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Use of Carbon-based Nanomaterials on the Cold Agglomeration of Iron Ore Fines

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Cold agglomerated iron ore mini-pellets (diameter 3–8 mm) with high mechanical strength were prepared. The use of carbon-based nanomaterials (carbon nanotubes and graphite nanoplatelets) as additives to the binder (liquid sodium silicate) promoted the increase of the mechanical strength of the agglomerate to about 285%. The dispersion of the nanomaterials into the binder combined with the resting time of the dispersed material were considered key points on the formation of agglomerates with high mechanical strength. The results have shown that the solely use of ultrasonic processor is inefficient to disperse the nanomaterials into the binder. However, using a resting period of approximately fifteen days, the dispersion of the nanomaterials has improved considerably. Subsequently, the increase in the mechanical strength of the agglomerate (mini-pellet) was related to the dispersion capacity of the nanomaterials in the sodium silicate.

KEY WORDS: nanomaterials; carbon nanotubes; graphite nanoplatelets; iron ore fines; cold agglomeration; mini-pellets.

1. Introduction

Nowadays, the iron ores extracted from the Iron Quadrangle in Minas Gerais State (Brazil) are originally from friable and/or compact itabirites.[1,2)] The obtained products are mainly composed by particles smaller than 0.15 mm (pellet feed), due to the fact that the itabirites are friable or they need to be submitted to a grinding process to release gangue and consequently concentrate the iron ore. The pellet feed needs to be agglomerated for to be used in blast furnace due to its granulometric distribution. It can be used directly in the sintering process up to 30 wt%. of the sintering blend without agglomeration. However, the agglomeration of pellet feed of good chemical quality with sizes close to the sinter feed size could be an important alternative to enhance the pellet feed market. Additionally, it promotes commercial and strategic benefits such as (*i*) regulate the market avoiding discounts permission; (*ii*) chemically correct cheaper sinter feeds (without physical and chemical quality); (*iii*) allow action over the mine split (ratio between sinter feed and pellet feed); and (*iv*) allow to meet the demand of sinter feed.

Among the technological alternatives to produce the agglomerate for the use as raw material in the sintering, cold agglomeration process shows to be interesting because of its lower cost as compared to the high temperature agglomeration processes (*e.g.*, conventional pelletizing). In this process, the agglomerate acquires mechanical strength by drying and consolidation of the binder at relatively low temperatures or at room temperature. A technology for producing cold agglomerated iron ore mini-pellets was reported by Dutra and Pimenta.[3)] In this technology, mini-pellets with diameters between 3 and 8 mm can be produced by a mixture of pellet feed (iron ore fines with particles smaller than 0.15 mm) and sodium silicate (binder). The mini-pellet and its production process minimizes some problems that are normally faced in the cold agglomeration process, such as high dosage of binder, large period of drying/curing, low mechanical strength when in contact with water, high generation of fines during handling/transporting and after submitted to high temperatures. Later, Dutra *et al.*[4)] reported a study concerning the influence of the drying temperature and atmosphere on the mechanical strength of iron-ore agglomerates and sodium silicate. The authors observed that the compressive strength of the agglomerates is influenced by the temperature and gaseous atmosphere during the drying and curing stage.

Improvements on the physical and metallurgical quality of the mini-pellets may be obtained by adjusting the raw materials. An increase on the mechanical strength of the binder, responsible for the union of the particles, may be able to improve the mechanical strength of the mini-pellet and, consequently, to improve their performance. An envisioned alternative refers to the development of a nanocomposite between sodium silicate and carbon-based nanomaterials. The choice for carbon nanomaterials, in relation to other inorganic nanomaterials, is associated to the

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absence of deleterious elements for the steelmaking, beyond the future availability and cost of processing. Moreover, it is well-known that carbon-based nanomaterials such as carbon nanotubes have good electrical and mechanical properties.[5] This type of nanomaterial can be used as reinforcement for several types of composite materials. In this sense, the use of nanometric materials combined with binders opens an enormous field of possibilities for its application in the agglomeration of ore fines. In our best knowledge, this is an unexplored area and there is a lack of literature concerning the application of nanomaterials on the agglomeration of iron ore fines. The present work deals with the application of carbon-based nanomaterials on cold agglomeration of iron ore fines. In this case, the nanomaterials are used to reinforce the binder (sodium silicate) and consequently to obtain iron ore mini-pellets of high mechanical strengths.

2. Experimental

The mini-pellets were prepared by mixing iron ore fines (pellet feed), liquid sodium silicate, carbon nanotubes and nanoplatelets of exfoliated graphite. The iron ore fines contained approximately 85% of particles below 0.15 mm with specific surfaces of 550 cm^2/g. The ore fines are originally from the Iron Quadrangle in Minas Gerais State, Brazil. A liquid sodium silicate, with a SiO_2/Na_2O molar ratio of 2.15, from PQ Silicas do Brasil has been employed for the tests. Multiwalled carbon nanotubes (NC7000) were purchased from Nanocyl, whereas the Nacional de Grafite supplied the nanoplatelets of exfoliated graphite (HC11).

The nanomaterials were dispersed into the silicate by using an ultrasonic processor (Sonics & Materials, model VCX 750) with an amplitude of 55%, a power of 750 W and a solid probe. The amount of nanomaterials dispersed into the silicate varied between 0.1 and 0.5 wt%. Amounts below 0.1 wt%, for instance 0.05 wt% were tested, however they did not give good results. The dispersion was carried out during 30 min in intervals of 5 min. A qualitative analysis of the dispersion was performed by placing a layer of the material in a glass plate and an image was collected in a stereoscope (Carl Zeiss, model Discovery V12).

After the dispersion, the mini-pellets were prepared by mixing pellet feed (~96%) with liquid sodium silicate containing nanomaterials (~4%). The mixture was carried out in an intensive mixer. For the complete homogenization of the mixture, the pellet feed was placed into the mixer during 2 min. Following this time, the silicate with nanomaterials and water were added to the pellet feed to reach a final humidity of 9.5%, and 2 min more of mixture was conducted. The mixture was pelletized in a disc (Lurgi, with a diameter of 0.80 m, rotation of 20 rpm, in an angle of 45° and a deep of 0.20 m). Finally, the samples were dried at a temperature of 150°C, for 3 h. The compressive strength was measured for 100 mini-pellets with sizes between 4 and 6 mm using a compression machine. The samples were characterized by Raman spectroscopy using a Horiba/Jobin-Yvon Labram-HR spectrometer, equipped with a laser of He-Ne (632.8 nm), and resolution of 1 cm^{-1} for typical counts of 60 s (objective 10×) after optimization of the signal.

3. Results and Discussion

The results of the compressive strengths of the mini-pellets, prepared varying the amount of carbon nanotubes into the silicate, are presented in **Fig. 1**. It was observed that the optimal amount of nanomaterial is 0.1 wt% in order to maximize the strength of the agglomerate with respect to agglomerates prepared without nanotubes (reference sample). In this respect, the compressive strength of the reference sample was 8.5 ± 2.2 daN, whereas the compression of the sample prepared with 0.1 wt% of nanotubes increased the strength up to 13.4 ± 2.0 daN (~58% higher than the reference sample). Several studies focused on the mechanical strength of composites containing carbon nanotubes have demonstrated that there is an optimal amount of nanomaterials in the matrix. Moreover, the composite tends to lose mechanical strength for higher amounts of nanomaterials due to the decrease of the ductility, which is attributed to the addition of stiff materials. This fact occurs due to the stress concentration effect of the agglomerated nanomaterial, which promotes the failure initiation of the material.[6–8] In this way, the dispersion of the nanomaterials into the binder (sodium silicate) plays an important role, as will be discussed later.

When preparing the dispersion of the carbon nanotubes into the silicate, it was observed an improvement on the quality of the dispersion if a time of resting was included after dispersing the nanomaterials and before preparing the mini-pellets. Therefore, periods between 0 and 25 days were employed to the dispersion of 0.1 wt% of carbon nanotubes into the sodium silicate before pelletizing the iron ore fines. The results of the compressive strength display a considerable increase on the strength of the materials with the time of resting, suggesting a strong influence of the time on the interaction between binder and nanomaterial. Immediately after dispersing, the gain in compressive strength was about 58% as observed and shown in Fig. 1. By increasing the time of resting, the gain in compressive strength of the mini-pellets was also observed, in which the optimal time with the highest gain was noticed after 15 days (increase of 133%), as shown in **Fig. 2**. However, resting times longer than 15 days did not result in any additional gain because of the formation of agglomerates.

In order to search for alternative materials to replace the

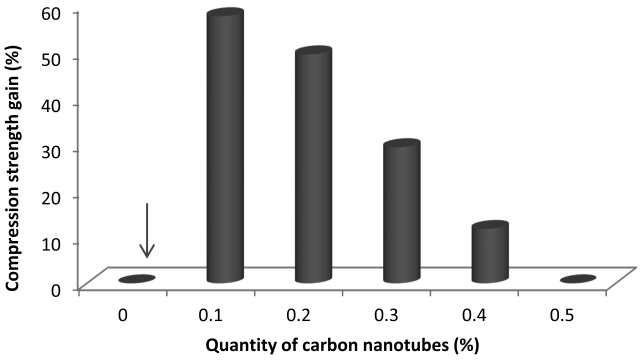

Fig. 1. Gain in the compressive strength of the mini-pellets with the increase of the carbon nanotubes quantity on the silicate. The gain is relative to a reference sample of mini-pellets prepared without the addition of carbon nanotubes.

carbon nanotubes in terms of costs, graphite nanoplatelets have been tested following the same procedures as the carbon nanotubes. However, the compressive strength of the mini-pellets by using only graphite nanoplatelets did not show any expressive gains (not discussed here). On the other hand, a mixture of carbon nanotubes (0.05 wt%) and nanoplatelets of graphite (0.05 wt%) dispersed into the sodium silicate demonstrated promising results concerning the mechanical strength of the mini-pellets. The time of resting of the dispersion was also investigated and 15 days have again shown to be the optimal time. The mini-pellets prepared with the dispersion after 15 days showed a compressive strength gain of about 284% as compared to a sample agglomerated with only sodium silicate and iron ore fines (**Fig. 3**). This result is in agreement with the observations reported by several studies concerning the use of carbon nanotubes and graphite in polymeric composites.[9,10] According to Kong,[11] there is a synergy between these two nanomaterials which favors the increase in strength by the formation of structured nets with higher Young modulus as compared with nets formed only by one of the nanomaterials individually.

Concerning the quality of the dispersion of the nanomaterials, images of thin layers of the dispersed materials, placed in a glass plate surface, were collected. The effect of the time of resting of the dispersion is clearly displayed in the stereoscope images (**Fig. 4**). It can be notice the quality of the dispersion depending on the time of resting of the material, again the optimal time is 15 days corroborating

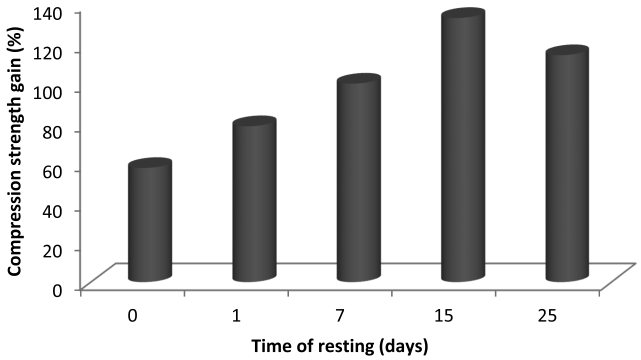

Fig. 2. Gain in the compressive strength of the mini-pellets with the increase of the time of resting of the carbon nanotubes dispersed into the sodium silicate, afterwards added to the iron ore fines for pelletizing. The gain is relative to a reference sample prepared without the addition of carbon nanotubes.

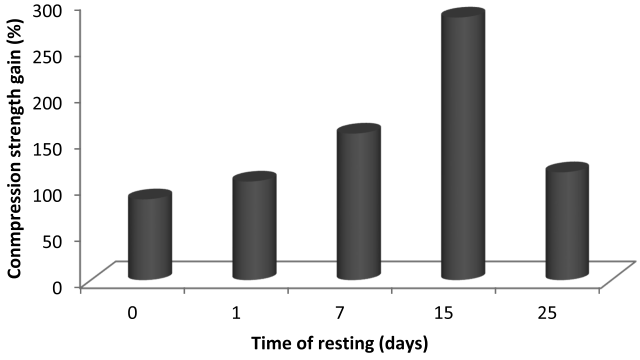

Fig. 3. Gain in the compressive strength of the mini-pellets with the increase of the time of resting of the carbon nanotubes and graphite nanoplatelets dispersed into the sodium silicate, afterwards added to the iron ore fines for pelletizing. The gain is relative to a reference sample prepared without the addition of carbon nanotubes and graphite nanoplatelets.

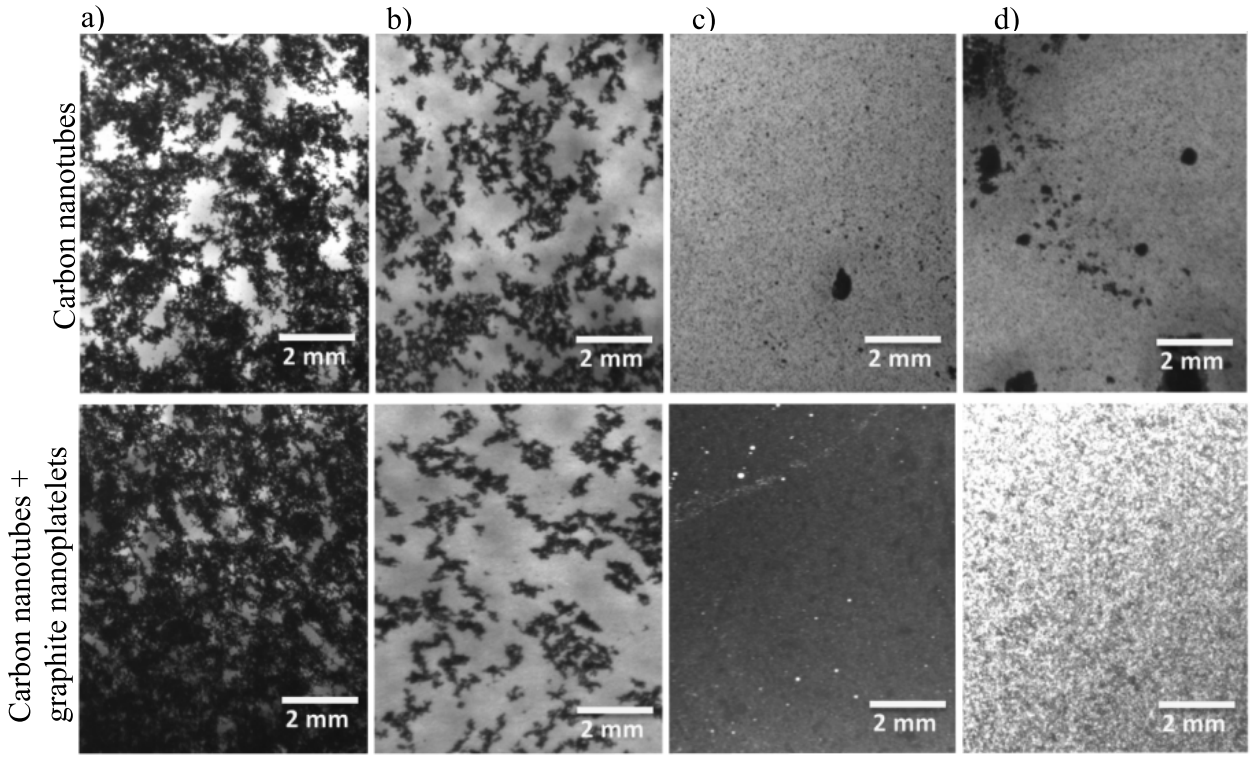

Fig. 4. Stereoscope images of the carbon nanotubes and graphite nanoplatelets into the sodium silicate without dispersion (a) and dispersed after: immediately (b), 15 days (c) and 25 days (d).

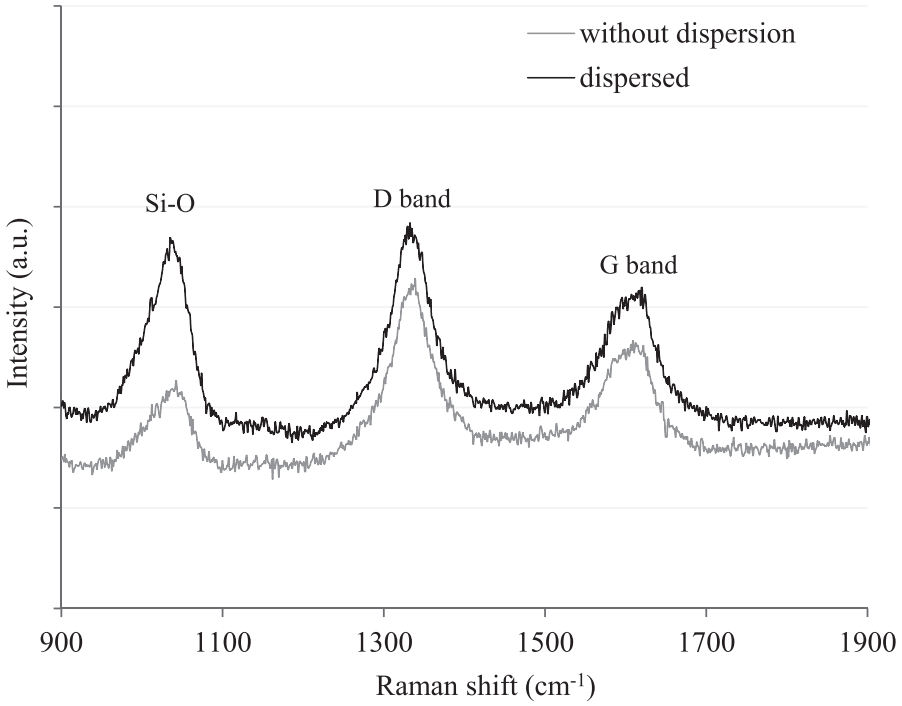

Fig. 5. Raman spectra of the nanomaterials dispersed into sodium silicate before and after the use of the ultrasonic processor.

the results of compressive strength of the mini-pellets. For less than 15 days, agglomerates were noticed. Therefore, the time of resting is very important when considering the complete dispersion of the nanoparticles in sodium silicate matrix. The resting time (15 days) was efficient and necessary to improve the dispersion of the nanomaterials, avoiding the formation of bundles or agglomerates capable of acting as points of weakness in the mini-pellets. A reagglomeration of the nanomaterial was observed for times of 25 days. This fact is believed to be explained by the curing process of the sodium silicate and also may be caused by the alkalinity of the silicate solution (pH ≈ 12), which is an aggressive condition for carbon nanomaterials when considering longer times of resting of the dispersion.

Ferreira[12] reported that the reinforcing nanomaterials have in general similar dimensions as of the polymeric chains of the matrix, resulting in others mechanisms responsible for the physical strength of the materials. One example is the chemical interaction between the components of the composite. Therefore, the present samples were characterized by Raman spectroscopy in order to observe if there are chemical interactions between the nanomaterials, silicate and iron ore. According to Ferreira *et al.*,[13] the G band (~1 580 cm^{-1}) is characteristic of all carbon-based materials with sp^2 hybridization. The D band (~1 350 cm^{-1}) is originated from the phenomena of double resonance. As the presence of structural defects is considered a necessary condition for the occurrence of this process, the intensity of the D band is used as a measurement of material crystallinity. The intensity ratio of the D and G bands (I_D/I_G) increases as the defects and disorder increase. The G' band (~2 700 cm^{-1}) is the vibrational mode of second order of the D band and, by the adjustment of this band, it is possible to indicate the number of dispersed graphene sheets. **Figure 5** shows that the ultrasonic processor did not cause any effect

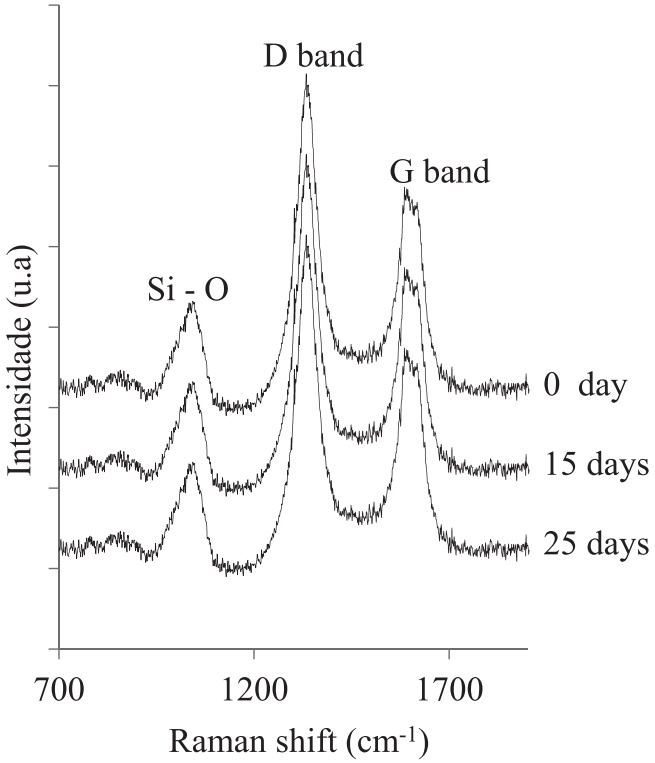

Fig. 6. Raman spectra of the nanomaterials dispersed into the sodium silicate with different time of resting.

on the dispersed material (nanocomposites). The spectra showed that the dispersing process of the nanomaterials by ultrasonic processor did not affect the Raman spectra of the samples, *i.e.* the intensity ratio of the D and G bands was unchanged. Moreover, the position of the silicate and nanomaterials bands was not altered, which suggests that the crystallinity of the nanomaterials was unaffected.

The influence of the resting time of the dispersed material (nanomaterials in sodium silicate) was also investigated by Raman spectroscopy (**Fig. 6**). It was observed the occurrence of the main silicate band, besides the D and G bands of the carbon-based nanomaterials. A small difference of the $I_{D/G}$ was noticed after 25 days of resting. Based on these observations, it is possible to suggest that no structure deterioration of the nanomaterials occurred for a time up to 25 days. According to Marega *et al.*,[14] the D band is often used to detect the efficiency of chemical functionalization of carbon nanotubes introducing sp^3 sites. It is indicated that no relevant chemical interactions took place on the present nanocomposites due to the D band, which had shown no modifications in its position as a function of the resting time.

Based on the presented results, it is indicated that the incorporation of carbon nanomaterials into sodium silicate is an alternative technology capable of greatly increasing the compressive strength of mini-pellets.

4. Conclusions

The incorporation of a mixture between carbon nanotubes and graphite nanoplatelets to sodium silicate results in an increase of approximately 285% in the compressive strength of the mini-pellets. The gain in compressive strength is maximized by forming a nanostructure which gives the sodium silicate film a larger mechanical strength, and non-relevant chemical interactions were observed. It was assumed that the mechanical strength gain of the mini-pellet is associated to the quality of dispersion of the nanomaterials into the sodium silicate matrix, thus avoiding the formation of regions of weakness in the mini-pellets. The reinforcement of the sodium silicate matrix by the nanomaterials is mainly physical. The action of the sodium silicate on the iron ore fines is the formation of thin films of silicate on the surface of the fines. This films are responsible to bond the particles, conferring a higher final compressive strength to the agglomerated material, after curing of the sodium silicate. Finally, the gains in compressive strength give the product quality to transoceanic shipping and performance improvements in its application in the steelmaking industry.

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