June 27, 1961 F. D. DE VANEY 2,990,268

PELLETIZED IRON ORE CONCENTRATE COMPOSITION AND PROCESS FOR MAKING THE SAME

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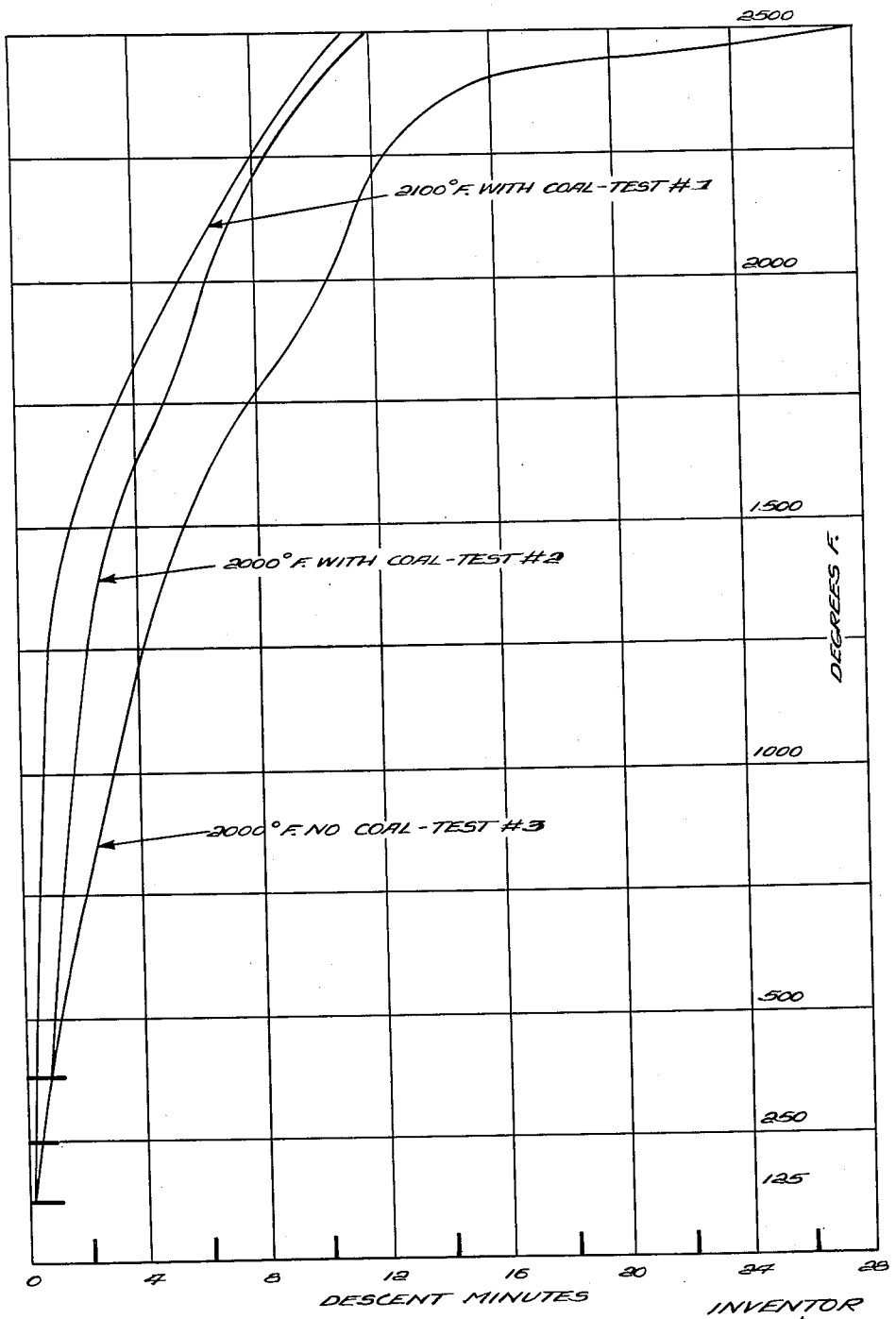


Fig. 1

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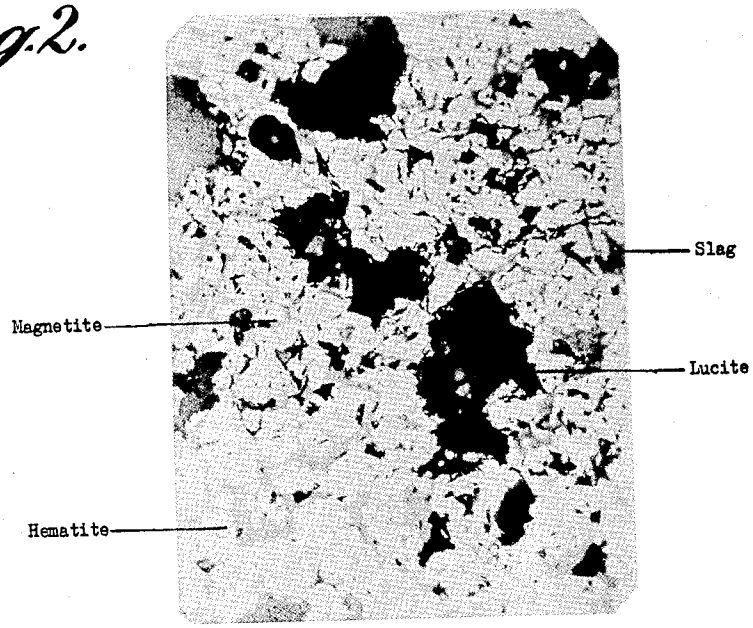
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Fig. 2.



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2,990,268

PELLETIZED IRON ORE CONCENTRATE COMPOSITION AND PROCESS FOR MAKING THE SAME

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2 Claims. (Cl. 75—5)

This invention relates to the art of producing blast furnace and open hearth, charge material of improved, and new, properties from low-grade iron ore materials, and is more particularly concerned with working up iron ore concentrates into intermediate products having enhanced utility in the production of pig iron and of steel. The invention includes both process and product aspects. A specific aspect of the invention is the provision of pellets of iron ore concentrates containing an added flux component.

Normally, iron ore contains more silica than it does bases, and hence is not self-fluxing. Accordingly, in the smelting of iron ore additions of potentially basically reacting flux materials have to be made to the burden. In current practice, iron ore is fed to the blast furnace as relatively unsized material, sometimes supplemented by sinter or pellets, and the flux (usually limestone or dolomite) is almost invariably added in the form of coarse material, all plus 2.0–2.5 inches in size. Because of the gross size of the limestone and of the ore, little fluxing obtains until the charge has descended to a considerable depth in the blast furnace.

In current blast furnace practice it is customary to add the flux component to the charge in the form of uncalcined limestone (or, dolomite), and hence it is necessary to calcine the latter, in the course of its descent through the blast furnace, in order to make the same effective as a reactive flux. Limestone calcines at about 1500° F. and dolomite begins to calcine at about 1300° F. In the case of either of these, calcination of the inside of the lump proceeds only as heat can be supplied to the immediate location of the reaction; accordingly, when working with lump stone complete calcination is not realized until after long-continued heating, to a top temperature well in excess of 1500° F. This means that uncalcined stone can get well down into the bosh in some instances.

Calcination (of the stone) uses up a substantial amount of the total heat input of the furnace—approximately 700,000–800,000 B.t.u. per ton of iron, or from about 10 to about 15% of the total heat load—and develops undesirably large amounts of carbon dioxide in the furnace gases.

These, and other, disadvantages inherent in conventional blast furnace practice have long been appreciated, and suggestions have been advanced for obviating them. Thus, it is known to modify the furnace charge by substituting a so-called "self-fluxing sinter" for a part of the coarse, loose, ore and limestone (or dolomite). According to that proposal, the coarsely crushed ore is mixed either with limestone or dolomite which has been crushed to minus one-fourth inch or somewhat finer or with "rice stone"—i.e., dolomite which has been crushed to minus one-half inch and then screened to remove all particles finer than one-eighth inch in diameter—the mixture sintered on a conventional (e.g., Dwight-Lloyd) sintering machine, and the sinter cake then broken up into coarse chunks for charging to the blast furnace.

Such so-called "self-fluxing sinter" has some advantages over charging loose burden. However, the ingredients of the product are quite coarse, are non-uniformly distributed, and are slow to react. The pre-slagged character of conventional sinter probably permits early slag

formation at lower temperatures, but such slag tends to carry iron oxide well down in the furnace thereby increasing the hearth heat load and the amount of direct reduction occurring there. The sinter product, moreover, has a less than desirable bulk density, viz., a bulk density of about 90 pounds per cubic foot.

According to the present invention, an iron ore concentrate—e.g., a concentrate from magnetic taconite or flotation concentrates from low-grade hematite ores or a gravity concentrate of non-magnetic oxidic compounds of iron from, e.g., siderite ores or the like—the particles of which are essentially all finer than minus 100 mesh in size and which include a large proportion of very fine material of the order of minus 325 mesh, in which concentrate the silica content is in excess of that which is slaggable by the basic components of the concentrate, is homogeneously mixed (*a*) with finely divided dolomite (or, limestone), the particles of which are all finer than 28 mesh and preferably much finer, in an amount sufficient to combine with the excess silica of the concentrate to yield a slag suitable for the production of pig iron in the blast furnace, together (*b*) with whatever additives (e.g., bentonite; soda ash; powdered coal) are to be incorporated in the resulting product and with an amount of moisture sufficient to make the homogeneous admixture plastic; the resulting moist mixture is formed into pellets (i.e., small balls) in any suitable balling apparatus (e.g., a balling drum or balling cone or equivalent balling means); and the so-formed pellets are indurated (heat treated)—in any suitable indurating apparatus such as an up-draft or down-draft sintering machine or any known variation thereof, or any known combination of horizontal grate machine-kiln, but preferably in a vertical shaft-type indurating furnace—at an elevated temperature well above the calcining temperature of the flux component content of the pellets and in the range 2000–2400° F. to insure their complete induration and the complete calcination of the dolomite stone.

As will be understood, in the course of being heated from room temperature (say, 60° F. to 2000° F.) and above in the induration procedure, the flux component of the pellets undergoes full calcination with release of the CO_2 contents of the carbonates ($CaCO_3$ and/or $MgCO_3$). Not only is this true, and not only are the pellets indurated, but also the heat-treatment effects slag-forming reactions between the basic and acidic components of the pellets. The addition of flux, in proper amount, therefore tends to increase the mechanical strength and ruggedness of the indurated pellets by reason of the in situ development of some slag in the pellets.

It is to be noted, in the above connection, that in the heat-treated pellets the eventual flux is by no means fully developed and that for full development of flux the conditions obtaining in the blast furnace (or, open hearth) are necessary; the carbonates have been fully calcined and a sufficient amount of flux has been created to sheathe the solid particles bonding them together. This means that there has been some, but not a major amount, of fluxing of the iron ore particles by reason of the induration treatments.

The foregoing procedure provides a product in which the iron oxides and the fluxing components are very intimately and uniformly admixed. This very close proximity of the particles (of iron oxide and fluxing components) renders their fusion easy and rapid higher up in the blast furnace, drastically reduces the time required for the reduction of the iron oxides to metallic iron. Since all of the CO_2 of the carbonates had been driven off during the induration treatment, the lower part of the shaft and upper part of the bosh are freed of a heavy

heat load—whereby more rapid heating of the stock column results—the estimated reduction in the thermal load is approximately 1,200,000 B.t.u. per ton of iron and about 75 pounds of coke are saved. The absence of the previously driven off CO_2 proves to be distinctly beneficial, in that the atmosphere in the area between the 1400 and 2400° F. isotherms of the furnace is more highly reducing than it otherwise would be; reduction of the iron oxides is initiated more quickly; a larger through-put is possible; and much less flue dust is produced as compared with a furnace burdened with merchant ore and standard lump flux components. The high bulk density of the product, viz., about 155 pounds per cubic foot, greatly increases the capacity of the blast furnace by the added amount of iron in the volume being smelted.

The product of the invention is a microscopically very porous indurated pellet characterized by the presence throughout of a slag bond which binds the ore particles and flux particles together. The greater part of the iron oxide particles thereof remain as discrete particles—surrounded by sheaths of slag acting as binder: the iron oxide particles are not significantly fused. The product is characterized, further, in that all of its iron content is in the highest state of oxidation, regardless of its initial oxidation state. That is to say, where the concentrate was derived from a magnetic taconite and contained magnetite as the sole or chief iron mineral, the iron content of the indurated pellets therefrom is all Fe_2O_3 and a substantial amount (40–20%) of the latter is in a magnetic form.

In the foregoing it has been assumed that in the usual case the iron ore concentrate will contain an excess of silica over that content which would be slaggable by the bases contents of the concentrate, and that, therefore, in the carrying out of the present invention the "added flux component" will be dolomite or limestone. However, the principles of the invention are equally applicable in a situation where the bases contents of the iron ore concentrate are in excess of the silica content: in such case, the "added flux component" is finely divided silica or mineral rich in silica and the amount added is sufficient to slag the excess bases of the ore.

While in the foregoing it has been stated to be preferable to add—to the iron ore concentrate—sufficient base-yielding flux component to combine with all of the excess silica of the concentrate, it is wholly within the intent and scope of the invention to add a somewhat lesser stoichiometric amount of the base-yielding flux component to the end that a substantial amount of flux is formed in the pellets but the pellets are not fully "self-fluxing." It is noted, in this connection, that the blast furnace operator conventionally uses 13 pounds CaO plus MgO for every 10 pounds of acidic components (disregarding oxides of iron) of the ore. In a situation where the excess acidic components of an iron ore concentrate would require—for forming a fully "self-fluxing" pellet—the addition of about 505 lbs. per long ton dry weight of the concentrate, of dolomite, it is within the concept of the present invention to reduce the dolomite content of the admixture to about 350 lbs./l.t., whereby to attain a substantial approach to true "self-fluxing." However, since the fullest advantages of the invention are associated with a fully "self-fluxing" product, it is preferred to make the flux component addition large enough to slag all of the excess silica (or, excess bases) of the concentrate.

The invention will be described in greater particularity, with reference to the following specific examples, illustrative of the application of the principles of the present invention to a concentrate from magnetic taconite in which the iron mineral was mostly magnetite, and with reference to the accompanying drawing in which:

FIGURE 1 is a chart showing, in graph form, temperature gradients obtaining at various levels of a shaft furnace in which the process of the invention is being carried out; and

FIGURE 2 is a photomicrographic showing of the interior of a pellet produced in accordance with the present invention.

TABLE NO. 1

Screen analysis of raw materials

Raw Material—Size	Conct., Percent Wt.	Dolomite, Percent Wt.	Furnace Feed, Percent Wt.
+28 Mesh	.08		.09
+35 Mesh	.08	.08	.09
+48 Mesh	.08	.16	.18
+65 Mesh	.31	1.17	.35
+80 Mesh	.08	.86	.27
+100 Mesh	.15	1.25	.62
+150 Mesh	.38	3.21	.89
+200 Mesh	3.30	7.99	4.06
+325 Mesh	11.67	19.73	12.90
−325 Mesh	83.87	65.55	80.55
Total	100.00	100.00	100.00

TABLE NO. 2

Chemical analysis of raw materials

Material	Iron	Phos.	Silica	Mang.	Alum.	Lime	Mag.	Sul.	Ig. loss
Concentrate	64.91	.006	7.98	.26	.18	.31	.19		
Dolomite	.99	.011	1.30	.03	.60	29.46	20.25	.009	46.90
Furnace Feed	56.28	.006	7.08	.23	.24	4.25	2.91	.001	6.33

In Examples Nos. 1 and 2, the pellet composition was as follows:

TABLE NO. 3

Raw pellet characteristics

Additives:	Lbs./l.t. conc.
Dolomite ____lbs__	350
Bentonite ____lbs__	12
Soda ash ____lbs__	1.5
Coal (powdered) ____lbs__	20
Drop test No.	18
Wet compressive strength	16.3
Dry compressive strength	56.5

In Example No. 3 the pellet composition differed from the above only in that no powdered coal was added.

To insure uniform mixing of the dolomite (and other "additives") with the magnetite concentrate, and to provide careful control of the moisture content of the balling drum feed, weighed portions of each were fed to a mixing drum, pulped with water, and then filtered, on a drum filter, to provide a homogeneous filter cake containing about 10% by weight of moisture. The filter cake was fed to the balling drum described in U.S. Patent No. 2,831,210, in which latter the mixture balled readily producing plus ⅝ inch raw pellets having good average physical properties as shown in Table No. 3 above.

The pellets were fed to the top of a column of similar pellets resident in the indurating furnace described in U.S. Patent No. 2,816,016 and therein were subjected to induration treatment.

After a preliminary trial run, a series of three induration experiments were conducted. In the preliminary run it was ascertained that when the combustion chamber temperature was maintained as high as 2300° F. the pellets column "hung-up" because of excessive softening (semi-fusion) of the pellets showing that combustion chamber temperature had to be maintained substantially lower than 2300° F.

In experiment No. 1 the combustion chamber temperature was maintained at 2100° F., and operating condition were held constant for a 17-hour run.

In experiments Nos. 2 and 3, the combustion chamber temperature was reduced to 2000° F. (as noted above, in experiment No. 3, the pellets contained no powdered coal).

TABLE NO. 4

Furnace operating data—Test No. 1

[2100° F. temperature of heating gas]

Feed rate	.59 l.t./hr.
Discharge rate	.54 l.t./hr.
Oil consumption	5.93 gal./l.t. fired pellets.
Air blow:	
Main shaft	196 c.f.m.
Combustion chamber	96 c.f.m.
Total	292 c.f.m.
Temperatures:	
Combustion chamber	2100° F.
Top stove—	
H	1880° F.
G	2115° F.
Bottom stove—	
E	1090° F.
D	650° F.
Pellet discharge	450° F.
Pressures:	
Top	0.25" mercury.
Middle	0.30" mercury.
Bottom	1.35" mercury.
Static	0.55" mercury.

TABLE NO. 5

Furnace operating data—Test No. 2

[2000° F. temperature (with coal)]

Feed rate	.59 l.t./hr.
Discharge rate	.54 l.t./hr.
Oil consumption	5.44 gal./l.t. fired pellets.
Air blow:	
Main shaft	210 c.f.m.
Combustion chamber	96 c.f.m.
Total	314 c.f.m.
Temperatures:	
Combustion chamber	2000° F.
Top stove —	
H	1860° F.
G	2100° F.
Bottom stove—	
E	1260° F.
D	820° F.
Pellet discharge	475° F.
Pressures:	
Top	0.25" mercury.

Middle	0.35" mercury.
Bottom	0.40" mercury.
Static	0.55" mercury.

TABLE NO. 6

Furnace operation data—Test No. 3

[2000° F. temperature (without coal)]

Feed rate	.54 l.t./hr.
Discharge rate	.59 l.t./hr.
Oil consumption	5.89 gal./l.t. fired pellets.
Air blow:	
Main shaft	184 c.f.m.
Combustion chamber	96 c.f.m.
Total	280 c.f.m.
Temperatures:	
Combustion chamber	2000° F.
Top stove —	
H	1740° F.
G	1960° F.
Bottom stove—	
E	1370° F.
D	890° F.
Pellet discharge	500° F.
Pressures:	
Top	0.30" mercury.
Middle	0.30" mercury.
Bottom	0.45" mercury.
Static	0.50" mercury.

The temperature data set out in Tables 4, 5 and 6 above were secured at the following thermocouple positions within the apparatus:

"Combustion chamber"—in inlet end of insulated passageway between combustion chamber and furnace shaft;

"H"—periphery of charge column substantially midway between top and bottom of upper stove;

"G"—periphery of charge column substantially midway between level "H" and level of introduction of heating gas from combustion chamber;

"E"—periphery of charge column adjacent to but beneath level of introduction of heating gas from combustion chamber;

"D"—periphery of charge column substantially midway between top and bottom of bottom stove.

TABLE NO. 7

Physical properties of fired pellets

Product	2,100° F. With Coal	2,000° F. With Coal	2,000° F. Without Coal
Test No.	#1	#2	#3
Size:	*Percent wt.*	*Percent wt.*	*Percent wt.*
+¾"	28.97	26.99	40.00
+½"	59.13	53.99	48.95
+⅜"	5.95	7.08	2.99
+3 Mesh	1.98	3.98	1.19
+10 Mesh	2.78	5.31	2.39
−10 Mesh	1.19	2.65	4.48
Total	100.00	100.00	100.00
Compression Tests, lbs	550	566	568
Tumble Test	95	93	91
Specific Gravity	3.94	3.74	3.63

TABLE NO. 8

Chemical analysis of fired pellets

Test No.	Product	Assay Percent							
		Iron	Ferrous Iron	Ferric Iron	Phos.	Sil.	Mang.	Lime	Magnesia
1	2,100° F. With Coal	58.16	.65	57.51	.006	7.65	.23	4.30	2.52
2	2,000° F. With Coal	58.16	.64	57.52	.006	7.68	.23	4.37	2.51
3	2,000° F. Without Coal	58.14	.66	57.48	.006	7.66	.23	4.28	2.55

In tests Nos. 1, 2 and 3, the readings of the traveling thermocouple, at the core of the furnace, were as shown in FIGURE 1 of the accompanying drawing, which shows in graph form the temperature gradients obtaining in these tests. It is noted in this connection that the instruments used were not capable of registering temperatures above 2500° F.

In spite of the high furnace core temperatures, no difficulty with fused pellets was encountered in tests 1–3 inclusive.

MINERALOGICAL STUDY OF FIRED PELLETS

Macroscopically, the pellets when broken open appeared to be a completely fused slag mass. However, polished cross sections through the pellets, when studied under the microscope, presented a very different "picture." The individual iron ore particles could be readily distinguished. In the case of the pellets fired at lower temperature, a combination of voids and glassy slag separated hematite particles on which the cusps had been blunted, and some of the dolomite residue could be distinguished. In the samples indurated at 2100° F., with added coal, many of the smaller grains were seen to have migrated together through what must have been a fairly fluid slag, and— apparently through the action of surface tension— to have been drawn together into spherical shapes, looking like clusters of grapes in a slag matrix. Slag appeared to be the principal factor governing bonding in all cases.

FIG. 2 is a photomicrographic showing, at 350 diameters, of interior of a pellet, with coal added, fired at a combustion chamber temperature of 2000° F.

In connection with the data set forth in Table No. 7, supra, it should be noted that the specific gravity or apparent density of the self-fluxing pellets (i.e., from 3.94 to 3.63, depending upon temperature of firing and upon amount of coal used in the pellets) is substantially higher than is the apparent density—3.50 to 3.35, depending upon amount of coal used—of pellets formed from the same ore concentrate and treated in the same manner but without the flux addition. This appreciable gain in density is due to the shrinking effect that takes place when such pellets are fired. This is undoubtedly due to the fact that there is a great deal more of the slag phase present under the flux-added condition which permits greater mobility of the particle and permits such shrinking. This added specific gravity is of great benefit in the blast furnace as it contributes to the amount of iron present in the charge, and it has a separate advantage for material used in the open hearth since its added specific gravity permits such pellets to sink through the slag layer much easier.

That the particle size of the added flux component has a significant bearing on the quality of the indurated "self-fluxing" pellets containing it is demonstrated by the findings of the following specific example.

The starting material was an iron ore (Hilton) concentrate, analyzing approximately

68.2% Fe
1.88% SiO_2
0.004% P
0.50% CaO+MgO

The screen analysis of the concentrate was substantially all minus 28 mesh with about 80 weight percent finer than 350 mesh. Because of its low content of acidic slag-forming component, the addition of 90 pounds of limestone (to one ton of concentrate) was sufficient to make the pelletized mixture self-fluxing.

Four comparative tests were run, in each of which 90 pounds of limestone was homogeneously admixed, with 1 ton of the concentrate plus (in each case)

1.6 lbs. soda ash and
12.0 lbs. bentonite,

the particle size of the limestone being varied as follows:

Test #1—all minus 14 mesh,
Test #2—all minus 28 mesh,
Test #3—all minus 65 mesh, and
Test #4—all minus 100 mesh.

In each instance the resulting homogeneous admixture was formed into small balls or pellets and the resulting pellets were indurated—in the manner described above—at a top temperature of about 2350° F. In each instance the dry compression strength of the unfired pellets and the compression strength of the indurated (fired) pellets were determined by standard procedure.

Pellets formed of the same mixture but containing no added limestone (or other base-yielding fluxing component) were found to have a dry compression strength (unfired) of 35 pounds, and a fired compression strength of about 1800 pounds.

The strength data of Tests 1–4, incl., were as follows:

Test No.	Dry (Unfired)	Fired
	Compression Strength, Pounds	Compression Strength, Pounds
1	34.3	1,610
2	37.7	1,720
3	41.2	1,965
4	42.6	2,000

There was a marked increase in quality as the maximum particle size of the added limestone was decreased. An examination of the fired pellets showed that those in which the coarser sizes of limestone had been used contained voids due to calcination of the relatively large pieces of limestone, whereas at sizes finer than 65 mesh no voids could be detected and the internal structure of the pellets was quite homogeneous. Accordingly, the addition of basic flux component as coarse as, or coarser than, 28 mesh, maximum, is harmful to the physical properties of the unfired pellets and also of the fired pellets notwithstanding the probability that the self-fluxing properties of the pellets containing the coarser limestone had not been seriously impaired. In sum, the flux component added to the fine magnetite concentrate, before pelletizing, should be as fine as minus 28 mesh or finer, because such fine material permits thorough mixing of the constituents and yields a more nearly homogeneous product.

As is stated hereinbefore, the thermal treatment leading to the product of this invention is not confined to the use of a shaft-type furnace, since said treatment can be effected equally well using known indurating apparatus of the traveling grate type which may employ either the updraft or the downdraft principle, provided only that the above-described conditions are observed.

I claim:

1. In the process of pelletizing iron ore concentrates, the particles of which are essentially all finer than minus 100 mesh and include a large proportion of material finer than 325 mesh, in which concentrate the iron oxides are associated with gangue material including acidic components in excess of the combined proportion of its basic components, according to which pelletizing process a moist concentrate is homogeneously admixed with finely divided solid carbonaceous fuel and bentonite and the mixture is formed into pellets and the pellets are indurated at an elevated temperature in excess of 1832° F., the improvement which consists in homogeneously admixing with the moist concentrate, prior to balling, a finely divided alkaline earth metal carbonate rock the particles of which are all minus 28 mesh, the amount of such added carbonate rock being such as to yield, upon calcination thereof, a slag-forming basic reagent in an amount sufficient to slag all of said excess acidic components, and heat-treating the resulting discrete pellets by contacting a mass of the discrete pellets with a stream of free oxygen-containing heating gas introduced into the pellets mass at a temperature of from about 2000° to

about 2100° F., the heat-treatment being continued for a period sufficient to effect (*a*) the complete calcination of the carbonate rock and (*b*) substantially complete combination of the calcined material with all of the acidic components of the pellets thereby substantially completely pre-slagging the gangue constituents of the pellets to the production of mechanically strong and rugged self-fluxing iron oxide concentrate pellets.

2. As a new product, a charge material for the blast furnace and for the open hearth, consisting essentially of discrete indurated pellets, each pellet consisting essentially of finely divided iron ore particles in a matrix of slag containing the nonferrous constituents of the iron ore in slagged form, the iron content of the pellets being in the highest state of oxidation and a substantial proportion of said iron content being in magnetic form, there being present in said slag matrix a content of basic slag-forming component amounting to from about 100% to about 130% of the stoichiometric equivalent of the content of acidic slag-forming component present therein, said pellets being mechanically strong, rugged and self-fluxing.

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