Biomass reduction of manganese ore in the presence of carbon monoxide

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Abstract. The ferromanganese industry is currently strained by the cost of production that is continuously increasing. Alternatives of reductants are being sought to try and alleviate the production costs namely solar energy, wind and biomass. Some studies on the possible use of biomass using the South African manganese ores were conducted and as preliminary results were generated. The South African manganese industry has focused more on the pre-reduction. The current paper focuses on the use of raw macadamia nut shells for the reduction of manganese ore in the presence of carbon monoxide. The feed and products were characterized using XRD, XRF as well as SEM and compared to products currently obtained using conventional reductants. The basicity of the feed was kept at around 1. The temperature was set at 1450ºC, a graphite crucible placed in a silica crucible to prevent any spillages. Comparisons between products obtained when raw macadamia nut shells and conventional reductants were used was done. It was found that macadamia nut shells have great potentials of replacing the conventional reductants used so far. The separation of slag from the metal needs imporvement as the slag structure was more needle-like and some metal entrapments were noticeable as compared to conventional process.

Keywords: Ferromanganese, biomass, carbon monoxide

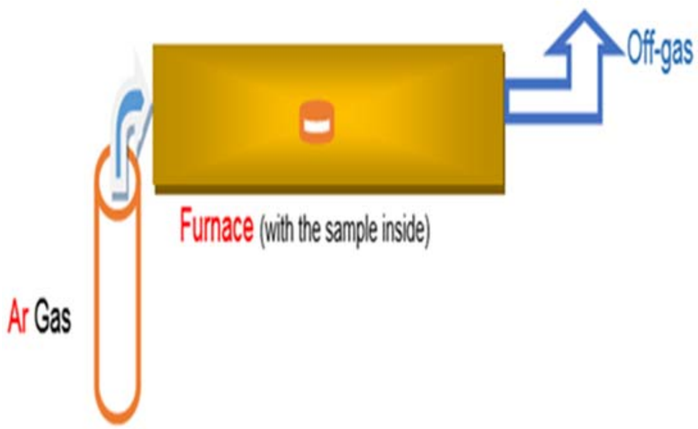
1 Introduction

The ferromanganese industry is encountering difficulties with regards to energy consumption that increases the cost of production of the alloy. The chemical composition of the raw material is said to have an impact on both metal recovery and energy consumption [1-4]. Also, reductants from different countries are currently used in the ferroalloy industry. In Brazil, the use of biomass energy in the steel industry is established. It was found that biochar which is produced using coconut from babassu at 1000 ºC through carbonization was a perfect replacement of coke in the blast furnace [5]. F.G. In order to reduce the CO_2 emissions a study in France has shown that substituting a certain amount of coke could be replaced by biomass taking into consideration the low mechanical strength of the of biomass [6, 7]. Although some investigations on the use of biomass in some areas of pyrometallurgy, the use of biomass in the production of ferromanganese is still open to depth investigations. The current investigation was conducted under carbon monoxide. It is a contribution and a continuation on the previous work where macadamia nutshells were used as reductant under argon.

2 Experimental

The manganese sample used in this experiment was sourced from South Africa. It was crushed and milled to -75 microns. The ore was analyzed using XRD for the mineralogy of the sample, XRF for chemical composition and SEM/EDS. The macadamia nutshells have also been sourced from the northern part of South Africa. On the biomass, sulphur, nitrogen, hydrogen and oxygen were determined using the ultimate analysis. Through proximate analysis moisture, volatiles matters, the fixed carbon as well as the ash content, the remaining residue containing inorganic matters after combusting the sample were determined. Also, XRD and XRF were used to analyze the macadamia nutshells. Two reduction experiments were conducted in this study. The first was conducted using raw macadamia nutshells only under argon gas and the second using raw macadamia nutshells under CO gas and a comparison was conducted thereof. The manganese ore was mixed with the required amount of macadamia nutshells and milled together with the aim to homogenize the feed. A graphite crucible was used for the experiments. The crucible was weighed before and after the experiment to assess whether there was any reaction between the crucible and the manganese ore. The graphite crucible was placed into a silica crucible to prevent any possible spillages from any probable defection of the graphite crucible. The feed was then placed into an alumina tube furnace that was set to reach a temperature of 1450^{o}C under either argon or carbon monoxide depending on what experiment as described above. The heating rate of the furnace was 8^{o}C/min. After reaching the desired temperature, the sample was kept for one hour and the furnace was switched off keeping the gas flowing until room temperature. The product was then removed from the furnace, weighed and prepared for characterization.

Experimental set up



3 Results and discussion

2.1 Materials

2.1.1 Manganese Ore. The manganese ore used in this study is from South African. The SEM, XRD and XRF analysis are presented in Figures 1, 2 and 3 below respectively.

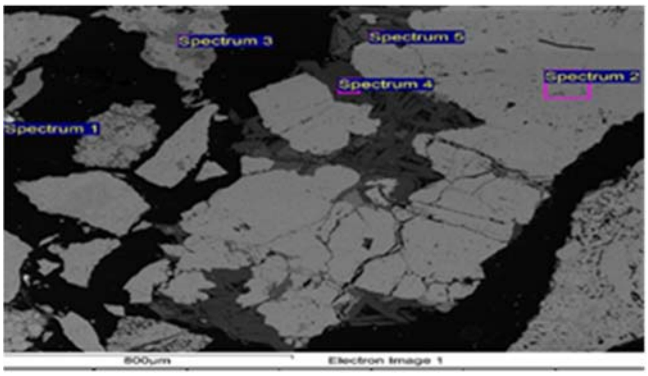


Figure 1. SEM analyses of the ore [3]

From the SEM picture, spectra were chosen to analyze possible minerals that are present in the ore. The Table 1 below provides different minerals that are present in the manganese ore used in the current study.

Table 1. SEM analyses of the spectra in Figure 1 manganese ore

Spectrum	Fe	Mn	Si	Al	Ca	Mg	Phases	Formula
1	-	6.6	-	-	1.06	-	Braunite	$Mn.Mn_6(SiO_4)O_8$
2	11.1	55.8	4.1	-	4.1	-	Bixbyte	$(Fe,Mn)_2O_3$
3	15.0	1.3	21.0	1.3	23.0	-	Hausmanite	$(Mn_3Fe)O_4$
4	0.54	0.45	19	9.6	-	25	Calcium iron silicates	$CaFeSi_2O_6$
5	-	1.0	3.5	2.1	54.0	8.0	Quartz	SiO_2

From Tbale 1, it can be seen that Braunite Bixbyte Calcium iron silicates, Hausmanite and quartz are phases that are present in the manganese ore used in the prsent work.

Table 2. XRF analyses of the manganese ore [3]

Compounds	**MnO_2**	**Al_2O_3**	**SiO_2**	**MgO**	**CaO**	**Fe_2O_3**	**Basicity**
%mass	66.85	0.93	4.89	1.03	5.29	19.56	1.15
Elements	**Mn**	**Fe**	**Ca**	**Mg**	**Al**	**Si**	**Mn/Fe**
%mass	65.80	21.31	5.89	0.99	0.77	3.56	3.1

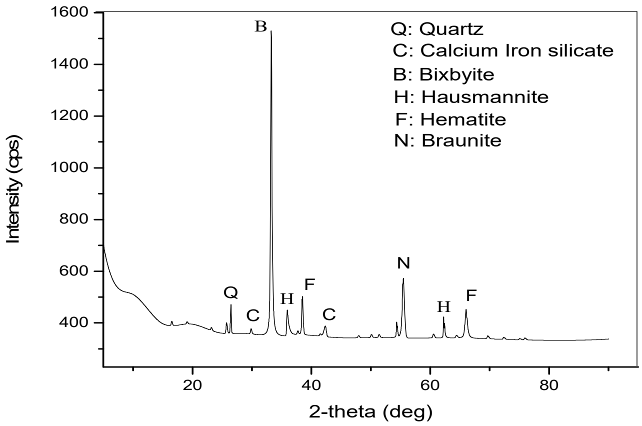


Figure 2 XRD analyses of the ore

From the XRD results, it can be seen that braunite, hematite, bixbyite, calcium silicate, hausmanite and quartz. The XRD analysis confirmed the results obtained with the SEM in figure 1.

2.1.1 Macadamia nut shells. The macadamia nutshells were characterized using the proximate and ultimate analyses. Results are provided in Table 3below.

Table 3. Proximate and ultimate analysis of the macadamia nutshells

	Parameter							
	Proximate analysis				**Ultimate analysis**			
	Fixed C	Volatiles	Ash	Moisture	H_2	N2	C	CV(MJ/kg)
Macadamia nutshells	19.2	72.6	0.7	7.5	5.9	0.2	48.7	18.5

*AR: As Received, CV: Calorific value, Fixed carbon by difference [100 - (Volatile matter + Moisture + Ash content)]

The calculated fixed carbon as per above estimation is 19,15%. The carbon fixed estimated in the macadamia is lower than the amount of fixed carbon found in the metallurgical coke that may contain more than 95% fixed carbon. This is an indication that raw macadamia nutshells are of low quality when comparing the amount of carbon fixed content with other carbon based reductants.

Table 4. Chemical composition of the raw macadamia nutshells

%	MgO	Al_2O_3	SiO_2	CaO	K_2O	SO_3	Na_2O	LOI%
Nutshells	0.01	0.07	0.20	0.08	0.09	0.04	0.01	99.50

From the analysis in Table 4 it can be seen that the silica, alumina as well as MgO are very low. This means they have no influence on the basicity of the final product. However, the loss on ignition is relatively high, thus the mass loss might be expected to be high as well.

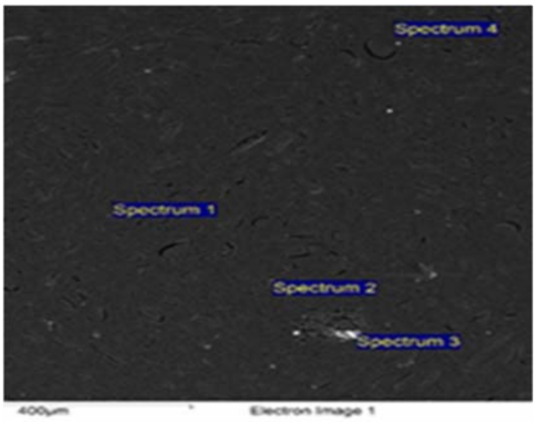


Figure 4. SEM-EDS analysis of raw macadamia

The chemical composition of the spectra in Figure 4 is provided in Table 5 below. It can be observed that carbon is the major component as opposed to potassium, silicon, calcium and magnesium. However, the volatile materials including moisture are also in considerable amount.

Table 5: Analysis of the spectra

Sample	Spectrum	C	K	Si	Ca	Mg
	1	70.67	-	-	-	-
	2	71.27	-	-	0.07	-
	3	77.57	0.42	0.06	0.96	-
	4	74.77	0.71	-	0.06	0.32

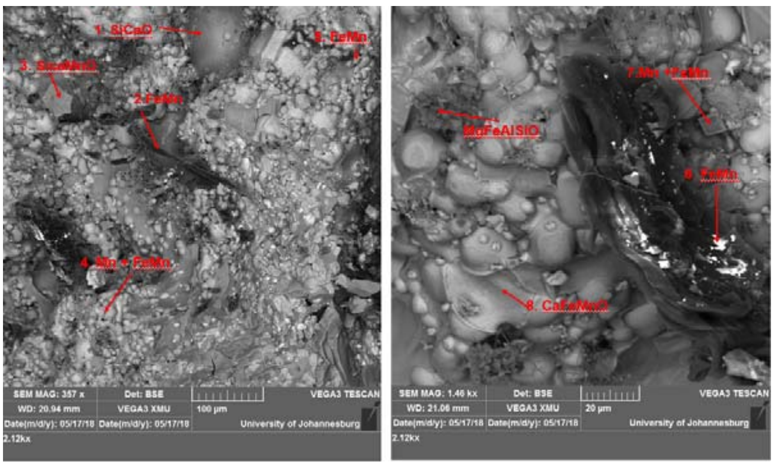


Figure 5. SEM-EDS analysis of slag and metal produced

The SEM analyses show images of mixed products. The miscibility of the metallic phase and the slag phase makes difficult to establish the mass balance.

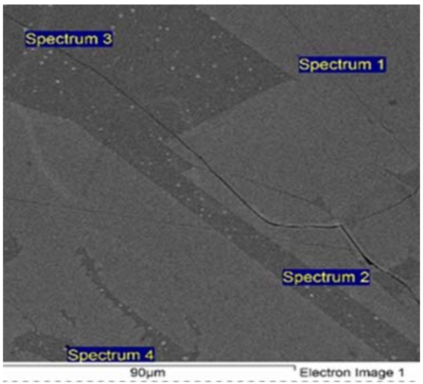


Figure 6. SEM-EDS analysis of slag

From the SEM image, it is observed that the slag was flaky as opposed to needle like structure that is generally observed. Table 6 below provides the spectra composition.

Table 6: Analysis of the spectra in Figure 6

Spectrum	Mn	Mg	Al	Si	Ca	Phases	Formulas
1	`3.23	4.01	-	18.10	17.79	Alpha calcium silicate	Ca_2SiO_4
2	6.01	0.59	8.04	17.71	19.08	Wollastonite	$Ca_3Si_3O_9$
3	6.99	0.79	5.12	19.32	17.72	Cordierite	$Mg_2Al_4Si_5O_{18}$
4	16.09	3.29	-	17.69	19.95		K_2MnO_4

Amongst the phases identified are dicalcium silicates so-called alpha calcium silicate, wollastonite and cordierite. These phases were also identified in the previous work where macadamia nutshells were used as reductants but argon was blown into the furnace instead.

Table 7: XRF results for slag products after reduction

%MgO	%Al_2O_3	%SiO_2	%CaO	%MnO	Basicity
2.12	1.83	24.74	27.47	28.62	1.11

Table 7 provides the XRF results of the slag produced. The percentage of MnO in the slag produced was 28.62%. This is far more improved slag compared to the slag produced in previous work with argon blown in the furnace where the MnO in the slag was 34.93% MnO [3]. Other oxides are in the same order than previous investigation [3]. However, the metal/slag separation remained a challenge since the miscibility of the two phases was pronounced.

Table 8: XRF of metal produced

	Mn%	Fe%	Si%	C%	Mn/Fe
Manganese Ore	65.80	21.31	3.56	-	3.09
Metal produced	63.75	32.11	1.21	3.05	1.93

From Table 8, it can be seen that the manganese content found in the alloy obtained using macadamia nutshells with flux was 63.75% Mn. The resulting Mn/Fe was relatively low. The amount of silicon was higher than 1% in the alloy.

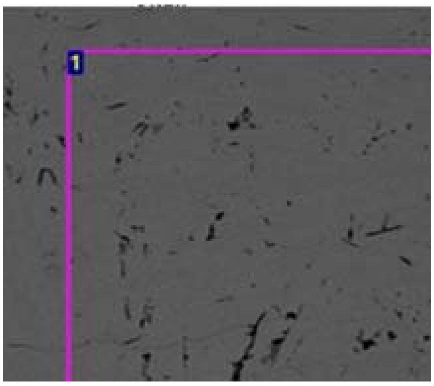


Figure 7. SEM/EDS for metals produced

For an estimation of the composition of the metal, one spectrum was chosen to get an idea on the composition of the metal.

Table 8: Analysis of the spectrum in figure 7

	Mn%	Fe%	Si%	Mn/Fe
Metal produced	62.8	29.9	1.2	2.1

The SEM was conducted in order to compare the results obtained using XRF. It transpired that although figures are different, they are not as far from each other. The overall comments are that, the metal produced is of better quality than the metal produced in previous work where macadamia nutshells were used at same basicity with same manganese ore but under argon. However, the phases present in the slag and the shape of the phases in the slag remained similar for experiment ran with carbon monoxide blown in the furnace along with the use of macadamia nutshells. This is an indication that the structure of the slag is more dictated by the macadamia nutshells.

Further, a considerable decrease in volume of material was observed. This could be attributed to the high volume of volatile matters that are present in the macadamia nutshells.

4 Conclusion

The use of macadamia nutshells as a reductant in the ferromanganese industry remains of good prospect. From the present work, it is concluded that:

1) With carbon monoxide was blown in the furnace along with the use of macadamia nutshells, the percentage of MnO in the slag produced was 28.62%. This was a far more improved slag compared to the slag produced in previous work when argon blown in the furnace where the MnO in the slag was 34.93% MnO
2) The metal produced is of better quality (with 63% Mn average) than the metal produced in previous work where macadamia nutshells were used at same basicity with same manganese ore but under argon.
3) Other oxides were in the same order than previous investigation [3]. However, the metal/slag separation remained a challenge since the miscibility of the two phases was pronounced. This would require a thorough investigation on the influence of macadamia nutshells on the viscosity of the slag for a better understanding
4) Phases present in the slag and the structure of the slag remained similar for experiments ran with carbon monoxide blown in the furnace along with the use of macadamia nutshells. This is an indication that the structure of the slag is more dictated by the macadamia nutshells

5) Further work is still needed to reach the level of industrial use of raw macadamia nutshells.

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