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(54) Title: METHOD FOR PRODUCING MINERAL ORE AGGLOMERATES USING A HEMICELLULOSE BINDER AND ASSOCIATED PRODUCTS

(57) Abstract: A method of preparing agglomerates of a mineral ore comprising mixing mineral ore particles and a binder to produce the agglomerates. The binder comprises hemicellulose in an amount effective to enhance the cohesiveness of the mineral ore particles. The agglomerates can be heated to produce pellets that are useful intermediates for refining products produced by the mining industry. Also provided are the mineral ore agglomerates produced in accordance with the method of the present invention.

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METHOD FOR PRODUCING MINERAL ORE AGGLOMERATES
USING A HEMICELLULOSE BINDER
AND ASSOCIATED PRODUCTS

- [01] This application claims priority to provisional U.S. Application Ser. No. 60/480,269, filed June 20, 2003, which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

- [02] This invention pertains to organic binders that are useful for the production of mineral ore agglomerates.

BACKGROUND OF THE INVENTION

- [03] In present day mining operations, iron ores are mined as an oxide intimately bound in silica. The iron must be separated from the silica via a beneficiation process that involves grinding the ore into very fine particles and separating the iron oxide from the silica, often in a flotation cell. The resultant iron ore slurry is filtered to provide an iron ore concentrate and then formed into green balls. The green balls are subsequently dried and indurated to produce durable iron oxide pellets, these pellets being referred to as taconite pellets. The evolution of the taconite industry and the revolutionary development of the taconite pelletizing process following the depletion of the high grade iron ore bodies in the United States are detailed in the book, Pioneering with Taconite by E.W. Davis, Minnesota Historical Society, St. Paul, MN. (1964).
- [04] Taconite pellets are articles of commerce that can be easily transported by rail or shipped from the mining operation to blast furnaces. Because blast furnaces are often geographically separated from the mining operations, the iron oxide pellets must be durable to provide stability during transport. The spherical geometry of the iron oxide pellets allows for ease of feeding the blast furnace and facilitates the flow of reductive gases which transform the iron oxide into elemental iron.
- [05] The process of forming the green balls or pellets from the iron oxide concentrate typically utilizes a binder. The binder imparts to the green ball sufficient strength to

survive the multiple handling steps involved in the process. Initial formation of the green balls is accomplished by feeding a mixture of iron ore concentrate and binder into a balling drum or rotogranulator. The resultant wet green balls are then transferred to a combination dryer-induration furnace, where moisture is removed and residual organics are burned away to form a hard iron oxide pellet convenient for shipping.

- [06] The most successful, cost-effective binder used in the formation of green pellets has been bentonite clay. Bentonite is typically added to a balling apparatus in an amount ranging from 15 to 20 pounds per ton of iron ore. However, because bentonite is an aluminum silicate, it adds silica back to a material that was previously beneficiated to remove the silica. Silica is undesirable in that it can lead to excessive slag and glass coatings on the pellets, both of which reduce the efficiency of the furnace. Bentonite also contains sodium and potassium, which are known to reduce the lifetime of furnace linings and to diminish the metallurgical properties of the iron. The negative effects of alkali metals on iron ore pellet characteristics are described by Ajersch et al., "4th International Symposium on Agglomerations," Iron and Steel Society Journal pp. 259-266 (1985).
- [07] Accordingly, much effort has been expended to replace bentonite with binders that do not contain silica. For example, the U.S. Bureau of Mines investigated the use of over thirty organic binders as substitutes for bentonite in agglomerating iron ore concentrate and found that guar gum, carboxymethyl cellulose, and gelled starch produced the greatest green strength spherical pellets. (Bureau of Mines, Report of Investigation 9230, Effectiveness of Organic Binders for Iron Ore Pelletization, by Larry A. Haas, Jeffrey A. Aldinger, and Robert K. Zahl). U.S. Patent 5,000,783 purports to disclose the use of a gelled starch and water dispersible gums, pectins, cellulose derivatives, vinyl polymers, and acrylic polymers. U.S. Patent 6,152,985 purports to disclose the use of a hydroxamated polymer made from a water-soluble ethylenically unsaturated monomer. U.S. Patent 6,071,325 purports to disclose the use of caustic with water soluble polymers such as guar, guar derivatives, carboxymethyl guar, hydroxypropyl guar, carboxymethylhydroxypropyl guar, modified starch, starch derivatives, carboxymethyl starch, pregelatinized starch, alginates, pectins, polyacrylamides and derivatives thereof, polyacrylates and copolymers thereof, polyethyleneoxides, cellulose derivatives, carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethylhydroxyethyl cellulose,

carboxymethyldihydroxypropyl cellulose, xanthan gum, dairy wastes, and wood related products.

- [08] Virtually all of the known organic binder substitutes for bentonite are costly. Moreover, the manufacture of organic binders, e.g., by synthesis or chemical derivation of natural polymers, often consumes finite petrochemical reserves, and the production processes can create hazardous waste streams.
- [09] In light of the foregoing, the invention seeks to provide a method of producing mineral ore products that incorporate a low-cost organic binder as a partial or complete substitute for bentonite. The invention seeks to provide a binder that may be prepared without significantly depleting petrochemical resources or generating significant waste streams.

BRIEF SUMMARY OF THE INVENTION

- [10] The present invention provides a method of preparing agglomerates of a mineral ore, the method comprising mixing mineral ore particles and a binder to produce the agglomerates. The binder comprises hemicellulose in an amount effective to enhance the cohesiveness of the mineral ore particles. The agglomerates can take the form of spheronized agglomerates (e.g., green balls). The spheronized agglomerates also can be heated to produce pellets (e.g., taconite pellets).
- [11] The present invention further provides agglomerates produced in accordance with the method heretofore described. The agglomerates preferably comprise mineral ore particles and a binder, wherein the binder comprises hemicellulose in an amount effective to enhance the cohesiveness of the particles. The agglomerates produced in accordance with the present invention can include spheronized agglomerates and pellets (such as taconite pellets), which are useful intermediates for the refinement of products produced by the mining industry.
- [12] The present invention further provides a mineral ore concentrate for forming mineral ore pellets, the concentrate comprising mineral ore particles having a moisture content of about 4 to about 30 weight percent; and about 0.01 to about 1 weight percent hemicellulose.

- [13] These and other advantages of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- [14] The present invention is directed to method for producing agglomerated products using a hemicellulose binder. The present invention is further directed to agglomerated ore products prepared with a hemicellulose binder.
- [15] Although the invention is discussed in its preferred embodiments in terms of iron oxide mineral ore particles, the invention is not limited thereto, and other particles may be agglomerated in accordance with the present invention. Such particles may include nearly any finely divided material, including most metallic minerals or ore. The predominant metal component in the ore may be iron, chromium, copper, nickel, zinc, lead, uranium or other metal. Mixtures of the above materials or any other metal occurring in the free or molecularly combined material state as a mineral, or any combination of the above, or other metals, or metal containing ores capable of pelletization, all may be agglomerated in accordance with the present invention. Also included within the purview of the invention are materials that contain iron, including iron ore deposits, ore tailings, cold and hot fines from a sinter process, and aqueous iron ore concentrates from natural sources or recovered from various processes. Iron ore or any of a wide variety of the following minerals may form a part of the material to be agglomerated: taconite, magnetite, hematite, limonite, goethite, siderite, franklinite, pyrite, chalcopyrite, chromite, ilmenite and the like. Minerals other than metallic minerals which may be agglomerated in accordance with the invention include phosphate rock, talc, dolomite, limestone and the like. Still other materials which may be agglomerated in accordance with the present invention include fertilizer materials such as potassium sulfate, potassium chloride, double sulfate of potassium and magnesium; magnesium oxide; animal feeds such as calcium phosphates; carbon black; coal fines; catalyst mixtures; glass batch mixtures; borates, tungsten carbide; refractory gunning mixes; antimony, flue dust from, for example, power generating plants, solid fuels such as coal, coke or charcoal, blast furnace fines and the like.
- [16] In accordance with preferred embodiments of the invention, initially iron oxide mineral ore and a binder are mixed and then formed into agglomerates. Mineral ore particles are

typically used in the form of a concentrate having a moisture content typically of 4% to about 30% by weight, preferably about 6% to about 12% by weight, based on dry weight of the mineral ore particles. The binder is typically in the form of a powder although any suitable form of the binder may be used.

- [17] A "binding effective amount" or "an amount effective to enhance the cohesiveness of the particles" will vary depending upon numerous factors known to the skilled artisan. Such factors include, but are not limited to, the type of particulate material to be agglomerated or pelletized, the moisture content of the particulate material, particle size, the agglomeration equipment utilized, and the desired properties of the final product, e.g. dry strength (crush), drop number, pellet size and smoothness. Though the invention is not limited to the following amounts, a binding effective amount of binder will typically be from about 0.01% to 1% by weight based on the dry weight of the particulate material.
- [18] Agglomerates preferably are formed by tumbling or other agitation, for example, using a balling drum or rotogranulator. Any agglomeration processes used in or similar to those used in the iron ore mining industry may be used. "Agglomeration" thus is deemed to encompass the processing of finely divided materials, whether in powder, dust, chip, or other particulate form, to form pellets, granules, briquettes, and the like.
- [19] Spheronized agglomerates are conventionally produced from iron oxide ore. The agglomerates thus produced are referred to as "green balls." The green balls preferably are sized so that at least 50%, preferably at least 60%, and more preferably at least 70% of the balls are retained by a 7/16 inch X 1/2 inch screen. Preferably, the green balls exhibit an average survival rate of at least about 6 when tested according to the 18-inch wet ball drop test set forth in more detail hereinbelow. Also, preferably the green balls have an average wet ball crush strength (as described in more detail hereinbelow) of at least about 1.5 psi (lb/in²), more preferably between about 1.5 and about 2.0 psi.
- [20] The resultant wet green balls may be then dried. Any suitable equipment such as a combination dryer/induration furnace or kiln, where moisture is removed and residual organics are burned away (typically in stages at a temperature of up to 2400° F to form a hard taconite pellet.

- [21] Drying of the wet balls and firing of the resultant dry balls may be carried out as one continuous step or as two separate steps. However, the balls generally must be dry prior to firing, because the balls will degrade or spall if fired without first drying them. It is therefore preferred that the balls be heated slowly to a temperature of at least about 2200° F, preferably to at least about 2400° F. and then fired at that temperature. In another embodiment, the balls are dried at low temperatures, preferably by heating, or alternatively, under ambient conditions, and then fired at a temperature of at least about 2200° F, more preferably at about 2400° F. Firing is carried out for a sufficient period of time to bond the small particles into pellets with enough strength to enable transportation and/or further handling, generally about 15 minutes to about 3 hours. Preferably, the taconite pellets thus formed have an average 3-inch dry ball drop survival rate (as set forth in more detail hereinbelow) of at least about 1.5 and an average dry ball crush strength of greater than about 3 psi.
- [22] In accordance with the invention, the binder comprises a hemicellulose. The hemicellulose binder used in accordance with the present invention can be produced from any suitable source of hemicellulose, and the source of hemicellulose is not critical. Suitable hemicellulose sources include natural, synthetic, or semisynthetic hemicellulose sources. Preferably, the hemicellulose is obtained from one or more abundant natural resources, such as by-products produced by the grain milling industry. Such by-products include, but are not limited to, corn hulls from the corn wet milling industry, corn bran from the corn dry milling industry, spent germ from the corn wet milling industry, and spent germ from the corn dry milling industry. These are all by-products from either the isolation of corn starch, corn protein, and corn oil in the case of the corn wet milling industry or from the isolation of corn flour and corn oil in the case of the corn dry milling industry. These byproducts are abundantly available and are of little economic value, being marketed primarily as excipients in animal feeds.
- [23] The U.S. hybrid corn crop is an enormous and stable source of hemicellulose, and the composition of the corn hulls does not vary significantly. The agricultural and corn wet-milling industry in the U.S., as well as the corn dry milling industry in the U.S., provide a reliable, low cost, and consistent source of hemicellulose-rich by-products. For instance, commercially produced corn hulls may contain the following components: hemicellulose (56%), cellulose (19%), starch (8%), protein (8%) fat (2%), acetic acid

(4%), ferulic acid (3%), diferulic acid (<1%), coumaric acid (<1%), and trace amounts of other materials such as phytosytosterols and minerals. Such materials can be chemically and/or physically bound together in the corn hulls.

- [24] Several procedures have been described for releasing these components from corn hulls. For example, the alkaline cooking of corn hulls is taught in the technical literature and is disclosed in patents U.S. 2,801,955, U.S. 3,716,526, U.S. 2,868,778, U.S. 4,038,481, and in WO 98/40413. The alkaline cooking of corn hulls to produce an adhesive composition upon drying for cellulosic materials is taught in the following patents: U.S. 5,855,659, U.S. 5,786,048, US 6,063,178, and US 6,179,905 B1. The isolation of corn hull hemicellulose from corn hulls is taught in the technical literature and is disclosed in the following patents: U.S. 2,801,955, U.S. 3,716,526, U.S. 2,868,778, U.S. 4,038,481, and in WO 98/40413. The treatment of corn hull hemicellulose with hydrogen peroxide is taught in the technical literature and in WO 98/40413. U.S. Patent 4,038,481 discloses the isolation of corn hull holocellulose, which is comprised mainly of corn hull hemicellulose.
- [25] Any suitable hemicellulose, or suitable combination of hemicelluloses, can be used in accordance with the present invention. It will be appreciated that hemicelluloses can be classified according to the production process by which they are produced.
- [26] Hemicellulose may be obtained in accordance with the process described in U.S. Patent 4,038,481 (Antrim et al.), referred to herein as the "Antrim" process. This type of hemicellulose is highly purified (greater than 90% hemicellulose) and is generally obtained via solvent extraction. A highly purified hemicellulose may be obtained by alkaline hydrolysis of corn hulls, followed by purification by ultrafiltration, an example of which is described in U.S. Patent Application No. 09/726,092.
- [27] Hemicellulose may also be obtained from alkaline-cooked destarched hulls, which can be prepared by destarching corn hulls, cooking the destarched hulls under alkaline conditions, and removing the insoluble materials there from. This type of hemicellulose contains roughly 60-70% hemicellulose. See, e.g., U.S. Patent 6,063,178.
- [28] Hemicellulose may be obtained from alkaline-cooked corn hulls without separating the insolubles or other materials, the product thus formed containing less than 50%

hemicellulose. This type of hemicellulose can be prepared by extrusion of alkali-treated corn hulls, an example of which can be found in U.S. Patent Application Nos. 09/901,342 (Example 3) and 09/864,779 (Example 3). These hemicellulose compositions are produced via alkaline extrusion-cooking of corn hulls obtained from a corn wet milling process. Hemicellulose may be prepared by jet cooking alkali-treated corn hulls, an example of which can be found in U.S. Patent Application Nos. 09/901,342 (Example 1), 09/864,779 (Example 1) and 60/216,083 (Example 1A). This hemicellulose composition is prepared via jet-cooking corn hulls under alkaline conditions using high pressure steam.

- [29] Hemicellulose may also be prepared by batch cooking alkaline treated corn hulls, an example of which can be found in U.S. Patent Application Nos. 09/901,342 (Example 2), 09/864,779 (Example 2) and 60/216,083 (Example 1B). This hemicellulose composition is prepared via batch cooking under alkaline conditions at atmospheric pressure.
- [30] Holocellulose, a highly refined mixture of hemicellulose and cellulose with few impurities, may be used in conjunction with the invention. Holocellulose contains roughly 70% hemicellulose. An example of holocellulose can be found in U.S. Patent Application Nos. 09/901,342 (Example 5) and 09/864,779 (Example 5), which describe the preparation of holocellulose.
- [31] In one preferred embodiment, the binder contains hemicellulose derived from extruded, preferably alkali extruded, corn hulls. In another preferred embodiment, the hemicellulose content in the hemicellulose binder is about 90% hemicellulose.
- [32] The binder may also contain components or mixtures of components derived from the hemicellulose sources, and/or other additives. Suitable additives include, for example, polymers (e.g., superabsorbent polymers), copolymers, and the like. Suitable superabsorbent polymers and copolymers include bentonite. Moreover, it is possible to form agglomerates using reduced levels of bentonite relative to the levels required in conventional green ball preparation.
- [33] The method of the present invention is particularly useful in the agglomeration of mineral ores, to provide wet green balls that with increased cohesiveness and strength relative to green balls prepared in the absence of a binder. The cohesiveness or strength

of binder-incorporated green balls may be measured by standardized test protocols, which are well known in the industry. Such tests include, for example, the 18-inch wet drop test, the 3-inch dry drop test, the wet ball crush strength test, and the dry ball crush strength test.

- [34] The following examples further illustrate the invention but of course should not be construed as in any way limiting its scope.

EXAMPLE 1

- [35] This example describes the preparation of an exemplary binder of the present invention, by extrusion-cooking commercial corn hulls with NaOH.
- [36] Corn hulls from a corn wet-milling process were extrusion-cooked with NaOH in a Wenger TX-144 Twin Screw Extruder according to the following conditions:

Extruder speed = 50 rpm
Feed Rate = 2500 pounds per hour
50% NaOH = 500 pounds per hour
Steam = 325 pounds per hour
Water = 100 pounds per hour
Barrel #1 Temperature = 190 °F
Barrel #2 Temperature = 240 °F
Barrel #3 Temperature = 260 °F
Barrel #4 Temperature = 330 °F
Barrel #5 Temperature = 330 °F

- [37] The extruded product was dried in a fluidized bed drier and ground into a powder. The resulting product can be used as a binder in the production of ore products.

EXAMPLE 2

- [38] This example describes the production of dry, green taconite pellets (spherical balls) using the binder produced according to Example 1. For comparison, taconite pellets containing no binder and pellets containing a non-hemicellulose commercial binder were produced.

Pellet Production

- [39] A 3,000 g dry basis sample of finely ground wet taconite concentrate, which had been commercially mined and beneficiated at an iron mine in the Mesabi Range of Minnesota, USA, was added to a mixer (Cincinnati Muller Division, National Engineering Company, Chicago, IL, Serial No. 8402007). The moisture content of the concentrate was 9.7%. Following the addition of the appropriate amount of dry pellet binder, the mixer was operated for two minutes. The contents of the mixer were then run through a shredder before being allowed to rest in an air-tight container for fifteen minutes.
- [40] An airplane tire (16-inch diameter) made to rotate at 60 RPM was used to produce green balls from the concentrate. First, 169 g of seed pellets were produced by placing small amounts of wet concentrate into the rotating tire and adding atomized water to initiate the formation of small balls. The resulting seed pellets were screened to be -3 mesh and +4 mesh.
- [41] The 169 g of seed pellets was returned to the rotating tire and more concentrate and atomized water were added over three minutes in order to grow larger balls. The larger balls were then allowed to roll for one additional minute.
- [42] The wet balls were unloaded and screened. The fraction greater in size than would pass through a 1/2 " screen was weighed. The fraction collected on a 7/16" X 1/2" screen was weighed and saved for evaluation. The fraction passing through a 7/16" X 1/2" screen was weighed.

Pellet Evaluation

- [43] Moisture: A portion of the balls were dried in a forced air oven at 100° C to 105° C to determine the moisture content.
- [44] 18 Inch Wet Ball Drop: Twenty balls were dropped from an 18" height onto a steel plate one at a time until either a crack appeared on the surface of the ball or the ball broke apart. The number reported in the table below is the average of the number of drops the twenty wet balls survived.

- [45] Wet Crush Strength: Twenty balls were subjected to a compression test at a loading rate of 0.1 inch per second one at a time. The number reported in the table below is the average of the crush strength of the twenty wet balls (psi).
- [46] 3 Inch Dry Ball Drop: Twenty oven dried (1000 °C to 1050 °C) balls were dropped from a 3" height onto a steel plate one at a time until either a crack appeared on the surface of the ball or the ball broke apart. The number reported in the table below is the average of the number of drops the twenty dry balls survived.
- [47] Dry Crush Strength: Twenty oven dried (1000 °C to 1050 °C) balls were subjected to a compression test at a loading rate of 0.1 inch per second one at a time. The number reported in the table below is the average of the crush strength of the twenty dry balls (psi).
- [48] Percent Correct Size Balls: The weight of the fraction of wet balls collected on a 7/16" X 1/2" screen was divided by the sum of the weights of the fractions collected on a 7/16" X 1/2" screen plus the weight of the fraction collected on a 1/2" screen plus the weight the weight of the fraction passing through a 7/16" X 1/2" screen.
- [49] The data generated in this example are shown in the following table.

75%	Binder Usage lb / ton	g per 3000g ore	Wet Ball Moisture	18-Inch Wet Ball Drop	Wet Ball Crush (psi)	Dry Ball Crush (psi)	3-Inch Dry Ball Drop	Percent Correct Size Pellet
Expectation	0.0 lb			6	1.5- 2.0	3	>1.5	
(Comparative Sample) No Binder		0.0	9.3	3.6	1.5	1.8	1.6	41%
(Comparative Sample) Proprietary Commercial Organic Binder System	0.751b	1.1	9.7	7.8	1.9	4.1	2.0	63%
Binder of Example 1	3.00 lb	4.4	10.0	5.0	1.5	2.9	1.9	72%
Binder of Example 1	6.00 lb	8.8	10.4	10.2	1.6	6.8	6.4	78%
Binder of Example 1	12.00 lb	17.6	11.1	20+	1.4	11.2	19.7+	72%
Interpolated Binder of Example 1	4.63 lb	6.8		7.8	1.5	5.0	4.3	

[50] The foregoing data demonstrate the effectiveness of the binder used in accordance with the present invention.

EXAMPLE 3

[51] This example describes the production of green balls and dry taconite pellets using corn hull hemicellulose. For comparison, taconite pellets containing no binder and pellets containing a non-hemicellulose commercial binder were produced.

[52] Pellet Production and Pellet Evaluation were performed as described in Example 2, except that highly pure (90%) corn hull hemicellulose was used in place of the binder of Example 1. The results of the data generated in this example are shown in the following table.

	Binder Usage lb / ton	g per 3000g ore	Wet Ball Moisture	18- Inch Wet Ball Drop	Wet Ball Crush (psi)	Dry Ball Crush (psi)	3-Inch Dry Ball Drop	% Correct Size Pellet
Expectation	0.0 lb			≥ 6	1.5- 2.0	≥ 3	> 1.5	
(Comparative Sample) No Binder		0.0	9.3	3.6	1.5	1.8	1.6	41%
(Comparative Sample) Commercial Organic Binder System	0.751b	1.1	9.7	7.8	1.9	4.1	2.0	63%
Corn Hull Hemicellulose	0.751b	1.1	9.3	5.4	1.7	2.7	1.9	50%
Corn Hull Hemicellulose	1.50 lb	2.2	9.7	7.8	1.6	4.2	2.1	70%
Corn Hull Hemicellulose	3.00 lb	4.4	9.9	11.1+	1.9	6.0	4.3+	66%

[53] The foregoing data demonstrates the effectiveness of the binder used in accordance with the present invention.

EXAMPLE 4

- [54] This example describes the production of an exemplary binder of the present invention, by jet-cooking commercial corn hulls with NaOH, followed by drum drying.
- [55] Dried corn hulls from a corn wet milling process of US Number 2 grade hybrid yellow corn were ground to a fine flour and assayed to contain approximately 6% moisture, approximately 8% dry basis protein, approximately 11 % dry basis starch, and approximately 5% dry basis fat. The ground corn hulls, 833 g dry basis, were mixed with 9,000 g tap water to form a slurry. NaOH (64.0 g) was added and the pH measured to be about 12.
- [56] The resulting slurry was continuously jet-cooked in a continuous jet cooker equipped with a Hydroheater Combining Tube which inflicts high shear into the slurry at the point of contact with the high pressure steam at ~ 150 psig. The jet-cooking conditions were: Temperature = 315 °F to 325 °F, Pressure = about 70 psig, Time = 12.6 minutes.
- [57] The jet-cooked product was dried with a drum dryer and ground into a powder. The resulting binder was used to produce green and dry taconite pellets (spherical balls). For comparison, taconite pellets containing no binder and pellets containing a non-hemicellulose commercial binder were produced.
- [58] Pellet Production and Pellet Evaluation was performed as described in Example 2, except that the binder prepared in this example was used in place of the binder used in Example 1.
- [59] The data generated in this example is shown in the following table.

	Binder Usage lb / ton	g per 3000g ore	Wet Ball Moisture	18- Inch Wet Ball Drop	Wet Ball Crush (psi)	Dry Ball Crush (psi)	3-Inch Dry Ball Drop	Percent Correct Size Pellet
Expectation	0.0 lb			≥ 6	1.5- 2.0	≥ 3	> 1.5	
(Comparative Sample) No Binder		0.0	9.3	3.6	1.5	1.8	1.6	41%
(Comparative Sample) Commercial Organic Binder System	0.75 lb	1.1	9.7	7.8	1.9	4.1	2.0	63%
Binder Prepared by jet cooking according to this Example	3.12 lb	4.6		7.8	1.5	5.0	4.3	75%

- [60] The foregoing data demonstrates the effectiveness of the binder used in accordance with the present invention.
- [61] The hemicellulose binders used in the present invention have the further advantage of minimizing the amount of sodium in the resulting ore products, e.g., minimizing the amount of sodium in green balls obtained produced from iron ore concentrate. In this regard, the hemicellulose used in accordance with the present invention advantageously can be prepared with very low concentrations of sodium.
- [62] It is thus seen that green balls can be prepared from hemicellulose.
- [63] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference.
- [64] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by

context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

- [65] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

WE CLAIM:

1. A method of preparing agglomerates of a mineral ore comprising mixing mineral ore particles and a binder and subsequently forming agglomerates from the particles and binder; wherein the binder comprises hemicellulose in an amount effective to provide cohesiveness.
2. The method of Claim 1 wherein the mineral ore comprises an iron oxide.
3. The method of Claim 1, said agglomerates comprising green balls of iron oxide ore, said method further comprising heating the green balls in a manner effective to produce taconite pellets.
4. The method of Claim 1 wherein the hemicellulose is produced from alkali-extruded corn hulls.
5. Agglomerates comprising mineral ore particles and a binder; wherein the binder comprises hemicellulose in an amount effective to provide cohesiveness.
6. The agglomerates of Claim 5 wherein the mineral ore comprises an iron oxide, said agglomerates comprising green balls.
7. Taconite pellets prepared by heating the green balls prepared in accordance with claim 6.
8. A method for providing taconite pellets comprising heating green balls until taconite pellets are formed, said green balls including an iron oxide and binder, said binder comprising a hemicellulose.
9. A method according to Claim 8, said hemicellulose comprising corn hull hemicellulose.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/019580

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B1/244

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EISELE T C ET AL: "A REVIEW OF BINDERS IN IRON ORE PELLETIZATION" MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW, GORDON AND BREACH, NEW YORK, NY, US, vol. 24, January 2003 (2003-01), pages 1-90, XP009033605 ISSN: 0882-7508	1-3, 5-8
Y	pages 4, 37, 50	4, 9
X	DATABASE WPI Section Ch, Week 198933 Derwent Publications Ltd., London, GB; Class H09, AN 1989-240026 XP002297078 & SU 1 458 377 A (KALININ POLY) 15 February 1989 (1989-02-15) abstract	1, 5

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

20 September 2004

Date of mailing of the international search report

07/10/2004

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/019580

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/005834 A (GRAIN PROCESSING CORP ; FREEMAN DANIEL R (US)) 23 January 2003 (2003-01-23) cited in the application claims 1, 13; example 3 -----	4,9
A	US 5 000 783 A (DINGEMAN DAVID L ET AL) 19 March 1991 (1991-03-19) cited in the application col.2, 1.56 - col.3, 1.2 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/019580

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
SU 1458377	A	15-02-1989	SU 1458377 A1	15-02-1989
WO 03005834	A	23-01-2003	US 2002028283 A1	07-03-2002
			CA 2453139 A1	23-01-2003
			EP 1404186 A2	07-04-2004
			WO 03005834 A2	23-01-2003
US 5000783	A	19-03-1991	US 5171361 A	15-12-1992