Effect of the Addition of Organic Binders on the Behavior of Iron Ore Pellets

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Abstract

The authors describe their experience with organic binders in pelletization plant. It started with carboxi-methyl-cellulose and hematite concentrates. The addition of sodium tri-poli-phosphate (TPP) was demonstrated to be essential. In pelletizing limestone fines, it has been shown to be possible to use dispersants like soda ash, for this particular case, it was possible to make use of no binder and to work only with the dispersant. This fact has been understood as a consequence of the dispersing effect of the chemicals. To check this hypothesis, a set of different kinds of organic dispersants were prepared to test on pellet feed, with the interesting results described herein.

The conclusion is a model for the behaviour of these binders as: 1 — the dispersion of colloidal particles on the surface of the particles to pelletise increases the viscosity in the liquid film between the particles, and 2 — it provides the physical way to link then by bridging. As a practical consequence, in principle, any dispersant may become the binder for pelletization and there is potential to achieve greater mechanical values than by using the conventional binders, bentonite and lime.

1. Introduction

The evolution of the steel industry in the last decades went in the directions of increasing the productivity of the blast furnaces, of saving coke, of keeping the uniformity of the product, of automating handling operations and of decreasing the man-power incidence. The evolution of the processes of direct reduction seeks, also, the same objectives. To reach them, one of the most important factors is the constancy of the metallurgical properties of the iron ore charge and its preparation in the form of pellets.

This tendency resulted mainly from the fact that the greater iron ore producers, with the progressive exhaustion of the richest ore bodies, must treat now lower grade ores, producing fine concentrates. As in this size they can not be used in the blast furnaces or in the direct reduction kilns, its metallurgical use depends on their agglomeration, mainly via pelletization.

The physical, chemical and metallurgical requirements for the pellets demand a narrow and continuous control of a series of process variables and their uniformity with time. The complexity of this problem is increased by the scale of the operations involved in each plant. This is of the order of three million metric tons of products per year. The fact that the product must have a low unitary value adds to that complexity.

The pelletization process is achieved by the agglomeration of ultra-fine particles of hematite, with the use of some binding agents. Spherical agglomerates, of about 8 to 20 mm diameter, are formed and then heated at high temperature.

The product, named pellet, presents the desired combination of chemical composition and compression and abrasion resistance when loaded in the blast furnace.

Furthermore, it conserves, and in general improves, in relation to the natural ores, some metallurgical

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increasing the viscosity of the liquid phase inside the capillaries; 

Companhia Vale do Rio Doce - Brasil maintains the integrity of the green pellets; helping, during heating, the formation of bridges, adequate to maintain cohesion. Therefore great difficulty, are not resistant to handling, and can't be used in the steel plants.

The pelletization technique, and its wide scale, resulted from research and development mainly done in North America, on their low grade ores, the taconites. It can be said that the pelletization, as today practised, constitutes a recent technique, begun at the end of the decade of 1950.

2. Theoretical Aspects

In the pelletization mechanism, the ore particles are kept together by surface moisture. The water film in the spaces between very close particles, or even in contact, acts as a capillary, where the phenomena of surface tension (very well known from the Physics) are manifested. The surface tension not only keeps the particles together but also allows the pellet to grow. As this water evaporates, the ball will dismantle itself, unless other mechanisms seem to maintain the cohesion of the particles.

It is a very well-known fact that the fine lamellar high grade hematite offers great difficulties to the formation of agglomerates. The spheres, formed with great difficulty, are not resistant to handling, and cannot be used in the steel plants.

Pellets with acceptable composition and diameter, and having the desired physical and metallurgical characteristics, can only be obtained by the use of additives. Thus must also be submitted to thermal processing in high temperatures to assure the constitution of new phases and the recrystallization, at least partial, of the original hematite.

Moreover, with high specific gravity minerals like hematite, the surface tension of water by itself is not adequate to maintain cohesion. Therefore “binders” must be added to the mixture, with the objectives of:

- increasing the viscosity of the liquid phase inside the capillaries;
- maintaining the integrity of the green pellets;
- helping, during heating, the formation of bridges, ceramic or iron oxide bonding, or still, the slagging in discrete points, so contributing to the resistance of the pellet after firing.

ULRICH and HAN’s work\(^1\) is one of the first ones to evidence the decisive influence of the formation of the new phases in the pellets. In summary, the new phases and the recrystallization of small granules inserted among the hematite crystals give to the heated pellets the properties of strength, porosity, thermal conductivity and reducibility, demanded by the good operation of the reduction kilns. Such a product presents better behaviour than natural ores, what explains the gains in productivity and coke economy in the blast furnaces. The processes of direct reduction are in general still more exigent in relationship to the characteristics of the charge but, in principle, it is always possible to adjust the production conditions so that they behave as demanded by those ovens.

ARIAS and MANHEIMER\(^2\), studying ore from CVRD\(^3\), clearly identified the textural modifications, and thus the alteration of the original nature of the hematite. At the temperature of 1100°C, the finest particles, of about 2 mm diameter, start to recrystallize and to grow. Such particles distribute themselves among larger lamellar granules. These manifest changes in shape. At such a temperature, also the silica gangue granules, those of lime, of limestone or of the added bentonite, start to constitute a new binding phase, which ULRICH and HAN\(^4\) believe to be a ferrite.

Increasing the temperature up to 1370°C, appreciably increases the pellet strength followed by an increase in the FeO grade, due to the transformation of part of the hematite in magnetite. Furthermore, and what is very important, significant changes in the chemical composition happen, lowering the sulphur and phosphorus grades\(^5\).

An appreciable growth of the grains is observed: grains which had 2 to 4 mm diameter at 1315°C grow to 7 to 15 mm when the temperature comes to 1400°C. The presence of fines is a factor of amount importance for the improvement of the pellet properties.

The chemical composition of concentrates for pelletization is very strict, specially for those destined to direct reduction. Specifically, they admit very low limits for contaminants.

The most widely used binder for iron ore is bentonite. This thixotropic clay-mineral gives the pellets the desired properties, has a low price and does not interfere with their metallurgical behaviour. However, the amount to be added is relatively high (about 5% by weight), which brings significant contamination with silica and alumina.

Chemical binders able to burn without leaving any residue would be extremely interesting. They would have over bentonite many advantages like:

\(^1\) CVRD – Companhia Vale do Rio Doce – Brasil

\(^2\) ARIAS and MANHEIMER

\(^3\) CVRD

\(^4\) ULRICH and HAN

\(^5\) ULRICH and HAN
as they are industrial products, they do not suffer quality variations;
the added amount may be reduced, what is important from the economic point of view.
Several products have been studied, such as carboxymethyl-cellulose (CMC), guar gum, hemicellulose, starch acrilate and many others. The disadvantages verified in practice are especially their price, the possibility of deterioration for some of the products and the bad results after firing.

3. Experimental Work

3.1 Preliminary experiments
In 1992, LIMA\textsuperscript{3,4,5} presented his PhD thesis on the use of CMC as a pellet binder. The previous published experience with the use of organic binders had taken pellets poor mechanical properties, especially hot, of very high production costs, or to very high moistures — to the point of causing the deformation of the pellet (ovalization) under its own weight. These problems were overcome by him via the addition of a dispersant, in the case the sodium tripolyphosphate (TPP).
The hematite concentrate was supplied by CVRD and the CMC by Ultraquímica São Paulo S.A. The pellets were built in a disk pelletizer 1 m diameter, 43° inclined, 19 rpm. The feed mixture was prepared in a Sympon mixer. After pelletization, 10 pellets were taken, randomly for the measure of the green strength and an other 10 pellets for the measure of the dry strength, another 5 pellets were finally tested as to the number of successive falls from the height of 45 cm.
After all, each lot was checked against the resistance to the thermal shock, according to CVRD's standards. The conclusions of this experimental work were the following ones:
- CMC presents good possibilities for use as a binder. It shows, however, significative result variations depending on the considered product. The greater the viscosity of the solution of CMC in water, the better is the binding power and the larger is the difficulty for dissolving it;
- by itself, CMC is not suited, because the resulting pellet does not resist to high temperatures, undergoes disintegrated. This problem was solved by the addition of TPP, which was the important contribution of LIMA;
- this dispersant improves the mechanical properties either green or after firing. There is an optimum value for its addition, which gives the best hot properties, as well as an optimum value for the rate CMC/TPP;
- the addition of soda ash to the CMC/TPP mixture has a synergetic effect.
In 1993, CHAVES\textsuperscript{6,7,8,9} studied, in North America, the problem of agglomerating limestone fines. He started to work using CMC and TPP, as well as bentonite and portland cement. In the effort to replace TPP for products of lower price, other dispersants were checked. Finally, the advantages and a convenience of soda ash were identified. The following step was to vary the rate CMC/soda ash in the mixture. It was verified that the mechanical properties of the pellet improved with the amount of soda ash and that the best results were attained with 100% of soda ash (that is to say — without CMC!).
In 1996, CASSOLA AND CHAVES\textsuperscript{10,11} worked with chemicals provided by Hoechst of Brazil (now Clariant) and a sample of pellet feed supplied by FERTECO, as will be described in sequence.
Two research lines were followed: the first one considered the classic modus operandi of using CMC plus TPP. The second one considered the substitution of CMC for alternative products.
The tests with CMC showed that TPP alone provided more resistance than the mixture CMC/TPP. This allowed the elaboration of the work hypothesis that: the truly important effect in the acquisition of mechanical strength for the pellets is due to the action of the dispersant and not to the action of the organic binder; this will be described later. To check this conclusion, Hoechst prepared different organic dispersant formulas which were tested and compared.

3.2 Systematic experiments
The research program consisted of the evaluation of the behaviour of different organic and inorganic binders, in different amounts. This was done via agglomeration through pelletization and characterization of the agglomerates with relation to their mechanical resistance.
The pellet feed sample was supplied by FERTECO. It was homogenised without previous drying. Representative samples were taken for size distribution analysis, chemical analysis, determination of the humidity and preparation of mixtures with the organic binders.
The characterization test had the purpose of determining the physical characteristics of the pellet feed. The humidity of the sample was determined by drying it for 105°C till constant weight. The actual specific gravity of the samples was determined in a
The picnometer and the chemical analysis were done via conventional methods. The results are presented in Table 1.

The size distribution analysis was done by dry screening with the Tyler series of sieves. The results are presented in Table 2.

### Table 1 Chemical analysis, humidity and actual specific weight

| Humidity (%) | Specific weight (g/cm²) | Oxide (%) | P₂O₅ | Al₂O₃ | SiO₂ | Fe₂O₃ |
|--------------|-------------------------|-----------|------|-------|------|-------|
| 9.02         | 4.4                     |           |      |       |      |       |

The mixtures were made in an Eirich muller mixer, model R-7, with capacity of 70 l and speed of 80 rpm. The minimum amount of material for each recipe was 3.0 kg for the pelletization tests. The tests were accomplished with moist ore or with dry ore, but the amount of chemicals added was always calculated on a dry basis.

For the test work, the following binders were used: P/D2114/E11, P/D2114/E12, P/D2114/E69, P/D2114/E21, P/D2114/E24, FONGRABOND, TPP, lime, limestone and bentonite.

As a research criterion, these three last products were always tested as a reference “standard” formulation. The organic chemicals are commercial line products or developed by Hoechst specifically for this program. For commercial reasons we are not able to provide their structural or physical-chemical characteristics.

The chemicals were diluted with mild agitation in a magnetic mixer/heater under low temperatures, so as to avoid any eventual degradation. The limestone, lime and bentonite were always added dry.

The chemicals dilution in the solutions varied due to their high viscosity. Every morning a fresh amount

### Table 2 Size distribution of the pellet feed

| Mesh Tyler (#) | FERTECO iron ore |
|---------------|------------------|
| % weight      | % cumulative     |
| -48+65        | 0.30             | 0.30            |
| -65+100       | 0.85             | 1.15            |
| -100+150      | 1.89             | 3.04            |
| -150+200      | 5.54             | 8.58            |
| -200+270      | 22.81            | 31.39           |
| -270+325      | 28.52            | 59.91           |
| -325+400      | 33.78            | 95.68           |
| -400          | 6.32             | 100.00          |

### Table 3 Pelletization tests results. Sample of iron ore from FERTECO

| Binders      | Crushing strength (N/pel) | Shock temperature (N/pel) |
|--------------|---------------------------|---------------------------|
|              | green | dry | 200°C | 300°C | 400°C | 500°C | 600°C |
| Iron ore     |       |     |       |       |       |       |       |
| Dosage (%)   |       |     |       |       |       |       |       |
| Lime         | 2.60  | 2.60|       |       |       |       |       |
| Bentonite    | 0.70  | 1.50|       |       |       |       |       |
| PD/2114/E11  | 0.05  | TPP | 1.10  | 1.70  | 1.90  | 2.00  | 1.60  |
| PD/2114/E11  | 0.10  | TPP | 0.50  | 1.26  | 1.21  | 1.00  | 1.82  |
| PD/2114/E11  | 0.15  |     | 0.55  | 1.76  | 1.70  | 1.50  | 1.54  |
| PD/2114/E12  | 0.05  | TPP | 0.10  | 1.60  | 1.46  | 1.00  | 1.20  |
| PD/2114/E12  | 0.10  | TPP | 0.05  | 1.38  | 1.43  | 0.80  | 0.80  |
| PD/2114/E12  | 0.15  |     | 0.34  | 1.60  | 0.90  |       |       |
| TPP          | 0.05  |     | 0.61  | 1.60  | 1.50  |       |       |
| TPP          | 0.10  |     | 0.70  | 1.60  | 1.50  |       |       |
| TPP          | 0.12  |     | 0.70  | 1.60  | 1.50  |       |       |
| TPP          | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
| TPP          | 0.20  |     | 0.70  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.05  |     | 0.70  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.10  |     | 0.70  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.10  | TPP | 0.05  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.12  |     | 0.70  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
| FONGRABOND   | 0.20  |     | 0.70  | 1.60  | 1.50  |       |       |
| PD/2114/E24  | 0.10  | TPP | 0.05  | 1.60  | 1.50  |       |       |
| PD/2114/E24  | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
| PD/2114/E24  | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
| PD/2114/E21  | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
| P/D2114/E69  | 0.15  |     | 0.70  | 1.60  | 1.50  |       |       |
of solution was prepared for that day. At the end of the day, the amount that had not been used was discarded.

The pelletization tests were done in a disk 1.2 m diameter with speed of 20 rpm and inclination of 45°.

The pellets were screened out when reached the range of 9.5 to 12.5 mm. The different binders were tested in varied amounts.

The pellets were submitted to the tests of successive falls either green and dry (for 105°C), green and dry strength resistance, thermal shock (200°C, 300°C, 400°C, 500°C and 600°C). Table 3 presents the results for the whole series and the experimental conditions.

Some additional tests were realized with another iron ore sample, supplied by MBR**). The results are presented in Table 4.

3.3 Analysis of the results

evaluation of the action of TPP

In this phase of the studies, an addition of .15% binders to the mixture was done. The rate TPP/binders varied from 0 to 100%. The tested binders were: P/D2114-E11, P/D2114-E12. Reference tests with the standard mixtures of lime + limestone and limestone + bentonite were also done. Figure 1 shows these results.

It was verified that TPP is superior to the other chemicals, providing the best results. Even so this product has the disadvantage of introducing phosphorus in the pellet, what is undesirable.

Other reagents, when used together with TPP showed better results but, by themselves did not show satisfactory results. This lead to the hypothesis of being the dispersing effect of the chemical the main agent for their performance.

In the sequence, the best level of TPP addition to the mixture was studied and alternative products to TPP were chosen, based on their dispersant properties.

evaluation of the variation of the dosage of TPP on the mixture

The best addition to the mixture, found to be around .15%, was optimised in this stage. Figure 2 shows the results. As one can observe, for all the addition levels (that varied of 0 to .15% TPP) there is a fall in the strength of the pellets at the level of .12% and, starting from there, the curve ascends up to .15, although .20% was the largest level tested. This behaviour repeats it self for the different sets of tests.

evaluation of the action of the other binders

(dispersants actives)

To verify if the dispersing characteristic of TPP was what in fact contributed for the improvement of the mechanical strength of the pellets, a series of tests was accomplished with other pure dispersants. These were FONGRABOND, P/D2114-E21, P/D2114-E69 and P/D2114-E24. The results were compared with the standard mixtures. The results are presented graphically in Figure 3.

TPP is again the product that provides the best mechanical properties. However, FONGRABOND presents similar results to those obtained with limestone + bentonite, being therefore a potential binder.
To evaluate the optimum addition level of FONGRABOND on the mixture, tests were carried out varying from 0 up to .20%. Figure 4 shows these results.

It can be observed that until the level of .20%, the mechanical properties of the pellets improve. As, in the level of .15%, these values are satisfactory, in the sequence of the studies this level was maintained.

4. Discussion of the Results and Conclusion

LIMA e CHAVES developed their experimental work based on the hypothesis that the effect of the mixture CMC/TPP was due to two different mechanisms that summed up to give the final result:

1 – the viscosity of the solution of CMC would improve the mechanism of capillary action by keeping the cohesion the particles into the green pellet;

2 – the dispersing action of TPP would disperse colloidal particles of limonite, always present on the surface of the hematite particles. This dispersion would act in two ways: increasing still more the viscosity of the CMC solution (contributing like this to the stability of the green pellet) and during firing, promoting the formation of iron oxide bridges between the particles. This mechanism is recognized for the sintering of the particles in the fired pellet.

CHAVES working with limestone, followed the same reasoning and verified that the soda ash alone was enough to allow stability to the green pellets. The limestone pellets were not fired, just cured.

It was verified that the cured pellet had remarkable mechanical properties. He interpreted this green behaviour as the result of the dispersing action of the soda ash on the colloidal particles of limestone and on the present clay-minerals.

The behaviour after curing was seen as the result of the chemical reaction:

\[ \text{CaCO}_3 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{CO}_3 + \text{CaCO}_3, \]

where the ions Ca\(^{2+}\) and Na\(^+\) of the solution and of the mineral surface are changed, forming bridges of carbonate between particles.

The verification of CASSOLA and CHAVES in the experimental work herein described is more comprehensive and completes the picture, allowing full understanding of the phenomenon. Effectively, the dispersion of the limonites on the surface of the hematite particles is the fundamental mechanism for the whole process. It assures the necessary viscosity to keep the green pellet stable, as well as it allows the construction of the iron oxide bridges that provide the stability to the burnt pellet. This is achieved without disturbing the other binding mechanisms such as slagging, melted points or sintering.

The main development is that this dispersion can be provided by any chemical that possesses such a dispersing action. Especially, organic dispersants that do not bring undesirable contaminants to the pellet (Al, Si, P, S) are interesting options to bentonite or lime.

Finally, the authors have shown to exist potential for the development of organic binders able to provide superior strength to that obtained with bentonite, limestone and lime.
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Author's short biography

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From 1972 to 1976 she studied mining engineering at the Escola Politécnica, University of São Paulo. She got his MSc. (1992) and PhD (1997) degrees at the same university in the field of flotation of salt type minerals. She worked six years at the Paulo Abib Engineers, a private consulting company; eight years at a phosphate mine in Jacupiranga, São Paulo, and since 1990 she is a research engineer in the Department of Metallurgy of the Institute for Technological Research of the State of São Paulo.

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