Review Article

Influence of dispersants on the rheological and colloidal properties of iron ore ultrafine particles and their effect on the pelletizing process—A review

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ARTICLE INFO

Article history:
Received 15 March 2013
Accepted 16 April 2013
Available online 7 November 2013

Keywords:
Iron ore
Pelletizing
Binder
Dispersant

ABSTRACT

The use of binders for iron ore pelletizing is required to: (a) increase the pellet strength before heating – green strength; (b) prevent the collapse of the pellets during firing, when the gases generated by water vaporization could cause cracks. Bentonite is the main binder used in industry, and its binding mechanism in iron ore pellets has been widely studied and understood. Efforts to solve the problems of using bentonite in iron ore pelletizing have focused on the employment of organic binders the composition of which presents dispersant properties. This review critically evaluates the current understanding of the influence of dispersants on the quality of iron ore pellets, by means of their action on the colloidal and rheological properties of iron ore ultrafine particles. Emphasis is given to obtaining parameters for practical application of this action in the pelletizing process in bench and pilot scales.

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1. Introduction

The use of ultrafine powders has increased substantially in various industrial fields, such as minerals, ceramic materials, chemical products, pigments and pharmaceutics, among others [1].

As a rule, a comminution process (grinding) takes place so as to obtain such materials. The work by Wang and Forsberger [2] gives an international overview on comminution technology to produce mineral powders, whose particle size, in most cases, is P_50 < 20 μm.

Much of the mentioned technology employs wet processing and makes use of an additive in order to enhance the efficiency of the process, either to facilitate the grinding itself or to reduce wear rates.

Posa [3] indicates that the processing of fine particles became a challenge in the mineral processing since the decrease of particle sizes is followed by a decrease of their mechanical forces. This makes the forces related to the electrostatic phenomena and to the discontinuity of the medium (viscosity) more significant.

The rheological properties in the mineral processing have been studied for many years now, and are becoming more and more attractive as the need to obtain ultrafine materials increases [1,3-5].

The mining industry makes use of a wide range of chemical products at various process stages, from inorganic products to
special synthetic polymers, in order to improve the rheology control of the production process.

A review by Pearse [6] summarizes various products used in mineral processing and their function at each step, i.e., depressants, collectors, pH controllers, clarifiers, dispersants, anti-caking, binders, and others.

In the case of iron ore mining, due to the recent shortage of high grade ores, the particle size of the final product is becoming finer and finer. Thus, the iron ore concentrate needs pelletizing to allow its use in the reduction processes, both in blast furnaces or direct reduction reactors.

Various types of organic binders (carboxymethyl cellulose, CMC, guar gum, hemicellulose, starch acrylate, polyacrylamides, among others) have been studied and implemented in the pelletizing step in an attempt to replace bentonite, the binder traditionally used.

As noted by Moraes [7], Lima [8] studied the use of CMC as a binder in the pelletizing of iron ore. In previous experiments, Lima [8] obtained pellets bonded by organic reagents. Such pellets did not develop sufficient strength, particularly after thermal treatment. Moreover, their production cost would be very high, or their production would demand a large amount of water to be added so that the pellets would deform under their own weight. These problems were solved by adding sodium tripolyphosphate (TPP) together with CMC.

Motivated by the results obtained by Lima [8], Casola and Chaves [9] conducted their research on iron ore pelletizing following two approaches: the first one using bentonite + CMC + TPP; the second one aimed the replacement of bentonite, CMC, and CMC + TPP with alternative products.

The tests showed that TPP alone was more effective in the pelletizing process than the mixture CMC + TPP. They hypothesized that the pellets develop strong mechanical properties owing to the binder action on the finer particles. Binder would increase the viscosity, leading to an increase in the strength of green pellets; and during heating, its predominant effect was on the dispersion of fine ore, with further crystallization/bonding of the dissolved grains.

Aiming to verify the action of the colloidisant agent on the pelletization process of iron ore concentrate, this review critically evaluates the current understanding of the influence of dispersants on the strength mechanism developed by pellets through its action on the colloidal and rheological properties of iron ore fines. Special emphasis is given to obtaining parameters for practical application of this action in the pelletizing process in bench and pilot scales.

### 2. Literature review

#### 2.1. Rheological parameters

Rheology is defined as the science that studies the deformation and flow of materials under the action of a force [1,3].

In the case of fluids, viscosity $\eta$ is a useful parameter and can be defined as the property that a fluid has to resist deformation, given by the ratio between shear stress $\tau$ and shear rate $\gamma$, as shown in Eq. (1).

$$\eta = \frac{\tau}{\gamma}$$

Traditionally, fluids can be classified into Newtonian or non-Newtonian. In the case of Newtonian fluids, the viscosity is constant, and this is variable in the case of non-Newtonian fluids, which means the shear stress varies non-linearly with the shear rate.

The rheology of suspensions, in the scope of mineral processing, is widely discussed [1,3,10–15].

Mewis and Spaul [16], in their review of rheology of concentrated suspensions, demonstrated the complexity of the rheological behavior of slurries, since it includes viscous, plastic and elastic phenomena of suspensions, and its importance for understanding the process data.

A typical mineral processing flowchart involves operations of comminution, separation by size, concentration, and transport which are carried out, when possible, in aqueous medium [17].

He et al. [1] brings a review of rheology of slurries at the stage of wet ultrafine grinding in the mineral industry. In this paper, the authors point out that the rheology in this step is highly complex and is influenced by many parameters such as solid concentration, size distribution and particle shape, temperature and pH of the slurry and the use of dispersants.

The study carried out by Shi and Napier-Munn [13] indicates that the effects of slurry rheology affect the Grinding Index of materials thus affecting their behavior.

Kawatra and Eisele [14] have highlighted that the rheology control of slurry in a grinding circuit requires the control of the percentage of solids, particle size distribution and temperature, and an on-line measurement of viscosity of the slurry.

Especially in the fine grinding and flotation operations, rheological aspects are widely discussed, but they need to be better understood [12].

#### 2.2. Influence of chemical additives

Ultrafine grinding has increased as the demand for ultrafine materials for industries has. The processing of very fine particles is a problem mainly because of their small mass and high surface area.

Sivamohan [18] reviewed the difficulties in recovering very fine particles in mineral processing. In this review, the author points out that particles with small mass lead to the following phenomena in the flotation process:

(a) low particle momentum;
(b) heterocoagulation;
(c) particle entrainment in concentrates;
(d) low probability of collision with a bubble; and
(e) difficulty in overcoming the energy barrier between particle and particle, and particle and bubble.

While the high surface area leads to

(a) a high dissolution rate in water;
(b) adsorption of a large quantity of chemicals;
(c) rigidity of froth;
(d) high pulp; and
(e) slime coating.

Table 1 shows a size classification proposed by Sivamohan [18].
In several steps of mineral processing, chemical additives are used aiming to minimize the effects of particle size and rheology of slurry [1,5,11,19–31]. The chemical additives used in each study, as well as their function in each case are summarized in Table 2.

2.3. Pelletizing of iron ore–binders

According to Moraes [7] and Lima [8], pellets are obtained by adding an appropriate amount of water to a powder; this is a fundamental factor in the formation and growth of pellets, which creates a surface tension that holds the mineral grains cohesive, thus allowing its handling.

This cohesive tension of fine particles due to water is called neutral tension. The neutral tension, however, is not sufficient to keep cohesive grains as dense as iron minerals. Furthermore, when the pellet is heated, the vaporization of water occurs and the pellets tend to disintegrate.

To prevent such effects, some additives, called binders, are added to the material, aiming to:

- increase the strength of pellets before heating (green strength);
- prevent the collapse of pellets in the initial stages of heating, when a large volume of gas generated by water vaporization tends to crack pellets.

Moisture and binder evenly distributed in the feeding process decisively contribute to improving the characteristics of pellets, especially in relation to the formation of undesirable agglomerates prior to the pellet itself.

In their review paper on organic binders for iron ore pelleting, Eisele and Kawata [32] use the principles suggested by Holley [33] to categorize binders into five groups, which are:

1. Inactive film: the binder forms an adhesive layer (film) on the particles, which promotes binding. Bonding may occur by capillary, adhesive or cohesive forces. Binding is usually reversible.
2. Chemical film: the binder forms a film on the surface of the particles, which undergoes a chemical reaction and hardens. Binding is generally irreversible.
3. Inactive matrix: the binder forms a more or less continuous matrix in which particles are embedded. Often, the binder is a material that needs heating to make it fluid, and then hardens after cooling and drying. Binding may be reversible upon heating.
4. Chemical matrix: the binder forms a nearly continuous matrix, which undergoes a chemical reaction that makes it bind. Binding by this mechanism is usually irreversible.
5. Chemical reaction: the binder reacts chemically with the material to be agglomerated, resulting in a very strong connection. This occurs to some specific materials, and binders of this type have not yet been developed for iron ore.

Bentonite is an effective, widely used binder in the iron ore pelleting process, and its low price is an important factor for its extensive use.

However, bentonite incorporates silica and alumina, which are undesirable contaminants to pellets. Additionally, it is a natural material with variable composition depending on its origin. The necessary amount to obtain a suitable binder effect is very large, around 0.5% by weight, which makes handling more difficult and increases logistics costs.

A number of attempts to replace bentonite as a binder for iron ore agglomeration make use of organic binders. Organic binders have advantages over bentonite, as they do not insert contaminants, are used in smaller amounts and can be eliminated during the pellet burning process.

The following patent documents may be cited as representative of the state of the technique:

- US 3,806,414 – describes a method for using a polymeric binder on wet iron ore, either alone or with bentonite. The binder in this case is a graphitized copolymer of acrylic acid with a polyhydroxyl compound, cellulose derivatives, starches, sugars, etc.;
- U.S. 3,893,847 – refers to a water soluble, high molecular weight substantially linear polymer used as a binder, for example, polyacrylamide;
- U.S. 4,767,449 – refers to a binder system composed of a polymeric binder, for example, polyacrylamide, dispersed in a non-aqueous medium and clay, for example, bentonite;
- U.S. 4,802,914 – refers to a process comprising the application of a polymeric binder to the mineral particles in the form of a powder or non-aqueous medium in the presence of sufficient water to bind the particles;
- U.S. 5,002,607 – refers to an agglomeration process comprising mixing the mineral particles to particles larger than 100 μm of a polymeric binder based on starch, cellulose or ethylenically unsaturated monomers;
- U.S. 5,102,455 – refers to an agglomeration process comprising the mixture of ore particles with a soluble, anionic polymer binder, preferably a copolymer of acrylamide and sodium acrylate, also including bentonite optionally, in a wet environment;
- US 5,306,327 – refers to a binder for mineral particles, based on natural starch and a soluble polymer, for example, pectin, or amide derivatives of cellulose, acrylic or vinyl polymers and others.

The state of technique is verified not to consider how to evaluate the influence of binders on the formation and on the quality of pellets.

Binders currently used by the industry act on the viscosity of the liquid phase, and the bonding of particles is obtained in any order, regardless of their size particle distribution.

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super colloids</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Colloids</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ultrafines</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Very fines</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Fines</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Intermediates</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Coarse</td>
<td>&gt;500</td>
</tr>
</tbody>
</table>

Table 1 – Size classification according to Sivamohan [18].
Table 2 – Chemical additives used and their function in the process.

<table>
<thead>
<tr>
<th>Material/process</th>
<th>Additive</th>
<th>Function</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore–ultrafine/recovery</td>
<td>Sodium hexametaphosphate</td>
<td>Dispersant</td>
<td>Particle size, Chemical composition, Stirring time, Zeta potential</td>
<td>[28]</td>
</tr>
<tr>
<td>Coal slurry/solid–liquid separation</td>
<td>Polyacrylamide</td>
<td>Flocculant</td>
<td>Filtration, Moisture content, Zeta potential</td>
<td>[27]</td>
</tr>
<tr>
<td>Fe₂O₄ in suspension/recovery</td>
<td>Sodium dodecylbenzene</td>
<td>Surfactant used as dispersant</td>
<td>Contact angle, pH, Average diameter, Zeta potential</td>
<td>[26]</td>
</tr>
<tr>
<td>Hematite/grinding</td>
<td>Acetone</td>
<td>Grinding aid</td>
<td>Hardness of hematite, pH</td>
<td>[25]</td>
</tr>
<tr>
<td>Bentonite/dispersion</td>
<td>Sodium dodecylsulphonate</td>
<td>Surfactant used as dispersant</td>
<td>Viscosity, pH, Size distribution</td>
<td>[24]</td>
</tr>
<tr>
<td>Dolomite/grinding</td>
<td>Polycarboxylic acid</td>
<td>Grinding aid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron ore fines/selective dispersion</td>
<td>Sodium humate</td>
<td>Dispersant</td>
<td>Stirring time, pH, Chemical composition, Viscosity</td>
<td>[22]</td>
</tr>
<tr>
<td>Hematite/dispersion</td>
<td>Polycrylic acid and polymethacrylic acid</td>
<td>Suspension stability</td>
<td>Zeta potential, Size distribution, Chemical composition</td>
<td>[21]</td>
</tr>
<tr>
<td>Minerals/fine grinding</td>
<td>Organic and inorganic dispersants</td>
<td>Rheology slurry control</td>
<td>Rotation, Viscosity, Temperature, Particle shape, Size distribution, Zeta potential</td>
<td>[1]</td>
</tr>
<tr>
<td>Iron ore pulp/dispersion</td>
<td>Sodium hydroxide and nitric acid</td>
<td>Dispersion stability</td>
<td>Percent solids, pH, Rotation, Zeta potential</td>
<td>[30]</td>
</tr>
<tr>
<td>Quartz/flotation</td>
<td>Polymer and surfactant</td>
<td>Cationic interaction</td>
<td>Time, Rotation</td>
<td>[19]</td>
</tr>
<tr>
<td>Minerals/grinding</td>
<td>Organic and inorganic dispersants</td>
<td>Grinding aid</td>
<td>Rheological parameters, Sedimentation, Percent solids, pH, Rheological parameters</td>
<td>[31]</td>
</tr>
<tr>
<td>Iron ore/grinding</td>
<td>Dispersants</td>
<td>Grinding aid</td>
<td></td>
<td>[29]</td>
</tr>
</tbody>
</table>

Bentonite promotes the formation of ceramic bridges between particles, which can minimize the number of pellets that collapse during firing. In case of other binders, this effect is generally favored by their crystallization or hardening, which creates physical connections between discrete points of the particles.

The ongoing work, conducted by this group, suggests a different interpretation for the process.

Our proposal is to study how a colloidal wrapping film is created from the contact of colloidal particles, particularly material and a colloidsant agent (as compared with the known action of a dispersant on the particles) during the formation of green pellets. This action ensures the interstitial viscosity necessary to keep the green pellets stable, as well as the stability of pellets during and after burning.
Colloidisant agents, in the sense used here, are elements, mixtures or compositions with the ability to promote the dispersion of the ultrafine fraction and the formation of a colloidal film around the iron ore particles (or agglomerates of particles) during pelletizing.

Such agents are polymers formed of monomers of acrylic, methacrylic, maleic, itaconic or vinylsulfonic acids, or their derivatives (vinyl, ethoxylated, propoxylated, sulfonic or phos- phonic). Sulphide or sulfonated condensates of formaldehyde with naphthalene, phenol or melamine are also colloidisant agents. Mixtures of two or more of the monomers mentioned above, as well as their acids and derivatives, and other co-polymerizable monomers such as vinyl acetate are other examples of colloidisant agents.

Regarding the use of bentonite as a binder, or bentonite together with organic binders, colloidisant agents should provide faster formation of green pellets, with the same or greater strength (both green and fired pellets) and lower contaminant content.

An advantage of this type of product is the effectiveness for any size of pellet feed. Unlike bentonite, their efficiency is not significantly affected by particle size distribution.

3. Conclusion

This review aimed to obtain parameters for the practical verification of the action of colloidisant agents in the iron ore pelletizing. Rheological parameters seem to be a good way to evaluate the effects of the application of binders which act as dispersants or vice versa.

From the studies surveyed, the rheological approach in mineral processing is strongly linked to the fine grinding step. However, the understanding of the binder action in the pelletizing process, through rheology concepts, has not yet been well investigated.

Furthermore, the state of the technique does not consider a way to jointly evaluate the influence of the binder on the formation mechanisms and on the quality of pellets.

In conclusion, this review allowed obtaining parameters for the proposition of a method to evaluate the effect of binders before the pelletizing step for iron ore.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

The authors thank FAPESP – Foundation for Research Support of São Paulo and Vale for the financial support to this project, within the Call Fapesp_Vale.

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