Abstract

Pelletizing iron ore fines is an agglomeration process that through a thermal treatment converts the ultra-fines fraction thereof into small balls ranging in size from 8mm (0.31 in.) to 18mm (0.71 in.), with adequate characteristics for feeding steel reduction works. The binder more used to make pellets is bentonite, which is an item of significant cost in the process. The present paper aims at evaluating the use of serpentinite instead of bentonite. The results obtained show that the full substitution of bentonite for serpentinite is unfeasible. However a potential does exist for using serpentinite and bentonite together in the iron ore palletizing process in the proportion of 1:1.

Keywords: iron ore pelletizing, serpentinite, bentonite.

Metallurgy and materials

Comparison between bentonite and serpentinite in the production process of iron ore pellets

Resumo

A pelotização dos finos de minério de ferro é um processo de aglomeração, que, através de um tratamento térmico, converte a fração ultrafina em esferas de tamanhos na faixa de 8mm (0,31 pol.) a 18mm (0,71 pol.), possuindo características apropriadas para alimentação das unidades de redução das usinas siderúrgicas. O ligante mais utilizado para a produção de pelotas é a bentonita, que é um item de custo significativo para o processo. Esse trabalho propõe uma avaliação do emprego do serpentinito em substituição a bentonita. Os resultados obtidos indicam que a substituição total da bentonita pelo serpentinito é inviável. Mas existe potencial para a utilização do serpentinito combinado com a bentonita, na razão 1:1, no processo de pelotização de minério de ferro.

Palavras chave: Pelotização do minério de ferro, serpentinite, bentonita.
1. Introduction

Serpentinite is a rock consisting almost wholly of minerals of the accessory group of serpentines, such as the antigorite, dolomite, magnetite and magnesite (NEWMANN and OLIVEIRA, 2003; BRANDÃO, 2007); it includes lizardite as one of the minerals of the serpentinite rock. These minerals are formed by the serpentization of igneous rocks, mainly peridotite (PELLANT, 1992).

The serpentinite may also have higher silica and lower MgO tenors, and under such conditions it is employed as an aggregate in civil construction (SENIOR ENGENHARIA, 2006).

For the last forty years, it has been used primarily as a flux (source of MgO) in the sintering process at integrated coke-using plants in Brazil (LEMOS et al., 1979). After the 2008 world economic crisis, the steel industry started to employ a metal load of high silica tenor, which makes the use of serpentinite unfeasible due to the high silica tenor of said rock. PIMENTA and his collaborators (2010) indicate the replacement of serpentinite by dolomitic limestone as a steel industry flux from 2010 on.

Other applications of serpentinite are its use as ornamental stones (ISMAEL, 2008); its use as aggregates in civil construction and as a base for asphalt pavements (RODRIGUEZ, 2007); its use as a flux in steel plants (WAGNER, 1972); and its use as a raw material for ceramic products (GUR’EVA, 2009). Possible uses include the potential treatment of mine acid drainage (BERNIER, 2005); in the carbon dioxide sequestering (TEIR, 2007); and its use in producing magnesium oxide (GLADIKOVA, 2007).

The production of iron ore pellets employing serpentinite as a source of MgO was already described by FONSECA (2003) and ARAGÃO et al. (2000). Notwithstanding these early experiences the use of serpentinite has been passed over in view of the presence of structural water, which causes a loss due to a greater calcination in comparison with other MgO sources. However when serpentinite is used in the production of ore pellets, the iron and its other chemical components, such as silicon oxide (SiO) and iron oxide (FeO), have not been taken into account, as well as their application as a clinging agent, the role of which is kept for the bentonite, an aluminum silicate that has various industrial applications and chemical resemblance with serpentinite.

During the pelletsitting process the ore is mixed with limestone, the binder and coal. The limestone functions to strengthen the raw and the burnt pellets; to hinder the rupture of the raw pellets while drying off inside the furnace; to supply CaO to the mixture to be processed; to accommodate the chemical and metallurgical features of the fired pellets; to lower the burning temperature required to make the acid cangue cling to the ore grains. The binder functions, usually bentonite, are to promote and ease the formation of the raw pellets during the pelletsitting operation; to give the raw pellets the conditions needed to resist transportation and handling that follow the unloading from the pelletsitting disc up to the indurating furnace; to optimize the dry and wet strength of the raw pellet; to improve the strength to the thermal shock during the drying phase.

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2. Methodology

For the pelletsitting tests the iron ore samples have come from Vale Company’s Fábrica Mine. The serpentinite under study is originated in the Corrego Dos Boiadeiros geologic formation, at Nova Lima County, State of Minas Gerais, where Pedras Congonhas extração arte Indústria Ltd. mines said rock since 1979. Utilized was the fines fraction that is the waste generated by the mining of the serpentinite. The bentonite came from Empresa União.

The mixtures developed were prepared in an intensive mixer manufactured by EI-RICH, model R 02, that has a capacity of up to 5.0 liters (9.08 dry pints). The pellets were produced using a tire pelletsitter with a three-phase 0.5 c.v. (0.493 hp) motor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>% bentonite mass</td>
<td>100</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>% serpentinite mass</td>
<td>0</td>
<td>50</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 1
Mixes made for the pelletsitting tests
Three types of pellets were produced, as described below in Table 1.

To perform the tests 200 kg (442 lb) of iron ore were used. The binder was used at ratios of 6kg/metric ton of ore, 54 kg/metric ton of limestone and 13.5 kg / metric ton of coal.

For the pellet size distribution tests, adopted was the Brazilian standard NBR ISO 2395 – Testing Sieves and Sieving Tests, and the standard ISO 9045 (industrial sieving), both enacted by ABNT – Brazilian Technical Standards Association. The sieves utilized comply with ASTM -11 – 70 specification, trade mark Bronzinox, and the maker of the mixer is Produtest. The test consists in sampling around 1.5 kg (3.31 lb) of pellets during the production thereof and sieving the resulting sample in the meshes between 5mm and 18mm, weighting the fractions obtained and calculating the percentage retained on each mesh.

For the humidity test the Brazilian standard NBR 3087 methodology was used. A stove at 110º Celsius and an analytical scale were used. The determination of the specific area was made through the Fischer parameter (Brazilian standard ABNT NBR 6221).

For the chemical analysis the X-ray fluorescent technique was used together with a Rigaku Simultix X-ray spectrometer (using cast lozenges).

The methodologies utilized for determining the water absorption, and determining colloids and swelling, have been the following:

Water absorption – to put a porous plate within a porcelain capsule suspended about 1 cm above the capsule bottom and resting on aluminum supports placed at the 4 corners and the center of the plate. Add distilled water up to the half of the plate. Get 2.00 grams of the sample on a rapid filtration paper. Place the paper with the sample on the porous plate within the receptacle for absorption. Wait for two hours. Weigh the sample together with the paper filter. Make a white test. Calculate the water absorption percentage.

Determination of colloids – agitate with a magnetic agitator 10.00 grams of the sample in 1000 mL for 10 minutes. Apply centrifuging for 15 minutes at approximately 1400 rpm to two aliquot parts of 100 mL. Weigh the floating liquid of one of the aliquot parts in a 250 mL beaker whose weight was previously determined. Dry completely in a stove at 105ºC. Cool in a desiccator and weigh the sample. The percentage colloidal tenor is the sample mass that remains in the beaker multiplied by 100.

Determination of swelling – add 2.00 grams of the sample, previously dried off at 105ºC, in fractions of about 0.1 gram in 100mL of distilled water contained in a test tube. Let the sample rest for 4 hours; read the sample volume in the test tube.

For tests of the number of raw pellet tumbles 15 pellets between 12,5mm and 10.0mm have been randomly picked. Roll every one of the raw pellets and let them fall freely and repeatedly from a height of 45cm until the first crack appears. Count and record how many tumbles each pellet had until the first crack occurred. The result will be the arithmetical average of the recorded figures and will be expressed in number of tumbles per pellet.

For the tests of raw pellets compression strength, 15 pellets will be randomly picked and a Kratos-trade-mark press is used, equipped with parallel pans, a 10kg capacity dynamometer, and a 0.005 kg/ pellet measuring precision. Dry pellets at 105 ± 5ºC should be cooled to the ambient temperature before the test. Record the load registered in the press scale at the rupture moment showed by the dynamometer finger. The result will be the arithmetical average of the recorded values and is expressed in kgf/pellet. In the case of the pellet firing the temperature and the test residence time were respectively 1320ºC and 24 minutes.

As references for the compression and abrasion strength tests the ABNT standards NBR 4700 and 6465 were used.

The tests were held in a pilot plant of a Brazilian company that produces iron ore pellets.

The chemical composition of the iron ore used in the pelletizing tests is shown in table 2. Tables 3 and 4 present the chemical composition and important physical-chemical properties of respectively the serpentinite and bentonite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>H₂O</th>
<th>FeT</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>P</th>
<th>Mn</th>
<th>CaO</th>
<th>PPC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass tenor</td>
<td>10.4</td>
<td>62.5</td>
<td>3.0</td>
<td>0.85</td>
<td>0.03</td>
<td>0.15</td>
<td>4.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*PPC = Loss on calcination.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Serpentinite</th>
<th>Bentonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeT</td>
<td>4.21</td>
<td>6.00</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.15</td>
<td>60.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.37</td>
<td>15.00</td>
</tr>
<tr>
<td>CaO</td>
<td>1.2</td>
<td>1.30</td>
</tr>
<tr>
<td>MgO</td>
<td>35.85</td>
<td>2.50</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
<td>1.00</td>
</tr>
<tr>
<td>P</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
<td>2.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>PPC*</td>
<td>11.09</td>
<td>7.00</td>
</tr>
</tbody>
</table>

*PPC = Loss on calcination.
Comparison between bentonite and serpentinite in the production process of iron ore pellets

As for the bentonite, the higher the sodium tenor, the greater the water absorption, and therefore the greater the swelling is. However, even worse is the peeling of layers because it requires more energy for opening the bladed mineral, that is, a trend to form isolating gel (need of a good sheering stress capable of overcoming the force among the clay-mineral).

The colloid, in turn, is important in the palletizing process, as it implies a greater covering area. The colloid means particles below 2µm, that is, a greater m²/gram of agglomerating action. The ideal is to have a high colloid tenor and a minimum swelling, but usually if one is high, the other will also be high. The water absorption is an indirect measure of swelling.

The binding materials normally present high specific surface. The bentonite specific surface determined for this research bentonite (table 4) is lower than that of lime, that is a good binder (6558.21 cm²/gram)(Bezerra et al., 2011)

When one compares serpentinite with bentonite, table 4, one sees that the water absorption, colloids, swelling, material fineness parameters are unfavorable to the serpentinite when the agglomeration process is considered. The same occurs in relation to the serpentinite low sodium tenor, table 3, in relation to bentonite.

As to the chemical parameters, the lesser SiO₂ tenor of the serpentinite is highlighted favorably in relation to the bentonite’s. But the high MgO tenor would limit the serpentinite utilization only in the production of pellets with a high MgO tenor.

Other parameters that do not favor the use of serpentinite as a binder is the predominance of fines (99% passing the 44µm sieve) and its high specific surface in relation to the bentonite.

Table 5 presents the raw pellets test results.

The mechanism of forming the pellets occurs from a phenomenon that involves a solid phase and a liquid phase, the former being characterized by the mixture of iron ore, binding agents and additive agents, and the latter by water (MENDES, 2009).

When humidity is increased or reduced, interference will occur in the size of the pellets and the speed in which they are formed.

The mixture no. 1 humidity is a typical one when only bentonite is used as a binder. The humidity of mixture numbers 2 and 3 were reached empirically so as to produce pellets with the same size of the pellets produced using only bentonite.

Table 5
Tests with raw pellets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tests Numbers</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Bentonite (kg/ton)</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Serpentinite (kg/ton)</td>
<td>0</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>8.8</td>
<td>8.5</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Number of tumbles/pellet at 45 cm in height</td>
<td>3.4</td>
<td>3.4</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Raw strength (daN/p)</td>
<td>2</td>
<td>1.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Dry strength (daN/p)</td>
<td>5.9</td>
<td>3.7</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows the number of pellet tumbles from a 45 cm (17,72 in.) height.

This test consists in carrying out consecutive raw pellets tumbles on a steel surface, from a 45cm height, in order to determine the average numbers of times that these pellets resist the tumble until the first crack appears.

The analysis of Figure 1 shows that test no. 2, that contains 50% of the serpentinite, presents a number of 45cm (17,72 in. )-tumbles near the tumbles of test 1, containing only bentonite. In this case, the palletizing process that uses the serpentinite alone, the reduction of the number of raw pellets tumbles decreases as much as reaching 26.5%.

Figure 2 presents the strength (kgf/pellet) for the raw pellets. This test shows the power necessary to destroy the raw pellet. Considering that the raw pellet should be handled until being transported to the furnace to be burnt, this information is of vital significance to avoid that the pellets arrive at the furnace without mechanical degradation.

The analysis of Figure 2 is similar to the analysis of Figure 1, i.e., it shows that test no. 2, that contains 50%w/w of serpentinite, presents a Strength (kgf/pellet) near the one obtained in test 1, containing only bentonite, with a strength reduction...
of 10%, while the no. 3 mixture presents a 40% strength reduction in comparison with mixture no. 1.

As to the strength of burnt or dry pellets Figure 3 presents the tests results obtained. This test shows the amount of power necessary for the mechanical degradation of the fired or dry pellet.

Considering that the fired or dry pellet should be transported up to a stock pile, where it shall be store piled, and in the future loaded into ships, wherein it will again be piled, such information is of vital importance to avoid destruction of the burnt and dry pellets along these operational phases.

One sees that the Strength drops as the bentonite tenor is reduced; the no. 2 test, that has 50% m/m of serpentinite, presents a loss of 37% in its strength, while the no. 3 test, that has 100% m/m serpen-
tinite, presents a strength loss of 67%.

Table 6 presents the results of the burnt pellets abrasion test.

In accordance with OLIVEIRA (2010), the results in the range of +6.3 mm should be higher or equal to 95%. Only test no. 3 didn’t reach said figure, although reaching a very near value (94.9%). As such, tests 1 and 2 are within the acceptable limits. For the -0.5mm range the results should be lower than 5%. Therefore, tests 1 and 2 are within the acceptance limits.

Table 7 presents the results of the compression strength tests of burnt pellets.

The compression strength test of burnt pellets shows which is the burnt pellets percentage that presents a mechanical
Comparison between bentonite and serpentinite in the production process of iron ore pellets

wear when submitted to a force lesser than 250 daN and when submitted to a force lesser than 100 daN. Considering that the fired or dry pellet should be transported up to a stock pile, where it shall be store piled, and in the future loaded into ships, wherein it will again be piled, such information is of vital importance to avoid destruction of the burnt and dry pellets in these operational phases.

The average strength of pellets produced with 50% bentonite and 50% serpentinite is 1.5% lower than the strength produced only with bentonite, but the pellet produced only with serpentinite is 14.9% lesser.

Regarding the percentage of pellets destroyed when submitted to a force lesser than 100 daN, those produced with 50% of serpentinite and 50% of bentonite showed an 0.8% increase in the quantity of destroyed pellets, while the use of only serpentinite increased that quantity by 1.6%.

These results show that there was a loss of strength of the burnt pellets whenever the serpentinite was used, and that the use of only serpentinite jeopardizes their strength.

Through the analysis of the full substitution of bentonite for serpentinite one sees a light fall in the SiO2 tenor (from 3.70% to 3.63%) and an increase of 0.18% in the MgO tenor.

4. Conclusion

Taking parameters Na2O – activation level, water and colloids absorption, the serpentinite is not characterized as a binder.

The use of 100% of serpentinite in the palletizing tests produced raw pellets with low compression strength. Also, in the firing phase the abrasion and compression results showed a worsening, which indicates the impossibility of the full substitution of bentonite for serpentinite.

In the fifty-fifty substitution (50% bentonite/50% serpentinite) an intermediate quality was obtained, which shows that such a combined application of the two products is feasible, provided the quality meets the needed required, a MgO tenor of around 0.20% is acceptable in an end product, and some process adjustment is carried out seeking to minimize the generation of fines during the firing phase.

Although the serpentinite doesn’t present a binding characteristic, due to its size distribution (99% passing the 325 mesh and high specific surface), it presents a potentiality to be used in a combined manner with the bentonite.

The use of serpentinite may reduce the cost of pelletizing iron ore, depending on the location site of this rock and the bentonite and the particularities process from the pelletizing producer.

It is recommended to carry out supplemental tests in order to confirm the results obtained and check the porosity and reducibility of the pellets manufactured and its microstructure. It is also possible to modify the percentages of serpentinite and bentonite in the mixtures and work with a more adequate size distribution in the serpentinite.

<table>
<thead>
<tr>
<th>Test number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size distribution</td>
</tr>
<tr>
<td>+6.3 mm</td>
</tr>
<tr>
<td>+0.5 mm</td>
</tr>
<tr>
<td>-0.5 mm</td>
</tr>
</tbody>
</table>

Table 6
Burnt pellets abrasion tests.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression Strength (daN/p)</td>
<td>403</td>
<td>397</td>
<td>343</td>
</tr>
<tr>
<td>Strength % (250 daN/p)</td>
<td>10.8</td>
<td>10.8</td>
<td>18.2</td>
</tr>
<tr>
<td>Strength % (100 daN/p)</td>
<td>0.6</td>
<td>1.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Strength% (78 daN/P)</td>
<td>0.4</td>
<td>1.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 7
Compression strength tests of burnt pellets.
Acknowledgments

To João Júlio Tolentino, Thiago Marchezi Doellinger and Vinicius Oliveira Fonseca for assistance and contribution in laboratory tests.

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