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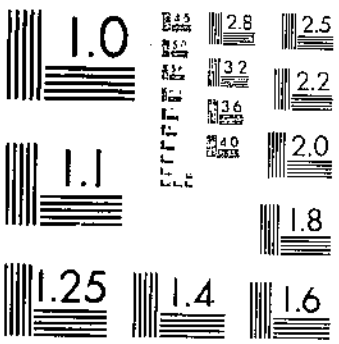
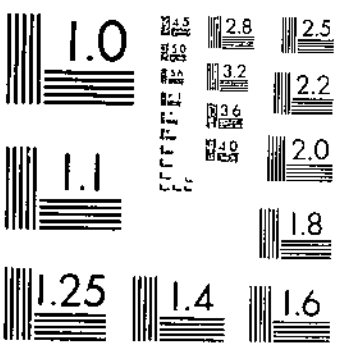



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

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Technical Bulletin No. 543 April 1937

UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

# BLAST-FURNACE PROCESSES FOR THE PRODUCTION OF PHOSPHATIC AND POTASSIC FERTILIZER MATERIALS

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CONTENTS



## INTRODUCTION

For more than 2 decades the Department of Agriculture has been investigating methods for the production of fertilizer materials that contain nitrogen, phosphorus, and potassium. An important object

[1] The experimental data of this report were obtained under the supervision and direction of P. H. Royster, who was directly in charge of the Bureau's blast-furnace operations. J. W. Turrentine, in charge of the Bureau's potash investigations, initiated the potash phase of this work and in conjunction with P. H. Royster was responsible for its direction. K. G. Clark, who was assistant in charge of the blast-furnace project, is responsible for the compilation and correlation of the data and the writing of this bulletin. The authors express to the American Agricultural Chemical Co. their appreciation for several tons of washed Florida land-pebble phosphate supplied free of charge at Alexandria, Va.; to the Armour Fertilizer Works for a carload of Tennessee blue-rock phosphate supplied free of charge at Washington, D. C.; to the International Agricultural Corporation for 2 carloads of Florida pebble phosphate matrix supplied free of charge at Mulberry, Fla.; to the Chicago & North Western Railway Co. for the free transportation of a carload of wyomingite from Council Bluffs, Iowa, to Chicago, Ill.; to the National Carbon Co., Inc., for a carbon-precipitator tube supplied free of charge at Washington, D. C.; to the Research Corporation for the use of a high-tension transformer and mechanical rectifier; to the Union Pacific Coal Co. for a carload of Rock Springs coal supplied free of charge at Rock Springs, Wyo.; to the Union Pacific Railroad Co. for permission to mine the wyomingite at Zirkel Mesa and for the free transportation of 2 carloads of wyomingite from Superior, Wyo., and 1 carload of Rock Springs coal from Rock Springs, Wyo., to Council Bluffs, Iowa; to F. G. Cottrell for his many helpful suggestions throughout the course of the investigation; to Mrs. C. E. Rist for the slag analyses; and to C. H. Kunsman, K. D. Jacob, and A. R. Merz for criticism of the manuscript.

[2] This investigation was carried out with funds supplied in part by the Winter Act, 70th Cong., 2d sess., Public, No. 781, and in part by funds appropriated to the Department of Agriculture for fertilizer investigations.

of the investigations is to assist in the development of improved methods for the commercial production of fertilizer materials. The present bulletin describes a phase of this research concerned with an investigation, by means of small-scale apparatus, of the technical feasibility and commercial practicability of producing phosphatic and potassic fertilizer materials by blast-furnace processes.

Extensive deposits of phosphate ores that contain sufficient phosphorus to be considered commercial sources of fertilizer occur in Florida and Tennessee. As the phosphate occurs in the ground, from 5 to 12 tons of material must be mined for each ton of phosphorus pentoxide ($P_2O_5$) obtained. More extensive and in general higher grade deposits occur in Idaho, Montana, Utah, and Wyoming. These deposits yield ores that contain approximately 25 to 35 percent $P_2O_5$ as mined. The present market for fertilizer in this country, however, is so largely centered in the Southern and in the Middle Atlantic States (*13*, *44a*)[3] that the cost of rail transportation from the western fields to the present eastern market has limited the development of these deposits.

Potash-bearing silicates in sufficient quantities to merit consideration as sources of potash are widely distributed in the United States. Notable among the deposits are the leucitic rocks of Wyoming, the greensands of New Jersey, and the shales of Georgia. The potash ($K_2O$) content of these rocks ranges from 3 to 7 percent in Georgia shale, from 4 to 7 percent in New Jersey greensands, and from 8 to 12 percent in wyomingite (*72*). The principal remaining constituents are largely silica, alumina, and iron, with smaller amounts of lime and magnesia. Each ton of $K_2O$ is accompanied, therefore, by from 7 to 32 tons of materials that must be mined, handled, treated, and discarded as waste or converted to marketable byproducts in any process proposed for potash production.

In attempting to develop an improved process for the commercial production of marketable phosphate or potash from the minerals available, the large tonnage of raw materials to be handled assumes primary importance. This is one of the reasons that the blast furnace was so early and so frequently suggested as an apparatus for the possible production of phosphates and potash. The blast furnace (*33*) as such has been used for many centuries for the production of pig iron, and more recently in a smaller way for the production of manganese alloys. The modern blast furnace is chiefly characterized by its ability to smelt enormous tonnages of raw materials at a low labor cost and with a relatively inexpensive fuel. In such a smelting process the volatile constituents of the charge are removed from the furnace in the exhaust gas; the reducible oxides in the charge are reduced to their respective chemical elements; and the irreducible oxides are converted into molten slag and discharged from the bottom of the furnace in the liquid state. The blast furnace thus provides a general furnace process adapted to volatilization, reduction, and melting.

Shortly after the Bureau of Chemistry and Soils was established in 1927, investigations of blast-furnace methods for the smelting of phosphate rock and potash minerals were undertaken. These investigations were continued until October 1933. From October 1933 to April 1934 the experiments on phosphate smelting were continued by the Tennessee Valley Authority, with use of the Bureau's personnel

[3] Italic numbers in parentheses refer to Literature Cited, p. 67.

and equipment. The blast-furnace experiments reported here cover the results obtained prior to October 1933.

## WORK OF OTHER INVESTIGATORS

### PHOSPHATE SMELTING

The proposal to smelt phosphate rock in the blast furnace for the production of elementary phosphorus was made as early as 1868 by Brison (*5*). From this date on, patents covering various furnace processes for the production of phosphorus and phosphoric acid have appeared with considerable frequency (*57, 74, 75*).

In 1915 the Bureau of Soils initiated an investigation of electric-furnace processes for the smelting of phosphate rock, and in 1916, in cooperation with the R. B. Davis Co., erected a semicommercial plant for the production of phosphoric acid (*9, 76*). In 1920–21 the first commercial furnace for the production of this acid was installed by the Federal Phosphorus Co. at Anniston, Ala. (*37, 38, 60*). So far as the writers know, the first attempt actually to smelt phosphate rock in a fuel furnace for the production of phosphorus or phosphoric acid was undertaken experimentally by the Bureau of Soils nearly half a century after Brison's proposal. The results of these experiments were reported by Waggaman, Easterwood, and Turley in 1923 (*75*). Although these results were not sufficiently conclusive to point the way immediately to the commercial adoption of furnace smelting as an economic process, sufficient progress was made to indicate the desirability of continuing and extending the investigation.

Easterwood (*14, 15*) reported that the experimental smelting of phosphate rock in the blast furnace was undertaken by the Victor Chemical Works at Chicago Heights, Ill., in 1924 and that a commercial installation was put in operation at Nashville, Tenn., in 1929. This installation was later replaced by a larger and improved plant. The Coronet Phosphate Co. constructed a blast-furnace plant at Pembroke, Fla., in 1931 (*73*), which has not been in operation since shortly after completion.

### POTASH AND COMBINED POTASH-PHOSPHATE SMELTING

The recovery of potash from relatively low-grade potash-bearing silicate rocks has also long been a subject of interest. Tilghman (*70, 71*), Blackmore (*4*), Rhodin (*55, 56*), McKee (*40*), and Cushmann (*12*) proposed producing water-soluble potash salts by fusion of naturally occurring potash rocks with lime and sodium or calcium chloride. In these processes the potash salt was to be recovered by leaching the cooled melt. Barclay and Simpson (*2*) proposed the recovery of potash salts from the fume collected from coke-fed furnaces.

In 1910–11 the Riverside Portland Cement Co., at Riverside, Calif., began the collection of fume from cement-kiln stacks and the recovery of its potash content (*62*). In 1911 Herstein (*27*) suggested producing cement from feldspar, limestone, and calcium chloride, and recovering potassium chloride from the fume collected. Later Brown (*6, 7, 8*), Spencer (*64, 65, 66, 67*), Ellis (*20*), Huber and Reath (*29*), Spackman and Conwell (*63*), Eckel and Spencer (*18*), and Spencer and Eckel (*68*) obtained patents on processes for the simultaneous production of cement and recovery of volatilized potash salts. These

processes consisted of calcining mixtures of feldspar and limestone with either calcium chloride or calcium fluoride.

In 1917 Chance (*10, 11*), in experimenting with one of the furnaces of the North Lincolnshire Iron Co., Ltd., reported data to show that the addition of sodium chloride to the charge or burden of iron furnaces increased the volatilization of potash. In Canada, Grauel (*1, 23, 24*) investigated the smelting of feldspar, coke, and limestone with calcium chloride or calcium sulphate in a blast furnace for the volatilization of the chloride or sulphate of potassium.

The suggestion to effect the simultaneous reduction of phosphates and volatilization of potash by smelting mixtures of phosphatic and potassic minerals was proposed in a patent issued to Hechenbleikner in 1929 (*25*). Data obtained from laboratory investigations of the simultaneous reduction of phosphate rock and the volatilization of potash from Georgia shale were reported by Ross, Mehring, and Jones (*58*) of the Bureau of Soils in 1924. In 1930 Pike (*50, 51, 52*) reported an investigation of the combined potash-phosphate blast-furnace process. He obtained patents (*53*) on such a process that used an oxygen-enriched cold blast, and believed the process would be economically attractive if oxygen could be obtained at $10 a ton.

## GENERAL FEATURES OF A BLAST FURNACE

### FURNACE STACK

The modern blast furnace as it is known today in the iron and steel industry is a vertical, cylindrical stack from 85 to 95 feet in effective height and from 20 to 30 feet in diameter. The shell is constructed of steel and is lined with firebrick. Air preheated to 800° to 1,600° F.[3a] and under a pressure of from 10 to 20 pounds per square inch is blown into the lower part of this shaft through from 10 to 16 water-cooled nozzles or tuyères. The amount of blast varies with the size of the furnace and ranges from 25,000 to 100,000 cubic feet per minute.

When in operation the furnace is kept filled from top to bottom with a charge of fuel, flux, and ore. These materials are charged into the furnace at the top in separate layers at frequent intervals. The fuel, almost invariably coke, is ignited at the blast entrance, where it is burned to produce a high temperature. The products of this combustion consist essentially of 35 percent of carbon monoxide and 65 percent of nitrogen diluted with from 1 to 2.5 percent of hydrogen, resulting from the variable amount of moisture contained in the air. When the fuel used is "run-of-the-oven" coke with a mean lump diameter of 5 to 10 inches, combustion is complete within 28 to 34 inches of the blast entrance (*35, 36, 48*).

During normal operation of the blast furnace the solids charged into the furnace descend continuously as the coke is burned by the blast while the mineral constituents of the charge are either reduced or are fused into slag. The hot gases that result from the combustion of the fuel flow continuously upward through the furnace and heat the descending charge. These gases are removed from the open space above the charge level or stock line through an exhaust pipe which is usually called the "downcomer." This continual passage upward of a stream of initially hot gas and the continual downward descent of an initially cold charge of solid particles constitutes one of the earliest examples of so-called countercurrent heat exchange.

[3a] Centigrade equivalents of Fahrenheit temperatures are tabulated on p. 72.

The upper and relatively cooler section of the furnace is termed the shaft. It is here that calcination of the carbonates and vaporization of the moisture in the charge occur, and, in iron smelting, that a large part of the ore is reduced by the carbon monoxide of the ascending gases.

Immediately below the shaft is a water-cooled section of an inverted cone, from 10 to 12 feet in height, called the "bosh", at the base of which the blast is admitted through the tuyères. In this section the reduction of the iron oxide is completed largely by solid carbon. The liquid metal formed flows downward to the bottom of the furnace, where it is retained as a bath of molten pig iron. At the same time the irreducible oxide constituents of the furnace are converted into a fluid slag which also flows downward, forming a slag bath, which floats on the metallic bath.

The portion of the furnace below the blast entrances, in which the molten metal and slag are collected and from which they are removed at regular intervals, is called variously the "crucible" or "hearth." It is usually from 6 to 8 feet in vertical height.

### MECHANISM OF COMBUSTION

The composition of the gas flowing through the interstices between the lumps of coke located nearest the blast entrance has been investigated by Perrott and Kinney (*48*), and Kinney, Royster, and Joseph (*36*) of the United States Bureau of Mines.

The investigations showed that as the oxygen concentration of the gas decreased the carbon dioxide concentration increased and reached a maximum at a point about 18 inches from the nose of the tuyère. From this point both the carbon dioxide and the oxygen concentration of the gas decreased with a corresponding increase in carbon monoxide until the gas consisted of carbon monoxide and nitrogen diluted with a small amount of hydrogen. The oxygen was found to have vanished at about 30 inches and the carbon dioxide at about 40 inches from the tuyère. More recently Eichenberg and Eilender (*19*) have found that the extent of the combustion zone increased slightly with increases of both the temperature and the rate of flow of the blast. It is evident from these investigations that the combustion process is completed in a relatively small portion of the furnace and that the blast furnace as a whole may be considered completely reducing in character.

Perrott and Kinney (*48*) and Kinney, Royster, and Joseph (*36*) found that, other factors being constant, the rate of disappearance of oxygen is dependent upon the effective surface exposed. This in turn depends largely on the size of the coke. Small coke not only presents a greater surface area per unit of volume but has narrower interstices between the lumps than large coke. When using small coke the combustion process is completed, therefore, in a smaller volume.

Since commercial furnaces operate on 5- to 10-inch diameter coke it is estimated that the combustion zone in a furnace using 1-inch coke would extend only 8 to 10 inches from the nose of the tuyère.

### TEMPERATURE OF COMBUSTION ZONE

It has not been found possible directly to measure the temperature existing in the combustion zone of a blast furnace. It is, of course, possible to sight an optical pyrometer down the hot-blast blowpipe and

to read the black-body temperature of the outwardly directed half of the coke lump lying immediately adjacent to the blast entrance. A very small area of the coke lump lying in the second layer from the blast entrance can be seen. It is not possible, however, to see further into the combustion zone than this small portion of the second lump. The temperatures observed in this zone are above the melting point of a platinum:platinrhodium thermocouple, and the gases are sufficiently reducing to be destructive to platinum. No particular interest attaches to the distribution of temperature within the combustion zone, since the restricted region which constitutes the combustion zone is not a functional part of the blast furnace when the furnace is used for effecting reduction. However the temperature of the gas as it leaves the combustion zone is of major engineering importance. It is fortunate that this temperature can be determined with satisfactory accuracy from available thermal quantities.

In the blast furnace, coke descends continuously into the combustion zone to replace that which is burned. In approaching the combustion zone each coke lump is heated by the countercurrent passage of gas to approximately the temperature of the gas leaving the zone. Since 1 pound of carbon requires 1.333 pounds of oxygen to produce 2.333 pounds of carbon monoxide, and since 4.418 pounds of nitrogen accompanies 1.333 pounds of oxygen in air, the product of combustion of 1 pound of coke carbon with dry air is 6.751 pounds of gas. The constituents of this gas are carbon monoxide and nitrogen, which being diatomic gases of the same molecular weight have the same specific heat. If $t_c$ is the temperature of the gas leaving the combustion zone; $m$, its weight (6.751 pounds per pound of carbon); $Q_a$, the heat of combustion of 1 pound of carbon to carbon monoxide (4,014 B. t. u.); $Q_b$, the sensible heat of the 5.751 pounds of air required to burn 1 pound of carbon, and $Q_c$, the sensible heat of 1 pound of carbon at the temperature $t_c$, then

$$t_c = \frac{Q_a + Q_b + Q_c}{m \times C_p}$$

where $C_p$ represents the mean specific heat of the gas from ordinary temperature to the temperature $t_c$. If the blast were not preheated, $t_c$ would be 2,876° F. At the lowest blast temperature encountered in present furnace practice, 800°, $t_c$ is 3,520°, and at the highest temperature, 1,600°, $t_c$ is 4,240°. For other blast temperatures the values presented in the tabulation below have been computed. These temperatures are subject to errors of probably not more than 100° to 150°, which are due to uncertainties in the values of the thermal quantities used.

| Blast temperature (°F.) | Theoretical maximum temperature of the gaseous products | Blast temperature (°F.) | Theoretical maximum temperature of the gaseous products |
|---|---|---|---|
| | °F. | | °F. |
| 77 | 2, 876 | 1,200 | 3, 890 |
| 200 | 2, 970 | 1,400 | 4, 070 |
| 400 | 3, 145 | 1,600 | 4, 240 |
| 600 | 3, 330 | 1,800 | 4, 410 |
| 800 | 3, 520 | 2,000 | 4, 575 |
| 1,000 | 3, 710 | | |

The value of $t_c$ in an actual furnace operation is less than that calculated, for two reasons: (1) The absorption of heat in the reduction by coke carbon of the moisture contained in the air, and (2) the loss of heat from the combustion zone by conduction, convection, and radiation to its surroundings. The decrease in $t_c$ due to (1) may be readily calculated for any given moisture content of the air. The decrease in $t_c$ due to the heat losses, however, is not readily measured. The total heat carried through the walls in the lower part of a blast furnace may be measured, but it has not been found possible separately to measure the heat lost from the combustion zone itself.

### THERMAL EFFICIENCY OF THE BLAST FURNACE

From the point of view of heating the charge, the temperature of the gases leaving the combustion zone is sufficiently high to melt any mineral mixture that might be charged into a blast furnace.

The efficiency of the blast furnace itself, considered as an apparatus for converting the chemical energy of the fuel consumed into useful heat, is at present relatively low. A pound of coke carbon has a heat of combustion of 14,157 B. t. u. when oxidized to carbon dioxide (*45, v. 5, p. 181*). Since the highest state of oxidation of carbon produced in the blast furnace is carbon monoxide, with the generation of 4,014 B. t. u. per pound of carbon (*45, v. 5, pp. 138, 181; 59, p. 330*) the heat-generating efficiency of a blast furnace cannot exceed 4,014 divided by 14,157, or 28.4 percent, when operating on a cold blast. When operating on a hot blast, this efficiency is increased.

The effect of the hot blast upon the furnace process as a whole is twofold. The chemical energy that leaves the furnace at the top in the form of carbon monoxide is converted in the stoves to sensible heat by combustion to carbon dioxide. This sensible heat is later returned to the furnace by the blast. This return to the furnace of the chemical energy of the fuel through the operation of the stove results in a direct increase in the heat-generating efficiency of the furnace according to the values presented in table 1. The introduction of the sensible heat of the blast into the combustion zone also increases the temperature, $t_c$, at which the products of combustion leave the combustion zone.

TABLE 1.—*Relation between blast temperature, blast composition, equivalent oxidation of carbon to carbon dioxide, and the heat-generating efficiency of the blast furnace*

| Blast temperature (°F.) | Oxygen blast [1] | | Air blast [2] | | Blast temperature (°F.) | Oxygen blast [1] | | Air blast [2] | |
|---|---|---|---|---|---|---|---|---|---|
| | Equivalent oxidation $C \rightarrow CO_2$ [3] | Heat-generating efficiency [4] | Equivalent oxidation $C \rightarrow CO_2$ [3] | Heat-generating efficiency [4] | | Equivalent oxidation $C \rightarrow CO_2$ [3] | Heat-generating efficiency [4] | Equivalent oxidation $C \rightarrow CO_2$ [3] | Heat-generating efficiency [4] |
| | *Percent* | *Percent* | *Percent* | *Percent* | | *Percent* | *Percent* | *Percent* | *Percent* |
| 77 | 0.00 | 28.35 | 0.00 | 28.35 | 2,200 | 6.47 | 32.99 | 30.03 | 50.51 |
| 200 | .35 | 28.61 | 1.66 | 29.56 | 2,400 | 7.13 | 33.46 | 34.05 | 52.75 |
| 400 | .93 | 29.02 | 4.45 | 31.54 | 2,600 | 7.79 | 33.93 | 37.24 | 55.03 |
| 600 | 1.52 | 29.44 | 7.25 | 33.55 | 2,800 | 8.47 | 34.42 | 40.47 | 57.35 |
| 800 | 2.11 | 29.87 | 10.08 | 35.57 | 3,000 | 9.15 | 34.91 | 43.75 | 59.70 |
| 1,000 | 2.71 | 30.30 | 12.94 | 37.62 | 3,200 | 9.85 | 35.41 | 47.08 | 62.08 |
| 1,200 | 3.31 | 30.73 | 15.83 | 39.70 | 3,400 | 10.56 | 35.92 | 50.45 | 64.50 |
| 1,400 | 3.92 | 31.16 | 18.77 | 41.80 | 3,600 | 11.27 | 36.43 | 53.88 | 66.96 |
| 1,600 | 4.55 | 31.62 | 21.75 | 43.94 | 3,800 | 12.00 | 36.95 | 57.35 | 69.44 |
| 1,800 | 5.18 | 32.06 | 24.77 | 46.10 | 4,000 | 12.74 | 37.48 | 60.88 | 71.97 |
| 2,000 | 5.82 | 32.52 | 27.82 | 48.29 | | | | | |

[1] Oxygen, 100 percent. [2] Dry air; oxygen, 20.92 percent.

[3] Percentage of carbon that would have to be burned to carbon dioxide in order to obtain with a 77° F. blast the same heat-generating efficiency as obtained with hot blasts at the tabulated temperatures when the carbon is completely burned to carbon monoxide.

[4] Percentage of the 77° F. heat of combustion of carbon to carbon dioxide that is generated by the combustion of carbon to carbon monoxide with blasts at the tabulated temperatures.

This increase in $t_c$ is important to the economical operation of furnace processes that involve reactions at elevated temperatures with the absorption of a considerable amount of heat. If specific heats of the combustion products are assumed constant, then the fraction of the heat generated in the combustion zone which is effective in maintaining such a reaction is $\frac{t_c-t_r}{t_c-77}$, where $t_r$ represents the temperature at which the reaction proceeds.

In a reaction proceeding at 2,400° F., with the low blast temperature of 800°, $t_c$ is 3,520°, and the fractional portion of the total heat generated that would be available for carrying out the reaction is

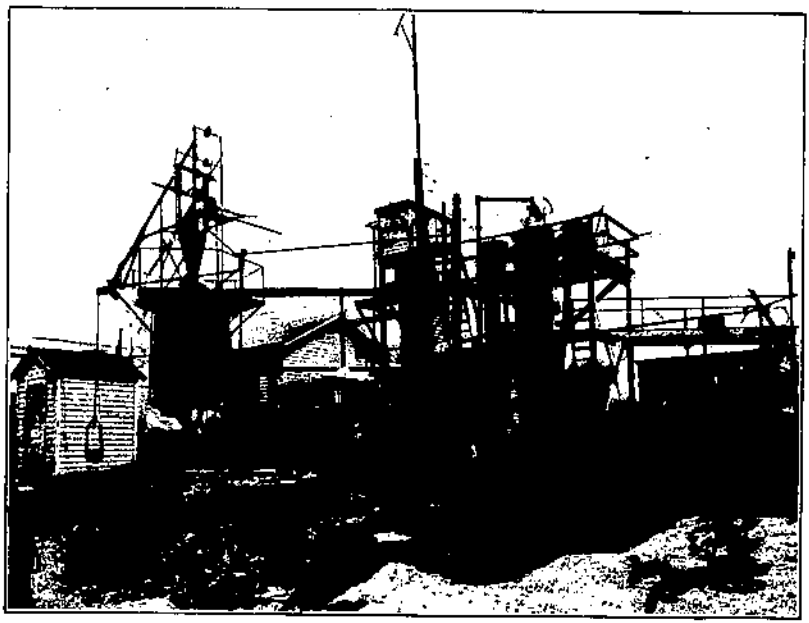

FIGURE 1.—Experimental blast-furnace plant, showing furnace stack, gas-cleaning equipment, and hot-blast stoves.

approximately $\frac{3,520-2,400}{3,443}$, or 32.5 percent. If the blast temperature were increased to the relatively high blast temperature of 1,600° this fraction would become $\frac{4,240-2,400}{4,163}$, or 44.2 percent. For a 2,000° blast temperature the value would be $\frac{4,575-2,400}{4,498}$, or 48.4 percent.

It is obvious, therefore, that high hot-blast temperatures are an economic necessity for blast-furnace processes absorbing any considerable amount of heat at elevated temperatures.

## THE EXPERIMENTAL BLAST-FURNACE PLANT

### FURNACE STACK

The blast-furnace plant used in this investigation is shown in figures 1 and 2.

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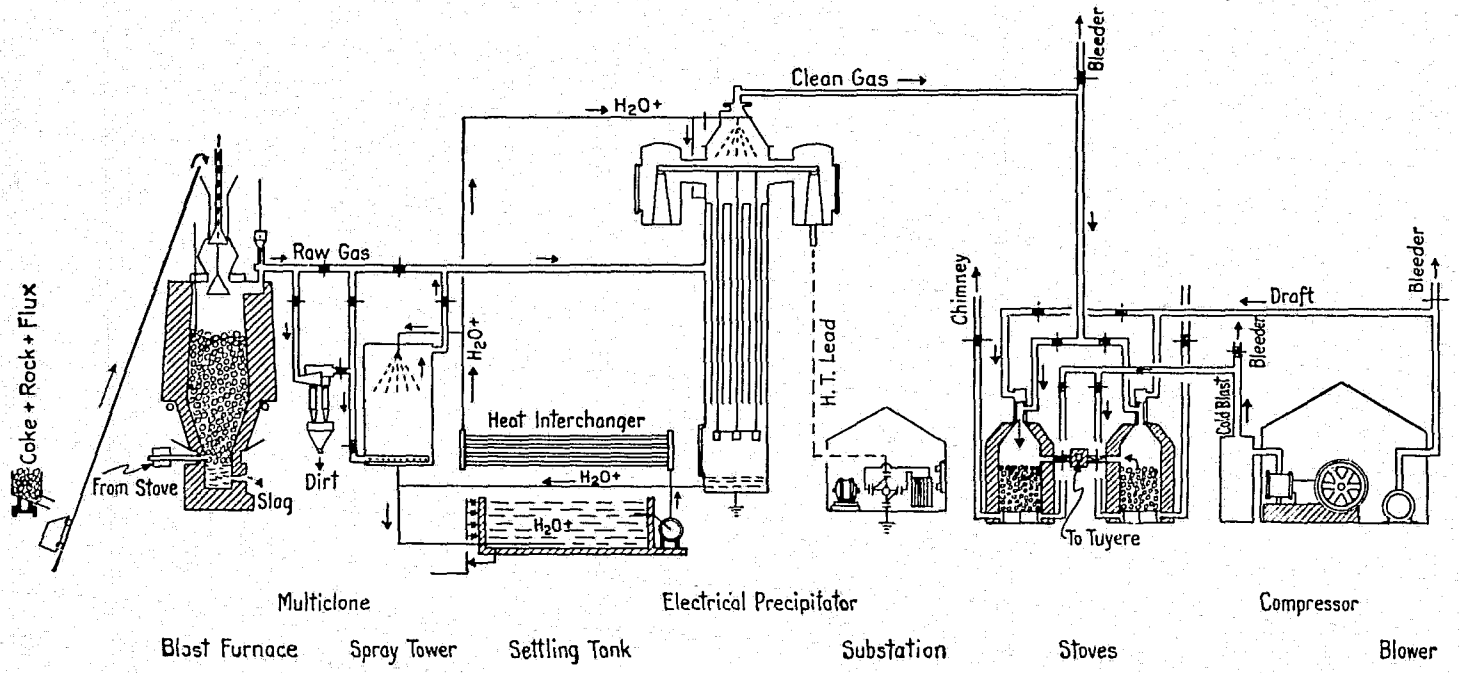


FIGURE 2.—Elevation of the blast-furnace plant.

The blast-furnace stack, fabricated by the Washington Navy Yard according to the Bureau's specifications, was welded and bolted as shown in figure 3. The over-all diameter was 6 feet 8 inches, and the height 19 feet 10 inches. The furnace was supported at the base of the mantle ring by four extra-heavy 6-inch pipes imbedded in concrete.

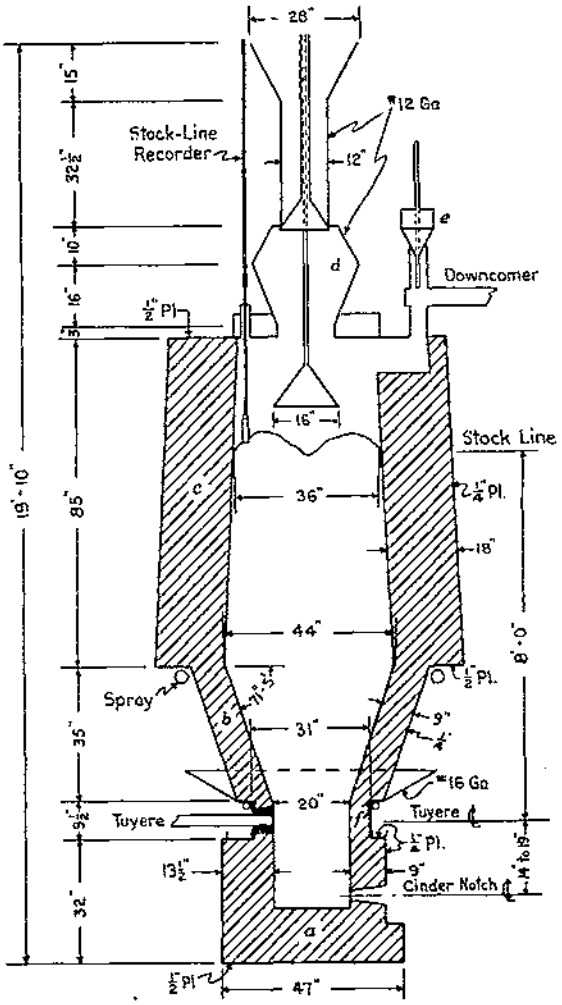


FIGURE 3.—Details of the experimental blast furnace: *a*, Hearth; *b*, bosh; *c*, mantle; *d*, gas seal and stock funnel; *e*, explosion valve; *f*, tuyère brest.

The hearth (*a*) was constructed from ¼- and ½-inch steel plate. It had a diameter of 47 inches and a height of 32 inches. A 13½-inch firebrick lining reduced the internal diameter to 20 inches, the depth to 18½ inches, and the cross-sectional area to 2.18 square feet. The capacity of the lined hearth was 3.36 cubic feet.

The bosh (*b*) was fabricated from ¼-inch steel plate. The upper and lower external diameters were 62 and 38 inches, respectively, and the height was 35 inches. The bosh was lined with 9 inches of firebrick, reducing the internal diameters to 44 and 20 inches, respectively. The bosh angle was 71°5'. The lined bosh had a capacity of 17 cubic feet and was externally cooled by a water spray.

The mantle (*c*) of the furnace was constructed from ¼-inch steel plate. It had upper and lower external diameters of 72 and 80 inches, respectively, and a height of 85 inches. An 18-inch firebrick lining reduced the internal diameters to 36 and 44 inches. The capacity of the mantle was 62 cubic feet. The in-wall batter was 1.13 inches per foot.

The furnace top was constructed of ½-inch steel plate. It was cooled by a water bath 42 inches in diameter and carried the lower bell seat and gas seal as shown in figure 4.

The gas seal and stock funnel (*d*) were constructed of 20-gage sheet. The lower bell was 16 inches and the upper bell 13 inches in diameter. Each of the bells was manually operated from the skip house by cable and counterweight.

The downcomer consisted of a horizontally placed standard 4-inch iron pipe approximately 22 feet in length. An explosion valve (*e*),

FIGURE 4.—The furnace top.

automatically operable at pressures in excess of 5 pounds gage, was installed at the furnace end of the downcomer. This valve could be operated manually from the skip house when necessary to reduce the top pressure in order to permit opening of the bells.

The height of the stock in the furnace was measured by a manually operated stock-line recorder.

The tuyère brest (*f*) was constructed from ¼-inch steel plate. It was welded to the hearth and had an external diameter of 31 inches and a height of 9.5 inches. It was protected by ½-inch copper cooling coils installed between a 4½-inch firebrick lining and the shell. The outer shell was also cooled by sprays, the water from which was collected in a gutter at the top of the hearth. The internal diameter of the tuyère brest was 20 inches, and its capacity was 1.73 cubic feet.

The hearth and tuyère-brest assembly (fig. 5), supported by jacks and wedges, was bolted to the bosh. This construction permitted ready removal of the hearth and tuyère-brest assembly for repairs and alterations to the furnace interior.

The blowpipe and tuyère was originally a standard 2½-inch iron pipe protected at the nose by several turns of ½-inch copper tubing,

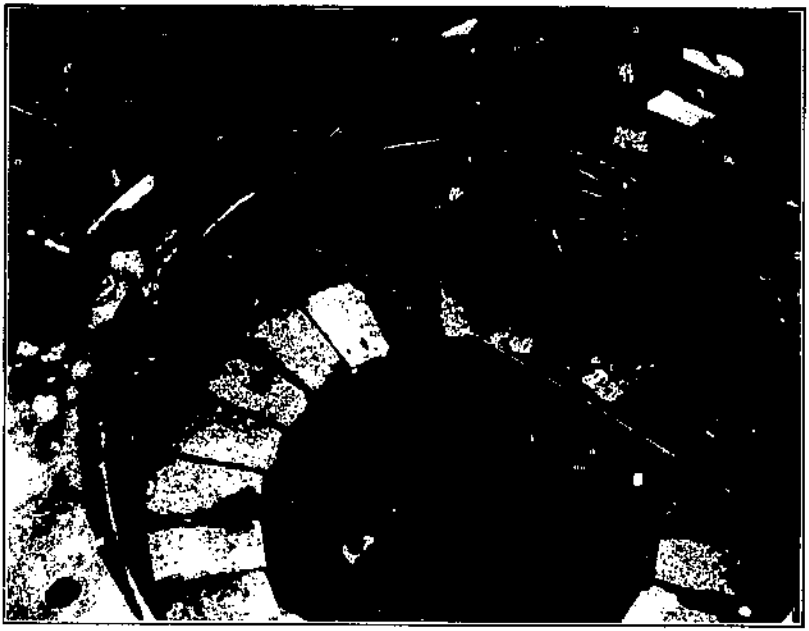

FIGURE 5.—Furnace crucible, under construction, showing copper water-cooling tubes and a portion of the lined blowpipe.

through which a flow of water was maintained. In later runs the blowpipe was a standard 6-inch iron pipe lined with 1½ inches of Armstrong insulating brick.

The position of the cinder notch ranged from 14 to 19 inches below the center line of the tuyère. The cinder notch was closed with a 1¼-inch diameter bot bar.

### BLOWING EQUIPMENT

Two single-stage compressors (fig. 6) were available for supplying the blast to the furnace. They were arranged either for individual or combined parallel operation and were equipped with adjustable automatic unloading devices for limiting the maximum deliverable pressure. The usual setting of the unloaders was 7 to 8 pounds gage.

One compressor had a 9-inch bore, 8-inch stroke, and 0.58-cubic-foot piston displacement per revolution. It was chain-driven at 325

revolutions per minute by a 20-horsepower electric motor. The other compressor had a 14-inch bore, 8-inch stroke, and 1.42-cubic-foot piston displacement per revolution. It was belt-driven at 275 revolutions per minute by a 25-horsepower electric motor.

Three rotary positive-pressure air blowers were available either individually or in parallel for supplying the draft air required in the stoves. Two of these blowers had a rotary displacement of 162 cubic feet and the other 338 cubic feet per minute at 200 revolutions per minute. Their normal operating pressure was 3 to 4 pounds gage.

FIGURE 6.—Interior of the enginehouse, showing one blower and the compressors.

One of the small blowers was chain-driven by a 7½-horsepower variable-speed electric motor. The other blowers were gear-driven at 200 revolutions per minute by 7½- and 10-horsepower motors.

### HOT-BLAST STOVES

The two hot-blast stoves were constructed as shown in figure 7. These were heated by burning cleaned blast-furnace gas with forced draft. Each stove had an over-all height of 7 feet 10 inches and a diameter of 48 inches.

The combustion dome and body of the stoves, as originally installed, had a 4½-inch firebrick lining. Later, to reduce heat losses, this lining was changed to 4½ inches of Armstrong insulating brick. The hot-blast outlet was a 4-inch port near the top of the stove. Two 4-inch ports near the base served as cold-blast and chimney-gas inlet and outlet, respectively. A 10-foot length of 4-inch pipe served as the chimney.

The burners of these stoves consisted of standard 8-inch iron pipe into which had been welded a header carrying 12 standard 1-inch iron pipes through which air for combustion was introduced. The gas was

led in around these pipes and mixed at the base of the burner with the air coming through them. The volume of the combustion zone was about 12 cubic feet.

The heat-transfer bed, supported by grate bars of ½-inch round rods, was 30 inches deep and 39 inches in diameter. The bed had a cross-sectional area of 8.3 square feet and a volume of approximately 21 cubic feet. The filling initially consisted of crushed firebrick passing a ½-inch and retained on a ¼-inch mesh screen (runs of June 8–10, Aug. 2–5, and Aug. 16–17, 1932). Later fillings (runs of Aug. 29–Sept. 3, and Oct. 10–13, 1932) were washed river gravel of the same size, or (runs of June 6–8, June 26–28, and June 29–30, 1933) river gravel that passed a ¾-inch and was held on a ½-inch mesh screen. The gravel weighed approximately 103 pounds per cubic foot and averaged 36 percent voids. The weight of the gravel filling for each stove ranged from 2,100 to 2,200 pounds. The surface of the pebble bed could be observed through a 2-inch port provided with a glass peep sight.

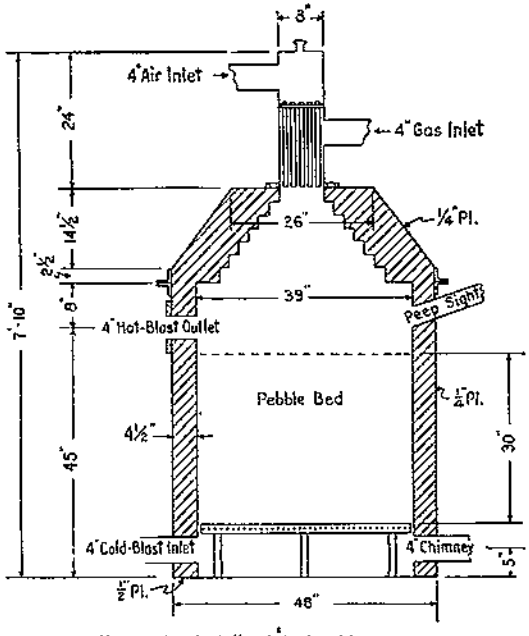


FIGURE 7.—Details of the hot-blast stoves.

Standard 4-inch quick-opening gate valves were installed to control the operation of the stoves and gas-cleaning equipment. The hot-blast valves were cooled by submersion in a water trough. The hot-blast main was of rectangular cross section. It was fabricated from ⅛-inch steel sheet and, with a 2½-inch firebrick lining, provided a duct 4 by 4½ inches. The initial firebrick lining was later replaced by one of Armstrong insulating brick of similar dimensions.

### GAS-CLEANING AND GAS-COOLING SYSTEM

The furnace gases were first led through a Multiclone (fig. 8) to remove a large portion of the dirt and fume normally accompanying such gases. The Multiclone, designed to recover 90 to 98 percent of a dust of which 90 to 95 percent would pass a 300-mesh sieve (0.0018 inch), consisted of two 6-inch tubes arranged for parallel gas flow. The rated capacity per tube ranged from 155 cubic feet per minute at 100° F. to 215 cubic feet per minute at 600° for a 2-inch water draft loss, and from 220 cubic feet per minute at 100° to 300 cubic feet per minute at 600° for a 4-inch draft loss.

The gases from the Multiclone were cooled in a spray tower preparatory to a final clean-up by an electrostatic precipitator. The cooling tower was 4 feet in diameter and 7 feet in height. The hot gases were

introduced near the base through a closed-end 6-inch pipe which was perforated with 1-inch drill holes on its lower side. The gases passed upward through the tower countercurrent to solid-cone water sprays produced either by several 2B and 4B Spraco nozzles, or by one no. 10A. The cooled moist gases were withdrawn near the top through a standard 4-inch pipe. The cooling water was discharged from the base of the tower through a 2-inch pipe to the settling tank, for sedimentation, cooling, and recirculation.

The electrostatic precipitator (fig. 9) had an over-all height of 23 feet 6 inches, and a main shell diameter of 3 feet 8 inches. The insulator compartments were 28 inches in diameter and 55 inches in height. Each insulator compartment and the upper and lower portions of the main shell were equipped with hinged cast-iron doors that closed entrance ports 20 by 31 inches. Numerous vents and drains, in addition to a 10-inch diameter explosion door, were incorporated in the construction.

The collecting electrodes were seven spiral-riveted steel tubes 8 inches in diameter and 12 feet long. They terminated at the top in a gastight header and were held in position at the base by steadying bars. The total cross-sectional area of the tubes was 2.44 square feet and the collecting area 176 square feet. The discharge electrodes, tied together at the base, were ¼-inch square steel twist rods each supporting a 15-pound weight. Each tube was equipped with two nozzles for continuous water washing and removal of the collected material. A large spray nozzle permitted periodic cleansing of the high-tension bus bar and discharge electrodes.

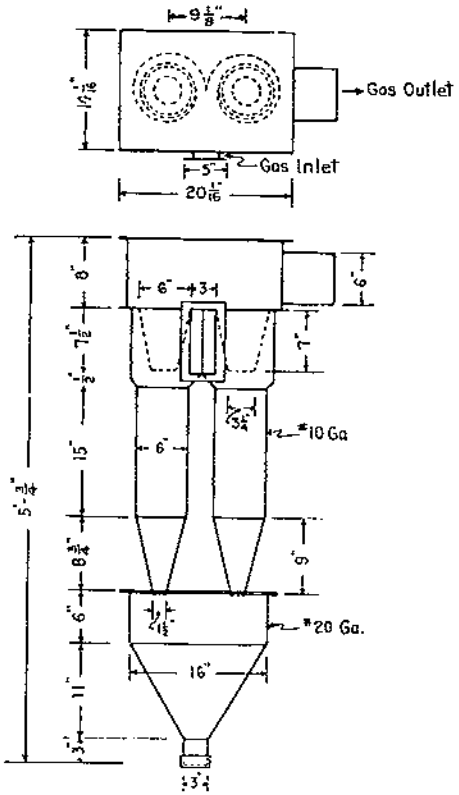


FIGURE 8.—Details of the Multiclone.

The gas entered the precipitator midway between the header and tube steadying bars and passed downward outside the tubes. It then passed upward through the tubes, where it was subjected to the precipitating action of an impressed voltage of 40,000 to 55,000 volts. The treated gases, discharging through a 10-inch port at the top of the precipitator, were led to the stoves or bled to the open air.

The gas-treating capacity of the precipitator, based on an average linear velocity of 5 feet per second, was 730 actual cubic feet per minute.

The substation for supplying the high-tension current required in the operation of the electrical precipitator was equipped with a high-tension transformer, synchronous motor with mechanical rectifier,

and the necessary control switchboard and meters. The mechanical rectifier had four 15-inch arms and was driven by a 750-revolutions-per-minute synchronous motor. The 5-kilovolt-ampere oil-filled transformer was equipped with 45-, 50-, 55-, 60-, and 65-kilovolt terminals.

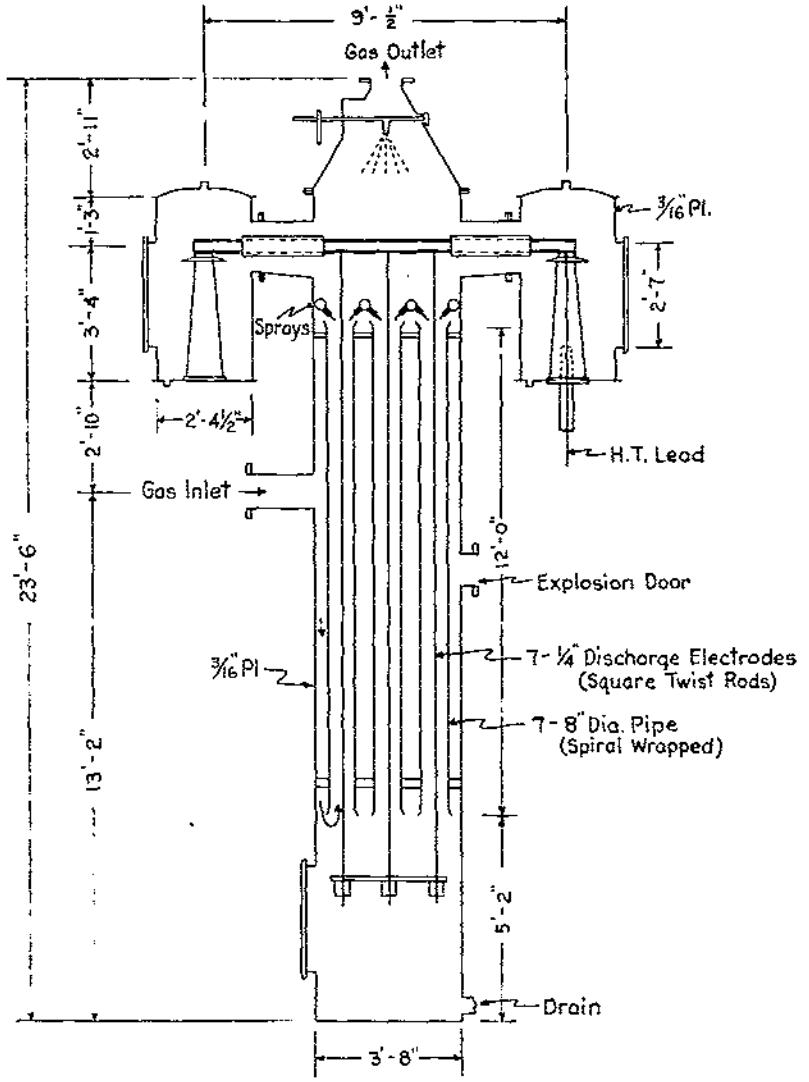


FIGURE 9.—Details of the electrostatic precipitator

A settling tank was provided to remove the sediment carried by the water discharged from the spray tower and precipitator. This tank was of concrete construction and lined with 18-gage galvanized sheet iron painted with asphalt. It had an inside diameter of 9 feet 7 inches, a depth of 36 inches, and walls 4 inches thick. The capacity of the tank was 1,600 gallons. A series of outlets at successive 4-inch levels permitted removal of the clarified water. Water from the

upper levels of the settling tank was circulated through a heat interchanger to the spray tower and precipitator.

The heat interchanger was constructed in three sections arranged for series flow. Each section of the interchanger consisted of a 12-foot length of 16-gage copper condenser tubing, ⅝-inch outside diameter, and held concentric within a 1-inch galvanized-iron pipe by a few drops of solder. It was capable of countercurrently cooling from 185° to 85° F. 4½ gallons of contaminated water per minute with the use of 14 gallons of cooling water initially at 72°.

#### HANDLING OF MATERIALS

Materials as received were piled in open bins (fig. 10). Before use they were transferred by a portable belt conveyor to working bins

FIGURE 10.—Experimental blast-furnace plant with stock piles and storage bins.

with hopper bottoms. They were weighed in a hopper mounted on a traveling platform scale car (fig. 11), and dumped directly from this into a skip car. The skip hoist was provided with automatic stops and dump and was driven by a 2-horsepower electric motor.

Slag was run from the cinder notch directly into cast-iron ladles (fig. 12) which held about 100 pounds. Two such ladles were used, each mounted on a rotating boom which allowed them to be swung around and emptied on a slag dump.

### PHOSPHATE SMELTING

#### APPLICABILITY OF THE BLAST-FURNACE PROCESS

The principal constituent of American continental phosphate rock is fluorapatite ($9CaO \cdot 3P_2O_5 \cdot CaF_2$) (*26*). Attempts to volatilize phosphorus pentoxide directly from phosphate rock have met with little

success, although phosphorus pentoxide boils below 1,112° F. (*45*). Displacement of the phosphorus pentoxide constituent by fusion with silica was investigated by Nielson (*46*), who found no such displacement with melts of tricalcium phosphate and silica up to 3,002°. Ross, Mehring, and Jones (*58*) calculated the decomposition temperatures of such volatilization reactions to be above 4,172°.

Since the thermal dissociation of phosphate rock to yield gaseous phosphorus pentoxide appears to take place at temperatures higher than those attained in present furnace practice, recourse must be had to the destruction of the phosphate molecule by reduction of the phosphorus pentoxide constituent to gaseous elementary phosphorus. Reduction of the phosphorus pentoxide constituent by carbon monoxide

FIGURE 11.—Storage bins, showing scale car and skip car.

was not detected by Nielsen at temperatures up to 2,282° F. Unpublished investigations carried out in the Bureau's laboratories confirm this result. Reduction of the phosphorus pentoxide constituent by solid carbon, however, has long been known and is the basis of all commercial processes for the manufacture of phosphorus. Mixtures of phosphate rock, sand, and coke have been smelted in electric furnaces for the production of phosphorus since about 1890 (*47*, *54*). Ross, Mehring, and Jones (*58*) and Jacob, Reynolds, and Hill (*32*) have shown that almost complete reduction of the phosphate is obtained when such mixtures are heated to 2,372° for 1 hour. This reduction reaction may be represented by the equation:

$$Ca_3(PO_4)_2+5C+3SiO_2=3CaSiO_3+5CO+1/2P_4$$

The heat of this endothermic reaction at room temperature is 4,144 B. t. u. per pound of phosphorus pentoxide reduced (*45*, *v. 5*,

*pp. 181, 182, 196, 197; 59, p. 330*). Similarly postulated reactions involving either more silica or none at all give values of the same order of magnitude (*58*).

The blast furnace is well adapted for carrying out such a reaction. Carbon at elevated temperatures is necessarily present, and the heat required for reduction is produced by combustion of coke rather than from relatively more expensive electric energy. In attempting to smelt phosphate rock in the blast furnace, combustion of coke and formation of slag occur as in iron smelting, but since the reducible oxide

FIGURE 12.—The cast house during a flush, showing slag discharging from the cinder notch into the slag ladle.

in the phosphate furnace charge is $P_2O_5$, the product is elementary phosphorus, a chemical element boiling at 536° F. (*45, v. 1, p. 102*). At the temperatures prevailing in the bottom of the phosphate blast furnace, phosphorus, of course, is a highly superheated gas which is carried upward through the furnace shaft to emerge from the stock line as a constituent of the furnace gas, though seldom amounting to more than 1 percent by volume.

### EXPERIMENTAL PROCEDURE

In carrying out the phosphate smelting experiments, the cold blast furnace was filled with coke from the bottom of the hearth to the tuyère level. A layer of wood charcoal was added, and additional coke was charged to fill the bosh. Above this, alternate layers of coke and of iron blast-furnace slag were charged. The charcoal at the tuyères was ignited with an acetylene lance. The blowers were started, and cold air was blown through the tuyères for about an hour.

Molten slag was removed from the hearth, usually from 20 to 40 minutes after the furnace was started. As rapidly as possible thereafter the gas from the furnace top was brought down through the gas-cleaning system and ignited in one of the stoves. This stove, after about an hour's heating, was used to heat the blast, while the other stove was placed "on gas." During normal operation the "on-gas" and "on-wind" periods of the stoves were 40 to 45 and 55 to 60 minutes, respectively. As soon as a hot blast was obtained the furnace was charged with the desired burden of phosphate rock, coke, and flux.

Before they were charged to the furnace the materials were weighed in the scale car with an accuracy of about 3 percent. All charges were based on 100 pounds of coke. Stock-line measurements were made before and after each charge in order to determine the intervals between charges necessary to maintain as nearly as possible a constant height of material in the furnace. Slag was removed from the furnace at intervals which were determined by the slag volume of the burden and the rate at which the furnace was being driven. These intervals usually ranged from 40 minutes to 1 hour. The temperature of the slag, as determined by an optical pyrometer and after an allowance of 101° F. as an emissivity correction, averaged about 2,532°. Samples of the liquid slag, taken as it ran from the furnace into the ladles, were reserved for analysis.

The rates at which the blast was delivered to the furnace and at which the gas and draft were supplied to the stoves were determined from measurements of their pressures, temperatures, and pressure differentials as they passed through a nozzle or an orifice installed in the delivery lines. The nozzle for measuring the blast was constructed according to the specifications of nozzle D–1 described by Bean, Buchingham, and Murphy (*3*, *p. 568*). The discharge coefficient of this nozzle was taken to be from 0.986 to 0.988 under normal operating pressures. The gas and draft orifices, 2 inches in diameter in a ⅛-inch brass plate, were calibrated in terms of the blast nozzle.

The hot-blast temperature was measured with a platinum:platinrhodium thermocouple in a silica protecting tube inserted into the hot-blast main as near the blast entrance to the blowpipe as possible. The electromotive force of this, as well as of all other thermocouples, was measured with a potentiometer. The cold-junction temperature was determined with a mercury thermometer. Temperatures of the cold blast, gas, and draft entering the stoves were measured with copper:constantan thermocouples. Chromel:alumel thermocouples were used to measure the temperature of the gas as it left the furnace top and as it left the stoves after combustion. Mercury thermometers were used to measure the temperatures of the gas that entered and left the spray tower.

Measurements of the pressures at the stove inlets, in the hot-blast main, and at the gas outlet from the furnace were made with water and mercury manometers.

At intervals samples of the gases leaving the blast furnace were taken over mercury in burettes mounted in a carrying rack. These samples were analyzed in a modified Orsat apparatus in which carbon dioxide, carbon monoxide, and oxygen were determined directly, hydrogen by combustion, and nitrogen by difference. Any oxygen present was assumed to have leaked in as air during the sampling,

and the analyses were corrected accordingly to an air-free basis. The losses of heat by conduction through the bosh walls and to the tuyère-nose, -seat, and -brest coolers were determined by means of the rise in temperature and the rate of flow of the water used in the respective cooling circuits.

#### DESCRIPTION OF EXPERIMENTS AND PRESENTATION OF DATA

Three series of experiments were made on the reduction of phosphate rock: (1) June 8–10, 1932; (2) October 10–13, 1932; and (3) June 29–30, 1933. The set-up of the apparatus was changed between each of these series of experiments or runs. The changes were largely confined to the gas-cooling and the phosphorus-collecting systems, although some improvements were effected in the stove construction and in the hot-blast delivery system.

#### FIRST EXPERIMENT

In this run (June 8–10, 1932), the gas-treating system consisted of (1) a Multiclone, (2) a spray tower, and (3) an electrostatic precipitator connected in series. Water to the spray tower was supplied by a no. 4B Spraco solid-cone spray nozzle. Exhaust water from the spray tower, discharged as waste, contained sufficient phosphorus in suspension to create a health hazard. The precipitator was operated without wash water. Occasional flushing was sufficient to remove the phosphorus and furnace fume from the tubes and rods. The insulator compartments of the precipitator were not steam-heated. The hot-blast stoves were lined with firebrick, and a bed of crushed and screened firebrick was used as the heat-exchange medium.

Condensation and recovery of phosphorus in this series of experiments were unsatisfactory in spite of the somewhat elaborate gas-cooling and gas-cleaning equipment provided. Dust was carried through the Multiclone, spray tower, and precipitator so that the gas supplied to the hot-blast stoves carried in suspension a considerable amount of dust. The cooling of the gas was inadequate, and a considerable amount of uncondensed phosphorus remained in the gas as vapor. Also, some phosphorus "fog" or "fume" was carried to the stoves. The introduction of this inadequately cleaned gas into the stoves interfered seriously with their operation since the interstices of the granular firebrick filling became clogged with entrapped dust and the resulting mass was subjected to some incipient fusion.

This deterioration of the firebrick bed interfered with the passage of both gas and air through the bed and lowered the efficiency of heat transfer. As a result, the blast temperature was rather low throughout the whole run. By reference to table 2 it is seen that the three tests exhibit the decreasing blast temperatures of 1,153°, 1,090°, and 831° F. Concurrent with this rapidly decreasing blast temperature, the coke consumption (column 31) increased from 4.11 to 9.71 tons per ton of $P_2O_5$ reduced. Considerable mechanical difficulty was experienced in operating the furnace in the latter part of this run when the stove passages had become clogged. The pressure required to force the gas through the stove increased. This, of course, increased the pressure at the top of the blast furnace itself, making the opening of the bells difficult and interfering with the introduction of the charge into the furnace. This run was terminated at the end of 64 hours.

TABLE 2.—*Phosphate blast-furnace operating data, 1932-33*

| Test no. | Date | Duration | Burden | | | | | | Height of stock line above tuyère | Wind blown [1] | Blast temperature | Blast humidity [2] | Hearth-heat loss | Furnace-top temperature | Blast pressure at— | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coke | Washed Florida land-pebble phosphate | Florida pebble phosphate matrix | Tennessee blue-rock phosphate | Limestone | Firebrick | | | | | | | Stove | Tuyère |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| | *1932* | *Hours* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Inches* | *Cu. ft. per min.* | *° F.* | *Lb. $H_2O$ per lb. air* | *B. t. u. per min.* | *° F.* | *Lb. per sq. in.* | *Lb. per sq. in.* |
| 1 | June 8 | 4.0 | 100 | 0 | 0 | 100 | 0 | 34 | 90.9 | 118 | 1,153 | 0.0038 | 1,645 | 327 | 2.9 | 2.8 |
| 2 | June 9 | 3.3 | 100 | 0 | 125 | 34 | 125 | 34 | | 115 | 1,090 | .0068 | 1,334 | 487 | 3.9 | 3.8 |
| 3 | June 10 | 1.0 | 100 | 0 | 125 | 34 | 125 | 34 | | 120 | 831 | .0063 | 1,200 | 568 | 3.2 | 3.1 |
| 4 | Oct. 11 | 1.5 | 100 | 60 | 30 | 0 | 0 | 0 | 52.0 | 119 | 718 | .0047 | 1,431 | 748 | 7.2 | 7.1 |
| 5 | Oct. 12 | 6.4 | 100 | 60 | 30 | 0 | 0 | 0 | 49.6 | 116 | 1,090 | .0032 | 1,471 | 648 | 7.0 | 6.8 |
| | *1933* | | | | | | | | | | | | | | | |
| 6 | June 29 | 4.1 | 100 | 100 | 0 | 0 | 0 | 40 | 81.5 | 215 | 1,580 | .0154 | 3,338 | 304 | 5.3 | 4.6 |
| 7 | June 30 | 4.0 | 100 | 100 | 0 | 0 | 0 | 40 | 85.0 | 166 | 1,467 | .0171 | 2,394 | 349 | 6.1 | |
| 8 | do | 1.0 | 100 | 120 | 0 | 0 | 0 | 37.5 | 87.4 | 202 | 1,447 | .0170 | 2,379 | 390 | 5.1 | |

| Test no. | Pressure drop across stove on wind | Top-gas composition | | | | Slag composition | | | | Slag | $P_2O_5$ | | | Coke [3] / $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CO_2$ | CO | $H_2$ | $N_2$ | $P_2O_5$ | CaO | $SiO_2$ | $\frac{CaO}{SiO_2}$ | | Charged | Reduced | Reduction | |
| 1 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| | *Inches water* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Weight ratio* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Percent* | *Weight ratio* |
| 1 | 1.9 | 1.30 | 35.37 | 2.60 | 60.73 | 4.65 | 31.12 | 36.59 | 0.851 | 123.5 | 27.01 | 21.27 | 78.75 | 4.11 |
| 2 | 3.4 | 6.05 | 33.85 | 1.70 | 58.40 | 4.54 | 42.19 | 33.75 | 1.250 | 224.8 | 22.46 | 12.25 | 54.54 | 7.14 |
| 3 | 2.5 | | | | | 6.02 | 43.49 | 36.05 | 1.206 | 223.4 | 22.46 | 9.01 | 40.12 | 9.71 |
| 4 | 2.1 | .47 | 36.14 | 1.12 | 62.27 | 6.31 | 42.48 | 34.70 | 1.233 | 74.1 | 21.32 | 16.64 | 78.05 | 5.26 |
| 5 | 4.0 | .32 | 37.68 | 1.83 | 60.10 | 6.34 | 48.14 | 32.80 | 1.468 | 70.0 | 21.32 | 16.88 | 79.17 | 5.18 |
| 6 | 20.3 | .84 | 37.79 | 2.71 | 58.66 | 5.08 | 40.67 | 33.81 | 1.203 | 114.7 | 30.21 | 24.38 | 80.70 | 3.59 |
| 7 | | 1.57 | 37.71 | 2.77 | 57.95 | 7.44 | 38.70 | 34.50 | 1.122 | 119.0 | 30.21 | 21.36 | 70.71 | 4.09 |
| 8 | | .35 | 37.32 | 2.00 | 60.33 | 5.53 | 42.92 | 32.72 | 1.312 | 127.9 | 36.25 | 29.18 | 80.50 | 3.00 |

[1] Measured at 32° F. and 29.92 inches of Hg.
[2] To convert to grains of moisture per cubic foot multiply by 565.
[3] Weight of 87-percent fixed-carbon coke per unit weight of $P_2O_5$ reduced.

SECOND EXPERIMENT

The gas-cooling and gas-cleaning equipment in this experiment (Oct. 10–13, 1932) consisted of (1) a baffled, water-cooled exhaust pipe or downcomer and (2) a continuously water-flushed electrostatic precipitator. Exhaust water from the precipitator was collected in the settling tank, and allowed to settle, and the supernatant water was recirculated. At frequent intervals additional water was introduced to the precipitater to remove accretions on the discharge electrodes. The water-cooled and baffled downcomer proved to be an efficient cooler of the furnace gases, but was subject to such frequent stoppage that it was abandoned on subsequent runs.

The sediment that collected in the settling tank was finely granulated and dark gray, and contained about 20 percent of phosphorus. After 78 hours of operation one of the high-tension insulators in the precipitator failed, and, because of the hazard of making repairs in the phosphorus-fouled gas line, the run was discontinued.

During this and succeeding runs a single bell was used, and the crushed firebrick filling of the stoves was replaced by washed and screened river gravel (p. 14).

THIRD EXPERIMENT

For the run of June 20–30, 1933, the firebrick lining of the stoves, hot-blast main, and blowpipe was replaced by Armstrong insulating brick with a thermal conductivity about one-fifth that of firebrick. The gas-treating equipment consisted of (1) the spray tower and (2) the precipitator. To reduce the condensation of volatile matter on the precipitator insulators, the insulator compartments were steam-heated. Water from the settling tank was cooled by the countercurrent heat interchanger (p. 17) before circulation to the spray tower and precipitator.

Throughout this run, smooth operation of the entire plant was marred only by the stoppage of the spray-tower inlet.

No experimental work was done after June 30, 1933.

For convenience in reporting and interpreting the data, each of these runs has been broken into test periods, of varying length, during which operating conditions were more or less uniform. The operating data for each of these periods are reported in table 2.

Table 3 shows the compositions of the dry raw materials. The coke, washed Florida land-pebble phosphate, Tennessee blue-rock phosphate, Florida pebble phosphate matrix, and limestone were charged to the furnace "as received." Both the coke and limestone were approximately 1 inch in mean diameter. The firebrick charged was crushed to pass a 4-mesh screen. The average moisture content of the materials charged into the furnace was: Coke, 5 percent; washed Florida land-pebble phosphate, 4½ percent; Tennessee blue-rock phosphate, 2 percent; Florida pebble phosphate matrix, 28 percent; limestone, 2 percent; crushed firebrick, 5 percent. From these data, the total slag-forming constituents, or slag volume, charged per round were calculated. The slag volume per round was also calculated from the number of pounds of CaO charged per round and the percentage of lime found by analysis of the slag. The value reported in table 2 is the mean of those obtained by these two methods. The maximum variation from the mean value reported was about 4 percent.

TABLE 3.—*Composition of materials*

[Dry basis]

| Material | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $P_2O_5$ | Undetermined |
|---|---|---|---|---|---|---|---|---|---|
| | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* |
| Coke [1] | 8.35 | 3.91 | 0.33 | 0.06 | 2.52 | ------- | ------- | ------- | 4.75 |
| Washed Florida land-pebble phosphate [2] | 6.90 | 2.13 | 46.50 | ------- | 1.91 | 0.20 | 0.72 | 31.63 | 3.31 |
| Florida pebble phosphate matrix [3] | 50.05 | 2.47 | 20.22 | .48 | 1.01 | .27 | .70 | 14.75 | 7.05 |
| Tennessee blue-rock phosphate [4] | 8.34 | ..... | 40.41 | ..... | .17 | ..... | .23 | 27.56 | 8.01 |
| Wyomingite [5] | 51.34 | 11.08 | 5.03 | 6.02 | 4.89 | 11.31 | 1.42 | 1.97 | 1.49 |
| Limestone [6] | ..... | ..... | 50.72 | .56 | ..... | ..... | ..... | ..... | 8.32 |
| Firebrick | 60.66 | 29.20 | .52 | ..... | 7.48 | ..... | ..... | ..... | 2.14 |

[1] Fixed-carbon, 80.08 percent.
[2] $CO_2$, 5.88 percent; $H_2O$, 0.76 percent.
[3] $TiO_2$, 0.13 percent; $ZrO_2$, 0.85 percent; $SO_3$, 0.55 percent; $CO_2$, 0.48 percent.
[4] $FeS_2$, 10.18 percent; $SO_3$, 3.20 percent; $H_2O$, 1.30 percent.
[5] $TiO_2$, 2.12 percent; $H_2O$, 1.83 percent.
[6] $CO_2$, 40.40 percent (calculated).

Tables 4 and 5 show the amounts of carbon used in the several furnace reactions. Column 2 of table 4 gives the pounds of fixed carbon charged per round, and column 3, the pounds of carbon charged in the form of carbonates. The sums of these weights, or the total weight of carbon charged, are shown in column 4. Column 5 shows the amounts of the carbon burned at the tuyère, that is, the fixed carbon in the coke that is burned to carbon monoxide by the free oxygen of the blast. These quantities were calculated in the following manner from the corrected top-gas analyses and the total weights of carbon charged. Each volume of carbon monoxide formed by the combustion of carbon with dry air is accompanied by $\frac{79.08}{2\times 20.92}$, or 1.89, volumes of nitrogen, where 79.08 and 20.92 are the volume percentages of nitrogen and oxygen in the air. Hence, the volume percentage of nitrogen in the top gas divided by 1.89 gives the volume percentage of carbon monoxide in the top gas that came from carbon burned by the blast. The latter quantity divided by the sums of the volume percentages of carbon monoxide and carbon dioxide in the top gas gives the fractional part of the total carbon charged (table 5, column 2) that was being burned at the tuyères at the time the sample was taken. That is:

$$\text{Carbon burned at tuyère} = \frac{\text{Percent } N_2}{1.89 \times (\text{percent CO} + \text{percent } CO_2)} \times \text{total carbon charged}$$

TABLE 4.—*Phosphate blast-furnace carbon balance*

[Pounds of carbon per round]

| Test no. | Input | | | Output | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fixed carbon in coke | Carbon as carbonates | Total carbon | Burned by $O_2$ in blast | Used for decomposing blast moisture | Used for reducing phosphates | Derived from calcination of carbonates | Total | Unaccounted for [1] |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* |
| 1 | 76.08 | 0.0 | 76.08 | 66.67 | 0.98 | 8.99 | 0.0 | 76.64 | −0.56 |
| 2 | 76.08 | 13.62 | 89.70 | 69.47 | 1.81 | 5.18 | 13.62 | 90.08 | −.38 |
| 3 | 76.08 | 13.62 | 89.70 | | | 3.81 | 13.62 | | |
| 4 | 76.08 | .95 | 77.03 | 69.35 | 1.20 | 7.03 | .95 | 78.59 | −1.56 |
| 5 | 76.08 | .95 | 77.03 | 64.46 | .78 | 7.13 | .95 | 73.32 | 3.71 |
| 6 | 76.08 | 1.53 | 77.61 | 62.30 | 3.69 | 10.36 | 1.53 | 77.88 | −.27 |
| 7 | 76.08 | 1.53 | 77.61 | 60.58 | 3.97 | 9.03 | 1.53 | 75.11 | 2.50 |
| 8 | 76.08 | 1.84 | 77.92 | 66.03 | 4.31 | 12.33 | 1.84 | 84.51 | −6.59 |

[1] Due to errors of analysis and undetermined reduction reactions (column 4 minus column 9).

TABLE 5.—*Utilization of fixed carbon in the phosphate blast furnace*

[Percent of fixed carbon charged]

| Test no. | Burned by $O_2$ in blast | Used for decomposing blast moisture | Used for reducing phosphates | Accounted for | Unaccounted for [1] |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* |
| 1 | 87.63 | 1.29 | 11.82 | 100.74 | 0.74 |
| 2 | 91.31 | 2.38 | 6.81 | 100.50 | .50 |
| 3 | | | 5.01 | | |
| 4 | 91.15 | 1.66 | 9.24 | 102.05 | 2.05 |
| 5 | 84.73 | 1.03 | 9.37 | 95.13 | −4.87 |
| 6 | 81.97 | 4.85 | 13.54 | 100.36 | .36 |
| 7 | 79.63 | 5.22 | 11.87 | 96.72 | −3.28 |
| 8 | 80.79 | 5.87 | 16.21 | 108.67 | 8.67 |

[1] Due to errors of analysis and undetermined reduction reactions.

The accuracy of this quantity is subject to the errors of gas sampling and analysis. It is truly representative when (1) all blast oxygen is converted to carbon monoxide, (2) the only source of nitrogen is the blast, (3) all the fixed carbon charged appears in the top gas, and (4) the carbonates are being calcined at the same average rate at which they are being charged. The tuyère-plane gas analysis investigations of Kinney, Royster, and Joseph (*36*) have shown that all the blast oxygen is converted to carbon monoxide.

The amount of nitrogen derived from the charge is small in comparison with that supplied by the blast and may be neglected. Some fixed carbon is carried out of the furnace by the top gas and by the ferrophosphorus formed, but its amount is small and usually within the limits of accuracy with which the total fixed carbon charged is known and may, therefore, be neglected. The variation of the instantaneous calcination rate from the time average is of little consequence in most phosphate smelting since the carbonates are

present only as minor impurities in the ores. However, when carbonates are present in appreciable quantities, as in tests 2 and 3 (table 4), it is only necessary to base the above calculation of the carbon burned at the tuyère on a time-average gas analysis obtained by averaging a number of individual analyses in order to obtain a representative value.

Since the heat generated in the furnace depends entirely on the carbon burned by the blast, it is convenient to express other quantities in terms of the carbon burned. In order to convert heat losses measured in ordinary time units to this unit carbon basis, the rate at which the blast is supplied and its composition must be known. Where the basis is the carbon burned by the blast the unit of time involved in the calculations is the time required to burn a unit weight of carbon.

The carbon used to reduce the moisture in the blast may be calculated from (1) the directly measured humidity of the blast or (2) the hydrogen content of the top gas, on the assumption that all the hydrogen therein is derived from the moisture of the blast. The latter method is obviously less accurate than the former, since some hydrogen certainly is derived from the volatile matter of the coke and since any water leaking into the furnace from the bosh and tuyère coolers would appear as hydrogen in the top gas. The carbon used to reduce the blast moisture was, therefore, calculated from the blast humidity. On the average, however, there was not much difference between the hydrogen content of the top gas and that calculated from the blast humidity, indicating that only negligible amounts of water leaked into the furnace from the bosh and tuyère coolers.

The carbon used in reducing phosphates was calculated from the equation $P_2O_5+5C=\frac{1}{2}P_4+5CO$ and the amount of phosphorus pentoxide reduced per round (table 2, column 29). The carbon unaccounted for is considered to have been mostly consumed in reducing other oxides present, such as the oxides of iron or carbon dioxide, though due in part to that removed in the ferrophosphorus formed and in the fume carried by the top gas, and to errors of analysis.

Table 6 gives a total heat balance for these tests. It is based on the burning of 1 pound of carbon by the free oxygen of the blast. This basis is more convenient for calculations, and the results are more easily interpreted than when the amount of carbon burned per unit of time is used as the basis. For the same reasons the heat balance is presented in terms of the carbon burned rather than on the basis of reduction of a unit weight of phosphorus pentoxide.

TABLE 6.—*Heat balance of the phosphate blast furnace* [1]

[1 pound of carbon burned by $O_2$ in blast]

| Test no. | Heat input | | | Heat output | | | | | | | | Heat unaccounted for [2] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Combustion of carbon | Sensible heat of blast | Total | Reduction of phosphates | Reduction of blast moisture | Calcination of carbonates | Vaporization and removal of water in charge | Sensible heat of dry top gas | Sensible heat of slag | Hearth-heat losses | Total | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *Per cent* |
| 1 | 4,014 | 1,548 | 5,562 | 1,321 | 68 | ------- | 155 | 455 | 1,265 | 967 | 4,231 | 1,331 | 23.4 |
| 2 | 4,014 | 1,469 | 5,483 | 720 | 122 | 141 | 247 | 778 | 2,216 | 830 | 6,063 | −580 | −10.6 |
| 4 | 4,014 | 909 | 4,923 | 1,006 | 84 | 80 | 322 | 1,197 | 738 | 860 | 4,287 | 636 | 12.9 |
| 5 | 4,014 | 1,548 | 5,472 | 1,008 | 57 | 80 | 333 | 1,055 | 752 | 907 | 4,282 | 1,190 | 21.7 |
| 6 | 4,014 | 2,230 | 6,253 | 1,052 | 275 | 128 | 209 | 428 | 1,235 | 1,111 | 5,088 | 1,165 | 18.6 |
| 7 | 4,014 | 2,077 | 6,091 | 1,487 | 306 | 128 | 227 | 518 | 1,368 | 1,041 | 5,065 | 1,026 | 16.8 |
| 8 | 4,014 | 2,039 | 6,053 | 1,877 | 304 | 154 | 227 | 574 | 1,354 | 842 | 5,332 | 721 | 11.9 |

[1] Reference temperature, 77° F. [2] Column 13 equals column 4 minus column 12.

### INTERPRETATION OF RESULTS

It has been explained that the major objective in the conduct of the furnace experiments described here was to determine the amount of fuel necessary to reduce the phosphatic constituents of phosphate rocks to elementary phosphorus by the blast-furnace process. Other factors are of economic importance, but as stated above, the major item of cost in this process is the fuel used. It is not possible to duplicate in a furnace apparatus as small as that used in these experiments the exact thermal conditions which will prevail in a furnace of commercial size. It is necessary, therefore, to subject these experimental results to a detailed analysis in order that a proper figure may be derived for use for forecasting the coke consumption in a commercial unit.

In attempting to interpret the thermal phenomena taking place in the phosphate blast furnace, it should be realized that the progress of the reduction reaction is controlled largely by the heat available for carrying out the reaction. The heat supplied to the furnace is derived from (1) combustion of the fixed carbon of the coke with the free oxygen of the blast, and (2) the sensible heat carried by the blast. The total heat supplied must be corrected for the heat lost to the cooling water and for that used in the decomposition of blast moisture in order to obtain the net heat available for smelting purposes. The net heat supplied per pound of carbon burned at the tuyères may be computed directly from quantities shown in table 6 (column 2+column 3−column 6−column 11).

The amount of $P_2O_5$ reduced when this amount of heat is available is obtained by dividing the weight of $P_2O_5$ reduced per round (table 2, column 29) by the weight of carbon burned at the tuyères per round (table 4, column 5). The net heat supplied and the corresponding amount of $P_2O_5$ reduced for each of the test periods are presented in table 7. These quantities have also been calculated for the series of experiments reported by Royster and Turrentine (*61, p. 225*) on the Bureau's small furnace, and they are included in this table.

TABLE 7.—*Net heat supplied and $P_2O_5$ reduced per pound of carbon burned at the tuyère*

LARGE EXPERIMENTAL FURNACE

| Test no. | Net heat supplied [1] | $P_2O_5$ reduced | Test no. | Net heat supplied [1] | $P_2O_5$ reduced |
|---|---|---|---|---|---|
| | *B. t. u.* | *Pounds* | | *B. t. u.* | *Pounds* |
| 1 | 4,496 | 0.319 | 6 | 4,867 | 0.399 |
| 2 | 4,532 | .178 | 7 | 4,757 | .359 |
| 4 | 3,978 | .243 | 8 | 4,907 | .453 |
| 5 | 4,507 | .265 | | | |

SMALL EXPERIMENTAL FURNACE [2]

| | | | | | |
|---|---|---|---|---|---|
| 1 | 4,160 | 0.185 | 5 | 4,448 | 0.223 |
| 2 | 4,246 | .172 | 6 | 4,655 | .251 |
| 3 | 4,302 | .181 | 7 | 4,800 | .320 |
| 4 | 4,324 | .226 | 8 | 4,894 | .315 |

[1] Total heat supplied per pound of carbon burned by $O_2$ minus the sum of the heat lost to the cooling water and the heat used for decomposing the blast moisture.
[2] Calculated from the results of Royster and Turrentine (*61, p. 226*).

The data contained in table 7 are plotted in figure 13.

A straight line was fitted to each set of data by the method of least squares. Test 2 on the large furnace was omitted from the least squares solution because its heat balance (p. 27) shows considerably more heat used than was supplied. Lines *a* and *b* represent the data for the large and small furnaces, respectively. The failure of these lines to coincide may be attributed to general experimental error and to the fact that the heat losses of the smaller furnace were measured less completely. Line *c* represents the arithmetical mean of lines *a* and *b*. Its intercept with the ordinate at zero reduction shows the amount of heat that must be supplied over and above the cooling-water heat losses and the heat used in blast-moisture reduction before any heat is available for phosphate reduction. This is 3,355 B. t. u. per pound of carbon burned at the tuyère. Its slope represents the heat absorbed in the reduction of phosphates, which is 4,167 B. t. u. per pound of $P_2O_5$ reduced, as compared with the theoretical value of 4,144 B. t. u. given on page 18. This is the heat of reduction at 77° F., since the value used for the heat of combustion was that at 77°.

In the above considerations the effect of operating variables, such as the amount, composition, and discharge temperature of the slag, height of stock line, and rate of driving, have been completely ignored. No correlation between these variables and the manner in which the individual points deviated from the values obtained by the least squares solution could be found. This simply means that the range of variation of any particular variable was insufficient to permit its detection. For this reason the intercept value of 3,355 B. t. u. per pound of carbon burned at the tuyère is taken as applicable to the mean of these operating conditions.

This threshold value of 3,355 B. t. u. per pound of carbon burned at the tuyères that must be present before any phosphate reduction can take place must have some fundamental significance. This large quantity of heat must escape from the phosphate-reduction zone unused. It can escape only as sensible heat of the slag and bosh gas leaving the zone, since the cooling-water heat losses have already been

taken into account. (Bosh gas is the mixture of carbon monoxide, nitrogen, and hydrogen resulting from the reaction of the blast with carbon.) The 3,355 B. t. u. unavailable for phosphate reduction is not

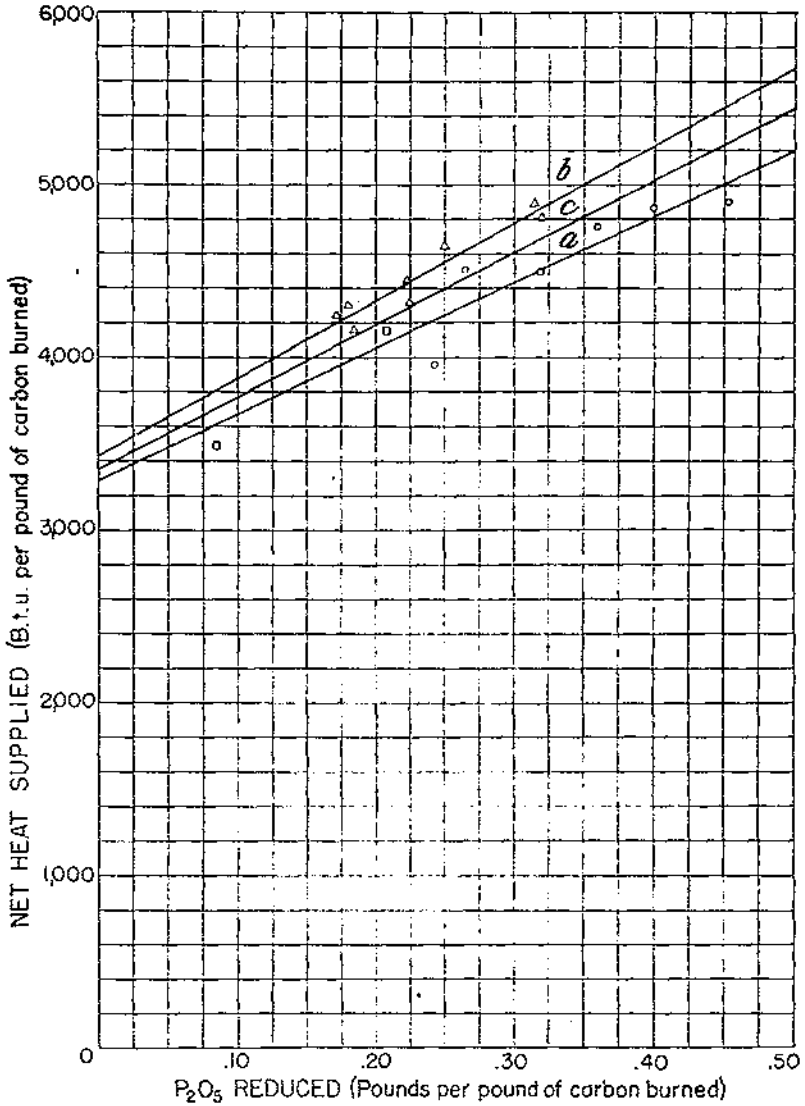


FIGURE 13.—Relation between the amount of phosphate reduced and the heat supplied, corrected for the heat lost to the cooling water and that absorbed in the reduction of the blast moisture: *a*, Large experimental phosphate furnace; *b*, small experimental phosphate furnace; *c*, mean of curves *a* and *b*. The small squares indicate results in the large experimental potash-phosphate furnace, the circles those in the large, and the triangles those in the small, experimental phosphate furnace, respectively.

the total sensible heat of the slag and bosh gas leaving the reduction zone but is the difference between the heat carried out of the zone by them and the heat brought into it by the descending slag or slag-forming materials and by the carbon from which the bosh gas was derived.

The net heat carried out by the slag is the product of the amount of the slag, its mean specific heat, and the difference between the temperature at which it enters and at which it leaves the reduction zone. The observed slag temperatures were about 2,552° F., from which it is estimated that the slag left the reduction zone at approximately 2,687°. On larger furnaces, where the heat lost from the crucible and in the process of flushing would be relatively smaller, the observed slag temperature should be higher and more nearly approach the temperature at which the slag leaves the reduction zone. The average slag volume for the present work was 1.65, for the previously reported tests on the small furnace, 1.30 (*61*), and for the mean of both series, 1.48 pounds of slag per pound of carbon burned at the tuyères. If the mean specific heat of slag at high temperatures is taken as 0.275, the net heat removed by the slag is $1.48 \times 0.275 \times (2{,}687 - t'_c)$, where $t'_c$ is the temperature at which the descending stock enters the reduction zone.

The net heat carried away by the bosh gas is the difference between the sensible heat of the bosh gas at the temperature $t_c$, at which it leaves the zone, and the sensible heat of the carbon at the temperature $t'_c$, at which it enters the zone. Because of the intimate contact between the descending stock and the ascending gases, it is not unreasonable to assume for practical purposes that the temperatures $t'_c$ and $t_c$ are the same. On this assumption, $t_c$ has been computed from the expressions for the net heat of the slag, the sensible heats of the bosh gas and carbon, and the experimentally determined value of 3,355 B. t. u. to be 2,255° F. It may be interpreted as the temperature below which no phosphate reduction occurs, and accordingly it is called the "effective critical temperature." It was unnecessary to take account of the sensible heats of the carbon, $P_2O_5$, carbon monoxide, and phosphorus involved in the phosphate reduction because the heat of reduction at 77° was used rather than that at $t_c$.

The average net heat carried out by the slag, that is the superheat, in these tests was, therefore, $1.48 \times 0.275 \times (2{,}687 - 2{,}255)$, or 175 B. t. u. The subtraction of this from the total of 3,355 B. t. u. leaves 3,180 B. t. u. as the heat carried out of the reduction zone by the bosh gas for a blast humidity [4] of 0.01. For a dry air-blast this value would become $\frac{2.89 \times 3{,}180}{2.97}$, or 3,095 B. t. u.

Although a number of approximations were involved in determining this superheat of the slag, its actual magnitude is small compared to that of the total heat leaving the reaction zone unused, and little error will be introduced if the experimentally observed heat unavailable for phosphate reduction is corrected in this way for variations in slag volume. Corrections may likewise be made for variations in the volume of bosh gas as a result of changes in air humidity.

The assumptions made in calculating the net heat carried away by the bosh gas were that (1) use may be made of the result of the extrapolation to zero reduction of straight line c, figure 13, (2) the slag was superheated to 2,687° F., and (3) the sensible heat of the bosh gas was sufficient at all times to heat up the charge, calcine the carbonates, and evaporate the moisture. Subsequent calculations will show that this last assumption is justified in almost all practical phosphate smelting.

[4] Blast humidity (H)=weight of water per unit weight of dry blast.

The determination of the net heat carried away by the bosh gas makes possible the calculation of the coke consumption to be expected in smelting any given phosphate rock. The superheat of the slag and the heat involved in the actual reduction of phosphate rock are most conveniently calculated on the basis of the amount of $P_2O_5$ reduced. On the other hand the amount of heat supplied, hearth-heat losses, blast-moisture reduction, and the heat carried off by the bosh gas depend on the amount of carbon burned by the free oxygen of the blast and are, therefore, more easily computed on the basis of the carbon burned at the tuyère. Hence, heat requirements are based on the reduction of 1 pound of $P_2O_5$, while the net heat available for this reduction is based on the combustion of 1 pound of carbon to carbon monoxide. The following tabulation shows a typical calculation in which test 7 on the large furnace is used as an example.

| | | B. t. u. |
|---|---|---|
| Hearth heat required per pound of $P_2O_5$ reduced: | | |
| $Q_1$ | For reducing phosphates | 4,167 |
| $Q_2$ | For superheating slag | 662 |
| $Q_3$ | Total hearth heat required | 4,829 |
| Hearth heat available per pound of carbon burned at the tuyère: | | |
| Heat supplied: | | |
| $Q_4$ | By combustion of C to CO | 4,014 |
| $Q_5$ | By sensible heat of blast including moisture, 1,467° F | 2,077 |
| $Q_6$ | Total heat supplied | 6,091 |
| Heat not available in hearth: | | |
| $Q_7$ | Lost by radiation and conduction: | |
| | (*a*) From hearth to cooling water | 1,031 |
| $Q_8$ | Used for reducing blast moisture, H 0.0171 | 306 |
| $Q_9$ | Carried out of reduction zone: [1] | |
| | (*a*) By the products of combustion | 3,095 |
| | (*b*) By the products of moisture decomposition | 145 |
| $Q_{10}$ | Total heat unavailable | 4,577 |
| $Q_{11}$ | Net available hearth heat, $Q_6-Q_{10}$ | 1,514 |
| Carbon required per pound of $P_2O_5$ reduced: | | *Pounds* |
| $C_1$ | For generating heat, $Q_3/Q_{11}$ | 3.190 |
| $C_2$ | For reducing blast moisture, 0.0657 $C_1$ | .2095 |
| $C_3$ | For reducing phosphates | .4225 |
| $C_4$ | Total carbon required | 3.822 |
| Coke [2] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption $=\frac{C_4}{0.87}=\frac{3.82}{0.87}$ | 4.39 |

[1] Sensible heat of the gaseous products of combustion and moisture decomposition minus the sensible heat of the carbon from which they were derived.
[2] 87-percent fixed-carbon coke.

The coke consumption calculated in this manner includes the total carbon required for supplying the heat, decomposing the blast moisture, and reducing the phosphates.

$Q_1$ is the heat of reduction of 1 pound of $P_2O_5$ as present in phosphate rock. The value taken, 4,167 B. t. u. per pound, is that represented by the slope of line c in figure 13.

$Q_2$ is the heat required to heat the slag from the critical temperature of 2,255° F. to 2,687°. It is equal to the amount of slag formed per pound of $P_2O_5$ reduced, 5.57 pounds in test 7, multiplied by the mean specific heat of 0.275 at these temperatures and by the temperature difference of 432°.

$Q_3$ is the total hearth heat required per pound of $P_2O_5$ reduced.

$Q_4$ is the heat evolved on burning 1 pound of carbon to carbon monoxide.

$Q_5$ is the sensible heat of the moist air required to burn 1 pound of carbon. For convenience the sensible heat of the dry air required

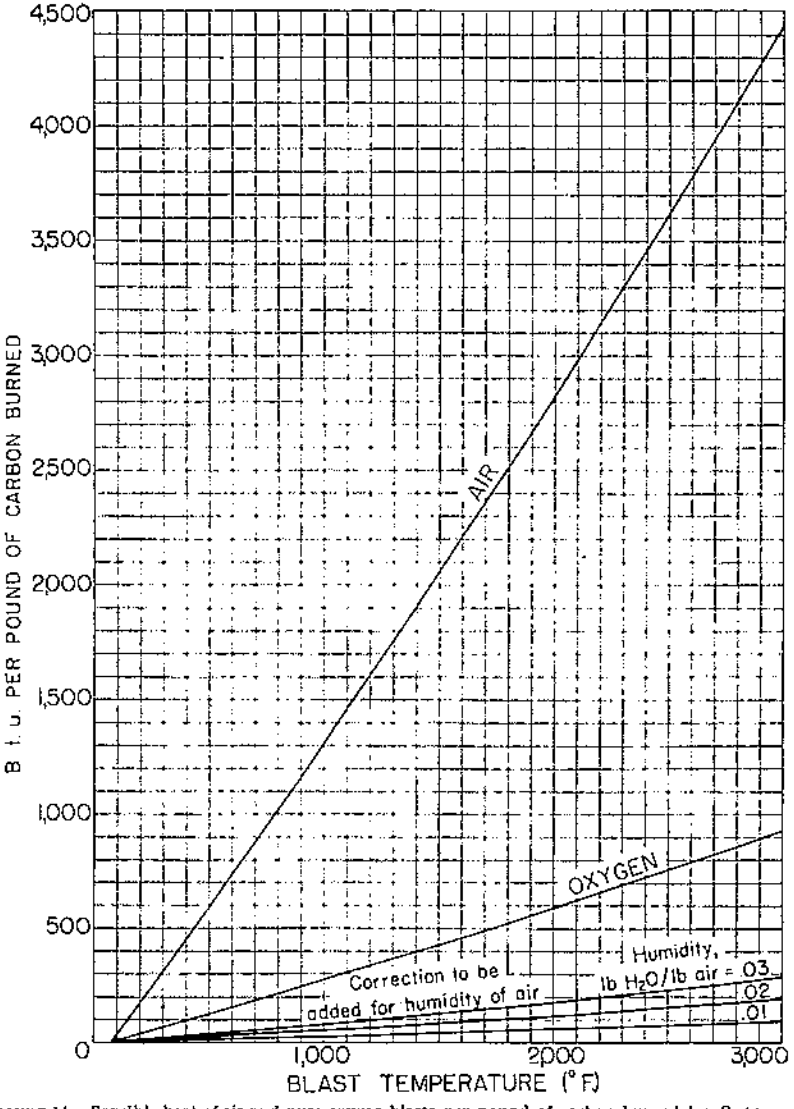


FIGURE 14.—Sensible heat of air and pure oxygen blasts per pound of carbon burned by $O_2$ to carbon monoxide.

to burn this much carbon and the corrections to be added for various humidities in order to obtain $Q_5$ at any blast temperature are shown in figure 14.

$Q_7$ is the total heat lost by radiation and conduction, $Q_{7a}$ is the heat lost to the cooling water. In these tests the entire surface of the fur-

nace from the bottom of the tuyère brest to the top of the bosh was water-cooled.

$Q_8$ is the heat used to reduce the blast moisture according to the reaction:

$$H_2O+C=CO+H_2$$

It is equal to 4,662×3.843, or 17,915 B. t. u. (*45, r. 5, p. 181; 59, p. 330*) multiplied by the humidity, in this case 0.0171 pound of water per pound of air.

$Q_9$ is the difference in the sensible heat of the bosh gas leaving and that of the carbon from which it was derived entering the reduction zone. For convenience this quantity has been separated into (1) the difference between the sensible heats of both the carbon monoxide and accompanying nitrogen resulting from the combustion of carbon with a dry blast and the sensible heat of the carbon consumed in the combustion reaction and (2) the difference between the sensible heats of both the carbon monoxide and hydrogen resulting from the reduction of the blast moisture and the sensible heat of the carbon consumed in the reduction. $Q_{9a}$ has a constant value of $\frac{2.89\times3,180}{2.89+(2\times0.03843)}$, or 3,095 B. t. u., for dry air per pound of carbon burned at the tuyère. $Q_{9b}$ is equal to $\frac{3,180-3,095}{0.01}$, or 8,500 B. t. u., times the blast humidity. In test 7, $Q_{9b}$ is 8,500×0.0171, or 145 B. t. u. $Q_9$, therefore, is 3,095+145, or 3,240 B. t. u.

$Q_{11}$ is the net hearth heat available for supplying the hearth-heat requirements.

$C_1$ is the amount of carbon which must be burned by the free oxygen of the blast in order to generate the heat required. In phosphate smelting it is the larger of the values obtained by dividing (1) the hearth heat required for reducing 1 pound of $P_2O_5$ by the net hearth heat available from 1 pound of carbon burned at the tuyère or (2) the total heat required for reducing 1 pound of $P_2O_5$ by the net total heat available from 1 pound of carbon burned at the tuyère. In this case, as in most phosphate smelting, it is the former.

$C_2$ is the carbon required by the moisture-reduction reaction given above under item $Q_8$. It equals 3.843 times the humidity expressed in pounds of water per pound of dry air.

$C_3$ is the carbon required for the phosphate-reduction reaction. Regardless of the composition of the phosphate rock the carbon required for reduction is determined by the equation:

$$P_2O_5+5C=\tfrac{1}{2}P_4+5\,CO$$

Thus $C_3$ is constant and equals 0.4225 pound of carbon per pound of $P_2O_5$ reduced.

To obtain the coke consumption the total carbon requirement, $C_4$, must be divided by the percentage of fixed carbon in the coke used.

An examination of the above tabulation indicates five ways for decreasing the coke requirements of the phosphate blast furnace:

(1) The slag-superheat requirement can be lowered by decreasing the slag volume. This can be accomplished by using a richer ore or by reducing a larger percentage of the $P_2O_5$ in the charge. In test 7

only 70 percent of the total $P_2O_5$ was reduced. Here as in most other tests the furnace was purposely overburdened. A reduction percentage of 90 should be a conservative estimate on a properly burdened furnace. In fact, one of the tests on the small experimental furnace shows 90.6 percent reduction (*61, p. 225*). The slag-superheat requirement is approximately 13 to 14 percent of the total hearth-heat requirements so that a drastic reduction in slag volume would be necessary before any material change in coke consumption could be expected.

(2) Coke consumption may be decreased by drying the blast. The coke consumption for a dry blast may be readily determined by making the proper changes in items $Q_5$, $Q_8$, $Q_9$, and $C_2$ of the tabulation. On changing these items to correspond to a dry blast, a coke consumption of 3.39 is found, as compared with 4.39 for a blast humidity of 0.0171. For a blast humidity of 0.01 a value of 3.94 is obtained. At higher blast temperatures, however, the magnitude of this saving would be less because of the smaller amount of wind blown per unit of heat supplied. The advisability of drying the blast depends upon the relative value of the coke saved and the cost of producing the dry blast.

(3) In these tests the heat losses to the cooling water amounted to more than 16 percent of the total heat supplied. Most of this heat is lost from those portions of the furnace where phosphate reduction is taking place. Consequently any decrease in this loss would result in increasing the available hearth heat by the same amount. In the illustrative calculation above, this heat loss ($Q_{7a}$) was 68.1 percent as large as the available hearth heat ($Q_{11}$). If the heat loss could be reduced by a half, the carbon burned at the tuyère would be reduced by $1-\frac{1}{1.340}$, or 25.4 percent, and the coke consumption would become 3.46, or a saving of 21.2 percent in the coke required. At higher blast temperatures this saving would decrease in relative importance, since a larger portion of the heat input would come from the sensible heat of the blast. Decreasing the hearth-heat loss offers an important means for reducing the coke consumption. An increase in furnace size should decrease the bosh-heat losses considerably because of the decrease in the ratio of bosh wall area to bosh volume. Tuyère heat losses, however, depend more on hot-blast temperature, combustion-zone temperature, and velocity of the blast. The blowpipe and tuyère were lined with Armstrong insulating brick prior to the experiments of June 1933, in order to reduce the loss of heat from the blast. Such insulation would be particularly advantageous when extremely high blast temperatures are used.

In actual commercial practice, these heat losses from the bosh are considerably less than in a small experimental furnace. Recently Marshall (*43, 44*) measured the cooling-water losses on some British iron blast furnaces. They range from 150 to over 400 B. t. u. per pound of carbon burned by the blast, which is much lower than the average of 940 B. t. u. found in this work. The higher blast temperature in use here would account for some, but by no means the major portion, of this difference. The estimated bosh-heat loss of 750 B. t. u. used for calculating the coke requirements for a commercial phosphate furnace (p. 42) may seem unreasonably high in view of this, but it must be remembered that hot blasts ranging from 2,000° to 3,000° F. are anticipated, and it seems advisable in general to use a conservative value.

(4) Coke requirements can be lowered by increasing the sensible heat of the blast. Theoretically the carbon monoxide in the top gas will supply more than two and one-half times as much heat as does the carbon from which it is formed. Hence, potentially there are over 10,000 B. t. u. per pound of carbon burned that can be converted into sensible heat of the blast. In actual practice this quantity is limited by the temperature to which the blast can be heated conveniently. Blast temperatures in excess of 2,000° F. have already been used.

In figure 14 the sensible heat of the air blast required to burn 1 pound of carbon is plotted against the blast temperature.

It is at once evident, therefore, that the principal opportunity for reducing the coke requirement lies in an increase of the blast temperature. Blast temperatures of 2,000 to 3,000° F. should lower coke requirements per ton of $P_2O_5$ reduced to 2½ and 1¾ tons, respectively. It must be emphasized that approximately one-half ton of coke is required chemically for the reduction of 1 ton of $P_2O_5$, regardless of the use of higher temperatures or other means for increasing the thermal efficiency. Thus the coke from which the required heat is obtained is roughly 2 and 1¼ tons, respectively.

(5) An additional way for lowering coke consumption in some instances would be to use an oxygenated blast. This would decrease the volume of nitrogen passing through the furnace and thus lower the net heat carried up the shaft by the bosh gas ($Q_9$ of the tabulation on p. 31). Figure 15 shows the variation in the available shaft heat with variation in composition of the blast.

For example, a pure oxygen blast would reduce this heat from 3,180 to $\frac{3,180}{2.97}$, or 1,071 B. t. u. It is important, however, that the net available shaft heat equal or exceed the heat required for preheating the stock, evaporating the moisture, and calcining the carbonates; otherwise, high-temperature heat available for phosphate reduction will be diverted to this use. With an oxygen-enriched blast less heat is carried into the furnace as sensible heat of the blast, and this must be taken into account in obtaining the net hearth heat available. This becomes increasingly important at high blast temperatures, as do also the shaft-heat requirements. In fact, when blast temperatures above the critical temperature are used, oxygenation would be a detriment regardless of whether or not the shaft-heat requirements were being met, because the sensible heat of the blast above this temperature would be used in phosphate reduction. Theoretically, it would be advantageous to add nitrogen to the blast in this case. Consequently, lower coke consumption will be obtained with a high-temperature air blast than could be attained with an oxygenated blast.

From the above considerations, it is evident that the hot-blast stoves are of considerable importance. In the iron blast-furnace plant the stoves are both larger and more expensive than the furnace stack itself. In good practice they may give blast temperatures between 1,400° and 1,600° F. The high cost of the stoves is due largely to the specially shaped firebrick checkers used as the heat-transfer medium. In an experimental installation the greatly increased heat losses would seriously lower the blast temperature attainable from this type of stove. Furthermore, funds were not available for installing such an elaborate stove assembly. From necessity, a better and

cheaper type stove was devised. The stoves used, described on page 13, gave during test 6 an average blast temperature of 1,580° in spite of the high heat losses due to their small size and to the make-

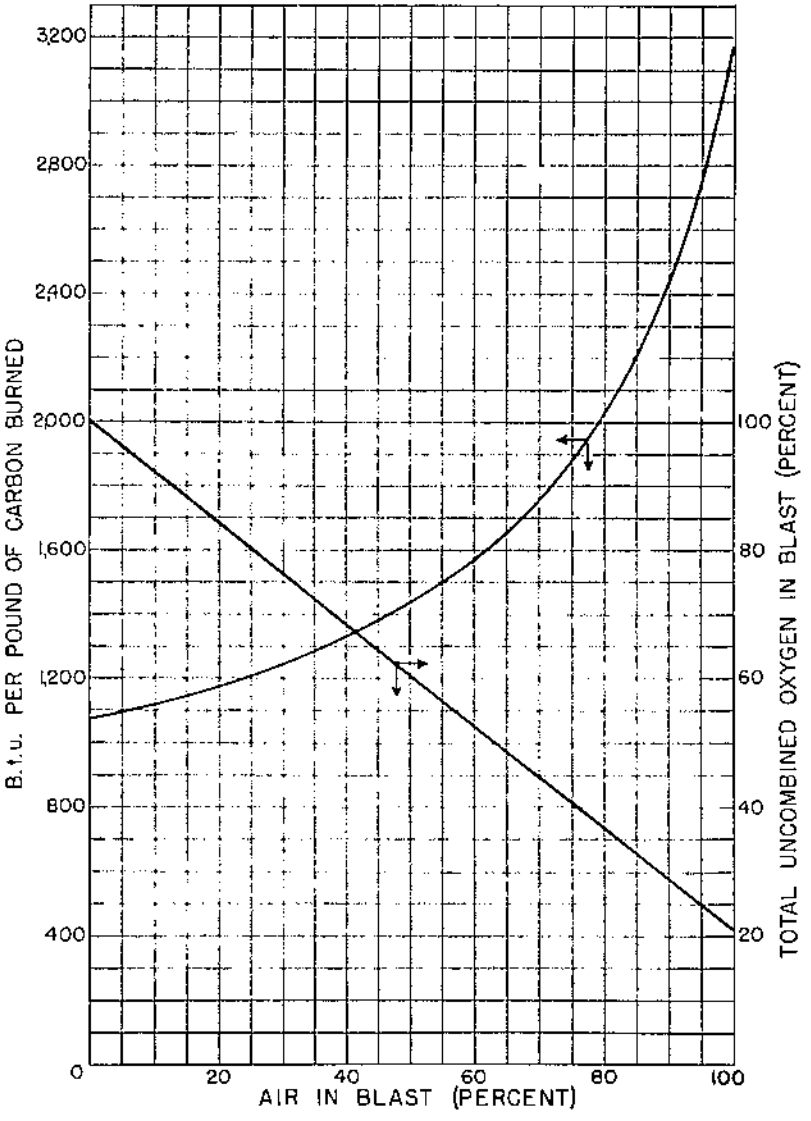


FIGURE 15.—Relation between the net heat carried out of the phosphate-reduction zone by the bosh gases and the composition of the air-oxygen blast mixture used. Air humidity, 0.01.

shift hot-blast valves. The initial drop in blast pressure amounted to less than 1 inch of water. Cleaning was effected by removing the inexpensive river gravel and replacing with new gravel. These stoves had the further advantage of supplying a blast of fairly uniform temperature. Figure 16 shows the record of a test period during which

blast-temperature readings were taken at 1-minute intervals. This period immediately followed the completion of test 7.

Calculations of reduced heat losses that may be reasonably anticipated on a larger installation indicate that blast temperatures in excess of 2,000° F. should be easily attained with this type of stove filling. In fact, temperatures of 2,400° appear to be possible without resort to a more refractory heat-transfer medium than ordinary river gravel.

In the early development of the phosphate blast furnace, considerable interest attached to the question of the degree of mechanical contact between the phosphate rock to be reduced and the carbo-

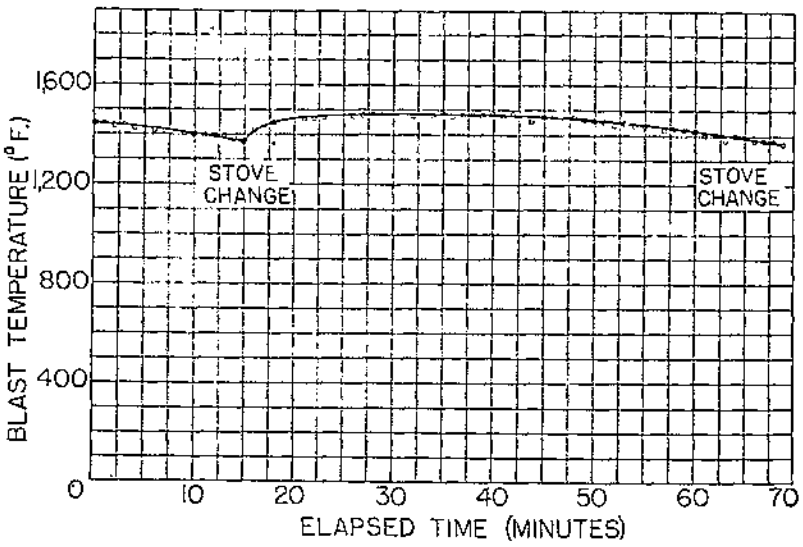


FIGURE 16.—Typical blast-temperature record in phosphate smelting, June 30, 1933.

naceous reducing agent. In the Department's earlier work (*75*), experiments were made only with briquetted charges. These briquets were made of finely ground phosphate rock and coke and were formed under high pressure by the use of various binders. The use of briquets in actual commercial operation has been reported by Easterwood (*14, 15*). In fact, it has generally been accepted by those interested in the development of the phosphate furnace that some preliminary treatment of the phosphate rock was necessary. Any operation involving the preliminary treatment of the rock before its charge into the furnace adds to the cost, which is reflected in the ultimate price of the fertilizer material to the consumer. Preliminary rock treatment, therefore, to be justified must result in an equal or greater reduction in some other item in the cost of operation.

In these experiments the phosphate, whether Tennessee blue-rock phosphate, washed Florida land-pebble phosphate, or Florida pebble phosphate matrix, was charged "as received." These phosphates differed greatly in mechanical condition, screen size, and moisture content. It was not found necessary to use any particular care in the manner in which the charge was put into the furnace. The experiments reported here when compared with the laboratory experiments cited (*31, 58*) regarding the temperature at which phosphate is

reduced by carbon and the amount of heat required by the reduction (*45, 58*) do not indicate that a compensating reduction in fuel cost would result from any such preliminary treatment of the rock.

In actual operation the relative proportions of the irreducible oxides must be such that a slag of suitably low viscosity is formed. In the ternary system lime-alumina-silica, however, the relative proportions of these oxide constituents may be varied over rather wide ranges without the production of slags that exhibit a viscosity sufficiently high to cause difficulty in furnace operation (*21*). In these experiments the ratio of lime plus magnesia to silica plus alumina in the charge ranged from 0.82 to 1.12.[5] No effort was made to determine the maximum or minimum limits of this base-acid ratio, but in the range employed no effect upon furnace operation was discovered.

This investigation of the smelting of phosphate rock in the blast furnace has resulted in three conclusions of considerable engineering importance: (1) That the fuel consumption may be greatly reduced by increasing the temperature to which the blast is raised; (2) that run-of-mine phosphate rock may be successfully charged into a phosphate blast furnace without preliminary treatment and that the mechanical condition or grade of the rock as charged is not particularly important from the standpoint of fuel consumption or of furnace operation; and (3) that the base-acid ratio of the charge may be varied widely without any sacrifice in the thermal efficiency of the process.

### DETERMINATION OF MATERIAL REQUIREMENTS

A careful study of the operation of the experimental furnace described in this bulletin indicates that the phosphate blast furnace has commercial possibilities in the fertilizer field. Although the primary purpose of this investigation was the study of the fundamentals of phosphate smelting rather than the making of a detailed cost analysis, certain important items in such a cost analysis can be estimated from the data obtained. For example, the percentage of phosphate reduced, the coke and flux requirements, and the blowing pressure have been determined.

The investigation has also developed an improved and cheaper hot-blast stove. It has shown that the phosphate furnace may be considerably shorter than the conventional iron furnace. The shaft of the phosphate furnace need only be sufficiently high to provide for the required heat interchange between the descending stock and ascending gases. The most suitable type of phosphorus-recovery system, however, is still in doubt because the limited time and money available restricted the investigation of phosphorus recovery to one particular method.

Phosphorus recovery may be accomplished by two general methods: Elementary phosphorus may be collected and subsequently oxidized and hydrated to phosphoric acid, or phosphoric acid may be recovered directly without separating the elementary phosphorus from the furnace top gas.

In the first method a large part of the dirt and fume carried by the top gas is removed by dust catchers, electrostatic precipitators, or other suitable devices while the gas is kept hot enough (about 250° F.) to prevent condensation of phosphorus. The gas is then cooled in a spray tower to a temperature sufficiently below its phosphorus dew point (*41*) to condense most of the phosphorus. Under suitable

[5] The lime-silica ratio ranged from 1.12 to 1.44.

conditions most of this condensed phosphorus may be collected in the spray tower, from which it may be withdrawn either as molten elementary phosphorus or as solid particles suspended in the effluent water. The condensed phosphorus that is not retained by the spray tower may be removed from the gas stream by an electrostatic precipitator. If the gas is not well cleaned prior to cooling, a considerable amount of dirt is caught with the phosphorus both in the spray tower and the precipitator. If the gas is not well cleaned the phosphorus is not so readily converted to phosphoric acid, but the sludge is much less hazardous to handle.

The second method of recovery may be carried out in several ways. The cleaned phosphorus-bearing top gas may be burned in the hot-blast stoves. This procedure has the apparent advantage of returning to the furnace both the heat of combustion of the phosphorus and the sensible heat of the top gas. Actually, however, the fuel value of the top gas by reason of its carbon monoxide content is far more than sufficient to produce the hot blast. The burning of the phosphorus in the stoves has the disadvantage that the amount of gas that must be treated for recovery of the product is larger. With a top gas that contains 40 percent of total carbon monoxide and hydrogen the volume of gas is approximately 75 percent greater after combustion than before. The burning of the gas in the stoves before removal of the phosphorus has the further disadvantage that $P_2O_5$ reacts with silicates at high temperatures, causing deterioration of the stove lining and heat-transfer medium. This, in stoves capable of producing the required high blast temperatures, would prove to be a serious handicap to economical phosphate smelting.

The most promising method for recovery of the phosphorus directly as phosphoric acid from the top gas seems to be that of preferentially burning the phosphorus. In this case, the dirt and fume are removed from the gas, and then sufficient air is admitted into the gas stream to burn the phosphorus. The $P_2O_5$ formed is removed as phosphoric acid by scrubbing towers and an electrostatic precipitator. The principal disadvantage of this method is that the gas line must be acid proof from the point at which air is admitted to beyond the collecting devices. It also introduces the hazard that sudden failure of the wind on the furnace might result in explosive mixtures of gas and air in the gas lines. However, this is not a new hazard since such irregularities are a source of explosions anyway.

In this investigation, only the collection of elementary phosphorus mixed with furnace fume and water as a sludge was studied. The results indicated that some other method might be better.

The amount of $P_2O_5$ actually recovered depends on the efficiency of the various parts of the recovery system as well as on the percentage of the phosphate reduced. Some phosphorus will combine with the iron present as an impurity to form ferrophosphorus, which may be tapped from the bottom of the hearth and used as such or converted into other useful products. A sample of ferrophosphorus made in these tests contained 23 percent of phosphorus, indicating that from 5 to 8 percent of the phosphorus reduced may leave the furnace in this form. With proper gas-cleaning and recovery equipment at least 95 percent of the phosphorus in the top gas should be recovered.

The estimation of the actual cost of constructing the furnace plant and recovery system is left to the blast-furnace construction engineer.

On the other hand, the material requirements can be presented here with a fair degree of accuracy. In order to simplify the presentation it was necessary to fix several variables as follows: The lime-silica ratio of the slag was assumed as 1.25, a figure which had been found satisfactory in the experimental tests. The temperature of the top gas was assumed to be 275° F. for the calculations based on total heat requirements. For calculations based on hearth-heat requirements it was unnecessary to assume a value for the top-gas temperature because the actual top-gas temperature will exceed that assumed for the calculation of the total heat balance over the range of blast temperatures for which the hearth-heat requirements are the controlling factors. In practice small errors made in estimating the total heat requirements will be reflected in variations of the top-gas temperature from the assumed value. Hearth-heat losses were fixed at 750 B. t. u. per pound of carbon burned at the tuyère in accordance with the discussion on page 34. Mantle-heat losses were assumed to be 10 percent additional. This is to be compared with shaft-heat losses amounting to 3.7 to 15.0 percent of the total heat losses on iron furnaces (*43, 44*). Slag was assumed to leave the reduction zone at 2,687°. The mean specific heat of slag was taken as 0.262 between 77° and 2,687°. The humidity was fixed at 0.01 pound of water per pound of dry air, a value differing but slightly from the average observed during these tests. Ninety percent of the phosphate charged was considered to be reduced, which although higher than reported in the present experiments (table 2), is a reasonable value to expect on a properly burdened commercial furnace.

Coke consumption was calculated in two ways: (1) On total heat requirements and (2) on hearth-heat requirements. As demonstrated on page 35, the hearth-heat requirement determines the coke consumption until the shaft-heat requirement exceeds the heat available in the bosh gas. For a given case the method that gives the higher coke consumption is the one that is applicable. Formally, coke consumption may be expressed as a function of the sensible heat of the blast and thus indirectly as a function of the blast temperature for each of the above methods of calculation. Simultaneous solution of these equations gives a sensible heat of the blast and consequently a blast temperature above which total heat requirements and below which hearth-heat requirements are controlling. This "critical blast temperature" depends on the relative amount of slag produced per unit of $P_2O_5$ reduced. Two examples are given, one for a washed Florida land-pebble phosphate and the other for a low-grade Florida hard-rock waste-pond phosphate. The analyses given in table 8 have been taken as representative of the materials.

TABLE 8.—*Chemical analyses of materials* [1]

| Material | $SiO_2$ | $Al_2O_3$ | CaO | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $P_2O_5$ | $CO_2$ | Combined $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* |
| Washed Florida land-pebble phosphate [2] | 0.90 | 2.13 | 46.59 | 1.91 | 0.26 | 0.72 | 31.63 | 5.88 | 0.76 |
| Florida hard-rock waste-pond phosphate [3] | 19.05 | 13.36 | 28.26 | 3.64 | .45 | .30 | 22.91 | 1.33 | 6.21 |

[1] Dried at 105° C.
[2] Free moisture as charged, 4.5 percent.
[3] Total water, organic carbon, and nitrogen, 6.87 percent; moisture as charged, 3.07 percent. Average analysis of 3 Florida hard-rock waste-pond phosphates. Jacob, Hill, Marshall, and Reynolds (*50, p. 22*).

The washed Florida land-pebble phosphate, which is high in lime with respect to silica, will require a siliceous flux, such as sand or gravel, if a lime-silica ratio in the slag of 1.25 is to be attained. The siliceous flux was assumed to contain 95 percent $SiO_2$. Since the waste-pond phosphate had a lime-silica ratio of 1.42 it was assumed to be self-fluxing within the limits of reasonable coke consumptions.

In calculating the coke consumptions on the basis of both the total or hearth-heat requirements it was necessary to know the relative amount of slag produced per unit of $P_2O_5$ reduced. In order to estimate this quantity the slag volume of each material and its relative proportion in the charge must be known or assumed. The expression, slag volume, is used to represent the weight fraction of the material charged that leaves the furnace as slag. On the basis of the analyses of table 8 the slag volumes of the materials were computed as 0.6391 and 0.7043 pound per pound of washed Florida land-pebble phosphate and Florida hard-rock waste-pond phosphate, respectively, a 90-percent reduction of the $P_2O_5$ being assumed in each case. The slag volumes of the siliceous flux and the coke were taken as 1.0 and 0.115 pound per pound, respectively. The following tabulation gives the slag volume calculated for the smelting of a washed Florida land-pebble phosphate under the conditions assumed:

| | *Slag volume, pounds per pound $P_2O_5$ reduced* |
|---|---|
| Washed Florida land-pebble phosphate | 2.245 |
| Siliceous flux [1] | $1.120-0.066\ \overline{CC}$ [2] |
| Coke [3] | $.115\ \overline{CC}$ |
| Total | $3.365+0.049\ \overline{CC}$ |

[1] $SiO_2$, 95 percent.
[2] $\overline{CC}$, coke consumption.
[3] Fixed carbon, 87 percent.

In this case each pound of the washed Florida land-pebble phosphate contains 0.3163 pound of $P_2O_5$ of which $0.9 \times 0.3163$, or 0.2847 pound, undergoes reduction. The slag formed from this rock, therefore, amounts to $\frac{0.6391}{0.2847}$, or 2.245, pounds per pound of $P_2O_5$ reduced. The siliceous flux required per pound of $P_2O_5$ may be calculated as follows: The ratio of lime charged to $P_2O_5$ reduced for this rock is $\frac{0.4650}{0.2847}$, or 1.633. The silica requirements are $\frac{1.633}{1.25}$, or 1.306, pound where 1.25 is the lime-silica ratio desired in the slag. The rock itself supplies $\frac{6.90}{28.47}$, or 0.242 pound, and each pound of coke charged supplies 0.063 pound. Hence flux must be added in some form to provide $(1.306-0.242-0.063\ \overline{CC})$ pound of silica per pound of $P_2O_5$ reduced, where $\overline{CC}$ is the pounds of coke charged per pound of $P_2O_5$ reduced. If the flux is 95 percent silica, $\frac{1.306-0.242-0.063\ \overline{CC}}{0.95}$, or $(1.120-0.066\ \overline{CC})$, pound of flux must be added per pound of $P_2O_5$ reduced.

The calculations of the coke required in smelting washed Florida land-pebble phosphate are illustrated in the following tabulations. In the first tabulation each item has the same significance as in the

tabulation on page 31. The coke consumption is based on hearth-heat requirements. The total slag volume, tabulated on page 41, multiplied by the mean specific heat of the slag, 0.275, and the degree of superheat, 432° F., gives $400+5.8\ \overline{CC}$, listed as $Q_2$.

| | | B. t. u. |
|---|---|---|
| Hearth heat required per pound of $P_2O_5$ reduced: [1] | | |
| $Q_1$ | For reducing phosphates | 4, 167 |
| $Q_2$ | For superheating slag | $5.8\ \overline{CC}+$ 400 |
| $Q_3$ | Total hearth heat required | $5.8\ \overline{CC}+4,567$ |
| Hearth heat available per pound of carbon burned at the tuyère: | | |
| Heat supplied: | | |
| $Q_4$ | By combustion of C to CO | 4, 014 |
| $Q_5$ | By sensible heat of blast, including moisture | $x$ |
| $Q_6$ | Total heat supplied | $x+4,014$ |
| Heat not available in hearth: | | |
| $Q_7$ | Lost by radiation and conduction: | |
| | (*a*) From hearth to cooling water | 750 |
| $Q_8$ | Used for reducing blast moisture, H=0.01 | 179 |
| $Q_9$ | Carried out of reduction zone: [2] | |
| | (*a*) By the products of combustion | 3, 095 |
| | (*b*) By the products of moisture decomposition | 85 |
| $Q_{10}$ | Total heat unavailable | 4, 109 |
| $Q_{11}$ | Net available hearth heat, $Q_6-Q_{10}$ | $x-95$ |

| | | Pounds |
|---|---|---|
| Carbon required per pound of $P_2O_5$ reduced: | | |
| $C_1$ | For generating heat, $Q_3/Q_{11}$ | $\frac{5.8\ \overline{CC}+4,567}{x-95}$ |
| $C_2$ | For reducing blast moisture | $0.0384\ C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225+1.0384\left[\frac{5.8\ \overline{CC}+4,567}{x-95}\right]$ |
| Coke [3] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x+4,702}{0.87x-89}$ |

[1] Based on the assumption of a 90-percent reduction of the phosphates and a lime-silica ratio of the charge equal to 1.25.
[2] Sensible heat of the gaseous products of combustion and moisture decomposition minus the sensible heat of the carbon from which they were derived.
[3] 87-percent fixed-carbon coke.

The calculation of the coke consumption on the basis of the total heat requirement is given in the second tabulation and was made principally to demonstrate that until blast temperatures in excess of 3,000° F. are reached the total heat requirement need not be considered. In the range where coke consumption depends on total heat requirements these calculations become less accurate. The many secondary reactions occurring in the shaft must be considered in detail. To include all of them is difficult and to determine to what extent they are occurring is frequently impossible. In the blast-temperature range where coke consumptions depend on hearth-heat requirements all shaft-heat requirements are satisfied by the heat carried up the shaft by the bosh gas. It is only with the heavy burdens made possible by high blast temperatures that the shaft heat required exceeds that available and that total heat calculations become necessary.

| | | | B. t. u. |
|---|---|---|---|
| Total heat required per pound of $P_2O_5$ reduced: [1] | | | |
| $Q_1$ | For reducing phosphates | | 4,167 |
| $Q_{12}$ | For producing slag | 33.5 $\overline{CC}$ + | 2,301 |
| $Q_{13}$ | For vaporizing and removing water | 2.25 $\overline{CC}$ + | 216 |
| $Q_{14}$ | For calcining carbonates and removing $CO_2$ | | 369 |
| $Q_{15}$ | For removing CO and $P_4$ resulting from reduction of phosphates | | 160 |
| $Q_{16}$ | Total heat required | 35.75 $\overline{CC}$ + | 7,213 |
| Heat available for smelting purposes per pound of carbon burned at the tuyère: | | | |
| Heat supplied: | | | |
| $Q_6$ | Total heat supplied (as in tabulation on page 42) | | $x$ + 4,014 |
| Heat not available for smelting purposes: | | | |
| $Q_7$ | Lost by radiation and conduction: | | |
| | (*a*) From hearth | | 750 |
| | (*b*) From mantle, 0.1×750 | | 75 |
| $Q_8$ | Used for reducing blast moisture, H = 0.01 | | 179 |
| $Q_{17}$ | Carried out in top gas: [2] | | |
| | (*a*) By the products of combustion | | 332 |
| | (*b*) By the products of moisture decomposition | | 10 |
| $Q_{18}$ | Total heat unavailable | | 1,346 |
| $Q_{19}$ | Net available heat, $Q_6 - Q_{18}$ | | $x$ + 2,668 |

| | | Pounds |
|---|---|---|
| Carbon required per pound of $P_2O_5$ reduced: | | |
| $C_1$ | For generating heat, $Q_{16}/Q_{19}$ | $\frac{35.75\ \overline{CC}+7,213}{x+2,668}$ |
| $C_2$ | For reducing blast moisture | 0.0384 $C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225+1.0384\left[\frac{35.75\ \overline{CC}+7,213}{x+2,668}\right]$ |
| Coke [3] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x+8,617}{0.87x+2,284}$ |

[1] Based on the assumption of a 90-percent reduction of the phosphates and a lime-silica ratio of the charge equal to 1.25.

[2] Sensible heat of the gases derived from the reaction of carbon with the blast. The sensible heats of the moisture removed from the charge, of the $CO_2$ derived from calcination of the carbonates, and of the CO and $P_4$ produced by phosphate reduction have already been allowed for in $Q_{13}$, $Q_{14}$, and $Q_{15}$.

[3] 87-percent fixed-carbon coke.

The items appearing for the first time in this tabulation are $Q_{7b}$ and $Q_{12}$ to $Q_{19}$, inclusive.

$Q_{7b}$ is the heat lost, by radiation and conduction, from the mantle.

$Q_{12}$, the total heat required to produce the slag, is equal to the slag volume tabulated on page 41, 3.365+0.049 $\overline{CC}$, multiplied by the mean specific heat of the slag, 0.262, and by the temperature interval, 2,687°—77° F.

$Q_{13}$ represents the heat required to vaporize all the water in the burden at the charging temperature, 77° F., and to heat it to the temperature at which it is assumed to leave the furnace, 275°. This was found from steam tables (*49*) to be 1,127 B. t. u. per pound of water.

$Q_{14}$ is the heat required to calcine the carbonates at the charging temperature and to heat the carbon dioxide formed to the top-gas temperature. The heat of calcination (*45*) was adopted as 1,739 B. t. u. per pound of carbon dioxide formed and the sensible heat (*16, 34, 39*) of this amount of carbon dioxide between 77° and 275° F. was taken as 43 B. t. u. Thus, $Q_{14}$ equals the weight of carbon dioxide produced by calcination per pound of $P_2O_5$ reduced multiplied by (1,739+43), or 1,782 B. t. u.

$Q_{15}$ is the difference in heat content between 77° and 275° F. of the phosphorus and carbon monoxide produced by the phosphate-reduction reaction. This correction is necessary since these products do not leave the furnace at the temperature at which they were charged. The value of 160 B. t. u. per pound of $P_2O_5$ reduced was taken for this quantity.

$Q_{17}$ is the sensible heat of the products of combustion and moisture decomposition that leave the furnace in the top gas.

$Q_{19}$ is the total heat supplied less such heat losses and consumptions as are more conveniently computed on the basis of carbon burned at

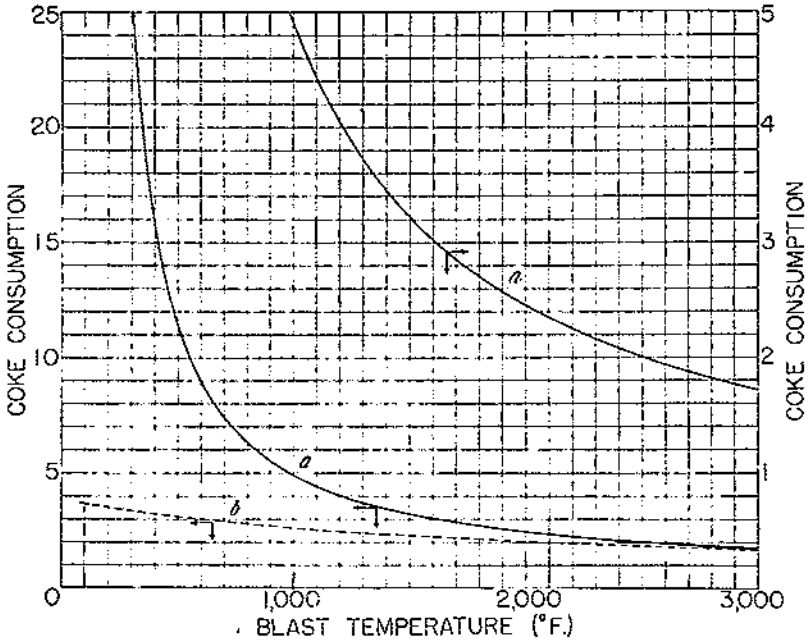


FIGURE 17.—Effect of the air-blast temperature on the estimated amount of 87-percent fixed-carbon coke required per pound of $P_2O_5$ reduced in a phosphate blast furnace smelting washed Florida land-pebble phosphate with a siliceous flux. Humidity, 0.01. Heat losses per pound of carbon burned at the tuyère: From hearth to cooling water, 750 B. t. u.; and from mantle, 75 B. t. u. Curve *a* is based on high-temperature heat requirements; curve *b* is based on total heat requirements.

the tuyère. It is the net heat per pound of carbon burned at the tuyères that is available to meet the heat requirements of the items constituting $Q_{16}$.

The relation between the weight of 87-percent fixed-carbon coke required for smelting washed Florida land-pebble phosphate and the air-blast temperature is given in figure 17.

The solid curve (*a*) of this figure represents the coke consumption based on hearth-heat requirements and was derived from the coke consumption equation of the tabulation on page 42. The broken curve (*b*) was similarly derived from the tabulation for the total heat requirements. Simultaneous solution of these two equations as described on page 40 gives a point of intersection equivalent to an air-blast temperature of 3,152° F., above which the total heat requirement becomes the controlling factor. This figure clearly demonstrates the necessity for high blast temperatures if low coke consumptions are to be attained.

In order to compare probable coke consumptions in smelting relatively low-grade phosphatic rocks with those for the above washed rock, the hearth and total heat requirements for a Florida hard-rock waste-pond phosphate were calculated. Since in this case no flux is to be added the slag volume of the charge is $\frac{0.7043}{0.9\times0.2291}+0.063\overline{CC}$, or $3.416+0.063\ \overline{CC}$.

The calculation of coke consumption in the smelting of a self-fluxing Florida hard-rock waste-pond phosphate on the basis of hearth-heat requirements, using the same assumptions as for the washed Florida land-pebble phosphate, is given in the tabulation below.

| | | B. t. u. |
|---|---|---|
| Hearth heat required per pound of $P_2O_5$ reduced: [1] | | |
| $Q_1$ | For reducing phosphates | 4,167 |
| $Q_2$ | For superheating slag | $13.7\ \overline{CC}+406$ |
| $Q_3$ | Total hearth heat required | $13.7\ \overline{CC}+4,573$ |
| Hearth heat available per pound of carbon burned at the tuyère: | | |
| $Q_{11}$ | Net available hearth heat (as in tabulation on p. 42) | $x-95$ |
| Carbon required per pound of $P_2O_5$ reduced: | | Pounds |
| $C_1$ | For generating heat, $Q_3/Q_{11}$ | $\frac{13.7\ \overline{CC}+4,573}{x-95}$ |
| $C_2$ | For reducing blast moisture | $0.0384\ C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225+1.0384\left[\frac{13.7\ \overline{CC}+4,573}{x-95}\right]$ |
| Coke [2] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x+4,799}{0.87x-97}$ |

[1] Based on the assumption of a 90-percent reduction of the phosphates.
[2] 87-percent fixed-carbon coke.

Similarly, the coke consumption calculated on the basis of total heat requirements is:

| | | B. t. u. |
|---|---|---|
| Total heat required per pound of $P_2O_5$ reduced: [1] | | |
| $Q_1$ | For reducing phosphates | 4,167 |
| $Q_{12}$ | For producing slag | $78.6\ \overline{CC}+2,336$ |
| $Q_{13}$ | For vaporizing and removing water | $2.25\ \overline{CC}+513$ |
| $Q_{14}$ | For calcining carbonates and removing $CO_2$ | 115 |
| $Q_{15}$ | For removing CO and $P_4$ resulting from reduction of phosphates | 160 |
| $Q_{16}$ | Total heat required | $80.85\ \overline{CC}+7,291$ |
| Heat available for smelting purposes per pound of carbon burned at the tuyère: | | |
| $Q_{19}$ | Net available heat (as in tabulation on page 43) | $x+2,668$ |
| Carbon required per pound of $P_2O_5$ reduced: | | Pounds |
| $C_1$ | For generating heat $Q_{16}/Q_{19}$ | $\frac{80.85\ \overline{CC}+7,291}{x+2,668}$ |
| $C_2$ | For reducing blast moisture | $0.0384\ C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225+1.0384\left[\frac{80.85\ \overline{CC}+7,291}{x+2,668}\right]$ |
| Coke [2] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x+8,698}{0.87x+2,237}$ |

[1] Based on the assumption of a 90-percent reduction of the phosphates.
[2] 87-percent fixed-carbon coke.

The relation between the coke consumption and the blast temperatures, as derived from the coke-consumption equations of these tabulations, is shown in figure 18.

Simultaneous solution of these equations shows that the blast temperature above which the total heat requirement is the controlling factor is 3,142° F., as compared with 3,152° for the washed land-pebble phosphate. A comparison of figures 17 and 18 shows that the grade of rock used had little effect on the coke consumption for a given blast temperature. The reason for this is that in each case there

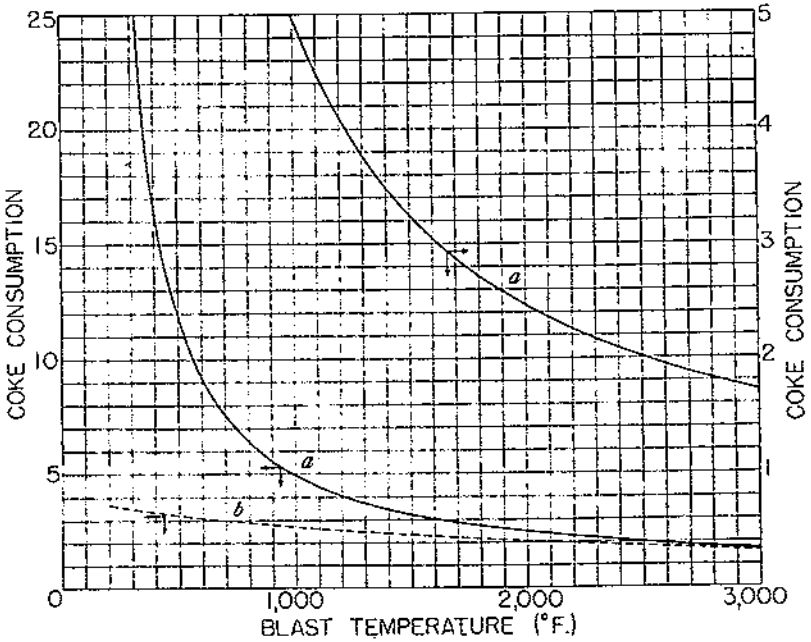


FIGURE 18.—Effect of the air-blast temperature on the estimated amount of 87-percent fixed-carbon coke required per pound of $P_2O_5$ reduced in a phosphate blast furnace smelting a self-fluxing Florida hard-rock waste-pond phosphate. Humidity, 0.01. Heat losses per pound of carbon burned at the tuyères: From hearth to cooling water, 750 B. t. u.; and from mantle, 75 B. t. u. Curve *a* is based on high-temperature heat requirements; curve *b* is based on total heat requirements.

was an excess of shaft heat so that coke consumption was determined by the hearth-heat requirement. The only factor in the hearth-heat requirement that differed in these cases was the slag volume.

Table 9 gives a concrete example of the estimated coke and material requirements for the smelting of Florida phosphates. Inspection of this table shows that, with air-blast temperatures of 1,000° F. or over, only 0.01 to 0.04 ton, or not over 1 percent, more total 87-percent fixed-carbon coke should be required to reduce 1 ton of $P_2O_5$ in the Florida hard-rock waste-pond phosphate than in the washed Florida land-pebble phosphate. The washed Florida land-pebble phosphate, however, also requires from 0.8 to 1 ton of a siliceous flux, whereas the Florida hard-rock waste-pond phosphate is self-fluxing.

TABLE 9.—*Estimated material requirements in phosphate smelting per ton of $P_2O_5$ reduced* [1]

| Blast temperature [2] (°F.) | Washed Florida land-pebble phosphate [3] | | | Florida hard-rock waste-pond phosphate [3] | |
|---|---|---|---|---|---|
| | Coke [4] | Phosphate | Gravel [5] | Coke [4] | Phosphate |
| | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* |
| 500 | 11.45 | 3.68 | 0.36 | 11.70 | 4.85 |
| 1,000 | 4.91 | 3.68 | .80 | 4.95 | 4.85 |
| 1,500 | 3.22 | 3.68 | .91 | 3.24 | 4.85 |
| 2,000 | 2.45 | 3.68 | .96 | 2.46 | 4.85 |
| 2,500 | 2.00 | 3.68 | .99 | 2.02 | 4.85 |

[1] Based on tabulations of pp. 42 and 43, assuming 90-percent reduction of the phosphate.
[2] Blast humidity, 0.01 pound of water per pound of air.
[3] Analysis as given in table 8.
[4] Fixed carbon, 87 percent.
[5] $SiO_2$, 95 percent.

From the above tables, tabulations, and figures, obtained in the determination of the material requirements for phosphate smelting and based on the interpretation of the results obtained from operation of the experimental furnace, it is at once evident that, with a satisfactory method for converting the phosphorus of the top gas to phosphoric acid before recovery or with a more satisfactory method for recovering the elementary phosphorus than was used in these investigations, blast-furnace methods for the production of phosphatic fertilizer materials offer attractive commercial possibilities. Air-blast temperatures of 2,000° F. and above, which should be readily and economically attainable by means of improved stoves of the type described, are particularly advantageous because with them the total coke requirement should be reduced to less than 2.5 tons per ton of $P_2O_5$ reduced. The precleaning of the top gas for the removal of dirt and fume, followed either by preferential oxidation of the phosphorus with hydration to phosphoric acid, or by condensation and direct recovery of the phosphorus for subsequent oxidation and hydration, appears to offer the best solution to the problem of recovering the product.

## POTASH SMELTING

### APPLICABILITY OF THE BLAST-FURNACE PROCESS

Potash smelting is a volatilization process that occurs without reduction. This is in contrast to phosphate smelting, which is a reduction process. In both cases the desired products leave the furnace in the top gas; in potash smelting as a fume and in phosphate smelting as a gas.

The only potash ore used in this investigation was wyomingite, an igneous rock containing several potash-bearing minerals, chief of which is leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) (*72*). Wyomingite is found in extensive deposits in the Leucite Hills of Sweetwater County, Wyo., and as mined contains from 8 to 12 percent of potash ($K_2O$). It cannot be readily concentrated, since its constituent crystals are microscopic in size.

Laboratory studies carried out in a small electric furnace have shown that the volatilization of potash from wyomingite is increased by the addition of such substances as calcium chloride, calcium car-

bonate, calcium fluoride, and sodium chloride (*42*). Practically complete volatilization of the potash was observed when mixtures of wyomingite, calcium carbonate, and calcium chloride were heated at 2,750° F. for 1 hour. It is supposed that under these conditions the potash escapes as the chloride and carbonate.

Thermal data on the various possible volatilization reactions are meager, but seem to indicate that the heat of reaction is small. It may be either exothermic or endothermic, depending on the reaction considered. The principal heat requirement for potash volatilization, therefore, is that for raising the furnace charge to temperatures at which the potash will volatilize. Since the blast furnace is well

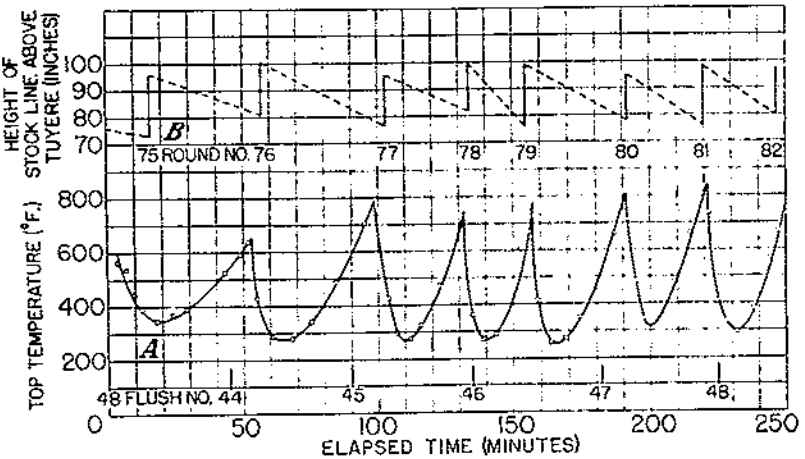


FIGURE 19.—Typical top-temperature (*A*) and stock-line (*B*) records in potash smelting, showing flushing intervals, August 3rd, 1932.

adapted to the heating and slagging of materials it should be readily applicable to potash-volatilization processes.

### DESCRIPTION OF EXPERIMENTS AND PRESENTATION OF DATA

The experimental procedure and observation of furnace-operating variables were almost identically the same in the potash as in the phosphate smelting tests on page 19. Operating conditions, however, were different. The amount of slag produced per unit of fuel was greater. At the same driving rate and with approximately the same flushing intervals larger volumes of slag were retained in the hearth between flushes. Collection of the potash fume could be made from the top gas at higher temperatures. The downcomer and gas lines were subject to more frequent stoppage, and the furnace was inclined to "hang." Figure 19 shows typical top-temperature and stock-line records during normal operation.

Three series of experiments were made on the smelting of wyomingite as follows: (1) August 2 to 5, 1932; (2) August 16 and 17, 1932; (3) August 29 to September 3, 1932, inclusive. The plant was altered slightly between each run.

(1) Run of August 2 to 5, 1932. In this run the gas-treating system, furnace, and stoves were the same as during the phosphate run of June 8 to 10, 1932 (p. 21). This run was characterized by high

furnace top pressures because dust and fume clogged the 4-inch downcomer and the spray-tower inlet. This run was terminated because of faulty precipitation and the frequent stoppage of the spray-tower inlet.

(2) Run of August 16 and 17, 1932. The potash-recovery system consisted only of the Multiclone and precipitator during this run. The stoppage of the gas lines was less serious than in the previous run as a result of removing the spray tower from the gas-cleaning circuit. Stock-line measurements showed rather irregular descent of stock in the furnace, and some difficulty was experienced in obtaining proper seating of the bells after a charge had been made.

(3) Run of August 29 to September 3, 1932. Before this run was started the double-bell assembly was replaced by a single bell. The crushed firebrick filling of the stoves was also removed and replaced by washed and screened river gravel (p. 14). The gas-cleaning equipment was left unchanged. As in previous runs some trouble was encountered with downcomer stoppage and low precipitation efficiency.

The three series of experiments have been broken down into test periods during which operating conditions were substantially uniform. The operating data for these periods are reported in table 10.

TABLE 10.—*Potash blast-furnace operating data, 1932*

| Test no. | Date | Duration | Burden | | | | | | Height of stock line above tuyère | Mean interval between flushes | Wind blown [1] | Blast temperature | Blast humidity [2] | Hearth-heat losses | Furnace top temperature | Blast pressure at— | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coke | Wyoming-ite | Limestone | Burned lime | Calcium chloride | $\frac{CaCl_2}{K_2O}$ | | | | | | | | Stove | Tuyère |
| 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| | 1932 | *Hours* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Mol ratio* | *Inches* | *Minutes* | *Cu. ft. per min.* | *°F.* | *Lb. $H_2O$ per lb. air* | *B. t. u. per min.* | *°F.* | *Lb. per sq. in.* | *Lb. per sq. in.* |
| 1 | Aug. 2 | 5.5 | 100 | 80 | 100 | 0 | 11 | 0.79 | 102.4 | 55 | 116 | 1,047 | 0.0127 | 1,410 | 412 | 3.1 | 3.0 |
| 2 | Aug. 3 | 9.1 | 100 | 80 | 100 | 0 | 22 | 1.58 | 98.8 | 60 | 114 | 934 | .0168 | 1,429 | 338 | 3.7 | 3.6 |
| 3 | Aug. 3 and 4 | 6.1 | 100 | 115 | 75 | 0 | 16 | .80 | 99.6 | 61 | 117 | 1,024 | .0155 | 1,425 | 428 | 3.8 | 3.7 |
| 4 | Aug. 4 | 1.9 | 100 | 115 | 75 | 0 | 16 | .80 | 94.9 | 57 | 118 | 1,175 | .0130 | 1,295 | ------ | 4.3 | 4.1 |
| 5 | Aug. 16 | 2.0 | 100 | 80 | 100 | 0 | 6 | .43 | 100.8 | 59 | 114 | 1,177 | .0098 | 1,709 | 399 | 2.0 | 1.9 |
| 6 | do | 1.9 | 100 | 80 | 100 | 0 | 6 | .43 | 98.4 | 56 | 116 | 1,404 | .0091 | 1,933 | 345 | 2.5 | 2.4 |
| 7 | do | 1.9 | 100 | 80 | 100 | 0 | 6 | .43 | 98.4 | 57 | 116 | 1,215 | .0124 | 1,658 | 304 | 2.5 | 2.4 |
| 8 | Aug. 29 and 30 | 11.0 | 100 | 130 | 115 | 0 | 10 | .44 | 92.1 | 60 | 117 | 1,308 | .0134 | 1,652 | 367 | 2.2 | 2.1 |
| 9 | Aug. 30 | 13.5 | 100 | 165 | 90 | 28 | 13 | .45 | 85.4 | 46 | 116 | 1,200 | .0146 | 1,772 | 527 | 2.5 | 2.3 |
| 10 | Aug. 31 | 2.0 | 100 | 80 | 100 | 0 | 8 | .57 | 82.3 | 40 | 117 | 1,335 | .0118 | 1,561 | 612 | 2.3 | 2.1 |
| 11 | do | 2.3 | 100 | 80 | 100 | 0 | 9 | .0 | 83.9 | 68 | 117 | 1,318 | .0151 | 1,826 | 570 | 2.4 | 2.2 |
| 12 | Sept. 2 | 3.8 | 100 | 130 | 115 | 0 | 20 | .88 | 84.6 | 46 | 117 | 1,206 | .0156 | 1,552 | 408 | 2.5 | 2.4 |

| Test no. | Pressure at furnace top | Pressure-drop across | | Top-gas composition | | | | Slag composition | | | | Slag | $K_2O$ | | | Coke [3] $\frac{\text{Coke}}{K_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Stove on wind | Furnace | $CO_2$ | CO | $H_2$ | $N_2$ | $K_2O$ | CaO | $SiO_2$ | $\frac{CaO}{SiO_2}$ | | Charged | Volatilized | Volatilization | |
| | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 |
| | *Lb. per sq. in.* | *Inches of water* | *Lb. per sq. in.* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Weight ratio* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Percent* | *Weight ratio* |
| 1 | | 2.9 | | 5.84 | 34.61 | 2.24 | 57.28 | 0.87 | 45.69 | 32.41 | 1.410 | 134.2 | 8.87 | 7.70 | 86.80 | 11.4 |
| 2 | | 2.9 | | 5.09 | 35.27 | 2.34 | 57.30 | .54 | 44.24 | 33.15 | 1.335 | 137.8 | 8.87 | 8.13 | 91.66 | 10.8 |
| 3 | | 3.2 | | 4.78 | 33.79 | 3.[illegible] | 57.74 | 2.81 | 33.52 | 40.30 | .832 | 153.0 | 12.75 | 8.45 | 66.27 | 10.3 |
| 4 | | 4.0 | | | | | | 2.94 | 32.60 | 40.20 | .811 | 155.2 | 12.75 | 8.19 | 64.24 | 10.7 |
| 5 | | 2.5 | | | | | | .38 | 46.30 | 33.98 | 1.363 | 130.0 | 8.87 | 8.38 | 94.48 | 10.4 |
| 6 | 0.4 | 2.9 | 1.9 | 4.49 | 36.01 | 2.53 | 56.97 | .72 | 46.40 | 33.09 | 1.402 | 130.0 | 8.87 | 7.93 | 89.46 | 11.0 |
| 7 | | 2.9 | | 6.78 | 34.19 | 2.45 | 56.58 | 2.32 | 44.05 | 36.10 | 1.220 | 139.4 | 8.87 | 5.64 | 63.59 | 15.5 |
| 8 | 1.1 | 4.6 | 1.0 | 6.01 | 33.59 | 2.01 | 58.39 | 3.17 | 38.97 | 35.18 | 1.108 | 183.6 | 14.41 | 8.59 | 59.61 | 10.2 |
| 9 | | 4.0 | | 6.00 | 30.36 | 2.16 | 61.48 | 4.45 | 36.29 | 38.38 | .946 | 232.4 | 18.27 | 7.95 | 43.52 | 11.0 |
| 10 | | 4.2 | | 4.59 | 35.51 | 2.80 | 57.10 | 2.84 | 42.48 | 32.49 | 1.307 | 138.4 | 8.87 | 4.94 | 55.69 | 17.7 |
| 11 | | 4.3 | | 3.16 | 38.33 | 2.75 | 55.76 | 2.31 | 39.61 | 34.12 | 1.161 | 137.4 | 8.87 | 5.70 | 64.26 | 15.3 |
| 12 | 1.1 | 3.7 | 1.2 | 6.73 | 31.10 | 2.95 | 59.22 | 2.29 | 38.98 | 37.35 | 1.044 | 189.5 | 14.41 | 10.07 | 69.88 | 8.7 |

[1] Measured at 32° F. and 29.92 inches of Hg.

[2] To convert to grains of moisture per cubic foot multiply by 565.

[3] Weight of 87-percent fixed-carbon coke per unit weight of $K_2O$ volatilized.

The compositions of the materials are given in table 3 (p. 24). The wyomingite charged was crushed to pass a 1-mesh and be retained on a 4-mesh screen. It contained 2 percent of water as charged to the furnace. The calcium chloride, which was charged in flake form, contained 76.5 percent of $CaCl_2$ and 23.5 percent of water. The slag volumes per round reported in table 9 were obtained in the manner described on page 23.

Tables 11 and 12 show the amounts of carbon used in the various furnace reactions. The items of table 11 were calculated as described on page 24.

TABLE 11.—*Potash blast-furnace carbon balance*

[Pounds of carbon per round]

| Test nr. | Input | | | Output | | | | Unaccounted for [1] |
|---|---|---|---|---|---|---|---|---|
| | Fixed-carbon in coke | Carbon as carbonates | Total | Burned by $O_2$ in blast | Used for decomposing blast moisture | Derived from calcination of carbonates | Total | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* |
| 1 | 76.08 | 10.80 | 86.88 | 65.05 | 3.48 | 10.80 | 79.03 | 7.85 |
| 2 | 76.08 | 10.80 | 86.88 | 65.38 | 4.22 | 10.80 | 80.38 | 6.50 |
| 3 | 76.08 | 8.10 | 84.18 | 65.70 | 3.90 | 8.10 | 77.76 | 6.42 |
| 6 | 76.08 | 10.80 | 86.88 | 64.67 | 2.26 | 10.80 | 77.73 | 9.15 |
| 7 | 76.08 | 10.80 | 86.88 | 63.48 | 3.03 | 10.80 | 77.31 | 9.57 |
| 8 | 76.08 | 12.42 | 88.50 | 65.46 | 3.36 | 12.42 | 81.24 | 7.26 |
| 9 | 76.08 | 9.80 | 85.88 | 70.23 | 3.94 | 9.80 | 83.97 | 1.91 |
| 10 | 76.08 | 10.80 | 86.88 | 65.46 | 2.98 | 10.80 | 79.24 | 7.64 |
| 11 | 76.08 | 10.80 | 86.88 | 61.78 | 3.60 | 10.80 | 76.18 | 10.70 |
| 12 | 76.08 | 12.42 | 88.50 | 73.35 | 4.40 | 12.42 | 90.17 | −1.67 |

[1] Due to errors of analysis and undetermined reduction reactions (column 4 minus column 8).

TABLE 12.—*Utilization of fixed carbon in the potash blast furnace*

| Test no. | Burned by $O_2$ in blast | Used for decomposing blast moisture | Accounted for | Unaccounted for [1] | Test no. | Burned by $O_2$ in blast | Used for decomposing blast moisture | Accounted for | Unaccounted for [1] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| | *Percent* | *Percent* | *Percent* | *Percent* | | *Percent* | *Percent* | *Percent* | *Percent* |
| 1 | 85.50 | 4.18 | 89.68 | 10.32 | 8 | 86.04 | 4.42 | 90.46 | 9.54 |
| 2 | 85.91 | 5.55 | 91.46 | 8.54 | 9 | 92.31 | 5.18 | 97.49 | 2.51 |
| 3 | 87.67 | 5.21 | 92.88 | 7.12 | 10 | 86.04 | 3.92 | 89.96 | 10.04 |
| 6 | 86.00 | 2.97 | 87.97 | 12.03 | 11 | 81.20 | 4.73 | 85.93 | 14.07 |
| 7 | 83.44 | 3.98 | 87.42 | 12.58 | 12 | 96.41 | 5.78 | 102.19 | −2.19 |

[1] Due to errors of analysis and undetermined reduction reactions.

In the phosphate runs practically all the carbon charged could be accounted for. In the potash runs, however, an average of 9.38 percent was used in some unaccounted-for manner.

Table 13 gives the total heat balances for each of these tests on the basis of 1 pound of carbon burned at the tuyère.

TABLE 13.—*Heat balance of the potash blast furnace* [1]

[1 pound of carbon burned by $O_2$ in blast]

| Test no. | Heat input | | | Heat output | | | | | | | Heat unaccounted for [2] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Combustion of carbon | Sensible heat of blast | Total | Reduction of blast moisture | Calcination of carbonates | Vaporization and removal of water in charge | Sensible heat of dry top gas | Sensible heat of slag | Hearth-heat losses | Total | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *B.t.u.* | *Percent* |
| 1 | 4,014 | 1,595 | 5,609 | 227 | 1,053 | 234 | 848 | 1,469 | 800 | 4,440 | 1,169 | 20.8 |
| 2 | 4,014 | 1,251 | 5,265 | 360 | 1,049 | 274 | 501 | 1,444 | 886 | 4,467 | 798 | 15.2 |
| 3 | 4,014 | 1,388 | 5,402 | 277 | 770 | 266 | 493 | 1,566 | 871 | 4,243 | 1,159 | 21.5 |
| 6 | 4,014 | 1,946 | 5,960 | 162 | 1,060 | 209 | 520 | 1,375 | 1,192 | 4,518 | 1,442 | 24.2 |
| 7 | 4,014 | 1,669 | 5,683 | 222 | 1,080 | 209 | 443 | 1,505 | 1,022 | 4,481 | 1,202 | 21.2 |
| 8 | 4,014 | 1,816 | 5,830 | 240 | 1,141 | 259 | 549 | 1,520 | 1,010 | 5,010 | 820 | 14.1 |
| 9 | 4,014 | 1,669 | 5,683 | 201 | 886 | 358 | 537 | 2,264 | 1,093 | 5,097 | −14 | −.3 |
| 10 | 4,014 | 1,852 | 5,866 | 211 | 1,048 | 234 | 1,039 | 1,444 | 954 | 4,930 | 936 | 16.0 |
| 11 | 4,014 | 1,885 | 5,899 | 270 | 1,109 | 209 | 681 | 1,519 | 1,116 | 5,204 | 695 | 11.8 |
| 12 | 4,014 | 1,667 | 5,681 | 279 | 1,075 | 279 | 619 | 1,764 | 940 | 4,965 | 716 | 12.6 |

[1] Reference temperature, 77° F. [2] Column 12 equals column 1 minus column 11.

A comparison of table 13 with table 12 shows that, in general, the amount of heat unaccounted for is roughly proportional to the amount of carbon unaccounted for. This is discussed further on page 54.

### INTERPRETATION OF RESULTS

In potash smelting there seems to be no relation between the net heat supplied and the amount of potash volatilized. When these quantities were plotted in a manner similar to that shown for phosphate smelting (fig. 13) they failed to show any correlation. This can only be interpreted to mean that the amount of heat involved in the volatilization reaction was too small to be detected, which substantiates the theoretical considerations on page 48 with regard to the magnitude of this quantity.

Since the amount of heat required for the volatilization reaction is too small to be detected, the heat used to supply the hearth-heat losses and to reduce the blast moisture is the major high-temperature heat requirement for potash smelting. Molten slag is removed from the hearth at high temperatures, but only a small part of the sensible heat involved is high-temperature heat because of the countercurrent exchange of heat between the slag-forming materials and the bosh gas in the furnace stack.

In potash smelting, therefore, the coke consumption is determined by the total heat requirements of the process and not by the hearth-heat requirements as in most phosphate smelting. As in all blast-furnace processes where coke-consumption calculations are permissible on the basis of total heat requirements, the only restriction is, that, after allowance has been made for the heat lost by radiation and conduction and used to decompose the blast moisture, the temperature and the heat content of the combustion products shall be sufficiently high to slag the charge.

The following tabulation, showing the estimated coke consumption for test 2, is an example. The method of calculation is roughly

analogous to that used to obtain the total heat requirements of the phosphate furnace (p. 43).

| | B. t. u. |
|---|---|
| Total heat required per pound of $K_2O$ volatilized: | |
| $Q_{12}$ For producing slag | 11, 590 |
| $Q_{13}$ For vaporizing and removing water | 2, 202 |
| $Q_{14}$ For calcining carbonates and removing $CO_2$ | 8, 456 |
| $Q_{15}$ Total heat required | 22, 248 |
| Heat available for smelting purposes per pound of carbon burned at the tuyère: | |
| Heat supplied: | |
| $Q_4$ By combustion of C to CO | 4, 014 |
| $Q_5$ By sensible heat of blast including moisture, 934° F | 1, 251 |
| $Q_6$ Total heat supplied | 5, 265 |
| Heat not available for smelting purposes: | |
| $Q_7$ Lost by radiation and conduction: | |
| (*a*) From hearth to cooling water | 896 |
| (*b*) From mantle, estimated as $0.1 \times 896$ | 90 |
| $Q_8$ Used for reducing blast moisture, $H = 0.0168$ | 301 |
| $Q_{17}$ Carried out in top gas: [1] | |
| (*a*) By the products of combustion | 440 |
| (*b*) By the products of moisture decomposition | 20 |
| $Q_{20}$ Used for direct reduction | 596 |
| $Q_{18}$ Total unavailable heat | 2, 343 |
| $Q_{19}$ Net available heat, $Q_6 - Q_{18}$ | 2, 922 |
| | *Pounds* |
| Carbon required per pound of $K_2O$ volatilized: | |
| $C_1$ For generating heat, $Q_{16}/Q_{19}$ | 7. 61 |
| $C_2$ For reducing blast moisture, $0.0646\ C_1$ | .49 |
| $C_3$ For unexplained direct reduction, $0.0994\ C_1$ | .76 |
| $C_4$ Total carbon required | 8. 86 |
| Coke [2] required per pound of $K_2O$ volatilized: | |
| $\overline{CC}$ Coke consumption, $C_4/0.87$ | 10. 18 |

[1] Sensible heat of the gases derived from reaction of carbon with the blast. The sensible heat of the moisture removed from the charge and of the $CO_2$ derived from calcination of the carbonates has already been allowed for in $Q_{13}$ and $Q_{14}$.
[2] 87-percent fixed-carbon coke.

The calculated value of 10.18 pounds of coke consumed per pound of $K_2O$ volatilized differs from the observed value of 10.8 by only 5.7 percent, which is well within the limits of error.

The items contained in this tabulation were evaluated as follows:

$Q_7$ is the measured heat loss to the bosh and tuyère coolers, to which an additional 10 percent has been added for shaft-heat losses. This estimate is justified by the observations of Marshall (*43*, *44*) on iron blast furnaces where he found that the shaft-heat losses averaged about 11 percent of the cooling-water losses.

$Q_8$ is calculated in the same manner as on page 33.

$Q_{12}$, the heat required to produce the slag, is equal to the amount of slag formed per pound of $K_2O$ volatilized multiplied by the mean specific heat, 0.262, and by the difference between the temperatures at which the slag-forming materials entered, 77° F., and at which the slag was assumed to leave the furnace, 2,687°.

$Q_{13}$ is the heat used to evaporate the water in the charge and to heat it to the top-gas temperature. It was calculated in the manner described on page 43.

$Q_{14}$, the heat used to calcine the carbonates and to carry the resulting carbon dioxide out of the furnace, was calculated in the manner described on page 43.

$Q_{17}$ is the sensible heat of the bosh gases leaving the furnace. In these tests this value is too low because the thermocouple was placed in the downcomer instead of directly above the surface of the stock. This may have caused a considerable error because the whole cross section of the mantle was exposed to an uninsulated water-cooled top and most of the heat lost to this cooler came from the sensible heat of the top gas and was not measured.

$Q_{20}$ Represents the heat used in unknown reduction reactions (see $C_3$ below) and is equal to 6,000 B. t. u. multiplied by the value for $C_3$. A plot of unaccounted-for carbon per pound of carbon burned at the tuyères (table 12, column 5) against unaccounted-for heat on the same basis (table 13, column 12) showed that they were roughly proportional and that 6,000 B. t. u. was a reasonable assumption for the heat of these reactions.

$C_1$ and $C_2$ are explained on page 33.

$C_3$ is difficult to account for. The top-gas analyses showed that more carbon-containing gases were present than were generated by combustion, calcination, and blast-moisture reduction. In test 2 the excess was equivalent to 0.0994 pound of carbon for each pound of carbon burned by the blast. This excess could only result from reduction reactions. Two such reactions are:

$$Fe_2O_3+3C=2Fe+3CO$$
$$CO_2+C=2CO$$

The wyomingite contained 4.87 percent of $Fe_2O_3$, which, if completely reduced to metallic iron by solid carbon, would have required in test 2 only 0.0265 pound of carbon per pound of carbon burned at the tuyère.

Carbon would be used by the second reaction if any calcination were to take place at temperatures exceeding about 1,850° F. At this temperature, this reaction is supposed to proceed at a sufficiently high rate to result in a noticeable carbon consumption. Although this temperature is above the normal dissociation temperature (about 1,650°) (*45*) of calcium carbonate, the rate of stock descent and the rate of calcination were such that some calcination may possibly have occurred at temperatures where the carbon dioxide would have been reduced by carbon. This would decrease the carbon dioxide concentration in the top gas below that required by the carbonates charged. On the average, sufficient carbon dioxide was present in the top gas in these tests to account for all the limestone charged. No definite conclusion can be reached, therefore, as to how this excess carbon was used. It is reasonably certain, however, that the carbon was consumed in direct reduction and that a corresponding amount of heat was absorbed (p. 52).

Any decrease in the heat requirements or increase in the net heat supplied would permit the charging of a heavier burden and presumably result in a decrease in the coke consumption per unit of $K_2O$ volatilized. The most obvious method for decreasing the coke consumption, aside from increasing the blast temperature, would be that of replacing the limestone flux by burned lime and thereby eliminating $Q_{14}$, which amounted to about 38 percent of the total heat requirements. This can be accomplished at a low cost by burning the limestone with waste blast-furnace top gas as fuel. The

replacement of limestone by burned lime would also remove the possibility of the consumption of carbon in the reduction of carbon dioxide and thus, perhaps, eliminate the heat used in the unknown reduction reactions. The coke consumption would also be decreased by drying the blast, decreasing the heat losses, and increasing the blast temperature, but not nearly so much as in phosphate smelting.

Since the amount of available heat determines only the amounts of materials that can be slagged and not the amount of potash volatilized, the question arises as to the factors responsible for the wide variations in the volatilization percentages. The base-acid ratio of the slag, the mol ratio of the calcium chloride to the potash charged, the length of time the slag is held at volatilization temperatures, and the actual temperatures prevailing in the hearth are possible factors.

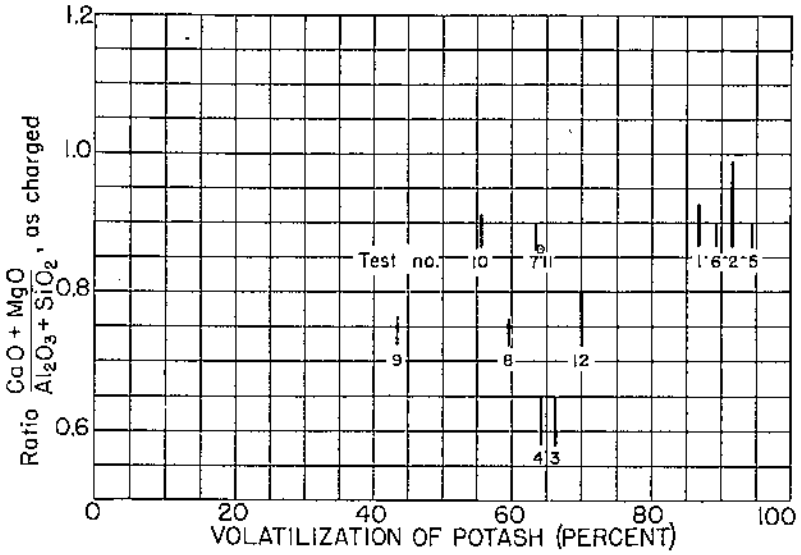


FIGURE 20.—Relation between the calculated base-acid ratio of the slag and the observed volatilization of potash, the length of the lines indicating the uncertainty in this ratio caused by the calcium chloride in the charge.

In figure 20 the percentage volatilizations are plotted against the weight ratios of lime plus magnesia to alumina plus silica in the charges.

There is some uncertainty in the actual value of these ratios due to the fact that a part of the calcium chloride charged left the furnace as a fume instead of as lime in the slag. The length of the vertical line for each test shows the extent of this uncertainty. It is evident that the volatilization approximated 90 percent only when the base-acid ratio approached 0.9 (tests 1, 2, 5, and 6). Conversely, the tests in which more acid slags were produced (tests 3, 4, 8, 9, and 12) showed poor volatilization. Not all the tests with the higher base-acid ratios showed good volatilization, indicating the existence of other influential factors. The use of calcium chloride seemed to be beneficial under some circumstances. In tests 2 and 5 the burdens were identical except that more than three and one-half times as much calcium chloride was charged in the former as in the latter. Volatilization was

roughly the same in each case. On the other hand, when relatively more acid slags were used, calcium chloride seemed to increase volatilization. In tests 3 and 4 twice as much calcium chloride was charged as in tests 8 and 9, and definitely higher volatilizations were obtained. It seems advisable to charge some calcium chloride since at least 0.43 mol of $CaCl_2$ was charged per mol of $K_2O$ in all the tests that showed good volatilization. It is best to keep the amount of calcium chloride as low as is consistent with good volatilization because the charging of large amounts of calcium chloride was observed to cause hanging of the stock in the furnace.

Comparison of the results of tests 10 and 11 indicates that a beneficial effect on volatilization is obtained by holding the slag in the hearth for longer periods. Test 10 (table 10) shows an abnormally low volatilization percentage, 55.69, in spite of a relatively basic slag and a 0.57 mol ratio of calcium chloride to potash, whereas test 11 shows a volatilization percentage of 64.26, which may be considered high in view of the fact that no calcium chloride was charged and that the slag was relatively low in lime. The mean time between flushes was 40 minutes in test 10 and 68 minutes in test 11.

Although only general conclusions regarding the effect of each of these variables could be drawn from the available data, these conclusions will be considered as working hypotheses for the estimation of the coke consumption to be anticipated in commercial practice. They are summarized as follows: (1) Coke consumption depends on the total heat requirements, (2) the weight ratio, $\frac{CaO+MgO}{Al_2O_3+SiO_2}$, must be as high as about 0.9 to obtain 90 percent volatilization, (3) the addition of small amounts of calcium chloride appears to be beneficial, and (4) volatilization may possibly be improved by prolonging the time of holding the slag in the hearth.

### DETERMINATION OF MATERIAL REQUIREMENTS

The economic feasibility of potash smelting depends to a large extent on the relative location of the raw materials, the furnace plant, and the market for the potash produced. Potash minerals do not ordinarily contain more than 8 to 12 percent of potash. They usually contain nearly equal quantities of potash and alumina and from 50 to 60 percent of silica. Because of their acidic character such ores require relatively large amounts of basic flux for smelting operations. As a result, about 12 to 15 tons of slag must be produced in the furnace for every ton of potash volatilized, which makes it imperative that the furnace plant be located close to the sources of both the potash-bearing rock and the limestone flux in order that transportation costs may be kept within practicable limits. The same is true of the fuel to only a slightly less extent.

The equipment required is not unusually elaborate. A dust catcher and an electrostatic precipitator or other fume-collecting device are needed in addition to the furnace stack, stoves, and blowing equipment. Particular attention should be paid to the design of the downcomer and the gas lines in order to prevent their clogging by the dirt and fume carried by the top gas. If the potash is not to be marketed in the form collected but is to be converted to the sulphate, phosphate, or nitrate, suitable auxiliary equipment must be provided for the transformation and for the regeneration of calcium chloride.

The purpose of this investigation, as stated elsewhere, was not a study of costs but of smelting principles. From the operating data it is possible to estimate the relative amounts of ore, flux, and fuel required in commercial operation. On the basis of the results it was concluded that potash volatilization depends on the composition of the charge and on the amount of heat required for slag production rather than on any thermal requirement of the volatilization reactions and that the fuel consumption, therefore, depends upon the total heat requirement for producing slag from a suitable charge. It was also concluded that 90 percent or more of the potash could be volatilized from charges having a weight ratio of $\frac{CaO+MgO}{Al_2O_3+SiO_2}$ of 0.9 and about 0.75 mol of calcium chloride per mol of $K_2O$. This amount of calcium chloride is probably in excess of the actual requirements and might be somewhat reduced in practice without seriously affecting the volatilization efficiency. The effect of the blast temperature on the coke consumption has been calculated for such conditions. The following tabulation gives these calculations for the smelting of potash from wyomingite with the use of a limestone flux. This tabulation is exactly similar to that described in detail on page 53.

Total heat required per pound of $K_2O$ volatilized:[1]

| | | B. t. u. |
|---|---|---|
| $Q_{12}$ | For producing slag | 140.2 $\overline{CC}$+9,429 |
| $Q_{13}$ | For vaporizing and removing water | 5.6 $\overline{CC}$+ 968 |
| $Q_{14}$ | For calcining carbonates and removing $CO_2$ | 115.7 $\overline{CC}$+6,353 |
| $Q_{16}$ | Total heat required | 261.5$\overline{CC}$+16,750 |

Heat available for smelting purposes per pound of carbon burned at the tuyère:

Heat supplied:

| | | |
|---|---|---|
| $Q_6$ | Total heat supplied (as in tabulation on page 42) | $x$+4,014 |

Heat not available for smelting purposes:

| | | |
|---|---|---|
| $Q_7$ | Lost by radiation and conduction: | |
| | (*a*) From hearth to cooling water | 750 |
| | (*b*) From mantle, 0.1×750 | 75 |
| $Q_8$ | Used for reducing blast moisture, H=0.01 | 179 |
| $Q_{17}$ | Carried out in top gas:[2] | |
| | (*a*) By the products of combustion | 413 |
| | (*b*) By the products of moisture decomposition | 10 |
| $Q_{20}$ | Used for direct reduction | 563 |
| $Q_{18}$ | Total unavailable heat | 1,990 |
| $Q_{19}$ | Net available heat | $x$+2,024 |

Carbon required per pound of $K_2O$ volatilized:

| | | Pounds |
|---|---|---|
| $C_1$ | For generating heat, $Q_{16}/Q_{19}$ | $\frac{262\ \overline{CC}+16,750}{x+2,024}$ |
| $C_2$ | For reducing blast moisture | 0.0384 $C_1$ |
| $C_3$ | For unexplained reduction | 0.0938 $C_1$ |
| $C_4$ | Total carbon required | 1.1322 $\left[\frac{262\ \overline{CC}+16,750}{x+2,024}\right]$ |

Coke[3] required per pound of $K_2O$ volatilized:

| | | |
|---|---|---|
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{21,798}{x+1,684}$ |

[1] Based on the assumption of a 90-percent volatilization of the potash, a lime-plus-magnesia to silica-plus-alumina ratio in the charge of 0.9 and a mol ratio of $CaCl_2$ to $K_2O$ charged of 0.75.

[2] Sensible heat of the gases derived from the reaction of carbon with the blast. The sensible heat of the moisture removed from the charge and the sensible heat of the $CO_2$ derived from calcination of the carbonates have already been allowed for in $Q_{15}$ and $Q_{14}$.

[3] 87-percent fixed-carbon coke.

Because the coke requirement for potash smelting is determined by the total heat requirement, it is possible to effect a considerable saving in this item if surplus top gas is used to burn the limestone before it is charged into the furnace. The following tabulation shows the calculation of the coke consumption when this is done.

| | | *B. t. u.* |
|---|---|---|
| Total heat required per pound of $K_2O$ volatilized: [1] | | |
| $Q_{12}$ | For producing slag | $140.2\overline{CC}+9,429$ |
| $Q_{13}$ | For vaporizing and removing water | $2.3\overline{CC}+769$ |
| $Q_{16}$ | Total heat required | $142.5\overline{CC}+10,198$ |
| Heat available for smelting purposes per pound of carbon burned at the tuyère: | | |
| $Q_{19}$ | Net available heat (as in tabulation on page 57) | $x+2,024$ |
| Carbon required per pound of $K_2O$ volatilized: | | *Pounds* |
| $C_1$ | For generating heat, $Q_{16}/Q_{19}$ | $\frac{143\overline{CC}+10,198}{x+2,024}$ |
| $C_2$ | For reducing blast moisture | $0.0384\ C_1$ |
| $C_3$ | For unexplained reduction | $0.0938\ C_1$ |
| $C_4$ | Total carbon required | $1.1322\left[\frac{143\overline{CC}+10,198}{x+2,024}\right]$ |
| Coke [2] required per pound of $K_2O$ volatilized: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{13,272}{x+1,839}$ |

[1] Based on the assumption of a 90-percent volatilization of potash, a lime-plus-magnesia to silica-plus-alumina ratio in the charge of 0.9 and a mol ratio of $CaCl_2$ to $K_2O$ charged of 0.75.
[2] 87-percent fixed-carbon coke.

The relations between the coke consumption and the blast temperature, as obtained from the two preceding tabulations, are shown in figure 21.

The analysis of the wyomingite used for making these calculations is given in table 3. This wyomingite was mined near Rock Springs, Wyo., and used for the blast-furnace tests. The limestone analysis [6] given in the following tabulation is that of limestone from a bed that runs through a part of eastern Idaho and southwestern Wyoming. An outcrop occurs near Sage, Wyo., about 4 miles from the railroad. Analyses of other Wyoming limestones are given by Eckel (*17*).

| Constituents: | *Percent* |
|---|---|
| $SiO_2$ | 2.6 |
| $Al_2O_3$ | .4 |
| $Fe_2O_3$ | .4 |
| MgO | 1.4 |
| CaO | 52.0 |
| $CO_2$ | 41.1 |
| Ignition loss | 1.8 |

The coke analysis assumed in these calculations was the same as that for the phosphate-furnace calculations. Such a coke presumably would be replaced by fuel produced by low-temperature carbonization of the coal mined in the vicinity of Rock Springs, Wyo. Analyses of this and other Wyoming coals are given by Fieldner, Cooper, and Osgood (*22, p. 72.*)

On the basis of these calculations the volatilization of 1 ton of $K_2O$ when a blast temperature of 2,000° F. is used would require 10.03 tons of wyomingite, 9.30 tons of limestone, 1.29 tons of 76.5-percent calcium chloride, and 4.78 tons of 87-percent fixed-carbon coke. If the lime-

[6] Private communication from W. W. Ruby, U. S. Geological Survey.

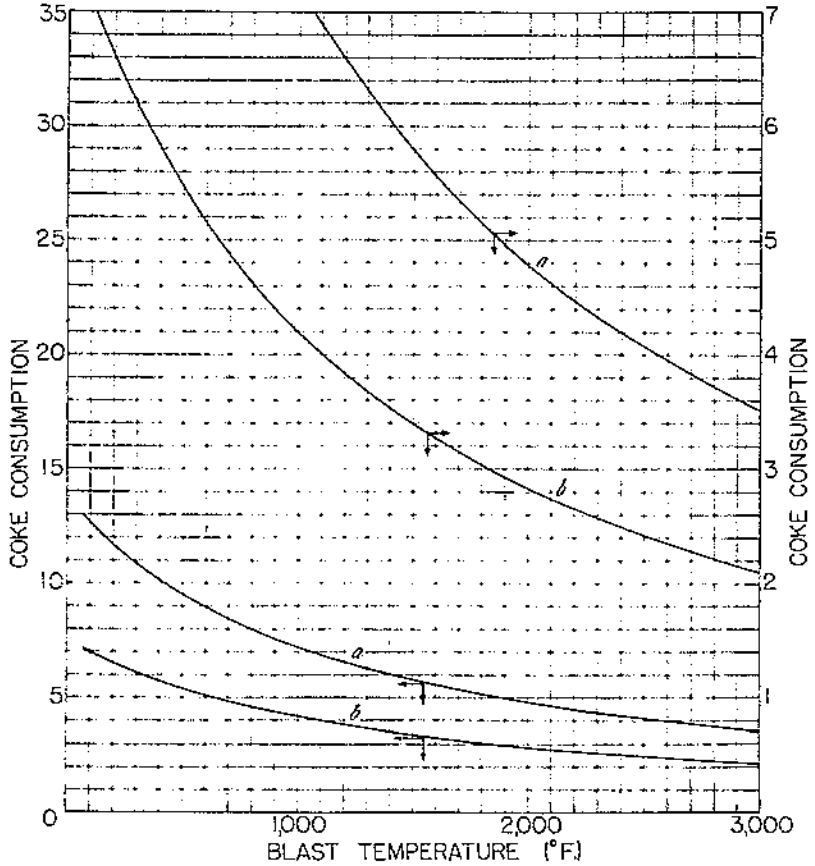


FIGURE 21.—Effect of the air-blast temperature on the estimated amount of 87-percent fixed-carbon coke required per pound of $K_2O$ volatilized in a potash blast furnace smelting wyomingite with limestone or burned lime and calcium chloride; humidity, 0.01. Heat losses per pound of carbon burned at the tuyères: From hearth to cooling water, 750 B. t. u.; and from mantle, 75 B. t. u. Curve *a* is based on limestone flux; curve *b* is based on burned lime flux.

TABLE 14.—*Estimated material requirements for smelting wyomingite per ton of $K_2O$ volatilized* [1]

| Blast temperature (° F.) [2] | Limestone flux [3] | | | | Burned lime flux [3] | | | |
|---|---|---|---|---|---|---|---|---|
| | Coke [4] | Wyomingite [5] | Limestone | Calcium chloride [6] | Coke [4] | Wyomingite [5] | Burned lime | Calcium chloride [6] |
| | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* |
| 500 | 9.51 | 10.03 | 9.71 | 1.29 | 5.41 | 10.03 | 5.44 | 1.29 |
| 1,000 | 7.22 | 10.03 | 9.45 | 1.29 | 4.18 | 10.03 | 5.33 | 1.29 |
| 1,500 | 5.77 | 10.03 | 9.30 | 1.29 | 3.38 | 10.03 | 5.26 | 1.29 |
| 2,000 | 4.78 | 10.03 | 9.19 | 1.29 | 2.82 | 10.03 | 5.21 | 1.29 |
| 2,500 | 4.07 | 10.03 | 9.11 | 1.29 | 2.41 | 10.03 | 5.17 | 1.29 |

[1] Based on tabulations on pp. 57 and 58 on the assumption of a 90-percent volatilization of the potash.
[2] Blast humidity, 0.01 pound of water per pound of air.
[3] Analysis of limestone as given on p. 58.
[4] Fixed carbon, 87 percent.
[5] Analysis as given in table 3.
[6] $CaCl_2$, 76.5 percent.

stone were burned with waste top gas the amounts of wyomingite and calcium chloride would not be changed, but the limestone would be replaced by 5.21 tons of burned lime and the amount of coke would be reduced to 2.82 tons. The estimated material requirements for other blast temperatures are given in table 14.

The conclusion is drawn from table 14 that commercial potash smelting appears feasible only when low-cost limestone and fuel are available. The information given in this bulletin in regard to the operating conditions involved in the blast-furnace process is, however, of fundamental importance because the existence of a technically feasible potash-furnace process should operate to set an upper limit to any future rise in the market price of potash.

## POTASH-PHOSPHATE SMELTING

### APPLICABILITY OF THE BLAST-FURNACE PROCESS

Combined potash-phosphate smelting appears to be attractive for three reasons: (1) The products can be converted to concentrated fertilizers that contain both potassium and phosphorus in an easily transportable form, (2) the furnace heat requirements would be better balanced between hearth and shaft, and (3) the ores are to a certain extent mutually fluxing. A product such as potassium phosphate would be less hazardous to ship and would, therefore, enjoy lower freight rates than elementary phosphorus or phosphoric acid. It would also be an advantage to ship potash combined with phosphoric acid as a phosphate rather than with hydrochloric acid as the chloride. The selling price of the usual commercial fertilizer would not, of course, warrant the cost of transportation from such areas as Idaho and Wyoming to the present southern and eastern markets.

The principal heat requirements for phosphate smelting occur in the hearth while for potash smelting they occur in the shaft. A combined smelting process, therefore, should use the heat generated in the blast furnace to better advantage although the actual extent of this advantage is not so great as might be supposed. With the low coke consumptions predicted for phosphate smelting with high blast temperatures a large excess of shaft heat is not available. For this reason as little potash should be produced as possible. The least that it would be convenient to ship would be that required to form monopotassium phosphate from the $P_2O_5$ produced. In this compound the weight ratio of $K_2O$ to $P_2O_5$ is 0.663, which is in excess of that which can be made with either the available shaft heat or by the use of a mutually fluxing mixture. The combined production of $K_2O$ and $P_2O_5$, however, requires less total heat and less flux than their production separately.

### DESCRIPTION OF EXPERIMENTS AND PRESENTATION OF DATA

One experiment was made on combined potash-phosphate smelting in the larger experimental furnace. This was made on September 2, 1932, as a part of the potash run of August 29 to September 3, 1932. The plant was not changed in any way for the tests on combined smelting. Burned lime, however, rather than limestone was used as a flux in order to reduce the shaft-heat requirements.

The run was divided into two short tests, one with the use of a low blast temperature of 448° F. and the other, of a medium blast temperature of 975°. The operating data, carbon balance, and heat balance are shown in tables 15, 16, and 17, which are similar to tables 2, 4, and 6 under phosphate smelting.

TABLE 15.—*Potash-phosphate blast-furnace operating data, 1932*

| Test no. | Date | Duration | Burden | | | | | | | Height of stock line above tuyères |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coke | Wyoming lime | Washed Florida land-pebble phosphate | Burned lime | Calcium chloride | $CaCl_2$ / $K_2O$ | $K_2O$ / $P_2O_5$ | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| | *1932* | *Hours* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Mol ratio* | *Weight ratio* | *Inches* |
| 1 | Sept. 2 | 2.0 | 100 | 135 | 50 | 50 | 18 | 0.76 | 0.851 | 87.4 |
| 2 | do. | 1.5 | 100 | 135 | 50 | 50 | 18 | .76 | .851 | 93.7 |

| Test no. | Wind blown[1] | Blast temperature | Blast humidity[2] | Hearth-heat loss | Furnace-top temperature | Blast pressure at | | Pressure drop across stove on wind |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Stove | Tuyère | |
| 1 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
| | *Cu. ft. per min.* | *° F.* | *Lb. $H_2O$ per lb. air* | *B.t.u. per min.* | *° F.* | *Lb. per sq. in.* | *Lb. per sq. in.* | *Inches water* |
| 1 | 119 | 448 | 0.0153 | 1,170 | 286 | 3.0 | 2.9 | 2.8 |
| 2 | 119 | 975 | .0150 | 1,497 | | 2.7 | 2.6 | 3.7 |

| Test no. | Top-gas composition | | | | Slag composition | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $CO_2$ | CO | $H_2$ | $N_2$ | $K_2O$ | $P_2O_5$ | CaO | $SiO_2$ | $\frac{CaO}{SiO_2}$ |
| 1 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
| | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Weight ratio* |
| 1 | 2.81 | 33.78 | 3.55 | 59.86 | 5.60 | 4.82 | 32.30 | 36.68 | 0.920 |
| 2 | | | | | .98 | 1.90 | 44.36 | 35.15 | 1.250 |

| Test no. | Slag | $K_2O$ | | | $P_2O_5$ | | | Coke | Coke[4] |
|---|---|---|---|---|---|---|---|---|---|
| | | Charged | Volatilized | Volatilization | Charged | Reduced | Reduction | $K_2O$ | $P_2O_5$ |
| 1 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 |
| | *Lb. per round* | *Lb. per round* | *Lb. per round* | *Percent* | *Lb. per round* | *Lb. per round* | *Percent* | *Weight ratio* | *Weight ratio* |
| 1 | 223.7 | 15.08 | 3.84 | 25.48 | 17.71 | 5.81 | 32.81 | 22.77 | 15.05 |
| 2 | 192.8 | 15.08 | 13.19 | 87.47 | 17.71 | 13.87 | 78.32 | 6.63 | 6.30 |

[1] Measured at 32° F. and 29.92 inches of Hg.
[2] To convert to grains of moisture per cubic foot, multiply by 565.
[3] Weight of 87-percent fixed-carbon coke per unit weight of $K_2O$ volatilized.
[4] Weight of 87-percent fixed-carbon coke per unit weight of $P_2O_5$ reduced.

TABLE 16.—*Potash-phosphate blast-furnace carbon balance*

[Pounds of carbon per round]

| Test no. | Input | | | Output | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fixed carbon in coke | Carbon as carbonates | Total | Burned by $O_2$ in blast | Used for decomposing blast moisture | Used for reducing phosphates | Derived from calcination of carbonates | Total | Unaccounted for [1] |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* | *Pounds* |
| 1 | 76.08 | 0.89 | 76.97 | 66.62 | 3.83 | 5.86 | 0.89 | 77.20 | −0.23 |
| 2 | 76.08 | .89 | 76.97 | | | | | | |

[1] Due to errors of analysis and undetermined reduction reactions (column 4 minus column 9).

TABLE 17. *Heat balance of the potash-phosphate blast furnace* [1]

[1 pound of carbon burned by $O_2$ in blast]

| Test no. | Heat input | | | Heat output | | | | | | | | Heat unaccounted for | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Combustion of carbon | Sensible heat of blast | Total | Reduction of phosphates | Reduction of blast moisture | Calcination of carbonates | Vaporization and removal of water in charge | Sensible heat of dry top gas | Sensible heat of slag | Hearth-heat losses | Total | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *Pct.* |
| 1 | 4,014 | 535 | 4,549 | | | | | | | | | | |
| 2 | 4,014 | 1,314 | 5,328 | 869 | 268 | 85 | 306 | 385 | 1,298 | 900 | 4,811 | [2] 517 | 9.70 |

[1] Reference temperature, 77° F. [2] Column 4 minus column 12.

The utilization of fixed carbon for test 2 is given in the following tabulation, and the composition of the materials charged is given in table 3 (p. 24.)

| | *Percent* |
|---|---|
| Burned by $O_2$ in blast | 87.57 |
| Used for decomposing blast moisture | 5.03 |
| Used for reducing phosphates | 7.70 |
| Accounted for | 100.30 |
| Unaccounted for [1] | −.30 |

[1] Due to errors of analysis and used in undetermined reduction reactions.

## INTERPRETATION OF RESULTS

The data from the two combined smelting tests are rather meager for definite conclusions. When, however, the net heat supplied and the amount of $P_2O_5$ reduced in these tests are correlated it is found that the data are well represented by line *b* of figure 13, which was obtained for independent phosphate smelting. This indicates that the high-temperature restrictions of phosphate smelting also apply to combined smelting processes.

Tables 16 and 17 show that the heat and carbon requirements are similar to those for phosphate smelting. They also show, in contrast to what was found in potash smelting, that neither carbon nor heat

was required for carrying out unexplained reduction reactions. This difference may possibly be attributed to the use of burned lime instead of limestone as the flux.

The weight ratio of the lime plus magnesia to the alumina plus silica charged was 0.82, the lime equivalent of the 0.76 mol of calcium chloride per mol of $K_2O$ in the charge being included. Potash-volatilization percentages of 25.46 and 87.47 were observed. The corresponding phosphate-reduction percentages were 32.81 and 78.32 with blast temperatures of 448° and 975° F., respectively.

Hignett and Royster (*28*), working with the Bureau's small furnace, obtained 90-percent volatilization of the potash by using slags of 0.9 base-acid ratio and relatively high calcium chloride to potash ratios.

From these considerations it is tentatively concluded that the heat requirements of the combined furnace may be computed in the same manner as in phosphate smelting. Furthermore, good potash-volatilization percentages may be obtained with slags having a base-acid ratio of 0.9 with the addition of 0.75 mol of calcium chloride per mol of potash charged.

### DETERMINATION OF MATERIAL REQUIREMENTS

The equipment required for combined potash-phosphate smelting is essentially the same as for the individual processes. Since the potash leaves the furnace as a fume, it may be collected from the top gas by means of a dust collector and precipitator before the gas is cooled sufficiently to condense the phosphorus. The phosphorus may then be collected by one of the methods described on pages 38 and 39.

Additional equipment would be required to convert the potash salts into phosphates. The hydrochloric acid recovered from this operation would be reconverted to calcium chloride and returned to the furnace.

The following tabulation shows the calculation of coke consumption based on the hearth-heat requirements for smelting a burden of wyomingite, Idaho phosphate rock, and burned lime:

| | | *B.t.u.* |
|---|---|---|
| Hearth heat required per pound of $P_2O_5$ reduced: [1] | | |
| $Q_1$ | For reducing phosphates | 4,167 |
| $Q_2$ | For superheating slag | $24.4\overline{CC}+1,150$ |
| $Q_3$ | Total hearth heat required | $24.4\overline{CC}+5,317$ |
| Hearth heat available per pound of carbon burned at the tuyères: | | |
| $Q_{41}$ | Net available hearth heat (as in tabulation on p. 42) | $x-95$ |
| Carbon required per pound of $P_2O_5$ reduced: | | *Pounds* |
| $C_1$ | For generating heat, $Q_3/Q_{41}$ | $\frac{24.4\overline{CC}+5,317}{x-95}$ |
| $C_2$ | For reducing blast moisture | $0.0384\ C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225+1.0384\left[\frac{24.4\overline{CC}+5,317}{x-95}\right]$ |
| Coke [2] required per pound of $P_2O_5$ reduced: | | |
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x+5,481}{0.87x-108}$ |

[1] Based on the assumption of a 90-percent reduction of phosphates, a lime-silica ratio of the charge equal to 1.0, a mol ratio of $CaCl_2$ to $K_2O$ charged of 0.75, and the volatilization of 91.2 ±2, or 0.963, pound of $K_2O$ per pound of $P_2O_5$ reduced.

[2] 87-percent fixed-carbon coke.

Similarly, the coke consumption calculated on the basis of total heat requirements is:

Total heat required per pound of $P_2O_5$ reduced: [1]

| | | *B. t. u.* |
|---|---|---|
| $Q_1$ | For reducing phosphates | 4,167 |
| $Q_{12}$ | For producing slag | $140\overline{CC}$ + 6,621 |
| $Q_{13}$ | For vaporizing and removing water | $2\overline{CC}$ + 574 |
| $Q_{14}$ | For calcining carbonates and removing $CO_2$ | 96 |
| $Q_{15}$ | For removing CO and $P_4$ resulting from reduction of phosphates | 160 |
| $Q_{16}$ | Total heat required | $142\overline{CC}$ + 11,618 |

Heat available for smelting purposes per pound of carbon burned at the tuyère:

| | | |
|---|---|---|
| $Q_{19}$ | Net available heat (as in tabulation on p. 43) | $x$ + 2,668 |

Carbon required per pound of $P_2O_5$ reduced:

| | | *Pounds* |
|---|---|---|
| $C_1$ | For generating heat, $Q_{16}/Q_{19}$ | $\frac{142\overline{CC} + 11,618}{x + 2,668}$ |
| $C_2$ | For reducing blast moisture | 0.0384 $C_1$ |
| $C_3$ | For reducing phosphates | 0.4225 |
| $C_4$ | Total carbon required | $0.4225 + 1.0384\left[\frac{142\overline{CC}+11,618}{x+2,668}\right]$ |

Coke [2] required per pound of $P_2O_5$ reduced:

| | | |
|---|---|---|
| $\overline{CC}$ | Coke consumption, $C_4/0.87$ | $\frac{0.4225x + 13,191}{0.87x + 2,173}$ |

[1] Based on the assumption of a 99-percent volatilization of potash, 99-percent reduction of phosphates, a lime-silica ratio in the charge equal to 1.0, a mol ratio of $CaCl_2$ to $K_2O$ charged of 0.75, and the volatilization of 91.2 lb., or 0.693, pound of $K_2O$ per pound of $P_2O_5$ reduced.

[2] 87-percent fixed-carbon coke

The items in these tabulations are calculated in the same manner as in the tabulations on pages 42 and 43 for phosphate smelting. They differ in magnitude because more slag is produced per pound of $P_2O_5$ reduced in combined smelting than in separate phosphate smelting.

The composition of the wyomingite used in these calculations is that given in table 3. The burned lime was assumed to have been made from limestone of the analysis given on page 58. The Idaho phosphate rock composition used, given in the following tabulation, is the mean of three analyses reported by Jacob, Hill, Marshall, and Reynolds (*30, p. 22*):

| Constituents: | *Percent* | Constituents—Continued. | *Percent* |
|---|---|---|---|
| $SiO_2$ | 8.67 | $Cr_2O_3$ | 0.13 |
| $Al_2O_3$ | 1.34 | $V_2O_3$ | .30 |
| CaO | 45.74 | $SO_3$ | 1.61 |
| MgO | .23 | $CO_2$ | 1.76 |
| $Fe_2O_3$ | .88 | F | 3.29 |
| $TiO_2$ | .07 | Cl | .03 |
| $Na_2O$ | .69 | $P_2O_5$ | 32.33 |
| $K_2O$ | .44 | Combined water | 1.10 |
| MnO | .003 | Moisture | .89 |

Figure 22 shows the effect of blast temperature on the calculated coke consumption for both the hearth and total heat requirements. It illustrates the conditions under which the hearth-heat requirements fail to yield proper coke-consumption values. The blast temperature (1,640° F.) at which total heat requirements become the limiting factor is much lower in this case because of the considerably greater slag volume.

According to these calculations with a 2,000° F. hot blast, 1 ton of $P_2O_5$ would be reduced and 0.663 ton of $K_2O$ would be volatilized from a charge consisting of 3.08 tons of 87-percent fixed-carbon coke, 3.05 tons of Idaho phosphate rock, 6.53 tons of wyomingite, 2.24 tons of burned lime, and 0.85 ton of 76.5-percent calcium chloride. The amount of coke required is about 0.63 ton more than required in

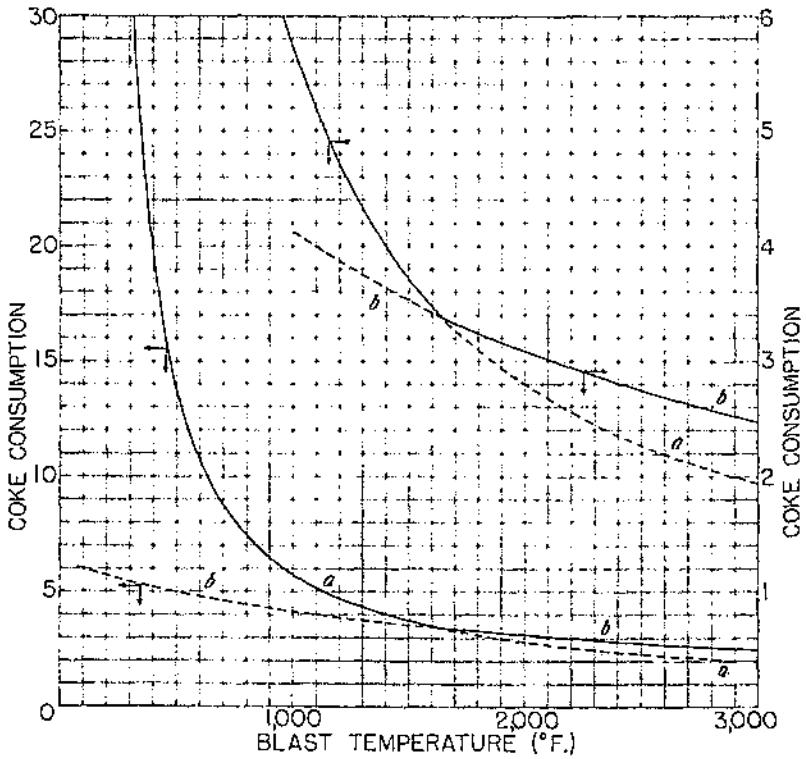


FIGURE 22. Effect of the air-blast temperature on the estimated amount of 87-percent fixed-carbon coke required per pound of $P_2O_5$ reduced in a potash-phosphate blast furnace smelting wyomingite and Idaho phosphate with burned lime and calcium chloride; 0.663 pound of $K_2O$ volatilized per pound of $P_2O_5$ reduced; humidity, 0.01. Heat losses per pound of carbon burned at the tuyères: From hearth to cooling water, 750 B. t. u.; and from mantle, 75 B. t. u. Curve *a* is based on high-temperature heat requirements; curve *b* is based on total heat requirements.

straight phosphate smelting. With this additional coke, 0.663 ton of $K_2O$ is volatilized. This is equivalent to 0.95 ton of coke per ton of potash, and is to be compared with 2.82 tons required for separate potash smelting. Comparison of the materials required for combined and independent smelting of 1 ton of $P_2O_5$ and 0.663 ton of $K_2O$ shows that the combined smelting may be carried out with the use of approximately 1.24 tons less of coke, 1.22 tons less of burned lime, and 0.96 ton less of gravel. The estimated material requirements for other blast temperatures are given in table 18.

TABLE 18.—*Estimated material requirements in potash-phosphate smelting per ton of $P_2O_5$ reduced* [1] [2]

| Blast temperature (° F.) [3] | Coke [4] | Wyoming-ite [5] | Idaho phosphate [6] | Burned lime | Calcium chloride [7] |
|---|---|---|---|---|---|
| | *Tons* | *Tons* | *Tons* | *Tons* | *Tons* |
| 500 | 13.85 | 6.53 | 3.05 | 3.21 | 0.85 |
| 1,000 | 5.71 | 6.53 | 3.05 | 3.18 | .85 |
| 1,500 | 3.69 | 6.53 | 3.05 | 3.29 | .85 |
| 2,000 | 3.08 | 6.53 | 3.05 | 3.21 | .85 |
| 2,500 | 2.71 | 6.53 | 3.05 | 3.21 | .85 |

[1] $K_2O$ volatilized, 0.668 ton per ton of $P_2O_5$ reduced.
[2] Based on tabulations on pp. 63 and 64, assuming 90-percent reduction and volatilization of the phosphate and potash.
[3] Blast humidity, 0.01 pound of water per pound of air.
[4] Fixed carbon, 87 percent.
[5] Analysis as given in table 3.
[6] Analysis as given on p. 64.
[7] Analysis of limestone given on p. 58.
[8] $CaCl_2$, 76.5 percent.

Combined potash-phosphate smelting thus would be economically more attractive than the separate processes, and the product would be cheaper to ship.

## SUMMARY AND CONCLUSIONS

The following conclusions may be drawn from the experiments on phosphate smelting:

Phosphate smelting is a reduction process that requires carbon for the reduction.

The heat required to carry out phosphate reduction in the blast furnace closely approximates that calculated for the reaction:

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = 3CaSiO_3 + 5CO + P_2$$

Only heat at or above 2,255° F. is available for carrying out the phosphate-reduction reaction. The amount of phosphate reduced is limited by the heat available above this temperature.

Within the limits 0.82 to 1.12, the base-acid ratio of the charge, $\frac{CaO + MgO}{Al_2O_3 + SiO_2}$, was not found to affect appreciably either the heat required by or the efficiency of the reduction process.

Phosphate smelting is technically feasible with low or medium blast temperatures but is commercially practicable for fertilizer production only if high blast temperatures are available.

The results of the potash-smelting experiments showed that:

The heat involved in potash-volatilization reactions occurring in the blast furnace was too small to be detected. The principal heat requirements of potash smelting are, therefore, the heat required to slag the charge, to decompose the blast moisture, and to satisfy the heat losses.

Volatilization to the extent of 90 percent was not realized from charges having a base-acid ratio, $\frac{CaO + MgO}{Al_2O_3 + SiO_2}$, less than 0.9.

The addition of calcium chloride increased the volatilization of potash from charges having low base-acid ratios. This effect was less pronounced for charges having base-acid ratios as great as 0.9.

Potash smelting is a technically feasible process, but is commercially practicable only if low-cost limestone and fuel are obtainable.

The results of the combined potash-phosphate smelting experiments showed that:

The combined smelting of potash and phosphate offers no technical difficulties not met in the two separate processes.

Combined smelting is commercially more attractive than the smelting of the same amounts of potash and phosphate independently because it requires less fuel and flux and yields a more easily transported product.

It must be emphasized that methods for recovering the products in all three processes require further investigation. It should also be pointed out that the indicated possibilities in these processes, especially in the phosphate and potash-phosphate processes, depend largely upon the development and application of stoves capable of economically producing blast temperatures several hundred degrees higher than in present iron blast-furnace practice. It is expected that the stoves used in this investigation will point the way to such a development (*60*).

In potash smelting the exact amount of calcium chloride required is uncertain, the consumption of carbon by some unknown reduction reaction is unexplained, and the full benefit of using burned lime as a flux is undetermined. These factors, as well as the applicability of carbonized Wyoming coal as a blast-furnace fuel, remain to be investigated.

The investigation of the combined potash-phosphate furnace must be extended before final conclusions can be drawn.

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## APPENDIX

TABLE 19.—*Equivalent temperatures*

| Temperature | | Temperature | | Temperature | | Temperature | |
|---|---|---|---|---|---|---|---|
| ° *F.* | ° *C.* | ° *F.* | ° *C.* | ° *F.* | ° *C.* | ° *F.* | ° *C.* |
| 72 | 22.2 | 612 | 322 | 1,407 | 797 | 3,100 | 1,704 |
| 77 | 25.0 | 648 | 342 | 1,500 | 816 | 3,142 | 1,728 |
| 85 | 29.4 | 700 | 377 | 1,580 | 860 | 3,145 | 1,729 |
| 100 | 37.8 | 718 | 381 | 1,440 | 871 | 3,152 | 1,733 |
| 185 | 85.0 | 748 | 398 | 1,640 | 893 | 3,200 | 1,760 |
| 200 | 93.3 | 800 | 427 | 1,650 | 899 | 3,300 | 1,816 |
| 250 | 121 | 831 | 444 | 1,700 | 927 | 3,330 | 1,832 |
| 275 | 135 | 900 | 483 | 1,800 | 982 | 3,400 | 1,871 |
| 286 | 141 | 934 | 501 | 1,850 | 1,010 | 3,500 | 1,927 |
| 300 | 149 | 975 | 524 | 1,900 | 1,038 | 3,520 | 1,938 |
| 304 | 151 | 1,000 | 538 | 2,000 | 1,093 | 3,600 | 1,982 |
| 327 | 164 | 1,024 | 551 | 2,100 | 1,149 | 3,700 | 2,038 |
| 338 | 170 | 1,047 | 564 | 2,200 | 1,204 | 3,710 | 2,043 |
| 345 | 174 | 1,000 | 588 | 2,255 | 1,235 | 3,800 | 2,093 |
| 349 | 176 | 1,100 | 593 | 2,282 | 1,250 | 3,810 | 2,143 |
| 367 | 186 | 1,112 | 600 | 2,300 | 1,260 | 3,900 | 2,149 |
| 390 | 199 | 1,153 | 623 | 2,372 | 1,300 | 4,000 | 2,204 |
| 399 | 204 | 1,175 | 634 | 2,400 | 1,316 | 4,070 | 2,243 |
| 400 | 204 | 1,177 | 636 | 2,500 | 1,371 | 4,100 | 2,260 |
| 408 | 209 | 1,200 | 649 | 2,552 | 1,400 | 4,172 | 2,300 |
| 412 | 211 | 1,205 | 652 | 2,600 | 1,427 | 4,200 | 2,316 |
| 428 | 220 | 1,209 | 654 | 2,687 | 1,475 | 4,240 | 2,338 |
| 448 | 231 | 1,215 | 657 | 2,700 | 1,482 | 4,300 | 2,371 |
| 487 | 253 | 1,300 | 704 | 2,750 | 1,510 | 4,400 | 2,427 |
| 500 | 260 | 1,308 | 709 | 2,800 | 1,538 | 4,410 | 2,432 |
| 527 | 275 | 1,335 | 723 | 2,876 | 1,580 | 4,500 | 2,482 |
| 536 | 280 | 1,348 | 731 | 2,900 | 1,592 | 4,575 | 2,524 |
| 565 | 296 | 1,400 | 760 | 2,970 | 1,632 | | |
| 570 | 299 | 1,404 | 762 | 3,000 | 1,649 | | |
| 600 | 316 | 1,447 | 788 | 3,002 | 1,650 | | |

TABLE 20.—*Vapor pressure of phosphorus (Mm. Hg.)* [1]

| Temperature (° C.) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.00775 | 0.00779 | 0.00847 | 0.00921 | 0.0100 | 0.0109 | 0.0118 | 0.0128 | 0.0139 | 0.0150 |
| 10 | .0163 | .0176 | .0190 | .0206 | .0222 | .0240 | .0259 | .0279 | .0301 | .0325 |
| 20 | .0350 | .0378 | .0405 | .0435 | .0468 | .0503 | .0540 | .0579 | .0621 | .0666 |
| 30 | .0714 | .0765 | .0819 | .0877 | .0938 | .100 | .107 | .115 | .122 | .131 |
| 40 | .139 | .149 | .159 | .169 | .180 | .192 | .204 | .217 | .231 | .246 |
| 50 | .262 | .278 | .295 | .313 | .332 | .352 | .374 | .396 | .420 | .445 |
| 60 | .472 | .499 | .528 | .559 | .591 | .625 | .660 | .698 | .737 | .778 |
| 70 | .823 | .867 | .914 | .964 | 1.02 | 1.07 | 1.13 | 1.19 | 1.25 | 1.32 |
| 80 | 1.39 | 1.46 | 1.54 | 1.61 | 1.70 | 1.78 | 1.87 | 1.97 | 2.07 | 2.17 |
| 90 | 2.28 | 2.39 | 2.51 | 2.63 | 2.75 | 2.89 | 3.02 | 3.17 | 3.32 | 3.48 |
| 100 | 3.63 | 3.81 | 3.98 | 4.17 | 4.36 | 4.56 | 4.76 | 4.98 | 5.20 | 5.43 |
| 110 | 5.69 | 5.92 | 6.18 | 6.45 | 6.73 | 7.02 | 7.32 | 7.64 | 7.99 | 8.30 |
| 120 | 8.66 | 9.01 | 9.38 | 9.77 | 10.0 | 10.5 | 11.0 | 11.5 | 11.9 | 12.4 |
| 130 | 12.9 | 13.4 | 14.0 | 14.5 | 15.1 | 15.7 | 16.3 | 16.9 | 17.5 | 18.2 |
| 140 | 18.9 | 19.6 | 20.4 | 21.1 | 21.9 | 22.7 | 23.6 | 24.4 | 25.3 | 26.2 |
| 150 | 27.2 | | | | | | | | | |

[1] *Computed from the equation of Mueller and Van Voorhis (31). Error not greater than 0.5 percent from 100° to 150° C. and not greater than 5 percent at 44°.*

TABLE 21.—*Estimated heat of potash-volatilization reactions* [1]

| Reactants | Products | Heat of reaction, 77° F. |
|---|---|---|
| | | *B. t. u. per lb. $K_2O$* |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ | $Al_2O_3 \cdot 4SiO_2 + K_2O$ | −1,346 |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2 + CaO$ | $CaO \cdot Al_2O_3 \cdot 4SiO_2 + K_2O$ | −1,190 |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2 + CaCO_3$ | $CaO \cdot Al_2O_3 \cdot 4SiO_2 + K_2CO_3$ | −196 |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2 + CaCl_2$ | $CaO \cdot Al_2O_3 \cdot 4SiO_2 + 2KCl$ | 403 |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2 + CaF_2$ | $CaO \cdot Al_2O_3 \cdot 4SiO_2 + 2KF$ | −284 |
| $K_2O \cdot Al_2O_3 \cdot 4SiO_2 + 2NaCl$ | $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 + 2KCl$ | 176 |

[1] Based on estimated heats of formation for $Al_2O_3 \cdot 4SiO_2$ and $CaO \cdot Al_2O_3 \cdot 4SiO_2$ of 1,216 and 1,310 kg calories per gram formula weight, respectively.

TABLE 22.—*Mean molal heat capacities at constant pressure* [1]

| Temperature (°F.) | Heat capacity for | | | | |
|---|---|---|---|---|---|
| | $N_2$, $O_2$, CO, NO, HCl, HI, HBr, or $F_2$ | $H_2$ or HF | $H_2O$ | $CO_2$ or $SO_2$ | C |
| | *B. t. u. per lb. mol per °F.* | *B. t. u. per lb. mol per °F.* | *B. t. u. per lb. mol per °F.* | *B. t. u. per lb. mol per °F.* | *B. t. u. per lb. atom per °F.* |
| 0 | 6.923 | 6.936 | 8.340 | 8.999 | 2.284 |
| 77 | 6.937 | 6.945 | 8.365 | 9.103 | 2.375 |
| 100 | 6.942 | 6.947 | 8.371 | 9.134 | 2.403 |
| 200 | 6.961 | 6.959 | 8.398 | 9.266 | 2.519 |
| 300 | 6.980 | 6.971 | 8.428 | 9.398 | 2.633 |
| 400 | 7.000 | 6.983 | 8.461 | 9.527 | 2.744 |
| 500 | 7.020 | 6.996 | 8.497 | 9.655 | 2.853 |
| 600 | 7.040 | 7.010 | 8.535 | 9.781 | 2.960 |
| 700 | 7.060 | 7.023 | 8.576 | 9.905 | 3.064 |
| 800 | 7.081 | 7.038 | 8.620 | 10.028 | 3.165 |
| 900 | 7.102 | 7.052 | 8.667 | 10.149 | 3.264 |
| 1,000 | 7.123 | 7.068 | 8.716 | 10.268 | 3.361 |
| 1,100 | 7.145 | 7.083 | 8.768 | 10.386 | 3.455 |
| 1,200 | 7.167 | 7.099 | 8.823 | 10.501 | 3.547 |
| 1,300 | 7.189 | 7.116 | 8.881 | 10.616 | 3.636 |
| 1,400 | 7.211 | 7.133 | 8.941 | 10.728 | 3.723 |
| 1,500 | 7.235 | 7.150 | 9.005 | 10.839 | 3.807 |
| 1,600 | 7.257 | 7.168 | 9.070 | 10.948 | 3.889 |
| 1,700 | 7.280 | 7.187 | 9.139 | 11.055 | 3.969 |
| 1,800 | 7.303 | 7.205 | 9.211 | 11.161 | 4.045 |
| 1,900 | 7.327 | 7.225 | 9.285 | 11.265 | 4.120 |
| 2,000 | 7.351 | 7.244 | 9.360 | 11.367 | 4.192 |
| 2,100 | 7.375 | 7.265 | 9.442 | 11.468 | 4.262 |
| 2,200 | 7.402 | 7.285 | 9.524 | 11.566 | 4.329 |
| 2,300 | 7.424 | 7.306 | 9.610 | 11.664 | 4.393 |
| 2,400 | 7.449 | 7.328 | 9.698 | 11.759 | 4.456 |
| 2,500 | 7.474 | 7.350 | 9.789 | 11.853 | 4.515 |
| 2,600 | 7.500 | 7.372 | 9.882 | 11.945 | 4.573 |
| 2,700 | 7.526 | 7.395 | 9.978 | 12.035 | 4.627 |
| 2,800 | 7.552 | 7.418 | 10.078 | 12.124 | 4.680 |
| 2,900 | 7.578 | 7.442 | 10.179 | 12.211 | 4.730 |
| 3,000 | 7.605 | 7.466 | 10.284 | 12.296 | 4.777 |
| 3,100 | 7.631 | 7.491 | 10.391 | 12.380 | 4.822 |
| 3,200 | 7.659 | 7.516 | 10.502 | 12.461 | 4.864 |
| 3,300 | 7.686 | 7.542 | 10.614 | 12.542 | 4.905 |
| 3,400 | 7.714 | 7.568 | 10.730 | 12.620 | 4.942 |
| 3,500 | 7.742 | 7.594 | 10.849 | 12.697 | 4.977 |
| 3,600 | 7.770 | 7.621 | 10.970 | 12.772 | 5.010 |
| 3,700 | 7.798 | 7.649 | 11.094 | 12.845 | 5.040 |
| 3,800 | 7.827 | 7.677 | 11.220 | 12.917 | 5.068 |
| 3,900 | 7.856 | 7.705 | 11.350 | 12.987 | 5.093 |
| 4,000 | 7.885 | 7.734 | 11.482 | 13.055 | 5.116 |

[1] Computed from equations of Eastman (*16*) for gases, and equation of Lewis and Randall (*39*) for carbon.

TABLE 23.—*Sensible heats above 77° F.*[1]

| Temperature (°F) | Sensible heat of— | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 pound of carbon | Blast required to burn 1 pound C to CO with— | | Products of combustion of 1 pound C to CO with— | | Moisture accompanying the dry air required to burn 1 pound C to CO (humidity[3]=0.01) | Moisture-decomposition products accompanying the products of combustion of 1 pound C to CO with dry air (humidity[3]=0.01) |
| | | Pure oxygen | Dry air[2] | Pure oxygen | Dry air[2] | | |
| | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* | *B. t. u.* |
| 77 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 100 | 4.7 | 6.7 | 31.9 | 13.3 | 38.5 | 0.6 | 1.0 |
| 200 | 26.7 | 35.8 | 171 | 71.5 | 207 | 3.3 | 5.5 |
| 300 | 50.0 | 65.0 | 311 | 130 | 376 | 6.0 | 10.0 |
| 400 | 76.2 | 94.4 | 451 | 189 | 546 | 8.8 | 14.5 |
| 500 | 104 | 124 | 593 | 248 | 717 | 11.5 | 19.0 |
| 600 | 133 | 154 | 735 | 307 | 889 | 14.3 | 23.6 |
| 700 | 163 | 184 | 878 | 367 | 1,062 | 17.2 | 28.1 |
| 800 | 196 | 214 | 1,022 | 428 | 1,236 | 20.0 | 32.7 |
| 900 | 230 | 244 | 1,167 | 488 | 1,411 | 22.9 | 37.4 |
| 1,000 | 265 | 275 | 1,312 | 549 | 1,587 | 25.9 | 42.0 |
| 1,100 | 301 | 305 | 1,459 | 610 | 1,764 | 28.8 | 46.7 |
| 1,200 | 339 | 336 | 1,606 | 672 | 1,943 | 31.8 | 51.4 |
| 1,300 | 379 | 367 | 1,755 | 734 | 2,122 | 34.9 | 56.1 |
| 1,400 | 419 | 395 | 1,904 | 797 | 2,303 | 38.0 | 60.9 |
| 1,500 | 461 | 430 | 2,055 | 860 | 2,485 | 41.2 | 65.7 |
| 1,600 | 503 | 462 | 2,206 | 923 | 2,668 | 44.4 | 70.5 |
| 1,700 | 547 | 493 | 2,359 | 987 | 2,852 | 47.7 | 75.3 |
| 1,800 | 591 | 525 | 2,512 | 1,051 | 3,037 | 51.0 | 80.2 |
| 1,900 | 637 | 558 | 2,666 | 1,116 | 3,224 | 54.4 | 85.1 |
| 2,000 | 683 | 590 | 2,822 | 1,181 | 3,412 | 57.9 | 90.1 |
| 2,100 | 731 | 623 | 2,978 | 1,246 | 3,601 | 61.4 | 95.0 |
| 2,200 | 778 | 656 | 3,137 | 1,312 | 3,793 | 65.0 | 100 |
| 2,300 | 827 | 689 | 3,294 | 1,378 | 3,984 | 68.7 | 105 |
| 2,400 | 876 | 723 | 3,454 | 1,445 | 4,177 | 72.5 | 110 |
| 2,500 | 925 | 756 | 3,615 | 1,513 | 4,371 | 76.3 | 115 |
| 2,600 | 976 | 790 | 3,777 | 1,580 | 4,568 | 80.2 | 120 |
| 2,700 | 1,026 | 824 | 3,941 | 1,649 | 4,765 | 84.2 | 126 |
| 2,800 | 1,077 | 859 | 4,105 | 1,718 | 4,964 | 88.3 | 131 |
| 2,900 | 1,128 | 893 | 4,271 | 1,787 | 5,164 | 92.5 | 136 |
| 3,000 | 1,179 | 928 | 4,438 | 1,857 | 5,369 | 96.7 | 141 |
| 3,100 | 1,230 | 963 | 4,605 | 1,927 | 5,569 | 101 | 147 |
| 3,200 | 1,282 | 999 | 4,775 | 1,998 | 5,774 | 106 | 152 |
| 3,300 | 1,334 | 1,035 | 4,945 | 2,069 | 5,980 | 110 | 158 |
| 3,400 | 1,385 | 1,071 | 5,117 | 2,141 | 6,188 | 115 | 163 |
| 3,500 | 1,436 | 1,107 | 5,290 | 2,214 | 6,397 | 120 | 168 |
| 3,600 | 1,488 | 1,143 | 5,465 | 2,286 | 6,608 | 124 | 174 |
| 3,700 | 1,539 | 1,180 | 5,640 | 2,361 | 6,820 | 129 | 180 |
| 3,800 | 1,590 | 1,217 | 5,817 | 2,434 | 7,035 | 134 | 185 |
| 3,900 | 1,640 | 1,254 | 5,998 | 2,509 | 7,250 | 140 | 191 |
| 4,000 | 1,690 | 1,292 | 6,175 | 2,584 | 7,457 | 145 | 197 |

[1] Computed from table 22. [2] Oxygen, 20.92 percent. [3] Pound $H_2O$ per pound dry air.

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