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FERRONIOBIUM ALLOY FINES AGGLOMERATION THROUGH BRIQUETTING

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Abstract

Brazil is the largest producer of Niobium alloys, with a production of 58,000 tons of Nb_2O_5 concentrate in 2016, corresponding to a 92.81% of the world production. The Brazilian Niobium ores grades vary from 0.51 to 2.71%. Ferroniobium (Fe-Nb) is an iron niobium alloy with niobium content of 60-70%. It is the main source for niobium alloying of HSLA steel and covers more than 80% of the worldwide niobium production. In 2014, Brazil produced 51,737 tons of Fe-Nb, being around 90% of it for exportation. In the final stage of the Fe-Nb production, the alloy needs to be crushed in a jaw crusher, which generate fine particles (around 26% of the feed below 10 mm at Niobras/CMOC). The selling price of the fine particles have a significant loss in the market, since the fine particles cannot be used directly in steelmaking. A process to agglomerate the Fe-Nb fine particles into briquettes with size and chemical composition similar to original products was developed. Organic binders were used as well as a lubricant agent. The briquettes were characterized both physically and chemically. For the physical characterization, the briquettes were tested for mechanical and water resistance, thermal shock and Brinell hardness. Briquettes containing addition of 3% of zinc stearate, 2% of iron powder, and 1% of water reached a Niobium content above 62% and contaminants levels of below the standard Fe-Nb specifications. The results indicate that Fe-Nb alloy fines can be technically and economically agglomerate by briquetting.
Keywords: Ferroniobium; Fines; Briquetting; Agglomeration.

1 INTRODUCTION

According to Mendes [1] Niobium is a trace element present in Earth crust with average grades between 0.3 and 1.0% of Nb_2O_5. However, some Brazilian deposits can reach exceptional grades around 3.0% due to supergene enrichment in weathered zones. It is a metallic, soft, ductile solid and has a high melting point (2,469°C) one of the highest of the periodical table. It is resistant to corrosion, mainly due to the formation of a thin film in the oxide surface, called passivation layer. It exhibit different oxidation numbers when combined, being +5 the most common. It do not react with hydrogen, air, water or acids at room temperature, except for hydrofluoric acid and its mix with nitric acid [2]. Its industrial applications include, but are not limited to, high-strength low-alloy steel (HSLA), stainless steel and super alloys. Its consumption in micro alloyed structural steels reaches above 80% of its demand [3].

Brazil holds the largest deposits Niobium in the world, distributed between the states of Minas Gerais, Amazonas, Goiás and Rondônia, with a total reserve around 10.8 Mt of pyrochlor exploitable reserves. Brazil is also the most important producer with an annual production around 88.8 ktons of Nb_2O_5 concentrate and 51.7 ktons of Fe-Nb alloy, with Nb content ranging from 60 to 70%. Canada holds the second position in the world marketing with approximately a reserve of 200 ktons and annual production around 5 ktons [4]. Figure 1 shows Brazilian's Niobium production between the years 2000 and 2014. It is possible to see a development in the Niobium marketing until 2010, when the steel marketing started to face a severe economic crisis. An improvement in the marketing was noticed after 2012 and 2014 end up being, together with 2009, the years with higher production in the period.

In 2017 the world's production of Fe-Nb was 124.200 tpy, been the largest players CBMM (100.000 tpy), Niobras (13.700 tpy), Niobec (9.000 tpy), and Taboca (1,500 tpy) [5]. Niobras is company from the Chinese group CMOC and is one of the three Brazilian companies that produce Fe-Nb. Situated in the state of Goiás, the company production is destined to exportation. After the aluminothermy, which is the final stage of the Fe-Nb production, the freshly produced

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alloy is grinded using a jaw crusher (see Figure 2). This stage generate particles under 10 mm, considered fine particles and not able to be used direct in the steelmaking process because only of their size. Other operations that generate fine particles are Fe-Nb screening and handling (especially the commutation between conveyor belts).

The total amount of fines produced can reach approximately 95 tons per month (equivalent to 26% of the total Fe-Nb production). Fe-Nb fine particles were divided in three different classes according to their granulometry and generation process: under 2 mm (type A), between 1 and 5 mm (type B) and between 3 and 15 mm (type C). Figure 3 shows samples of the three types of fines.

The agglomeration process aim in produce material with size adequate to the future application and the correct choose between the available methods depends on a very

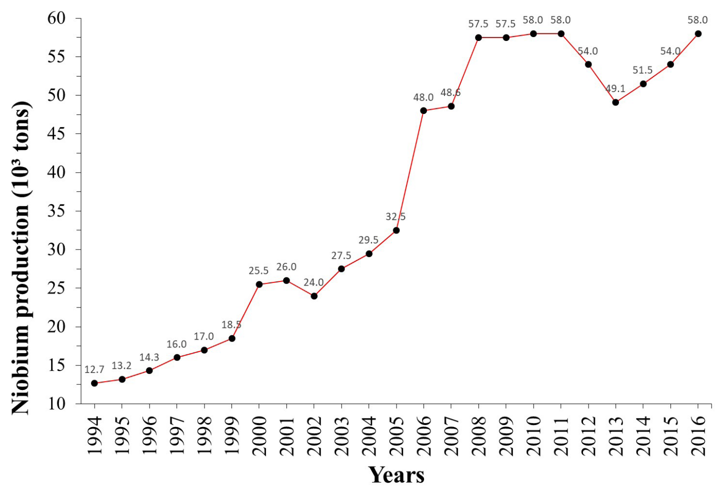

Figure 1. Brazilian's Niobium production (1994-2016) [4].

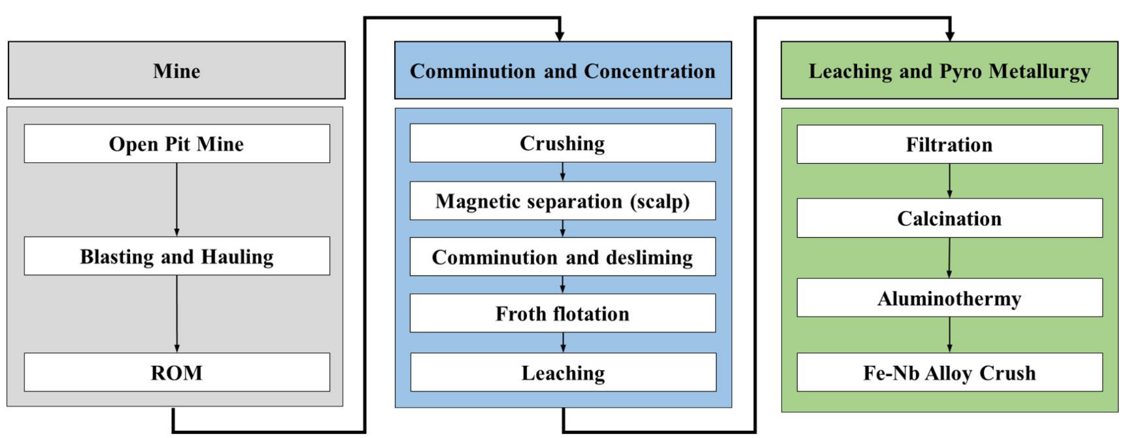

Figure 2. Fe-Nb alloy production flowsheet.

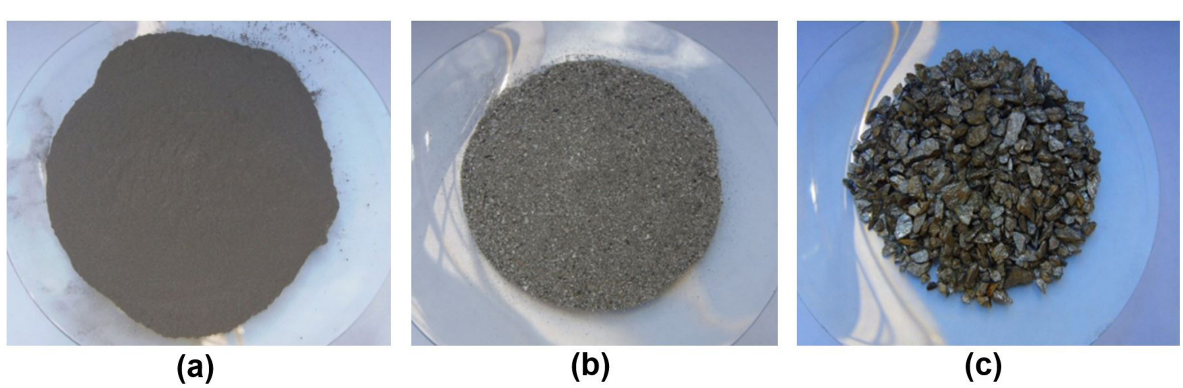

Figure 3. Fe-Nb fine particles: (a) under 2 mm (or type A), (b) between 1 and 5 mm or type B and (c) between 3 and 15 mm or type C.

careful analyses. According to Carvalho and Brinck [6], this involves not only laboratory work in order to produce the agglomerate, but also its physical and chemical characterization. Among the agglomeration techniques, the most important ones in mineral processing are pelleting, sintering and briquetting. Some important work were performed in this field, such as Moraes and Kawatra [7], which tested how binders successfully used in the pelletizing of Brazilian hematitic iron ores, using disk pelletizer, would perform in the processing of an American magnetite concentrate by balling drums. Although the results were very good, the operational cost of the pelleting was relatively high when compared with the other two methods. Telles et al. [8] developed a sintering process to agglomerate electric arc furnaces dust in order to recycle this material in the steelmaking. In their process, the dust had to be first agglomerated as micro-pellets and then sintered. Lucena et al. [9] were able to produce a low-cost charcoal wastes briquetted to be used in blast furnaces and for energy generation using a piston extruder. On the other hand, Silva et al. [10] were able to agglomerate limestone fines using a batch briquetting process. In both case the operational cost where small.

Taking in consideration the fact that the Fe-Nb fine particles has very small moisture content, high melting point (1,900 °C) and is very abrasive the briquetting was choose as the most feasible technique to agglomerate the fine particles.

2 METHODOLOGY

2.1 Briquettes Production

Samples of the Fe-Nb fines produced from gridding, screening, and handling were sent to two different companies in Brazil to be agglomerated (Höganäs and Renova). Höganäs used a piston extruder and Renova a high-pressure roll press. Each company produced two different briquettes composed by a blend of the fine particles type composition (see Table 1). The briquettes were labelled as H (for Höganäs) and R (for Renova) followed by the percentage of the fines on it. The main differences in the two processes were the manufacture costs and briquettes geometry.

The organic binders used were zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) and zinc palmitate ($Zn(C_{16}H_{31}O_2)_2$) in a proportion of 70 and 30% respectively. Iron powder with very low impurities grade was used as lubricant. The proportion, in weight, of addictions was 3% of binder, 2% of iron powder, and 1% of water. The homogenization of the particles was performed in a mixing tank, where the fine particles were added first and then water and the binders. Samples were sent to XRD on a PANalytical's AXIOX MAX and NDIR spectroscopy on a Quimitron's QCS-2010 at Niobras chemical lab.

Table 1. Briquettes composition regarding the fine particles type

Briquettes	A	B	C
R100-0-0	100	0	0
R0-100-0	0	100	0
H50-40-10	50	40	10
H60-40-0	60	40	0

2.2 Fe-Nb Briquettes Characterization

2.2.1 Shatter test

Shatter test (or Impact Resistance Test or Drop Test) determines the briquette strength to withstand repeated drops, simulating impacts that occur naturally during handling and transportation. According to Carvalho and Brink [6] for uncured briquettes, 3 drops from 30 cm are considered a reasonable value. Eighteen briquettes from each type were submitted to shatter tests from 30, 50, 75, 100, 125 and 150 cm height.

2.2.2 Uniaxial compression and tension

A compressive load was applied direct to the briquette using a hydraulic press until the briquette rupture, as described by the Brazilian Association of Technical Standards (ABNT) NBR 12767/92 [11]. To evaluate the tension resistance the method created by Professor Lobo Carneiro was used. This method calculates the tensile strength through a diametric compression test (Falcão and Soares [12]). Altogether twenty-six briquettes where used in both tests). Briquettes manufactured by Renova could not be tested using Lobo Carneiro test because of their geometry.

2.2.3 Water absorption

According to Cunha et al. [13] in this test, briquettes must be complete submerged in water for 24 hours. After this time, the briquettes must be removed from water and put to rest in room temperature for 10 minutes in order to remove the water layer adsorbed in their surface and then weighted. Then they must be dried in a drying oven at 80°C for 2 hours. In order to return the briquettes to room temperature they must be put to rest again for 20 minutes and weighted again. The amount of water that is absorbed by the briquette is important when the briquettes can be stored in open areas [6]. Altogether forty-eight Fe-Nb briquettes where tested.

2.2.4 Thermal shock

The shock temperature can be defined as the maximum temperature that the briquette resist without lose more than 10% of its mass, without collapse or explode, during a fast temperature elevation. Briquettes were weighted and placed in a steel cylinder with holes in the lid and placed in a muffle oven with temperatures ranging from 300 to 550 °C for 20 minutes. The briquettes were removed from the oven and let to rest in room temperature before a new weighing. The maximum temperature reached was the temperature when the briquette start to combust (defined as ignition temperature). Sixty briquettes where submitted to thermal shock test.

2.2.5 Brinell hardness test

The diameter of the tungsten carbide indenter used was 10 mm with loads ranging from 500 to 3000 kg. During the test, the load was maintained constant for 30 s (Callister and Rethwisch [14]). Twenty-five briquettes where used measure the Brinell hardness.

2.2.6 Tumbler drum test

The tumbler drum test is derived from the R-556 of the MICUM standard for coke of the International Organization for Standardization (ISO). In this test, 1.5 kg of briquettes were placed in a steel test drum (29 cm long and 30.5 cm diameter) fitted with four steel angles with 6.5 cm wider, fixed lengthwise inside the drum. The drum was rotated at 25 rpm for eight minutes (200 revolutions in total).The material was then sieve-analysed to measure the size reduction that has occurred.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fe-Nb Fines

Figure 4 shows the granulometric analyse of the Fe-Nb particles before the agglomeration. It is possible to notice that particles type A (under 2 mm) and type B (between 1 and 5 mm) were well classified, fitting into their label. On the other hand, particles type C (between 3 and 15 mm) where actually smaller than expected. In fact, particles type C were smaller than 7 mm.

Table 2 shows the chemical results of the Fe-Nb fine particles compared to a standard composition of the alloy as expected by the steelmaking market. Due to mineral associations at Niobras mine, the main contaminants are P, Ti and Mn. All three fine particles types are chemically adequate for steelmaking.

3.2 Fe-Nb Briquettes Characterization

3.2.1 Shatter test

Figure 5 summarizes the average resistance of the briquettes regarding the number of drops at different heights supported in the shatter test. It was possible to notice that cylindrical briquettes manufactured by Höganäs had a high tendency in complete fragment themselves after a few drops, even from the smallest heights. The higher resistance was observed for the briquette R-0-100-0. For heights higher than 100 cm all type of briquettes showed a similar behaviour, losing 5% or more of their initial mass in less than 10 drops.

3.2.2 Uniaxial compression and tension

Figure 6 shows the average results found in the uniaxial compression test for the four types of briquettes and the results for the uniaxial tension test for the cylindrical

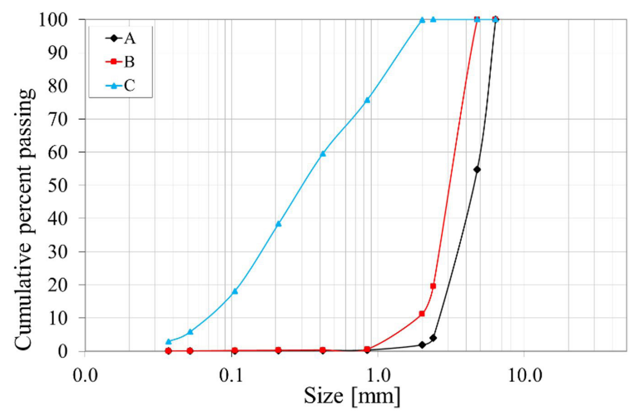

Figure 4. Granulometric analyse of the Fe-Nb fine mixes before the agglomeration. Type A (under 2 mm), type B (between 1 and 5 mm), and type C (between 3 and 15 mm).

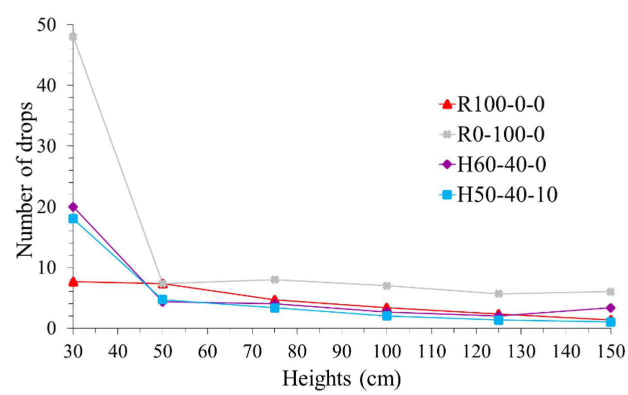

Figure 5. Average shatter test results.

Table 2. Standard Fe-Nb composition and chemical composition of the fine particles

Elements (%)	TYPE			
	Standard	A	B	C
Nb*	62-67	64.56	65.17	65.25
P*	< 0.20	0.15	0.17	0.15
Fe*	25-30	29.18	28.65	27.97
Ti*	< 1.00	0.33	0.25	0.24
Mn*	< 0.50	0.30	0.30	0.35
Si*	< 3.00	2.95	2.85	2.68
Ta*	< 0.50	0.31	0.31	0.29
Pb*	< 0.20	0.19	0.19	0.18
Al*	< 1.00	0.40	0.31	0.23
C**	< 0.15	0.14	0.14	0.13
S**	< 0.15	0.07	0.09	0.07

* XRD results and ** NDIR results.

briquettes. Briquettes manufactured by Höganäs obtained the higher results and this could be related with their geometry, once the cylindrical shape provides a better contact surface with the hydraulic press. The soap shaped briquettes had a poor contact surface, with normally one contact point and not a proper surface. Regarding the tension resistance, the cylindrical briquettes showed a resistance around 50% of the compression resistance. Compared with other materials this is a high value. Concrete, for example, shows tension resistance around 10% of the compression resistance.

3.2.3 Water absorption

Briquettes supported the immersion in water for 48 hours without any physical degradation or decomposition, remaining almost intact. Figure 7 shows the water absorption test results. It is possible to notice that all briquettes had their mass increased at least by 1% after 48 hours of immersion in water. Although the Renova briquettes had the high mass gain during the test, the briquettes behaviour was quiet unusual, since a plateau was expected describing a water saturation level. Explanations for this behaviour could be the hydration of the binder agents, such as the iron powder, or chemical reactions of the Fe-Nb alloy with water.

3.2.4 Thermal shock

Since the Fe-Nb alloy was produced through aluminothermy, it was expected that all combustible material were complete consumed in that stage, but that was not the case. Every test performed at temperatures above 600 °C ignited the briquettes. The flame produced remained burnt around 12 hours after the briquettes ignition. Figure 8 shows the average fragments percentage generated at different temperatures during the tests. No clear pattern could be observed between the briquettes behaviour regarding the fragments generation during the test. It is possible to highlight that the briquette R100-0-0 supported 100 °C more than the briquette R0-100-0 and H50-40-10 before they start combusting.

3.2.5 Brinell hardness test

Figure 9 shows the average results found in the Brinell test. As expected, the found results were quite low for all briquettes since they are agglomerated materials, formed mainly by the mechanical forces. Therefore, their indentation resistance must be low and, in this case, compatible with a polymeric material or minerals with Mohs hardness bellow gypsum.

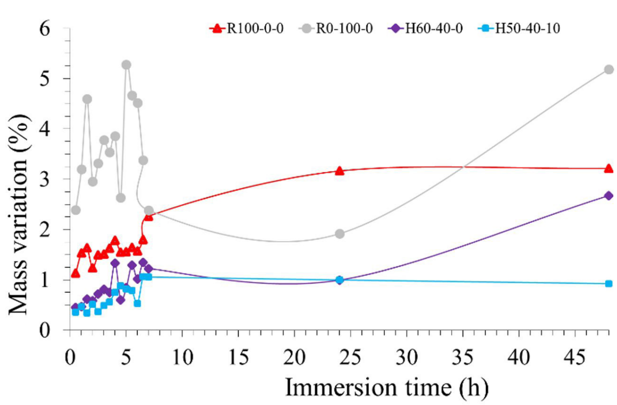

Figure 6. Average uniaxial breakdown load (compression and tension) results.

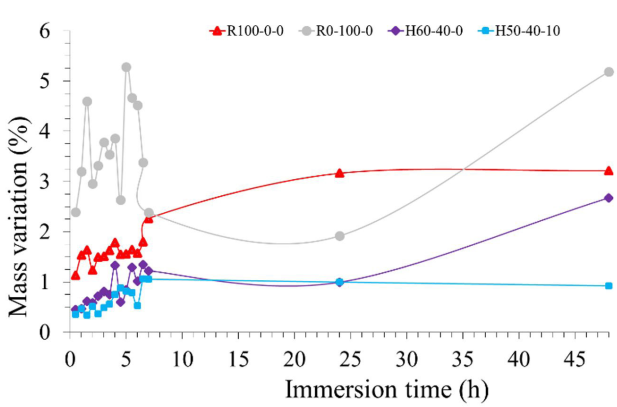

Figure 7. Average water absorption test results.

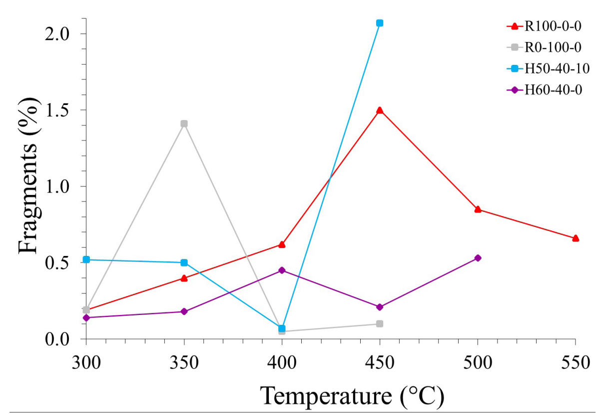

Figure 8. Average briquettes fragments percentage generated at different temperatures.

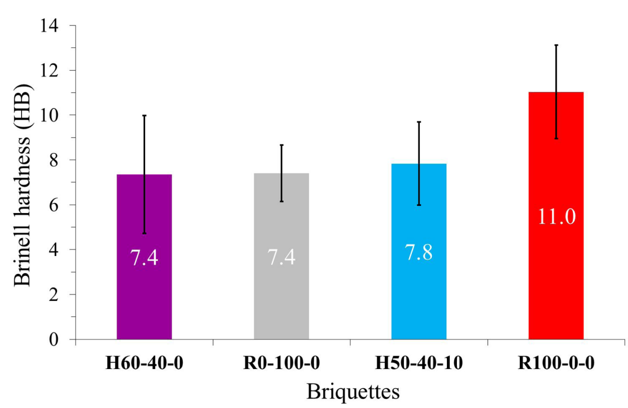

Figure 9. Briquettes average Brinell hardness.

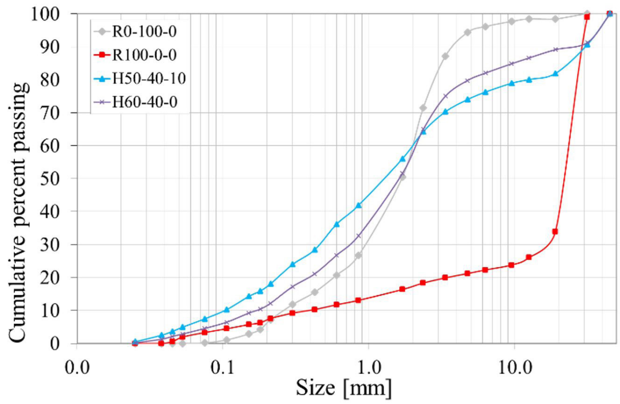

Figure 10. Granulometric analyse of the briquettes after the tumbler test.

3.2.6 Tumbler drum test

Figure 10 shows the average granulometric analyse of the briquettes after the tumbler test. Considering the material passing in sieve with aperture 3/4" (or 19 mm) only the briquette R100-0-0 had a considerable resistance, producing 34% of its mass bellow this aperture. This result is consistent with the Brinell hardness result, since the R100-0-0 was the briquette hardener one and the tumbler test evaluate the shear resistance of the material. The other briquettes had results above 80% of passing (98.5% for R0-100-0, 89.2% for H60-40-0 and 81.9% for H50-40-10).

4 CONCLUSIONS

Regarding the shatter test, all tested briquettes succeeded in the test considering the literature parameters. However, the found results were heterogeneous and a trend could not be stablished. Briquettes manufactured by Höganäs (cylinders) showed results slightly more homogeneous than the ones manufactured by Renova.

It was possible to notice in the uniaxial compression test that briquettes manufactured by Höganäs had better results, however showing a standard deviation higher than Renova's briquettes. This fact may be due to the geometry of them, once Höganäs' briquettes have a better stress distribution because of their cylindrical shape. The same briquettes showed a higher than expected uniaxial tension resistance.

All briquettes were able to resist the water absorption test retaining their shapes. For higher immersion time Höganäs' briquettes complete disintegrate, not retaining either shape or mechanical resistance. In some briquettes, immersed for 48 hours, it was possible to notice some oxidation spots on them. Only one briquette (R0-100-0) did not gain mass after the test.

Regarding the thermal shock, all briquettes were successful. Although it was not possible to stablish a trend from the obtained results, the briquettes ignition temperature was stablished bellow 550°C (450°C for R0-100-0 and H50-40-10, 475°C for H60-40-0, and 550°C for R100-0-0).

Briquettes showed a low Brinell hardness, which was expect once they were only agglomerated through mechanical stress, without the addition of any kind of chemical binder. At last, regarding the tumbler test all types of briquettes generated fine particles during the test. Although the briquette R100-0-0 showed a higher resistance compared with the others.

Summarizing the found results both fabrication methods can be industrially adopted for briquette production with parameters acceptable by the steelmaking marketing. All fine particle blends tested were successful regarding the briquette chemical composition and mechanical properties. It was not possible to choose one manufacture method between the two tested because the found results were quite different. In the end, the authors suggest the adoption of the cylindrical briquettes manufactured by Höganäs as the best choice, combining good results in most of the tests and the lower manufacture costs.

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