

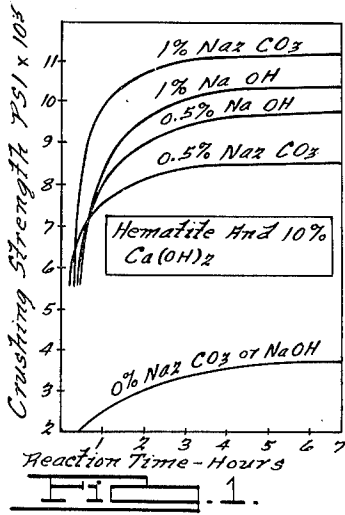
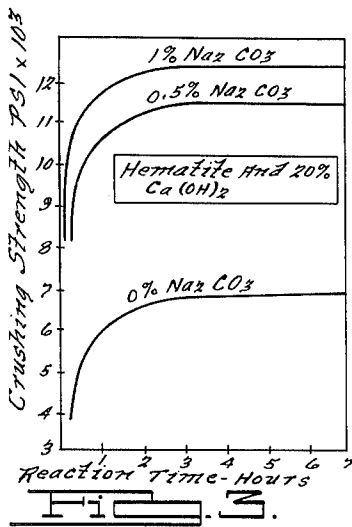
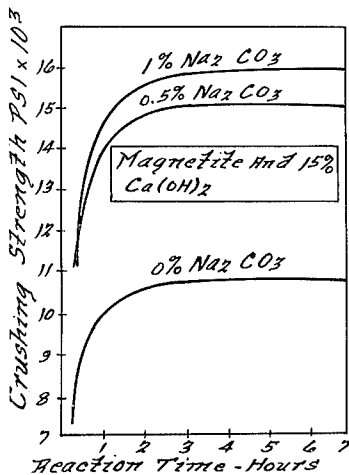
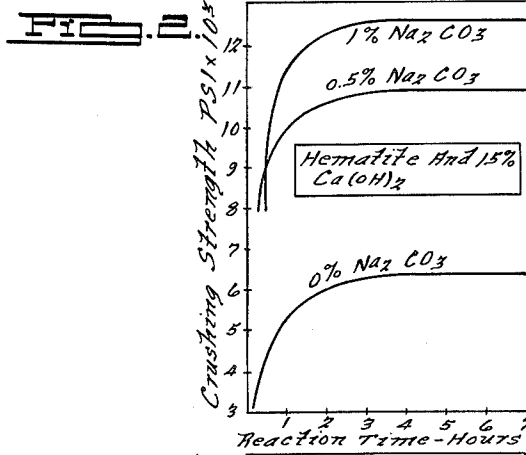
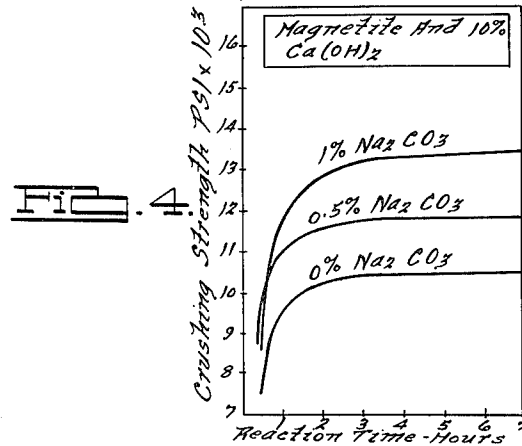
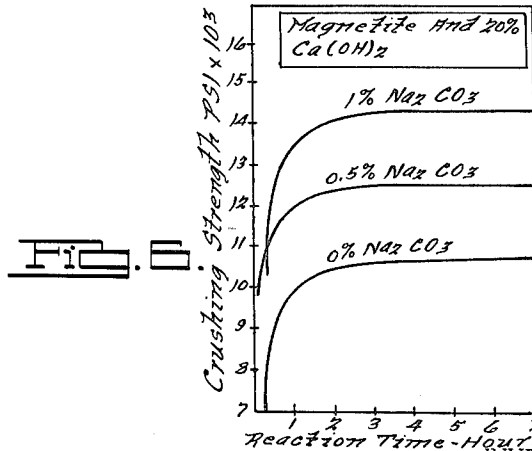
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3,235,371

AGGLOMERATED MINERAL PRODUCTS AND METHOD OF MAKING SAME

Filed Sept. 10, 1962



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3,235,371

**AGGLOMERATED MINERAL PRODUCTS AND
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5 Claims. (Cl. 75—3)

The present invention broadly relates to the treatment of ores, and more particularly to a novel ore agglomerate and to an improved method of making the agglomerate. More specifically the present invention is directed to the formation of agglomerates from finely particulated metallic and non-metallic minerals, and particularly iron ore concentrates which are in a finely particulated state and which must be agglomerated to facilitate subsequent handling of the ore and the smelting thereof during subsequent processing.

A large variety of processes are commercially employed for the beneficiation of low grade ores to remove therefrom the undesirable constituents or gangue and to upgrade the ore into a concentrate of high valuable mineral content. It is conventional in such ore dressing operations to pulverize or grind the low grade ore as mined to a relatively fine particle size in order to free the locked gangue of silica and other impurities therein enabling physical separation thereof from the valuable minerals in the ore. The concentration of the pulverized ore relies on the differences in the physical properties of the mineral and gangue such as the differences in their specific gravity, surface energy, magnetic permeability, and the like, enabling separation thereof by techniques such as gravity, flotation, magnetic concentration, and the like. In order to achieve the necessary degree of concentration of the low grade ore, it is frequently necessary to subject the ore to one or successive pulverizing operations wherein the ore is reduced to a fineness in particle size less than about 4 mesh.

Due to the dusting and packing tendency of ore concentrates or other minerals obtained directly from the mine or subsequent refining operations in such a finely particulated state, in addition to the difficulty of handling and transporting such ores, it has been found desirable and in some instances necessary to agglomerate the finely divided particles into relatively large sized lumps in which they can be conveniently handled, transported, and smelted. In the methods heretofore employed or proposed for use, the finely divided ores have been agglomerated by sintering molded lumps or globules of the finely particulated ore at relatively high temperatures such as, for example 2200° F. for prolonged periods of time wherein incipient fusion of the particles takes place to form a friable mass which is thereafter crushed and screened. Alternatively, pelletizing processes have been employed wherein the finely particulated ore is mixed with bentonite and lime or crushed limestone and thereafter heated at temperatures of about 2400° F. to about 2500° F. to form hardened pellets. In still other agglomerating processes heretofore known, suitable binders such as sodium silicate, coal tar, bitumen, spent sulfite liquor, etc. are mixed with finely particulated ore after which the ore is pressed or extruded into lumps which may then be heated for prolonged periods of time at an elevated temperature to form integrally bonded masses.

Each of the foregoing heretofore known processes have one or more inherent disadvantages which are overcome in accordance with the practice of the present invention. For example, the use of various binders for forming agglomerates of the finely divided ore introduces materials in the resultant agglomerates which are carried over into subsequent smelting operations resulting in

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increased quantities of impurities and slag formation and in a corresponding reduction in the efficiency of the operation. Alternatively, the use of such high temperatures for prolonged periods of time for effecting a hardening of the molded lumps or pellets constitutes a tedious and costly operation in view of the massive equipment and high energy required and frequently produces agglomerates having insufficient strength to resist breakage and attrition during subsequent handling and storage.

It is accordingly a primary object of the present invention to provide an improved agglomerate of a finely particulated ore and to provide an improved method of forming the agglomerate which overcomes the disadvantages present in processes of similar purpose heretofore known.

Another object of the present invention is to provide a novel agglomerate of a finely particulated mineral which incorporates therein a controlled quantity of a fluxing agent substantially uniformly distributed throughout thereby facilitating subsequent smelting operations and avoiding the necessity of a separate addition of such fluxing agents during the smelting operation.

Still another object of the present invention is to provide an improved agglomerate of a finely particulated mineral or mineral concentrate which is of high strength and impact resistance enabling relatively rough handling thereof during shipment and storage without incurring any appreciable breakage or attrition of the agglomerate.

A further object of the present invention is to provide an improved process for forming agglomerates of a finely particulated mineral which overcomes the need for massive and expensive processing equipment and which is simpler and substantially more economical than agglomeration techniques heretofore known.

A still further object of the present invention is to provide an improved agglomeration process wherein burnt limestone can be employed for mixing with wet ore concentrates or minerals facilitating a rapid reduction in the moisture content in the ore to within a desirable moisture range avoiding the necessity of employing heat or special drying techniques to remove the undesirable moisture content thereof.

Still another object of the present invention is to employ an improved agglomeration process for finely divided minerals and mineral concentrates wherein relatively low temperatures can be employed to promote the hardening reaction of the agglomerates thereby providing for a substantial savings in the cost of heat energy.

A still further object of the present invention is to provide an agglomerate of finely divided ore and to provide a method of making the agglomerate whereby the resultant agglomerate is substantially devoid of carbonate compounds that, if present, decompose during subsequent smelting operations and liberate carbon dioxide gas which effects a dilution of the conventional smelting gases employed and concurrently reduces the efficiency of the smelting operations.

The foregoing and other objects and advantages of the present invention are achieved by employing a hydrothermal reaction for forming hard, crush-resistant porous agglomerates of finely particulated metallic and non-metallic mineral concentrates and fines, incorporating therein controlled proportions of the oxides, hydroxides and carbonates of calcium and magnesium as well as mixtures thereof in the presence of heat, pressure and moisture. In a preferred form of the present invention small controlled quantities of the oxides, hydroxides and carbonates or bicarbonates of the alkali metals can be added further promoting the hydrothermal reaction and effecting the formation of higher strength agglomerates.

The composition of the mixtures and agglomerates as herein disclosed and claimed are described in terms of percentages by weight unless otherwise indicated. It will also be understood that the fluxing and binding agent, namely the oxide, hydroxide and carbonate of calcium and magnesium are expressed in the subjoined claims in terms of a weight equivalent basis calculated as calcium oxide (CaO) or magnesium oxide (MgO) as the particular case may be. Similarly, the oxide, hydroxide and carbonate or bicarbonate of the alkali metals such as potassium and sodium are expressed in terms of a weight equivalent basis calculated as sodium oxide (Na₂O) or potassium oxide (K₂O), as the particular case may be. It will be further understood that the term "finely particulated" mineral or mineral concentrate encompasses finely divided minerals and mineral fines such as hematite, magnetite, chromite, pyrolusite, wolframite, scheelite, cobaltite, cassiterite, zincite, smithsonite, sphalerite, phosphate rock, galena, pyrite, bauxite, cuprite, malachite, chalcocite, copper oxide, and the like, derived from natural sources or conventional ore concentrating operations, as well as mixtures thereof.

The present invention is particularly adaptable for agglomerating iron ore concentrates into high strength crush-resistant agglomerates of a desired size and configuration in which they are eminently suitable as a charge material to blast furnaces. In accordance with the practice of the present invention, concentrates of conventional iron bearing ores such as hematite and magnetite, for example, which are concentrated so as to conventionally contain from about 45% to about 70% iron calculated as Fe and the balance gangue which is comprised primarily of silica can be inexpensively and simply agglomerated either alone or in admixture with fines from other sources into high strength agglomerates incorporating a homogeneous distribution of a non-gas producing fluxing agent. In order to effect a purification of low grade iron ores, it is conventionally necessary to grind or pulverize the ore to a particle size ranging from about 4 mesh to less than about 400 mesh or fine enough to unlock the iron oxide minerals and thereby facilitate separation of the major portion of the mineral from the gangue. This separation is conveniently achieved by either one of the conventional wet separation techniques well known in the art such as froth flotation and/or magnetic processes; for example, wherein the resultant iron ore concentrate produced is in the form of an aqueous slurry from which it can be filtered resulting in a filter cake generally containing between about 5% to about 15% water. Iron or other mineral concentrates which are concentrated by dry methods can be simply blended with water in the amount of about 1% to about 14% so as to properly form a cohesive mass of the finely particulated mineral.

The appropriate proportion of the fluxing or binding agent can be added and substantially homogeneously mixed with the finely particulated mineral or mineral concentrate either by directly mixing the two dry particulated materials, by admixing slurries of the two materials followed thereafter by filtration, or by blending the dry fluxing and binding agent into the wet filtered mass of the mineral or concentrate. The particular blending technique employed will vary depending on the particular form in which the mineral is available as well as the desired water content of the blended mixture in order to facilitate the preliminary formation of pellets, briquettes or extrusions of the wet mixture.

Any one of a number of suitable molding, pelletizing, briquetting or extrusion techniques can be satisfactorily employed for forming compacted lumps or agglomerates of the wet green mixture which are thereafter subjected to the hydrothermal reaction under controlled temperature, pressure and moisture conditions effecting a hardening of the lump into a porous crush-resistant agglomerate. The average size and size distribution of the particles of the mineral as well as the particle size of the flux-

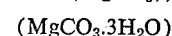
ing and binding agent in addition to the water content of the green mixture will vary depending on the mineralogic characteristics of the mineral or mineral concentrate and the particular molding, pelletizing or extruding technique employed. For example, when a pelletizing process is employed for forming the preliminary green agglomerates such as by employing a drum or disk to form spherical pellets of the desired size, it is generally preferred to control the water content of the admixture within a range of from about 3% to about 10% and to include fines of less than about 325 mesh representing at least about 20% of the mixture which has been found to facilitate the formation of spherical masses by this technique. On the other hand, when the preliminary formation of the green agglomerates is achieved through a briquetting roll press, for example, lower moisture contents such as about 5% are preferred and the size of the particles in the mineral and the size distribution thereof is less important. It will be apparent from the foregoing that the particular size range of the particles in the mixture as well as the quantity of water contained therein can be optimized for each specific mineral and mineral concentrate and for each specific technique employed for forming the green unreacted agglomerates.

A further factor influencing the size of the particulated mixture is that relating to the ultimate strength of the reacted agglomerate. Generally, it has been found that an increase in the crushing strength of the agglomerates is obtained as the fineness in size or as the percentage of extremely fine particles is increased which is believed to be directly attributable to the increased surface area per unit volume of the material providing an increase in the total area of the resultant bond.

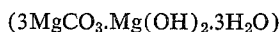
In view of the foregoing considerations, the mineral or mineral concentrate may conventionally have a range of fineness in particle size ranging from about 4 mesh size to subsieve sizes, and preferably ranging below about 20 mesh with at least half less than 270 mesh. The particular size range or degree fineness in size of a mineral concentrate will generally be determined by the mineralogic character of the material, the particular process employed for beneficiation of the low grade ore and the economic considerations involved therein. It has been found that conventional commercially available concentrates have a degree of fineness of particle size of this general magnitude and are eminently satisfactory for agglomeration in accordance with the practice of the present invention.

The composition of the agglomerates comprising the valuable mineral, the gangue or impurities, the flux or binding agent, the accelerating agent if desired, and other suitable additives as may be desired to facilitate the subsequent reduction and smelting of the agglomerates must be controlled within certain limits in order to obtain the benefits of the invention. With respect to the metallic or non-metallic mineral concentrate such as iron ore concentrate, for example, it has been found that the type and concentration of the conventional impurities therein, such as silica, alumina, carbonates, bicarbonates, sulfates, sulfites, phosphates, oxides, hydroxides, magnesium, calcium, sodium, potassium, etc., is relatively unimportant to obtain the requisite strength of the cured agglomerate.

In addition to the mineral constituent which is present in the form of an oxide, hydrated oxide, sulfide, carbonate, phosphate, etc., and the residuary impurities in the mineral or mineral concentrate, the agglomerate contains from about 1% up to about 30% of the fluxing or binding agent calculated as calcium oxide (CaO). Binding agents suitable for forming the agglomerates comprising the present invention include calcium carbonate such as aragonite and calcite, calcium hydroxide, calcium oxide, dolomite (CaO.MgO.2CO₂), magnesite or magnesium carbonate (MgCO₃), mesquitine



hydromagnesite or basic magnesium carbonate



magnesium hydroxide, magnesium oxide, as well as mixtures thereof. Of the foregoing materials, the hydroxides and oxides of calcium are preferred particularly in view of economic considerations and of these, calcium hydroxide constitutes the preferred constituent. In some instances, however, burned lime or calcium oxide is preferably employed which when admixed with a wet mineral concentrate reacts with the water content thereof effecting the formation of calcium hydroxide, resulting in a corresponding decrease in the net water content of the mixture and through the exothermic reaction generates heat which acts to heat the mass causing further evaporation of water. This feature is particularly desirable when wet minerals or mineral concentrates are available having water contents in excess of that desirable for achieving optimum molding pelletizing, briquetting or extruding efficiency whereby the water content can be reduced to the desired level without the need of employing extraneous heat or other drying equipment.

The quantity of the flux or binding agent employed as hereinbefore set forth, may range from about 1% up to as high as 30% or more of the admixture. It has been found that by employing the flux or binding agent in amounts less than about 1% inadequate strength is obtained, in some instances, of the resultant reacted agglomerate whereby it is rendered relatively fragile and susceptible to breakage and attrition during subsequent handling in transportation and storage. Accordingly, the quantity of the flux and binding agent is preferably controlled in an amount greater than about 1%.

The upper limit of the concentration of the fluxing and binding agent is dictated by the quantity of the silica and other slag forming impurities in the mineral concentrate in order to achieve satisfactory fluxing thereof during the subsequent smelting operations. It is generally desirable to employ an amount of fluxing and binding agent sufficient to satisfactorily flux the gangue contained within the agglomerate. Amounts in excess of this quantity do not appreciably improve the strength of the resulting agglomerate and serve only to dilute the ore mineral content of the agglomerate and thus would constitute an uneconomical practice. Conventionally, the quantity of the flux and binding agent calculated as the weight equivalent of calcium oxide is controlled within a range of about 5% to about 20% and usually about 10% for most iron ore concentrates. For typical commercial iron ore concentrates which contain from about 60% to 67% iron calculated as Fe, and from about 3% to about 10% silica, a quantity of the flux and binding agent ranging from about 7% to about 11% has been found eminently satisfactory for achieving a high strength agglomerate and for providing efficient fluxing of the agglomerate during subsequent blast furnace operation.

The particle size of the flux and binding agent may generally range from about 60 mesh to less than about 400 mesh and preferably all less than about 270 mesh. A size range of the flux and binding agent coarser than about 20 mesh increases the difficulty of effecting a substantially uniform distribution thereof throughout the mixture and provides insufficient surface area in some instances to obtain the requisite high strength bond. It is for this reason that the size of the finely particulated flux and binding agent or mixtures thereof be controlled within ranges below about 60 mesh and preferably with at least half of the material in sizes less than about 270 mesh. For agglomerating purposes there is no lower limit of particle fineness, this depending on the degree of grinding required to unlock the ore mineral.

In addition to the foregoing constituents it has been found that the inclusion of an oxide, hydroxide, carbonate or bicarbonate of the alkali metals such as po-

tassium or sodium or blends thereof to the mixture in amounts ranging up to about 1% calculated on a weight equivalent basis of sodium oxide (Na_2O) or (K_2O), has provided an acceleration of the hydrothermal reaction and a corresponding increase in the strength of the resultant agglomerate. Concentrations of the accelerator agent in excess of about 1% also provide an improvement in the strength of the resultant agglomerate, but concentrations in excess of about 1% are usually unduly corrosive to the blast furnace linings during subsequent smelting of the pellets. For this reason, it is preferred to restrict the quantity of the accelerator to a maximum amount of about 1%. On the other hand, while concentrations as small as only one tenth of a percent produce a measurable increase in the strength of the resultant agglomerate, it is generally preferred to include the accelerator agent in amounts ranging from about .25% to about .75%. Of the foregoing accelerator agents, the hydroxide, carbonate or bicarbonate of sodium are preferred primarily because of economic considerations of which the hydroxide and the carbonate are the preferred forms.

The accelerator agent is preferably added to the mixture in the form of an aqueous solution which may range in strength or concentration from about 10% by weight up to about 75% by weight and preferably a 50% solution. It is also contemplated that the accelerator agent can be added in dry form while in a finely particulated state but due to the hygroscopic nature of these materials and their toxicity and corrosivity, it is preferred to employ aqueous solutions which provide the further advantages of handling and uniform distribution throughout the mixture. The particular concentration of the aqueous solution of the accelerator agent can be varied consistent with the consideration of such factors as the water content of the initial green mixture and the optimum water content desired consistent with the particular type of molding, pelletizing, briquetting or extruding operation to be employed for preliminarily forming the green agglomerates.

Other extraneous or suitable additive materials may also be included in the mixture which do not deleteriously affect the subsequent hydrothermal reaction and the strength of the cured agglomerate. Additives such as these may be desired depending upon the particular type of smelting operation to be performed avoiding a separate addition of this additive material to the smelter in which it is not as uniformly distributed as in the case wherein it is preliminarily incorporated in the agglomerate.

As hereinbefore set forth, the mixture of the mineral concentrate together with the flux and binding agent, either through the formation of an aqueous slurry of the constituents followed by filtration or the dry mixing of the constituents followed thereafter by the addition of water or a solution of the accelerator agent for achieving a wet mixture suitable for molding, pelletizing, briquetting or extrusion, or by mixing the dry flux and binding agent with a wet concentrate, provides for a homogeneous mixture wherein the fluxing agent is uniformly distributed throughout the agglomerate substantially improving the fluxing characteristics of the agglomerate and the efficiency of the subsequent smelting operation. Any one of a number of well-known mixing or blending apparatuses can be satisfactorily employed for the purpose of achieving a substantially homogeneous blend of the several constituents comprising the green mixture.

The resultant green mixture of the finely particulated mineral incorporating a controlled quantity of the flux and binding agent together with a small amount of the accelerator agent, if desired, and other additives if desired is thereafter subjected to a molding, briquetting, pelletizing or extruding operation wherein the wet mixture is formed into green agglomerates of the desired size and configuration consistent with the achievement of optimum

strength and smelting characteristics. The agglomerates are preferably formed of a relatively compact configuration such as in the form of cylinders, spheres, eggs, pillows etc., in which they are substantially devoid of any thin sections or sharp angularities which are susceptible to fracture or breakage during handling. The particular configuration of the green agglomerates is also controlled so that the nesting characteristics of a plurality thereof are such as to prevent tight compacting preventing the passage of a heated moisture-laden fluid therethrough during the subsequent hydrothermal processing. Agglomerates of the general configuration hereinabove set forth provide satisfactory open stacking characteristics wherein the surfaces of the individual agglomerates are not obscured and provide sufficient bed porosity to facilitate the circulation of a hot pressurized fluid therethrough. These same porosity characteristics are also desirable during the subsequent smelting operation of the agglomerates, facilitating movement of the reducing gases and the like through the agglomerate charge.

The resultant green agglomerates during prior handling and molding, pelletizing, briquetting, or extrusion usually lose a portion of their moisture content. A net moisture content within a range of from about 3% to about 8% represents the preferred range of moisture content during the hydrothermal reaction. Moisture contents of less than about 3% generally do not provide sufficient cohesion of the mass whereas moisture contents in excess of about 8% are sometimes undesirable because the mass is too plastic to retain a molded, balled, briquetted or extruded shape. It is for this reason that the moisture content of the green agglomerates prior to the hydrothermal reaction is preferably controlled within a range of from about 3% to about 8% and more usually from about 4% to about 5%.

The resultant green agglomerates are thereafter charged to a chamber or pressure vessel in which they are heated to an elevated temperature under pressure and in the presence of moisture to effect a hardening and bonding of the individual particles into an integral high strength agglomerate. The particular hydrothermal reaction which occurs is not completely understood but it has been found that pressure, temperature, time and moisture content contribute toward the reaction and the strength of the resultant agglomerate. By increasing the pressure and/or temperature, the rate of reaction is increased enabling stronger bonds to be obtained for the same length of time or enabling agglomerates of equal strength to be produced in a shorter time. Experimental analyses suggest that the hydrothermal reaction results in the formation of a bond comprising a reaction product of the fluxing and bonding agent, water, the impurities in the mineral such as silicon dioxide and alumina, as well as with the oxide, hydrated oxide, carbonate, phosphate, etc., of the mineral itself. During subsequent smelting, any hydroxides or carbonates in the agglomerate tend to decompose liberating water or carbon dioxide gas which escapes and accentuates the porosity of the agglomerate.

It will be apparent from the foregoing that the temperature, pressure, time and amount of alkali hydroxide, carbonate or bicarbonate to produce a reacted agglomerate from a specific type of finely particulated material of satisfactory strength are interrelated and these variables must be correlated and optimized in accordance with available equipment and economic considerations to provide agglomerates of the desired strength. The application of heat to the green agglomerates may be achieved in any one of a number of methods such as by employing steam, heated moisture-laden air such as flue gases saturated with moisture and by direct or indirect heating and the like. Since heat is necessary to promote the hydrothermal reaction and represents a significant cost factor of the process, economic considerations such as the availability of waste heat and recovery sources will conventionally dictate the particular heating medium and temperatures em-

ployed consistent with achieving a hardening of the green agglomerates within commercially practical time periods. Of the foregoing techniques, the use of steam has been found eminently satisfactory since it simultaneously provides a source of heat energy and moisture necessary for the hydrothermal reaction. Steam under pressure has been satisfactorily employed for effecting a hardening of the agglomerates within a reasonable time that are of the requisite strength and crushing resistance.

In consideration of the foregoing factors, it has been found that temperatures ranging from about 200° F. up to about 700° F. can be satisfactorily employed to achieve a hardening of the green agglomerates within reasonable time periods. The maximum temperature usable is dictated by that at which fusion or unwanted thermal decomposition of the additive constituents or of the mineral occur which in the case of iron ore concentrates is about 2200° F. In this latter instance it is preferred that temperatures of less than 600° F. be employed for curing iron ore agglomerates. The lowest temperature suitable for initiating the hydrothermal reaction is about 200° F. but in view of economic considerations as to the curing time required for achieving satisfactory strength, a temperature of at least about 300° F. and preferably about 400° F. is employed. In addition, while the hydrothermal reaction can satisfactorily be performed at atmospheric pressure, it is preferred to employ pressures greater than atmospheric up to pressures approaching the capacity of a conventional pressure vessel so as to decrease the time and improve the strength of the resultant cured agglomerate. When steam is employed as the heating medium, the pressure and temperature thereof are interrelated and are selected to achieve optimum curing characteristics depending on attendant economic considerations. Similarly, the quantity of moisture in the fluid or disposed in contact with the green agglomerates during the curing reaction should be maximized to achieve the hardening reaction within a reasonable time.

In order to further illustrate the composition of the agglomerates and the method of making them in accordance with the practice of the present invention, the following examples are provided. It will be understood, however, that these examples are provided solely for the purposes of further illustration and the specific compositions and conditions employed are not intended to be limiting of the scope of the invention as herein described and as set forth in the subjoined claims.

EXAMPLE I

A dry hematite concentrate derived from iron ore as mined in the state of Michigan and concentrated by a froth flotation technique, was employed for forming agglomerates in accordance with the practice of the present invention. The hematite iron ore concentrate had a chemical composition and a size distribution as set forth in the following table:

Analysis of hematite iron ore concentrate

Composition		Size Analysis	
Constituent	Percent	Mesh Size	Percent
FeO.....	0.39	-35 +48.....	0.25
Fe ₂ O ₃	90.09	-48 +65.....	0.50
SiO ₂	7.39	-65 +100.....	2.75
Al ₂ O ₃	0.69	-100 +150.....	10.75
CaO.....	0.23	-150 +200.....	15.00
MgO.....	0.05	-200 +270.....	13.00
MnO.....	Trace	-270 +325.....	18.00
S.....	0.032	-325 +400.....	6.25
P ₂ O ₅	Trace	-400.....	33.50
Volatile.....	0.56		
			100.00

The dry hematite concentrate was mixed with approximately 4 to 5% water for a period of time until a substantially uniformly moist blend was obtained. There-

after, a bonding and fluxing agent comprising finely particulated calcium hydroxide was added to the blended mixture of the hematite concentrate. The calcium hydroxide was derived from calcined precipitated calcium carbonate which was thereafter mixed with water, dried and screened, resulting in a finely particulated calcium hydroxide having a particle size of less than about 325 mesh. The amount of calcium hydroxide employed was varied in three different batches to provide concentrations of about 10%, 15%, and 20%, respectively. To aliquot portions of each of these batches were added 0.5% and 1% by weight of sodium carbonate in the form of an aqueous solution. To separate portions of the batch containing calcium hydroxide, a sodium hydroxide accelerator agent also was added in amounts of 0.5% and 1%.

The resultant blended mixtures were thereafter briquetted in a cubic mold under a pressure of 24,000 p.s.i., forming one inch cubic briquettes. The green briquettes were thereafter charged into a 2-gallon high-pressure autoclave which was provided with electrical heating elements into the bottom of which about .4 gallon of water was placed and thereafter the autoclave was heated to a temperature of about 380° F. under a pressure of 200 p.s.i. Individual samples of each of the green briquettes were reacted for controlled periods of ½, 1, 3, 5, and 7 hours, effecting hydrothermal hardening of the briquettes. Thereafter, the briquettes were removed from the autoclave and dried at a temperature of about 230° F. prior to further physical and chemical analyses.

EXAMPLE II

A second series of agglomerates was prepared in accordance with the present invention employing a magnetite iron ore concentrate of Canadian origin having a chemical and size analysis as set forth in the following table:

Analysis of magnetite iron ore concentrate

Composition		Size Analysis	
Constituent	Percent	Mesh Size	Percent
FeO	27.52	-35 +48	
Fe ₂ O ₃	63.49	-48 +65	0.25
SiO ₂	8.23	-65 +100	0.25
Al ₂ O ₃	0.66	-100 +150	0.10
CaO	0.02	-150 +200	0.20
MgO	0.05	-200 +270	0.90
MnO ₂	0.03	-270 +325	6.25
S	0.005	-325 +400	6.25
P ₂ O ₅	0.062	-400	85.80
Volatile	0.23		
			100.00

The dry magnetite concentrate was blended with water to provide a water content ranging from about 4% to about 5%. After a substantially homogeneous moist mixture was obtained, a fluxing and bonding agent comprising calcium hydroxide of the same type employed in Example I was added in amounts of 10%, 15%, and 20%. Aliquot portions of each of the batches were separately employed to which aqueous solutions containing sodium carbonate in an amount equal to 0.5% and 1% by weight were added forming a homogeneous green mixture. Each of the batches was thereafter subjected to briquetting in a manner as described in Example I and were hardened in the autoclave in the same manner as the briquettes comprised of the hematite iron ore concentrate.

The hardened briquettes or agglomerates prepared in accordance with Examples I and II were subjected to crushing tests in a hydraulic press by which a load was applied at a rate of 500 pounds per second. The direction of the application of the crushing load was made in the same direction as the briquetting pressure and in directions perpendicular to the direction of briquetting pressure. The results of these tests were averaged to obtain

an average crushing strength of the agglomerates. In addition, test specimens of each of the briquettes were held for a period of 5 hours while immersed in boiling water to determine the resistance of the hardened agglomerates to moisture.

The test results obtained on the several test specimens are graphically illustrated in FIGURES 1-6. FIGURE 1 portrays the relative crushing strength of the hematite iron ore concentrate containing 10% calcium hydroxide without and with varying percentages of the sodium hydroxide and sodium carbonate accelerator agent. FIGURE 2 is similar to FIGURE 1 illustrating the crushing strength of the hematite concentrate incorporating 15% calcium hydroxide and varying proportions of the sodium carbonate accelerator agent, whereas FIGURE 3 illustrates the effect of employing 20% of the fluxing and bonding agent with similar proportions of the accelerator agent. FIGURES 4-6 illustrate similar test data obtained on the agglomerates prepared from the magnetite iron ore concentrate employing varying proportions of the calcium hydroxide bonding and fluxing agent and sodium carbonate accelerator agent.

It will be apparent from the data as portrayed in FIGURES 1-6 that increases in the crushing strength are obtained as the duration of the hardening period in the reactor is increased and as the percentage of the bonding and fluxing agent in the agglomerate and the quantity of accelerator agent added is increased. It is further apparent that the use of higher quantities of the bonding and fluxing agents do not appreciably increase the strength of the agglomerate as indicated by a comparison of the strengths obtained between the agglomerates containing 15% and 20% of the bonding and fluxing agent. This is apparently due to the fact that a prescribed quantity of the bonding and fluxing agent enters into the reaction and any amount in excess thereof merely acts as a diluent in the agglomerate.

It is also apparent from these data that the curing time to achieve a satisfactory crushing strength is appreciably reduced by including higher proportions of the bonding and fluxing agent and by adding a small amount of the accelerator agent thereto. Both sodium hydroxide and sodium carbonate produce substantial increases in the resultant crushing strength of the cured agglomerate. The sodium carbonate under the influence of heat, pressure, moisture and calcium hydroxide in the autoclave is believed to decompose and reacts with water forming sodium hydroxide which is thought to activate the surfaces of the iron ore particles thereby accelerating the hydrothermal reaction.

It will also be apparent from the data as illustrated in FIGURES 1-6 that the agglomerates made from the magnetite concentrate had substantially higher crushing strengths than corresponding agglomerates made from the hematite iron ore concentrate. These data suggest that the finer sizes of magnetite iron ore concentrates are more conducive to bonding by the hydrothermal reaction than hematite iron ore concentrates, although in both cases satisfactory high strength agglomerates are obtained.

To determine the effect on the strength of the briquettes or agglomerates as encountered during typical blast furnace operations, specimens of the agglomerates made from both the hematite and magnetite iron ore concentrates incorporating varying proportions of the flux and bonding agent and accelerator agent were heated over a period of 4 hours to an elevated temperature (1832° F.) and held at that temperature for a period of about 1 hour in a neutral atmosphere and thereafter tested. These data indicate that only minor increases in the crushing strengths of the agglomerates occurred after being subjected to high temperatures. Similar tests were conducted employing a reducing atmosphere (29% H₂, 22% CO, 48% N₂, and 1% CO₂ by volume). While some reduction occurred under these conditions, the agglomer-

ates still retained the major proportion of their high crushing strengths.

Minerals and mineral concentrates other than iron ore concentrates can be satisfactorily agglomerated in accordance with the practice of the present invention. The following additional example is provided to illustrate other typical minerals in oxide, hydrated oxide, sulfide, carbonate, etc. form from which high strength crush resistant agglomerates can be satisfactorily made.

EXAMPLE III

A series of other typical minerals which can be satisfactorily agglomerated in accordance with the practice of the present invention are listed in the following table. Each of these minerals in a finely particulated state were agglomerated in accordance with the method previously described in connection with Example I. Blends were prepared of each mineral with 15% by weight calcium hydroxide (11.1% equivalent CaO) of the same type employed in preparing the hematite iron ore agglomerates set forth in Example I. In addition, the blended mixtures contained 1% by weight sodium carbonate as an accelerator agent.

Each of the green blended mixtures of the minerals were briquetted forming cylindrical briquettes having a diameter of 3/4 and a length of 3/4 inches and rounded ends. The green briquettes were thereafter subjected to the hydrothermal curing reaction in accordance with the method previously described in Example I for a period of 7 hours. The specific mineral, its chemical analysis and the crushing strength of the resultant briquettes are set forth in the following table:

Mineral analysis and crushing strength of briquettes

Mineral	Chemical Analysis		Crushing Strength, Pounds
		Percent	
Chromite (Cr ₂ O ₃ +Fe ₂ O ₃)	Cr ₂ O ₃	9.80	716
Pyrolusite (MnO ₂)	MnO ₂	73.60	283
Wolframite (FeWO ₄)	WO ₃	73.10	967
Scheelite (CaWO ₄)	WO ₃	43.50	1,012
Cobaltite (CoAsS)	Co	17.80	1,150
Cassiterite (SnO ₂)	SnO ₂	46.70	844
Zincite (ZnO)	ZnO	64.23	384
Smithsonite (ZnCO ₃)	ZnCO ₃	90.05	1,957
Sphalerite (ZnS)	ZnS	95.83	444
Phosphate Rock (Ca ₃ (PO ₄) ₂)	Ca ₃ (PO ₄) ₂	76.80	400
Galena (PbS)	PbS	81	767
Pyrite (FeS)	FeS	70.41	667
Bauxite (Al ₂ O ₃)	Al ₂ O ₃	55.00	1,200
Cuprite (Cu ₂ O+Fe ₂ O ₃)	Cu	6.15	833
Malachite (CuCO ₃ +Cu(OH) ₂)	CuCO ₃ .Cu(OH) ₂	87.36	410
Chalcocite (Cu ₂ S)	Cu ₂ S	72.37	365
Copper Oxide (Cu ₂ O.CuO)	Cu	84.11	250

It should also be pointed out that a reaction time of 7 hours was employed to assure substantial completion of the hydrothermal curing reaction. Reaction times substantially shorter than 7 hours can be employed to produce agglomerates of these minerals which are of satisfactory strength and crush resistance.

It will be apparent from the foregoing that the agglomerates formed in accordance with the practice of the present invention are unique in structure and composition and provide for substantial improvement in the handling and storage of finely particulated ores. Such agglomerates can be simply and economically made in accordance with the method comprising the present invention thus providing a significant advancement in the technology of ore

dressing and treatment. While it will be apparent that the preferred embodiments herein illustrated are well calculated to fulfill the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

What is claimed is:

1. The method of making a mineral agglomerate which comprises the steps of providing a finely particulated moist mineral having an average particle size of less than about 4 mesh and a moisture content of from about 3% to about 14%, admixing therewith a finely particulated bonding agent selected from the group consisting of calcium hydroxide, calcium oxide, magnesium hydroxide, magnesium oxide, and mixtures thereof, in an amount greater than about 1% up to about 30% until a relatively uniform mixture is obtained, adding to said mixture an accelerator agent selected from the group consisting of the oxides, hydroxides, carbonates and bicarbonates of the alkali metals in an amount of about .25% to about 1% calculated as the oxide form, forming the blended said mixture into compact discrete masses, and thereafter contacting and heating said masses under pressure by steam to a temperature of from about 200° F. to about 700° F. and maintaining contact for a period of time sufficient to form hard and integrally bonded masses.

2. The method of making an iron ore agglomerate which comprises the steps of providing a finely particulated moist iron ore containing from about 45% to about 70% iron calculated as Fe and the balance gangue having an average particle size of less than 20 mesh and a moisture content of from about 3% to about 14%, admixing with said iron ore a finely particulated bonding agent selected from the group consisting of calcium hydroxide, calcium oxide, magnesium hydroxide, magnesium oxide, as well as mixtures thereof in an amount of from about 5% to about 20% until a relatively uniform mixture is obtained, blending into said mixture an accelerator agent selected from the group consisting of the oxides, hydroxides, carbonates and bicarbonates of sodium and potassium in an amount of about .25% to about 1% calculated as the oxide form, forming the blended said mixture into compact masses, and thereafter contacting and heating said masses under pressure by steam to a temperature of from about 200° F. to about 700° F. and maintaining contact for a period of time sufficient to form hard and integrally bonded iron ore agglomerates.

3. The method of making a mineral agglomerate as set forth in claim 1, wherein said mineral is bauxite.

4. The method of making a mineral agglomerate as set forth in claim 1, wherein said mineral is chromite.

5. The method of making a mineral agglomerate as set forth in claim 1, wherein said mineral is pyrolusite.

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