CHAPTER 11.1

Pretreatment for Pyrometallurgy

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This chapter covers the various pretreatments used to prepare mineral concentrates and direct-shipping ores so that they are suitable feed for smelting operations. These pretreatments are necessary to ensure that the smelter feed can be handled easily, has the proper chemical composition, and has the correct physical form to behave well in the smelting operation. These properties will vary depending on the smelting operation. Specifically, blast furnaces require feed particles that are large enough not to be entrained in the airstream and blown out of the furnace, while providing enough bed permeability that the reducing gases can flow through easily (Poveromo 1999). At the other extreme, flash smelting furnaces require a dry, free-flowing material with particles small enough to react quickly with the furnace gases.

Mineral concentrates are typically moist powders, and consist of specific minerals that may contain chemically bound volatiles such as carbon dioxide (CO_2) or water. The basic operations that are used to prepare the concentrates for smelting are those that remove volatiles and adjust the particle size and particle chemistry. These processes are

- Drying and calcination,
- Precombination with reductants and fluxes, and
- Agglomeration and other processes that alter physical properties.

CALCINATION

Calcination processes consist of heating minerals to decompose them into a gas phase and a solid phase. The most common applications of calcination are heating of hydrates to drive off water, and heating of carbonate minerals to drive off carbon dioxide.

Chemically Bound Water

A wide range of minerals contain water of hydration, with water included in their crystal structure. Removing this water requires higher temperatures than simple removal of surface water, which evaporates fully at only 100°C. Examples of common minerals that contain chemically bound water are gypsum ($CaSO_4 \cdot 2H_2O$) and goethite (FeO-OH, which is a composition equivalent to $Fe_2O_3 \cdot H_2O$), along with many others. Removal of this water requires heating and results in changes in the crystalline structure of the mineral. The products from removal of chemically bound water tend to be either powders or highly porous solids.

Carbon Dioxide

Carbonate minerals contain the CO_3^{-2} anion as part of their crystalline structure. Prominent examples are $CaCO_3$, $CaMg(CO_3)_2$, and $FeCO_3$, among many others. Upon heating, these carbonates decompose to their corresponding oxides, releasing CO_2 gas. The decomposition temperature is highly variable, with some carbonates decomposing at a few hundred degrees whereas others (such as $CaCO_3$) require temperatures above 900°C.

Other Volatile Components

Ore concentrates may also contain volatile organics, either natural or added in the course of processing. Many of these can be removed by simple vaporization, although in an oxidizing atmosphere some will partially combust, leaving a carbonaceous residue that will need to be burned away to remove it.

BLENDING AND FLUXING

If the concentrate is to be sent to a smelting operation, it is often beneficial to pre-blend it with components that will be necessary reactants in the smelter. By pre-blending, it is possible to achieve better contact of the ore with its reactants, resulting in more complete reactions and shorter reaction times.

Fluxes

Fluxes are materials that will improve melting of gangue minerals and removal of impurities during smelting. The most common of these are CaO and MgO, which are readily available from the minerals limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Because limestone and dolomite are insoluble, they can be ground and combined with the mineral concentrate slurry before the slurry is filtered, which provides

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uniform blending with the ore (Malysheva and Chemyshev 1974; Roorda et al. 1981; Abouzeid et al. 1985; Bleifuss and Goetzman 1991). When the ore concentrate is then either heated to fire pellets, or smelted, the carbonate minerals decompose to their oxides, which then react with the silica and alumina gangue to produce slags with sufficiently low melting points to be practical. One issue to be careful of is that these minerals can reduce filtration rates by changing the surface chemistry of the mineral particles, so a mineral concentration plant that is filtration limited may have much reduced capacity when it adds flux to its concentrate slurry before filtration.

Integral Reductants

When the mineral concentrate is an oxidized form that needs to be reduced to metal, it can be helpful to combine the ore with a solid reductant (Goksel et al. 1987). In the case of iron oxides, carbonaceous reductants combined directly with the ore concentrate reduce the time taken for reduction to only 10–15 minutes, compared to several hours using gaseous reductants such as CO. The reason for the more rapid reduction with the combined reductant is that the carbonaceous solids are already where they are needed, and they do not need to diffuse in from the gas phase. If a mixture of ore concentrate and reductant is formed into pellets and heated, the pellets will self-reduce to produce metal and gases, even in an oxidizing atmosphere, because the reducing gases produced inside the pellet flow outward, preventing oxygen from entering the pellet.

Most work using integral reductants uses either coal or coke breeze, which are nearly pure carbon, low-cost, and stable in contact with moisture. Many other organics that are not essentially pure carbon will also perform well, including starches, flour, agricultural by-products like sugarbeet pulp and bagasse, molasses, wood pulp, plastics, and a broad spectrum of similar substances. These other materials will begin to decompose at lower temperatures than coke breeze, which can lead to more rapid reduction of the metal oxide in the pellet. Many of them are also capable of acting as binders, which makes them very useful additives if the ore concentrate is to be pelletized or briquetted. They can also generate volatile organic acids and soot, which must be considered in the construction of smelters using such materials as reductants.

Although there are advantages of including integral reductants in pellets produced for smelter feed, it can sometimes be a problem to accomplish this. Many pelletization processes depend on heating the pellets to harden them, and during the heating any integral reductant will burn away before it ever has a chance to contribute to reduction in the smelter. Use of reductants to make self-reducing pellets therefore depends on the use of a cold-bonding process to harden the pellets, rather than high-temperature hardening.

AGGLOMERATION

Agglomeration processes form fine particulates into larger shapes, and then bind them together to give the agglomerates sufficient mechanical strength that they can be handled and processed. These shapes can be spherical balls, cylinders, briquettes, or random-shaped masses, depending on the processes used to produce them. The bonding can be due to addition of specific binders to hold the fine particles together inside the agglomerates, or due to thermal treatments that cause the particles to sinter and fuse together (Poveromo 1999).

Sinter and Nodule Plants

Sinter plants produce agglomerates by heating the fine particles sufficiently that they fuse together, and no supplemental binder is used. These are primarily used for iron oxide concentrates that consist of particles of about a few millimeters in diameter. The particles to be sintered are combined with a solid fuel (typically coal or coke breeze) and placed on a heat-resistant traveling grate while drawing air down through the particle bed. The bed of particles is then ignited on the surface, causing it to burn at a temperature of approximately 1,300–1,480°C. As the bed of particles is carried along by the traveling grate, the flame front travels down through the bed, progressively sintering it throughout its entire depth. After the fuel burns out, the resulting fused, porous material is cooled and screened into appropriate sizes for use as furnace feed, typically 25 mm × 6 mm. Agglomerates larger than this can be crushed to size, and fines can be recirculated back through the process.

The sinter product is subject to abrasion and breakage during handling, so sinter plants are typically located very close to the furnaces that they feed. In addition to agglomerating ores, they are also used for recycling in-house fines such as furnace dusts and mill scale. It is difficult to run a sinter plant without leakage of combustion gases, so they are not favored in areas where emissions regulations are stringent.

Nodulizing is similar to sintering in that it does not require the addition of binders, but it differs in that the concentrate is not directly combined with a fuel. In a nodulizing plant, fine concentrate is fed to a rotary kiln that is operated at a sufficiently high temperature that portions of the fines are beginning to melt.

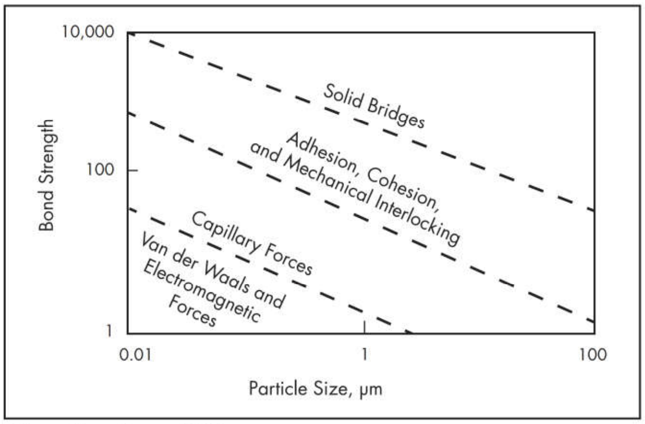
As the charge is tumbled in the kiln, it rolls into roughly spherical nodules that are bonded together by the molten portion of the fines. After the nodules exit the kiln, they are very durable and high strength. The process has the advantage of being largely insensitive to feed variables such as moisture content and particle size. However, it also has the disadvantages of high fuel consumption, difficulty in preventing the formation of "rings" of sintered material adhering inside the kiln, nonuniform nodule size, and low nodule porosity leading to poor reducibility. As a result, nodulization has fallen out of general use.

Pelletization

Pelletization is a two-step process, where the fine particles are first agglomerated by rolling them into a "green ball" that is held together by moisture and a binder material. The green balls are then hardened in a second step, usually by drying and heating sufficiently for the individual particles in the ball to sinter together. The resulting pellets are uniform in size, durable, and sufficiently porous to be easily smelted (Sastry and Fuerstenau 1972; Abouzeid et al. 1979).

The particles making up pellets are held together by capillary forces, adhesional and cohesional forces, electrostatic and van der Waals forces, and mechanical interlocking of grains. The relative strengths of these forces are shown in Figure 1. Note that the bonding strength increases as the particle size decreases, due to the increased particle surface available over which bonding can occur (Stone and Cahn 1968).

Different forces dominate at different points in the pelletization process. Freshly made wet pellets are primarily bonded together by capillary forces, with small contributions by van der Waals and electrostatic forces. After the pellets are



Adapted from Sastry 1996a

Figure 1 Relative strengths of different bonding mechanisms as a function of particle size

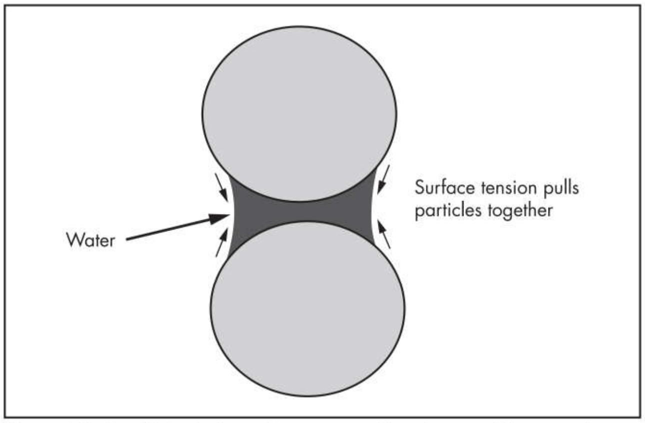


Figure 2 Particles being drawn together by capillary action

dried, the loss of moisture eliminates the water responsible for the capillary forces, and if the pellets are to hold together, the water is replaced by adhesional and cohesional forces from the binder. In the case of certain cold-bonding binders, the particles can also be held together by covalent bonds that result from chemical reactions. Firing of pellets forms solid bridges between mineral grains, giving the maximum strength. Mechanical interlocking is usually not significant unless the pellets are composed of ductile particles, and the pellets are compressed with sufficient force for the particles to deform around one another and lock together.

For pelletization to be successful, the feed ore must (1) have a sufficiently fine particle size distribution; (2) be moist enough that the individual mineral grains can stick together into pellets, but not be so moist that the ore becomes "muddy"; and (3) contain a binder to hold the pellet together during the period between drying and final hardening.

Binders

The availability of a suitable binder is key to making the pelletization process work. It is possible to form green balls using only water to bind the balls together, with the surface tension of the water drawing the mineral grains together as shown in Figure 2. This occurs when there is enough water present to bridge between particles, but not so much that the pore space is entirely filled with water, which, depending on the size distribution of the ore, typically occurs at approximately 9%–12% moisture by weight. However, the pellets must be dried before they are fed to a pyrometallurgical process, and it is necessary to have a non-evaporating binder to keep the balls from immediately falling apart again after they are dried. Binders also help to make the moist ore more plastic than it would be otherwise, resulting in more uniform and controllable pellet growth. Many different binders are possible, depending on the nature of the material being pelletized and the desired final pellet properties.

Binders can be classified into five groups, based on their mechanism of action (Holley 1982):

1. **Inactive film.** The binder is an adhesive material that adheres to the mineral grain surfaces and binds them together through capillary forces, adhesional forces, and cohesional forces. Green pellets bonded with inactive film binders can be broken up and re-agglomerated because the binding action is reversible.
2. **Chemical film.** The binder film undergoes an irreversible chemical reaction on the particle surfaces, causing the pellet to harden.
3. **Inactive matrix.** The binder is added at a high enough dosage that it forms a continuous matrix that the particles are embedded in. The binder is a material such as tar, pitch, or wax that is either made into a fluid emulsion in water, or heated enough to make it fluid. It then hardens upon drying or cooling. The high viscosity of the binder may require high compaction forces to form the pellets.
4. **Chemical matrix.** Similar to the inactive matrix, except that the hardening of the binder is an irreversible chemical reaction, such as the hardening of portland cement.
5. **Chemical reaction.** The binder and mineral particles undergo a chemical reaction to bond very strongly together. This could include dissolution and recrystallization of the mineral particles.

In most cases, ore pelletization uses film binders because they are used at low dosages. They may be inactive films such as clays or organic binders, or active films such as cements, as shown in Figure 3.

Bentonite. Bentonite clay is the most widely used binder for ore concentrate pelletization, due to its ease of handling, effectiveness at low dosages, low cost, and ability to continue acting as a binder all the way up to sintering temperatures. It is normally used as an inactive film type of binder. Bentonites are primarily composed of the clay mineral montmorillonite, which consists of aluminosilicate layers with a net negative charge, held together by exchangeable cations between the layers. There are two primary types of bentonite: sodium bentonites, where the exchangeable interlayer cations are mainly Na^+ ions; and calcium bentonites, where the interlayer cations are Ca^{2+} ions (Grim 1968). Clays other than bentonite can be used, although they are somewhat less effective due to their lesser swelling ability in water (Ehrlinger et al. 1966; Haas et al. 1987).

Sodium bentonites have a very high water-absorption capacity, because the monovalent sodium ions are readily solvated by water molecules. This allows water to be drawn between the layers, with the clay absorbing as much as 900% of its weight in water. Calcium bentonites have much lower water absorption capacity, as illustrated in Figure 4. The

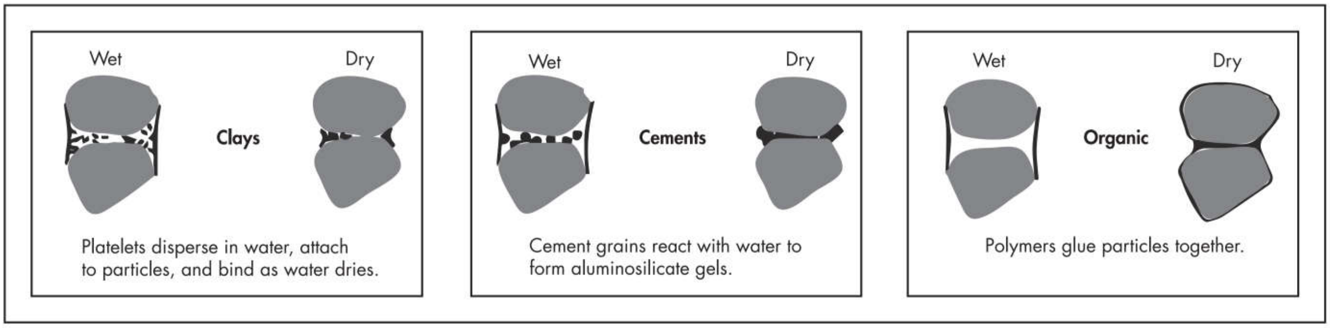


Figure 3 Binding of mineral particles by binders of different types

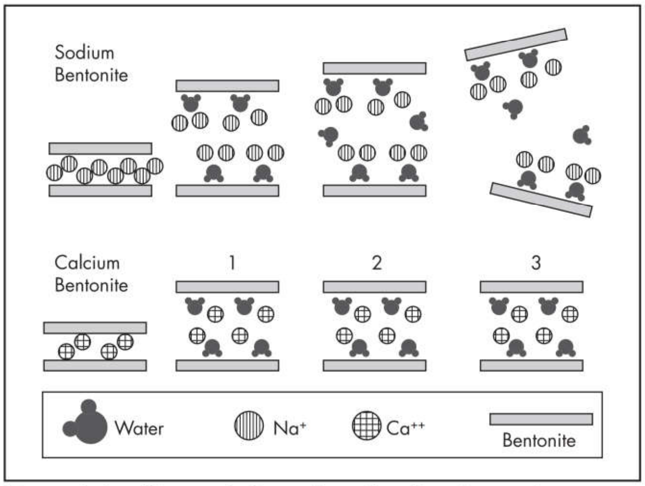


Figure 4 Swelling and dispersion of sodium bentonite versus calcium bentonite

divalent calcium ions bond more strongly than the monovalent sodium ions; therefore, the calcium bentonite does not hydrate as readily and has much less water absorption capacity.

The expansion of the bentonite allows the clay platelets to be spread over the surface of the particles being bonded. The platelets then bridge between the particles. The effectiveness of the binder can be enhanced by altering the mixing conditions. For example, Figure 5 shows glass beads bonded by bentonite. In Figure 5A, the beads and bentonite were combined using a conventional mixer, whereas the material in Figure 5B was mixed by passing it between a set of compression rolls 20 times. The compressive shear mixing used to produce sample B clearly spread the bentonite much more thoroughly over the surfaces of the particles being bonded. This improvement in mixing approximately doubles the green pellet strength produced by the bentonite at any given dosage (Kawatra and Ripke 2001, 2002).

Bentonite has several applications other than as a binder for mineral agglomerates, so many different tests for measuring the quality were developed for each of these applications. These tests that may be reported by bentonite suppliers include the following:

- Batch balling
- Enslin water absorption
- Alumina plate water absorption
- Grit content
- Moisture content
- Size distribution
- Marsh funnel
- Gel strength
- Colloid content
- Chemical analysis
- Methylene blue uptake
- Free swelling
- Exchangeable cations by atomic absorption spectroscopy
- Glycolated layer expansion

Not all of these tests are relevant to mineral agglomeration, as many of them relate to the use of bentonite in moisture absorption, gelling, and water purification applications. Further details on these tests are provided elsewhere (Eisele and Kawatra 2003).

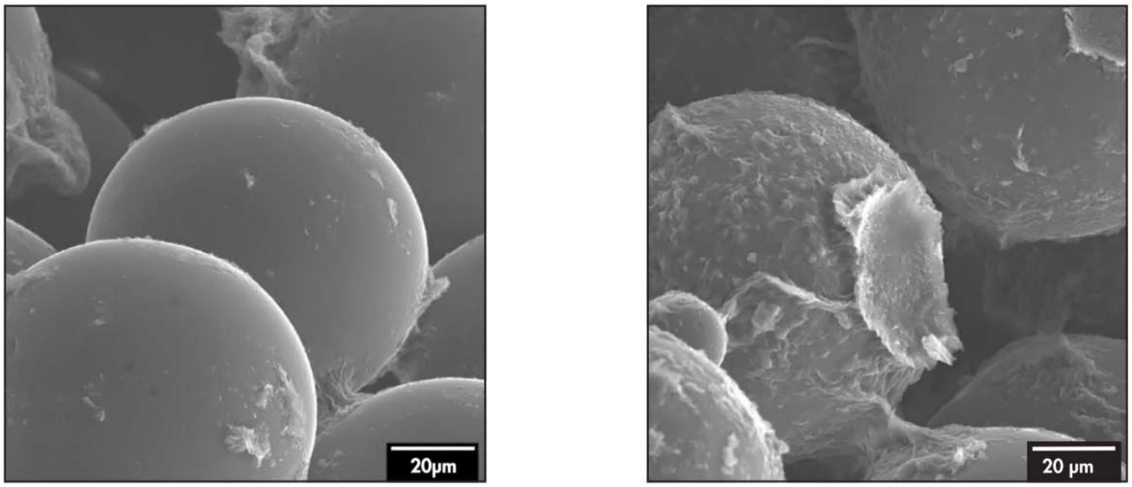
The most useful test for evaluating the value of bentonite as a binder is the batch balling test, where the bentonite is actually used to make pellets using the exact mineral that is to be agglomerated. The procedure for batch balling has never been fully standardized, so each ore producer typically uses its own ore concentrate, apparatus, and specific procedures, which makes it difficult to compare bentonite performance between different laboratories. The most nearly standardized procedure is that developed by the Bentonite Users Committee (1982a, 1982b), which is as follows.

Equipment

- A 600-6 airplane tire (40.6 cm diameter × 15.24 cm wide), mounted to rotate at 52 rpm, with access to one side for adding feed mix and removing pellets
- Model no. 1, Cincinnati Muller, 30.48 cm diameter
- Screens: 4.75 mm, 3.35 mm, 13.2 mm, 12.5 mm, and either 2.0 mm or 1.7 mm
- Spray bottle filled with distilled water
- Balance accurate to 0.1 g, with 3-kg capacity
- Scoop for removing balls from tire
- Airtight, moisture-resistant containers for seeds and balls

Materials

- At least 2,500 g of mineral to be agglomerated (dry weight). This should be at the appropriate moisture content for pelletization, which varies from 8.5% moisture to 12% moisture depending on particle size distribution and mineralogy.
- Dry, powdered bentonite, in sufficient quantity to reach the desired dosage in the material to be agglomerated. For iron ores, a typical dosage is near 0.5%–0.66% bentonite by weight.



A. 0 Passes

B. 20 Passes

Source: Kawatra and Ripke 2001

Figure 5 Effect of compressive shear mixing using compression rolls on the distribution of bentonite over glass bead surfaces

Procedure

- Weigh out the appropriate amount of bentonite for the quantity of ore being agglomerated.
- Spread the concentrate uniformly in the muller, and distribute the bentonite uniformly over the top of the concentrate.
- Mix for 3 minutes. If the mix is clearly too dry, additional water can be slowly added ahead of the muller wheel after 1 minute of mixing.
- Remove material from the muller, and force through either 2.0-mm or 1.7-mm screen to delump the material.
- Start the balling tire rotating, and take approximately 700 g of the ore/bentonite/water feed mixture to use to produce seeds. Add a small amount of the feed mixture, spraying lightly with water to start seed formation.
- When the top size of the seeds approaches 4.75 mm, use the scoop to remove the seeds from the tire, and screen them at 4.75 mm and 3.35 mm. Discard the +4.75-mm material, save the 4.75 × 3.35-mm seeds in a sealed container, and return the –3.35-mm material to the balling tire. Resume adding feed mixture and spraying with water, and repeat the screening procedure until approximately 34 g of seeds have been produced.
- Return the 34 g of 4.75 × 3.35-mm seeds to the balling tire, and slowly add more feed mixture over a 6-minute period, spraying water as needed to cause the seeds to enlarge into pellets. When the pellets approach the target size, remove the pellets and screen them at 13.2 mm and 12.5 mm. Discard the +13.2-mm material, retain the 13.2 × 12.5-mm balls for testing, and if additional balls are needed, return the –12.5-mm balls to add additional feed mixture and enlarge them to the target size.

Pellets produced using this procedure can then be tested as green pellets, or dried and fired for additional tests as appropriate.

Bentonite is an extremely popular binder due to its acceptable cost, availability, and effectiveness. The primary limitation to its use is the silica content, as a typical bentonite is approximately 35% SiO_2. After processing the ore concentrates to remove silica, it is somewhat counterproductive to then re-add silica as a component of the bentonite. Much of the interest in replacing bentonite as a binder is therefore to use a binder that is at least lower in silica, or even entirely free of it.

Other inorganic binders. Inorganics other than bentonite clay that can potentially be used as binders include sodium hydroxide, potassium hydroxide, soluble salts, portland cement, lime, calcium carbonate, magnesia, and sodium silicate. Only a few of these have been used industrially for ore concentrate agglomeration, due to issues with cost, contamination, and low strength. Most do not have performance as good as bentonite clay. The inorganic binders that have been used are primarily portland cement, lime, and calcium carbonate.

Portland cement. Portland cement is primarily used for cold-bonding applications, where it is intended to form pellets that reach high strength at room temperature (Dutta et al. 1992, 1997; Go and Tate 1982; Iyengar et al. 1968). It is most effective as an "active matrix" binder, where it forms a continuous matrix bonding the mineral grains together. This requires a dosage of approximately 10% portland cement by weight, with sufficient moisture for the cement to chemically react with the moisture and harden. Cement has been used in the Grancold and COBO processes for forming iron ore pellets. The Grancold process formed wet pellets that were bedded in loose iron ore concentrate powder for 3–6 days to prevent them from sticking together while hardening. The pellets were then stockpiled for an additional 30 days to reach a high enough strength for processing (Svensson 1969). Although the pellets produced were reported to be adequately fluxed by the lime in the cement and to have good reduction properties, the long curing time made it uncompetitive (Linder and Thulin 1973). The COBO process used steam curing to accelerate the hardening, but the added cost of the steam made this process uncompetitive as well (Doughty 1975).

Lime. Lime can be used alone as a binder, as it will hydrate in water and bond mineral particles together (De Souza 1976). This action is enhanced if silica is present, as lime and silica will react in the presence of water to form calcium hydrosilicates. This can make use of the silica gangue already present in the ore concentrate, and therefore does not necessarily add more silica. If the natural silica is not sufficiently reactive, it is possible to add pozzolanic materials such as coal fly ash to react with the lime, producing a material very similar to portland cement (Eisele et al. 1998a, 1998b).

The process can be considerably accelerated by operating under hydrothermal conditions. The basic process is to combine ore concentrate, CaO, sufficient water for pelletizing, and any other additives desired in the pellet. After the green pellets are formed, they are autoclaved for 1–2 hours in 2,070 kPa steam at approximately 200°C to develop the amorphous calcium hydrosilicates (Goksel et al. 1987) The disadvantage of this approach is the need to convey pellets into and out of a pressurized autoclave, which adds considerable process complexity and cost.

Calcium carbonate binder. Calcium hydroxide reacts with carbon dioxide to form calcium carbonate, which is stable up to approximately 900°C. If ore is combined with approximately 7.5% calcium hydroxide, along with sufficient water to make the material adhesive, it can be pelletized using standard equipment. The pellets are then treated with CO_2 gas, so that the carbonation reaction can proceed:

$$Ca(OH)_2 + CO_2 * CaCO_3 + H_2O$$

Although this produces pellets with compressive strengths in the range of 200–500 lb/pellet, it has not been widely pursued industrially because of the cost of the CO_2 treatment and the need for producing large quantities of calcium hydroxide.

Organic binders. A broad range of organic materials exist that are sufficiently "sticky" that they have been at least considered as ore binders. Those that were reported as having been tested for this application are listed in Table 1.

Table 1 Organic materials that have been tested as binders for ore pelletization

Paper by-products • Hemicellulose • Caustic leonardite • Naphthalene sulfonate • Lignin sulfonates	Dairy wastes • Lactose • Whey permeate • Whey	Starches • Alkalized • Nongelled • Gelled
Cellulose derivatives • Carboxymethyl cellulose • Hydroxyethyl cellulose • Carboxyhydroxyethylcellulose	Starch/acrylic • Guar gums	Natural gums • Guar gums • Xanthan gums
Tars	Molasses	Humic acids
Bitumens	Ethylene oxide	Sawdust/wood flour
Polyacrylamides	Polyvinyl alcohol	Peat moss

Although using low-cost organics such as dairy wastes, molasses, or paper by-products as binders is very attractive, in general their usefulness is limited both by difficulty in transporting and storing them without rotting, and by their generally poor performance compared to purpose-manufactured binders. As a result, ore pelletization with organic binders has been limited to only a few products. The organic binders that have been commercialized are the Alcotac series (Ciba Specialty Chemicals), which are acrylic copolymers, and the Peridur series (AkzoNobel), which are cellulose derivatives (Kortman et al. 1987).

The primary advantage of organic binders is that they do not contribute silica to the finished pellet, making it easier to meet the product silica specification and increasing plant productivity. They are also reported to produce more uniform pellets that are less likely to spall during preheating. Some of these binders can also be added at considerably lower dosage than bentonite while still achieving comparable strength. For example, Peridur at a dosage of 0.1 wt % gives the same pellet dry compressive strength as bentonite at 0.5 wt %. This is largely offset by the higher cost of the organic binders compared to bentonite.

A serious problem with organic binders is the fact that, when the green pellets are heated to harden them, organic binder ignites and burns away starting at approximately 250°C, whereas ores such as magnetite do not begin to oxidize and recrystallize to form interparticle bonds until over 600°C. Other ores, such as hematite, require even higher temperatures to bond together, over 1,100°C. As a result, organic binders are not able to hold pellets together over most of the temperature range during preheating. This causes pellets to be excessively fragile, leading to high levels of dust production and pellet breakage.

There are options for reducing the problems with binders burning away during preheating. One is to increase the ignition temperature of the binder. Unfortunately, carbon compounds are not sufficiently stable in oxidizing environments, and will need significant advances in technology to find a "backbone" molecule that will outperform the existing molecular structures. Another option is to use "straight-grate" firing kilns that handle pellets more gently than the more common "grate-kiln" systems. The downside of this is that straight-grate firing has more issues with mechanical reliability and variation in pellets quality than the grate-kiln systems do.

Binder blends. The most promising approach to reducing the thermal stability issues with organic binders is to blend them with inorganic additives. These additives may be binders such as bentonite or lime, or may be compounds that are not binders by themselves but that melt or react with the ore particles to bond them together while the organic portion burns away.

AkzoNobel experimented with sodium tetraborate as a "pellet strengthener" additive for Peridur binder. When added at a rate of 4 parts sodium tetraborate/1 part Peridur, the pellet quality during preheating increased markedly, due to the ability of the sodium tetraborate to melt at a moderately low temperature (743°C). More recently, calcined colemanite ($Ca_2B_6O_{11}$) in combination with carboxymethylcellulose binder has given pellet strengths at 1,000°C that are comparable to the strengths using bentonite, and roughly twice the strength achieved using organic binders alone (Sivrikaya et al. 2013).

Funa, an organic binder produced by alkali extraction of humic acids from coal (Qiu et al. 2003), is considered a blend of organic and inorganic materials, since it contains approximately 40%–50% humic acid and 20%–25% inorganics such as silica, alumina, calcium salts, and iron salts. These inorganic components remain after the humic acid portion burns away, and as a result the Funa binder has excellent high-temperature performance. Because it is more hydrophobic than bentonite, the pelletization performance with Funa binder is reported to be very different, with slower pellet growth rate than when bentonite or other organic binders are used.

Bentonite can also be combined with organic binders such as starch, where the starch reduces the quantity of bentonite needed to produce satisfactory pellet strengths while the bentonite provides strength to the pellet during heating. This combination has occasionally been used on an industrial scale. In most cases the performance improvement has not been considered sufficient to warrant the added complexity.

In some cases, binders must not be blended because their modes of action are fundamentally incompatible. For example, lime cannot be combined with bentonite because the lime is a cementitious binder that works by reacting calcium hydroxide with silicates (Ripke and Kawatra 2000). The effectiveness of bentonite as a binder depends on its ability to absorb moisture and expand, and this ability depends on it having sodium ions present as its exchangeable cations. The calcium from lime displaces the sodium from the bentonite, converting it into the much less effective calcium bentonite. As a result of this phenomenon, experiments combining bentonite with a lime-based binder showed that the performance of the blended binder was dramatically worse than either the bentonite or the lime-based binder alone.

Balling Devices and Operations

The two most common types of pelletization devices are balling disks and balling drums. A balling disk consists of a shallow pan, tilted at an angle from the vertical, and rotating around its axis, as shown in Figure 6.

Moistened feed and binder are added to the angled, rotating pan. As the pan rotates, the forming pellets roll over the fresh feed, layering material on their surfaces and growing. Material that is not picked up by a rolling pellet is scraped off of the pan surface, producing more "seed" pellets. The forming pellets sort themselves by size, with the largest pellets rising to the top, so the pellets of the finished size discharge over the edge of the disk. The pellet size is adjusted by varying the feed rate.

A balling drum consists of a sloping cylindrical drum rotating around its long axis, with feed and recirculated pellets entering the uphill end and pellets discharging onto a screen at the downhill end, as shown schematically in Figure 7. Unlike the disk pelletizer, the screen in the drum pelletizer circuit provides positive control of pellet size. These are normally operated with a significant circulating load, with pellets passing through the drum two to three times before reaching the finished pellet size.

The formation of pellets from fine particles proceeds through three mechanisms, as shown in Figure 8. During nucleation, individual particles adhere together to form "seed" pellets a few millimeters in diameter. These seeds are large enough to begin rolling in the pelletizer. As they roll, they can coalesce with other, similarly sized pellets merging into a single pellet, which leads to a rapid increase in size while reducing the number of pellets present. Or, they can accumulate layers of unagglomerated fines onto their surfaces, which leads to slow, steady growth in size while keeping the number of pellets constant. During continuous operation of a pelletizer, all three of these mechanisms proceed simultaneously (Sastry and Fuerstenau 1972; Sastry 1996a, 1996b).

The forces compacting the individual grains into the pellets depend on the pellet mass and the size of the contact point between the pellet and the material being picked up. For example, consider the growing pellet shown in Figure 9. If we assume the mass of the pellet is 1 g, and the ore grain being picked up is 25 μm in diameter, then the entire weight of the pellet is being supported by the cross section of the 25-μm grain, which is equal to $n(0.0025/2)^2 = 4.91 \times 10^{-6}$ cm^2. The force exerted by the weight of the 1 g pellet is equal to its mass multiplied by gravitational acceleration, which is $0.001(9.81) = 0.00981$ N. The pressure exerted by the pellet on the ore grain is $0.00981/(4.91 \times 10^{-6}) = 1{,}998$ N/cm^2, which is equal to 19,980 kPa. Although the actual pressures developed are likely to be lower than this value, clearly the pressure can nevertheless be quite high. The high point pressures developed lead to a firm, well-compacted final pellet.

Green Ball Quality Determination

The quality of pellets for firing depends on their ability to survive the handling and drying process while they are transported from the pelletizing device to the kiln. The three primary quality tests are shown in Table 2 (ASTM 1997). The virtue of these tests is that they can be performed very quickly and are therefore useful for quality control.

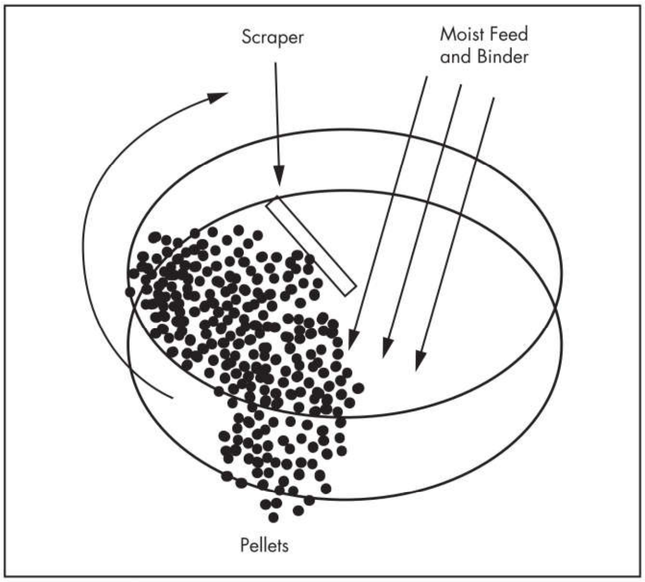


Figure 6 Disk pelletizer

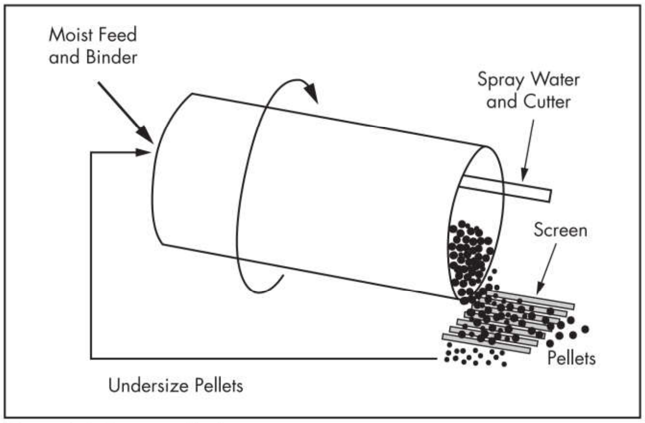


Figure 7 Drum pelletizer

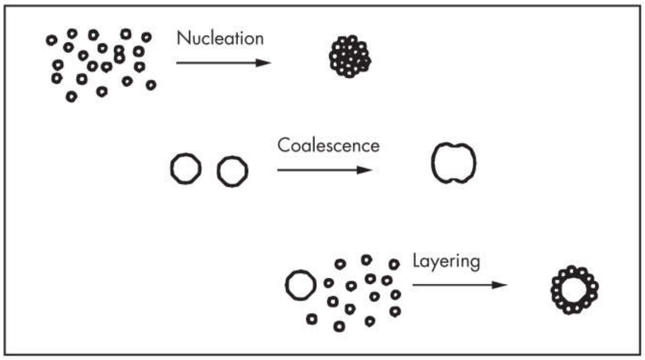


Figure 8 Pellet growth mechanisms

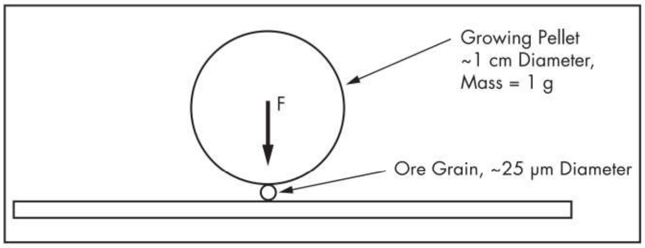


Figure 9 Estimation of compaction pressure during formation of a rolled pellet

Pellet Firing

The moist green pellets are primarily held together by capillary forces and typically have crushing strengths of about 10–15 N/pellet. This is not strong enough for handling and processing, which typically require strengths of about 1,800 N/pellet or higher. To achieve these strengths, the pellets are normally heated sufficiently that the mineral grains recrystallize and sinter together. This heating process must be carried out using appropriate heating rates to fully develop the final pellet strength.

Drying. The drying stage removes the moisture from the pellet. This must be done slowly so that the water vapor can escape without developing high internal steam pressure that can cause the pellets to spall their surfaces or explode. The drying stage is carried out on a moving grate and takes approximately 4 minutes.

Preheating. The preheating stage brings the pellet temperature up to the point where sintering can begin to occur. If there are carbonate minerals present, such as siderite, ankerite, dolomite, or calcite, the preheating stage will also calcine them to drive off their chemically bound CO_2. During the preheating stage, the pellet strength is entirely due to the binder, since water has already been evaporated and sintering has not yet begun. The preheating stage typically takes approximately 3 minutes.

Sintering. Pellets begin to sinter at approximately 930°C and are heated to 1,260°C for full sintering. If the ore is a mineral that can be oxidized, such as magnetite (Fe_3O_4), it will fully oxidize during the sintering step.

Sintering requires approximately 3 minutes to allow the pellet to fully harden. If the pellets are heated too quickly they may not sinter properly, leading to a shell of material surrounding a loose core, which results in a very weak pellet.

Table 2 Test procedures for "green" pellets, before firing

Test	Procedure	Use of data
Wet-knock	Repeatedly drop undried pellets 46 cm onto a steel plate, and count the number of drops needed for visible fracturing to occur. Repeat for at least 20 pellets, and calculate an average value.	Measures the ability of the wet pellet to remain intact during handling. Satisfactory values are between 5 and 10 drops.
Wet-crush	Undried pellets are crushed using a compression testing apparatus, with a compression speed of 40 mm/min. The peak load before fracture is recorded. Repeat for at least 20 pellets, and calculate an average value.	Measures the ability of the pellets to be stacked on each other without fracturing. Satisfactory values are greater than 11 N/pellet.
Dry-crush	Pellets are dried at 105°C for at least 1 hour (weigh before and after drying to determine moisture content). Crush as for the wet-crush test. Repeat for at least 20 pellets and calculate an average value	Measures the ability of the pellets to maintain their strength during the early stages of drying. Satisfactory values are greater than 22 N/pellet.

Cooling. Pellets are cooled with air. Allowing 5 minutes for cooldown will minimize the thermal shock to the pellets, and also allow the recovery of heat to be recycled to the process. The hot air exiting the coolers is then used as the air to feed the sintering, preheating, and drying stages, with combustion in the sintering stage used to provide heat for the whole process. The airflows must be designed to ensure that the air entering the drying stage is not saturated with moisture from fuel combustion, as this would interfere with drying.

Determining final pellet quality. The final pellets must have sufficient mechanical strength to survive intact during handling and be sufficiently free of fine particles that they will perform well in the pyrometallurgical operation. The three most important parameters are the fired crushing strength, the tumble test results, and the Q index (Sportel et al. 1997).

Fired crushing strength is determined by placing a single fired pellet on a compression testing machine and applying an increasing load until the pellet fractures. This is repeated for at least 20 pellets and the results averaged. For blast furnace feeds, this should be greater than 1,780 N/pellet.

Tumble tests are performed using ASTM Test Procedure E279. It consists of placing 11.33 kg of fired pellets into a steel drum of the dimensions specified in the standard. It is then rotated at 24 rpm for 200 revolutions. The pellets are then removed from the drum and screened to determine the percent coarser than 6.3 mm (the Tumble Index), and the percent finer than 600 µm (the Abrasion Index). The tumble test results are also used to calculate the Q index by multiplying the wt % coarser than 12.7 mm by the Tumble Index.

Briquetting

Like pelletization, briquetting typically requires a binder to hold the particles together in the agglomerate (Messman 1977). The key difference is that briquetting applies considerable mechanical force to the material to compress it together, rather than depending on only the weight of a growing pellet to provide compression (Koizumi et al. 1988). Briquetting is useful for materials that do not have an appropriate particle size distribution for pelletization. The limitation of briquetting is that the devices are considerably lower capacity than

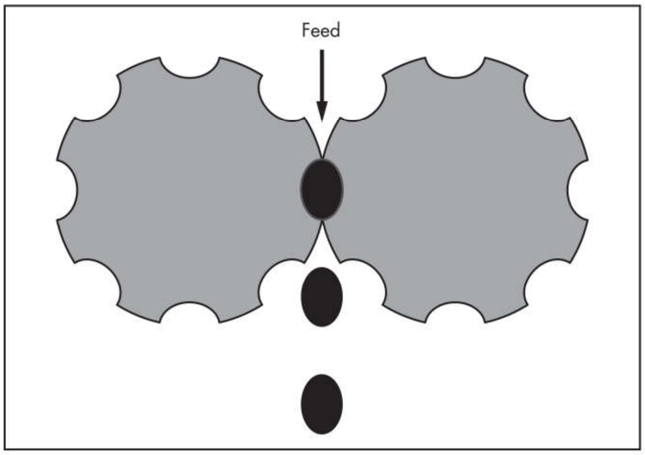


Figure 10 Schematic of a briquetting roll compressing powder into briquettes

pelletization drums and disks, and costs are higher due both to the energy needed for the compression and to the higher mechanical wear. The compression forces in briquetting are most commonly applied using briquetting rolls, which consist of rolls with pocketed surfaces that compress the initial particulates, as shown schematically in Figure 10. The size of the briquettes depends on the shape of the pockets in the briqueting rolls.

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