Carbothermic Reduction of Manganese Ore Fines Using an Organic Binder

M.R Malatji and MK. Wa Kalenga

***Abstract*—**Fines resulting from processing fines often pose environmental risks and result in the loss of valuable metal when stored or disposed of as they are not amenable to heat treatment in their fine state. Inorganic binders were found to negatively affect the quality of the product by introducing impurities. The present study focused on the effect of using an organic binder, Alcotac CB6, on ore agglomerates in terms of mechanical and water-retention properties as well as reduction behaviour. The findings indicate that a drying time of 48hrs is recommended for air-drying. The increase in binder quantity was found to make the briquettes less susceptible to disintegration. In terms of reduction behaviour, increasing the binder content induced difficulties in reduction, where the oxide with the least energy requirements in terms of thermodynamics was preferably reduced, and thus was present in higher proportions in the final product.

***Keywords*—** Alcotac CB6, Briquettes, Manganese Ore Fines, Mechanical Properties, Drop Test, Carbothermic Reduction.

I. INTRODUCTION

Manganese is a crucial raw component in the production of high-quality steel. Mn ores are currently being at a very high rate as a result of the rise in steel demand in developing nations. The steel sector consumes 95% of the manganese ore produced annually, with the remaining 5% going to other industries like the chemical, paint, fertilizer, and battery industries [1]. It has been noted that there is a correlation between the products, with the production of Mn ferroalloys accounting for around 1% of the production of steel overall. The production of Mn ferroalloys accounting for around 1% of the production of steel overall. According to the criteria and specifications for the final steel's chemical composition, various grades of Mn ferroalloys are manufactured. Silicium manganese (SiMn), high-carbon ferromanganese (HC-FeMn), and refined ferromanganese (medium-carbon (MC-FeMn) and low-carbon (LC-FeMn) are the three major categories of Mn ferroalloys [2].

After mining, manganese ores are subjected to size reduction and concentration techniques, in an attempt to make the ore more susceptible to the subsequent treatment processes, and to remove the gangue associated with that specific ore. The desirable product from these processes is a concentrate of the required particle size, rich in the mineral of interest, in this case pyrolusite. The manganese concentrate is then treated in Electrical furnaces to obtain purer manganese in a liquid state. Other purification steps may be taken before its utilization in steel applications. During the mining, handling, and processing activities, the production of fines is inevitable due to breakage of large particles because of compression, abrasion, attrition and impact of the ore particles with one another and the equipment during beneficiation and handling [3]. The fines generated as a result, contain substantial amounts of the valuable mineral (Pyrolusite). Processing these fines will present some economic benefits for the company as less valuable metal (Mn) will be lost in the overall operation. The problem encountered during the processing of these fines is that they cannot be charged into the furnace, as they tend to get displaced by shockwaves generated in the electric arc furnace when the arc is formed. The reason they get displaced is because of their very low mass which makes it difficult for them to withstand the high-pressure wave formed by the arc. These shockwaves are as a result of rapid heating of the material in the furnace and gas expansion. Consequently, these fines will not be reduced, and the overall recovery of Manganese ores remains low. This necessitates the focus on treating these fines and making them amenable to heat treatment in the furnace charging.

Experience has demonstrated that close size control of the raw materials results in the efficient and smooth functioning of manganese ferroalloy smelting furnaces. For the gas to be spread throughout the load, the raw materials must ensure adequate permeability. Particularly harmful, are the fines in the raw materials, which lead to poor charge porosity, high power consumption per ton of alloy, significant fume and dust losses, and low productivity. Producers of alloys favor lump and agglomerated ores. High-quality fines are frequently agglomerated, typically using a sintering process at the mine or the customer's factory. Agglomeration processes to be considered include Sintering, Pelletizing and Briquetting. Manganese ores require more effort to pelletize than the majority of iron ores do. The technique is more expensive because stronger manganese ore pellets need higher temperatures (>1150 to 1250C). Manganese dioxide (MnO2) and manganic oxide (Mn2O3) dissociate in endothermic processes when green pellets are heated, increasing the fuel requirement. Additionally, for pelletizing, the material would need to be finely ground. Therefore, compared to iron ore,

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pelletizing manganese ore appears to be a rather expensive approach, while there have been recorded attempts to pelletize fine manganese ores (flotation enhanced) into 12 to 15 mm size pellets using low temperature drying [4].

There is a large capital investment requirement for the sintering and pelletizing operations, as well as a high cost for grinding and burning [4]. Therefore, briquetting is more favorable than other agglomeration methods because it is low cost, as it is a cold bonding process and offers flexibility in terms of particle size, eliminates the need for roasting agglomerates and earlier grinding. Briquetting is accomplished by agglomerating particles via electrostatic and Van der Waals forces between particles, moisture-related capillary bridges, and the addition of binders that provide adhesion and cohesion forces. Furthermore, by including binders, the fine and coarse particles are held to the surface of each other, thus preventing segregation. These particles stick together to create larger, more durable agglomerates when subjected to external stimuli. To avoid the formation of fines within electric furnaces, which leads to gas collection, pressure builds up, and eventually explosions, it is essential to make sure that agglomerates are stable [5].

Prior to the development of vibro-pressing and stiff vacuum extrusion, roller presses were a commonly utilized tool for briquetting in the field of ferrous metallurgy. The briquetted mixture is supplied into the space between two rolls that are rotating in the opposite direction. These rolls have proportionately positioned cells in the shape of semi-briquettes that are placed in a checkerboard pattern on their surfaces. Convergence of cells, the capture of the material, and its sealing compression occur while the rollers are rotating. The Bilateral compression of the material results in a more even distribution of its density by volume. Afterward, the cells diverge as the rolls revolve, and under its weight, the briquette exits from the cell [6].

In previous studies, inorganic binders have been used to form agglomerates from fine ores. Inorganic briquette binders often come in the forms of clay, lime, plaster, cement, sodium silicate, and sodium silicate. Industrial briquette binder, civilian briquette binder, and environmental protection briquette binder are the three categories into which inorganic binder can be divided. The inorganic binders have several great benefits, including good hydrophilicity, low cost, non-pollution, and strong adhesion. In addition to having strong bonding capabilities, organic binders also produce briquettes with high crush and drop test strengths [7]. Bentonite, which is an inorganic binder, has been used in the agglomeration of ores, especially iron ores. Despite all its benefits, using bentonite as a binder has several drawbacks, such as the dilution of pellets, the high price and scarcity of a quality binder, the high cost of its transportation, and the significant energy expenses involved in bentonite's preparation for technical processes. Bentonite and other inorganic binders are known to introduce additional silica into the furnace, which leads to increased energy requirements in separating the hot metal from the slag. The mechanical strength and thermal stability of the briquettes made with organic binder are poor at high temperatures, despite the fact that organic binder is easily decomposed at those temperatures [6].

II. METHODOLOGY

A. Characterization

A basic manganese ore sourced from Nchwaning was subjected to X-Ray Fluorescence (XRF) analysis to accurately determine its grade. The reductant (metallurgical coke) was also characterized using proximate analysis to determine its moisture, volatile matter, ash content which enabled the determination of its fixed carbon content. Silica, which functioned as a flux was also analyzed using XRF.

B. Experimental Procedure

The first step in the procedure was to determine the stoichiometric amount of metallurgical coke required to fully reduce the ore taking into account the major constituents in the ores which were iron oxide and manganese oxide. The amount of flux(silica) required to achieve the basicity of one taking into consideration acidic and basic compounds in the ore. The size analysis of the components was determined. The ore was milled to 80% passing 1mm to narrow the size difference the components. 6 different batches of ore, coke, flux and varying binder amount were formed and homogenized. The batches were then mixed with water to form wet mixtures which were then used to form briquettes. A briquetting machine was used to form briquettes with a height of about 1cm. The briquettes were air-dried for moisture removal. The change in the weight of the briquettes was recorded every 24hrs for a period of 96hrs to monitor the moisture released by the briquettes. After a period of 96hrs, three of the briquettes were investigated for mechanical stability by subjecting them to drop tests, which were performed 3 times, at a height of 2m for each briquette. The degree of disintegration was recorded for varying binder amounts. The remaining briquettes (3) were subjected to heat treatment at 1400°C for a period of 1hr. The effect of binder amount on reduction behavior was investigated.

III. RESULTS AND DISCUSSION

This section of the paper focuses on the results obtained from moisture removal, drop tests and carbothermic reduction.

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A. *Moisture Evaporation*

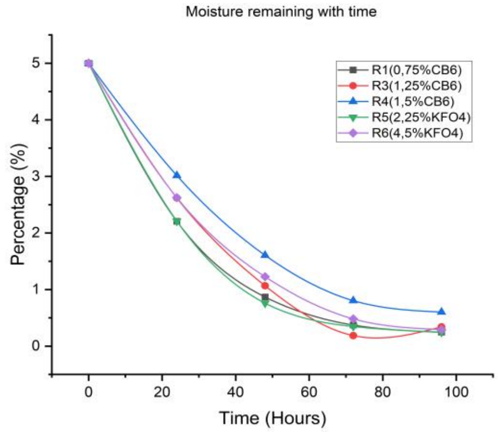

Fig. 1: The change in the moisture of the briquettes recorded every 24 hours.

The graph in the figure above shows the change in the moisture content of the briquettes over a period of 96 hours. The moisture was first recorded from the moment the briquettes were created and thereafter every 24hrs until a period of 96 hours was reached. All the briquettes had an initial moisture of 5%. It can be observed that at a time of 24 hours, sample R4(1.5% of binder) had the highest moisture remaining with a percentage of 3.01%, with R3 and R6 having moisture of 2.62% and R1 and R5 having moisture of 2.21%. After a period of 96 the moisture remaining, sample R4 has the highest moisture remaining with 0.6% with the other briquettes having a final moisture ranging from 0.24% to 0.34%. By analysing the curves representing the moisture evaporation of R1 and R5, the curves follow the same path, indicating that they release moisture at the same rate. It should be noted that R1 had a binder content of 0.75% CB6 whereas R5 had a binder content of 2.25% KFO4. This shows that CB6 has a greater binding ability than KFO4.

Most of the moisture released by the time of 48 hours, this can be seen by the steep slope between the time of 0 and 60 hours. After 60 hours, the slope becomes gentle, indicating that the change in moisture is very little. In terms of production, it would not be very economical to leave the briquettes to dry out for a period greater than 60 hours, since the moisture released after that period is not too significant.

B. *Degree of Disintegration*

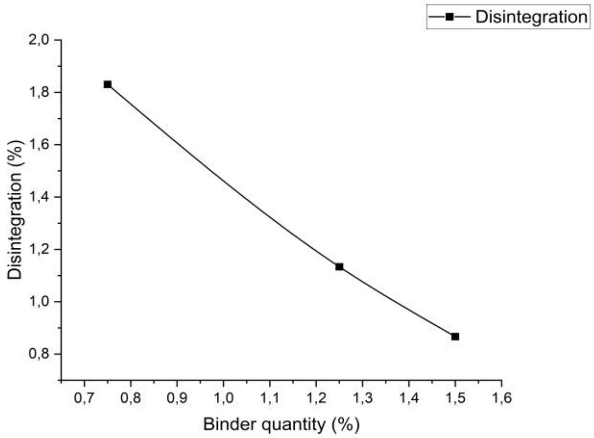

Fig. 2: A plot showing the degree of disintegration with varying binder amounts.

The drop test was performed on three briquettes each containing the binder amounts, 0.75%, 1.25% and 1.50% by weight. This specific experiment was conducted to investigate the effect of binder quantity on the structural integrity of the briquettes and their resistance to disintegration. Upon the completion of the drop test, it was observed that the disintegration values recorded were 1.831%, 1,134% and 0,867% for binder quantities of 0.75%, 1.25% and 1.50%, respectively. The general trend that can be observed is that as the binder quantity increases, the disintegration of the briquettes decreases. This signifies that increasing the binder quantity increases the overall strength of the briquettes.

At a microscopic level, the increased binder quantities introduce a greater number of adhesive bonding sites throughout the briquette structure. These additional bonding sites create a more extensive and robust network of adhesive forces acting upon the individual particles that comprise the briquette. The binder effectively forms bridges between particles, encapsulating them in a cohesive matrix that resists separation under mechanical stress. Furthermore, the higher binder content may also contribute to a more uniform distribution of adhesive forces throughout the briquette. This uniformity can help in distributing applied stresses more evenly, preventing the formation of weak points or stress concentrations that could lead to fracture or disintegration.

C. *Carbotherm*ic Reduction

For the carbothermic reduction test, three briquettes containing binder containing binder quantities of 0.75%, 1.25% and 1.50% were charged into the furnace at a temperature of 1400°C, for a period of 1hr. Following the carbothermic reduction experiment the fully reduced parts of the samples were analysed using SEM-EDS. The results are displayed and discussed below. The parts that were analysed are the Manganese-Iron phases formed after the carbothermic reduction process.

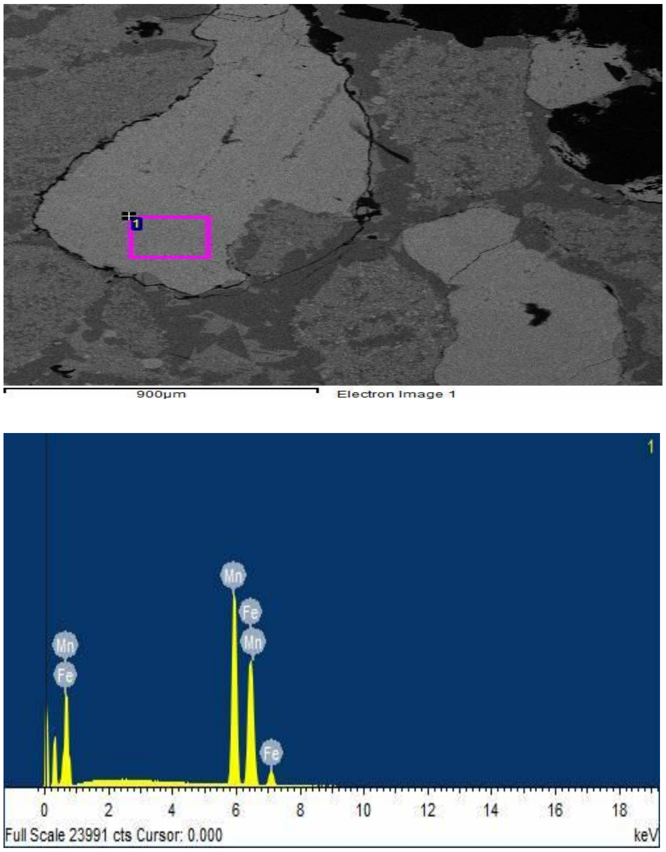

Fig. 3: SEM-EDS micrographs and spectrum for the sample containing 0.75% of organic binder.

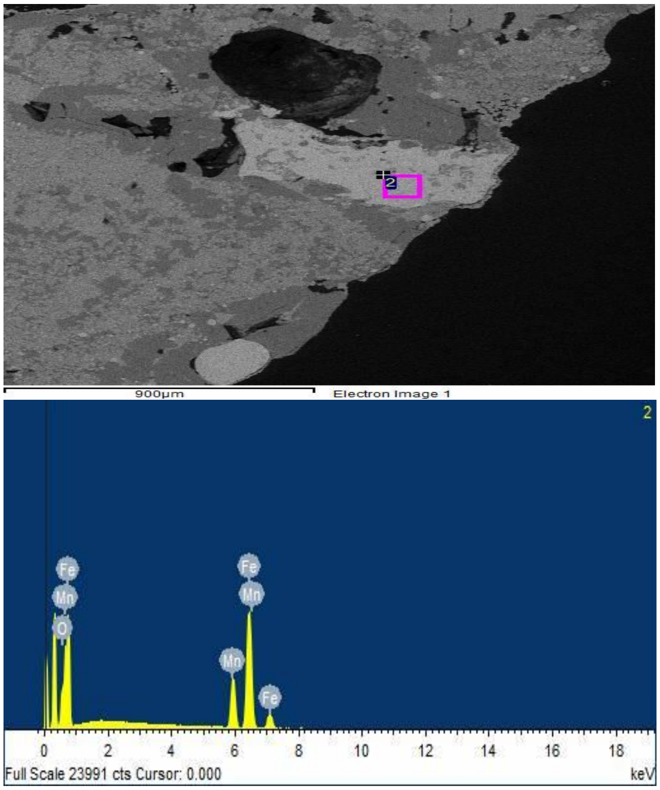

Fig. 4: SEM-EDS micrographs and spectrum for the sample containing 1.25% of organic binder.

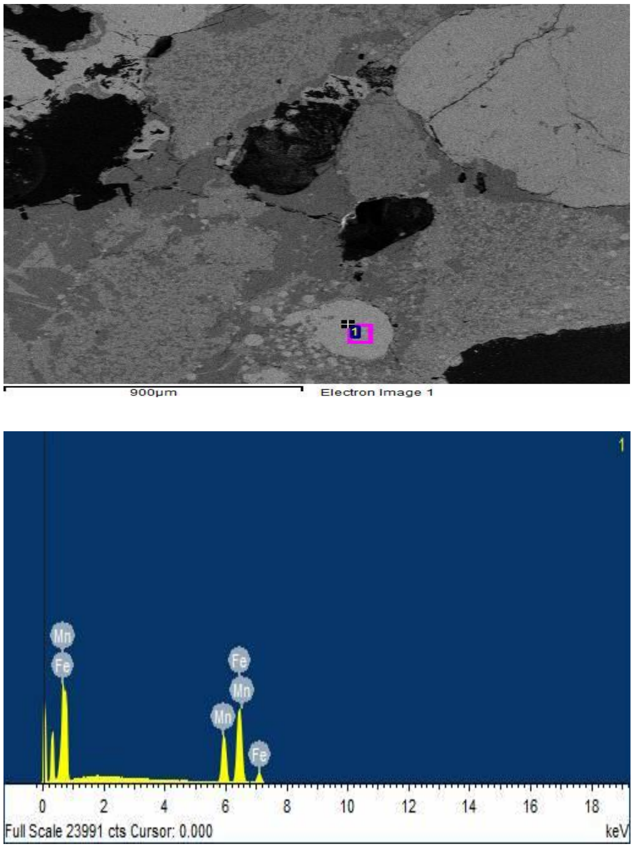

Fig. 5: SEM-EDS micrographs and spectrum for the sample containing 1.25% of organic binder.

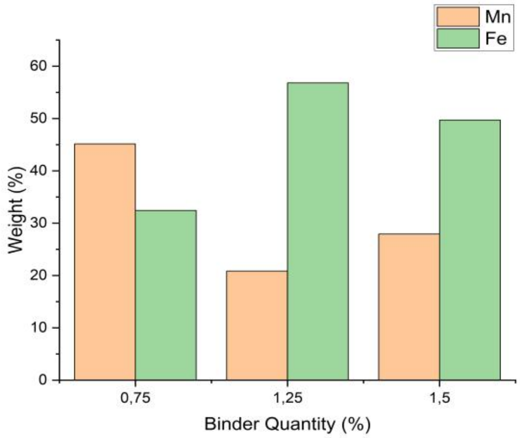

Fig. 6: A graph showing the metal phase analysis different binder quantities.

The graph was constructed using the weight percentages. The formation of an Mn-Fe with MnO occurring in a granular phase was predicted by Huang et al. in 2017. For sample R1, containing 0.75% of the CB6 binder, the weight percentages of Manganese and Iron were 45.14% and 32.43%, respectively. The weight percentages detected for R3(1.25% of the CB6 binder) was 20.85% and 56.80% for Manganese and iron respectively, and lastly the proportions of Manganese and Iron in the briquette containing 1.5% of CB6 were 27.93% and 49.70%. The general trend that can be observed is that as the binder quantity increases, the proportion of Iron increases, whereas the proportion of Manganese decreases. Is important note that the remaining percentage represent weight percentage of oxygen, which was most likely attached to manganese as result of manganese being irreducible at the operating temperature.

This is due to the fact that higher binder contents may induce difficulties in reduction by making the briquettes more dense and less porous/permeable such that heat and reducing gases cannot properly move throughout the briquettes and effectively reduce it. In such difficult reduction conditions, the oxide which is more thermodynamically favored will get reduced to a greater degree. In this case, Iron oxide is more thermodynamically favoured to being reduced than Manganese oxide, as a result, the iron will be reduced more and therefore will be present in greater proportions. This relationship is illustrated in the graph above.

IV. CONCLUSION AND RECOMMENDATIONS

This research aimed to investigate the effects of organic binder on the mechanical properties and reducibility behaviour of briquettes. In order to investigate the effect on the mentioned characteristics, experiments were conducted, and results were obtained. After the analysis of the results, it can be concluded that, CB6 should be used in fine ore agglomeration, since it has a binder ability than KFO4, which means it is more effective at smaller dosages. Binder quantity is the proportional to the moisture needed to activate the binder, i,e. the higher the dosage of the binder used, the higher the amount of water that will be needed to activate the binder, consequently, the time required for let the briquettes release moisture will increase. In cases where air-drying is preferred to reduce energy requirements, a drying period of 48 hours is recommended, minimal moisture is removed after that period. It was observed that the binder quantity significantly affected the structural stability of the briquettes. An increase in the binder quantity led to less disintegration of the briquettes when subjected to mechanical stress. In terms of reducibility, higher binder dosages may inhibit effective reduction of the briquettes due to higher densities and low porosity. As a result, the oxide which is thermodynamically favoured will get reduced to a greater extent.

It is recommended that the reduction is performed under settings that simulate plant conditions where the charging the material in the furnace is more turbulent, and the conditions lead to the displacement of fines during furnace operations, instead of the setting in which these experiments were conducted. That will ensure that the same principles used in this project can be applied at a larger(plant) scale without the fear of attaining contradicting results.

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