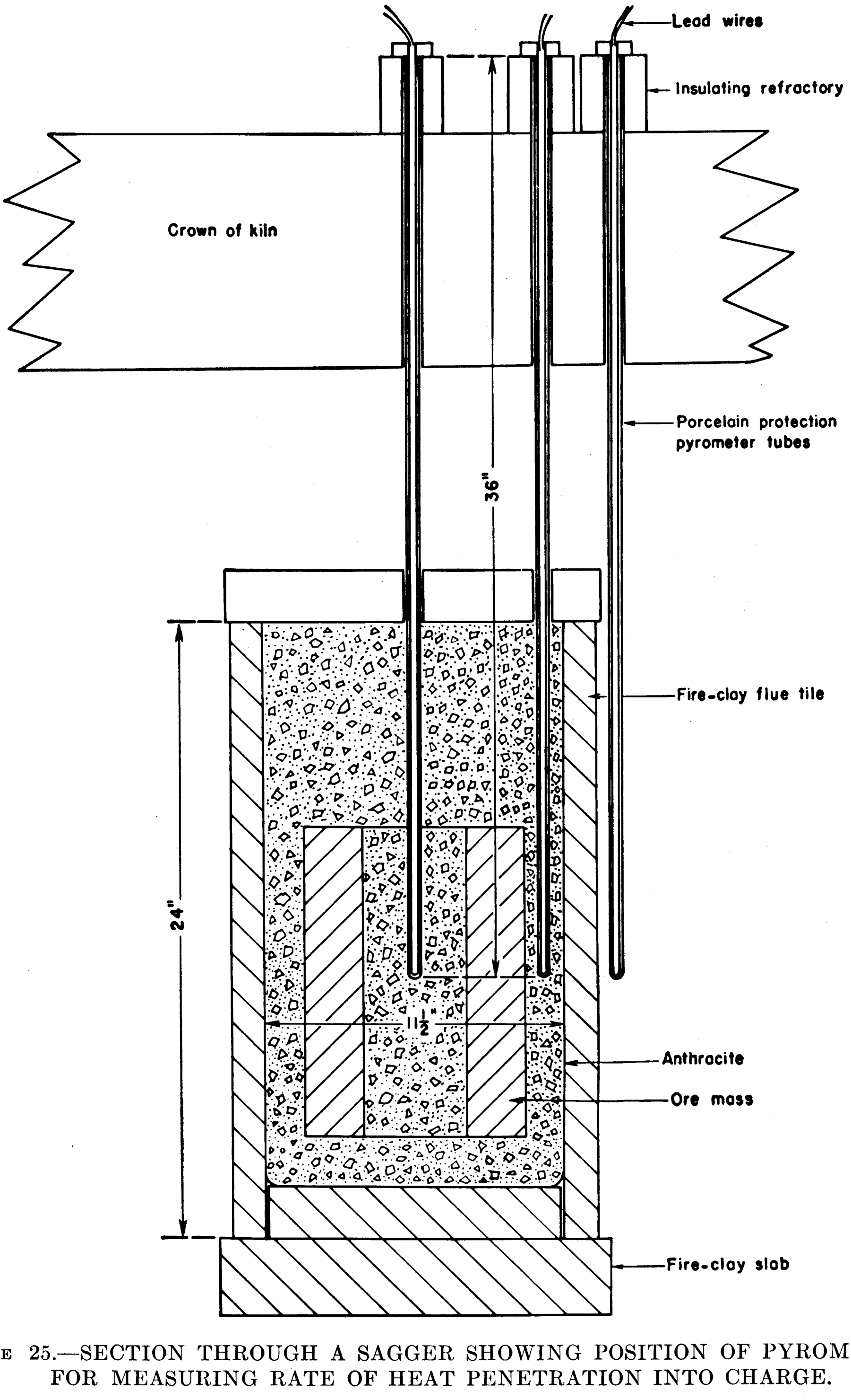
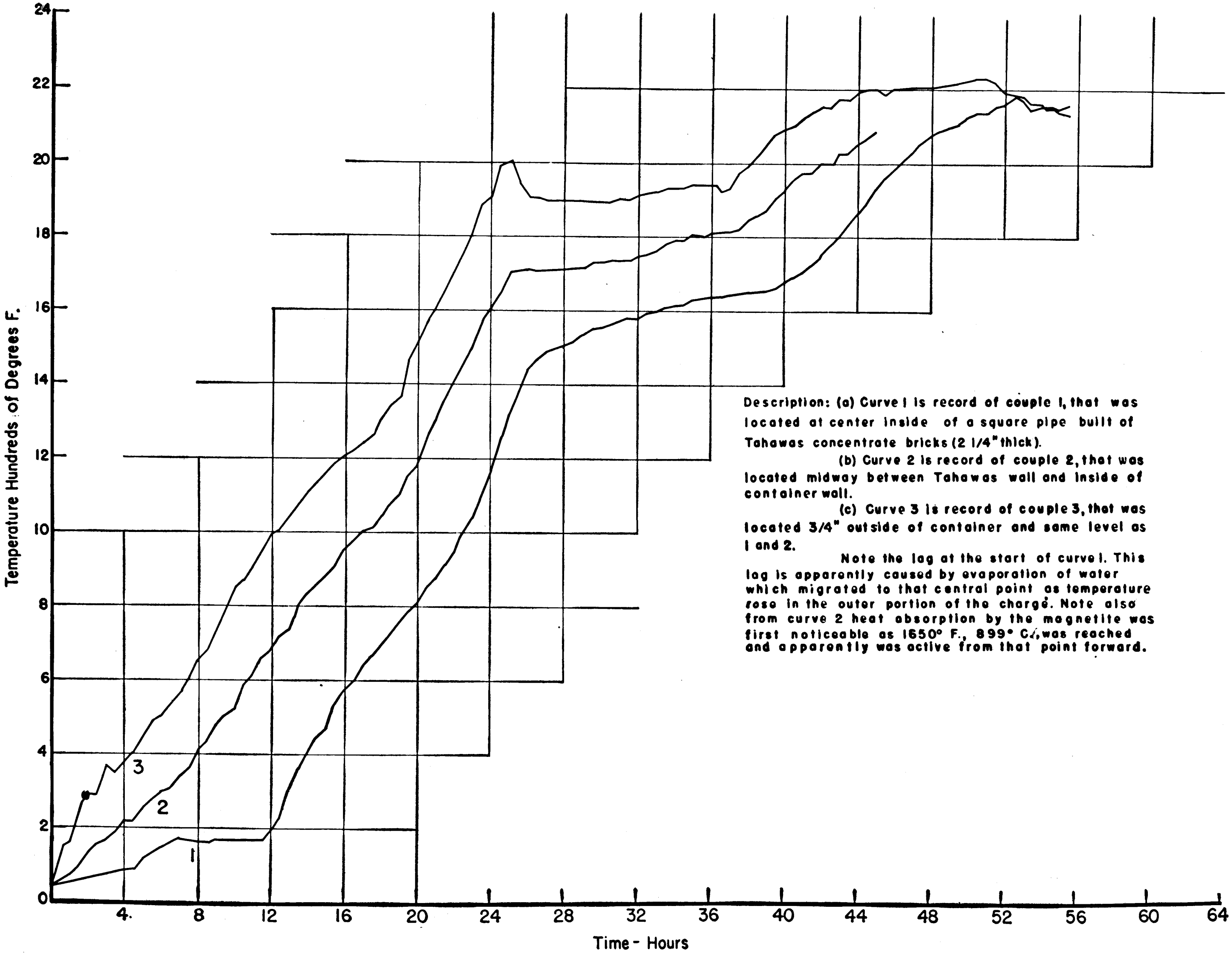


FIGURE 25.—SECTION THROUGH A SAGGER SHOWING POSITION OF PYROMETERS FOR MEASURING RATE OF HEAT PENETRATION INTO CHARGE.



Description: (a) Curve 1 is record of couple 1, that was located at center inside of a square pipe built of Tahawas concentrate bricks (2 1/4" thick).

(b) Curve 2 is record of couple 2, that was located midway between Tahawas wall and inside of container wall.

(c) Curve 3 is record of couple 3, that was located 3/4" outside of container and same level as 1 and 2.

Note the lag at the start of curve 1. This lag is apparently caused by evaporation of water which migrated to that central point as temperature rose in the outer portion of the charge. Note also from curve 2 heat absorption by the magnetite was first noticeable as 1650° F., 899° C., was reached and apparently was active from that point forward.

Figure 26.—TIME-TEMPERATURE CURVES, FIRST EXPERIMENT IN DOWNDRAFT TEST KILN.

final sponge was so friable that small amounts of it were lost; hence, weight-loss data cannot be exact. Change in weight noted in the sponge mass, however, from 81 pounds before reduction to 58.5 pounds after reduction, indicates virtually complete reduction. For analytical determinations every alternate brick of the square ore mass was selected, and samples were taken by boring an evenly distributed system of ½-inch holes through the least dimension of each.

That very intense reducing conditions (high percentage CO) are required for the reduction of iron oxide to sponge was indicated from a series of draw trials made with Denver Fire Clay Co. crucibles (5 inches in diameter by 8 inches high) with close-fitting lids luted in place. Even with the relatively slight leakage that occurred under these conditions and with some unburned coal remaining in each crucible, the reduction of the respective ore masses was so slight, both in the crucibles that were drawn from the kiln during the progress of the burn and those that were removed on its completion, that comparisons could not be made.

In a second test in the test kiln Tahawus concentrate and crude Clinton hematite, which in the first test had not been bonded into tough masses of sponge iron either separately or in mixture, were again included for comparison with Scrub Oak magnetite concentrate, with the same friable result. This lack of bond development in Tahawus and Clinton masses was evident, in spite of the fact that the Scrub Oak sponge mass was satisfactorily bonded.

In this second test the kiln load was composed chiefly of crucibles 5 inches in diameter and 8 inches high and a few 3½ inches in diameter and 5½ inches high; the lids were luted on all crucibles. The temperature was raised rapidly in this test, the rate of heating being governed by what it was believed the crucibles would stand; cone 1 (2,057° F., 1,125° C.) was reached in 9⅔ hours. This test was run to determine what effect such rapid heating would have upon bond formation in Tahawus concentrate and in the impure Clinton hematite. Repeated series of crucibles drawn from the kiln, both at this temperature and at higher temperatures, failed to reveal any special bond-developing effect.

This test confirmed the finding of the first experimental downdraft-kiln test that these impure ores are not firmly bonded into a tough mass by mere heat treatment in this manner. Likewise, the test showed that pure Scrub Oak magnetite concentrate was suitably bonded by this treatment. However, the fact that iron oxides differ greatly in bond development during firing was not forcibly brought to attention until the first test on DeGrasse magnetite concentrate was made in the tunnel kiln; repeated experiments in downdraft kilns later disclosed that all purer materials reduced on this project (including the pure synthetic rouge hematite) bonded more readily at sufficiently high temperatures than did these impure Tahawus and Clinton materials.

TESTS IN COMMERCIAL DOWNDRAFT KILNS

Six tests were conducted in downdraft kilns of the commonly known multiple-stack, rectangular type. The first four were made in a 15-foot kiln, and the following two tests were made in 25-foot kilns.

TABLE 28.—*Results of tests in commercial downdraft kilns*

Test No.	Kiln No.	Type of ore	Weight of ore, pounds	Time	
				Days	Hours
1	6	Mixed	2,050	5	7½
2	6	do	15,000	5	4
3	6	Chateaugay (wet)	24,000	4	12
4	6	Chateaugay	20,000	8	16
5	9	do	36,000	7	22½
6	7	do	36,000	7	18

ARRANGEMENT OF REDUCING AGENT AND ORE MASS

In the early burns in downdraft kilns both the anthracite mixed with the ore and that surrounding it were ground to pass a 4-mesh screen to insure adequate reaction surface between the carbon and the surrounding gases and, if necessary, to make contact with the ore particles. After experiments with Rice-size (5/16-inch diameter) anthracite had proved that the fine carbon dust was not necessary for reduction, the Rice size was used throughout most of the downdraft burns. This size insured relatively large interstices through which gases might circulate in definite directions. Later, after it had finally become established that reduction takes place within approximately an inch of the source of carbon, Nut-size anthracite (¾-inch to 1½-inch) was used where it was desired to mix carbon with the ore because it is believed that these larger ash particles rise from a molten bath of metal, whereas dust-size particles of ash may remain scattered through the melt. Sponge iron produced from masses of ore surrounded by graded sizes of carbonaceous material had a clean carbon-free surface. Sponge iron produced from masses of ore surrounded by closely sized carbon had a rough surface contaminated by pieces of carbon. The tests disclosed that noncarbon ore masses will reduce to a depth of 1.25 inches, and this fact led to consideration of ore columns no thicker than 2.5 inches.

A few tests were made with various proportions of anthracite up to 25 parts by weight to 100 parts of ore. The standard proportions in tests 1 through 3 were 8 parts of anthracite to 100 parts of ore. At that time it was realized that larger percentages gave higher percentages of reduction under the procedure in downdraft-kiln burns. Hence, in tests 4 to 6, 10 parts of included coal was used to 100 parts of ore. In addition, a rather thorough experiment was made in which a proportion of 16 parts of included coal was compared with 8 parts in pigs 10½ inches in diameter and 46 inches high.

ORE SIZING

In the early stages of the project, impure Tahawus magnetite concentrate and impure Clinton hematite ore were employed largely as experimental materials. Under the conditions of the experiments these materials did not bond readily into a tough mass of sponge. Therefore, some work was done on reduction of size-graded masses of ore. Exactly correct size gradations for maximum density were not attempted, as it was thought that commercial practice might never be confronted with this problem. Instead, ore graded as received, ore further reduced by swing hammer mill, and ore that had been ground to minus-200-mesh and/or minus-300-mesh (air-floated) were used in equal parts by weight.

USE OF LIME

In some of the early experiments lime was used with the anthracite contained in the ore mass and in that surrounding it. Five percent of minus-16-mesh limestone also was used. Later, however, no lime was added to contained anthracite, because any calcium sulfate or calcium sulfide produced would be retained in the sponge. At the same time the proportion of lime in the surrounding anthracite was somewhat arbitrarily reduced to 2 parts of hydrated lime by weight to 100 parts of ore.

CHARGING AND UNLOADING CONTAINERS

With suitable equipment, charging can be done economically in the form of pigs, disks, and pipes. As the ore is much heavier than the carbon, this fact must be taken into account in vibrating or transporting filled containers. If the containers are filled in place in ceramic kilns, both the ore and the carbon can be introduced through the holes in the crown of the kiln or be elevated mechanically within the kiln. Filling can be done by means of suitable equipment such as contained sheet-iron forms attached to guides supported at the top of the container and surmounted by receiving funnels. In forming pigs, disks, and pipes ore and carbon can be charged almost simultaneously. Where dense, tough sponge is not objectionable, it is to be expected that commercial operators would resort to wet charging, as it not only eliminates the dust nuisance but also increases the weight per unit volume charged. During unloading, suction for dust removal would seem to be desirable; whether hydrated lime or limestone is used as a sulfur trap in charging, the burnt lime that results on reduction tends to make an unpleasant dust during unloading.

Table 29 gives the analytical results of representative samples of sponge iron made in periodic kilns.

TABLE 29.—*Periodic-kiln sponge-iron analyses, percent*

Sample No.	Total iron	Metallic iron	Reduction	Sulfur	Phosphorus	Silica (SiO_2)	Lime (CaO)	Magnesia (MgO)	Alumina (Al_2O_3)	Titania (TiO_2)	Manganese
58	86. 2	81. 3	94. 3	0. 25	0. 006	--------	--------	--------	--------	--------	--------
150	90. 4	87. 9	97. 2	--------	--------	--------	--------	--------	--------	--------	--------
57	83. 1	80. 9	97. 4	. 72	. 025	--------	--------	--------	--------	--------	--------
218	82. 6	73. 8	89. 3	. 69	--------	--------	--------	--------	--------	--------	--------
220	83. 2	70. 2	84. 4	. 65	--------	--------	--------	--------	--------	--------	--------
54	88. 7	83. 9	94. 6	. 36	--------	--------	--------	--------	--------	--------	--------
110	91. 9	88. 6	96. 4	. 13	. 22	--------	--------	--------	--------	--------	--------
73	88. 9	87. 7	98. 7	. 09	. 024	--------	--------	--------	None	--------	--------
56	87. 2	85. 5	98. 1	. 08	. 03	--------	--------	--------	--------	--------	--------
55	86. 6	85. 2	98. 4	. 12	. 027	--------	--------	--------	--------	--------	--------
52	69. 7	62. 8	90. 1	. 39	. 006	--------	--------	--------	--------	--------	--------
119	64. 2	55. 6	86. 6	. 27	. 012	--------	--------	--------	--------	11. 0	--------
51	69. 3	62. 9	90. 8	. 36	. 008	3. 71	1. 0	0. 90	2. 86	14. 46	--------
245	86. 7	81. 4	93. 9	--------	--------	6. 31	--------	--------	--------	--------	--------
180	57. 8	49. 2	85. 1	. 56	. 89	17. 32	10. 79	4. 16	4. 50	. 23	--------
167	86. 0	82. 3	95. 7	. 10	1. 06	4. 64	--------	--------	2. 52	. 10	0. 801
236–1	67. 7	56. 9	84. 0	. 19	. 107	22. 45	--------	--------	--------	--------	. 090
181	55. 3	49. 5	89. 5	3. 40	. 12	18. 94	--------	--------	5. 33	. 18	. 177
207	95. 3	88. 3	92. 65	. 16	. 006	--------	--------	--------	--------	--------	--------

The degree of reduction of sponge-iron pigs made from Chateaugay magnetite concentrate containing added carbon varied regularly from surface to center of pig and from ends inwardly but did not vary vertically beyond the end effects. This conclusion was based upon two pigs, each 10½ inches in diameter and 46 inches long, and on two carbon contents—8 parts and 16 parts of anthracite to 100 parts of ore. Similar regularity, based upon fewer values, was found for sulfur. It was therefore concluded that samples taken at a transverse plane in the middle of the length of the pig were reasonably representative of the pig as a whole. In pigs containing up to 16 parts of anthracite to 100 parts of magnetite concentrate the degree of reduction decreased from the outside of the pig toward its center. Furthermore, in 8½-inch, pipe-shaped, noncarbon pigs reduction in the outer zone was relatively high, in the intermediate portion it was somewhat lower, and in the region immediately surrounding the pipe, it was relatively high. Samples of pigs and pipes were therefore taken by drilling a series of holes vertically in each direction from the sample plane. Disks were sampled by means of two sections 1 inch wide cut across and through the disk at right angles to each other.

SUMMARY

Sponge iron in formed masses to duplicate the two types made in a ceramic plant at Höganäs, Sweden, can be produced by carbon reduction in a common shale-brick plant without alteration of the plant. Magnetites, hematites, limonites, and other materials containing iron oxide, such as mill scale, can readily be reduced to sponge iron in tunnel kilns or periodic downdraft kilns built to operate at temperatures up to 1,150° C. (2,102° F.).

Iron oxide, with or without admixed carbon, can be reduced to sponge iron, the noncarbon masses reducing at depths of 1¼ inches from the source of carbon. The sponge iron contains virtually no combined carbon, regardless of whether the solid reducing agent is mixed with the ore.

Ten parts of hydrated lime in 100 parts of surrounding anthracite reduces the effect of sulfur to such an extent that little or no sulfur concentrated in the outer portions of the sponge-iron mass, whereas 2 parts and less hydrated lime results in such a concentration of sulfur.

When reducing carbon is mixed with the ore to be reduced, its sulfur content will be largely transferred to the reduced iron. Saggers loaded with all the carbon packed around the iron ore, if lime is mixed with the carbon, can be expected to produce sponge iron of much lower sulfur content, like the Swedish disks, but they require a longer heating period.

REDUCTION IN THE TUNNEL KILN AT BINGHAMTON, N. Y.

The tunnel kiln was of the Harrop design. It was first built for use with natural gas as fuel; later it was changed to an oil-fired and finally, without being redesigned, to a coal-fired kiln shortly before the present project was started. The waste hot gases from the tunnel kiln, largely cooling air, were used for drying clay wares. This tunnel kiln is 44 cars long. The loaded cars pass through the kiln from end to end. When one car was drawn from the kiln every 2 hours, an 88-hour schedule was achieved. That is, during the 88-hour period the load on a given car is first gradually heated to the maximum temperature of the kiln; it is held at this temperature for a definite period as the car advances in the kiln; it is then cooled nearly to room temperature and is ready to be unloaded from the car as it emerges from the kiln.

The tests on sponge iron in the tunnel kiln were made on mixed carlots of ore and the company's regular shale brick and hence were made on the company's regular brick-firing schedule. As became apparent later, the sponge-iron pigs were too large in diameter to be completely reduced during a shale-brick schedule, and many of the charged saggers containing partly reduced material from one firing schedule were repassed through the tunnel kiln.

The sponge iron made in the tunnel kiln was produced from *both carbon-free and carbon-containing masses, charged as slabs* (*2½ inches thick*) *and as 3-, 4-, 4½-, and 5½-inch-diameter pigs* surrounded by coal (usually anthracite) in *4- and 6-inch round and 6½-inch* (*inside dimensions*) *rectangular saggers* (1-inch wall) made of *Mount Jewett semi-fire-clay.*

Table 30 gives the analytical results on a few of the runs made in the tunnel kiln with the following mixtures:

1. Tahawus titaniferous magnetite concentrate mixed with 8 parts by weight of anthracite, charged as a 5-inch-diameter pig.

2A–D. Clinton hematite mixed with 25 parts by weight of bituminous coal, charged as pigs of the following diameters: A, 3-inch; B, 4-inch; C, 6-inch; D, 8-inch.

3A. Mineville magnetite concentrate mixed with 8 parts of anthracite; 3B, same but wetted; both charged as 5½-inch pigs.

4A. Tahawus titaniferous magnetite concentrate mixed with 8 parts of ½-inch anthracite; 4B, same but wetted.

5. Mineville magnetite-concentrate bricks: A, On side of car; B, on top of car; C, preliminary run; D, same as C but passed through tunnel kiln a second time.

6. Tahawus titaniferous magnetite concentrate mixed with 8 parts of anthracite: A, Pig surrounded by ½-inch anthracite; B, surrounded by 5⁄16-inch anthracite (Rice); C, surrounded by minus-4-mesh anthracite.

When brickyard sponge was being produced at Binghamton, the methods of sampling used selected the extremes of variation. These extremes are reflected in the analyses shown in table 30. The composition of the lots of sponge iron sampled varied widely not only from pig to pig but within a single pig. The analyses of table 30 represent a stage in development and do not represent the high uniformity of fully adopted processes either in downdraft or in tunnel kilns.

At the end of this project a test run was made in a muffle-type tunnel kiln of the Hartford Faience Co., Hartford, Conn. Using pipe-shaped pigs, a percentage reduction of 74.7 was obtained, although the kiln was being operated on a 72-hour cycle. The temperature, however, corresponded to cone 10 (2,300° F., 1,260° C.), which is considerably higher than the range of cone 1 (2,057° F., 1,125° C.) to cone 02 (2,003° F., 1,095° C.).

No full carload lots of ore were reduced in the tunnel kiln, because they would have necessitated such radical changes in heat distribution throughout the kiln as to make it unsatisfactory for the company's shale-brick product; moreover, experiments had not progressed sufficiently to warrant production on the tonnage basis for which tunnel kilns are especially adapted.

TABLE 30.—*Analyses of tunnel-kiln sponge iron, percent*

No.	Total iron	Metallic iron	Reduction	Sulfur	Phosphorus	Other
1	67.38	55.34	82.0	0.05	0.01	0.79 V_2O_5.
	67.25	53.67	79.8	.05	Nil	.79
	66.07	53.92	81.5	.07	.04	
2A	57.3	54.7	95.4	----------	----------	
2B	57.2	54.0	94.4	----------	----------	
2C	50.0	49.2	98.4	----------	----------	
2D	54.7	50.0	91.5	----------	----------	
3A	80.1	47.4	59.3	.07	.23	
3B	82.5	55.3	67.0	.10	.22	
4A	65.5	47.4	72.4	.28	.008	
4B	62.8	35.6	56.7	.24	.004	
5A	84.7	74.8	88.3	----------	----------	
5B	70.6	66.3	93.9	----------	----------	
5C	88.7	76.7	86.5	----------	----------	
5D	91.7	87.3	95.2	----------	----------	
6A	68.3	48.2	70.6	.35	.01	0.28 Mn and 0.04 combined carbon.
6B	67.9	50.2	73.9	.36	.01	
6C	67.1	52.4	78.1	.35	.01	

COMMERCIAL-SCALE EXPERIMENTAL PRODUCTION OF SPONGE IRON AT CANTON, OHIO

The data obtained in the investigations conducted at East Sparta, Ohio, and at Binghamton, N. Y., formed the basis for commercial-scale experimental production of sponge iron. Since the market for sponge iron was then virtually nonexistent, it was planned to produce enough sponge iron to supply certain producers of steels for tests to determine the value of domestic sponge iron as melting stock.

On October 4, 1943, the contract was signed for experimental commercial production of sponge iron, known as project 963, at Canton, Ohio. Laboratory-scale tests were continued at College Park, Md., as an integral part of the large-scale tests at Canton.

The project was prematurely concluded by a fire on August 4, 1944, that destroyed the shed, tools, mechanical equipment, and 1,500 saggers.

SELECTION OF SITE FOR PROJECT

The plant of the Stark Brick Co., Canton, Ohio, was selected as the site of this sponge-iron project. The company was financially sound, its plant was well-maintained, its kilns were suitable for any desired range of firing temperatures, and the personnel was progressive and capable of working out technical and production problems. Nearly all the equipment necessary for manufacturing sponge iron was available at the plant. The plant was on the main line of the Wheeling & Lake Erie Railroad and was near the source of all the materials needed in the manufacture of sponge iron as well as near the steel plants where the sponge iron was to be tested.

SAGGERS

The saggers used in this project were 8- by 8-inch columns (inside dimensions) 24 inches high, with ¾-inch walls. To expedite getting the project under way, 2,500 flue liners were purchased. They were made from an Ohio buff-burning shale that became very brittle after one firing and could not be re-used. Near the fireboxes, where the heat was around 1,250° C., these flue liners softened, and some failed completely.

A die for extruding hollow clay columns and another for extruding solid clay ends, 2 inches thick by 11 inches wide, were made in the plant machine shop and installed in the 16-inch Riddell, horizontal, de-aired brick machine.

A mixture of 40 percent minus-8-mesh grog and 60 percent by weight of ground upper stratum of the local fire clay was extruded through the 8- by 8-inch die and cut in 24-inch lengths. These square hollow tiles were then placed on drier cars. The die was then changed to 2- by 11-inch size, and a column was extruded and cut in 11-inch lengths. These lengths were pressed into flat, cup-shaped slabs to fit the ends of the square columns.

To seal the ends to the square columns to form saggers, an unfired slab was placed on the floor of the kiln, cupped side up, and leveled with clean white sand. High-temperature cement was spread around the edge of the slab, and the square column was placed on top. Another slab was placed on top of the column, cupped side up, and the operation repeated until the stack was as high as the kiln would permit. The preliminary firing not only baked the clay and grog mixture but also fused the bottom slab to the column, forming a sagger with a gastight bottom. Early attempts to stick the bottoms to the hollow columns immediately after they were extruded and while in a soft, plastic state, by green welding with a heavy clay slip, met with failure.

The general idea at first was that a sagger must be free from cracks and in virtually perfect condition, with a smooth, square, upper edge so that, as each sagger was placed on top of the one below, in building up a bung, the bottom of the top sagger would serve as a cap for the sagger underneath. Repeated tests showed that, even with a gap as much as ½ inch showing around the top edge of the sagger, reduction was above 95 percent and the sulfur content was below 0.02 percent. This fact permitted the use of saggers that otherwise would have been discarded and refuted the previous premise that the sagger top must be virtually gastight. Gas formed by reduction of iron ore must have an avenue of escape.

The first batches of saggers were made from the best grade of local clay and stood firing very well. Later, this type of clay was not available, and a run-of-mine clay was substituted. The result, while fair, was not as good as the original mix, and the average life of saggers was shortened materially. However, there were enough saggers from the original mix to last until the end of the project, thus giving some data for life tests.

At project 981, Salisbury, N. C., some standard 8- by 8- by 24-inch flue liners made from 80 percent raw North Carolina pyrophillite and 20 percent Missouri plastic bond clay were purchased from the Pomona Brick & Tile Co., of Pomona, N. C. These flue liners have stood repeated firings on a fast schedule through the tunnel kiln at that project and have proved superior to any other saggers tried to date. It is recommended that such a mix be thoroughly investigated.

Since a period of approximately 2 weeks is required to complete a sponge-iron periodic-kiln cycle, there were not enough firings during the term of this project to give the complete life story of the saggers in use. It is believed that the better grades of Ohio fire clays (such as those mined in the Oak Hill district), blended with at least 20 percent of a more refractory clay, will serve very well as sponge-iron saggers.

A square sagger is more efficient than a round sagger for producing rectangular pigs[70] of sponge iron. It is also more easily made, as a square column will pass through a standard brick-and-tile, off-bearing extrusion assembly without the necessity of altering the assembly. A round column requires a special off-bearing assembly with rounded cradles to hold the column in shape while it is being cut into proper lengths. Comparative life tests of square and round saggers have not been made.

Can Charging of Saggers.—In using the method of can charging developed by the Bureau of Mines at College Park, Md., approximately 3 inches of reducing mixture was placed in the bottom of each sagger. Two 2- by 6- by 28-inch rectangular, bottomless, 22-gage, sheet-iron cans were then placed side by side in the sagger with about ¾-inch space between them and about 1-inch space around the sides next to the sagger. Figure 27 shows the charging operation. Ore was fed through a flexible hose from the ore bin into the canisters, while reducing mixture was fed through another flexible hose from the mixture bin into the space surrounding the canisters. The cans were then withdrawn, leaving two rectangular columns of ore surrounded by reducing mixture. This method was used with variations as to thickness of columns and bottom and top layers of reducing agent.

All raw materials were shipped in open gondolas and were naturally very moist when they arrived at the project. As they had to be dried to permit flow through the charging apparatus and to prevent sticking to the charging

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[70] The term "pig" is used throughout this report to designate a coherent mass of sponge iron and was suggested by operators of open-hearth furnaces.

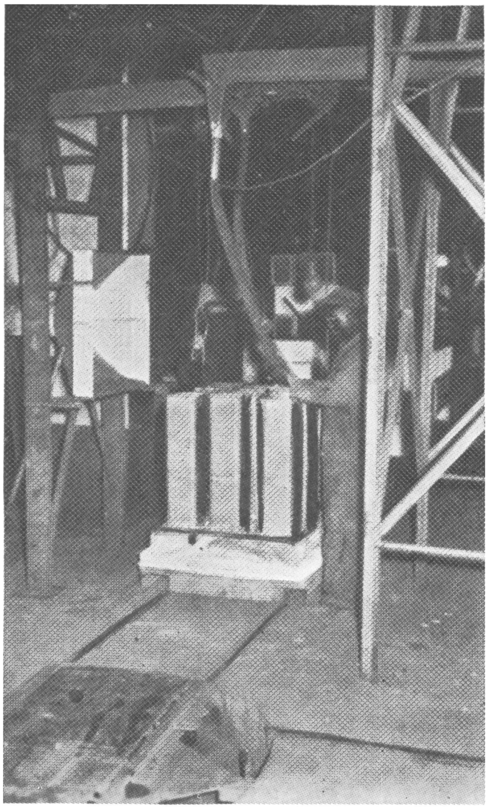

FIGURE 27.—SAGGER-CHARGING OPERATION: ORE CONCENTRATE IS BEING FED INTO CANISTER THROUGH FLEXIBLE RUBBER HOSE AT LEFT; REDUCING MIXTURE IS BEING FED THROUGH HOSE AT RIGHT; DUST IS REMOVED BY MEANS OF HOOD SHOWN AT LEFT.

cans, a homemade rotary drier was built, making use of a piece of 16-inch by 20-foot secondhand pipe, discarded drier car wheels, and a second-hand set of sprockets and chain. This contrivance was mounted in a furnace, and external heat was applied to the drum of the drier by three hand-fired, coal-burning fireboxes.

All the magnetite ores were fine enough to pass a 6-mesh screen, but the hematite ores had to be ground before use. A dry pan with ¼-inch slots was used for this purpose. It handled the moist hematite very well and ground it at the rate of 3 to 4 tons an hour. This ore had to be trucked from an outdoor stockpile to the grinder and then returned to the rotary drier.

The anthracite and limestone were hand-loaded into the drier, which mixed the two materials as it dried them. The mixture was then conveyed up into one of the overhead steel bins. The ore or ores were likewise put through the same rotary drier and elevated into a second overhead bin.

EXTRUSION OF IRON ORES

Charging iron ore into saggers in the form of vertical slabs suggested the idea that ores could be extruded through a standard brick machine.

After some preliminary trials in a small 3-inch machine at the Eastern Experiment Station, College Park, Md., further experiments were conducted with the help of research engineer William Ramsey, of the Stark Brick Co., in its laboratory, using a 4-inch, deaired machine designed and built by the Stark Brick Co. The maximum-size die for this machine was 2¼ by 1⅜ inches, inside dimensions. When 1.5 percent of bentonite was used as a plasticizing agent, not only Mahoning hematite but also magnetite that had been screened to minus-20-mesh and finer could be extruded. The resulting sponge iron produced from these 2¼- by 1⅜- by 12-inch extrusions showed a density ranging from 1.39 for Mahoning hematite to 4.42 for magnetite.

These results were so promising that a full-scale run through a 16-inch-diameter Riddell brick machine was tried.

Mahoning hematite, containing 1.5 percent added bentonite, extruded very well. Three columns of different cross-sectional size were extruded successfully—5½- by 6½-inch, 6½- by 7-inch (fig. 28), and 2¼- by 7-inch. A mixture of 50:50 Mahoning hematite and Mineville magnetite also extruded very well. Straight magnetite was not tried, as there was not enough magnetite left to continue experiments. This extrusion was so successful that the last two kilns of sponge iron produced were loaded with nothing but extruded ores, and can charging was eliminated. The capacity of the large machine loaded with 6½- by 7- by 20-inch extruded pigs (fig. 29) was approximately 30 tons an hour.

KILN FIRING

After loading the kiln, which held approximately 2,200 saggers, the fires were lighted, and the temperature was raised as rapidly as possible, without damaging the refractories, to approximately 1,100° C. (2,010° F.). This process required 60 to 70 hours, depending on the kiln and local atmospheric conditions. The temperature was held within the range of 1,100° C. (2,010° F.) to 1,150° C. (2,110° F.) for a minimum of 40 hours (in some tests, as long as 60 hours) to equalize the temperature from the top to the bottom of the kiln and to allow enough time to complete the reduction. According to Ross[71] and Walker,[72] this reduc-

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[71] Ross, Donald W., Production of Sponge Iron in a Shale-Brick Plant: Bureau of Mines Rept. of Investigations 3822, 1945, 27 pp.

[72] Walker, J. P., Reduction of Iron Ore in Clay and Steel Containers (Saggers): Bureau of Mines Rept. of Investigations 3819, 1945, 30 pp.

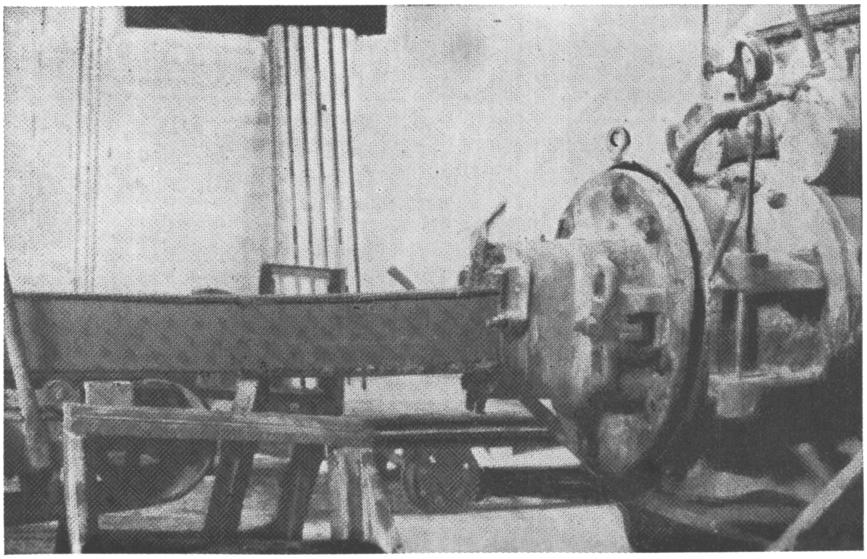

FIGURE 28.—EXTRUSION OF MAHONING HEMATITE THROUGH BRICK MACHINE; SIZE OF COLUMN EXTRUDED, 6½ BY 7 INCHES.

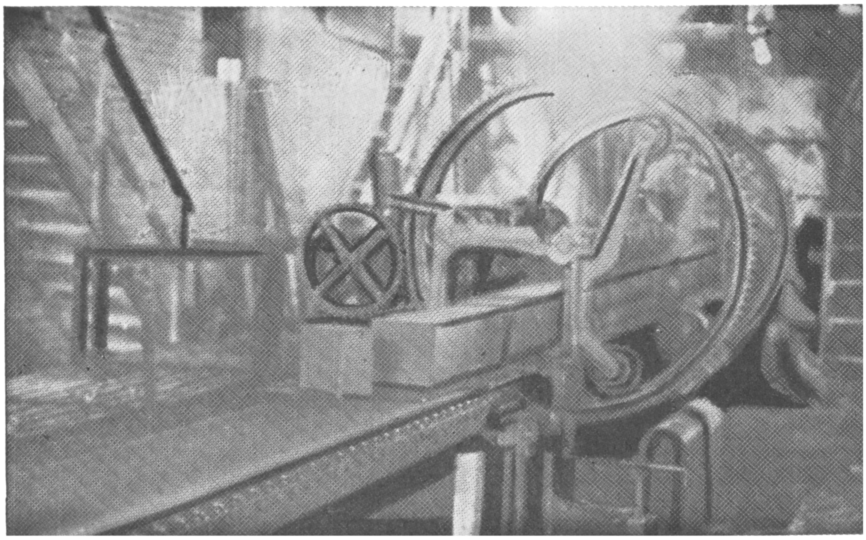

FIGURE 29.—VIEW SHOWING 6½- BY 7-INCH EXTRUDED COLUMN BEING CUT TO PROPER LENGTH BY STANDARD BRICK-CUTTING ASSEMBLY.

tion cycle is complete when the temperature in the center of the core mass equals the temperature outside the sagger. The cross-sectional size of the sagger and the thickness of the ore body being reduced governs this time cycle. For the type and size of saggers and ore charges used in this project the time cycle was fixed as the minimum required to complete the reaction.

At the conclusion of the burn the fireboxes and ashpits were closed with steel plates and luted tightly with fire clay, and the stack damper was closed to reduce to the minimum reoxidation of the sponge iron from passage of air through the kiln. When the kiln temperature had dropped to approximately 500° C. (932° F.), the stack damper was opened, and the stack suction was allowed to pull air through the kiln. At 350° C. (662° F.) the fireboxes were opened, and the kiln doors were partly opened; at 200° C. (392° F.) the doors were opened wide, the crown damper was opened, and a suction fan was placed in the door to pull air through the kiln. Five to six days was required to safely cool the kiln to atmospheric temperature.

The kiln was unloaded with the kiln crane, eight saggers being placed on a skid and the skid picked up by a lift truck and carried to the unloading station. Here the saggers were dumped, at first by hand and then by a mechanical device.

REDUCING AGENTS

Buckwheat No. 5 anthracite was chosen as the most economical and most efficient reducing agent for this particular area.

Experiments at College Park, Md., showed that anthracite or noncoking bituminous coal, coke, or coke breeze may be used for reducing iron ore to sponge iron. High-sulfur coals did not impart their sulfur to the sponge iron when properly admixed with limestone. Tests were made to determine the effect of particle size of reducing agents on the reduction of iron ores. Two sizes of reducing agents were used—minus-6-mesh and minus-20-mesh run-of-crusher. In a 4-hour heating period the 20-mesh reducer gave approximately 60-percent reduction, while the 6-mesh gave approximately 45 percent. As the heating periods were increased to 8, 12, and 16 hours, reduction for the two particle sizes approached each other in regular curves. At 16 hours these curves crossed, and at 20 hours the 20-mesh reducer gave approximately 92-percent reduction while the 6-mesh gave approximately 94 percent.

Apparently, the finer reducing agent is more active; but as the reduction period progresses, ash and the mass settle readily into the voids and retard circulation of the reducing gases.

DESULFURIZING AGENTS

Experimental work at College Park, Md., proved that finely ground limestone is the most efficient and most economical desulfurizing agent of all materials tested for brickkiln sponge iron. The limestone decomposes gradually throughout the reduction period, and the carbon dioxide evolved aids the circulation of reducing gases and reacts with the hot reducer to form more carbon monoxide. It was found that for a 24-hour reduction period 20 percent limestone with 80 percent reducer was the most efficient desulfurizing mixture; but for the longer periods used at Canton 15 percent limestone was found to be equally efficient. The sponge iron produced at Canton with 15 percent limestone and 85 percent reducer contained less than 0.02 percent sulfur.

Dolomitic limestone was found to act as an efficient desulfurizing agent, but reduction of iron oxide was slightly lower, probably because the dolomitic limestone decomposed at a temperature too low for the carbon dioxide evolved to react with the reducer and form carbon monoxide. Limestone decomposes slowly at a temperature higher than dolomite, and at the end of a 24-hour reduction period about 25 percent of the limestone remains undecomposed.

The cost of limestone analyzing over 90 percent $CaCO_3$ was $3.60 a ton delivered. If all of the carbon dioxide evolved from the complete decomposition of 100 percent limestone reacts with the hot reducer to form carbon monoxide, a ton of limestone would be equivalent to 302 pounds of anthracite (valued at approximately $1.11) of the grade used at this project.

One test kiln was charged with Scrub Oak magnetite with a reducing mixture consisting of 90 percent minus-8-mesh anthracite and 10 percent lime hydrate. The sponge iron from this kiln contained 0.047 to 0.085 percent sulfur.

USE AND RECOVERY OF USED REDUCER

Experiments at College Park, Md., showed that, when minus-6-mesh run-of-crusher anthracite was used as reducer, the unburned coal remaining in the sagger after the reduction of ore to sponge iron may be recovered by passing it over a 28-mesh screen. Most of the minus-28-mesh coal was consumed in the firing, as less than 1 percent passed through the screen although 15 percent of the unused coal was minus-28-mesh. When recovered coal was used as a reducer, with various percentages of limestone, the percentage of reduction was higher and the percentage of sulfur in the resulting sponge iron was lower, as shown in table 31.

Analyses of the unused and recovered reducer are shown in table 32.

The equipment necessary for recovering used reducer was not available at Canton; however, tests were made in which the used reducer was re-used without screening. In some tests the reducer was used coal, and in others it was a mixture of equal parts of used and unused coal.

TABLE 31.—*Effect of limestone in the charge on the sulfur in the resulting sponge iron*

Sample No.	Reduction, percent		Limestone used, percent	Sulfur, percent
	Unused coal	Recovered coal		
4180	95.0		5	0.057
4181	95.0		10	.041
4183	96.2		20	.014
4266		96.0	5	.009
4267		96.0	10	.008
4268		95.3	20	.008

TABLE 32.—*Analysis of unused reducer recovered after reduction of ore to sponge iron, percent*

	Moisture and volatile matter	Ash	Fixed carbon	Total sulfur
Unused coal	6. 64	17. 6	75. 8	1. 23
Recovered coal	. 81	25. 2	74. 0	1. 22

When all used reducer with 15 percent added limestone was employed, analysis of the resulting sponge iron showed 94.4-percent reduction and 0.005 to 0.007 percent sulfur. Analysis of the sponge iron reduced with a mixture of used and unused reducer with 15 percent added limestone showed 92.8- to 97.9-percent reduction and 0.007 to 0.019 percent sulfur. These tests merely indicate that the carbon in the used reducer is active and that the sulfur is fixed; re-use of reducer containing spent limestone and ash is not economical because of its bulkiness and the heat capacity of the inert materials.

SAGGERLESS SPONGE-IRON EXPERIMENTS

Saggerless sponge-iron tests were made in a 10-foot-diameter, semicommercial kiln having a single transverse flue, the remainder of the floor being solid.

Over this central flue, flue liners were placed vertically to allow passage of heat from the fireboxes. A 2-inch layer of a reducing mixture consisting of 85 percent No. 5 Buckwheat anthracite and 15 percent limestone was spread over the floor. A layer of extruded Mahoning hematite pigs measuring 5⅝ by 6⅝ by 24 inches was laid edgewise, with approximately 1½-inch space between each pig. This space was packed with reducer, and approximately a 1½-inch layer of reducer was spread over the top. In this manner four layers were built up, representing 6 tons of ore. (In saggers this kiln capacity was only 2 tons.) The top layer was covered with reducer 4 inches deep, and over this was spread an additional 2 to 3 inches of used reducer as a protective blanket. On this layer were placed two courses of firebrick splits laid flat as an additional protection.

The kiln was fired according to the following schedule:

0 to 84 hours to reach 1,120° C. (2,050° F.).
84 to 132 hours at 1,120° C. (2,050° F.).

It was planned to hold the heat for at least an additional 48 hours, but the research engineer for the Stark Brick Co. feared that the gases generated in the mass would explode and insisted that the firing be stopped.

Approximately 120 hours was allowed for cooling before the kiln was opened, but the mass was still too hot for removal and required 3 more days to reach atmospheric temperature. The results showed an average of only 6-percent reduction, but the Mahoning hematite had been reduced to magnetite.

The kiln, from which only one sample had been drawn, was refired according to the following schedule:

0 to 48 hours to reach 1,120° C. (2,050° F.).
48 to 126 hours at 1,120° C. (2,050° F.) to 1,160° C. (2,110° F.).

Analysis of the resulting sponge iron follows:

TABLE 33.—*Analyses of samples of sponge iron from the refired run, percent*

Sample No.	Total Fe	Metallic Fe	Reduction	S (evolved)
4644	79. 4	50. 3	63. 3	0. 007
4645	82. 6	63. 8	77. 2	. 006
4646	84. 3	68. 4	81. 0	. 007
4647	84. 0	68. 0	81. 0	. 007
4648	75. 3	32. 4	43. 0	. 006
4649	69. 5	23. 7	34. 1	. 001

The sulfur was expected to run exceptionally high in this particular test, but the analytical results showed only 0.001 to 0.007 percent. The percentage of reduction ranged from 34.1 to 81.0 percent.

Another experiment was tried in a large sponge-iron-kiln fire. A 2- by 2-foot area on the kiln floor was blocked off, and four walls of hollow tile were built up with vertically set flues to allow heat flow down from the top into the floor flues. These hollow tiles were standard 10-cell 4- by 8- by 12-inch building tiles. The bottom of this walled-off area was then covered with approximately 3 inches of reducing agent. Two columns of extruded Mahoning hematite pigs measuring 6½ by 7 by 20 inches were stacked on edge, five high, with roughly 1-inch clearance between the stacked pigs and the inner walls. Another stack of extruded hematite pigs measuring 2 by 7 by 20 inches was piled on edge between the stack of larger pigs, with approximately 1- to 1½-inch clearance between these and the outer stacks of larger pigs. All the vertical space was packed with reducing mixture. One-half to 1 inch of reducer was spread over each layer, and approximately 4 inches of reducer was spread over the top; the whole mass was covered with fire-clay slabs.

The kiln was fired according to the following schedule:

69 hours to reach 1,093° C. (2,000° F.).
51 hours at 1,093° C. (2,000° F.) to 1,171° C. (2,140° F.).
51 hours to cool.

Analysis of a 2¼- by 6½-inch pig taken from near the hollow-tile wall showed 43.3-percent reduction and 0.011 percent evolved sulfur. In a similar position a 6½- by 7-inch pig showed lower reduction owing to the larger cross section—32.4-percent reduction and 0.011 percent evolved sulfur. In the center reduction ranged from 1.0 to 5.8 percent and the sulfur from 0.014 to 0.003 percent.

Insufficient reducing agent was used in this test, as was evinced when the kiln was opened. Nearly three-fourths of the ore was left exposed and was poorly covered by the residual ash and limestone. Evidently the iron reoxidized excessively owing to lack of tight enough setting of the walls.

This experiment should be tested further, using 2½- by 7- by 24-inch pigs (thinner cross section), greater interspacing between the layers, a kiln with more flues evenly distributed over the floor, and vertical flues spaced more closely. Elimination of saggers greatly increases kiln capacity, representing 2.5 tons of sagger sponge iron versus 6 tons by this method. However, this 6-ton load would be reduced somewhat by increase in the flue areas and reducing agent, but any difference could be offset by stacking the charge higher. Termination of the project stopped further investigation.

To produce 45 tons of sponge iron it is necessary to heat to 1,100° C. and hold at this temperature 2,400 saggers weighing 69 pounds each, or a total of 84.3 tons. Moreover, only 60 percent of the kiln volume is utilized.

REDUCTION OF CAN-CHARGED v. EXTRUDED ORE MASSES

At the beginning of the project the size of the pigs was heldat 2 by 2 by 16 inches. As the project progressed, the length of the pigs was increased from 16 to 18 inches and finally to 20 inches and the ore charge per sagger from two 16-pound to two 20-pound charges and finally to two 24-pound charges. The thickness of the reducing agent placed in the bottom of the sagger was changed from 4 inches to 1 inch; and the top or protecting reducer layer was reduced from 4 to 2 inches; the resulting percentage of reduction remained as high as at the beginning of the tests.

The cross-sectional area was then increased, first by increasing the width from 6 to 6¾ inches (the percentage of reduction remaining as high as at first) and then by increasing the thickness from 2 to 2¼ inches and finally to 2½ inches.

It was found that, with magnetite ground to pass 8-mesh (at least 50 percent passing 100-mesh), the charging cans for an 8- by 8- by 24-inch (inside dimensions) sagger should measure 2¼ by 6¾ inches and the height of the ore column 19 inches. The bottom bed of reducer was 2 inches thick, and the top layer was 3 inches. These dimensions left a space of ¾ inch between the vertical ore slabs and 1¼ to 1⅜ inches of reducer surrounding the slabs next to the sagger walls. The charge per sagger was approximately 0.1 pound of ore per cubic inch, and the two ore columns measuring 2¼ by 6¾ by 19 inches (288.6 cubic inches) weighed 28.86 pounds per slab of 57.72 pounds of dry ore per container. A charge of this size included approximately 40 pounds of reducing agent consisting of 85 percent Buckwheat No. 5 anthracite and 15 percent crushed limestone.

Mill scale ground to pass 4-mesh charged in 2½- by 7- by 19-inch vertical columns weighed 35 pounds per slab or 70 pounds per sagger and with 37 pounds of reducing agent showed 97.1- to 99.8-percent reduction.

Cranberry, N. C., magnetite concentrate, ground to pass 65-mesh, charged in 2½- by 7- by 19-inch vertical columns with the standard reducing agent mentioned showed 98.4-percent reduction. This ore, charged in 2- by 6½- by 19-inch vertical columns with the same reducing agent showed 100.0-percent reduction. In both instances, the sulfur content was 0.017 percent.

A mixture of minus-8-mesh Scrub Oak magnetite and Mahoning hematite, blended in the ratio of 50:50 by volume or 60:40 by weight, showed a reduction of 96.5 to 99.3 percent when charged in vertical slabs measuring 2½ by 7 by 19 inches.

Aside from the large 6½- by 7-inch extruded ore columns from which are made partly reduced sponge iron for the Great Lakes Steel Corp., the only columns approaching the sizes of the can charges were made with a 2¼- by 6½-inch die.

A test on this size of extruded ore was made in which 5½ tons of dry-pan Mahoning ore ground to minus-4-mesh yielded 270 pigs 20 inches long, weighing 40 pounds each. One percent of bentonite was used as a plasticizing and binding agent. A second run was made in which 729 2¼- by 6½- by 20-inch pigs were made from 2 parts of Mahoning hematite and 1 part of Mineville magnetite by volume admixed with 1 percent bentonite as a plasticizing and binding agent. These pigs weighed approximately 42 pounds each owing to the use of the heavier magnetite.

The extruded pigs from both runs were air-dried for 24 hours but were still somewhat moist. These moist pigs were placed vertically in the saggers in the same position as the can-charged columns. As the fire had destroyed the drying equipment, moist reducing agent from the outdoor stockpile had to be used. Consequently, it could not be poured into the saggers, and being more bulky its total weight was lower than it otherwise would have been.

TABLE 34.—*Effect of lower carbon content of the charge on reduction of the resulting sponge iron*

Sample No.	Total Fe, percent	Metallic Fe, percent	Reduction, percent	S (evolved), percent
4762	80.8	56.8	70.3	0.062
4763	72.8	41.5	57.0	.073
4764	87.5	82.8	94.6	.012
4765	87.0	75.8	87.1	.027
4766	87.3	79.5	91.1	.036
4767	86.0	67.5	78.5	.046
4768	85.5	68.8	80.5	.026

Only 30 pounds of reducing agent per sagger, instead of the usual 37 pounds, could be tamped around the ore columns. This weight of reducing agent, coupled with the fact that 80 pounds of extruded hematite ore per sagger was charged instead of the usual 57 pounds, yielded a poorly reduced product, as shown in table 34.

Theoretically, the charge contained much more carbon than was needed to complete the reduction, but past experience has shown that, to have enough carbon to reduce the ore completely in the minimum time and to prevent the sponge iron from oxidizing during cooling, approximately 37 pounds of reducing agent must be used to 57 pounds of magnetite or 40 pounds of reducing agent to 50 pounds of hematite; the higher oxygen content of the hematite requires more carbon.

A small run was tried, using 1 part of Mineville magnetite to 2 parts of Mahoning hematite by volume or 40 percent of magnetite to 60 percent of hematite by weight. These pigs weighed 42 pounds each or 84 pounds per sagger; 30 pounds of moist reducing agent could be tamped around the columns. In this test the magnetite required less carbon, and higher reduction was obtained, as shown in table 35.

This particular blend made the best grade of sponge iron, with respect to percentage of reduction and low sulfur content, produced at the project.

TABLE 35.—*Higher ratio of carbon to oxygen in charge results in higher reduction to metal*

Sample No.	Total Fe, percent	Metallic Fe, percent	Reduction, percent	S (evolved), percent
4769	90.3	89.5	99.1	0.013
4770	90.3	88.8	98.3	.015

SPONGE IRON PRODUCED FROM VARIOUS ORES

Sponge iron was produced from:

Scrub Oak, N. J., magnetite concentrate.
Mahoning, Minn., hematite.
Sterling high-phosphorus hematite.
Tahawus, N. Y., high-titanium magnetite concentrate.
Mineville, N. Y., magnetite concentrate.
Mill scale.

It was also produced from the following mixtures:

Mahoning hematite and Tahawus magnetite, 1:4.
Mineville magnetite and Mahoning hematite, 1:2.
Chateaugay magnetite and Mahoning hematite, 1:1.
Mill scale and Mahoning hematite, 3:3.
Mill scale and Scrub Oak magnetite, 1:1.

Analyses of various iron oxide materials and of the sponge iron produced from them are shown in table 36 (p. 87).

Scrub Oak Magnetite Concentrate.—In all, 197 tons of Scrub Oak magnetite concentrate was converted to sponge iron in 2- by 6½- by 18-inch pigs.

Mahoning Hematite.—A total of 390 tons of this ore was reduced to sponge iron. Enough ore was used to produce approximately 10 tons of a pure hematite sponge iron, while the remainder was blended with other ores to produce more coherent pigs. The pure ore was extruded, dried, and then charged in the saggers. When hematite is reduced to sponge iron, a large shrinkage in volume occurs, and the resulting sponge iron has approximately the same bulk density (3.5) as the original mass. The sponge-iron pigs contain numerous cracks that are hard to free of all spent mixture.

Sterling (High-Phosphorus) Hematite.—Approximately 7 tons of this ore was reduced to sponge iron in special shapes to be used for the production of wrought iron direct from sponge-iron pigs.

Special charging cans, cross sections of which measured 1 by 4 inches and 1 by 6 inches, were made to form sponge-iron pigs of the same cross-sectional dimensions. Four of these 1- by 4- by 18-inch and 1- by 6- by 18-inch pigs were charged into standard 8- by 8- by 24-inch saggers, allowing 2 inches for a bottom bed, 4 inches for a topping cover, and approximately 1 inch between each vertical pig and around the inner wall of the sagger of standard reducing agent. With a regular kiln load, the charge was fired 100 hours to bring it to 1,093° C. (2,000° F.) and was held at 1,099° C. (2,010°F.) to 1,149° C. (2,100° F.) for 42 hours. Inspection of both sizes of pigs showed that a 1-inch cross-sectional thickness was too thin to be entirely self-supporting. The pigs buckled during firing and quite frequently stuck together.

Tahawus (High-Titanium) Magnetite Concentrate.—Approximately 30 tons of this ore was received from project 925 at Binghamton, N. Y. Several pigs of sponge iron were produced from the pure ore to be used in melting tests conducted at College Park, Md.

Sponge iron produced from Tahawus magnetite is very friable, and tests were made at College Park to find methods for producing coherent pigs. Blending 1 part of Mahoning hematite with 4 parts of Tahawus magnetite by volume gave coherent sponge-iron pigs. The remainder of the ore, blended with Mahoning hematite, was reduced to 2- by 6½- by 19-inch sponge-iron pigs.

Mineville Magnetite Concentrate.—Approximately 15 tons of this ore was received from project 925 at Binghamton, N. Y. A small quantity of the pure ore was reduced to sponge iron in 2- by 6½- by 19-inch pigs to observe its physical characteristics. The sponge iron, which was approximately 97 percent reduced, was coherent and otherwise of excellent quality. As this ore was high in phosphorus and somewhat low in iron, it was blended with Mahoning hematite in the proportion of 1 part of magnetite to 2 parts of hematite. The physical characteristics of the sponge iron produced were excellent, but the phosphorus was still too high to produce steel except by a basic open-hearth method.

Chateaugay Magnetite Concentrate.—Approximately 20 tons of this ore was received from project 925 at Binghamton, N. Y. It was low in total iron and was blended with Mahoning hematite in the proportion of 1 part of magnetite to 1 part of hematite by volume.

Mill Scale.—A local steel plant gave the project 106 tons of mill scale in exchange for sponge iron. The bulk of the sponge iron produced here was made from mill scale used alone or blended with other ores. The mill scale was of high purity and when ground to pass 8-mesh produced an excellent chemical and physical grade of sponge iron. When the mill scale was blended with other ores available to this project, it raised the total iron content and produced a denser and more coherent sponge iron.

SPECIAL SPONGE IRON FOR THE GREAT LAKES STEEL CORP., DETROIT, MICH.

The Great Lakes Steel Corp. asked the Bureau of Mines[73] to prepare a special sponge iron for experimental use in open-hearth steel production. The corporation specified a sponge-iron pig 6 to 7 inches in cross section and 4 to 24 inches long; the center of the sponge-iron shell was to be unreduced, and the reduction was not to exceed 50 percent.

A preliminary can charge, using a form 7 by 7 inches square in which ¼-inch-mesh Mahoning hematite was charged, gave the following data:

The size of sponge-iron pig was 7 by 7 by 19 inches.

A center-cut cross section, which was very difficult to saw because the outer crust was so well metallized, showed a shell of sponge iron surrounding an unreduced core. This sponge-iron shell was approximately 1 inch thick at the sides, while at the corners where reduction had penetrated from two directions it was rounded and was 1¼ to 1¾ inches thick. Chemical analysis showed approximately 50.0-percent reduction.

The Great Lakes Steel Corp., however, felt that it would rather have a thinner shell of sponge iron and a higher percentage of unreduced center. A 6½- by 7-inch column of Mahoning hematite was extruded successfully and cut into 21-inch lengths. These extruded pigs, each weighing 115 pounds as compared to 83 pounds for 7- by 7- by 20-inch can-charged pigs, were lowered by a hand-operated block and tackle into 8- by 8-inch rectangular saggers in which 1½ inches of reducing agent had first been placed in the bottom. The space between the extruded pig and the sagger walls, which ranged from ½ to ¾ inch, was filled and hand-rammed with a wet, stockpiled standard reducing agent, the only one available. The whole was then filled with approximately 1½ inches of reducing agent, and the loaded saggers were shoved into the kiln on a roller-type conveyor and stacked four high. No mechanical equipment was available for this work, as it had been destroyed by fire.

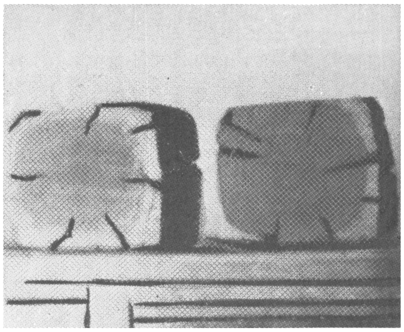

FIGURE 30.—PARTLY REDUCED SPONGE IRON PRODUCED FOR GREAT LAKES STEEL CORP., DETROIT.

In all, 110 tons of Mahoning hematite, including 71 tons donated by the Great Lakes Steel Corp., was converted to 85 tons of this special form of sponge iron.

The sponge-iron shell surrounding the partly reduced core ranged in thickness from ⅙ to ½ inch at the sides and from 1 to 1⅛ inches at the corners at the center cross section (fig. 30). A representative analysis of this shipment showed 22.9-percent reduction; no other determinations were made.

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[73] Through Alexander A. Dow, senior industrial engineer, acting as contact man between the iron and steel industry and the Bureau of Mines.

TABLE 36.—*Analyses of various iron oxide materials and of the sponge iron produced from them*

Iron oxide material	Analysis of iron oxide material, percent								Analysis of sponge iron, percent										
	Fe	SiO_2	S	Al_2O_3	CaO	MgO	P	TiO_2	Iron		Reduction	SiO_2	S	Al_2O_3	CaO	MgO	P	TiO_2
									Total	Metal								
Scrub Oak magnetite concentrate	66.90	5.71	0.004	1.05	0.10	0.13	0.008	------	87.80	84.00	95.70	7.54	0.01	1.10	0.00	0.51	0.017	0.70
Mahoning hematite	62.40	4.11	.004	1.35	.11	.20	.049	------	87.3	79.1	90.6	5.75	.025	1.89	.15	.28	.051	.056
Sterling high-phosphorus hematite	55.13	5.45	.076	1.64	.19	.30	.399	------	82.6	81.6	98.8	8.44	.009	2.55	.30	.47	.500	------
Tahawus magnetite concentrate	55.87	4.75	.270	4.26	.70	1.64	.007	10.22	71.8	70.8	98.6	3.83	.250	4.98	------	5.03	.009	12.70
Blended ore	57.18	4.62	.220	3.67	.58	1.35	.015	8.18	78.6	73.2	93.2	3.04	.078	4.25	.10	.43	------	10.92
Mineville magnetite concentrate	67.89	2.67	.020	.79	.18	.58	.220	.79	89.1	86.1	96.7	2.46	.015	------	------	------	.170	------
Chateaugay magnetite concentrate	65.70	4.18	.080	4.32	.00	.00	.010	.75	85.5	83.5	92.7	2.59	.031	------	------	------	.039	------
Mill scale	71.00	1.32	.270	------	------	------	------	------	91.4	89.0	97.4	------	020	------	------	------	------	------
Mill scale, 60, and Mahoning hematite, 40 parts by volume	------	------	------	------	------	------	------	------	90.0	89.4	98.3	------	.020	------	------	------	------	------
Mill scale, 50, and Scrub Oak concentrate, 50 parts by volume	------	------	------	------	------	------	------	------	91.2	88.5	97.0	------	.015	------	------	------	------	------

Total Tonnage of Sponge Iron Produced.—A total of 468 tons of sponge iron was produced and shipped. This included 85 tons of partly reduced sponge iron for Great Lakes Steel Corp. and 42 tons stored at Pittsburgh, set aside for Bureau of Mines melting tests; the remainder was consigned to various steel and wrought-iron companies. Analyses of the iron oxide materials and of the sponge irons produced from them are shown in table 36.

Fire Damage.—On August 4, 1944, fire destroyed the building used for housing all Bureau of Mines equipment used at the project. All mechanical equipment was completely destroyed, and of 3,500 saggers only 2,000 were salvaged. Fortunately, 86 tons of sponge iron awaiting shipment was only slightly damaged. On account of this fire it was necessary to end the project before all commitments for sponge iron had been filled.

LARGE TUNNEL KILN, SALISBURY, N. C.

The Isenhour Brick & Tile Co., Salisbury, N. C., signed a cooperative agreement with the Bureau of Mines whereby a tunnel kiln and accessories were made available for investigating the manufacture of sponge iron in tunnel kilns. The 29-car kiln, made by the Allied Engineering Co., is 200 feet long, 56 inches wide, and 60 inches high; the cars are 49 inches wide at the top and 84 inches long. The kiln was fired with fuel oil and coal in alternating fireboxes. The fuel oil was Standard Oil Co. Industrial No. 4, containing 0.0075 percent sulfur, and the coal was 2- by 4-inch Egg containing 38 percent volatile matter, 3 percent ash, and 0.05 percent sulfur. The kiln is provided liberally with pyrometers and heat controls and operates top and bottom within ±10° C.

The accessories included a J. C. Steele double 18-inch-auger deairing pugmill, complete and in excellent condition.

Special acknowledgment is due John H. Isenhour, manager of the Isenhour Brick & Tile Co., for his technical advice and interested cooperation, which enabled Kenneth M. Smith and S. E. Burton to adapt their experience with periodic kilns to the manufacture of sponge iron in the tunnel kiln, and for his many later suggestions and help at points of difficulty, not only in operating the large kiln but more especially in the troublesome sagger and extrusion problems.

SAGGERS

The standard saggers used in the tunnel-kiln campaigns were extruded at the Isenhour plant from the following mixture:

	Size	*Percent*
Calcined pyrophyllite	minus-6-mesh	70
Ohio (Oak Hill) fire clay	minus-12-mesh	10
Fire-clay grog	minus-6-mesh	20

The rectangular saggers were of various sizes, most of them 5½ by 7½ inches, inside diameter, and 24 inches high, with ¾-inch walls closed at the bottom. As at the Stark Brick Co. plant, it was found that extruded sagger bottoms did not stand up well and had to be re-pressed. The re-pressed bottom, with a ¾-inch groove pressed into it to accommodate the end of the sagger, was cemented to the sagger with high-temperature cement, while both were in the green state, and the saggers were then fired at 1,370° C. The cost was $0.60 each. These saggers weighed 42 pounds each, and the minimum capacity was 30 pounds of sponge iron per trip through the kiln. At an estimated life of 15 trips through the kiln, the cost of saggers per ton of sponge iron produced was approximately $2.70.

The use of pyrophyllite (a North Carolina product) was suggested by the unexpectedly excellent performance of 600 8½- by 8½- by 24-inch commercial flue liners, purchased from the Pomona Terra Cotta Tile Co., Greensboro, N. C., at $0.495 each, and 1,000 11- by 11- by

2-inch bottoms at $0.31 each, which were used in preliminary runs while preparations were under way for extruding saggers at the Isenhour plant. These saggers were made from raw instead of calcined pyrophyllite and Missouri instead of Ohio fire clay and showed longer life than any ceramic saggers used by the Bureau in its brickyard sponge-iron campaigns. Possibly, the pyrophyllite at the high firing temperature[74] is less susceptible to embrittlement by carbon monoxide than ordinary refractory clays; but experience at Salisbury confirms the findings at Canton that the life of a sagger depends largely on the art of sagger manufacture. A special lot of 360 pyrophyllite saggers—presumably of the same composition but measuring 7 by 11 by 27 inches, with a ⅝-inch wall—also purchased from the Pomona Terra Cotta Tile Co., cracked on the first trip through the furnace, and the several lots of standard saggers extruded at the Isenhour plant showed varying resistance to thermal shock.

ORES

Most of the sponge iron made by the Bureau of Mines in tunnel kilns at Salisbury was of the premium grade hitherto furnished only by the Swedish Höganäs plant. The high grade was due to use of a superconcentrate made by the Bureau from Cranberry magnetite.[75] About 300 tons of this superconcentrate was available, of which 34 tons was made into sponge iron in the large tunnel kiln.

The only other large lot of sponge iron made at Salisbury was 24 tons of nonpremium grade made from pyrite sinter, of which 34 tons was purchased from the Tennessee Copper Co., Copperhill, Tenn. Analyses of these materials follow:

Sinter:	*Percent*	Superconcentrate:	*Percent*
Fe	67.8	Fe	69.7
SiO_2	1.9	SiO_2	1.77
Al_2O_3	.85	Al_2O_3	[1]0.01– .05
CaO	1.2	CaO	[1].05– .10
MgO	.78	MgO	[1].05– .10
Zn	.23	Zn	----------
Cu	.13	Cu	----------
Mn	.09	Mn	[1].01– .05
S	.06	S	.021
P	.007	P	.008

[1] Spectrographic.

Various other commercial iron ores, both magnetite and hematite, were used, alone or in mixture, for making test runs in 1– to 18-sagger lots.

REDUCING AND DESULFURIZING AGENTS

The reducing agent was coke breeze purchased locally at a cost of $2.50 a ton delivered; it contained 79 percent fixed carbon and 0.51 percent sulfur.

The desulfurizing agent was ground limestone purchased from the Gager Lime Manufacturing Co., Sherwood, Tenn., at $2.75 a ton plus $2.00 freight per gross ton. The standard reducing mixture, consisting of 85 percent coke breeze and 15 percent limestone, thus cost $2.84 a ton.

CANISTER CHARGING

A special 28- by 36-foot building, with 10-foot clearance under the roof truss, was built for storing, drying, and charging ore and reducing mixture.

A roller conveyor under the overhead bins carried the saggers during charging. The section of the conveyor directly under the bins was set upon springs in such a manner that the sagger could be vibrated during loading with an off-balance ⅓-hp. motor to pack the ore and reducing agent more firmly in the sagger. The conveyor extended forward about 30 inches to a point where the sagger could be picked up with a small overhead monorail hoist and loaded on the tunnel-kiln cars in two tiers.

PUG CHARGING

Much work was done on extrusion of Cranberry, N. C., magnetite concentrate with an auger-type, deairing, clay-working machine. The most satisfactory results were obtained from 1.5 percent Cere-amic flour and 0.5 percent Trueline binder. The Cere-amic flour gave the pugs enough strength to permit handling during the drying operation, and the Trueline binder, which has a resinous base with a melting point of approximately 100° C., gave additional strength to permit handling while the pugs were being charged into the sagger. A 2- by 4-inch die was used for all extrusions, and the pugs were cut 20 inches long.

SPONGE-IRON PRODUCTION

Preliminary experiments in which the charged saggers were placed on the cars with the brick company's ceramic ware showed that a 72-hour heating cycle was ample to insure optimum reduction; the time cycles for runs in the large tunnel kiln were as follows:

Heating up	hours	12
Reduction period	do	34–48
Cooling down	do	12–20
Maximum temperature	°C	1,120–1,150

Six reduction runs, totaling 69 cars producing about 3,000 pounds of sponge iron per car,

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[74] Norton, F. H., Refractories: McGraw-Hill Book Co., Inc., New York, 2d ed., 1942, pp. 508–509.

[75] Lamb, Frank D., and Woodard, D. A., Pilot-Plant Production of High-Grade Magnetite Concentrate, Cranberry, N. C.: Bureau of Mines Rept. of Investigations 3980, 1946, 7 pp.

were made. The saggers of the first three runs with Cranberry magnetite concentrate were canister-charged, the fourth run was made up of canister- and pug-charged saggers, and the last two runs were pug-charged; the resulting pigs of sponge iron, whether canister- or pug-charged, appeared identical. Analysis of the sponge-iron pigs follows:

	Percent
Total Fe	94. 1
Metallic Fe	91. 9
Reduction	97. 7
S (evolved)	. 017
Si	. 71
P	. 006
C	. 35
Bulk density	2. 50

The 24 tons of sponge iron made from pyrite sinter in the same six runs was not of premium grade. Analysis of a representative pig of this sponge follows:

	Percent
Total Fe	92. 4
Metallic Fe	86. 5
Reduction	93. 6
Si	1. 03
S (evolved)	. 072
P	. 004
Cu	. 16
Zn (spectrographic)	0. 01-. 05
C	. 10
Bulk density	2. 25

Small experimental lots of sponge iron made from mixtures of pyrite sinter and Cranberry magnetite concentrate were of excellent grade.

Analyses of many samples taken from several saggers on a car showed the same degree of reduction—95±2.5 percent—independent of the position on the car (lower or upper tier, corner, inside, or outside), which indicates a remarkably even distribution of heat in the tunnel kiln. This is an important advantage of tunnel kilns over periodic kilns in which there is always a small proportion of saggers containing underreduced sponge and frequently some that are overheated, whereas the product issuing from the cool end of a tunnel kiln is so uniformly reduced as to require no inspection or sorting, once the temperature-time cycle has been adjusted properly to a given set of operating conditions.

Other advantages of the tunnel kiln over the periodic kiln for making sponge iron are:

1. Greater ease in loading and unloading, resulting not only in a saving of man-hours of labor but also in less mechanical breakage of costly saggers (probably more important).
2. Lower fuel costs when the tunnel kiln is properly designed for heat recuperation.

The manufacture of sponge iron in tunnel kilns is also susceptible to a greater degree of mechanization than the manufacture in periodic kilns. Thus, multiple charging has been proposed, that is, charging not one sagger at a time but a whole tier of saggers simultaneously. This seems feasible for canister charging, but opinion differs as to whether it can be applied advantageously to pug charging. So, too, metal containers would seem to be out of the question with periodic kilns but easily manageable in tunnel kilns.

SMALL TUNNEL KILN, SALISBURY, N. C.

Eketorp,[76] in a paper describing practice at the sponge-iron plant in Höganäs, Sweden, intimates that the reason the process is used at only one plant probably is that it depends on the skill of ceramists experienced in making good refractory saggers. Undoubtedly, the process would be more attractive to metallurgists if metal containers could be substituted for the ceramic saggers; work with the large tunnel kiln was discontinued at this point, because it was decided to study the possibilities of using metal containers and to develop a technique for charging saggers.

For these purposes, a small, oil-fired, experimental tunnel kiln was built at the Isenhour plant by the Harrop Ceramic Service Co., of Columbus, Ohio. It was 57½ feet long, with 32½ inches inside car clearance and 28$\frac{3}{16}$ inches vertical clearance over the car top. The kiln had a capacity of 15 cars moved by an adjustable-speed rack-and-pinion-type pusher mechanism outside the kiln, the cars being moved by means of a bar inserted through the end wall of the kiln.

The small experimental kiln consisted mainly of the fire-zone section, with very short preheat and cooling zones. This type of design does not permit heat recuperation, and consequently the heat losses were relatively high. In fact, the stack temperature was about 540° C. when the kiln was in operation.

The small, experimental, Harrop tunnel kiln was designed, laid out, and installed by J. B. Zadra, at that time supervising engineer of the College Park Branch, Bureau of Mines, College Park, Md.

Cranberry magnetite concentrate was used exclusively in this experimental tunnel kiln and was reduced in most runs in a standard 64-hour temperature-time cycle: 16 hours for preheating, during which time the kiln temperature increased from 590° to 1,090° C.; 32 hours for moving a car through the reducing zone, where the temperature ranged from 1,090° to 1,180° C.; and 16 hours in the cooling zone from which the car emerged at a temperature of 90° to 120° C.

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[76] Eketorp, Sven, [The Höganäs Sponge-Iron Process]: Jernkontorets Ann., vol. 129, No. 12, 1945, pp. 703-721.

TABLE 37.—*Analysis of sponge iron, 64-hour cycle, percent*

Total Fe	Metallic Fe	Reduction	Sulfur	Carbon
95. 0	89. 8	94. 5	0. 027	0. 33

Table 37 gives the average chemical analysis for 75 individual samples taken from 17,000 pounds of sponge iron in the first continuous run of 17 days.

The low average reduction in this run (94.5 percent) may be ascribed to some heavy pigs 2 to 2½ inches thick. The comparatively high carbon content was interpreted later to indicate too long exposure to carburizing conditions after a high degree of reduction had been effected. Small-scale tests support the contention that final carbon content can be held at 0.05 percent maximum and reduction at 95 percent minimum when the time at the reducing temperature is held to a minimum and the sagger is removed from the kiln while its temperature is still in the reducing range.

Another run on a time cycle of 56 hours—28 hours in the reducing zone and 14 hours each for preheating and cooling, but at a slightly higher average reducing temperature—seems to confirm this concept. Table 38 gives the average chemical analysis of 190 analytical samples taken from 45,000 pounds of sponge iron produced in this run.

CONTROLLING CARBON CONTENT

The problem of controlling conditions that determine the percentage of carbon in the finished sponge iron has not been solved unequivocally. Apparently, the carbon content increases regularly with the time of heating continued after reduction is virtually complete, when the metallic iron formed absorbs carbon to form iron carbide; this diffuses into the interior of the pig. It seems possible, therefore, to meet the request of acid open-hearth operators for a carbon content just sufficient to reduce the residual ferrous oxide in the sponge. The saturation of solid iron by carbide corresponds to about 1.5 percent carbon at 1,000° C., the carbide (Fe_3C) separating as the temperature falls to the transformation temperature of 768° C., where the carbon held dissolved in the gamma iron is 0.80 percent while the excess separated as carbide would be subject to reoxidation if the sagger atmosphere were favorable. Since the carbon necessary to reduce the ferrous oxide remaining in the sponge pig that shows 97-percent reduction is only about 0.5 percent, the desired end appears attainable by proper procedure.

TABLE 38.—*Analysis of sponge iron, 56-hour cycle, percent*

Total Fe	Metallic Fe	Reduction	Sulfur	Carbon
96. 3	94. 4	97. 9	0. 010	0. 14

Low carbon of the order of 0.005 to 0.05 percent, as desired by electric-furnace operators making 18–8, requires that reduction be stopped as soon as it reaches 97 percent, for example. This is the normal procedure at Höganäs and was followed at Canton, where periodic kilns permitted the use of Walker's criterion for completeness of reduction. The tunnel kiln is not equipped with a pilot thermocouple for determining the exact time when the charge just reaches the temperature in the kiln; hence, it is somewhat more difficult to establish the heating cycle requisite for a given carbon content.

GLOMERULE CHARGING EXPERIMENTS

An ore glomerule is a sphere formed by allowing a finely divided, plasticized ore mass to roll on the inner surface of a rotating horizontal drum. The plasticizing agent in this instance is water. As the material rolls over, it picks up additional matter and increases in diameter in concentric layers. According to an unpublished report on Preparation of Glomerules from Wet Pulverized Materials, compiled by the author, the ore must be pulverized so that about 50 percent is minus-200-mesh and should contain 12 to 20 percent of water, depending on the type of ore and the mesh size. The Cranberry magnetite concentrate met the size requirement (78.5 percent minus-150-mesh) closely enough for glomerulizing, and previous experiments in the periodic kiln, in the Bureau of Mines rotary kiln, and in a shaft furnace had shown that magnetite glomerules were unusually permeable to gases and that the reduced glomerule had a relatively high bulk density.

It was expected that the reduction with glomerule charging would proceed more like the "mix" method than like the Swedish layer method and hence would take less time at the reducing temperature, besides permitting more rapid charging, and would yield a denser product in a form more suitable for open-hearth melting.

The procedure for glomerule charging was as follows: The ore was conducted from the drier to a bin, from which it was fed by means of a rotary disk feeder to a pugmill. In the pugmill the ore was thoroughly mixed with about 15 percent of water and extruded through a perforated plate with ¾-inch openings into the glomerulizing drum. As the extruded material emerged from the perforated plate, it was broken by its own weight into cylinders approximately ¾ inch in diameter by 1 inch in length, which fell on the inner surface of the drum and were formed into spheres by the rolling action. The finished glomerules rolled out the discharge end of the drum onto a combination screening and charging device, which separated the optimum-size material from the fines and oversize. The screening and charging device discharged the optimum-size glomerules, consisting of all material ¾ to 1½ inches in diameter, directly into the saggers. The fines and oversize material were returned to the pugmill by a belt conveyor and reworked.

The glomerulizing drum was similar in construction to a rotary drier. It was fabricated from ¼-inch steel plate and was 27 inches in diameter by 9 feet in length. The drum was carried on rollers and was set at a slight slope (0.5 inch per foot), so that the material would roll toward the discharge end. It was driven by a belt from a 1-hp. motor and fed by a 12- by 42-inch pugmill fabricated from 10-gage black sheet iron. Ore feed to the pugmill was controlled by an adjustable rotary disk feeder having a capacity of 100 to 1,500 pounds of ore per hour, and water feed was controlled by a needle valve. The pugmill was operated by a ½-hp. motor connected to a shaft through a reducer.

As originally designed, the inner surface of the glomerulizing drum was smooth. Instead of rolling, the wet ore merely slid, and only a small proportion formed into glomerules. To eliminate sliding and produce a rolling action, small fins of ¼-inch welding rod were welded to the inner surface parallel to the axis.

The moisture content of the ore was quite difficult to control. The apparatus produced satisfactory glomerules for an hour or so and then, for no apparent reason, made glomerules as large as billiard balls or as small as peas. A study of the situation indicated that some additional means of controlling the moisture content of the ore within the glomerulizing drum was necessary. Further study indicated that the most satisfactory glomerule resulted when a wet nucleus was permitted to roll over in dry ore and thus build up a glomerule in concentric layers. The following additions were made to the glomerulizing equipment in an effort to meet these conditions and to allow the glomerules to form in what appeared to be their natural manner.

A screw conveyor driven by a ½-hp. motor through a reducer was inserted into the charging end of the glomerulizing drum so that dry ore could be fed at distances of 3 and 6 feet, respectively, from the charging end. The position of the dry-ore feed was controlled by manually controlled gates on the conveyor. Ore could be fed in either or both positions or shut off entirely, as necessary. Two water lines were inserted from the discharge end so that a water spray could be played on either or both streams of dry ore. A barrier 1 inch high was placed in the drum 3 feet back from the discharge end to prevent fine material from rolling down too fast. Between the barrier and the discharge end, 1 foot from the barrier, a screen 1 foot wide with ½-inch openings was built into the periphery of the drum to remove fines that had crossed the barrier. The fines discharged onto a belt conveyor, which returned them to the pugmill, and the formed glomerules were permitted to roll on a clean surface at the discharge end of the drum, which materially increased their strength. The finished glomerules then rolled out of the drum onto the screen and charging mechanism.

The screening and charging mechanism was similar in construction to an apple or orange sorter. It consisted of two screens made of parallel bars with hoppers underneath. Material from the glomerulizing drum was discharged onto the smaller screen, the openings of which were set for the minimum size desired. Undersize material fell through the screen into a hopper, from which it was discharged onto a belt conveyor and was returned to the pugmill. Oversize material rolled over the second screen (the bars of which were set for the maximum size) and was conducted back to the pugmill by the belt conveyor. Optimum-size glomerules fell through the second screen into a hopper, from which they rolled by gravity down a pipe and into the sagger. The pipe was telescoped so that it could be adjusted to reach any one of three saggers across a car. The reducing agent was fed onto the stream of glomerules as it passed from the pipe into the sagger.

Some difficulty was experienced in controlling the respective quantities of ore and reducing mixture when glomerules were charged. With this equipment, weighing the charge was impracticable because too much time was required, and rehandling the glomerules resulted in about 40 percent loss from breakage. The problem was solved by taking the average charge weight of 50 saggers loaded by hand, the raw materials for which had been carefully weighed. The average charge weight per sagger for the 5- by 8- by 28-inch pyrophyllite saggers was found to be 48 pounds of ore, 35 pounds of coke, and 6 pounds of limestone. Variation in weight of ore for the 50 saggers was 4 pounds and in reducing agent 2 pounds. An adjustable batching bin was adjusted to hold 41 pounds of reducing mixture. The reducing mixture was then fed from the batching bin by means of a flexible rubber hose to merge with the glomerules as it ran into the sagger. The system was checked by weighing loaded saggers at intervals during the charging. From the known weight of the sagger and the known weight of the added reducing mixture the weight of the ore charged could be determined with reasonable accuracy. It was found to check well with the predetermined average.

This glomerulizing and charging equipment could produce and charge 1,000 to 1,100 pounds of glomerules an hour. Glomerule size was chosen to range from ½ inch to 1½ inches in diameter; glomerules larger than 1½ inches in diameter do not reduce consistently. The yield of the glomerulizing equipment was 85 to 95 percent.

REDUCTION OF GLOMERULES

Glomerule-charged saggers were used in the first three runs of the small experimental tunnel kiln, yielding 11,500 pounds of sponge iron. These first three runs were unsatisfactory because of several interruptions due to various causes; these probably account for the poor metallization (76.9-, 83.9-, and 90.6-percent reduction, respectively). The results of the first run are obviously too unsatisfactory to permit deductions; the other two runs, while passable, yielded a sponge iron high in carbon (averaging 0.40 and 0.94 percent, respectively). These high carbon contents may indicate the necessity of scrubbing metallized glomerules to remove reducing mixture from the relatively large surface as compared with pigs; possibly, too, the time the glomerules were held at the reducing temperature was much too long, with consequent absorption of carbon. The high-sulfur contents (0.070 and 0.050 percent, respectively) indicate adherence of reducing mixture, but the 0.016 percent sulfur and 0.94 percent carbon of the third test and best glomerule metallization must be interpreted as indicating carburization after reduction. Discontinuance of the whole project when the war ended left this question unanswered.

An unexpected difficulty was the tendency of the metallized glomerules to stick to the sagger wall and to weld together in a more or less compact mass within the sagger during reduction. They were extremely difficult to dislodge, and in many instances a sagger was broken in the unloading operation. A tar coating on the inner wall of the sagger was effective in eliminating sticking to the sagger wall. The problem of glomerules welding together within the sagger was never satisfactorily solved, although it was investigated to the extent that fine coke was added to the discharge end of the glomerulizing drum and the glomerules were allowed to pick up a layer of coke about 1/16 inch thick.

Despite the two unsolved difficulties (capricious behavior of the glomerulizing machine and sticking in the saggers), glomerule charging has been described in detail as far as it has been studied, because its potential advantages merit more study than could be given in this prematurely discontinued tunnel-kiln campaign.

PRODUCTION IN THE SMALL KILN

In the course of operation of the small tunnel kiln 46 tons of sponge iron was produced in seven continuous runs—approximately 6 tons of glomerules and 40 tons of canister-charged pigs. Table 39 summarizes the raw materials used, the average quality as determined by chemical analysis, and the quantity of sponge iron produced in the seven runs.

Runs 1, 2, and 3 had to be curtailed owing to overheating of the car wheels, failure of the pusher mechanism, sinking of the furnace, and other causes. During run 4 broken saggers fouled the wipe seal and prevented movement of the cars; repairing this trouble made five

TABLE 39.—*Summary of raw materials used, sponge-iron quality, and sponge iron produced in the experimental tunnel kiln at Salisbury, N. C.*

Run No.	Type of charge	Raw materials, pounds			Fuel oil, gallons	Total iron, percent	Reduced iron, percent	Reduction, percent	Sulfur, percent	Carbon, percent	Sponge iron produced, pounds
		Ore	Coke	Limestone							
1	Glomerules	8, 339	2, 691	230	2, 487	87. 7	67. 5	76. 9	0. 070	-------	4, 839
2	Glomerules	6, 307	2, 295	303	1, 892	90. 5	75. 9	83. 9	. 050	0. 40	4, 365
	Pig	2, 296	1, 020	283	-------	94. 3	87. 4	92. 6	. 024	. 33	1, 648
3	Glomerules	2, 825	845	145	1, 781	92. 8	84. 1	90. 6	. 016	. 94	2, 338
	Pig	8, 207	3, 748	1, 232	-------	90. 2	70. 9	78. 6	. 024	. 17	6, 530
4	Pig	10, 373	4, 110	1, 185	5, 106	94. 3	89. 2	94. 6	. 019	. 27	8, 223
5	do	22, 293	9, 413	1, 415	4, 972	95. 0	89. 8	94. 5	. 027	. 33	17, 386
6	do	30, 603	13, 127	2, 790	3, 825	96. 4	95. 4	99. 0	. 010	. 14	21, 105
7	do	35, 094	13, 877	3, 883	4, 160	96. 2	93. 4	97. 0	. 011	. 14	25, 275

warming-up periods necessary during this run.

Runs 4 and 5 were made on the 64-hour cycle and runs 6 and 7 on the 56-hour cycle. Comparison of the average chemical analyses for these runs (table 39) indicates that some degree of success was achieved in correlating sponge-iron quality with operating procedure.

Practical operating problems, difficulty in procuring enough saggers, and premature termination of the project prevented carrying these experiments to their logical conclusion.

Of the premium-grade sponge iron made from Cranberry superconcentrate in the small tunnel kiln, 31 selected tons of sponge was shipped to Redding, Calif., where it was used as the base of high-quality alloy steel melted in the Bureau's experimental 5-ton arc furnace. The following incident relating to the porosity of sponge iron is quoted from an unpublished preliminary report of the Redding pilot plant.

> The pigs were dark gray in color and showed no evidences of reoxidation.
>
> Due to lack of storage space at Redding, the sponge iron was stacked in one end of the pouring pit upon receipt. Subsequently, this pit was accidentally flooded with water, which resulted in a thorough soaking of the sponge iron. The flooded material was dried with oil burners and in an electrically heated drying oven. The flooded and dried pigs all showed evidence of reoxidation and were colored reddish brown on the outside. When these pigs were sawed or broken, the brown layer was found to range from 1/32 to 3/8 inch in thickness.
>
> Analyses of 265 samples from this shipment were supplied by the Salisbury plant. Two samples were taken at Redding, one of the material as received and the other from pigs that had been water-soaked and then dried. The weighted average of the Salisbury analyses, together with analyses of the Redding samples, are tabulated below.

TABLE 40.—*Analysis of Cranberry sponge iron (tunnel kiln), percent*

Sample	Total Fe	Metallic Fe	Reduction	C	Mn	SiO_2	P	S
Salisbury (average)	96. 0	92. 9	96. 8	0. 19	--------	--------	--------	0. 015
Redding (as received)	95. 0	90. 6	95. 4	. 16	0. 08	2. 1	0. 010	. 021
Redding (flooded and dried)	94. 2	88. 4	93. 8	. 13	. 09	2. 1	. 012	. 019

> These analyses would indicate that the flooded material was not as badly reoxidized as would have been expected from its appearance.

These results confirm Dalrymple's laboratory study (at College Park) of water-soaked brickyard sponge iron, according to which a sponge of bulk denisty 2 to 2.25 might be expected to form 0.8 to 1.4 percent oxide when dried after water soaking.

METAL SAGGERS

The commercial possibilities of producing sponge iron by the brickkiln method depends largely on the cost of saggers per ton of sponge iron produced. Walker believes that the use of saggers is the least satisfactory feature in the manufacture of sponge iron in brickkilns.

Metal saggers have three advantages over ceramic saggers:

1. Greater strength.
2. Higher heat conductivity.
3. Thinner wall section, permitting a large increase in kiln-car capacity.

These advantages are offset by the following disadvantages:

1. High initial cost of heat-resisting-alloy saggers.
2. Damage due to possible overheating.

Dr. Richard Cole and associates at the Bureau of Mines laboratory in Raleigh, N. C., investigated the use of both carbon-steel and alloy-steel containers. Four heat-resisting-alloy containers were tested to solve the scaling problem encountered with plain carbon steel. These containers were centrifugal castings made from SAE 446-type chrome steel. They weighed 104 pounds, were 8 inches in diameter by 27 inches in length, and had a 1/2-inch wall thickness. The containers held 30 pounds of sponge iron and cost $50.00 each. Their average life in this experiment was four trips through the tunnel kiln. They withstood the oxidizing atmosphere of the furnace quite well, inasmuch as their external surface was smooth and apparently undamaged. They failed from the inside out owing to carbon absorption from the contained reducing mixture. Analytical results on turnings taken from the outside and inside of one of the chrome-steel saggers showed that the carbon content had increased from 0.44 percent on the outside to 2.46 on the inside, which was in contact with the coke. The increase in carbon lowered the melting point of the metal and formed a material similar to high-chrome cast iron. All evidence of failure was on the inside, where the high-carbon metal actually melted.

Walker's observation regarding the shortening of reduction time as a characteristic of metal containers was confirmed by a comparative run on a 36-hour time cycle—16 hours for preheating, 13 hours at 1,090° to 1,200° C., and 8 hours for cooling. Pig size was 2 by 4 by 20 inches for both ceramic saggers (Isenhour 5- by 8- by 28-inch pyrophyllite), each loaded with

TABLE 41.—*Chemical analyses of sponge iron produced in ceramic saggers and metal containers, percent*

	Total Fe	Metallic Fe	Reduction	Sulfur	Carbon
Ceramic sagger	84.9	40.2	47.6	0.130	0.18
Metal container	94.9	87.6	92.4	.010	.32

42 pounds of ore, and for the 28-percent heat-resisting chrome-steel containers, each loaded with 51 pounds of ore. Table 41 shows the results of this run.

The results obtained at Raleigh from tests on containers made of a chromium cast iron containing 32 percent chromium, 5 to 6 percent total carbon, 0.7 percent silicon, and 0.1 percent manganese are encouraging. The appearance of several such containers after about 10 cycles justifies a life expectancy of at least 100 cycles and possibly several hundred cycles at 1,090° C. The life tests indicated that pouring procedure is important in centrifugally casting these containers and that a ceramic-mold lining is desirable to control the cooling rates, especially in casting the larger sizes. Both vertical and circumferential cracks appeared in containers cast by pouring the metal into the mold too slowly. Except for some castings from metal containing more than 3.5 percent silicon, no cracks appeared in small castings made by rapid pouring or in large castings made in lined molds. The effect of metal composition on the life of cast saggers is shown in table 42.

TABLE 42.—*Effect of composition on life of saggers*

Melt	Number of cycles	Hours above 1,000° C.	Weight loss, percent	Composition, percent				Remarks
				Cr	C	Si	Mn	
C	40	800	19	25.0	------	------	------	Scaled heavily at 1,125° and 1,150° C.; very slightly at 1,100° C.[1]
10	6	130	Trace	26.7	5.1	2.6	3.15	Moderate scaling; cracked on second cycle.
13	5	110	do	28.4	3.7	4.9	1.20	Very slight oxidation; very brittle.
18	6	130	do	24.3	4.6	1.8	------	Thin scale over entire outside surface.
21	6	130	do	30.0	5.5	1.9	------	Coated with mold lining; no corrosion.
22	6	130	do	29.5	5.7	2.0	------	Do.
23	8	178	do	30.8	5.4	.7	------	Slight oxidation; small area of scale.
24	8	178	do	35.0	5.6	.5	------	Slight oxidation.
25	8	178	do	24.2	4.7	.5	------	Slight oxidation; thin scale and shallow pits.
26	8	178	do	29.9	5.9	1.2	------	Small area of very thin, loose scale.
27	8	178	do	30.7	5.5	.7	------	Small areas of 1/16-inch scale.

[1] Maximum temperature, 1,100° C. except for 2 cycles with saggers from melt C.

NOTE.—30 melts were made in which the composition varied in the range of Cr, 23.8–35.8; C, 3.53–6.19; Si, 0–8.6; and Mn, 0–3.15 percent.

SAGGER CHARGING

The distinctive feature of the Bureau of Mines method of charging saggers is the use of vertical pigs of ore surrounded by reducing mixture. That this is a great improvement over the original Swedish method of charging alternate layers of ore and reducing mixture is attested by the fact that the Höganäs plant introduced vertical pig charging in October 1944 and announced[77] that this new method of charging allows it to guarantee a more uniform sponge of higher quality as regards sulfur and metallic-iron content. Unfortunately, the Swedish vertical pig-charging method is described merely as "a new packing machine that sets the cakes of concentrate vertically in the saggers," and "the cakes of sponge are uniform and have a convex, easily cleaned exterior." Convex cakes could hardly be made, either by canister charging or by extrusion; hence, it is a fair guess that the new Swedish packing machine is some kind of briquetting machine.

The personnel at the Raleigh station of the Bureau of Mines have further improved canister charging by perfecting a semiautomatic machine for charging eight saggers at a time; based on pug or glomerule charging, the machine, in their opinion, will give much lower charging costs per ton of product than any method thus far investigated. This reduction in cost would have little significance at Höganäs, because the kiln is of the periodic type, for which stacking and unloading represent the major outlay for labor. Multiple charging, however, should make the tunnel-kiln procedure even more advantageous because, after the saggers are charged on the car, the labor costs for putting the loaded car through the tunnel kiln and unloading it are relatively small.

Another feature of Bureau of Mines procedure in the manufacture of brickyard sponge

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[77] Eketorp, Sven, [The Höganäs Sponge-Iron Process]: Jernkontorets Ann., vol. 129, No. 12, 1945, pp. 703–721.

iron, which is a direct consequence of vertical pig charging, is disregard of the injunction to lute tops on saggers. The necessity for an airtight seal has proved less essential than is usually stated. In some instances, a crack in the lower end of a sagger may result in poorly reduced sponge iron, but the observation made at Canton that loosely fitting sagger tops do not affect percentage reduction has been amply confirmed at Salisbury. The saggers drawn from the cool end of the tunnel kiln are still two-thirds to three-fourths filled with reducing mixture, with 3 to 5 inches of the pig protruding; the exposed surface of the pigs is slightly discolored (bluish), but only the most careful chemical analysis can detect the very slight oxidation of the surface.

This fact indicates that the function of limestone in regulating conditions within the sagger during the heating and cooling cycle may be even more important than its desulfurizing action. The aid to gas circulation that the carbon dioxide evolved from the limestone provides cannot be questioned because charges containing no limestone require a longer time at the reducing temperature and often are unevenly and poorly reduced. Fortunately, the dissociation-temperature curves for limestone and for the reaction $2CO \rightleftharpoons CO_2 + C$ correlate well with the conditions indispensable for the optimum reduction of iron oxides during heating and for preventing reoxidation of reduced iron on cooling. Furthermore, the continuous but gradually decreasing evolution of carbon dioxide from the limestone during cooling seems to maintain a $CO : CO_2$ ratio, which shifts with decreasing temperature in such a way as to avoid deposition of the finely divided carbon always obtained when carbon monoxide is cooled to 700° C. in contact with iron. This (unproved) hypothesis of the function of limestone in the sagger charge, if correct, would encourage belief in the possibility of empirically proportioning the temperature-time curve in the tunnel kiln to yield the maximum percentage of reduction for any given set of conditions, which, if followed, would guarantee a steady flow of a uniform quality of sponge iron.

Several additional items in the manufacture of brickyard sponge iron need further study. The most important of these are: (1) Control of carbon content in the sponge iron and (2) disposition of the large quantity of reducing mixture left after the saggers are unloaded.

Although most of the Bureau's sponge-iron pigs contained 0.10 to 0.15 percent carbon, contents of 0.3 to 0.4 percent were common, and in a few instances the carbon content was still higher. The tables in this report give some points of departure for controlling the carbon content in brickyard sponge iron, but the data are insufficient for duplicating the Höganäs guaranty that carbon content can be kept to 0.10 percent or less or for meeting the request of certain domestic steel mills that the carbon content be just enough to reduce the 2 to 4 percent residual iron oxide in Bureau of Mines wartime sponge iron.

The problem of disposing of surplus reducing mixture suggests the possibility of saving carbon by re-using the coal, which seems to be activated by passage through the kiln. The residual reducing mixture contains an undetermined quantity of undissociated limestone but enough caustic "burnt" lime to make the dust irritating to the nose and throat during unloading. The Bureau did not consider this matter in its brickyard sponge-iron campaigns other than to show how, on a laboratory scale, 95 percent of the contained Buckwheat anthracite could be recovered from one such mixture. A plant operating continuously probably would have to install dust collectors, at least at the unloading station, and eventually disposition of the accumulated waste material might become a problem.

A simple beneficiation step on the waste fuel should recover granular fuel and unburned limestone to be re-used, probably with addition of fresh limestone.

COSTS

The small Harrop tunnel kiln was not adapted for determination of costs, and hence the following estimate of the costs of manufacturing brickyard sponge iron in tunnel kilns is based primarily on the experience with the 200-foot tunnel kiln. The first set of cost estimates was made by E. S. Beebe, project engineer, who provided the data discussed in the first part of this section. Beebe's first estimates were checked by J. B. Zadra, who has wide experience as production engineer in metallurgical plants. His cost data for tunnel kilns as of January 5, 1945 (excluding the cost of the ore), are as follows:

Plant—25 tons per day:	
One kiln, 54 inches by 84 inches by 260 feet.	
Cost of plant and equipment, $76,400.	
Amortization, 20 years.	
Cost per ton of sponge	$0.38
Saggers:	
Cost, 80 cents each.	
Life of saggers, 15 fires.	
Cost per ton of sponge iron	2.60
Reducing mixture:	
$2.84 per ton.	
25 percent re-used.	
Cost per ton of sponge iron	1.07
Fuel:	
Cost per ton of sponge iron	2.88
Power:	
Cost per ton of sponge iron	1.44

Labor:		
10 laborers at 60 cents per hour.		
3 kiln operators at 75 cents per hour.		
1 superintendent at $1.25 per hour.		
Cost per ton of sponge iron		$3.28
Fixed costs per ton of sponge iron:		
Interest	$0.307	
Insurance	.055	
Taxes	.071	
Maintenance	.079	
Office expenses	.24	
Total		.75
Total cost of producing 1 ton of sponge iron in a tunnel kiln (exclusive of ore)		$12.40

It is believed that this cost of producing sponge iron in the tunnel kiln can be reduced materially by proper mechanization and further development in operational technique. The costs were computed in 1944 and require correction to present conditions.

CONCLUSIONS

The results of this investigation show that:

1. Brickyard sponge iron can be produced advantageously in large tunnel kilns, such as are used for the production of refractory ceramic ware.
2. A cost of $12.40 (1944 economy) per ton of sponge iron can be set for manufacture in a slightly larger tunnel kiln but under virtually the same conditions and same operational technique as at Salisbury, N. C. This cost does not include price of the ore, selling costs, and profit.
3. Better mechanization, such as multiple charging, and other developments in operational technique should lower costs materially.
4. The percentage of reduction and sulfur content of the sponge can be controlled satisfactorily. Carbon content is usually about 0.1 percent but as yet cannot be fully controlled.
5. Saggers made from pyrophyllite instead of clay have given excellent results.
6. The use of metal containers instead of ceramic saggers warrants further study.
7. The grade of the sponge iron produced is a direct function of the grade of iron ore used, and a high-quality product requires high-grade iron.
8. Sulfur in the fuel is trapped effectively by limestone mixed with it, but only about 30 percent of the sulfur in the ore is removed.

USE OF SPONGE IRON IN STEEL PRODUCTION [78]

Sponge iron served as the main source of iron and steel before the blast furnace was developed. It was generally produced in shaft furnaces and converted directly into wrought iron by the so-called blooming process, in which the sponge iron is heated to a temperature slightly below the fusion point of iron and then mechanically worked to remove the impurities. Conversion to wrought iron in this manner involved considerable manual work and loss of iron as a high iron oxide slag. Largely because of the cost of this operation, sponge-iron methods were replaced by blast furnaces.

The literature contains few references to the use of sponge iron in steel production, but numerous articles indicate outstanding physical properties of steels produced from sponge iron.

In 1932–33 the Bureau of Mines, in cooperation with Henry Disston & Sons, Inc., conducted an investigation of the properties of steel produced from a 50 : 50 charge of Höganäs sponge iron and scrap and from an all-scrap charge. Two 4-ton heats of 1-percent carbon steel were prepared in an electric furnace from these charges. This work was not published in detail but was reported only briefly in a section of Report of Investigations 3229.[79] Determination of extensive physical properties of these steels revealed only slight differences, except for damping capacity. The damping capacity of annealed and normalized samples from the sponge-iron heat was twice that of identically treated steel from the all-scrap heat. For parts subjected to vibration in addition to other stresses, a steel with high damping capacity is considered desirable.

Maier[80] reports a melting test in which 31,000 pounds of granular sponge iron constituted the charge of a basic open-hearth furnace run in 1935. This sponge iron was made from pyrite cinders and was put into light steel canisters for charging into the open hearth with 4.3 pounds of coke per 100 pounds of sponge iron. The carbon content at melt-down was 0.98 percent, which was considered satisfactory. The slag was quite acid and attacked the furnace banks. The heat required 1 to 1½ hours longer than regular heats made with scrap charges. The steel produced had a normal composition and behaved satisfactorily in fabricating tests. Its physical properties were similar to those of steel of about the same composition produced from a scrap charge. However, wire drawn from the steel made from sponge iron had slightly higher tensile strength and ductility than wire normally produced from all-scrap charges.

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[78] Buehl, R. C., Royer, M. B., and Riott, J. P., Use of Sponge Iron in Steel Production: Bureau of Mines Rept. of Investigations 4096, 1947, 74 pp.

[79] Fitterer, G. R., and Freeman, H., Use of Sponge Iron in the Production of High-Quality Steels in the Electric-Arc Furnace: Bureau of Mines Rept. of Investigations 3229, 1934, pp. 61–63.

[80] Maier, C. G., Sponge-Iron Experiments at Mococo: Bureau of Mines Bull. 396, 1936, 81 pp.

Tholand[81] reviews the use of sponge iron in the production of steel and compiled much information on the physical properties of steels produced from sponge iron. His data indicate that a superior steel can be made by using sponge iron. He stated that in the production of low- and medium-carbon steel in an open hearth 7 to 15 percent of sponge iron added to the charge increased the ease with which billets could be pierced for the manufacture of seamless tubing and reduced hot shortness and the tendency of the steel to crack. Steels are claimed to have a greater hardenability range without excessive grain growth when made from a charge containing sponge iron. Wire made from sponge iron was shown to have higher strength, greater ductility, and greater reduction in area than similar wire produced from scrap. Short logs are given of several heats made in basic electric and acid open-hearth furnaces.

It is worthy of note that the Swedish sponge iron imported every year into the United States sells for more than twice the price of the best scrap used by the steel industry. Its high purity is due to selection of specially pure iron ore. It is used in special electric and crucible steels, particularly in cutlery. A saw-manufacturing company is the largest user. Because of the limited supply of ore, the tonnage of Swedish iron received in the United States is always lower than the demand.

Améen[82] gives cost data on the production of steel from sponge iron and discusses briefly the melting of sponge iron of a high gangue content in a 10-ton basic electric furnace. The sponge iron analyzed:

	Percent		Percent
Total iron	77	Carbon	0. 5–1
Metallic iron	65	Phosphorus	. 012
Reduction	85	Sulfur	. 012
Gangue	19		

He stated that during the melt-down period the electric furnace operated more smoothly on sponge iron than on normal scrap. Excess slag resulting from the high gangue content of this sponge iron was removed during the early stages of the melting operation.

Johannsen[83] discusses the melting of "Krupp-Renn blooms" in basic electric and basic open-hearth furnaces. In most of the tests the charge was very high in sulfur (0.3 to 0.8 percent) and phosphorus (0.2 to 0.8 percent). No details were given of the electric-furnace heats, but it was claimed that no difficulty was experienced in converting the blooms into good steel. One heat in a stationary 15- to 20-ton basic open hearth was described in detail. Because of the high sulfur (0.32 percent) and phosphorus (0.64 percent) contents of the charge, it was necessary to employ four slags. The final steel contained 0.057 percent sulfur and 0.035 percent phosphorus.

COMPARISON OF SPONGE IRON AND SCRAP

Sponge iron resembles scrap more closely in its chemical composition and behavior in melting furnaces than other raw materials, such as cold pig iron or hot metal, used as melting stock in the production of steel. Nevertheless, sponge iron differs from scrap both in chemical composition and physical characteristics, and these differences must be considered in comparing sponge iron with scrap as a melting stock for the production of steel.

Sponge iron may be produced as a granular material or as a sintered mass, depending on the method of manufacture. Most of the sponge iron used in this investigation was produced at brick plants[84][85] in the form of a sintered mass or pig measuring approximately 2 by 6 by 24 inches. When viewed at low magnification, this sponge iron is seen to consist of small particles of approximately the size and shape of the ore used, which are sintered together in a porous structure.

In the production of sponge iron it is difficult to effect complete reduction, that is, remove all the oxygen from the ore. Consequently, sponge iron generally contains a small quantity of unreduced iron oxide. The oxide in sponge iron reacts with the carbon and silicon in a steel bath during melting and changes the bath composition; or, if insufficient carbon and silicon are present, the oxide enters the slag and attacks the refractories. Therefore, the oxide contained in sponge iron and that resulting from reoxidation must be considered in preparing furnace charges in order to obtain a bath of proper composition at melt-down.

Although it was realized that sponge iron produced from highly concentrated ore would be most satisfactory for conversion into steel, ore-concentrating equipment was not readily available during the war, and therefore much of the sponge iron employed in this investigation was produced from normal blast-furnace-grade "ore" without beneficiation. Sponge iron produced from such ore contained a relatively large proportion of other unreduced oxides, such as silica, alumina, and titania (6 percent silica, 2 percent alumina, and 0 to 1 percent

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[81] Tholand, N. K. G., Sponge Iron, Material for Electric Steel: Blast Furnace and Steel Plant, vol. 17, No. 9, 1929, pp. 1350–1355, 1362.

[82] Améen, Einer, Swedish Sponge Iron: Iron Age, vol. 153, Jan. 20, 1944, pp. 55–59; Jan. 27, 1944, pp. 56–65.

[83] Johannsen, Freidrich, [The Present Status of the Krupp-Renn Extraction Process]: Stahl u. Eisen, vol. 59, No. 37, 1939, pp. 1041–1046.

[84] Ross, Donald W., Production of Sponge Iron in a Shale-Brick Plant: Bureau of Mines Rept. of Investigations 3822, 1945, 27 pp.

[85] Smith, Kenneth M., and Burton, S. E., Manufacture of Sponge Iron in Periodic Brickkilns: Bureau of Mines Rept. of Investigations 3841, 1945, 38 pp.

titania). These unreduced oxides are not present in appreciable quantities in the usual scrap and pig-iron charges, although they do form to some extent as a result of oxidation during the melting and refining of normal charges. As previously mentioned, most of the sponge iron employed in these tests was in the form of pigs, so that it was not possible to concentrate the material after reduction.

The unreduced iron oxide in sponge serves to displace some of the iron ore normally added with the open-hearth or electric-furnace charge to remove carbon contained in the pig iron or high-carbon steel scrap. The resulting oxides of carbon cause the charge to boil after it has melted and thereby promote good mixing and bring metal and slag into close contact to cause transfer of slagging material into slag, transfer of phosphorus from metal to slag, and other important reactions. Probably 10 percent of the metal in an open-hearth cast comes from iron ore or from iron oxide in the scrap. The slag-forming oxides in sponge iron are the objectionable oxides. They unite with the lime added to the charge to form slag and form a deeper layer of slag than is desirable. They also attack the basic lining of the furnace if they come in contact with it before they meet the lime in the slag. More rapid loss of lining results.

Sponge iron entering an open hearth in the form of powder melts slowly. Even powdered metal is a heat insulator. Therefore, if sponge iron is produced in finely divided form, it must be briquetted or pelletized in some manner to promote more rapid melting. All Bureau of Mines work on sponge iron during the period 1942 to date has been directed toward producing it in the form of pigs or other shapes suitable for rapid melting.

ANALYSIS OF SPONGE IRON

Analyses of typical sponge irons used in the melting tests and of the ores employed in the production of these sponge irons are listed in table 43.

PURPOSE OF TESTS

The main purpose of the tests was:

1. To acquaint plant metallurgists and operating personnel with the use of sponge iron should a national emergency require substitution of sponge iron for scrap.
2. To ascertain the reaction of company executives, metallurgists, and operating personnel to the use of sponge iron.
3. To determine the melting characteristics of sponge iron, that is:
   (*a*) Whether the use of sponge iron requires a change in operating procedure and, if so, the best method of operation.
   (*b*) Maximum quantity of sponge iron that can be used successfully in various types of furnaces without adverse effect upon the operation.
   (*c*) Effect of sponge iron upon furnace capacity and rate of production.
   (*d*) Minimum degree of reduction of sponge iron when it is used as an appreciable fraction of the charge in various types of furnaces.
   (*e*) Maximum quantity of gangue minerals that sponge iron can contain without seriously interfering with the operation of the furnace, causing erosion of the refractories, or retarding the rate of production.

COOPERATIVE ARRANGEMENTS

Apparently, the purpose of the tests could best be attained by using sponge iron in place of scrap in the regular processes of steel plants. It was desirable to include plants with all types of furnaces, that is, open-hearth furnaces and electric furnaces lined with both acid and basic refractories. To obtain data on a large number of tests with the limited quantity of sponge iron available, the material was distributed to plants with relatively small furnaces (capacity of 40 tons or less). Plants were also chosen to include the production of most types of steel (low- and high-carbon, alloy, and stainless steels) and methods of fabrication (rolling, forging, and casting). The geographical location of the plants was also considered to avoid long-distance shipments of the sponge iron.

Plants that appeared to be suitable for the tests were visited by a representative of the Bureau of Mines. If the plant personnel expressed an interest in the trial melts, informal agreements were made for the trial of a specified quantity of sponge iron, depending on the furnace capacity and the desire of the cooperating group to investigate the utility of sponge iron as a raw material for steel making. The tests were attended by one or more representatives of the Bureau of Mines whenever it was feasible to make the necessary arrangements. The cooperating companies generally furnished operating data on the heats and sometimes similar data on comparison heats in which no sponge iron was employed. Many of the plants made physical tests on the steels produced and in some instances the Bureau of Mines personnel made additional physical tests.

ACKNOWLEDGMENTS

The Bureau of Mines appreciates the cooperation of the various steel producers whose personnel spent considerable time and effort conducting these tests without any financial remuneration. Members of the Bureau staff who observed these tests are grateful for the courteous treatment extended to them by company officials and operating personnel. The following companies cooperated in the investigation:

TABLE 43.—*Analyses of typical sponge irons used in melting tests and of ores used in the production of sponge iron, percent*

Element	Ores						
	Cranberry, N. C., magnetite concentrate	Scrub Oak, N. J., magnetite concentrate		Mahoning, Minn., hematite	60 percent Scrub Oak, 40 percent Mahoning, by weight	Mill scale	Sunrise, Wyo., hematite
Total iron	69.7	66.2		62.4	------	71.0	50.8
Phosphorus	.008	.014		.049	------	------	.05
Sulfur	.021	.004		.014	------	.27	.05
Silica	1.8	5.6		4.1	------	1.3	12.3
Alumina	------	1.1		1.4	------	------	4.6
Lime	------	.1		.1	------	------	.6
Magnesia	------	.1		.2	------	------	------
Titania	.07	.5		.04	------	------	------
	Sponge iron						
	Slab	Granular	Slab	Slab	Slab	Slab	Pellets
Total iron	94.1	90.8	87.8	87.3	85.9	91.4	89.5
Metallic iron	91.9	77.7	84.0	79.1	81.2	89.0	87.9
Reduction	97.7	85.6	95.7	90.6	94.5	97.4	98.2
Ferrous oxide	2.8	16.9	4.9	10.5	6.0	3.1	2.1
Carbon	.09	.24	.19	------	.46	.62	1.7
Phosphorus	.010	.005	.017	.051	.027	.020	.08
Sulfur	.014	.059	.010	.025	.046	.013	.13
Silica	1.5	1.6	7.5	5.8	7.0	1.7	4.4
Alumina	.3	1.3	1.1	1.9	3.6	None	------
Lime	1.0	1.7	None	.2	1.2	None	------
Magnesia	.3	Trace	.5	.3	------	None	------
Titania	.1	.8	.7	.06	.3	------	------
Manganese	.06	.2	.03	.8	.3	.6	------
Chromium	.02	------	<.02	------	------	.8	------
Nickel	.01	------	<.02	------	------	.1	------
Copper	.05	.02	<.02	------	------	.1	------
Vanadium	.01	------	<.02	------	------	------	------

ELECTRIC-FURNACE COOPERATORS

Allegheny Ludlum Steel Corp., Brackenridge, Pa.
Carpenter Steel Co., Reading, Pa.
Crucible Steel Co. of America (Halcomb Steel Division), Syracuse, N. Y.
Henry Disston & Sons, Inc., Philadelphia, Pa.
Dodge Steel Co., Philadelphia, Pa.
Rustless Iron & Steel Corp., Baltimore, Md.
Simonds Saw & Steel Co., Lockport, N. Y.
Timken Roller Bearing Co., Canton, Ohio.
Universal-Cyclops Steel Corp., Bridgeville, Pa.
Vanadium-Alloys Steel Co., Latrobe, Pa.
Vulcan Crucible Steel Co., West Aliquippa, Pa.

OPEN-HEARTH-FURNACE COOPERATORS

American Locomotive Co., Latrobe, Pa.
Baldwin Locomotive Works (Standard Steel Works Division), Burnham, Pa.
Central Iron & Steel Co., Harrisburg, Pa.
Colorado Fuel & Iron Corp., Denver, Colo.
Edgewater Steel Co., Oakmont, Pa.
Erie Forge & Steel Co., Erie Pa.
Follansbee Steel Corp., Toronto, Ohio.
Great Lakes Steel Corp., Detroit, Mich.
Harrisburg Steel Corp., Harrisburg, Pa.
Heppenstall Co., Pittsburgh, Pa.
Mackintosh-Hemphill Co., Pittsburgh, Pa.
Phoenix Iron Co., Phoenixville, Pa.
John A. Roebling Sons Co., Trenton, N. J.
Stanley Works, Bridgeport, Conn.
Worth Steel Co., Claymont, Del.

MELTING TESTS AT STEEL PLANTS

The cooperating plants furnished extensive data on the tests made with sponge iron. These data were supplemented with notes taken by Bureau of Mines observers. Data were obtained on 51 heats made with sponge iron and 7 comparison melts made with scrap. The plants are designated by letters rather than by names.

The tests are grouped by type of furnace employed—basic electric, acid electric, basic open hearth, and acid open hearth. The terms "basic" and "acid" refer to the composition of the refractories of the furnace and the slags employed. In basic furnaces the lower side walls are lined with magnesite brick, and the bottom usually is built up by sintering into place granular magnesite or dolomite. Most of the slags used in such basic furnaces are more than half lime (CaO). Acid furnaces are lined with silica brick, and the slags are composed largely of silica and iron oxide. All the electric furnaces used for the sponge-iron tests were 3-phase, Heroult-type, arc furnaces.

BASIC ELECTRIC-FURNACE TESTS

Tests were made in seven plants in arc furnaces of 6 to 10 tons capacity; 12 to 48 percent of sponge iron was used in the charges. Armor plate, plain carbon steel, high-speed steel, and stainless steel were produced. All of the steel met prescribed specifications.

BASIC OPEN-HEARTH-FURNACE TESTS

A series of melting tests was carried out in industrial steel plants to demonstrate the utility of sponge iron as a charge constituent in the production of steel by the basic open-hearth process. The sponge-iron tests were made in furnaces of 50 to 125 tons capacity. The quantity of sponge iron used in the various test charges ranged from 5 to 25 percent of the furnace charge, depending mainly on the attitude of the operating officials of the cooperating company toward radical departures from established practice. Generally, the quantity was conservative because of the desire to approach gradually any problems that might arise from its use. Such conservativeness cannot be condemned, because the tempo of steel production for war purposes did not justify possible loss of 50 to 125 tons of metal by introducing too much of a charge constituent for which no previous data as to its effect on regular operating practice were available.

Tests were made in nine plants. Furnace operations did not differ significantly from normal plant practice.

ACID OPEN-HEARTH-FURNACE TESTS

Tests were made in six plants. The quantities of sponge iron in the charges ranged from 3.0 to 21.0 percent. Carbon tool steel, steel castings, and forge-grade steels were produced.

SPONGE IRON AS A SCRAP SUBSTITUTE DURING A NATIONAL EMERGENCY

The tests showed that sponge iron can be substituted for part of the scrap normally used for producing steel in open-hearth and electric furnaces. It has been found advantageous to use highly concentrated ore or mill scale for the production of sponge iron. However, when concentrating equipment is not available, moderate quantities of sponge iron suitable for use in steel-making operations can be produced from better grades of blast-furnace ores.

Sponge iron produced from commercial ores without special concentration was used successfully in quantities up to 10 percent of the charge of open-hearth furnaces without interfering with normal operation.

The use of sponge iron constituting 10 percent of open-hearth charges represents a considerable decrease in the quantity of purchased scrap required by steel plants. For example, consider first open-hearth furnaces using hot metal charges to the extent of 50 percent of the furnace capacity. Assuming that the scrap returned from plant operations amounts to 20 percent of the furnace charge, a 10-percent sponge-iron addition would replace one-third of the purchased scrap. For cold-metal operations in which pig iron usually constitutes approximately 30 percent of the furnace charge and return scrap 20 percent, a 10-percent sponge-iron replacement would be equivalent to about one-fifth of the purchased scrap. Sponge iron would therefore help to alleviate a scrap shortage even though only 10 percent of this material is used in open-hearth charges.

The sponge iron used in most of the melting tests was produced at brick plants; cost calculations for this process [86] indicate that the material can be produced for $10.66 a ton, exclusive of the cost of ore. On the basis of these figures, the cost of producing sponge iron at brick plants would be slightly below the selling price of pig iron in most sections but slightly above the price for scrap established during the emergency period. As sponge iron would have to compete with scrap, private enterprises could not undertake the production of sponge iron by this process (except for special application) without some form of financial aid. This fact, however, does not prove that brickkiln sponge iron is too expensive to warrant consideration as a scrap substitute during an emergency. Although selling price is normally a good indication of value and production costs, it ceases to be reliable when prices are regulated by law, plants are erected with government funds, and production is subsidized, as during the recent war. In comparing the desirability of sponge-iron processes with the blast-furnace method as an emergency source of raw material for steel making, one should consider that the construction of blast furnaces and associated equipment requires critical items (steel, heavy fabricating equipment, and labor), which must be taken from other production at a time when such production is badly needed.

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[86] Smith, Kenneth M., and Burton, S. E., Manufacture of Sponge Iron in Periodic Brickkilns: Bureau of Mines Rept. of Investigations 3841, 1945, 38 pp.

Blast furnaces and associated equipment require 1 to 3 years to construct and put into operation. Some of the blast furnaces that were constructed as rapidly as possible when the scrap shortage became evident operated about 3 years before hostilities ended, whereas other units were never completed. On the basis of a 1,200-ton (daily capacity) blast-furnace installation cost of approximately 6 million dollars during the period 1941–45, the investment per ton during the emergency period would be approximately $4.50, $6.90, and $13.70 for furnaces that operated 3, 2, and 1 years, respectively. Therefore, if sponge iron could be produced at an existing brick or cement plant without great expenditure for equipment and at a cost that was not excessively high, compared to blast-furnace operation (for example, $10 per ton above blast-furnace costs), the total cost (erection plus operation) per ton of product made during the emergency would be comparable to that of blast-furnace and coke-oven installations that were not completed until near the end of the emergency period. In such instances, sponge-iron processes would have the advantage of earlier production and smaller requirements for critical materials and therefore are worthy of consideration if a similar situation should arise, as it did in 1951.

When the shortage of scrap became evident in 1941–42, the immediate application of sponge-iron processes to relieve part of the scrap shortage was limited by lack of operating data on processes that could utilize idle equipment. The recent investigations of the Bureau of Mines have supplied considerable data, but, nevertheless, additional pilot-plant operations would be desirable.

UTILIZATION OF SPONGE IRON IN GENERAL STEEL PRODUCTION

The Bureau of Mines observers had the opportunity to discuss the utilization of sponge iron with the personnel of the cooperating plants during the progress of the tests. Executives in many of these plants expressed an interest in the possibility of producing or purchasing sponge iron provided it could be made or obtained at a price comparable to that of scrap. Many of the plants in which the sponge-iron tests were run were too small to warrant the operation of a blast furnace, and these plants therefore must rely on the purchase of suitable scrap and pig iron at a price low enough for competitive operation. In periods of scrap shortages, as during the war period, it is difficult for such plants to find enough suitable scrap and pig iron for their operation. Operators of acid-lined furnaces who require scrap and pig iron low in sulfur and phosphorus have greater difficulty in obtaining raw materials than producers using basic furnaces.

Plants in some parts of the country that use a charge consisting largely of low-grade scrap are now having difficulty with high-residual alloying elements—copper, nickel, tin, and antimony. For example, the metallurgists at one plant mentioned that their residual elements are now approximately as follows:

TABLE 44.—*Residual elements in charges of low-grade scrap*

Element	Range, percent	Average, percent
Copper	0. 15–0. 70	0. 30
Nickel	. 10–1. 00	. 40
Tin plus antimony	. 04– . 1	. 05

When the residual elements in the charge are high (table 44), the metal product does not deep-draw satisfactorily, and difficulty is experienced in hot-forming operations. Such plants would benefit by the substitution of sponge iron or pig iron for part of the scrap they are now using.

USE OF HIGH-GRADE SPONGE IRON IN THE PRODUCTION OF SPECIAL STEELS

The plant tests indicated that high-grade sponge iron has special value for the production of some grades of tool steels in basic electric furnaces. Such steels are a premium product for which quality is more important than cost of production. During the melting tests some producers of tool steels expressed a desire to purchase sponge iron even though the cost might be considerably above that of high-grade scrap. Consequently, it appears that there is a market for high-quality sponge iron for use as a melting stock in basic electric furnaces.

CONCLUSIONS

1. **Utility.**—Sponge iron can be used to replace part of the scrap iron normally employed in the production of steel. The maximum percentage of sponge iron that can be substituted without requiring an appreciable change in furnace operation or without reducing furnace capacity depends on the grade of sponge iron, type of furnace employed, and operating procedure.

2. **Physical Properties.**—Steels for which sponge iron constituted part of the furnace charge met chemical specifications, were processed without difficulty by the usual procedures, and had physical properties that were at least as good as those of normal raw materials.

3. **Storage.**—Sponge iron oxidizes readily

when stored outdoors for extended periods during rainy weather. The tests demonstrated that oxidation interferes with the effective utilization of sponge iron as a melting stock in steel production. Therefore, it should preferably be used within a few days after receipt or should be stored under cover.

Losses due to rusting during storage for several months have not been serious.

4. Use of Sponge Iron in Basic Electric Furnaces.—Sponge iron is a desirable charge material for basic electric furnaces, and company officials expressed an interest in the possible use of sponge iron to improve steel quality. High-quality steels with rigid chemical specifications are generally produced in basic electric furnaces. In the production of such steels difficulty is often experienced in meeting specifications for residual alloying elements (nickel, copper, chromium, and tin) and phosphorus. Sponge iron has been produced that is very low in these elements and therefore is a premium raw material for the manufacture of certain grades of tool steel.

Well-reduced sponge iron in the form of slabs with low sulfur (0.014 percent), phosphorus (0.008 percent), and silica (1.5 percent) contents was found to be very satisfactory when used to the extent of 50 percent of the furnace charge at plant A.

Sponge iron with a relatively high silica content (6.5 to 7 percent) made from blast-furnace-grade ore without special concentration constituted 25 percent of the furnace charge at plant C and 32 percent at plant E. The heats were satisfactory, but the slag volume was abnormally large because of the high gangue content of the sponge iron. Both of these plants employed a two-slag practice; that is, the oxidizing slag was removed after melt-down, and constituents were added to form the reducing slag. When this grade of high-silica sponge iron was used in single-slag practice, the tests indicated that about 15 percent sponge iron in the charge was the maximum amount that could be used satisfactorily.

Granular sponge iron constituted 18 percent of the furnace charge at plant E. The only difficulty experienced was some sticking of the sponge iron to the side walls. If granular sponge iron is loaded so that it is in the center of the charge, it should be a satisfactory raw material for basic electric furnaces. Granular sponge iron has low density, but if properly charged it would flow into the voids between scrap; therefore, the use of a moderate proportion of granular sponge iron should decrease the volume of a furnace charge. At some plants the use of granular sponge iron might avoid the necessity for charging more than once and might thus decrease the operating time.

5. Use of Sponge Iron in Acid Electric Furnaces.—Acid electric furnaces are generally used in making steel castings. For many types of steel castings a metal low in sulfur and phosphorus is desirable, but neither of these elements is removed by an acid slag. Therefore, company personnel was interested in the possibility of producing castings of low sulfur and phosphorus contents by using sponge iron in the charge. To be desirable as melting stock in acid electric furnaces, sponge iron should contain little sulfur and phosphorus (below 0.02 percent for each element). Data were obtained from only a few tests in which sponge iron constituted a quarter to half of the charge in acid electric furnaces. In these tests reactions between the iron oxide of the sponge iron and the carbon in the bath appeared to cause more trouble than in basic electric-furnace tests, indicating the need for a well-reduced sponge iron in acid electric practice. However, this difficulty possibly could be overcome through the development of the proper charge composition and loading procedure. The slag volume in these tests was somewhat greater than for normal operation. This caused no trouble in the furnace but was undesirable in the ladle during the casting operations. This disadvantage could probably be overcome through a change in the operating procedure, such as the removal of part of the slag while the heat was in progress.

6. Use of Sponge Iron in Basic Open-Hearth Furnaces.—Sponge-iron slabs with a high silica content (about 7 percent) can be used to replace scrap in a basic open-hearth furnace to the extent of about 12 percent of a cold-metal charge without any appreciable change in operating procedure or reduction in furnace capacity (plant I). No tests were made with a higher percentage of sponge iron of this grade, as an excessive slag volume would have resulted from the high silica content of the sponge iron.

Sponge-iron slabs made from mill scale with a lower silica content (2 to 3 percent) were used to replace scrap to the extent of 20 percent of the furnace charge (plant J). The carbon at melt-down in these heats was lower than in the regular heats at this plant; this fact indicates that the proportion of pig iron or carbonaceous material in the charge should be increased over that normally employed. In other respects, this percentage of sponge iron in the furnace charge caused no operating difficulties.

Results of the furnace tests indicated that the slabs of sponge iron preferably should be charged on top of scrap and then covered with additional scrap to prevent oxidation of the sponge iron by exposure to the heating flame. Use of less ore in the charge is indicated to compensate for iron oxide in the sponge.

Sponge iron made in the form of dense pellets in a rotary kiln was used as half of an open-hearth charge at plant L. The pellets were placed in piles on the bottom of the furnace, followed by hot metal after apparent fusion of the sponge iron. The heat required 2 hours longer than for normal operation, so apparently the pellets had fused only superficially before the hot metal was added. A change in operating procedure, such as the use of smaller quantities of sponge iron charged on top of the scrap, probably would give more satisfactory results.

7. Use of Sponge Iron in Acid Open-Hearth Furnaces.—A high-quality sponge iron was used successfully as 20 percent of an acid open-hearth charge at plant R. Sponge iron with a relatively high silica content (6.5 percent) was employed as 13 percent of an open-hearth charge without interfering with normal operation (plant T). However, the carbon and silicon content of the furnace charge should be increased above that used in normal operation to compensate for the iron oxide remaining in the sponge iron because of incomplete reduction and oxidation during melting. The sponge iron should be placed in the middle of the charge and covered with some additional charge material to reduce oxidation during the melting period. The reaction of company executives and plant personnel was generally favorable to the use of sponge iron low in sulfur and phosphorus.

8. Sponge Iron as a Scrap Substitute.—Sponge-iron processes warrant consideration as a means of alleviating a scrap shortage during a war or other national emergency. Sponge iron can be made with equipment constructed for other purposes (brick plants and cement kilns), and therefore production could begin in a short time, with only a small expenditure for minor changes in plant facilities. Possible higher production cost for sponge-iron processes operating on a small scale, compared to blast furnaces, might be offset by the high cost and time required for new blast-furnace construction.

The economic use of sponge iron as a raw material for general steel production in normal years depends on the development of processes for producing this material on a large scale at low cost. Such processes would appear most applicable to sections of the country that lack coking coals suitable for blast furnaces but have ores and reducing agents satisfactory for sponge-iron production. At the present stage of development of sponge-iron processes it appears economically feasible to produce a high-purity material on a relatively small scale for use in the manufacture of special steels in electric furnaces.

MILITARY TESTS IN THE BUREAU OF MINES PILOT PLANT AT SHASTA DAM, CALIF.[87]

An electric-furnace pilot plant was constructed by the Bureau at Shasta Dam, near Redding, Calif., in 1946, under authority of a congressional appropriation for investigating resources of raw materials for steel production. The initial problem investigated was the production of steels and ferrous alloys from sponge iron of a grade that could readily be produced from available domestic ores. The major objectives of this work were the determination of operating problems and costs involved in melting sponge iron in an electric-arc furnace and investigation of the properties of steels and alloys produced from sponge iron on a semicommercial scale compared with similar materials produced from scrap.

This investigation entailed the production of more than 175 tons of various grades of steel and other ferrous alloys in a 4-ton basic electric furnace using several different types of sponge as melting stock. Heats were also made from scrap charges melted under operating conditions as nearly identical to the sponge-iron heats as possible for comparison of operating data and properties of the alloys.

The furnace used was a basic-lined, 3-phase, direct-arc furnace of the Heroult type. The shell diameter was 8 feet, and nominal holding capacity was 4 to 5 tons. The plant was adequately equipped for production of ingots in sizes ranging from 30 to 1,700 pounds. The pilot-plant equipment and methods of operation have been described fully by Stephens and Morning.[88] Figure 31 is a photograph of the furnace.

DESCRIPTION AND ANALYSES OF SPONGE IRONS

Sponge iron produced from three different ores by various processes was used in the melting tests. Briquetted sponge iron produced from Shasta County, Calif., magnetite ore by a rotary-kiln process at the Laramie, Wyo., sponge-iron pilot plant of the Bureau of Mines was used as charge material for most of the heats. In addition to heats made with the regular briquetted rotary-kiln sponge iron produced from Shasta ore, unbriquetted granular sponge iron made by this process from the same ore was used in three heats, and this same sponge iron, briquetted with additional carbon, was used in one heat. The briquets were 5 inches in diameter and 2 to 3 inches thick, with a specific gravity of 4.4 to 4.6.

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[87] Stephens, W. W., and Morning, J. L., Pilot-Plant Production of Steel from Sponge Iron: Bureau of Mines Rept. of Investigations 4498, 1949, 21 pp.

[88] Stephens, W. W., and Morning, J. L., Adapts Pilot Plant to Manufacture of Alloy Steel: Steel, vol. 120, No. 18, May 5, 1947, pp. 116–122.

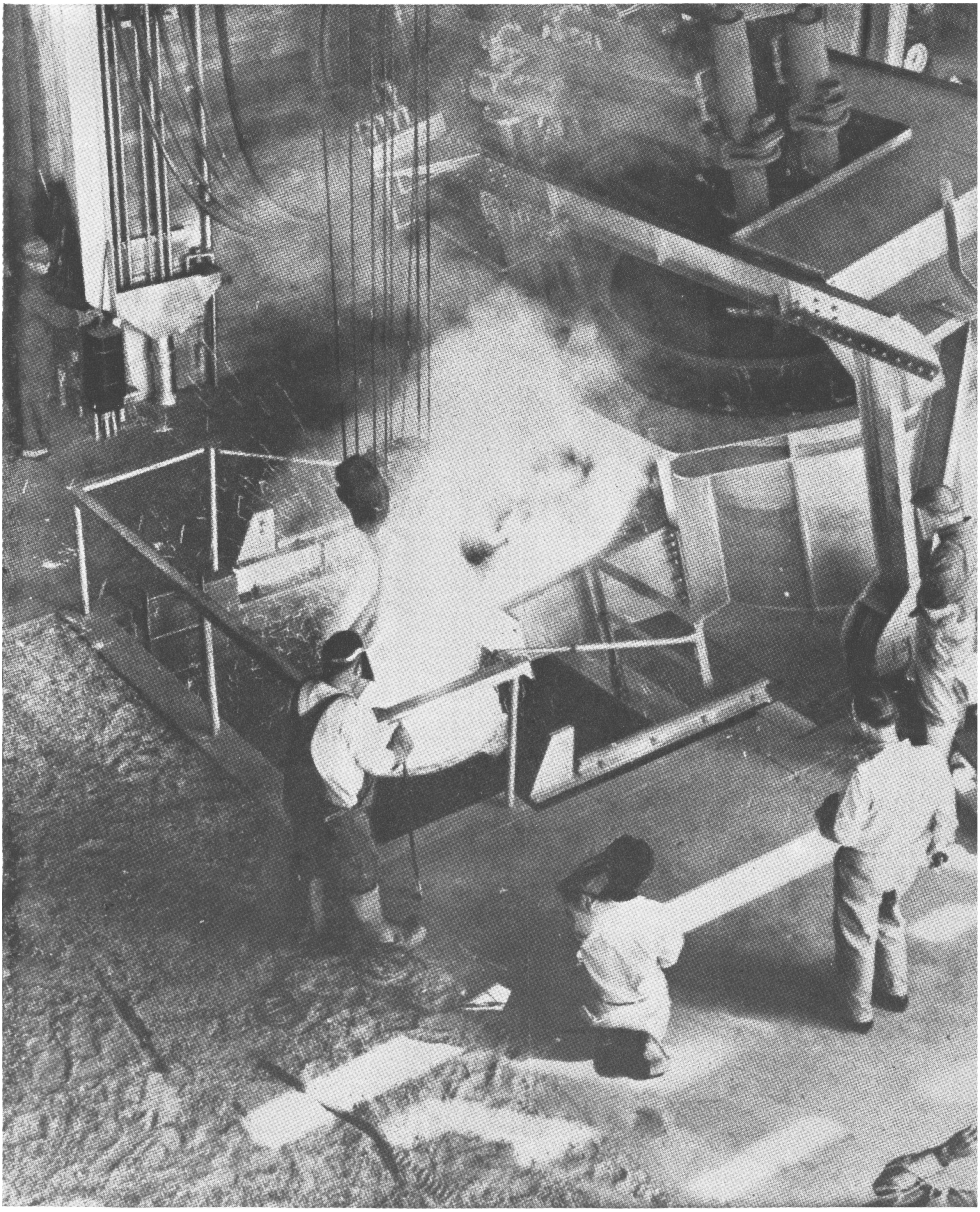

FIGURE 31.—TAPPING A HEAT OF STEEL FROM A PILOT-PLANT FURNACE.

A premium grade of sponge iron made from pure Cranberry, N. C., magnetite concentrates in a ceramic tunnel kiln at the Bureau of Mines Salisbury, N. C., sponge-iron pilot plant was used as melting stock in nine heats. This material was in the form of porous pigs 1¾ to 2 inches thick, 4 to 6 inches wide, and about 20 inches long, with a specific gravity of 2.5 to 3.0.

One heat was made with granular sponge iron produced from Scrub Oak magnetite concentrates in rotary-kiln pilot-plant tests conducted by the Bureau at the plant of the National Radiator Co., Johnstown, Pa. The test (No. CIX) in which this material was produced was described in an earlier publication.

Analyses of the sponge irons and the ores used in their production are given in table 45.

REDUCING AGENTS, FLUXES, AND ALLOYS

Successful melting of sponge iron for steel production requires the addition of some form of reducing agent to the charge to complete reduction of the iron oxide in the sponge and to prevent the charge from melting down with an extremely low percentage of carbon in the bath and consequent high-iron slag. The literature contains many references to various reducing agents used for this purpose, including graphite, charcoal, coke, silicon carbide, ferrosilicon, manganese, silicomanganese, and pig iron.

Enough burned lime to form a slag with a lime-silica ratio of about 2 to 1 was charged in all heats.

Lump magnetite ore from the Shasta County, Calif., deposits was used where required for oxidation of carbon. Other fluxes used were fluorspar and silica sand, which met the usual specifications for furnace-grade material. Cement clinker was used in some heats as a basis for the reducing slag.

The alloying materials were standard commercial ferro-alloys. Most of the manganese additions were electrolytic manganese metal (because it was on hand), but in a few heats chromium was added as electrolytic chromium metal. Both of these electrolytic metals were products of the Bureau of Mines pilot-plant operations at Boulder City, Nev.

TYPES OF ALLOYS AND FURNACE PRACTICE

The alloys produced ranged from low-carbon rimmed steels and ingot irons to standard chromium-nickel stainless types such as AISI types 304 and 316. They included plain, carbon-killed steels containing 0.16 to 1.07 percent carbon, alloy steels of the 1300, 4100, 4300, 4600, 5100, 6100, and 8600 series, and a number of special iron-manganese and iron-chromium alloys and chromium-manganese stainless steels. Six heats of plain carbon steel were made from sponge iron by following single-slag practice, and two heats were made by using a single "turned" slag (a single slag oxidizing during the first part of the heat and made reducing or "turned over" during the latter part of the heat by adding fine coke and ferrosilicon). The remaining 53 heats, in which sponge iron constituted 100 percent of the charge, were made by the double-slag process, in which the original or oxidizing slag was removed completely and a second slag was built up and maintained in a reduced condition.

Four additional heats used sponge iron as part of the charge material, and eight heats were made with all-scrap charges for comparison of operating data with the sponge-iron heats.

CHARGING PROCEDURE

The specific gravity and form of the briquetted sponge iron permitted placing the entire charge for a heat in the furnace at one

TABLE 45.—*Analyses of sponge irons used in pilot-plant melting tests and of the ores from which the sponge iron was produced, percent*

Ores	Total iron	Metallic iron	C	Mn	S	P	SiO_2	Al_2O_3	CaO	MgO	Reduction, percent
Shasta County, Calif., magnetite ore	60.57	--------	--------	0.15	0.34	0.013	5.50	2.28	3.0	--------	--------
Cranberry, N. C., magnetite concentrates	69.7	--------	--------	[1] 0.01-.05	.021	.008	1.77	[1] 0.1-.5	[1] 0.05-.10	[1] 0.05-0.10	--------
Scrub Oak, N. J., magnetite concentrates	66.2	--------	--------	--------	.004	.014	5.6	1.1	.1	.1	--------
Sponge irons											
Shasta briquetted sponge:											
Lot 1	87.4	72.7	0.50	.10	.059	.009	2.70	1.2	1.25	.5	83.2
Lot 2	85.3	70.7	.59	.12	.103	.017	3.43	1.1	2.1	.5	82.9
Lot 3	87.1	72.0	.78	.14	.054	.019	3.10	1.1	1.5	.4	82.7
Lot 4	89.3	81.2	.66	.13	.053	.019	2.68	.8	1.35	.65	90.9
Lot 5 (with additional carbon)	84.0	73.0	2.14	.15	.072	.027	3.46	1.0	2.0	.8	86.9
Shasta granular sponge	85.0	76.1	1.04	--------	.085	--------	3.86	--------	1.6	--------	89.5
Cranberry brickkiln sagger pigs	95.0	90.6	.16	.08	.021	.010	2.1	.4	.35	.12	95.4
Scrub Oak granular sponge	92.1	83.4	.90	--------	.054	.009	1.2	1.0	--------	--------	90.6

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[1] Spectrographic analysis.

time without resorting to back-charging. Therefore, the only charging problem when using this material is the distribution of lime and reducing agent in the charge.

To prevent any possible erosion of the furnace bottom by the first slag formed during the melt-down, about 20 percent of the required lime was shoveled onto the bottom and banks of the furnace before any sponge iron or reducing agent was charged. If much more lime than this (about 80 to 100 pounds) was placed on the bottom, it generally resulted in building up the bottom. Another 40 percent of the required lime was shoveled onto the furnace banks after the sponge iron was charged, and the remaining 40 percent was added during the melt-down at the discretion of the furnace operator.

The distribution of the reducing agent in the charge apparently has little effect upon over-all carbon recovery as long as it is not placed so near the top of the charge as to burn off excessively during the early part of the melt-down.

The most satisfactory method found for distributing the carbon in a charge of 6,400 pounds of sponge was to place about 1,000 pounds of sponge iron in the bottom of the charging bucket, half of the required carbon, 2,000 pounds more sponge iron, the remaining carbon, and finally the rest of the sponge iron. In larger heats the second addition of carbon was placed higher in the charge, so that it was covered by about 50 percent of the total sponge iron in the charge.

A major operating difficulty with the briquetted Shasta sponge was the tendency of the briquets to weld together at a comparatively low temperature, to bridge over in the furnace, and hang on the banks.

The possibility of improving the melting characteristics of the briquetted sponge by mixing the granular sponge with the required quantity of lime or carbon, or both, and then briquetting the mixture became obvious rather early in the program. Unfortunately, most of the sponge iron used in the melting tests had been made and briquetted some time before the tests were begun. Only one lot of 6,240 pounds of briquetted sponge made by adding carbon before briquetting was available. This made up the charge for one heat of alloy steel. These briquets were somewhat softer and more easily broken than those made without additional carbon but withstood normal handling without excessive breakage. The charge melted down very rapidly and exhibited no tendency to stick together or bridge over in the furnace. In any commercial melting of a charge containing a large proportion of sponge iron, it appears that briquetting of the required reducing agent with the sponge would offer a distinct advantage in furnace operation.

MELTING METHODS AND CHARACTERISTICS

No particular difficulty was experienced in striking or maintaining an arc on any of the sponge-iron charges. With some of the granular material, it was necessary to place a steel bar under the electrodes when first starting the furnace to provide a conductive path for striking the arc. With this material, several minutes was required to get the arcs well started; they then could be maintained without difficulty. The arc could be started promptly on the briquetted or sagger type of sponge, with a number of small arcs forming between the briquets or pigs throughout the top part of the charge. All of the sponge-iron charges melted smoothly and quietly compared with the scrap charges.

The melt-down of the sponge-iron heats was generally started by turning the power on the 145-volt tap for about the first 25 minutes, or until the electrodes were well buried in the charge. Melting was then continued at 225 volts until the charge was almost completely melted down, when the voltage was reduced to prevent damage to the refractories.

With either the briquetted or sagger-type sponge, there was no difficulty in getting the electrodes to bore down through the charge in the early part of the heat to form a molten pool on the bottom of the furnace, so that melting then proceeded in a normal manner. On the other hand, dense packing of the granular sponge-iron charges made it extremely difficult for the electrodes to work down into the charge, with the result that the bath tended to form on top of the charge. The charge therefore melted slowly and was difficult to melt off the bottom.

The Cranberry, N. C., sagger-type sponge, which was more completely reduced and contained less silica than the Shasta sponge, caused much less difficulty in sticking or bridging. The pigs of this material, as received, were about 20 inches long, and their keying action when charged into a furnace of this size made the charge rather bulky and difficult to work down in the furnace. It was found advisable, therefore, to break the pigs to a length of about 6 inches before being charged so that they could be handled more easily in the furnace. The low specific gravity of this material made it necessary, however, to resort to back-charging when the furnace was operated at full capacity.

The slag volume in melting high-silica sponge irons in a basic furnace is necessarily large and adds to the heating time and power consumption both from power required for melting the slag and because of its action in insulating the bath from the heat of the arcs. The only remedy for this condition is to pour off as much of the slag as possible early in the heat. Naturally, this cannot be done until the slag is molten and the bath level is high enough to allow the slag to run out of the door when the furnace is tilted. In most of the heats very little slag could be poured off until the charge was about two-thirds melted.

The action during the melt-down of a sponge-iron heat differs from that occurring with the ordinary scrap heat. With sponge iron, a vigorous boiling action starts almost with the first formation of molten metal and continues throughout the entire melt-down period. This boiling action tends to limit the amount of power going into the furnace and increases the time required to melt the charge. On the other hand, it insures adequate slag-metal contact and uniformity of bath composition and temperature and should almost completely eliminate undesirable gases in the bath.

Samples taken during the melt-down indicate that when the carbon is placed near the bottom of the charge, the first molten metal formed is very high in carbon. As melting proceeds, the sponge-iron works down into the bath, its iron oxide content acting much the same as an ore addition in boiling out the carbon in the bath. The carbon content of the bath continues to drop until the charge has completely melted.

A log of a typical heat of alloy steel made with briquetted Shasta sponge iron is given in table 46 and serves to illustrate the general progress of the melting and refining of a sponge-iron heat.

POWER CONSUMPTION AND HEAT PERIODS

The furnace could be operated only intermittently, and most of the heats were started with a cold furnace. Seven heats, however, were made with the furnace either at operating temperature from a previous heat or preheated by arcing on pieces of graphite electrode placed on the bottom of the furnace.

Although the data in table 47 indicate that about the same length of time is required for sponge-iron and scrap heats made in a hot furnace, the time required to melt down a sponge-iron charge in a cold furnace was generally 20 to 30 minutes longer than for a scrap heat of similar size, so that under commercial operating conditions the productive capacity of a given furnace, in tons per hour, when melting sponge iron would be possibly 15 percent lower than when melting scrap.

COSTS

Consideration of the cost of melting sponge iron as a substitute for scrap may be based best on the increased operating costs involved in producing a ton of molten steel from a sponge-iron charge as compared with an all-scrap charge. For all practical purposes, cost of refractories, molds, alloying elements, and incidentals should be identical for a given location and type of steel produced. As the time required to make a heat with sponge iron is longer than with scrap, a slightly greater furnace capacity would be required for melting sponge iron. For briquetted sponge iron made from Shasta County, Calif., ore the decrease in furnace capacity amounts to about 15 percent.

In a relatively small steel-making installation such as might be associated with a sponge-iron production plant, this decrease in furnace capacity could be compensated by use of larger furnaces. Thus, for example, where an arc furnace with a shell diameter of 11 feet might be required to produce 25,000 tons of ingots per year from scrap, a furnace with a shell diameter of 12 feet would be required to produce the same quantity when charging 100 percent sponge iron. Under these conditions no additional labor costs would be involved, and the costs shown in table 48 have been calculated on this basis. In a larger plant, where extra furnaces would be required to provide the increased capacity, the extra labor would have to be considered in determining the increased operating costs in melting sponge iron.

When melting scrap, a cost is involved in preparation to make it suitable for charging to the furnace, which is not involved in charging sponge iron, so that the following comparisons are based upon prepared scrap. The estimated extra costs involved in melting briquetted Shasta sponge iron of two different degrees of reduction are shown in table 48. The unit costs are based upon present conditions at the location of the pilot plant.

As 2,409 pounds of lot 1 sponge iron or 2,357 pounds of lot 4 would be required to produce 2,000 pounds of steel at 95-percent recovery of the total iron whereas only 2,105 pounds of scrap would be needed, the value of these two materials as a direct substitute for prepared scrap at $20 per net ton would be $14.20 and $15.17 per net ton, respectively.

If prepared scrap costs $40 per net ton, the value of these two grades of sponge iron as a direct substitute for scrap would then be $31.67 and $33.03 per net ton, respectively.

TABLE 46.—*Log of sponge-iron heat, AISI type 8642 steel*

[Power consumption = 1,117 kw.-hr. per net ton tapped]

CHARGE DATA

Charge materials	Weight, pounds
Lime	300
Briquetted Shasta sponge iron, lot 4 (89.3 percent total Fe, 90.0 percent reduced)	8,000
Carbon briquets (85 percent fixed C)	160
Electrolytic nickel squares	93
Electrolytic manganese	25

Time from power on, hr. min.	Additions and remarks	Weight of addition, pounds	Samples: Metal No.	Samples: Slag No.
0:00	Power on 145 v			
0:25	Change tap 220 v			
0:29	Slag sample			1
0:29 to 1:19	Lime, added 25 to 70 pounds at a time during this period	200		
1:29	Samples		1	2
1:39	Partial slag-off			
1:46	Lime	30		
1:59	Samples, all melted		2	3
2:15	Samples		3	4
2:21	Slag-off			
2:29	Electrolytic Mn added on bare bath	57		
2:29	Second slag-on:			
	Cement clinker	120		
	Coke	15		
2:40	Ferrochrome (70.05 percent Cr)	48		
2:41	Fine 50 percent ferrosilicon	3		
2:41 to 3:59	Fine coke added, 1 to 3 pounds at a time, to condition slag	16		
2:49	Samples		4	5
3:01	Electrolytic nickel	6.5		
3:16	Wash metal (3.5 percent C)	300		
3:17	Electrolytic Mn	4		
3:31	Sample		5	
3:54	Ferromolybdenum (63.3 percent Mo)	26		
3:58	Ferrosilicon lump (50 percent Si)	24		
4:00	Aluminum pig, poled in	5		
4:04	Final furnace sample		6	6
4:05	Tap temperature, 2,935° F. (optical); ladle addition, calcium silicon.	10		

SAMPLE ANALYSES

Sample No.	Metal samples, weight, percent: C	Mn	Si	P	S	Cr	Ni	Mo
1	0.97	0.08			0.062			
2	.41	.07	0.004	0.020	.064			
3	.28	.06	.002	.013	.056			
4	.27	.85			.051		0.44	
5		.90			.031			
6	.45	.91		.015	.019	0.54	.61	0.20
Ladle analysis, average of 3 samples	.44	.88	.37	.015	.020	.54	.60	.23

TABLE 46.—*Log of sponge-iron heat, AISI type 8642 steel*—Continued

SAMPLE ANALYSES—Continued

Sample No.	Slag samples, weight, percent						
	CaO	MgO	SiO_2	Al_2O_3	FeO[a]	MnO	Cr_2O_3
1	40.7		33.4		3.7	5.0	
2					3.7	3.9	
3	38.1	18.6	25.5	9.3	5.5	2.7	
4	42.9	7.7	27.3	10.7	8.2	3.1	
5					1.5	4.1	0.9
6	54.2	7.0	20.4	18.0	.4	.1	.3

[a] Total iron calculated to FeO.

TABLE 47.—*Comparison of power consumption and heat periods in melting sponge iron and scrap, two slag heats*

Charge material	Number of heats	Average weight tapped, net tons	Average time from power on to tap, hr. min.	Average power consumption, kw.-hr. per net ton tapped	Increased power consumption over comparison scrap heat, kw.-hr. per net ton
Small heats charged in cold furnace:					
Shasta briquetted sponge, lots 1, 2, and 3	23	2.427	5:30	1,592	318
Shasta granular sponge	2	2.534	5:38	1,618	344
Scrub Oak granular sponge	1	2.561	5:23	1,476	202
Cranberry sagger sponge, pigs	8	2.513	5:27	1,515	241
Shasta briquetted sponge, lot 5	1	2.380	4:48	1,597	323
Scrap, comparison heats	4	2.630	5:01	1,274	
Large heats charged in cold furnace:					
Shasta briquetted sponge, lots 1, 2, and 3	10	3.414	6:20	1,424	317
Shasta granular sponge	2	3.365	6:38	1,539	432
Cranberry sagger sponge, pigs	1	4.049	7:15	1,346	239
Scrap, comparison heat	1	3.523	4:44	1,107	
Small heats charged in hot furnace:					
Shasta briquetted sponge, lot 2	1	2.341	4:41	1,346	
Shasta briquetted sponge, lot 4	1	2.719	4:32	1,251	
Large heats charged in hot furnace:					
Shasta briquetted sponge, lot 4	3	3.595	[1] 4:40	1,127	198
Scrap, comparison heat	1	3.747	[1] 4:50	929	

[1] Actual time to melt down a scrap charge 20 minutes less than average for 3 sponge-iron heats. Time lost on scrap heat working out carbon before slag-off.

TABLE 48.—*Extra costs for melting 100-percent sponge-iron charge above costs for melting all-scrap charge*

Item and unit cost	Shasta briquetted sponge			
	Lot 1—87.4 percent total iron, 83.2 percent reduced		Lot 4—89.3 percent total iron, 90.9 percent reduced	
	Quantity per net ton tapped	Cost per net ton tapped	Quantity per net ton tapped	Cost per net ton tapped
Extra power at 4 mills per kw.-hr. ... kw.-hr.	300	$1.20	200	$0.80
Flux, lime at $12 per net ton ... pounds	125	.75	125	.75
Reducing agent at $20 per net ton ... do	55	.55	40	.40
Depreciation and interest on difference in cost of plant		.02		.02
Ferromanganese at $168 per gross ton ... pounds	10	.75	10	.75
Extra electrodes at $15 per cwt ... do	4.5	.68	3	.45
Total extra cost per net ton tapped		3.95		3.17

SUMMARY

Operating difficulties increased with increasing gangue and iron oxide content of the sponge iron. Major difficulties experienced were excessive slag volume, violent boiling action during melt-down, and tendency of sponge-iron briquets to weld together at low temperatures, thereby causing the charge to bridge over and stick on the furnace banks. Melting characteristics of briquetted sponge iron were improved by adding enough carbon to the briquets to complete reduction of the iron oxide in the sponge. Sponge iron that had been briquetted was more easily handled and melted than granular sponge or the more porous sagger-type pigs.

Increased costs for production of steel from an all-sponge charge compared to an all-scrap charge are estimated at $3.17 per net ton tapped for a briquetted sponge iron containing 89.3 percent total iron, 90.9 percent reduced, and $3.95 per net ton tapped for sponge iron containing 87.4 percent total iron, 83.2 percent reduced. Value of these two analyses of sponge iron as a direct substitute for prepared scrap at $20 per net ton is calculated at $15.17 and $14.20 per net ton, respectively.

The residual-alloy content of steels produced from sponge iron was considerably lower than that of comparison steels produced from scrap

COMMERCIAL PRODUCTION OF SPONGE IRON

HÖGANÄS PROCESS

A ceramic kiln at Höganäs, Sweden, has been used for about 40 years to make some 10,000 tons of premium-grade sponge iron a year. The kiln, with an effective length of over 900 feet, is ring-shaped and is built underground with two traveling firing zones. Burners and airports are progressively opened and closed to make the burning zones move around the kiln. Saggers are stationary in the kiln and are handled through two loading and two unloading openings. About 3 days is required to heat the saggers to 2,100° F. They are held at this temperature for 80 hours and then cooled. The total cycle is about 12 days.

The Höganäs process requires 14,300,000 B. t. u. per ton of sponge iron. During reduction carbon monoxide and hydrogen are given off from the saggers. By admitting air to the kiln in carefully controlled positions and quantities these gases are burned and provide nearly 98 percent of the heat needed.

In the earlier years of operation the ore, limestone, and coal were placed in alternate layers about 3 inches thick in saggers 14 inches in diameter by 6.5 feet high. In later years the size of the saggers was decreased to 10 to 12 inches in diameter by 10 to 12 inches in height. About 1,000 kg. of coal is used per metric ton of sponge iron produced.

The latest description of the Höganäs procedure [89] shows rectangular cakes, measuring 375 by 250 by 60 mm. (approximately 14¾ by 9¾ by 2¼ inches), obtained by their new method, in which magnetite concentrate formerly charged in alternating horizontal layers is now charged in vertical cakes. Even before the Swedes, the Bureau of Mines adopted canister and pug charging of vertical "pigs" of iron ore surrounded by a reducing mixture containing 15 percent limestone. Eketorp does not mention limestone, probably because the 30 percent ash of Swedish coal contains calcium carbonate; but Tigerschiöld,[90] in his description and cost figures for the early phases of the Höganäs process, gives 190 kg. of limestone to 800 kg. of coke breeze as reducing mixture for 1,420 kg. of 70- to 71-percent magnetite superconcentrate to make 1 metric ton of sponge iron analyzing 96 to 96.5 percent Fe, 1.5 to 2.0 percent O_2, and 1.5 to 2.0 percent gangue.

The greater part of the sponge iron produced at Höganäs is used by the Swedish steel companies making high-quality special steels. Small tonnages were sold in the United States in 1950 at about $83 a ton. Some of the output is used to make powdered iron, which sold for $180 a ton in the United States.

WIBERG PROCESS

Wiberg [91] experimented with the reduction of iron ore by carbon monoxide in a shaft furnace at Woxna, Sweden, in 1920. His results are an important contribution to the application of gaseous reduction to large masses of iron ore.

A furnace of 10,000 metric tons annual capacity has been operated continuously at Söderfors Works, Sweden, since 1941. Sintered Vintjarn ore is used largely, and the average reduction is about 85 percent. No really satisfactory lump ore has been available. Most of the ores available at a reasonable price disintegrate and gradually choke the shaft with fines or soften, stick in the furnace, and form large lumps that will not discharge. The maximum diameter of furnace feed is 2½ inches. It is more economical to use sizes smaller than 2½ inches, as rates of reduction are much slower for larger sizes.

A schematic drawing of a larger plant for producing 60 tons of sponge iron daily is shown in figure 32.

A sealed hopper on top of the furnace holds about 15 tons of feed. A valve between this hopper and the furnace is opened periodically to fill the shaft.

The upper zone of the shaft furnace is a preheater, in which about 25 percent of the spent reducing gas is burned with air to heat the ore to 955°–980° C.

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[89] Eketorp, Sven, [The Höganäs Sponge Iron Process]: Jernkontorets Ann., vol. 129, No. 12, 1945, p. 717 (fig. 13).

[90] Tigerschiöld, Magnus, [The Sponge Iron Problem]: Blad f. Bergshandteringens Vänner, vol. 20, 1932, pp. 219–289.

[91] Wiberg, F. M., Method of and Furnace for Reducing Ores and Oxygen Compounds Utilized as Ores: United States Patent 1,401,222, Dec. 27, 1921.

Améen, Einer, Swedish Sponge Iron: Iron Age, vol. 153, Jan. 20, 1944, pp. 55–59, 150; Jan. 27, 1944, pp. 56–65.

Cavanagh, P. E., Direct Reduction of Canadian Iron Ore in the Wiberg Furnace: Ontario Research Foundation, unpublished manuscript.

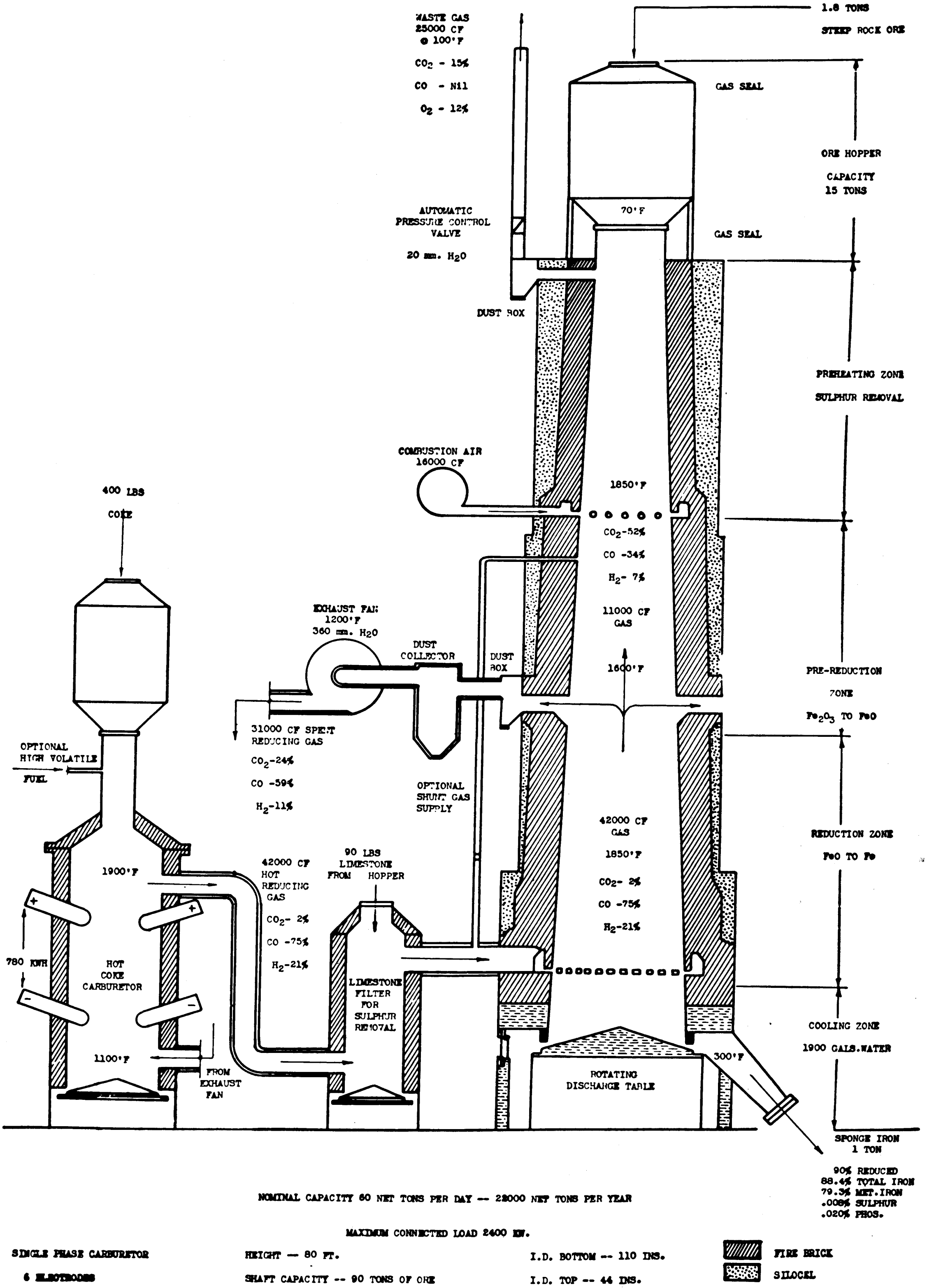

FIGURE 32.—WIBERG FURNACE.

TABLE 49.—*Volume and analyses of gas used in the Wiberg furnace*

Gas to—	Cubic feet per ton of sponge	Temperature, °C.	Analysis, percent				
			CO_2	CO	H_2	N_2	H_2O
Shaft	42, 000	980	2. 0	75. 2	21. 5	1. 0	0. 5
Circulating fan	33, 000	650	23. 9	59. 4	11. 2	1. 0	5. 0
Prereduction zone	9, 000	1, 010	51. 2	33. 0	7. 2	1. 0	9. 0

The preheated ore enters a prereduction zone, where it is reduced to FeO. As the reaction is slightly endothermic, the temperature decreases to about 870° C. Only 25 percent of the reducing gas is passed through the prereduction zone.

The temperature increases in the reduction zone when FeO is reduced to Fe. The sponge iron enters the cooling zone at 955° C. to 1,010° C. If the temperature becomes higher than this, sticking and hanging of the charge occurs with most ores.

The entire column of material in the shaft is supported by a water-cooled, eccentric, rotating table, which discharges sponge iron continuously around the periphery of the shaft. A rotating flat ring transports the sponge iron to a single discharge port.

The discharged sponge-iron is received in an airtight steel can holding about 4 tons. When the can is filled, it is removed and sealed. The cans are used for storage and transportation of the sponge iron to the electric-arc smelting furnace.

The efficiency of the Wiberg process depends on withdrawal and regeneration of the partly spent reducing gas. By withdrawing three-fourths of the reducing gas below the prereduction zone the gas volume in the upper part of the shaft is only slightly greater than that needed for prereduction. The volume of gas withdrawn from the shaft is passed through the electrically heated carburetor, where the CO_2 is converted to CO and the water vapor reacts to form H_2.

The volume and analyses of the gas used in the Wiberg furnace are shown in table 49, and analyses of ores used and of the sponge iron produced are shown in table 50.

TABLE 50.—*Analyses of ores used and of the sponge iron produced in the Wiberg furnace, percent*

Product	Total Fe	Metallic Fe	Reduction to metal	SiO_2	S	P	C	Moisture
Kiruna lump	68. 8	--------	----------	4. 5	0. 042	0. 019	--------	8. 0
Vintjarn sinter	62. 6	--------	----------	10. 5	. 010	--------	--------	--------
Steep Rock	59. 3	--------	----------	6. 0	. 028	. 020	--------	6. 2
Kiruna sponge	92. 6	83. 6	90. 3	3. 8	. 008	. 018	1. 22	--------
Vintjarn sponge	82. 0	71. 5	87. 0	10. 0	. 005	. 015	. 70	--------
Steep Rock sponge	90. 7	85. 5	94. 0	9. 0	. 008	. 020	. 70	--------

MAKING IRON POWDER IN THE TUNNEL KILN

IN GERMANY

Gottschalk[92] reviews reports describing the procedures developed by the Germans[93] for making iron powder.

The descriptions of German methods for making iron powders and their use in the manufacture of shell-rotating bands, as reported by Comstock,[94] Krebs,[95] and Ivery,[96] indicate that the centrifugal powders made by DPG suffered in competition with iron powders made by other methods because of the oxide content unavoidably acquired during manufacture. Apparently, this excess of oxide could not be removed at the rate demanded by the war emergency by reducing in hydrogen; therefore experiments with solid-carbon reduction were made in a ceramic kiln found available at the North German Stoneware Co., Inc., in Bremen.

This Dressler indirectly fired, muffle-type tunnel kiln was 164 feet long and operated with 27 cars 5.68 feet long and 3.28 feet wide, each loaded to a height of 3.61 feet with 60 ceramic saggers. The saggers were approximately 18 inches long, 8½ inches wide, and 8 inches high. The kiln was heated by producer gas having a heating value of about 135 B. t. u. per cubic foot generated from coke in a revolving-grate producer. "Locks" at both ends of the kiln prevented access of air while cars were being pushed in or pulled out.

FINISHING THE REDUCTION OF CENTRIFUGAL POWDERS

Two types of centrifugal powders were studied—SL and S—the former carburized to about 2 percent C and the latter carbon-free. Although the experiments did not include Mannesmann powders, made by quenching a stream of molten iron in steam, it is thought that the procedure for SL and S powders (table 51) is suitable also for finishing the reduction of Mannesmann powders.

The carburized powders are self-reducing; that is, the carbon present is sufficient to reduce the oxide present and yield a product containing less than 0.1 percent C. The carbon-free powders require the addition of 3.3 percent charcoal or 9 percent sawdust before being charged in saggers.

TABLE 51.—*Treatment of SL and S powders*

Carbon, percent	Average peak temperature, °C.	Hours above 800° C.	Percent reduction
1. 69–1. 44	1, 025–1, 110	8. 8–12. 3	97. 4–97. 9
1. 39–1. 32	975–1, 030	9. 3–10. 5	95. 1–96. 8
. 52	1, 055–1, 065	18. 0–19. 0	95. 3–96. 1

Degree of reduction increases with temperature, reaching an optimum at about 1,025° C. It should be stated here that standard specifications allow higher contents of oxygen in reduction powders.

As compared with centrifugal powders, the blocks of reduction powders have a smaller bulk density and are very spongy and hence readily comminuted.

The specific volume, after tapping, decreases with increasing temperature, as desired. At the maximum temperature bulk volumes on tapping were 45 to 50 cc. per 100 grams. Extrapolation indicates that a further increase of 50° C. in maximum temperature should certainly suffice to attain the specified bulk volume of 35 to 40 cc. per 100 grams of reduction powders.

CRUSHING AND GRINDING IRON POWDER

Comstock[97] makes the following statement:

> The annealed powder on being taken from the furnace was in the form of brittle cake. It was broken out from the trays and crushed and sieved in a standard plant embodying jaw crusher, rotary drum pulverizer, and vibratory screen coupled with the usual elevator gear. Unsintered scrap rings were put back into powder form by first breaking in a specially designed crusher and then pulverizing in a standard rotary-type grinder and screening.

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[92] Gottschalk, V. H., Making Iron Powder in the Tunnel Kiln: Bureau of Mines Inf. Circ. 7473, 1948, 16 pp.

[93] Making Iron Powder in the Tunnel Kiln, translated from FIAT microfilm reel H–46, frames 9190–9209, 9280–9299, 9339–9357, and 9377–9384 (PB L 70042), which represent the four original research reports, Nos. 2005, 2008, 2010, and 2012, respectively, of the Metallgesellschaft, Inc.

[94] Comstock, Gregory J., German Powder Metallurgy: FIAT Final Rept. 772 (PB L 39354–R), June 17, 1947, pp. 52–74.

[95] Krebs, Heinrich L., Sintered Iron Shell Rotating Bands: FIAT Final Rept. 979 (PB L 78261), Mar. 19, 1947, 8 pp.

[96] Ivery, W., The Production of Powdered Iron and Sintered Iron Driving Bands in Germany: BIOS Final Rept. 1323 (PB L 79189), January 1945, 120 pp.

[97] See footnote 94.

Krebs[98] describes the powder mill as follows:

> Iron and other metals and alloys which are to be pulverized may be fed into the mill in various forms, such as wire, granules, chips, borings, shavings, turnings, or crushings.
>
> The pulverizer is built on the well-known principle of the beater or hammermill type, in which the resulting particle size is governed by the length of time of treatment and the mesh size of the screen at the discharge end.
>
> The material is introduced into the mill by means of a continuous feeder. Two propellers or beaters, made of hard sintered metals or of manganese steel of great hardness, whirl the metal particles against one another. By this impact they break up into powder form. In order to keep the powder in constant suspension so as to continually expose the powder to the action of the hammer as well as to prevent oxidation from the air, a constant stream of inert gas is fed into the disintegration chamber. Particles of sufficient fineness are continuously discharged through a screen. The shape and size of the particles are governed by the speed and spacing of the hammers. The iron particles have a characteristic disk or plate shape.

Ivery,[99] discussing Mannesmann powders, shows the difference in results when grinding in a mortar and in a small roller mill. According to Ivery, ball milling this type of powder proved unsuitable, and eventually a fluted roller mill, as used with other powders, was adopted.

BUREAU OF MINES EXPERIMENTS

The Bureau of Mines wartime development of the Höganäs process culminated in the adaptation of ceramic tunnel kilns for carrying out the solid-carbon reduction of iron ores, and comparison with the German technique should further advance the art.

The Bureau of Mines made sponge iron from magnetite concentrate in a 200-foot tunnel kiln using time cycles ranging from 58 to 80 hours, distributed as follows:

Heating	hours	12
Reduction period (that is, time above 900° C.)	hours	34–48
Cooling	do	12–20
Maximum temperature	°C	1, 120–1, 150

Comparison of the results of experiments in the Bremen kiln with those obtained by the Bureau of Mines indicates that the sponge-iron pigs made by the Bureau could be crushed and ground to powder suitable for powder metallurgical purposes.

Producers of magnetite concentrates might well consider the production of iron powder in tunnel kilns according to the procedure described under Manufacture of Sponge Iron in Ceramic Kilns (pp. 69–96).

Where magnetite ore is already being beneficiated by magnetic separators, the installation of a 300- to 500-foot direct-fired tunnel kiln having a maximum daily capacity of 35 to 60 tons of sponge iron could meet a possible future demand for 5- to 6-cent (per pound) iron powder suitable for making articles by powder metallurgical methods. The ease of procuring cheap coke breeze or cheap Buckwheat anthracite, both of which have proved satisfactory for solid-fuel reduction of magnetite, and the indicated possibilities for further mechanization of tunnel-kiln procedure are factors favorable to the economics of such production, however difficult and costly the final crushing and grinding of sponge-iron pigs may prove to be. The spread between prices of highest quality Swedish sponge iron ($73 a ton) and 9-cent Swedish iron powder ($180 a ton) would seem to be wide enough to cover costs of comminution and of making a special superconcentrate by using the rotating-field magnetic separator.

INVESTIGATION BY ONTARIO RESEARCH FOUNDATION

Beginning in 1946, the Ontario Research Foundation[1] made a thorough investigation of possible methods of relieving the serious shortage of scrap that existed in Canada at that time. Available information concerning the successful commercial plant in Sweden, experimental work in Germany during the war, and experimental work in the United States up to 1946 was studied. Much of this information has been published.[2] Laboratory- and plant-scale experiments were conducted to determine:

1. How to make sponge iron in existing brickkilns with minimum expenditure for extra equipment.
2. Improvements that could be made to insure production of high-grade sponge iron in specially designed equipment.
3. Whether sponge iron suitable for iron powder could be produced.
4. Time needed to reach production stage.

IMPROVED CHARGING METHODS

The canister-charging method used by the Bureau of Mines was improved to permit automatic charging of wedge-shaped ore columns around a central core of reducing mixture. The outer and thicker part of each ore column was heated first and maintained at reduction temperature for a longer time. Since there is no ore

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[98] See footnote 95.

[99] See footnote 96.

[1] Cavanagh, P. E., The Tunnel Kiln Sponge Iron Process: Ontario Research Foundation, unpublished manuscript. (Used by permission.)

[2] Cavanagh, P. E., Economics of Ferrous Smelting in Canada: Trans. Canadian Inst. Min. and Met., vol. 60, 1948, pp. 205–212. Manufacture of Sponge Iron in Kilns: Jour. Canadian Ceram. Soc., vol. 17, 1948, p. 77. Commercial Production of Sponge Iron: Iron Age, vol. 163, No. 21, 1949, pp. 67–71, 82.

in the center of the sagger, heat penetration into the ore is more rapid, and reduction is uniform throughout the ore column.

Development in the United States of a vacuum extrusion machine, which delivers the extruded column downward, permits a further improved charging method: A hollow, cylindrical assembly of wedge-shaped columns connected at the thicker outer part of each column may be extruded direct into a sagger placed below the extruder and automatically cut off. Such an assembly of columns will stand alone in the sagger. The sagger may then be moved automatically to a charging bin and filled with reducing mixture.

Extrusion charging increases the production of sponge iron from the same sagger volume; because the surface of the ore mass is smooth, there is less tendency for the reducing mixture to stick to the surface of the resulting sponge iron.

Table 52 shows the effect of the charging method on the density of iron oxide charges.

Sponge iron can be produced in the normal cycle used in firing brick in standard tunnel kilns. Also existing brickkilns can be converted quickly to making sponge iron. If proper materials are charged into the kiln, a satisfactory sponge iron is sure to be produced.

A rough estimate of the cost of producing sponge iron in a tunnel kiln is the production cost of a ton of brick made in the same kiln plus the cost of the ore and the cost of the saggers per ton of sponge iron. Five dollars may be considered a conservative estimate of sagger cost per ton of sponge iron.

TABLE 52.—*Effect of charging method on density of iron oxide charges*

Iron oxide	Density		
	Canister		Extrusion
	Loose	Vibrated	
Mill scale, minus-80-mesh	2. 02	3. 05	3. 9
Magnetite, minus-80-mesh	2. 40	3. 05	4. 0
Hematite, minus-20-mesh	1. 50	1. 70	3. 1

SUMMARY OF IRON-POWDER PRODUCTION

The results of this investigation show:

1. The tunnel-kiln process is a method for producing relatively large tonnages of sponge iron suitable for processing into iron powder.
2. The purity and properties of iron powder depend mainly on the iron oxide material used.
3. Lower reduction temperature is advantageous. At 1,950° F. the particles of reduced iron oxide do not sinter together strongly. The soft, crumbly cakes of sponge iron are easily broken in a hammermill into particles corresponding in size to the original iron oxide particles.
4. Raw iron oxide material can be ground more cheaply and easily to a size finer than the required iron-powder grain size than hard sponge-iron cakes can be ground to specified grain size.
5. It is more economical to produce sponge iron about 95 to 97 percent reduced in the tunnel kiln and to finish reduction in the annealing process.
6. Iron powder made in Canada by this method compares in quality to Swedish powder selling in New York at 50 percent above the cost of Canadian powder.

IRON-POWDER INDUSTRY

The use of iron powder by chemical and metallurgical industries has greatly increased during the past few years. The National Bureau of Standards[3] has published a list of 2,253 United States patents, up to January 1, 1947, pertaining to powder metallurgy. They are classified under four main headings: Production, handling and working, alloying, and applications.

The greater part of the iron powder used in the United States in 1950 was supplied by a Swedish firm at Höganäs, Sweden. It was made by processing sponge iron produced from magnetite superconcentrates in a large brick-kiln. The balance was supplied by several smaller companies in North America, each using a different method of manufacture; the largest producer used a two-diameter rotary kiln to make sponge iron from mill scale. The sponge iron was processed to make iron powder.

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[3] National Bureau of Standards, United States Patents on Powder Metallurgy: Pub. M 184. (Obtainable from Superintendent of Documents, Washington, D. C.)

SPONGE IRON AS A CHEMICAL REAGENT

That sponge iron may be widely used in certain chemical and metallurgical operations that require finely divided metallic iron of high porosity and strong chemical reactivity is conceivable. Sponge iron has many advantages as a precipitant of metals from solution. Such use in copper metallurgy has been advocated for many years,[4] and interest in it has been revived recently.[5] The probable expansion of the practice of leaching copper ore in place,[6] developed successfully by the Ohio Copper Co. in Utah and by the Shannon Copper Co. in Arizona, will increase the use of iron as a precipitant. The successful commercial use by the Tintic Standard Mining Co., at Harold, Utah,[7] of the Holt-Dern process for lead-copper-silver ores has increased the use of metallic iron for precipitating lead from solution in recent years.

Steel scrap is now being used as a precipitant; whether sponge iron will displace it will depend on the relative costs and economic value of the two forms of iron. Steel scrap is relatively expensive at many ore-reduction plants, because they are so far from scrap-producing centers. On the other hand, steel scrap is relatively cheap in some parts of the West, where there are no steel mills, the great consumers of scrap. As the western steel industry develops, the demand for and the price of steel scrap will increase. That place value of steel scrap is now gradually increasing is evidenced by a study of western scrap prices during the past 15 years. The cost of scrap at steel plants maintains a rather definite relation to the cost of pig iron. In eastern steel centers the difference in cost per ton is only $2 or $3. In the West this margin is, of course, wider, but it is becoming narrower. Certain classes of steel scrap, such as can clippings, used cans, and other so-called low-grade scrap, are disproportionately low-priced, but this decided advantage will diminish as the western iron and steel industry grows.

The use of a large tonnage of sponge iron—for example, 50 tons a day—in a plant or a district where cheap ore and fuel are available should allow sponge iron to be produced more cheaply per unit of iron than steel scrap. Conceivably, too, the savings in labor, floor space, and equipment might easily make the use of sponge iron profitable, even though its iron was more expensive than steel scrap. Against these advantages must be weighed the disadvantage of producing a lower-grade precipitate from sponge iron than is made in good practice from scrap. The metallic-iron content of sponge iron will vary with the grade of ore used but as a rule will range from 75 to 85 percent. In consequence, foreign material amounting to 15 to 25 percent of the sponge iron used will be introduced into the precipitate.

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[4] Lunge, George, Manufacture of Sulfuric Acid and Alkali, with the Collateral Branches: New York, vol. 1, pt. 3, 1913, pp. 1506–1516.

Greenawalt, W. E., Hydrometallurgy of Copper: New York, 1912, pp. 273–277.

Croasdale, Stuart, Leaching Experiments on Ajo Ores: Trans. Am. Inst. Min. Eng., vol. 49, 1914, pp. 610–658.

Laist, F., and Frick, F. F., Precipitation of Copper from Solution at Anaconda: Trans. Am. Inst. Min. Eng., vol. 49, 1914, pp. 694–700.

[5] van Barneveld, C. E., and Leaver, E. S., Leaching Nonsulfide Copper Ores with Sulfur Dioxide: Bureau of Mines Tech. Paper 312, 1923, p. 87.

Richard, T. A., The Chino Enterprise: Eng. and Min. Jour.-Press, vol. 117, 1924, pp. 13–20.

Oldright, G. L., Keyes, H. E., and Wartman, F. S., Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas: Trans. Am. Inst. Min. and Met. Eng., vol. 73, 1926, pp. 84–98; discussion, pp. 98–107.

[6] Oldright, G. L., Leached Areas of Ohio Copper Mines, Bingham Canyon, Utah: Min. and Met., vol. 4, 1923, pp. 518–521.

Anderson, A. E., and Cameron, F. K., Recovery of Copper by Leaching, Ohio Copper Co. of Utah: Trans. Am. Inst. Min. and Met. Eng., vol. 73, 1926, pp. 31–55; discussion, pp. 55–57.

Engineering and Mining Journal-Press, Roasting and Leaching Without Mining: Vol. 120, 1925, p. 722.

[7] Allen, H. P., and Madge, W. C., Chloridizing Mill of the Standard Reduction Co.: Trans. Am. Inst. Min. and Met. Eng., vol. 73, 1926, pp. 317–338; discussion, pp. 338–341.

Ralston, Oliver C., Hydrometallurgy of Lead: Trans. Am. Inst. Min. and Met. Eng., vol. 70, 1924, pp. 447–466; discussion, pp. 466–470.

PRECIPITATION OF COPPER

The Chino Copper Co. experimented with sponge iron to determine whether it could be used to precipitate copper from solutions obtained by treating pulp containing sulfide and carbonate ores with sulfuric acid. The metallic copper and undissolved copper sulfide were recovered by froth flotation.

H. E. Keyes and W. A. Sloan, of the Bureau of Mines, have experimented with sponge iron as a precipitant of copper. The following conclusions are taken from their report:

1. Tests comparing sponge iron with detinned tin-plate scrap and massive steel scrap showed that sponge iron is a rapid and efficient precipitant; the resultant cement copper quickly settles and is finely divided as compared with the product from scrap iron. Under favorable conditions the precipitated copper can be recovered by flotation. Detinned tin-plate scrap is slower in its action than sponge iron but produces a pure, high-grade copper precipitate. Massive steel scrap is extremely slow as a copper precipitant; its surface soon becomes covered with a plating of copper, which greatly retards further action and must be removed frequently. Sponge iron made in an indirect-fired muffle was more active than most of the samples made in the direct-fired kiln, although under some conditions the direct-fired kiln gave a sponge iron that appeared to be as chemically active as that from a muffle-type furnace and to yield as high-grade cement copper.

One test with excess iron in a copper sulfate solution containing 4.87 percent Cu and 0.22 percent H_2SO_4 gave the following schedule for complete precipitation of the copper: Sponge iron No. 1, 14 minutes; sponge iron No. 2, 20 minutes; and detinned scrap, 45 minutes. With massive steel scrap, precipitation virtually ceased in 3 hours, and only 10 percent of the copper was precipitated. Another test with 20 percent excess metallic iron in a solution containing 4 percent Cu and 0.20 percent H_2SO_4 gave the following quantities of metallic iron that had been replaced in given time intervals: Sponge iron No. 1, 96.4 percent in 8 minutes; sponge iron No. 2, 82.2 percent in 10 minutes; detinned scrap, 99.8 percent in 75 minutes; and massive steel scrap, 29.3 percent in 3 hours. Sponge iron No. 1 was produced by indirect firing in a muffle-type furnace, and sponge iron No. 2 was made in the direct-fired kiln. The slightly slower precipitation rate of the direct-fired product was due to its having denser and slightly rounded particles of metallic iron. Smaller size particles of ore were used to produce the indirect-fired product; this fact probably accounts for its greater porosity.

2. Results showed that the theoretical quantity of copper could not be precipitated by sponge iron unless the acid concentration of the solution was 0.05 to 0.1 percent H_2SO_4. An increase of acid caused re-solution losses when the precipitation was so conducted that atmospheric oxidation of the cement copper was permitted. Under these conditions a solution containing 2 percent copper showed less effect of varying acidity than did a solution with higher or lower initial concentration of copper. Furthermore, for a short precipitation period (6 minutes or less in these tests) the maximum percentage of copper was precipitated from solutions containing 2 percent copper, regardless of acid strength. In later tests, however, when atmospheric oxidation of the precipitate was inhibited, re-solution was considerably minimized; therefore the above conclusions would have to be modified if oxidation of cement copper could be prevented by type of precipitator.

3. In using batch processes for complete precipitation an excess of at least 7.5 percent of active sponge iron must be used and the temperature allowed to rise to at least 50° C. A larger excess would be required if a lower temperature or less active sponge iron was used. In a continuous precipitation process use of the countercurrent principle would produce a higher grade of copper precipitate and avoid loss of copper in the discard solution through excess acid or ferric sulfate.

4. The rate of precipitation was greatly accelerated by increasing the temperature.

PRECIPITATION OF LEAD

COMMERCIAL OPERATIONS

At the Tintic Standard mill detinned tin-plate scrap is used to precipitate lead in the treatment of brine solutions resulting from chloridizing, roasting, and leaching operations.[8] The solution that results from leaching contains 2 to 5 pounds H_2SO_4 per ton, 12 to 15 percent chlorine as chloride, 0.5 to 1.5 percent lead, and 0.1 percent copper. It is first agitated with sponge copper to precipitate the silver, then passed over tin-plate cuttings to recover the copper, and finally heated to 75° C. and passed through other boxes containing tin-plate cuttings to precipitate the lead. The

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[8] Allen, H. P., and Madge, W. C., Chloridizing Mill of the Standard Reduction Co.: Trans. Am. Inst. Min. and Met. Eng., vol. 73, 1926, pp. 317-338; discussion, pp. 338-341.

boxes are kept as full as possible of cuttings, and 2 of the 15 boxes are cleaned each day. The cuttings are removed and washed, while the precipitate is sluiced to a drain box and recovered, without further drying, for shipment to the smelter.

Best results are obtained when the tin-plate scrap has been detinned and the solution is kept at 75° C. during precipitation of the lead. Massive forms of iron or steel scrap used earlier were slower and harder to clean than the detinned scrap. Even with detinned cuttings, removal of the metallic precipitate is tedious and costly. The precipitate contains about 70 percent lead, 5 percent copper, 5 percent iron, and 20 percent water.

To avoid the necessity of using such hot solutions (about 75° C.) and to eliminate the costly cleaning required when heavy scrap was the precipitant, T. P. Holt, of the Tintic Milling Co., experimented with sponge iron and later used it commercially for several months. The sponge iron was made in a direct-fired kiln. (See Operation of a 2½-Ton Furnace, p. 26.) After leaching, the solution—which had about the same composition as that used at the Tintic Standard plant—was freed of most of its gold, silver, and copper; it was then passed to three sponge-iron precipitation boxes placed in series.

Each box was 50 feet long, 4 feet 8 inches wide, and 4 feet deep. About 12 inches from the floor a filter bottom was built of 2- by 2-inch boards placed together cornerwise with wooden strips 1 by ¾ inch on top and running lengthwise of the box to act as shoveling guides when sponge lead was removed from the boxes. Sized hematite placed on this form, level with the top of the shoveling guides, was the filtering medium. A layer of sponge iron topped the bed of ore. The solution passed through the sponge iron by downward percolation and circulated through the three boxes in a countercurrent manner, the rich solution passing first through the nearly spent precipitant.

Lead was precipitated rather rapidly at normal temperatures, and work continued for a long time at a solution temperature of 32° C.; better results, however, were obtained by heating to 40° C. Most of the heat required for this higher temperature was obtained from the waste gases from the sponge-iron furnace. A precipitate containing 40 percent lead and 20 percent iron was ordinarily obtained, but at times products were made containing more than 60 percent lead. The plant was shut down before entirely satisfactory methods of precipitation could be developed.

EXPERIMENTAL WORK

After Holt finished the work described, Oldright and Miller,[9] of the Bureau of Mines, experimented with sponge iron as a precipitant of lead, obtained fundamental information relative to the rates of precipitation under various conditions, and developed apparatus in which precipitation can be conducted rapidly and efficiently. The experiments demonstrated that sponge iron could be used successfully in precipitating lead from large quantities of solutions, and the grade of precipitate, consumption of iron, and operating conditions made the precipitation of lead by sponge iron desirable.

The precipitator, patterned after the MacDougall roasting furnace, consisted of a cylindrical shell containing seven floors or hearths on which the sponge iron was agitated by rabble arms attached to a vertical shaft at the middle of the shell. The sponge iron passed downward over the seven floors, where it was gradually replaced by lead and other precipitated metals from the solution moving upward through the precipitator.

After preliminary experiments in the laboratory of the Intermountain Experiment Station the small precipitator was operated almost continuously for 15 days at the Tintic Standard plant, using part of the regular mill solution as it flowed to the lead-precipitation boxes. Although the precipitation of lead was satisfactory at ordinary temperatures, the rate was increased materially by raising the temperature of the solution. The capacity of the precipitator was increased 30 percent by raising the temperature from 60° to 70° C., and operators at the Tintic Standard plant found that best results were obtained when leaching was done with solutions coming from the lead-precipitation boxes at temperatures of 55° to 70° C.; at lower temperatures the rates of percolation and solution were too low. Therefore, in these later tests the solution in the precipitator was kept within the range of 60° to 75° C.

The results indicated that the method is suitable for large-scale work. Solution was treated at the rate of 1 liter a minute. Calculations showed that one multiple-floor precipitator 20 feet in diameter would be large enough to treat the 1,000 tons of solution now going to the 15 lead-precipitation boxes daily. These boxes are 5 feet wide, 30 feet long, and 18 inches to 3 feet deep.

In this type of precipitator the lead is precipitated on the sponge iron in the form of

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[9] Oldright, G. L., Keyes, H. E., Miller, Virgil, and Sloan, W. A., Precipitation of Lead and Copper from Solutions on Sponge Iron: Bureau of Mines Bull. 281, 1928, 131 pp.; Rept. of Investigations 2812, 1927, 4 pp.

small, hard granules and does not stick or ball when being handled. Lead that had been precipitated with sponge iron in other types of precipitators, such as launders, rotating cylinders, gravity percolators (upward or downward), and air-stirred agitators, was always matted or balled and hard to handle.

The MacDougall-type precipitator is automatic, easy to operate, and does not require laborious handling of materials. The precipitate and the barren solution are of uniform composition. When excess sponge iron was used and all the lead was removed from the solution, the precipitate contained about 70 percent lead; but when all the metallic iron was replaced and 80 to 90 percent of the lead was recovered, the lead product contained 79.5 percent lead, 7 percent copper, 9.3 percent total iron, 0.9 percent metallic iron, and 3 percent insoluble.

OTHER USES OF SPONGE IRON

Other uses of sponge iron probably will be developed once production has been established on a large scale. Some experiments have been made to determine whether sponge iron can be used for the production of hydrogen from steam—the iron oxide formed in the process to be converted to sponge iron.[10]

Interest is also being shown in the possibility of using sponge iron in place of the more common forms of finely divided iron as a reagent in processes of organic chemistry; the iron oxide formed as a result of the reduction reaction, now a waste product, would be converted to sponge iron and thus used again.

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[10] Jaubert, G. F., Hydrogen by Autocombustion: United States Patent 1,040,204, Oct. 1, 1912.
Keller, Hans, Producing Hydrogen: United States Patent 1,286,650, Dec. 3, 1918.
Abbott, L. S., Process of and Apparatus for Producing Hydrogen: United States Patent 1,345,905, July 6, 1920.
Bray, S. W., and Balfour, I. H., Manufacturing of Hydrogen: United States Patent 1,360,876, Nov. 30, 1920.

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