

Review of Organic Binders for Iron Ore Agglomeration

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Introduction

Iron ore pellets are one type of iron-rich, intermediate product used during primary iron and steel making. During pellet production, fine-grained iron containing minerals are liberated from low-grade ores, concentrated, and agglomerated into round balls that are thermally hardened to form “pellets”. Pellets are then transported to Blast Furnace or Direct Reduction operations where they are reacted with reducing gases and melted to produce iron; iron is further refined and shaped into the wide variety of steel-based industrial and consumer products in use today.

Over the years, pellet production has become increasingly more prevalent with the increased exploitation of low-grade iron ores and increased iron and steel consumption around the world. In 2010, world iron ore pellet production was 388 Mt. It could be argued that the current pellet production process has been enabled by the use of binders – practical experience has shown that it would be nearly impossible to agglomerate iron ore using rotary drums and discs without using a binder.

Eisele and Kawatra (2003) reviewed every binder type that had been tested for iron ore agglomeration and concluded that inorganic bentonite clay “is still the dominant binder”, although it is expensive and is not silica-free (Eisele and Kawatra, 2003). Organic binders have significant potential as a bentonite replacement as evidenced by their successful use in the U.S. iron ore pellet market. This manuscript reviews organic binders applicable for iron ore agglomeration.

How do binders affect agglomeration?

Agglomeration processes combine small, discrete particles into larger aggregates, where the individual particles are still discernible (Ennis and Litster 1997). During iron ore agglomeration or pelletization, moist iron concentrate particles and flux materials are rolled into balls with the aid of a binder (Figure 1). Balls tumble and grow in rotating drums and discs. While agglomerates are held together by the surface tension and capillary forces when wet, they will fall apart upon drying unless binders are present. Binders, typically bentonite clay or an organic material, help hold balls together and ease the agglomeration process.

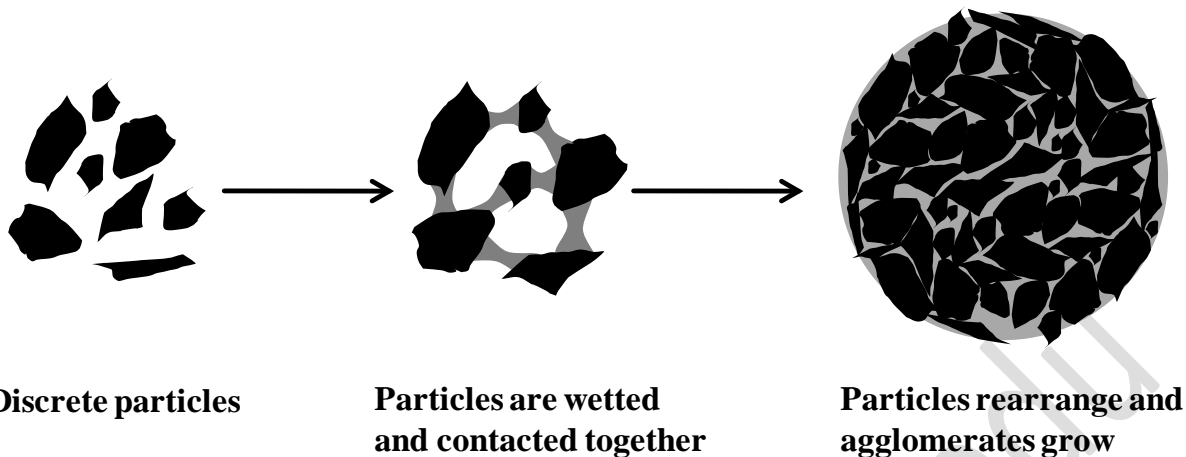


Figure 1 Green-ball growth during iron ore agglomeration. Individual iron ore particles are wetted, and pellet ‘seeds’ are nucleated. During agitation in the rotating drum or disc, small seeds can grow by consolidation of individual granules and layering of new feed material (Iveson et al 2001).

Iron ore agglomeration is a wet agglomeration process, and moist “green-balls” are subsequently dried and heat hardened at high temperatures to make pellets; the presence of binders affects the entire process from green-ball formation to pellet hardening. In green-balls, binders interact with moisture and mineral particles, affecting capillary forces (Tigershiold and Ilmoni 1950; Rumpf 1958) and viscous forces (Wada and Tsuchiya 1970; Forsmo et al 2006) which bond individual particles together. The presence of clays and organic binders help for a variety of reasons:

- *Binders help control transport of moisture during the wet agglomeration process.* Binders increase the viscosity of moisture within the green-ball structure, and slow the transport of moisture from the green-ball interior to the green-ball surface. This phenomenon controls green-ball growth rates which depend on free moisture at the agglomerate surfaces. Certain binders can also help lessen green-ball spalling during drying. Spalling occurs when steam builds up too fast in the green-ball structure and forces grains apart. Usually, thermal shock temperature is increased with binders, so hotter drying gases can be used: this may decrease time and energy requirements for drying green-balls (Smythe 1974).
- *Binders can help control excess moisture present in the agglomeration feed.* Agglomeration dynamics depend critically on moisture content in the feed material, so industrial pelletizing plants set tight constraints on filter-cake moisture levels sent to pelletizing drums and discs. Too little moisture and nucleated seeds will not grow or small clusters of seeds may form that are difficult to enlarge; under these conditions, the final green-balls are porous and weak. Too much moisture produces rough green-ball surfaces, enables rapid and uncontrollable green-ball coalescence, and in extreme cases, turns the agglomerating material to “mud”. In the second case, certain binders can be added to absorb excess moisture, producing a better green-ball and more stable agglomeration process.

After green-balls are formed, moisture is removed by drafts of high-temperature air. As moisture evaporates, the main cohesive forces holding particles together lessen (Rumpf 1958) which could cause balls to crumble. However, clays and organic binders concentrate at and adhere to particle contact points (Ball et al 1973), forming mechanical bridges and films which increase dry ball strength.

Following drying, balls are heated to temperatures up to 1300 °C. Whether binders contribute to bonding at this stage depends on which binder is used. Bentonite is a low melting temperature silicate (Grim, 1978). The liquid phase (due to bentonite) wets particles, envelops and melts quartz, and pulls particles together and increases pellet density. The liquid phase may act as a diffusion medium, promoting sintering of iron oxide grains in the pellet. Upon cooling, it adds additional solid bonds. Contrarily, purely organic binders burn away during thermal treatment, (begin burning generally around 300 °C), and have not been shown to aid the iron oxide sintering and recrystallization processes. Liquid phase properties are determined entirely by the mineralogy of the pelletizing concentrate. In general, the absence of an additional silicate mineral is the fundamental difference between bentonite and organic binders.

Many factors are considered when choosing a particular binder for iron ore agglomeration. For example, with bentonite, it is well known that using a western, or Wyoming, bentonite with high sodium to calcium ratio results in good pellets across a wide range of conditions (Nikol and Adamiak, 1973). Oftentimes, a single type of organic binder can be modified a number of ways, each producing vastly different binder properties. Consequently, the following factors should be considered when choosing a particular binder for agglomeration:

1. How effective is a particular binder? What binder dose is required to meet all pellet quality metrics?
2. What is the binder composition? Are any deleterious elements introduced into the pellet structure through the binder?
3. How expensive is the binder? What is the binder cost per ton pellets produced, and what costs are incurred upstream and downstream of pelletizing when using the chosen binder?
4. What equipment is required for binder application? Can current equipment be used, or are new designs, with associated capital costs, required?

Regardless which binder is selected, green-balls must survive the agglomeration process and finished pellets must meet chemical, physical and metallurgical specifications demanded (and paid for!) by pellet consumers. These constraints vary from consumer to consumer, but general requirements and test procedures are summarized below.

Desirable pellet properties

In general, iron ore pellet makers and consumers desire pellets that a) are strong enough to physically withstand transportation and reduction processes without deformation or breakage; b) have a narrow size distribution; c) are easily reduced; and d) have appropriate chemical contents (such as high iron and low impurity (e.g. SiO₂, P, S) levels, and a certain degree of basicity).

Physical properties

Physically, iron ore pellets should be uniformly sized, strong, and abrasion resistant. Ideally, mono-sized pellets would be best, as a uniform pellet size distribution promotes high bed

permeability with correspondingly low pressure drops and power consumption during heat hardening. Good permeability is also desired during pellet reduction. A narrow size distribution is achieved by screening pellets to 9-12 mm in diameter (Meter, 1980). Approximately 90 % of industrial pellets are in this size range. The top size was chosen based on decreasing reducibility and mechanical strength with pellet size, while particles that are too fine would be blown out of the top of blast furnaces during operation.

Green-balls are subjected to considerable handling and loading events during agglomeration: sizing green-balls on screens and roller bars; conveying green-balls between the balling unit and induration machine; and static loading in the travelling grate. Green-balls should not plastically deform; spall during drying; or disintegrate when dry, which produces dust and fines. Dust coats furnace walls increasing wear and thermal loads, decreases bed permeability and must be captured and recycled. Green-ball quality tests include compressions tests and a shock test. Wet and dry ball strengths and plasticity are measured by a “drop test” and “compression test” (Table 1). A thermal shock test measures green-balls’ resistance to spalling while drying, and may be one of the most important indicators of a binder’s performance (de Lima and Chaves, 1993) (Table 1).

After hardening, pellets are shipped considerable distances from pelletizing plants to blast furnaces or other points-of-use. High strength and abrasion resistance are required to minimize fines and dust generation during transport and iron making. Pellet strengths are measured by a compression test and by tumbling pellets in a rotating drum. Common fired pellet quality tests are shown in Table 1.

Table 1 Desirable properties of iron ore pellets (Meyer, 1980; Geerdes, Toxopeus, et al., 2009)

Pellet Property	Test Procedure	Typical Values
Compression strength	Moist, dry or fired pellets are individually compressed to failure and the maximum load is recorded. ISO 4700	> 2.5 kgf/pellet (dry) > 150 kgf/pellet (fired)
Size distribution	Pellets are sieved on a set of screens from 6.3-15mm. ISO 4701	> 90 % 9-12 mm
Drop strength	Green-balls are individually dropped from 45 cm onto a steel plate.	> 4-5 drops to fracture
Thermal shock	Green-balls are placed in a preheated furnace at temperatures ranging from 100-1000 ° C for 10 min. Temp. at which 90 % of pellets survive is "shock temp".	> 350 °C
Tumble and Abrasion Indices	Pellets are sieved on 500 mesh and +6.3 mm screens after tumbling in a standardized drum. ISO 3271	> 90 % pellets +6.3 mm < 5 % fines -500 mesh
Reducibility	Pellet weight is recorded as pellets are reduced under standardized gas composition and temperatures. ISO 4695	> 0.5 % min ⁻¹ (dR/dt) ₄₀
Low-temperature breakdown	Pellet size distribution is measured after static reduction and tumbling. ISO 4696	> 80 % pellets + 6.3 mm

Metallurgical properties

Iron ore pellets are ultimately converted to pig iron, hot metal or other iron rich products. In the Blast Furnace for example, the pellets travel down the furnace counter-current to the high-temperature reducing gas flow. The reducing gases remove oxygen from pellets, soften and eventually melt solid particles which accumulate as separate molten metal and slag layers on the hearth.

Metallurgical tests (Table 1) gauge pellets' behavior during reduction under somewhat-representative process conditions. Reducibility is generally determined by heating pellets in a controlled reducing atmosphere and measuring the weight change as oxygen is evolved from the pellet. High pellet reducibility is desired. Poor furnace operation is driven by poor burden permeability which reduces efficient reducing gas use. So, low temperature reduction-disintegration, softening-melting, and swelling characteristics are measured to indicate whether pellets produce unwanted fines or slump together too soon.

Chemical content

Modern iron-making processes require feed with high iron content to make iron in an efficient and productive manner. For example, efficient blast furnace operations need feed exceeding 58 % iron (Geerdes, Toxopeus, *et al.*, 2009). Coal or gas based direct reduction processes are typically fed material with iron contents exceeding 64 %, and pellets fed to the MIDREX process are typically 67-69 % iron (Chatterjee, 1994). Considering hematite (Fe_2O_3) is approximately 70 % iron, a pellet feed of 69 % iron implies gangue contents as low as 1.3 %. Clearly, the chemical make-up of binders added during agglomeration can greatly affect the composition of iron ore pellets, especially high purity pellets. The relationship between acid gangue content ($\text{SiO}_2 + \text{Al}_2\text{O}_3$), basic flux materials ($\text{CaO} + \text{MgO}$), and iron content in iron ore pellets is shown in Figure 2.

The graph shown in Figure 2 illustrates how gangue and flux quantities affect iron ore pellet iron content. The graph, constructed assuming fired pellets contain only hematite, acid gangue, and basic fluxes derived from a 50/50 mixture of limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), is bound by typical values observed in industrial pellets. Notice that basicity is plotted along the x-axis. Basicity is a ratio of the basic to acid oxides found in pellet slag; basicity affects pellet microstructure and properties, as well as the properties of the blast furnace iron making slag. To read Figure 2, choose the line representing pellet gangue content and follow along to the appropriate basicity level – the ordinate will be pellet iron content.

The vertical line (Figure 2) represents a basicity ratio of 1. Pellet “acidity” increases to the left of this line. Acid pellets tend to be strong in compression, have poor reducibility, and are sensitive to swelling during reduction (especially when basicity is between 0.2 and 0.7) (Geerdes, Toxopeus, *et al.*, 2009). Pellet basicity increases moving to the right along the horizontal axis. Basic or fluxed pellets require more energy input during induration than acid pellets due to flux decomposition: limestone and dolomite decompose during firing, forming lime, magnesia and gaseous carbon dioxide. Fluxed pellets tend towards better metallurgical properties than acid pellets (Geerdes, Toxopeus, *et al.*, 2009).

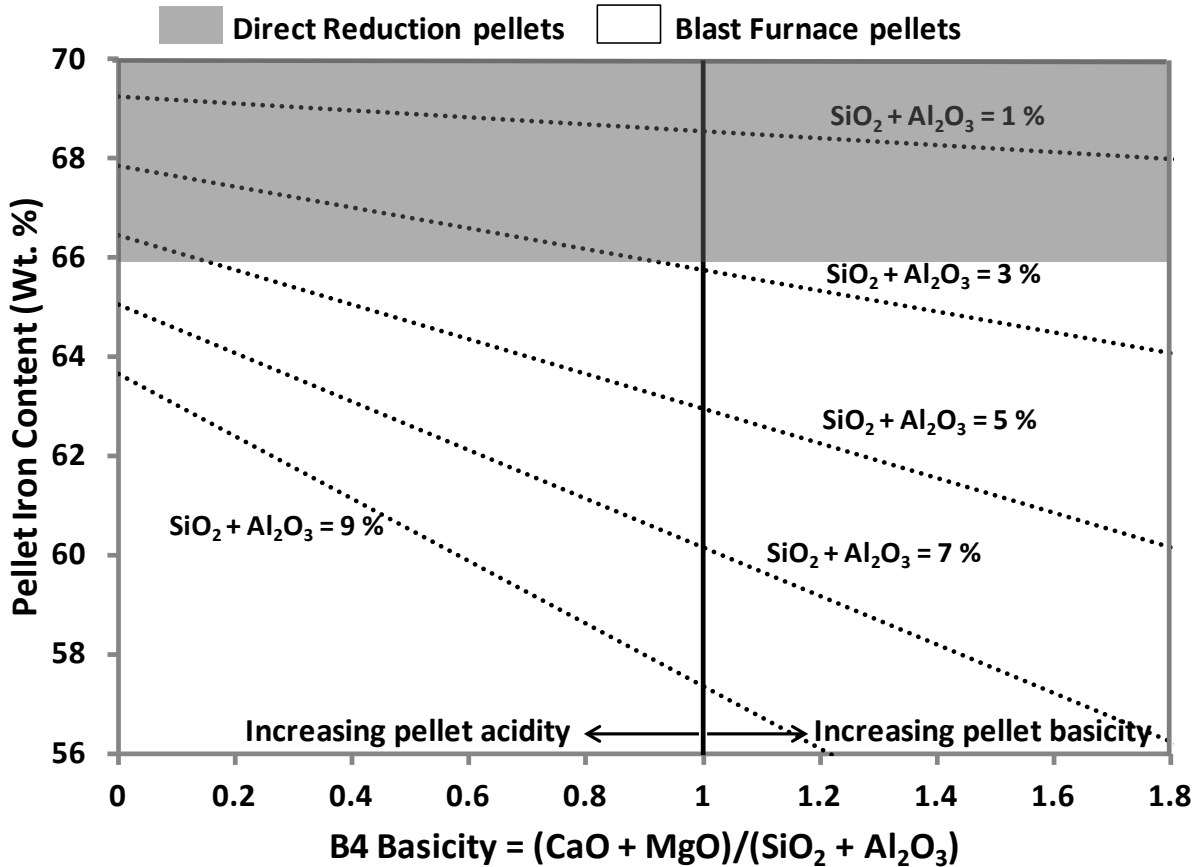


Figure 2 Effects of flux and gangue quantities on the iron content of iron ore pellets. The graph was constructed assuming fired pellets contain only hematite (Fe_2O_3), gangue, and basic oxides ($CaO + MgO$) originating from a 50/50 mixture of limestone ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). (After Mourao, 2008)

Organic binder development

Iron ore pelletizers have tried using inorganic and organic binders since developing the agglomeration process (Meyer, 1980; Eisele and Kawatra, 2003). Initially, inorganic bentonite use dominated for economic reasons and its ability to improve pellet physical quality at all stages of agglomeration. Over time, research into organic binders increased due to rising bentonite costs and the desire to lessen silica contents in iron ore pellets.

Organic material tested ranged from synthetic chemicals such as acrylamides, naturally occurring materials (such as cellulose and starch) and their derivatives, to waste-and by-products from other industries (e.g. animal and dairy wastes, wood processing liquors, and heavy hydrocarbons) (Nalco Chemical Co., 1968; Wilson, 1980; Eisele and Kawatra, 2003). Some binders were unsuccessful; some binders produced acceptable pellets in the laboratory, but failed during pilot testing and at an industrial scale; other binders produced acceptable pellets during industrial balling trials but were not fully incorporated into plant operation.

The underlying reasons for organic binder “success” or “failure” is difficult to discern from reported literature as binder characterization is practically non-existent. One reason for limited characterization could be that there are very few “independent” studies—many have been put forth by organic binder producers who are naturally reluctant to divulge the proprietary characteristics of their products. However, it is generally thought that purely organic binders only enhance green-ball formation, and pellet firing schedules can be adjusted to achieve high quality fired pellets. Green-ball quality increases with a binder’s ability to control and thicken water during agglomeration, and its tendency to form adhesive films after drying.

Three organic materials, sodium carboxymethylcellulose, corn starch, and sodium acrylate-acrylamide copolymers, have been used industrially as binders by the U.S.A. iron ore industry.

Use of organic binders by the U.S.A. iron ore industry

In the U.S.A, iron ore pelletizers have produced saleable pellets using three different organic binders (Table 4): sodium carboxymethyl cellulose (CMC), modified corn-starch, and synthetic acrylamide-sodium acrylate copolymers. CMC is derived from the natural polymer cellulose, which is a widely available around the world. During CMC production, cellulose is digested with sodium hydroxide and reacted with mono-chloroacetic acid to make it water soluble (Whistler, 1973). The CMC-based Peridur binders were used after 1986 at Eveleth Mines (Now United Taconite) in Minnesota, but are not currently in use in the U.S. (Karkoska, Sankey, et al, 1995).

One U.S.A. iron ore pellet plant has used a modified corn-starch based binder to reduce bentonite doses required for agglomeration (Personal Reference, 2011). Starch can be isolated from other sources (e.g. potato, wheat, rice, tapioca), but production from corn is more prevalent (Swinkels, 1985); modified corn-starch is also successfully used as an iron ore flocculant (Keranen, 1986). As natural starch in its raw form is not soluble in water, it is cooked or causticized to increase solubility and binding power.

The third commercial organic binder type is synthetic acrylamide-sodium acrylate copolymers. These petrochemical-based “anionic polyacrylamide” binders are produced by reacting the monomers acrylamide and acrylic acid in a controlled reactor. The acrylamide content – the anionic fraction – and the molecular weight can be controlled by varying reaction conditions. Proprietary additives can be added which render these polymers less soluble, but increase their ability to form gels with a higher swelling capacity (Allen, 1993). The Alcotac line of polyacrylamide binders replaced Peridur binders at United Taconite, and has been used since 1993 (Karkoska, Sankey, et al., 1995).

The percentage of pellets produced with each particular class of binder is shown in Figure 3. To generate the graph, pellet quantities produced at each operating plant were classified according to published binder use. Although organic binders are used internationally for agglomeration, data was not available for comparison.

Comparatively, it is clear that bentonite use still dominates the iron ore market. Including pellets manufactured with bentonite-corn starch composite binders, bentonite is present in approximately 90 % of US iron ore pellets. Polyacrylamide bonded pellets make up the remainder.

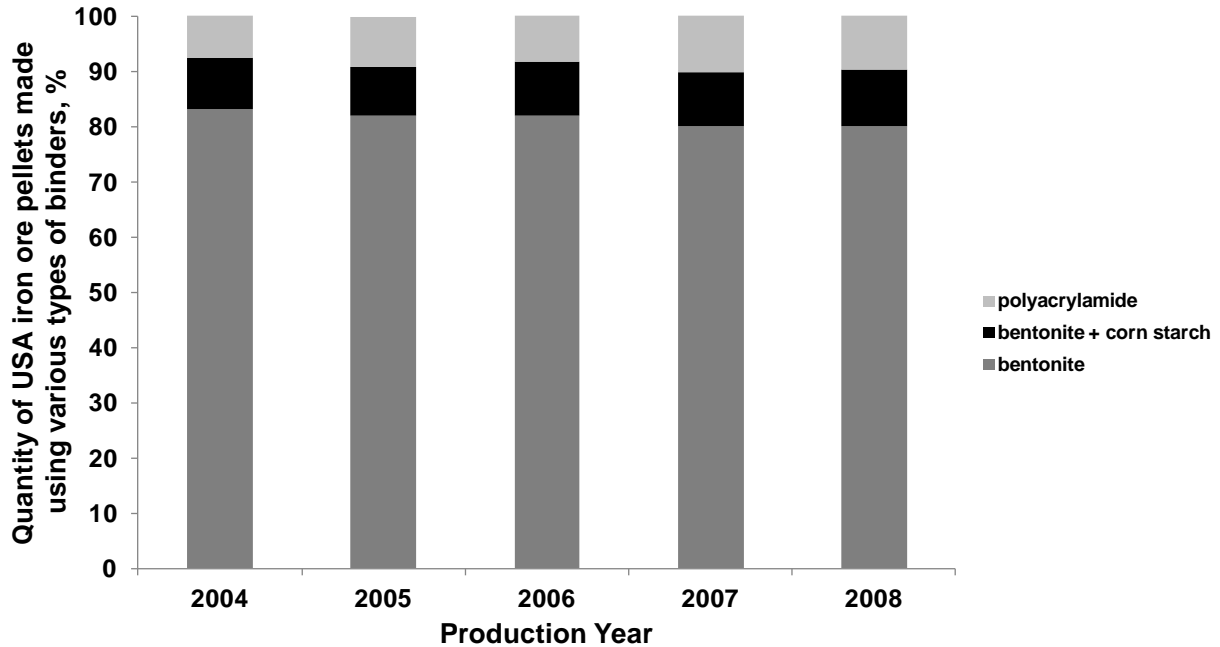


Figure 3 *Quantity of USA iron ore pellets made using different types of binders. Bentonite alone accounts for approximately 81 % of pellets; bentonite-corn starch composite binder accounts for approximately 10 % of pellets; the remaining 9 % are polyacrylamide bonded pellets. (Data compiled from Skillings Mining Review.)*

Looking at the market share of the three binders (Figure 3), one might ask why would polyacrylamide and corn starch – or any other organic binder – be used? Are there benefits to using organic binders? Are there certain drawbacks or common problems associated with organic binders that have limited their use by industry? Some organic binder pros and cons are discussed below.

Benefits to using organic binders

Organic binders may be used for a variety of reasons, but perhaps the most reported benefit is a reduction in pellet silica content. The traditional binder, bentonite clay, generally increases iron ore pellet silica content by 0.5 %; the true value depends on bentonite dose and composition. Organic binders are combusted during the high-temperature firing process, and may leave virtually no ash residue among the pellet structure for slag formation. This is illustrated by Table 2, which presents mass loss profiles of some organic binders tested in a Bureau of Mines study (Haas et al., 1989).

Table 2 summarizes loss-on-ignition values (LOI) of various classes of organic binders (Haas et al., 1989). In general, the organic binders lost 85 – 100 pct. of their mass by 1000 °C. The remaining material is most likely inorganic ash, which is present naturally in the organic material. Certain contaminants are also be introduced during processing. High sodium and chlorine concentrations in the cellulose derivatives evidences the latter (NaCl is a side product during reaction), while certain starches, for example, contain appreciable quantities of phosphate groups (Swinkels, 1985).

Table 2 *Combustion behaviors of various organic binders (Haas et al., 1989)*

	Loss On Ignition	
	(percent of initial weight)	
	300 °C	1000 °C
Cellulose derivatives	34 - 53	83 - 95
Dairy wastes	58 - 70	95 - 100
Natural gums	67 - 85	91 - 100
Wood products	51 - 85	85 - 96
Starch-acrylic copolymers	23 - 58	79 - 84
Starches	51 - 91	87 - 100
Coal products	12 - 31	65 - 78

Lowering gangue or silica contents in iron ore pellets may be beneficial for a number of reasons: Lower silica contents require less flux to achieve certain basicity levels (Figure 2), and ultimately reduce slag volumes in blast furnaces and other ironmaking operations. Direct reduction ironmaking processes have tight gangue tolerances and limited slag handling capabilities, so strict control over silica is important. It has been reported that each 1 % reduction in silica can reduce energy and flux costs by \$2.50 USD per ton hot metal (Schmitt, 2005).

Secondly, if pellets are meeting silica specification with bentonite binder, then replacement with a silica-free binder will allow the target silica concentration in the agglomeration feed to be raised. Raising target silica levels will tend to lower grinding costs, reduce iron losses to tailings, and allow more material to reach agglomeration.

A second major reason reported for using organic binders is that organic binders increase fired pellet porosity and reducibility. Panigrahy et. al., (1990) studied the microstructures of iron ore pellets made with peat-moss and bentonite binders, and attributed high porosity in fluxed pellets (basicity from 0.2 – 1.6) to peat moss combustion before a liquid slag phase formed. With lower ash contents and correspondingly lower flux levels in the peat-moss and other organically bonded pellets, insufficient slag quantities are available for bonding; pellet porosity has been shown significantly higher in organic-binder pellets compared to bentonite.

Increasing pellet porosity typically improves pellet reducibility. Reducibility can be defined as the ease of oxygen removal from oxides in the pellet during the reduction process. A higher volume of macro and micro pores in the pellet microstructure corresponds to more surfaces being in contact with the reducing gases at any time. Consequently, less time is required to achieve a given percent reduction. For example, replacing bentonite with an organic binder improved taconite pellet porosity by 29.1 %, in pellets prepared for blast furnace iron making (Lyons et al 1986). Pellet reducibility correspondingly increased by 16.7 %. This is illustrated in Table 3.

Improving metallurgical parameters of iron ore pellets is beneficial for many reasons, but it ultimately results in more efficient use of reducing gases in the blast furnace and other iron making processes. Iron-makers at the Middletown Blast Furnace have been able to 1) reduce fuel

costs during ironmaking by 6 % using pellets made with organic binders as feed; and 2) increase hot metal production by 2.6 % (Lyons et al 1986).

Common drawbacks to organic binder use

Fired pellets made with organic binders historically have had low compression strength and abrasion resistance. This could be due to higher porosities and less glassy phases in those pellets. Pellet strength generally increases with decreasing porosity, and more-so lowering the volume of large macropores which concentrate stress-fields in pellet structures. Ranade, Ricketts, et al., (1986) reported that CMC binder test pellets tended to produce more -150 micrometer dust particles during tumble testing than bentonite-bonded pellets which produce larger chips and fines. Poor Abrasion Indices and compression strengths may have been ultimately caused the narrower pellet size distribution.

It was hypothesized that the narrower size distribution and organic binder burn-out improved bed permeability to such a degree that the magnetite pellets oxidized earlier than expected on the grate (Ranade, Ricketts, et al., 1986). Consequently, less heat was provided by oxidizing pellets in the firing zone; a significant fraction of process heat available for sintering results from magnetite oxidation. These problems were corrected by altering furnace operating conditions.

Green-balls made with organic binders sometimes grow too fast, and have moist, rough surfaces. Slower growth and higher recycling loads in rotary drums (commonly associated with higher viscosity binders) produces stronger, more spherical balls. Lower surface moistures may enable better classification between finished green-balls and fine particles on roller decks and screens, resulting in less dust issues in furnaces and while shipping and handling fired pellets.

Higher surface moistures may be associated with certain organic binders at agglomerations conditions above an optimal water content. Excess water is rapidly exuded to pellet surfaces where it enables rapid green-ball growth, coalescence and dust pick-up. Some iron ore binder patents claim to solve this problem by altering molecular structure and functional groups in an organic binder, or by addition of other hydrophilic organic polymers.

Characteristics of organic binders and their effects on agglomeration

Iron ore agglomeration is a complex, dynamic process. Some conditions that may change between pellet plants, or even within a single process, include moisture content of the concentrated iron ore; composition and pH of the moisture; residual process additives adsorbed onto concentrate particles or dispersed within the moisture; the sizes and shapes of concentrate particles; and mineralogy. Ideally, an organic binder will be insensitive to many of these process changes and be able to firmly bond pellets together across a wide variety of conditions. However, the binding properties of organic binders may depend on their respective molecular structures.

Table 3 Porosity and isothermal reduction of pellets at Middletown No. 3 blast furnace trial (Lyons et al 1986).

	Bentonite	Organic
Porosity (%)	25.4	32.8
Reduction (%)	68.3	79.1
ISO 7215		

Ideal organic binder structure

Qiu et al (2003) proposed the general structure of an ideal organic binder (Table 4). According to the authors, the binder structure should contain 1) hydrophilic functional groups to promote binder dispersion into moisture and to enforce concentrate wettability; 2) polar functional groups to promote binder adhesion to ore particles; and 3) a mechanically strong and thermally stable “backbone”. The authors suggest an ideal structure containing any of the following functional groups, $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, and $-\text{COO}^-$, which are hydrophilic and polar, along an organic backbone composed of phenol rings and double and triple covalent bonds.

As seen in Table 4, the ideal structure generally describes the three common organic binders, CMC, anionic polyacrylamide, and corn starch. However, all of these have saturated carbon-carbon bonds along their backbone structure. These bonds are not as strong as double and triple covalent bonds (Chang 1998), which would tend to decrease their thermal and mechanical stability. Furthermore, triple covalent bonds are highly energetic and reactive.

In the past, the effects of binder molecular structure on iron ore agglomeration have not been directly reported. Molecular structure characteristics of polymers such as CMC and polyacrylamide have been related to adsorption properties onto iron oxides (Hoogendam et al 1998; Lee and Somasundaran 1989; Lee and Somasundaran 1991). Only recently have studies been reported which relate functional group contents in coal-derived, organic binders to its interaction with iron ore surfaces, and their effects on agglomeration (Han et al 2010; Zhang et al 2011; Jiang et al 2011; Han et al 2012). These studies confirm the hypothesis that altering 1) molecular structure and 2) ratios of different types of molecules affects binder performance.

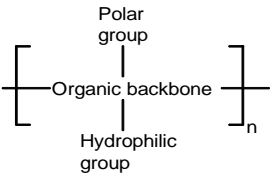
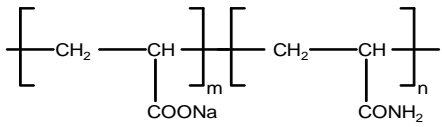
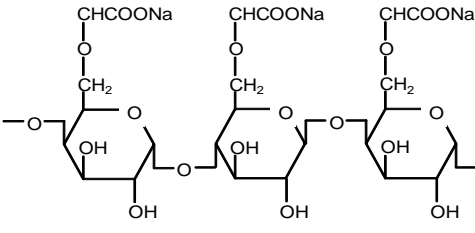
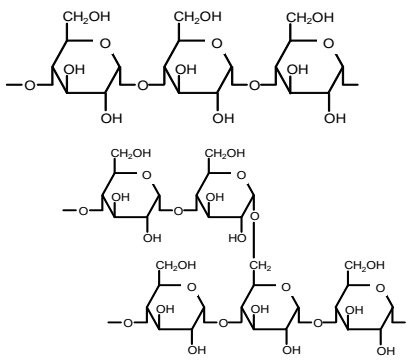
It does appear, however, that best results come from an organic structure with multiple functionalities; in other words, a variety of functional groups are incorporated along the polymer structure. Multiple functionalities, for example, can help uncoil and rapidly disperse organic binders into the agglomeration feed. A more branched, networked, or gel-like structure may also inhibit complete adsorption to concentrate particles; limit hydrophobic bonding between polymer molecules; and retain green-ball water.

After an organic material has been identified as a potential iron ore binder, certain characteristics can be altered to adjust its physical properties and performance as a binder. For example, molecular weight, degree of substitution, and purity are the main characteristics a consumer could specify when selecting a CMC binder. Goetzman et al. (1988) conducted a comprehensive study of molecular weight, degree of substitution and purity on the performance of a CMC binder.

Effects of molecular weight on agglomeration

Molecular weight (MW) essentially indicates the size of the polymer molecules making up the organic binder. MW controls viscosity, solubility and other mechanical and thermal properties of the binder; viscosity and mechanical and thermal strengths increase with MW while solubility decreases. Usually, the molecular weight of a binder is not reported directly, but indicated either by 1) viscosity of a low concentration (1 – 2 %) binder solution, or 2) intrinsic viscosity (Allen 1993).

Table 4 Molecular structures of the ideal organic binder (after Qiu et al, 2003), and three commonly used organic binders. Modified corn starch and copolymers of acrylamide and sodium acrylate are used as bentonite replacements in US iron ore agglomeration.

Binder name	Molecular structure	Common characteristics
Ideal binder		<ul style="list-style-type: none"> •Polar and hydrophilic functional groups include NH₂, OH, COOH, and COO⁻ •Organic backbone incorporating double covalent bonds and phenol rings • See Qiu, et al., (2003) for reference
sodium acrylate-acrylamide copolymer		<ul style="list-style-type: none"> •Typically contains 30-50 % sodium acrylate •Typical intrinsic viscosity, (indicating molecular weight), is 4-11 dl/g • See Allen (1993) for reference
Sodium carboxymethylcellulose		<ul style="list-style-type: none"> •Typical degree of substitution is 0.4 - 0.8 •Typical degree of polymerization is 500 - 2000 • See Whistler (1973) for reference
Corn starch (composed of amylose and amylopectin)		<ul style="list-style-type: none"> •Amylose (upper molecule at left) is a linear molecule with α(1→4) bonds, and degree of polymerization of 350-1000 •Amylopectin (lower molecule at left) is a branched molecule with α(1→6) bonds, and degree of polymerization >1000 •Normal corn starches contain approximately 25 % amylose and 75 % amylopectin •See Swinkels (1985) for reference

Intrinsic viscosity is commonly used to qualitatively indicate a particular polymer's molecular weight (e.g. low, high MW). Flow times of various concentrations of a polymer solution through a known distance in a standard tube are measured; the data is used to extrapolate a viscosity at 0 % concentration (or intrinsic viscosity).

The effect of CMC viscosity on the quality of green-balls is shown in Figure 4. Pellet drop strength is shown for both 9.2 and 9.5 percent moisture at a CMC dose of 1.0 lb/LT. Drop strength initially increased significantly with molecular weight and then either a) leveled off, or b) continued increasing, depending on green-ball moisture content. For example, at 9.5 percent moisture the drop number increased from 4.3 to 10.5 when the 1 percent CMC viscosity was increased from 10 to 2900 cps. The authors suggested that at the higher moisture level, the higher molecular weight binder was able to more fully extend into the liquid and attain its maximum thickening effect. The green-ball wet and dry compression strengths did not seem to be affected by the molecular weight of the CMC.

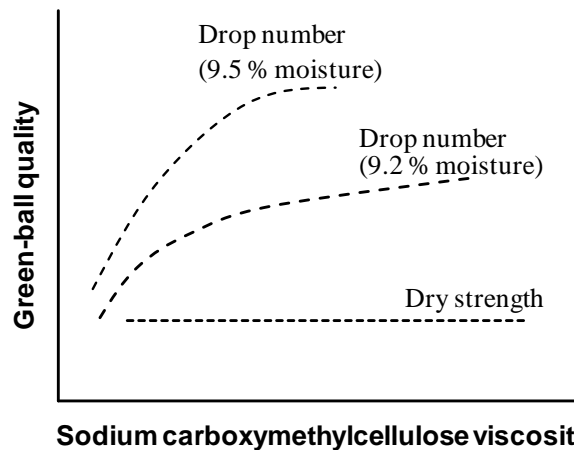


Figure 4 Effect of CMC viscosity on the quality of green-balls. Molecular weight is indicated by the viscosity of a 1 or 2 % CMC solution. Polymer degree of substitution is constant at approximately 0.8. Pellets made using Eveleth taconite concentrate. (General trends taken from Goetzman et al 1988)

At a constant degree of substitution, small changes in the dose of the medium and high viscosity CMC affected the green ball drop strength much more than the low viscosity CMC (Figure 5).

Effects of degree of substitution on agglomeration

The Degree of Substitution (DS) of a CMC binder indicates the quantity of available hydroxyl groups (-OH) that have been replaced by sodium carboxymethyl groups (-CH₂COONa) along the natural cellulose backbone. DS—similar to the ionic nature of an acrylamide/sodium acrylate copolymer binder—controls solubility, adsorption, and sensitivity to salts in the binding solution. Higher DS would tend to increase solubility and the decrease interaction effects between the binder and various ions in solution.

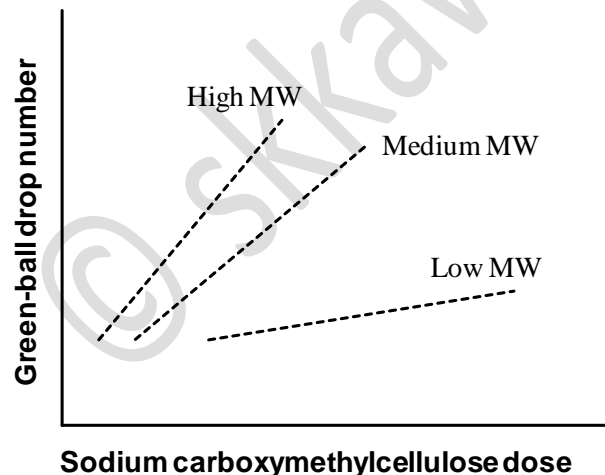


Figure 5 Effect of CMC dose on the drop strength of green-balls. Pellets were made at 9.2 % moisture. High MW had a viscosity (1 %) of 2920 cp; Med. MW had a viscosity (2 %) of 780 cp; Low MW had a viscosity (2 %) of 29 cp. All at constant degree of substitution of 0.8. (General trends taken from Goetzman et al, 1988)

The effects of DS during agglomeration are not as pronounced as MW effects. Goetzman et al (1988) varied DS from 0.5 to 1.3 at a constant MW and noticed negligible changes in green-ball quality at 9.2 % moisture. As the CMC dose was increased from 1.0 to 1.5 lb/LT, however, wet drop increased slightly with DS. The authors attributed this to incomplete solubility of the low DS binder. However, their hypothesis was not tested on higher MW material, which would have lower solubility than the medium MW binder studied.

Additionally, a minimum DS is needed to dissolve any appreciable quantity of CMC, as unmodified cellulose is not soluble. Below a DS of 0.4-0.5, CMC is not soluble unless great care is taken to get even substitution along the cellulose backbone (Whistler, 1973).

Effects of organic binder purity on agglomeration

Binder purity depends on both the manufacturing process used during its production and the costs to purify the product. The effects of impurities on pelletization could range from negative to beneficial, depending on the type of impurity and its content in the agglomerating material. This was illustrated by Goetzman et al (1988), who added sodium chloride (NaCl) and sodium glycolate (Na-glycolate) to a high-purity CMC binder. NaCl and Na-glycolate are two common impurities found in CMC products that are introduced during the manufacturing process.

At doses found in commercial products, NaCl was found to sometimes affect pelletization while Na-glycolate did not (Goetzman et al 1988). NaCl decreased both wet drop and dry strength when using a high MW CMC, but had negligible effects on lower MW binders. Increasing salt concentration is well known to inhibit the expansion of CMC in solution (Whistler, 1973), and the higher MW CMC would already have fewer tendencies to dissolve due to the MW effects at the moisture content used for agglomeration.

Effects of water chemistry on organic binders

Iron ore process water is not pure, but contains significant quantities of dissolved solids. Major elements include Ca, Mg, and Na at concentrations near 100 mg/l immediately prior to agglomeration (Haselhuhn et al 2012). As seen in Figure 6, divalent cations (Ca^{++} , Mg^{++}) are transported by mineral surfaces to the agglomeration process (Westerstrand and Ohlander 2010), and can be at concentrations as high as 1000 mg/l in pellet moisture (Kawatra and Ripke 2003). The negative effects of cations on pelletization with bentonite clay are understood from work directly with plant-moistened concentrates (Rice and Stone 1972; Engesser 2003; Kawatra and Ripke 2003) and the common practice of “activating” calcium-bentonite clay with soda ash. When present, cations may degrade the performance of certain organic binders as well.

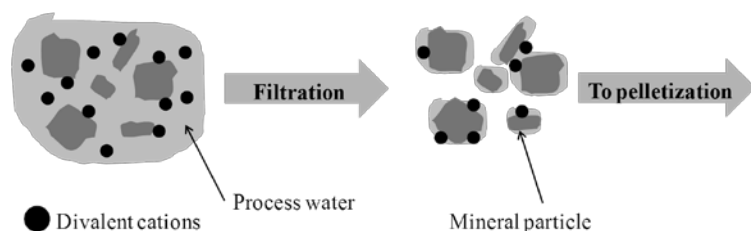


Figure 6 Divalent cations are transported from the iron ore concentrator to agglomeration.

Allen (1993) reported improvements in agglomeration with “Alcotac” anionic polyacrylamide binders after washing the iron ore concentrates. Better green-ball quality was also achieved on ore moistened with water softened by carbon dioxide or sodium carbonate additions, both of which precipitate Ca^{+2} ions as CaCO_3 (Allen 1993). Goetzman et al (1988) found similar improvements on green-ball quality when concentrates from Evtac and Minntac mines in Minnesota were washed with distilled water prior to agglomeration using CMC binders. Furthermore, intentionally increasing the Ca^{2+} concentration from 0 to 208 ppm in green-ball moisture reduced wet drop from 5.6 to 5.0 drops, wet compression from 3.1 to 2.7 lb., and dry compression from 4.0 to 2.6 lb. (Goetzman et al 1988). All point to or suggest that ionically charged organic binders are sensitive to water chemistry.

Generally, water soluble anionic polyacrylamide and CMC binders are salts of monovalent cations, such as sodium. In moisture, the binder molecules unravel and extend, in part due to ionic repulsive forces from the charged $-\text{COO}^-$ groups. The presence of divalent cations can shield those repulsive forces, causing the binder molecules to stay more tightly coiled and decreasing the viscosity of the pellet moisture (Whistler 1973).

As a consequence, current organic binders are often a combination of a particular polymer binder and inorganic additives/activators. Additives such as sodium carbonate (Na_2CO_3) serve to soften the pellet moisture by precipitating calcium and magnesium out of solution as solid carbonates, and may act as a fluxing agent during sintering (Eisele and Kawatra 2003). Both green-balls and fired pellet quality tend to increase when binder additives are used during agglomeration.

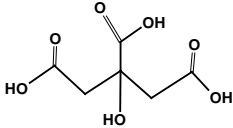
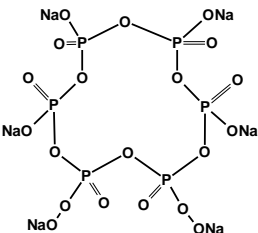
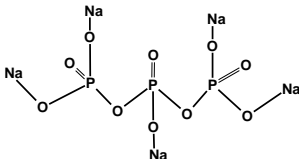
Effects of additives on organic binders

Organic binders are commonly used in conjunction with activators or inorganic additives. The most well-known is sodium carbonate (Na_2CO_3), but boron-containing minerals such as colemanite, and dispersants such as tripolyphosphate, citric acid, and sodium silicate have been used as well. Additives may increase green pellet quality, but are more primarily used to increase the strengths of preheated and fired pellets. Common additives used in conjunction with organic binders are shown in Table 5.

Sodium carbonate

Sodium carbonate, commonly called soda ash, is added to CMC and anionic polyacrylamide binders. Soda ash has also been added to the cellulose derivative carboxymethyl-hydroxyethyl cellulose (Banyai et al, 1990). Ionic or charged organic binders are sensitive to water chemistry, in a similar manner as bentonite. Consequently, soda ash is added to soften pellet moisture and speed binder dissolution and dispersion. Quantities of soda ash added during agglomeration may make up to 50 percent of the binder by weight (Karkoska, 2012), but the dose varies with ore and process conditions. Sodium carbonate use resulted in higher and more stable water contents in Alcotac bonded pellets (Allen, 1993).

Table 5 Additives are commonly used to increase the quality of pellets made with organic binders. Dispersants are added to sequester divalent cations that interfere with binder function, while borate minerals are low melting-temperature slag formers.

Additive name	Structure	Additive description
sodium carbonate (soda ash)	Na_2CO_3	<ol style="list-style-type: none"> 1) soda ash is a low-cost water softener for agglomeration 2) soda ash is commonly added to anionic polymers which are sensitive to divalent salts in pellet moisture 3) soda ash may make up to 50 % by weight of the organic binder dose (Karkoska, 2012)
citric acid		<ol style="list-style-type: none"> 1) citric acid is added as a sodium salt (sodium citrate) to anionic polymers such as CMC 2) functions as a chelating agent, and sequesters harmful elements present in the agglomeration feed 3) dosed at 0.1 lb/ton to 2.2 lb/ton (Steeghs and Schmitt 2005)
sodium silicate	$\text{Na}_2\text{O} \bullet \text{SiO}_2 \bullet x\text{H}_2\text{O}$	<ol style="list-style-type: none"> 1) sodium silicates are inorganic polymers that can act as binders or dispersants 2) $\text{Na}_2\text{O}:\text{SiO}_2$ ratio is commonly 1:1 to 1:4 3) sodium silicate may compose up to 75 % of the total binder weight (Schmitt and Smeink 2007)
sodium hexametaphosphate (SHMP)		<ol style="list-style-type: none"> 1) SHMP is a common dispersant in mineral processing 2) SHMP sequesters elements that interfere with the organic binder structure 3) SHMP may make up to 50 % by weight of the organic binder dose (Banyai et al, 1989)
borax pentahydrate	$\text{Na}_2\text{B}_4\text{O}_7 \bullet 5\text{H}_2\text{O}$	<ol style="list-style-type: none"> 1) borax pentahydrate is a soluble sodium salt with a melting temperature of 200 ° C (Schmitt, 2005) 2) increases pellet quality by adding additional slag phases to the pellet microstructure
sodium tripolyphosphate (TPP)		<ol style="list-style-type: none"> 1) sodium tripolyphosphate is a common dispersant 2) TPP functions as a chelating agent, and sequesters harmful elements present in the agglomeration feed 3) the organic binder dose may consist of 30-50 % by weight of TPP (Banyai et al 1989)
colemanite	$2(\text{CaO})3(\text{B}_2\text{O}_3) \bullet 5\text{H}_2\text{O}$	<ol style="list-style-type: none"> 1) colemanite may be calcined before use 2) has a melting temperature of 986 °C 3) functions as a low-melting temperature slag former 4) generally a B_2O_3 dose around 0.3 % is sufficient for enhanced strength (Malysheva et al, 1996)

Boron containing compounds

Iron ore has been agglomerated with natural minerals containing boron to increase the strengths of preheated and fired pellets (Roorda et al 1975; Akberdin et al 1999; Schmitt 2005; Schmitt et al 2005; Sivrikaya and Arol 2011). Natural borate minerals, such as colemanite and borax, have low melting temperatures which promote the sintering of iron ore grains and add additional slag-bonding phases to the pellet. The mechanisms behind these effects were clarified with pure boron oxide (B_2O_3) having a melting temperature of 450 °C (Malysheva et al 1996; Dolitskaya 2001).

During pellet induration, B_2O_3 melts at 450 °C producing localized regions of a borate melt and imparting minimal liquid-phase strengthening (Malysheva et al 1996). As temperatures rise to 1000 °C, pellet strengths increase from 10 to 100 kg/pellet as the borate melt absorbs small grains of iron ore, silicate and flux, and penetrates into intergranular pores. The low temperature melt develops a better connected microstructure. Above 1000 °C, the silicate phases begin

melting and become more fluid (or less viscous) due to the presence of B_2O_3 . Strength is enhanced as hematite grains grow, which increases with boron addition; pellet strengths exceeded 300 kg/pellet when sintered at 1250 °C with B_2O_3 (Malysheva et al 1996; Dolitskaya 2001).

In general, silicate melts become less viscous and are present at lower temperatures when B_2O_3 is present in the pellet charge (Akberdin et al 1999). Consequently, organic binders have been coupled with colemanite and borax to improve their performance as binders. The organic portion improves green pellet quality while the inorganic borate strengthens the preheated and fired pellets. Sivrikaya and Arol (2011) found that 0.43 percent B_2O_3 (as 1 % calcined colemanite) added to 0.1 % CMC, 0.05 % Ciba DPEP06-007, or 0.1 % corn starch produced pellets with fired strengths exceeding 500 kg per pellet. Comparatively, these pellets were stronger than those made with 0.5 % bentonite.

Similar to bentonite, as the quantity of B_2O_3 exceeds a certain value, pellet reducibility and even mechanical strength can lessen. Increasing B_2O_3 content from 0.3 to 2.0 wt % in a magnetite concentrate decreased the degree of reduction (obtained in a Linder test) 38.9 to 6.4 percent; at the same doses, the strength of pellets roasted at 1250 °C decreased from >400 to nearly 300 kg/pellet (Malysheva et al 1996). Increasing the quantity of slag minerals from colemanite and borax decreases pellet porosity and hinders the diffusion of reducing gases into the pellet. In pellets with a relatively high volume percent of slag phases, the slag serves as a weak link during mechanical loading.

Clearly, borate minerals can act synergistically with organic binders to improve the quality of iron ore pellets (Table 6). But, blast furnace operators may hesitate to use them until their effects on downstream iron and steelmaking operations are understood. Boron dissolves in pig iron, increasing its hardenability and brittleness, and affecting other properties (Sato et al 1986). Consequently, pellets agglomerated with borate minerals could be used to produce boron-alloyed steels (Akberdin and Kim 2008); tolerable boron limits vary with steel grade, and some can only tolerate 4-5 ppm boron (Schmitt 2005). If borate minerals are to function as an iron ore binder, their effects on blast furnace and direct reduction ironmaking processes must be established.

It has been suggested that the additives disperse colloidal particles into the pellet moisture: the colloidal particles would increase binder viscosity and be subsequently deposited at contact points in pellets as moisture evaporates during drying (Cassola and Chaves 1998). Wet drop, wet compression, and dry compression strengths of CMC bonded pellets increased after addition of the dispersant TPP (0.02 %) as shown in Table 7 (de Moraes and Kawatra 2010).

The dispersant sodium silicate can also act as a binder in its own right, and has been used for foundry sand applications (Owusu, 1982). Sodium silicate cross-links into a stable, glassy structure during drying and heating that is capable of holding agglomerates together (Eisele and Kawatra, 2003). At a dose of 1.5 percent, sodium silicate bonded iron ore pellets had dry compression strength of 52.6 N/pellet, compared to 38.3 N/pellet for bentonite bonded pellets (0.66 %) (de Moraes and Kawatra, 2010).

Table 6 Effects of calcined colemanite on the quality of green and fired hematite pellets (Sivrikaya and Arol 2009b).

Binder	Moisture, %	Wet Drop	Compression strength, kg/pel	
			1000 °C	1300 °C
None	6.9	2.2	19	254
0.5 % bentonite	7.5	3.4	50	381
0.1 % Technical CMC	8.4	4.7	20	321
0.1 % Ciba	9.6	10	21	288
0.1 % Tech. CMC + 0.5 % calcined colemanite	8.5	4	121	535
0.1 % Ciba + 0.5 % calcined colemanite	8.9	8.5	118	512

Summary of individual organic binders for iron ore agglomeration

A wide variety of organic binders have been tested for iron ore agglomeration over the years. A feature common to most of these materials has been their ability to form a gel in water, and increase the viscosity of pellet moisture to the level required for agglomeration. Individual binders are discussed in this section.

Anionic acrylamide binders

The petrochemical-based anionic, acrylamide copolymers (Table 4) are commonly prepared by reacting sodium acrylate and acrylamide monomers under controlled conditions. The production process is extremely versatile, as a variety of molecular weight and ionic variations are possible. In other words, these synthetic binders can be tailored for each specific plant and the requirements of their pelletizing process.

Floform 1049V, an anionic polyacrylamide binder manufactured by SNF Floerger, was tested in a 120 tons/h pelletizing facility (Chizhikova et al 2003a). Floform 1049V fully replaced bentonite at a binder dose of approximately 0.20 kg/ton. Pellets fired at 1200 °C had a compressive strength over 3000 N/pellet, and impact strength of 96.5 %. The content of total iron in fired pellets also increased by 0.3-0.4 % when polyacrylamide replaced bentonite as binder.

Table 7 Effects of the dispersant sodium tripolyphosphate (TPP) on the strength of CMC bonded pellets (de Moraes and Kawatra 2010).

Binder	Dose (%)	Moisture (%)	Wet drop	Compression strength, N/pellet					
				Wet	Dry	300 °C	500 °C	700 °C	900 °C
Bentonite	0.66	9.5	3.2	19	38.3	19.9	43	101.9	119.9
CMC	0.04	8.9	2.4	16.9	15.9	10.9	19	67.7	51.2
CMC + TPP	0.04 + 0.02	9.1	2.9	19.6	21.5	147	26.7	89.8	89.3

Of interest during this study, the optimum moisture content for pelletization was lower than when using bentonite (Chizhikova et al 2003a), perhaps because of the better moisture distribution within pellets. Polyacrylamide binders more evenly distribute moisture compared to inorganic binders like bentonite (Chizhikova et al 2003b). The lower moisture requirements correspondingly increased the cost of electric power for filtration by 20 %. While this would tend to reduce energy requirements for pellet drying, overall energy requirements may be higher due to the higher temperatures usually needed for firing pellets made with organic binders..

A second polyacrylamide binder, NS 99340 (manufactured by Neo Solutions), has been tested in a 3 month, full-plant trial in Minnesota. While binder testing was not complete at the time of this writing, initial results suggest pellet quality specifications were met at a very low binder cost per ton of pellets (Karkoska 2011).

Sodium carboxymethylcellulose (CMC)

CMC (Table 4) can be derived from natural cellulose obtained from a variety of sources. Cellulose is digested with sodium hydroxide, and reacted with monochloroacetic acid. The manufacturing process replaces hydroxyl groups (-OH) along the cellulose structure with sodium carboxymethyl groups (-CH₂COONa). Because CMC is derived from natural materials, the make-up of the feedstock varies from source to source: the cellulose content of wood varies from 40-50 percent while cotton contains 90-99 percent cellulose (Hon 1989). Consequently, binder properties may vary depending on the source; this has been observed with CMC flocculants, but has not been directly reported with binders.

A large number of studies have shown that carboxymethyl cellulose derived materials effectively bind iron ore pellets [Goetzman 1988; Haas 1989; Martinovic 1989; Steeghs 1989; de Souza 1984; de Moraes 2008; Sastry 1985; Kortmann 1987; Roorda 1975]. Good quality pellets were produced both at a lab scale and using industrial equipment. Physical and metallurgical properties that can be obtained are shown in Table 8 below.

In general, when using CMC binders, good quality pellets can be made at significantly reduced doses compared to bentonite: the quantity of CMC added for successful agglomeration was only 5-15 percent by weight of the consumption of bentonite (de Souza et al 1984). Because of the small doses used, some have argued that organic binders must be fully dispersed throughout the concentrate for full effectiveness; this might be difficult with such small quantities of binder. However, two optical tracer studies showed non-uniform binder dispersion (from Pekay mixing) still results in acceptable quality pellets (de Souza, Mendonca, et al., 1984; Ranade, Ricketts, et al., 1986).

Table 8 *Physical and metallurgical properties of iron ore pellets obtained with the CMC binder Peridur XC-3 (Steeghs 1989)*

Test	Result
Tumble Index (ASTM E279)	+90 % > 6.3 mm
Compression strength (ISO 4700)	450-675 lbs/pel
Porosity, %	25-26
Reduction (ISO 4695)	0.7-1.1

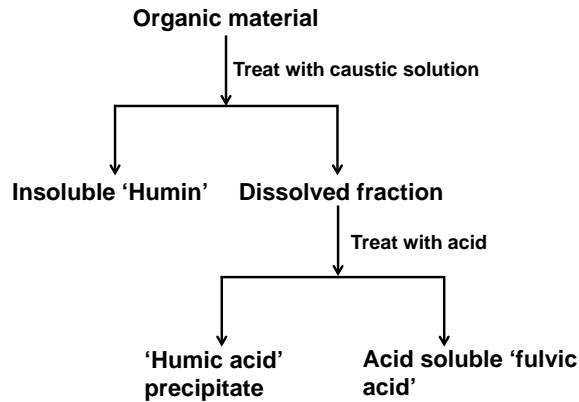


Figure 7 Preparation of humic acid (after Stevenson 1994). “Humic acid” binders are taken from the entire caustic solution, and so contain both humic acid and fulvic acid.

Humic substances

Humic substances are products of organic matter decomposition, and are widely distributed across the globe. They are found in soils as well as peat moss, carbonaceous shale, lignite, brown coal, and other materials (Stevenson 1994). The chemical structure of humic matter is still a topic of debate (Sutton and Sposito 2005; Piccolo 2001); one view is that humic substances are a collection of colloidal particles held together by hydrophobic interactions and hydrogen bonds. This view might suggest that humic-based binders may tend to excessively adsorb to mineral surfaces during agglomeration, and limit its water thickening effects.

Humic substances have historically been characterized into three fractions based on their solubility under various pH conditions (Figure 7): Humin is the insoluble fraction; humic acid is alkaline soluble but not acid soluble ($\text{pH} < 2$), and fulvic acid is soluble under all pH conditions (Stevenson 1994).

Humic-rich materials such as brown coal (Kashiring, 1969), seaweed (Quon, 1990), and peat moss (Godin, 1987; Martinovic, 1989; Panigraphy, 1985; Panigraphy, 1990; Vincze, 1971) are usually added in conjunction with caustic soda or causticized before use as a binder. The organic material has been reported to form a colloidal gel after treatment (Fine and Wahl, 1964). In either case, humic acid and fulvic acid are present in varying quantities depending on binder feedstock, so pellet quality may vary considerably with humate binder. Humic acid and fulvic acid have different thermal stabilities, and interact with ore surfaces to varying degrees, which affects their agglomeration characteristics (Han et al 2010; Zhang et al 2011; Jiang et al 2011; Han et al 2012).

Humate based binders have been successful in lab scale pelletization tests. These materials were digested with sodium hydroxide before agglomeration. An example of this can be seen from results given in Table 9 using peat moss as a binder.

As indicated in Table 9, green-ball quality using caustically treated peat moss was nearly equal to agglomerates made with bentonite. Dry performance, indicated by a 12” drop and a compression test, was superior when using caustically treated peat moss as binder. Industrially acceptable pellets were produced at reasonable peat moss + NaOH doses.

Table 9 Evaluation of unfired pellets made with peat moss and sodium hydroxide as binder (Vincze and Cavanagh 1971)

Binder	Moisture (%)	12 in. drops		Compression strength, lbs	
		Wet	Dry	Wet	Dry
Bentonite 16 lbs/ton	9.2	16.5	2.3	3.5	14.2
Peat moss 12 lbs/ton NaOH 1-2 lbs/ton	9.4-10.1	9.5-12.8	2.2-4.1	2.4-2.6	13.7-14.6
Peat moss 16 lbs/ton NaOH 0.6-2.68 lbs/ton	9.8-10.6	12.8-15.3	3.0-5.2	2.4-2.6	11.6-18.9

While some humate binders produced reasonable quality pellets in laboratory tests, others have decreased the “ballability” of the ore (Fuerstenau 1975; Nalco 1968). (Ballability is commonly defined as the ability to form pellets during agglomeration.) One such binder was reported to form a “mass of mud” during an industrial trial (Fuerstenau 1975). It was hypothesized that under the industrial balling conditions, the pellet surfaces oversaturated with moisture and caused balling to stop. This might indicate an inability of humates to retain moisture inside the pellet structure, which is necessary for successful balling.

A humate based binder with improved ballability was recently developed at Central South University in China. The binder, Funa, is made from caustically treated lignite (Qiu et al 2003a; Qiu et al 2003b; Qiu et al 2004a; Qiu et al 2004b). Its composition is significantly affected by the mined coal fed to the extraction process, and inorganic alumino-silicates make up to 30 % of the binder (Qiu et al 2004b). Han, and Jiang et al., (2012) reported that the inorganic fraction complements the fraction by crosslinking and is necessary for good quality pellets.

Both Funa and bentonite reduced green-ball growth rates at increasing binder doses. (Qiu et al 2004a). However, Funa reduced ball growth more than bentonite, as evidenced by green-ball diameters measured after 20 minutes. Ball diameters with Funa binder were 9 mm, compared to 10 mm with bentonite, both at a 1.5 % dose. The difference was attributed to a larger increase in liquid viscosity in the pellet pores for Funa bonded pellets compared to bentonite bonded pellets. The higher viscosity would slow water transport to the pellet surface, impeding pellet coalescence and growth.

Table 10 Effects of binder addition on the quality of green pellets made with a humate based binder, Funa (Qiu et al 2004a)

Binder	Dose (%)	Wet drop	Compression strength, N/pellet	
			Wet	Dry
None	---	3	11	10
Bentonite	1.5	10	24	40
Funa	1.5	23	23	260

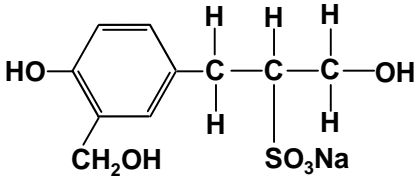


Figure 8 General structure of lignosulfonate monomer. Lignosulfonates are complex polymers consisting of a 6-carbon ring with a 3-carbon tail. Replacing hydrogen are various amounts of $-OH$, $-CH_2OH$ and $-SO_3Na$ groups. (After Hatakeyama and Hatakeyama 2010)

The effects of Funa on wet and dry compressive strengths and wet drop values were also established and compared to bentonite. Pellets were prepared from a magnetite concentrate and agglomerated with 0-2 % binder. Funa bonded pellets were stronger than bentonite bonded pellets in both wet drop and dry compression. However, bentonite performed slightly better in wet compression, as displayed in Table 10 at a dose of 1.5 %.

Funa has not been tested in traditional pellet firing conditions, perhaps because it is unstable above 200-250 °C. Instead, pellets were cured by “cold bonding” and used for DRI production (Qiu et al 2003a). Optimal cold bonding was performed under blowing air (0.8-1 m/s) at 200-250 °C, which resulted in relatively weak cold bonded pellets (268 N/pellet) compared to sintered bentonite bonded pellets (2200 N/pellet). However, the cold bonded pellets had a similar abrasion resistance to the bentonite bonded pellets. The Funa bonded pellets were also more porous which resulted in a higher reducibility. Overall, the cold bonded pellets had better reduction performance than sintered bentonite bonded pellets, but inferior mechanical properties.

Lignin based binders

Lignin is an important natural biopolymer that helps provide bonding and structure in plant tissues. It has been reported that 12-39 % of wood constituents are lignin, which has historically been considered an unwanted product during paper and pulp manufacturing (Hatakeyama and Hatakeyama 2010). During pulp production by the sulfite method, insoluble lignin is made soluble by incorporating SO_3^- groups into the lignin structure (Figure 8) and separated from cellulose. Lignin is then burned for heat or recovered from solution and sold to other industries for use as a binder (e.g. dust suppressants).

While the exact lignosulfonate structure is not known, they are considered to be complex polymers. General features of a lignosulfonate monomer unit include a phenylpropanoid unit (6-carbon aromatic phenyl group with a 3-carbon propene tail) with various amounts of $-OH$, $-CH_2OH$, and $-SO_3Na$ groups substituted onto the side groups. The anionic SO_3^- group makes the binder water soluble while hydrogen and $-OH$ groups lend themselves for hydrogen bonding.

Lignosulfonate binders were tested in the Bureau of Mines organic binder study (Haas et al 1989) and in direct-reduction pellets (Chellan et al 2004). As waste products from wood processing, lignosulfonates have the potential to be relatively cheap. However, these binders introduce sulfur into pellets which can be emitted as SO_x during firing or require higher slag volumes during ironmaking.

Lignobond DP001, a lignosulfonate-based material manufactured by Lignotest SA, was used for agglomeration of magnetite-coal composite pellets for DRI use at a 1 % dose (Chellan et al

2004). Thermal treatments ranged from 500-900 °C. Crushing strengths of pellets +11.2-12.7 mm in diameter were reportedly greater than 22 N/pellet; however, the actual values were not reported.

In the Bureau of Mines study (Haas et al 1989), lignin sulfonates were comparable to bentonite (0.5 %) at significantly reduced doses. At a dose of 0.1 percent, lignin sulfonate bonded pellets met dry strength values of greater than 5 lbs./pellet, but had wet drop numbers just below the target 3.5 drops to failure. The fired strength target of 300 lbs./pellet was not reached until 1250 °C for lignin sulfonate, whereas bentonite surpassed it at 1200 °C. However, lignin sulfonate bonded pellets were more reducible than the bentonite bonded pellets. This could probably be attributed to an increase in pellet porosity, although it was not determined.

Lignosulfonates are naturally hydrophilic and have helped ease agglomeration under difficult circumstances. Coal is a naturally hydrophobic mineral and often agglomerated with hematite and other iron ores as a solid fuel. Lignobond DP001 increased coal wettability in disc pelletizers (Chellan et al 2004) which would reduce large air inclusions in pellets and increase their strengths. Lignosulfonates have also been added to starch binders to reduce the 'tackiness' of pellet surfaces and reduce their growth rates (Dingeman et al 1994).

Dairy waste

Dairy wastes include a number of compounds such as whey and whey permeate, which remain after industrial cheese-making. These are basically composed of simple sugars (lactose), proteins and minerals. The backbone of, lactose, is filled with hydroxyl groups which render the molecule water soluble and adhesive.

Ferretti and Chambers (1979) used a 25 percent lactose solution as a binder for magnetite ore. Pellets produced on an extruder were cured at 300 °C in air, which resulted in an abrasion resistant product (Tumble Index of 1 % - 28 mesh). The reducibility (t_{90}) of these pellets was also favorable.

Haas et al (1989) also tested dairy wastes as a potential organic binder. Pellets produced using lactose whey, and whey permeate had dry and fired strengths in the range produced with bentonite (0.5-1.0 percent); however, pellet moisture and drop strengths were lower. Reducibility improved when using dairy waste, as the t_{90} value decreased from approximately 225 to 180 min.

Drawbacks associated with dairy wastes include easy microbial degradation and rot, and they cannot be stored or shipped easily.

Pulp and papermill sludge

One reported drawback to bentonite is that its transportation to the mine is a significant fraction—approximately 10 percent in 1989—of the overall binder cost (Haas et al 1989). Consequently, in the search for alternative binders, sources nearby iron ore pelletizers have been of interest. Pulp and papermill sludges have been one of those investigated in the past. Pulp and papermill sludges present a low cost, readily available source of wood fibers, clays (such as kaolinite), and inorganic fillers (lime) which can be used to strengthen iron ore pellets.

Haas et al (1989) evaluated sludges from 5 different sources as an iron ore binder. The sludges had a wide range of fiber, colloid, and ash contents, and were added to the concentrate in a variety of physical states. Wet sludge was more effective than dry sludge, perhaps due to poor rehydration of the binder. However, the improved pellet performance using wet sludge was offset by more difficult mixing and/or filtration of the pelletizing feed. In general, pellets with good physical quality were obtained at approximately double the dry-equivalent weight as bentonite.

As expected when using organic binders, metallurgical properties of the sludge-bonded pellets were better than bentonite bonded pellets. Pellet reducibility, R_{40} (reduction rate at 40 pct. reduction, pct/min), was over 30 percent higher using wet sludge as a binder. This may have been explained by the noticeable increase in porosity that occurred when using the paper sludge as binder. Porosity at 1 percent bentonite was approximately 21 pct; the lowest porosity measured for sludge-bonded pellets was approximately 24 pct. However, pellet degradation during reduction, or RDI, was slightly lower than bentonite (1 pct), although it did exceed the minimum target values.

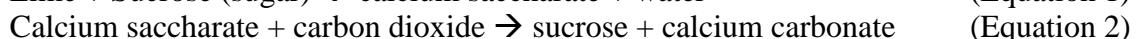
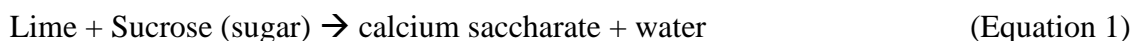
Although not discussed in the paper (Haas et al 1989), using pulp and paper sludge did not significantly reduce gangue levels in the fired pellets. Chemical analyses of silicon and aluminum in fired, sludge-bonded pellets were in the same range as 0.5-1.0 pct bentonite bonded pellets. Pulp and paper sludge contain significant quantities of inorganic minerals and clays, which would remain in the binders after firing. This could also have contributed to increased strengths obtained during firing.

Although positive results were obtained on a lab scale, pulp and papermill sludge proved inferior during pilot scale testing (Goetzman 1989). Major problems reported were the method to fully disperse the binder into the concentrate while keeping moisture at an optimal level, and the inferior quality of fired pellets compared to bentonite. Pulp and papermill sludges also rot quickly and cannot be stored or shipped easily.

Molasses

Molasses is a by-product of the sugar refining process. It consists of the thick solution left after sugar is crystallized out of sugar cane or sugar beet juices (Hebeda, 2001). Major components include sugars unrecovered during processing (30-60 wt %), proteins (<10 wt %) and the various inorganic minerals (<10 wt %) found in the sugar cane or sugar beet crop. The residual nutrition content allows molasses to be used as an animal feed supplement, so it may never be realized as a viable replacement for bentonite.

Molasses is typically used in conjunction with lime, which provides an ample supply of calcium for reaction with sucrose sugar (Equation 1). Calcium reacts with sucrose and forms a calcium-sucrose complex (calcium saccharate), which further reacts with CO_2 from the air to form calcium carbonate and recrystallized sucrose (Equation 2). Essentially, the sugars act as a catalyst during this reaction (Hebeda, 2001; Sah 2010) and form a binding calcium carbonate network.



For full strength development, these binders may be cured for many days, or reacted with concentrated streams of CO₂.

A 3 percent molasses dose was successfully used to pelletize unfluxed iron ore concentrate from the Sokolovsko-Sarbaiskoye Mining-concentration Combine (Tleugabulov 2009). Green pellets were then a) dried and roasted at 1200 °C before metallization, or b) dried and directly metallized at 950 °C. The dried and roasted pellets reportedly had greater mechanical strength and a metallization degree of 0.65-0.7. Unroasted pellets were weaker but nearly completely metallized (0.98). Dried pellet strength from pre-roasted concentrate with a molasses binder was within 10-15 kg/pellet.

Molasses was also used as a binder in conjunction with calcium hydroxide or slaked lime, dextrose and sodium polyacrylate (Sah 2010). Pellets were made in a disc pelletizer using 10 % calcium hydroxide and 5 % molasses. The pellets were then cold bonded by passing CO₂ gas over them for a set period of time. The highest compressive strength using molasses was 299 N/pellet using slaked lime and reaction under CO₂ for 6 minutes. The authors claim this is just below the required 300 N limit for pellets fed to a rotary kiln or hearth. Using dextrin instead of molasses resulted in strength of 357 N/pellet at the same conditions.

Heavy hydrocarbons

Heavy hydrocarbons such as bitumen, naphthalene, and fuel oil have been considered for iron ore pelletization. They are available naturally or as oil and coal refining products and residue. Bitumen is highly viscous, hydrophobic, and may be hard to mix into the concentrate. Consequently, wetting agents may be required for pelletizing when bitumen is used as a binder. Ionic sulfonate groups can be incorporated into the bitumen molecular structure to increase its solubility in water (Suzuki and Gomi 1974).

Bitumen was used as a binder on high purity concentrates for DRI use (Ahier 1981; Ansari 1984). Bitumen was softened at 180 °C and mixed with concentrate in a high energy mixer for 1 hour of mixing and cooling. 5 % bitumen was used; higher doses became too sticky to pelletize. Pellets were hardened at low temperatures to polymerize the bitumen and bake out volatile components. Maximum pellet performance was achieved at 200 °C: 250 kg compression strengths were achieved on 1.27 cm diameter pellets during conventional pelletizing (Ansari 1984); compression strengths over 220 kg were achieved on 6 mm diameter pellets after a double baking treatment (200 °C for 16 hrs followed by 200 °C for 1 or 4 hrs) (Ahier 1981). Critically, the double baking treatment improved pellet strengths over the temperature ranges needed for DRI production.

Earlier studies using bitumen may have not considered fuel oil as a binder due to its sulfur content. However, fuel oil-iron ore composite pellets have been successfully produced using fuel oil as both the binder and reducing agent (El-Geassy 2001). Baharian iron ore and a locally produced heavy oil fraction were mixed and agglomerated into pellets approximately 15 mm in diameter. Fuel oil dosages were kept below 15 % to limit the creation of a “sticky massive product” (El-Geassy 2011) Pellets were cold bonded at 120 °C for 24 hours, but no strengths were reported.

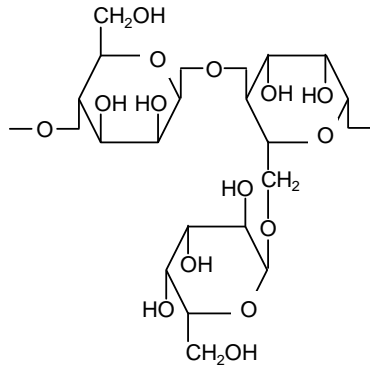


Figure 9 General structure of guar gums (Whistler 1973). Guar gums are mainly composed of high molecular weight polysaccharides, such as is shown here, and proteins.

Guar gum

Guar gums are nonionic, high molecular weight polysaccharides produced from the endosperm of the guar bean. Guar gums form viscous, colloidal dispersions in water, and are composed mainly of starches and protein (Figure 9). A chemical analysis on a typical Jaguar gum showed the polysaccharide component to be 78-82 % and protein 4-5 % of the material (Ogbonlowo 1987). The abundance of hydroxyl groups along the relatively linear guar gum molecule may lead to good adsorption on hydrated oxide surfaces, which is one suggested functions of a binder. Guar gums should be relatively insensitive to varying water chemistry due to their nonionic structure.

Guar gums were effective iron ore pellet binders (Haas et al 1989; Ogbonlowo 1987; Wada and Tsuchiya 1970). In the Bureau of Mines (BOM) study, green pellet properties using 0.1 % guar gum were superior to .5 % bentonite; fired pellets were also sufficiently strong, like most other organics tested. Jaguar gums produced similar quality pellets as the BOM test at 0.1 % doses (Ogbonlowo 1987). However, on average, the guar gums performed poorly in the thermal shock test. Wet pellets were placed for 30 minutes in a preheated muffle furnace at 900 °C; the fraction that survived without fracture was reported as the percent survival.

Dextrin and modified starch

Dextrins are starch derivatives, produced by hydrolyzing starch in acid, or by roasting unmodified starches (Whistler 1973). A wide variety of product solubility and viscosity can be produced, by varying the extent of reaction during decomposition. Similar to other natural gums, the properties can also vary depending on starch source. Corn has proven to be a widely abundant, stable supply of starch and dextrin over the years, and is used in a wide variety of binding applications.

Dextrin was also used for ore-coal composite pellets for sponge iron production (Agrawal 2000; Agrawal 2001). Pellet handling in the plant environment required ~ 30 kg/pellet dry strengths; this was met with a 4 % dextrin dose. Pellets 10-12 mm in diameter were prepared on a disc pelletizer and cured in air for 3-4 days. Varying the -325 mesh fraction increased dry strength up to 50 kg/pellet at 40 % - 325 mesh. Above this value, pellet strength stabilized. Based on these optimized results, plant trials were conducted in an 8 t/day rotary kiln.

Pellets were prepared with 4 % dextrin, and using concentrate sized to 45.6 % -325 mesh. The pellets were air cooled for 4-7 days. Consistent strengths of 35-40 kg/pellet were produced.

The potential for starch to fully replace bentonite as an iron ore binder may be seen by good binding properties, such as its insensitivity to variations in plant water chemistry, and its current use in industry. Approximately 0.1 lb/ton corn starch is added as a partial bentonite replacement at one operating US iron ore pellet plant. However, pellets made solely with starch as binder tend to have sticky surfaces, which results in very rough pellet surfaces (Dingeman and Skagerberg 1991; Dingeman et al 1994), as well as exhibit very high growth rates. Rough surfaces would lead to high dusting rates in kilns and abrasion during pellet transport and handling, which are undesired. Both observations suggest starch alone is not capable of 'holding' water inside the pellet structure, and this problem has been corrected by additions of other gums or water soluble polymers (Dingeman and Skagerberg 1991; Dingeman and Skagerberg 1994).

Pellet consumption by blast furnace or direct-reduction processes

Historically, the majority of iron ore pellets have been consumed by blast furnaces. Consequently, iron ore pellets made with organic binders have had to meet the stringent physical and metallurgical specifications required by this process, such as compression strengths exceeding 400 lbs/pellet and tumbler indices of +95 % > 6.3 mm.

The production of iron ore pellets using organic binders are now often reported for use in direct reduction ironmaking processes (Agrawal et al 2000; Agrawal et al 2001; Chellan et al 2004; Qiu et al 2003a). Pellet burden fed to direct reduction processes should have high iron and low impurity contents. Consequently, iron units fed to direct reduction now consist almost entirely of pellets produced from upgraded ores.

Organic binders may be ideally suited to the production of DRI pellets, again depending on furnace design (such as in rotary hearth furnaces) and process requirements. For example, pellets fed to rotary hearth processes may not be hot-fired in the traditional sense ($T > 1200-1300\text{ }^{\circ}\text{C}$), suggesting that pellets do not need to be as physically strong as blast furnace pellets. Instead, pellets are "cold-bonded". During cold-bonding, pellets are cured at lower temperatures or reacted with gases (such as CO_2) to produce a stable, structurally sound pellet that meets process requirements.

Conversely, certain DR shaft furnace designs require more stringent pellet strengths as coke does not mechanically support the burden like in blast furnaces (Agrawal and Oshnock, 1995). As DRI production continues to increase in the future (Figure 10), organic binders may become more prevalent. The quality requirements for each direct reduction process should be reviewed and made available.

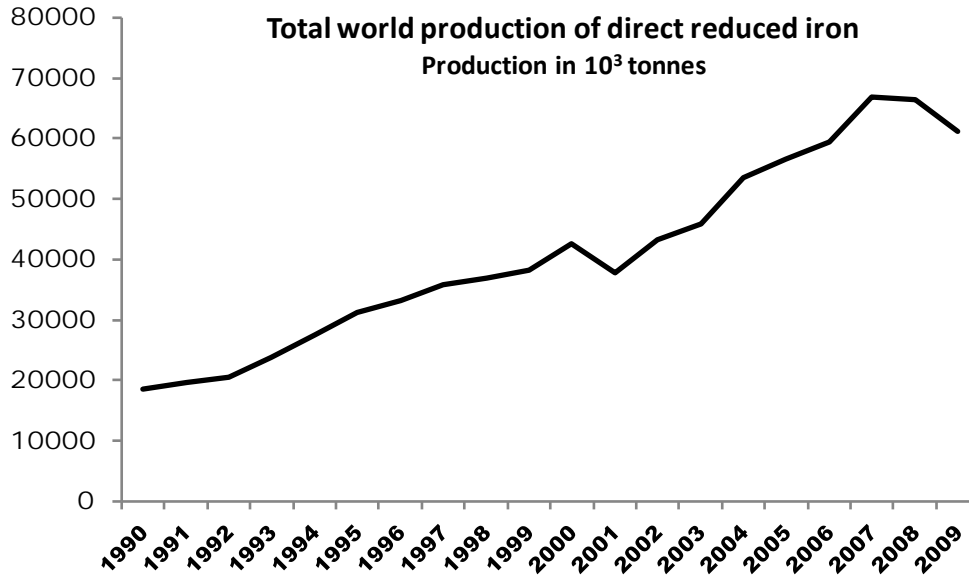


Figure 10 Total world production of direct reduced iron, 10³ metric tons (World Steel Association 2011). Total DRI production has increased approximately 6.5 percent per year since at least the early 1990's.

Conclusions

Organic binders affect the entire iron ore agglomeration process: adding natural or synthetic polymers helps control moisture contents in pellets, aids ballability, and binds fine ore particles together before heat hardening is completed during induration. Bentonite has historically performed these functions well and it still dominates binder consumption in the US; however, it adds additional silica and alumina to the finished pellets, which may or may not be desired by iron ore pellet consumers (e.g. blast furnaces and direct reduction ironmaking processes). Hence, research into appropriately designed organic binders continues.

“Successful” organic binders have typically been water soluble gums or crosslinked polymers which can absorb water and increase the viscosity of pellet moisture at small doses, and form adhesive films on drying. On an industrial scale, these functions have been met with sodium carboxymethylcellulose binders, copolymers of acrylamide and sodium acrylate, and corn starch. Sodium humates with a high content of inorganic minerals have also been reported to be a good binder for industrial cold-bonding.

In general, using organic binders has resulted in poor physical quality of preheated and fired pellets. This problem has been addressed by 1) adding dispersants to organic binders to control the distribution of ultrafine pellet particles; 2) adding low melting temperature slag-forming minerals to the agglomeration feed; and 3) adjusting pellet firing conditions. Benefits obtained with any particular additives should be weighed against any detrimental effects seen in downstream ironmaking operations.

Iron ore pellets produced with organic binders are now commonly reported for use in direct reduction processes. These pellets have not been fired at exceedingly high temperatures,

suggesting process physical requirements are not as stringent in certain furnace designs. Organic binders are chemically suited for DRI pellets due to their low content of impurities. The quality requirements for each direct reduction process should be reviewed and made available.

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