Aug. 26, 1952 P. H. ROYSTER 2,608,481

HEAT-TREATING SOLIDS

Filed Sept. 26, 1947 3 Sheets-Sheet 1

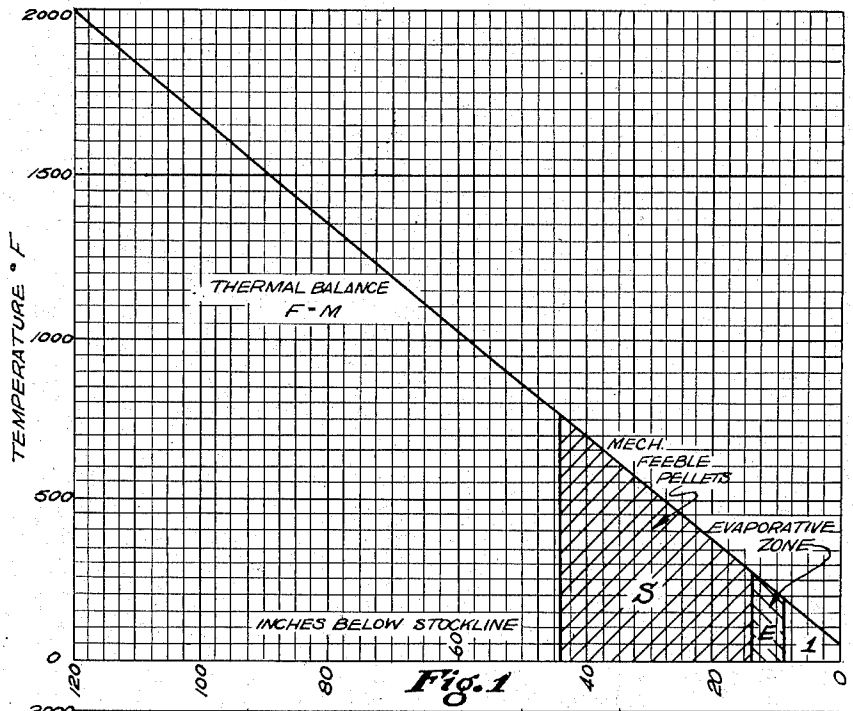

Fig. 1

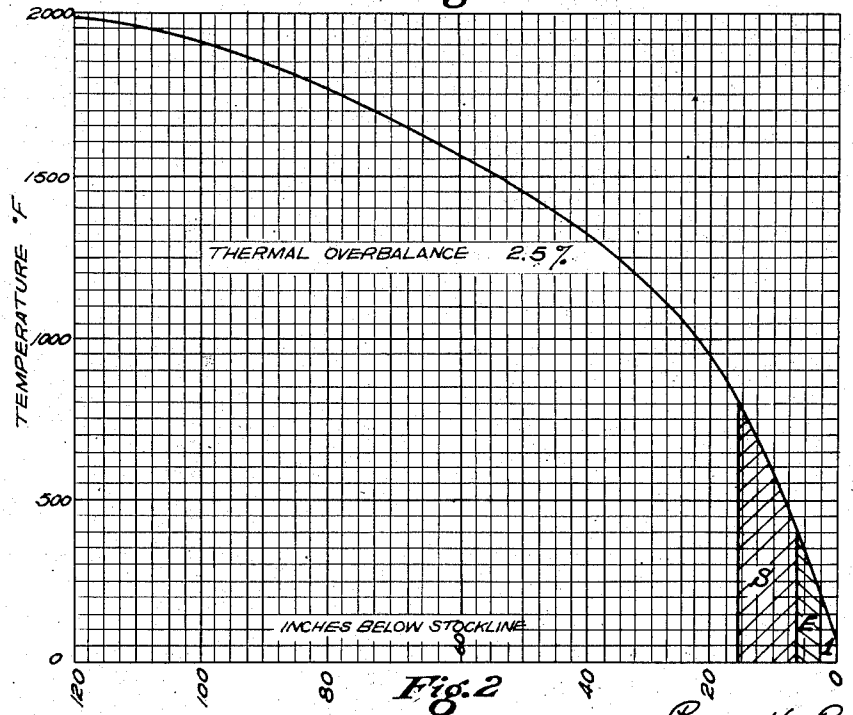

Fig. 2

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HEAT-TREATING SOLIDS

Filed Sept. 26, 1947 3 Sheets-Sheet 2

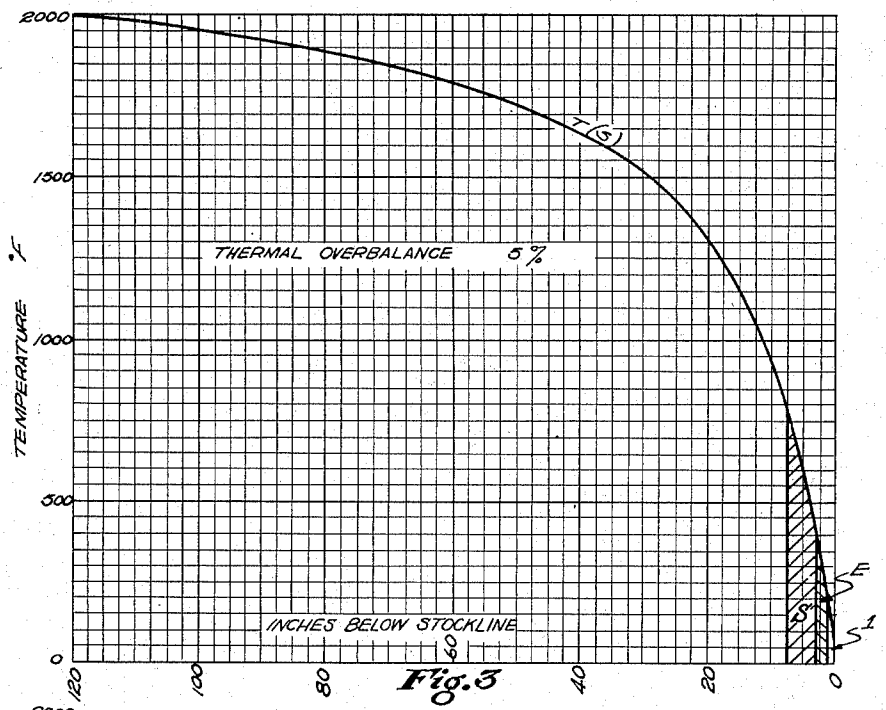

Fig. 3

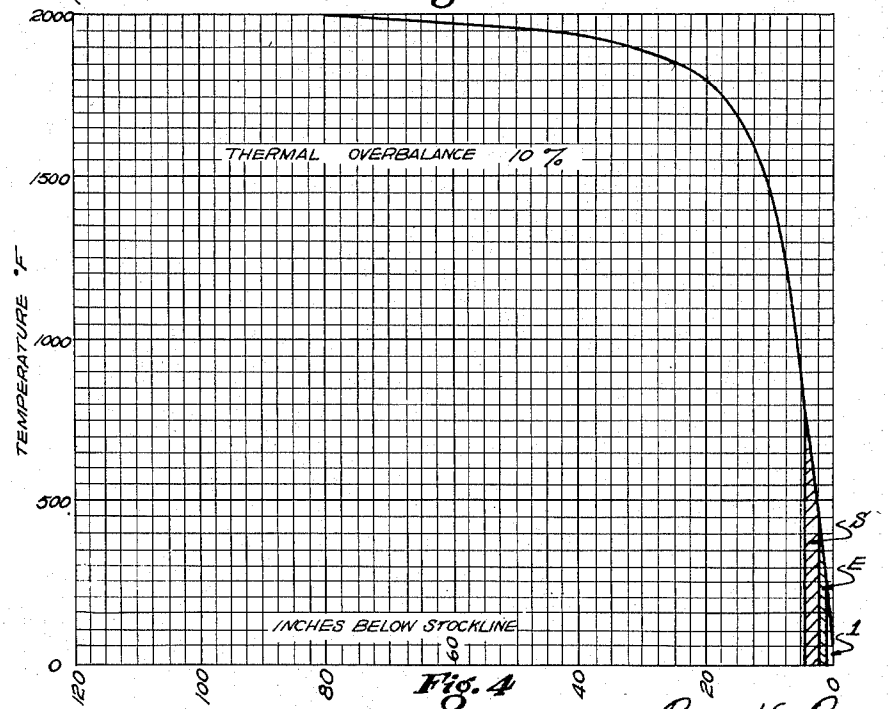

Fig. 4

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HEAT-TREATING SOLIDS

Filed Sept. 26, 1947 3 Sheets-Sheet 3

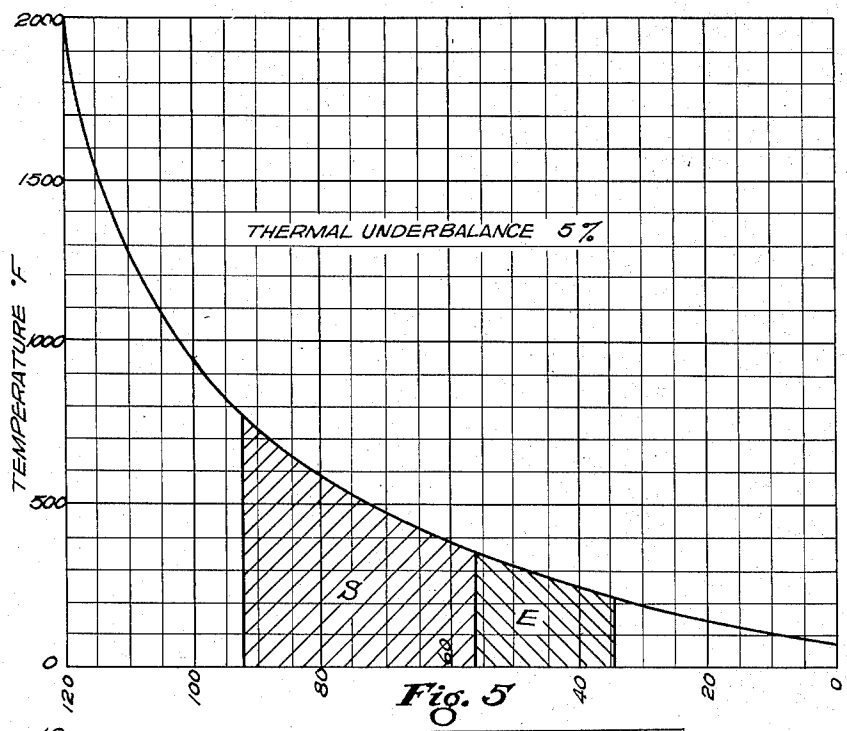

Fig. 5

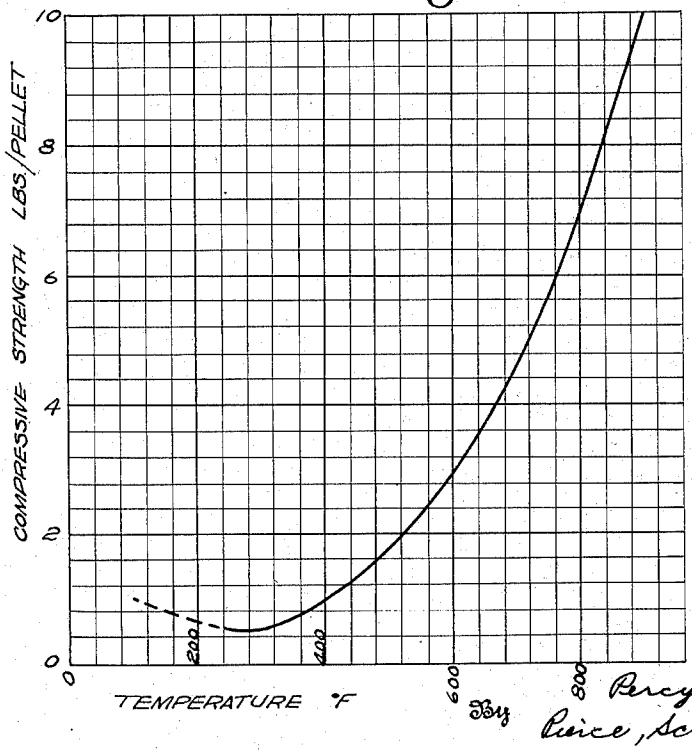

Fig. 6

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2,608,481

UNITED STATES PATENT OFFICE

2,608,481

HEAT-TREATING SOLIDS

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Application September 26, 1947, Serial No. 776,351

1 Claim. (Cl. 75—5)

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This invention relates to the art of working up aggregates of finely divided iron ore concentrates, and is concerned more specifically with the step of indurating raw pellets formed of moist oxidic iron particles resulting as product from beneficiating a low grade oxidic iron ore material such, for example, as the ferruginous cherts known in Minnesota as "taconites." The present application contains subject matter in common with my application Serial No. 605,861, filed July 19, 1945, now Patent No. 2,533,142, and is to be considered as a continuation-in-part thereof.

Beneficiation methods involve more or less fine grinding of the low grade iron ore material, with the result that the beneficiated product is in a state of subdivision too fine to be directly usable in the blast furnace and hence requires the practice of some type of "agglomerating" operation whereby the fine particles may be formed into masses of a size and structure usable in the blast furnace. One operable mode of so "agglomerating" iron oxide particles is to mold the finely divided material into pellets (or small spheroidal masses) by subjecting them to a rolling action while somewhat moist. The disclosure of U. S. Patent No. 2,411,873 to Charles V. Firth is here referred to for a full disclosure of one operable mode of carrying out a pelletizing step.

When the pellets have been formed in optimum size (viz., one-fourth inch to 1.5 inches diameter) from particles having a desired size distribution, and with the moisture content controlled—between 5 and 15% by weight—to the optimum amount for the particular ore and particular particle size distribution, they enjoy in freshly formed (moist) state a certain degree of mechanical strength. Thus, they may be dropped three times from a height of 6 inches onto a steel plate without serious fracture or deformation: when piled carefully on themselves they can support an 18–32 inch layer of themselves without the lowest layer of pellets being crushed under the superimposed gravitational burden.

However, even if this degree of mechanical strength could be retained upon drying out, it would not be sufficient to permit shipping the raw pellets in mass or any other handling usual with ores per se. It is essential to indurate the raw pellets before they are industrially acceptable. An operable mode of indurating the raw pellets involves heat-treating the latter to an elevated temperature near to but below the fusing point of the ore material. When thermally indurated under optimum conditions, the pellets assume a mechanical strength equal or substantially equal

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to that of pieces (of equivalent size) of the original ore material and hence may be shipped or otherwise handled in mass without crushing or serious fracturing.

Drying out of the initially moist raw pellets, which is inevitable in any process for thermally indurating them, is attended by a marked reduction in mechanical strength. Upon loss of the moisture from between and on the particles constituting the pellets, the resulting dry, raw pellets become extremely fragile and frangible, exhibiting only about one-third to one-fifth the strength of the moist raw pellets: they fall apart when dropped a few times through a distance as little as an inch or two, and they scarcely can sustain a load of as much as a foot of pellets carefully piled upon them.

When the temperature of the dry raw pellets is raised to about 400° F., the pellets regain their original (moist state) mechanical, e. g., compressive, strength; with further temperature rises they progressively increase in strength, and when a temperature of the order of 780°–800° F. has been reached the pellets have acquired several (e. g., six or more) times their original mechanical strength and are, therefore, said to have been "incipiently hardened." Increasing the temperature above 780–800° F. confers additional strength upon the incipiently hardened pellets up to the point of optimum induration. The temperature range between about 200 and about 800° F. may properly be termed the "sensitive range" in the heat-treating of the pellets, and constitutes the interval during which the greatest care must be taken to relieve the frangible, fragile pellets from mechanical shock and from imposed pressure. This sensitive range is of importance in any thermal induration process wherein—as is the case here—the moist raw iron oxide pellets are continuously or intermittently added to the upper surface of a continuously or intermittently descending column of iron oxide pellets, in greater or lesser degrees of induration, gravitationally descending in countercurrent to the flow of a heating gas. In such case, a pellet must have been carried through the sensitive range before there has been superimposed upon it a greater weight than the pellet can sustain without fracture or deformation.

A second difficulty is encountered in the heat hardening of these pellets. If attempt is made to carry the pellets rapidly through the sensitive range at too high a rate of heating, the sudden release of steam derived from the initial moisture content causes the pellets to fly apart or "spall."

The maximum rate of heating which can be used safely without encountering serious spalling depends upon the diameter of the pellets as well as upon their moisture content and the size distribution of the constituent ore particles. In actual practice, the pellets may vary in diameter from ¼ inch to 1½ inches, with ⅜–¾ inch as a commonly encountered size. With a ¾ inch pellet, for example, rates of heating of several hundred degrees per minute up to 650° to 750° F. per minute may be employed without encountering serious spalling, whereas with the larger sized pellets a somewhat slower rate of heating should be adhered to.

Therefore, in carrying out the thermal induration by the general process referred to above, the rate of heating must be carefully controlled between an upper and a lower limit: the pellets, once they are dried, must be hurried through their sensitive range in order to avoid their crushing under the progressively superimposed pressures, whereas the rate of heating must be limited to prevent fission or spalling under the thermal shock.

According to the process of the present invention, this control of the rate of heating through the sensitive range is effected by establishing and maintaining a thermally "over-balanced" operation in which the heat capacity of the ascending stream of heating gas exceeds the heat capacity of the pellets in the descending column thereof, during equal times, by a few (e. g., between about 2.5 and about 10) percent and sufficient to effect the heating of a layer or layers of the initially substantially unheated moist oxidic iron pellets through drying to incipient hardening in a zone, in said column, the lower boundary of which zone is not more than about 18 inches below the stockline or upper surface of said column. The overbalanced condition, and its desired extent, will now be more specifically described, with reference to the accompanying drawings, in which:

Fig. 1 is a graph showing temperature distribution in a column of iron oxide pellets being heat-treated under thermally balanced operation;

Figs. 2, 3 and 4 are graphs showing temperature distributions when operating at 2.5%, 5% and 10%, respectively, of thermal overbalance;

Fig. 5 is a graph showing temperature distribution when operating at 5% of thermal underbalance; and

Fig. 6 is a graph illustrating changes in mechanical strength as initially moist iron oxide pellets are progressively heated from 60° to about 900° F.

In the present process, the raw wet pellets are charged in a more or less continuous fashion onto the upper surface or "stockline" of a descending column of pellets maintained within a suitable heating chamber or shaft furnace. A continuous flow of a heating gas, e. g., air, or air mixed with combustion products, is passed continuously upwardly through this column whereby to effect heating of the pellets in a conventional counter-current manner. It is of importance to limit the total height of the column from the stockline measured downwardly to the locus of the introduction of the heating gas to a minimum. In a furnace suitable for commercial tonnages, which may range in diameter from 10 feet to 20 feet, it is seldom practical to limit the height of the column to a figure less than 10 feet for example. Satisfactory final mechanical strength of the heat hardened pellets can be attained at temperatures ranging from 1700° to 2300° F., i. e., near but not exceeding the "fusion point" of the ore material. If such a counter-current heating is undertaken in a column 16 feet in diameter and 10 feet tall, in which raw pellets are charged on the stockline at 60° F. and the heating gas is introduced at 2000° F. at a plane 10 feet below the stockline, maximum thermal efficiency will be realized when the heat capacity of the ascending heating gas per minute is exactly equal to the heat capacity of the pellets moving downwardly per minute. That is to say, if G represents the pounds of ascending gas per minute, and if C_p is the specific heat of the gas, the products $G \times C_p$ may be termed F and represents the heat capacity per minute of the heating gas stream. Similarly, if S represents the pounds of solids passing a given horizontal plane, and s represents the specific heat of the solids, the product $S \times s$ may be designated as M and represents the heat capacity of the descending solids per minute. When $F=M$, the heating operation is termed "thermally balanced." In the example at hand, with the average diameter of the pellets ¾ inch, the solids are heated in a uniform manner from stockline to the plane of gas influx at a rate of 16.16° F. per inch and will attain a temperature of 1986° F. 10 feet below the stockline. In like manner, the ascending gas stream will be cooled at the rate of 16.16° F. per inch and will emerge from the stockline at 74° F. In this 10 ft. vertical column, the gas at each point will be 14° F. hotter than the pellets at the same point. This difference between the gas temperature T(g) and the solid temperature T(s) is the "thermal head" which is effective in transferring heat at the gas-solid interface.

If 20,000 C. F. M. (cu. ft. per minute) of a diatomic heating gas is blown upwardly through the column and if 1450 G. T. (gross tons) of raw wet pellets per day is charged on the stockline (9.5% moisture—1320 G. T. per day of dried pellets), the operation will be in thermal balance, and the ratio of gas to dry solids will be 9.79 cu. ft. per pound or 8.86 cu. ft. per pound of wet pellets. Reference to Fig. 1 indicates the temperature of distribution in this 10 ft. vertical column in the "ideal" case in which the flow both of gas and solids is uniform across any horizontal plane and in which the loss of heat through the walls of the furnace is negligibly small.

It will be observed from Fig. 1 that under "balanced" operation the pellets attain the temperature 212° F. at an elevation 9 inches below the stockline. It has been found that some 3 to 9 inches of vertical height is required to remove the moisture from the pellets and that section of the vertical column lying between 9 inches and 14 to 17 inches below the stockline may be termed the "evaporative zone" and is shown in fine shading in Figure 1. In a zone from the 14 inch level down to a plane 45 inches below the stockline, the temperature of the pellets is less than 780° F. and in present language is said to be in the "sensitive condition." This region of mechanical feebleness or fragility is shown in dotted shading in Figure 1. It is obvious that the pellets in the layer lying 45 inches below the stockline have merely been restored to the mechanical strength of the original wet pellets, are unable to support the 45 inches of overlying pellets and will be crushed by the pressure imposed on them even in the absence of any shock due to mechanical motion. Such an operation, although exhibiting maximum thermal efficiency, is utterly

impractical when heat-hardening raw pellets of iron ore particles. It is necessary, therefore, to contract the extent of the sensitive region and to elevate the 780° F. isotherm nearer the stockline. This is readily accomplished by increasing the amount of heating gas forced upwardly through the column while holding the rate of charging of pellets constant.

The thermal distribution in the column when 20,500 cu. ft. of gas is employed is shown in Fig. 2. In this operation, the heating is said to be "over-balanced" to the extent of 2.5%, e. g., F is 2.5% greater than M, and the ratio of heating gas to moist pellets is 9.09 cu. ft. per each pound of the moist pellets. It is seen that the evaporative zone has been brought nearer the stockline and diminished in vertical extent. Evaporation of moisture becomes rapid at a distance of only 3 inches below the stockline and the pellets are essentially dry on reaching a level 7 inches below the stockline. The sensitive zone in Figure 2 extends from 9 inches to 16 inches below the stockline. The location and extent of the evaporative zone and of the sensitive zone are shown as shaded regions in Figure 2. With carefully controlled size of particles and with a highly efficient rolling operation, the mechanical strength of the pellets is usually sufficient to permit an operation with this temperature distribution in the pellet column.

In the more usual cases of practical operation, it is preferred that a thermal over-balance of 5% be employed, which condition is attained by blowing 21,000 C. F. M. while charging 1450 G. T. of wet pellets per day; the ratio here is 9.96 C. F. per pound of dry pellets or 9.39 cu. ft. per pound of wet pellets. The temperature conditions obtaining in the column with the 5% thermal over-balance are shown in Figure 3. The evaporative zone extends from 1.5 inches to 3.5 inches below the stockline and the sensitive zone has been contracted to lie from 3.5 to 8 inches below the stockline as is indicated in the shaded region. The crowding of the several isotherms into proximity of the stockline by employing thermal over-balance in this manner and to this extent results in a temperature distribution which permits satisfactory treatment of the pellets without causing serious crushing or spalling.

It is noted that the thermal gradient near the stockline is 16.2° F. per inch in Figure 1; is 41° per inch in Figure 2; and is 98° F. per inch in Figure 3. That is to say, by employing 2.5 to 5.0 percent over-balance, the "normal" 16° F. per inch temperature gradient is increased to 250 and 600 percent respectively. In the three illustrated examples above, the "average gradient" in the upper half of the ore column is 24° F. per inch in Figure 2 and 28.2° F. per inch in Figure 3. The "average thermal gradient" in the lower half of the column is 8.4° per inch in Figure 2 and 4.0° per inch in Figure 3. The effect of thermal over-balance is to "bow" the temperature-distance curves upwardly making them concave when viewed from below in Figures 2 and 3. Equally well it can be stated that thermal over-balance increases the average thermal gradient in the upper half of the charge column and simultaneously decreases the average thermal gradient in the lower half of the column as compared with the straight line temperature distribution shown in Figure 1.

The exact amount of over-balance required in any practical operation will depend (1) on the heat capacity of the ascending gas stream which will depend upon the composition of the gas; (2) on the heat capacity of the ore itself, including its moisture content, as well as on the state of oxidation of the iron content, i. e., whether hematite or magnetite; (3) on the average size of the pellets and on the distribution of sizes about the average; and (4) on the degree of uniformity of flow of (*a*) the gas ascending the column, and (*b*) the pellets descending the column. The effect of the variations in the above listed factors encountered in usual practice is seldom great and it is an unusual circumstance that the ratio of gas to solid will exceed the range of 8 to 14 cu. ft. per pound of pellets charged.

The loss of thermal efficiency due to thermal over-balance is seldom a determining criterion since the extent of over-balance required will usually lie between 2.5% and 10%. The heat distribution has been found to be extremely sensitive to the ratio of gas to solid. If the gas volume is too low, the isotherms are distributed at too low a level below the stockline and collapse of the pellets in their mechanically feeble condition results, causing clogging of the interstices between pellets and serious "channeling" of the gas in its upward flow through the column. This irregular gas flow distorts the isotherms in the column from their normal loci as horizontal planes and the temperature conditions within the column become chaotic. On the other hand, if a thermal over-balance much in excess of 10% is employed, the rate of heating in the neighborhood of the stockline becomes excessive and the moisture in the ore is driven out at too rapid a rate, thus causing fracturing of the pellets during drying and the somewhat explosive spalling of the pellets.

When 22,000 C. F. M. of diatomic heating gas, per day, is blown upwardly in the example used here as an illustration, the temperature distribution is as shown in Figure 4. In this operation about 9.75 cu. ft. of the heating gas are used per each pound of the moist pellets. It is observed that the temperature gradient at the stockline is 400° F. per inch, that the pellets attain the temperature 2000° F. 16 inches below the stockline and that the evaporative zone and sensitive zone have been brought to within two inches of the stockline. In this operation the temperature of the gas exhausting from the stockline is 450° F., representing a substantial loss to the thermal efficiency of the process. The rate of descent of the pellets through the column is almost exactly one inch per minute (over-all density of the wet pellets 127 lbs. per cu. ft.). The rapid impingement of gas at 1250° F.—the temperature obtaining 3 inches below the stockline (cf. Figure 4)—on the four uppermost layers of ¾ inch pellets subjects these pellets to dangerously rapid drying, and spalling of the pellets may be encountered. Successful operation can thus be realized by the controlled use of thermal over-balance which will, in general, be confined inside the critical range of 2.5% to 10%.

An important application of my invention concerns the indurating of pellets formed by rolling moist fines composed of concentrates produced from the magnetic concentration of iron bearing materials, particularly the taconite deposits occurring in the Lake Superior region.

In pelletizing magnetite fines, I maintain a continuously descending column of pellets within a vertical cylindrical refractory lined chamber 24 feet inside diameter, with a vertical height between the blast entrance and the stockline of 16

feet. The pellets analyze 65.2% Fe (dry basis) and contain 10.3% H_2O as charged. The wet over-all density is 127 lbs./cu. ft., and the average size of the pellets is 0.55 inch. I maintain through this vertical column of pellets the upward flow of 67,000 cu. ft./min. of heated gas flowing counter-current to the descending column of pellets. When the heated gas is produced by burning 171 lbs./min. of fuel oil with 65,000 cu. ft./air, the entrance temperature of the hot gas into the lower level of the column (blast entrance) is or may be about 2180° F. and the composition of the gas entering the column is: 6.6% CO_2; 7.3% H_2O; 10.4% O_2; and 75.8% N_2. The mean specific heat of this gas mixture between 60° F. and 2180° F. is 0.0215 B. t. u. per standard cubic foot per degree F. The mean specific heat of the dry pellets, over the same temperature range, is 0.236 B. t. u. per pound per degree F. Were it not for the heat absorbed in the evaporation of the moisture and the heat generated from the oxidation of the Fe_3O_4, initially in the raw pellets, into Fe_2O_3 thermal balance would be attained when I charge 6850 lbs./min. (44 G. T. per day) to produce 6150 lbs./min. of dry pellets. The ratio of gas-to-ore here is 9.78 cu. ft./lb. of wet pellets or 10.83 lbs./min. of dry pellets.

In actual practice, it is, of course, not permissible to ignore the heat absorbed and generated in the evaporation of moisture and the oxidation of magnetite, respectively, since the evaporation heat amounts to 17% and the oxidation heat to 22% of the total. In order to determine the thermal balance, it is desirable to construct a heat balance which reads as follows:

Heat Absorbed	B. t. u./min.
Sensible heat: 6520 lbs. dry pellets at 2180° F	3,400,000
Evaporation of moisture (10.3%)	685,000
Total	4,085,000
Heat Supplied:	
67,000 cu. ft./min	3,209,000
Heat of oxidation of Fe_3O_4 to Fe_2O_3	876,000
Total	4,085,000

It is noted here that the over-all heat supply and heat requirements are equated in order to determine the "calculated" thermal balance of 67,000 cu. ft./min. of heating gas with 7275 lbs./min. of wet pellets (6520 lbs./min. dry pellets). The ratio here is 9.20 cu. ft./lb. of wet pellets and 10.22 cu. ft./lb. of dry pellets.

In operation, three factors may tend to render a calculation such as that above somewhat unreliable in carrying out my process: (1) the temperature of distribution in the upper dozen inches of the charge column is subject to severe temperature distortion from the curves illustrated in the accompanying figures, due to the absorption of heat required to evaporate the water from the wet pellets, which causes local flattening of the temperature-distance diagram; (2) the generation of 207 B. t. u./lb. of Fe in the oxidation of magnetite to ferric oxide causes an upward bulge in the temperature curve in the zone immediately below the evaporation zone in the charge column, the heating effect of the ore oxidation being 20% greater than the cooling effect of evaporation; and (3) the possible failure of the ascending gas stream to achieve uniformity of flow across any horizontal cross-section of the charge column—a disturbing effect which is accentuated by failure of the charge column to exhibit uniformity of downward mass flow across the same horizontal sections of the column. It is all well and good, from a theoretical standpoint, to adjust the flow of gas and pellets to agree with the thermal calculations and to exhibit a ratio of gas-to-pellets at some predetermined figure. Actually, where the flow of pellets downwardly through certain horizontal sections of the column exceeds the average, and where (as likely as not) the upward flow of gas through that area is less than the average, the ratio of gas-to-pellets will diverge markedly from the overall average, with the result that too rapid heating of the raw pellets in one area of the furnace section will cause objectionable spalling, due to rapid heating, while, concurrently, the raw pellets are heated too slowly in other areas in the same horizontal section with frequent crumbling and disintegration of the pellets which have been subjected to too great compressive forces due to too great a superposed burden of pellets in the column.

It has been found, therefore, that although the heat balance is sufficiently accurate to determine the order of magnitude of the flow of gas required for thermal balance per pound of pellets, it is not a completely satisfactory criterion to guide the operator in controlling the present process. It has been found, however, that observations of the temperature in horizontal sections several feet below the stockline constitute a very effective method of controlling the temperature distribution in the charge column.

In the present example, the temperature 8 feet below the stockline (mid-section of the column) will read 1120° F. when in thermal balance (average of inlet gas temperature 2180° F. and pellet temperature 60° F.). A few percent overbalance in the ore-pellet ratio will cause the temperature at mid-section to rise several hundred degrees above 1120° F., and the temperature observed at this mid-section will vary greatly in response to minor, if not immeasurably small, variations in the gas-pellet ratio. Since the temperature observed at any cross-section is lower in the furnace at the loci of the zones of ore oxidation and moisture evaporation is greatly amplified as a result of small variations in the gas-pellet ratio, I have found that it serves as the most convenient and reliable method of controlling the necessary overbalance which is the basic feature of my present invention.

In any operating case, in practice it is necessary for the operator to determine the optimum temperature of his probe thermocouple located at or near the mid-section of the column by observing the physical character of the indurated discharge from the column. This is readily ascertained in any operating example of practice, but is difficult to define in general terms due to the wide variation in the specific heat of the pellets and gases employed, as well as the more significant deviations from uniformity of flow exhibited by the pellets in their descent.

I claim:

The process of heat hardening pellets of magnetite fines which comprises forcing a stream of an oxidizing gas mixture comprising air and gaseous products of combustion of a carbonaceous fuel, said oxidizing gas mixture being initially heated to a temperature between 1000° F. and the fusion temperature of the magnetite fines, upwardly in countercurrent heat exchanging contact with a continually descending column of the pellets initially containing about 10% moisture,

and maintaining the heat capacity of the ascending oxidizing gas mixture from 2.5 to 10% in excess of the heat capacity of the descending pellets by controlling the volume of the oxidizing gas mixture used to between 9.09 and 9.75 cubic feet per each pound of the initially moist pellets whereby the pellets are heated to incipient induration temperature by the time they have descended into said column a distance between about 5 inches and not more than 16 inches from the top thereof.

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