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Compressive Strength of Manganese Ore Fines and Molasses – Role of Binder Content, Raw Materials Size, and Heat Treatment

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***Abstract*—The manganese is one of the most used metals in the World. The beneficiation of manganese ores consists of sizing steps. After beneficiation, up to 50 % of the material mined is deposited in tailing dams due to its low particle size despite owing a proper chemical composition. Thus, briquetting stands as an alternative process which allows the use of such fines. To ensure a good performance of the briquettes in the manganese ferroalloy production furnace, it is important that the agglomerates have suitable compressive strength. Hence, this work aims to study the compressive strength of briquettes made of fine-grained manganese ore and molasses (as binder) and the influence of particle size distribution and heat treatment. It was produced different batches of briquettes with diversified parameters regarding binder content (5, 7,5 and 10 %), particle top size (0,250, 1,00 and 2,00 mm) and heat-treating temperature (without, 200, 300 and 400 ˚C).Based on the results obtained, the briquettes that showed the best compressive strengthhad a maximum particle size of 0,250 mm, with 10% of molasses, heat-treatment temperature of 200 °C, which resulted in a 33.3 MPa of compressive strength.**

***Index Terms*— Briquetting, Manganese ore fines, Agglomerates.**

I. INTRODUCTION

The manganese is one of the most used metals in the World [1]. The main use of manganese is as an alloying metal in steel in which it is added as ferroalloy [2]. Among the main manganese minerals there are pyrolusite (MnO_2) and Cryptomelane (KMn_2O_{16}) [1]. The beneficiation of manganese ores consists of sizing steps [3]. After beneficiation up to 50 % of the material mined is deposited in tailing dams due to its low particle size despite owing a proper chemical composition [2].

The manganese ferroalloy is produced in Submerged Arc Furnaces (SAF) and uses manganese lumpy ores as main raw material. Coke is used as reductant and limestone as flux which complete the main particulate raw materials charged inside the reactor [2].

The SAF is depicted in Figure 1 it is a circular furnace equipped with three Søderberg electrodes placed in the centre of the furnace [2]. Electricity flows from the electrode tip to the charge immediately below heating it which results in production of slag and metal [2].

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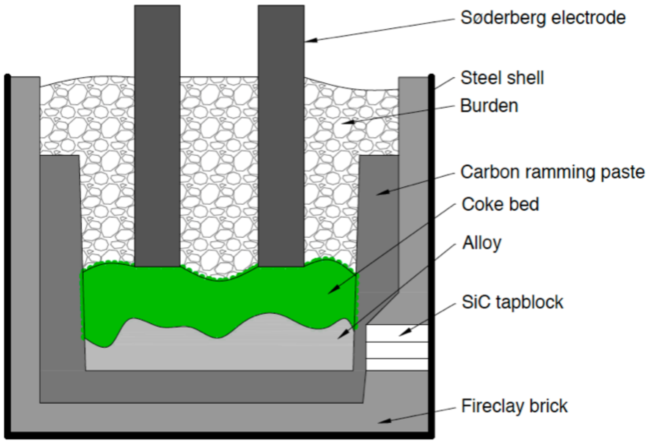

Figure 1. Schematic diagram of the submerged arc furnace [1].

There are two zones within the furnace: the prereduction zone and the coke bed zone. In the prereduction zone the higher manganese oxides are reduced to MnO by the CO gas produced in the coke bed zone. In the coke bed zone, the charge melts and a MnO-rich slag is produced. The MnO is then reduced by carbon, which produces CO that promotes the prereduction reactions. The Figure 2 presents a schematic diagram of the reactions within the furnace.

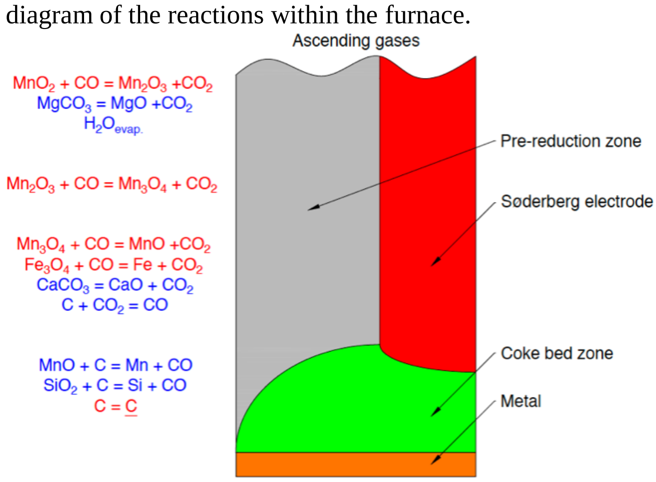

Figure 2. Main reactions in the submerged arc furnace [1]

The particle size is a key parameter of the charge, since it assures a good furnace performance and stable operation. The presence of fines in the charge materials fills in the spaces among the larger particles causing channelling of the gases. This undermines the prereduction reactions efficiency since they are gas-solid reactions, thus depending on contact between the phases [1, 4]. If the prereduction reactions are delayed to higher temperatures, it would result higher carbon consumption as the carbon demanded by such reactions is produced through Boudouard reaction. Furthermore, it also raises the energy consumption of the furnace [1–4].

Thereby, briquetting of manganese fines is an alternative to charge these materials in the furnace. The use of this process is promising as the fine-grained materials had suitable chemical composition. Thus, the compressive strength is an important parameter because a proper mechanical performance would prevent them to behave as fines inside the furnace [2].

Thus, this work has as aim study the compressive strength of briquettes made of fine-grained manganese ore and molasses (as binder) and the influence of particle size distribution and heat treatment. This work is based on the hypothesis that there is a set of parameters regarding raw materials top-size and heat treatment temperature that raises the compressive strength of the agglomerates up to a suitable standard.

To pursue the main aim of this work, the following specific objective were pointed: assess the influence of binder content in the compressive strength; evaluate the influence of the raw material's top-size in the compressive strength; measure the impact of heat treatment in the compressive strength of the briquettes.

II. Materials and Methods

The experiments were performed in the Metallurgy Laboratory of the Federal Institute of Mato Grosso do Sul. The fine-grained manganese ore as well as the binder (molasses) used in the work were provided by a local industry.

The raw materials were sieved in three different top-sizes: 0,250, 1,00 and 2,00 mm. To study the influence of the binder content in the compressive strength each of the different top-sizes samples were mixed with 5, 7,5 and 10 % of molasses. For every set of parameters, 5 specimens were produced to be tested. Table 1 presents the different parameters, regarding particle top-size and binder content, for each batch of briquettes produced.

Particle top size [mm]	Binder content [%]		
0,250	5,0	7,5	10,0
1,00	5,0	7,5	10,0
2,00	5,0	7,5	10,0

Table 1. Particle sizes and binder content of the different batches of briquettes.

Furthermore, briquettes with three different binder content (5, 7,5 and 10 %) which the top-size was 0,250 mm were made to study their compressive strength after heat treatment under 200 ˚C. In order to further explore the influence of the heat treatment on the strength of the agglomerates, a batch whose top size was 0,250 mm and the molasses content was 10 % was also produced. This batch was heat treated in 300 and 400 ˚C. Table 2 presents the set of parameters, regarding particle top-size and binder content, of the study of the influence of the heat treatment temperature on the compressive strength of the briquettes.

Temperature [˚C]	Binder content [%]		
200	5,0	7,5	10,0
300	-	-	10,0
400	-	-	10,0

Table 2. Heat-treatment temperature and binder content of the different heat-treated batches of briquettes.

The raw materials were weighted and mixed in a Becker with the use of a propeller. The briquettes were produced in a die and punch with an inner cavity of 10 mm (Figure 3), the briquetting cavity was lubricated with engine oil. The mixture was placed inside the die and was pressed in a hydraulic press at 1 ton of pressure. The briquettes were released from the die and were stored for 7 days.

Figure 3. The cylindrical die and punch.

The briquettes from the batches presented in the Table 1 were then tested to its compressive strength in an EMIC multipurpose mechanical device with a charge cell of 20 kN. In the Figure 4, a batch of briquettes is presented.

Figure 4. A batch of briquettes made with 0,250 mm top size raw material and 7,5 % of molasses.

The agglomerates showed in Table 2 were heat treated in a furnace. The heating rate was 10 ˚C/min and the materials were kept at the target temperature for 1 hour. The compressive strength data for this batches was obtained as previously described.

III. Results and Discussion

The results obtained by the experimental procedure previously mentioned were presented in Table 3.

Furthermore, it is presented the set of parameters for each batch of tested briquettes.

Raw materials top size and binder content influence			
Top size [mm]	Binder [%]	C. S. [MPa]	Other parameters
0,250	5,0	3,2	Cure: 1 week
	7,5	6,1	
	10,0	4,5	
1,00	5,0	5,8	
	7,5	5,4	
	10,0	3,6	
2,00	5,0	3,5	
	7,5	4,0	
	10,0	3,2	
Heat treatment and binder content influence			
Temperature [˚C]	Binder [%]	C.S. [MPa]	Other parameters
200	5,0	8,3	Cure: 1 week Top size: 0,250 mm
	7,5	14,3	
	10,0	33,3	
Heat treatment temperature influence			
Temperature [˚C]	Binder [%]	C.S. [MPa]	Other parameters
300	10 %	8,9	Cure: 1 week
400		12,5	Top size: 0,250 mm

Table 3. Set of parameters and compressive strength [C. S.] of the tested briquettes.

The Figure 5 shows the influence of binder percentage in the compressive strength in specimens made with different particle top-sizes. In the briquettes which the top size was 0,250 mm there was an increase in the compressive strength with the raise of the binder content. The batches whose top size was 1,00 and 2,00 mm, the increase of the binder content decreased the compressive strength.

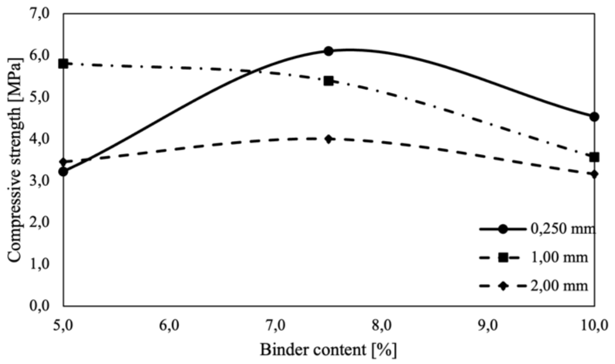

Figure 5. Compressive strength *versus* binder content.

The Figure 6 presents the influence of binder content in the compressive strength as well as a comparison between batches with and without heat treatment at 200 ˚C. The heat treatment increases compressive strength of the specimens. As the binder content increases, the compressive strength of the heat-treated samples also increases. Furthermore, the compressive strength of the non-heat-treated samples remains slightly stable when the binder content was rise.

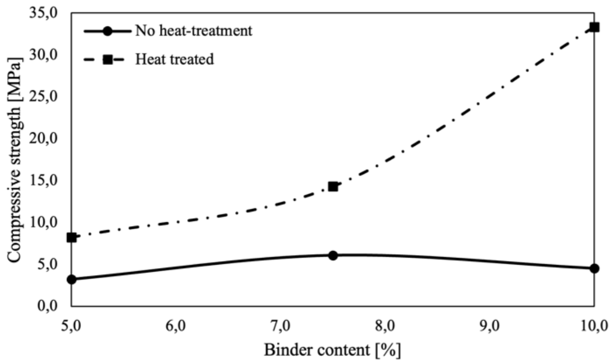

Figure 6. Compressive strength *versus* binder content and the influence of heat treatment.

Figure 7 shows the relation between compressive strength and heat-treatment temperature in a batch of briquettes made with top size of 0,250 mm and 10 % of binder content. The increase of heat-treatment temperature decreases the compressive strength. However, for the data presented, the compressive strength of the samples which the temperature was 400 ˚C is somewhat higher than the 300 ˚C specimens.

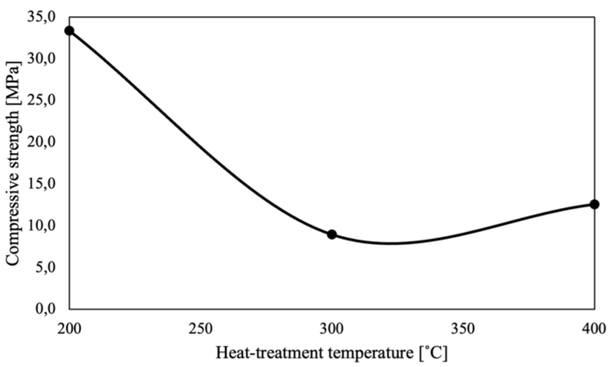

Figure 7. Compressive strength *versus* heat-treatment temperature.

Figure 8 depicts the relation between the bulk density and compressive strength. The labels for the data presented are summarized in Table 4. The data is clustered by batch, since it was made 5 measurements for each set of parameters. The plot also shows no correlation between bulk density and compressive strength.

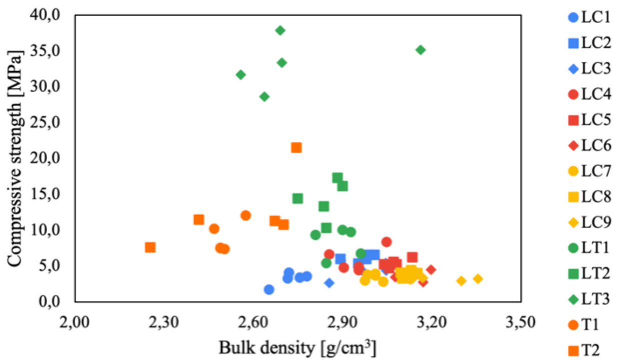

Figure 8. Compressive strength *versus* bulk density.

To confirm the low correlation between bulk density and compressive strength, the Table 4 is presented. The table presents the coefficient of determination (R2) for each batch of tested specimens. The presented data, make a clear on the statement that the compressive strength is not correlated with the bulk density.

Raw materials top size and binder content influence			
Top size [mm]	Binder [%]	Label	R^2
0,250	5,0	LC1	0,5114
	7,5	LC2	0,2706
	10,0	LC3	0,1754
1,00	5,0	LC4	0,1969
	7,5	LC5	0,6812
	10,0	LC6	0,0656
2,00	5,0	LC7	0,0380
	7,5	LC8	0,2348
	10,0	LC9	0,0352
Heat treatment and binder content influence			
Temperature [˚C]	Binder [%]	Label	R^2
200	5,0	LT1	0,0001
	7,5	LT2	0,1118
	10,0	LT3	0,1581
Heat treatment temperature influence			
Temperature [˚C]	Binder [%]	Label	R^2
300	10 %	T1	0,3946
400		T2	0,4252

Table 4. Label and coefficient of determination of each batch of briquettes.

The cohesion mechanisms of briquettes as well as the binder demand were previously described by Eisele and Kawatra [5]. According to the authors, the compressive strength is connected to the particle size distribution of the raw materials. Fine-grained particles are important, since they have high superficial area which contributes to van der Waals intermolecular forces that bind two or more particles together. Due to the higher superficial area of the fines, there is a need to higher amount of binder to provide the proper connection between the particles. In contrast, coarser particles have lower superficial area, consequently, they have lower need of binder to maintain the agglomerate cohesion. Thus, to raise the binder content may cause the formation of a film of binder in the particles surface which lower the compressive strength of the briquettes.

The mechanism previously described by Eisele and Kawatra [5] based the explanation to the results observed in Figure 7. The increase of binder content increases the compressive strength of the briquettes whose top size was 0,250 mm due to interaction between the molasses and raw materials surface. As the binder content was raised, more particles were connected raising the compressive strength. However, the further increase of molasses content may form a film of the binder between the particles, which lowers the strength of the agglomerate. The decrease of superficial area by the increase of particle size of the raw materials lowers the compressive strength at lower binder contents as it was shown.

The effect produced by the heat treating of the briquettes was previously described by Hartel and Shastry [6] and de Jesus [1]. According to Hartel and Shastry [6], the heat treating at 200 ˚C led to proper conditions to crystallization of the sugar present in molasses. Furthermore, the higher binder content allowed the formation of a higher quantity of crystals. The increase of the heat-treating temperature may have caused molasses decomposition, thus, instead of crystallization, it was observed the bind phase decomposition, which explains the lower compressive strength results found in samples heat treated at 300 and 400 ˚C. The molasses decomposition was also observed by de Jesus [1] at such temperatures in thermogravimetric tests.

Da Luz [3] and Baptista [7] explained the compressive strength of briquettes as result of an effective packing, hence a high densification of the briquetting mixture. According to da Luz [3], the compressive strength of the briquettes is related to its bulk density. The results, presented in Figure 7, showed divergent results from what is stated in the literature. Furthermore, the hypothesis that may explain the low correlation between bulk density and compressive strength results is that there were other parameters that affected the compressive strength, such absence/presence of surface defects as well as charge homogeneity.

IV. Conclusion

Briquettes with manganese ore fines and molasses were successfully produced. The briquettes made with raw material with 0,250 mm of raw materials top size, 7,5 % of molasses, and 2,00 mm and 5 % presented the best compressive strength. The briquettes heat treated at 200 ˚C presented the best results among the set of tested parameters due to the proper environment to molasses crystallization. In briquettes whose heat-treatment was carried out at 300 and 400 ˚C, binder decomposition may have occurred, which explain the decrease in the compressive strength. It was also possible to conclude that, for the tested data, the bulk density was not a parameter that influenced the compressive strength of the agglomerates.

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