

EFFECT OF TEMPERATURE AND TIME ON THE WEIGH LOSS AND PHASES DURING CARBOTHERMIC REDUCTION OF BASICMANGANESE ORE IN PRESENCE OF PKS AND HYDROGEN

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Abstract

Generic coke for carbothermic reduction has become for decades a global threat to the environment. Studies on mass losses during carbothermic reduction using generic coke has been largely investigated for different types of manganese ore. However, the use of greener process and their impacts on different parameters remain insufficient. The current study investigates the use of a combination of hydrogen, argon and biochar on the mass loss during carbothermic reduction of basic south African manganese ore. Temperature varied from 1200 to 1500°C with 100°C. H₂/Ar ratio varied at 25/75, 50/50 and 75/25 ratio for each temperature and their impact on the mass loss assessed. A comparison study between the mass loss when hydrogen was used and when biochar only was used was conducted. Results demonstrate a general trend of increasing mass loss with temperature increase as well as time increase. However, in presence of hydrogen the mass loss has a higher mass loss than when biochar is used alone.

Keywords: Metallurgy, Manganese, Carbothermic reduction, mass loss, hydrogen

1. INTRODUCTION

The pyrometallurgical sector is among the major contributors to global warming due to the intensive use of fossilized reductants. Anthracite, coke and coal used as reducing agents in metallurgical processes contribute to carbon footprint and climate change. About 10% emission is ascribed to the metallurgical industry mainly generated during carbothermal reduction [1]. Efforts to significantly reduce carbon emissions are being sought for through the transition to biomass, hydrogen-based processes, and by implementing new technologies [2], or a combination of them [3]. There have been several investigations into the use carbon-based materials produced from renewable or recycled materials as alternative reducing agents. Biochar derived from biomass, particularly, shows the potential to replace coke and t reduce the emission due to its abundance, availability, and physicochemical properties. Furthermore, biochar has several environmental benefits because It is neutral because the amount of CO₂ released is absorbed during the photosynthesis process and, therefore, suitable to mitigate global warming [4], [5]. Biomass as a substitute for metallurgical coke presents a great potential to reduce the carbon footprint because of their physical and chemical properties that are like those of metallurgical coke [6]. The pyrolysis temperature, residence time, inert gas flow rate, heating rate and pressure all play an important role on the nature of the biochar [7,8]. Hydrogen is also currently being explored not only as an alternative reductant but as additive to biomass [9-12] and growing interest in use of hydrogen as a reductant in the metallurgical sector [13, 14]. The current study aims at assessing the effect of hydrogen-argon ratio on the mass loss during high carbon ferromanganese production.

2. MATERIALS, EQUIPMENT AND EXPERIMENTAL METHODS

2.1 Materials and equipment

South African basic Manganese ore was used in this study. Hydrogen and Argon with 99.96% and 99.98% purity respectively from Afrox were used. Experiments were conducted using a TGA furnace to measure mass loss. Alumina crucibles were used for better assessments of the reduction process.

2.2 Experimental method

The impact of hydrogen on the reduction was examined by adding hydrogen to the furnace. Argon and Hydrogen were blown simultaneously throughout the experiment. Three different gas ratios (H₂/Ar) including H₂/Ar: 25/75, 50/50, and 75/25 were used at 1200, 1300, and 1400°C for 30, 60 and 120 minutes. The mass losses were recorded at different temperatures and duration of the experiment and assessed accordingly.

3. RESULTS AND DISCUSSION

The weight loss at different H₂/Ar volume ratios at 1200°C is recorded in **Table 1** and trend shown in **Figure 1**.

Table 1 Recorded weight loss (g) at different H₂/Ar volume percentages ratios at 1200 °C.

Time (min)	H ₂ /Ar (volume percentage) ratio		
	25/75	50/50	75/25
30	7.42	7.50	7.57
60	7.44	7.57	7.77
120	7.57	7.76	7.82

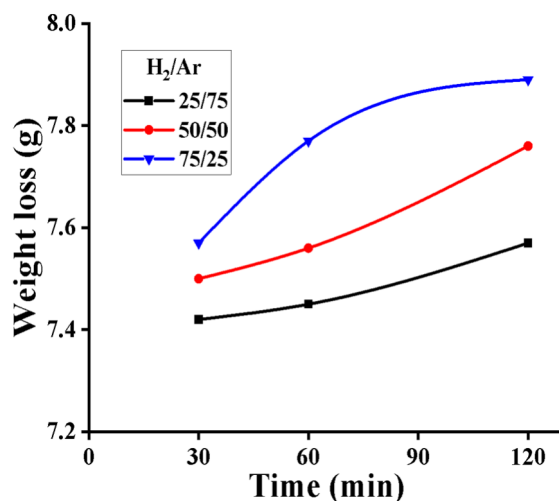


Figure 1 Weigh loss measured at different times at 1200°C

Observations made from **Figure 1** indicate that the weight loss increased with increasing H₂/Ar ratio. However, the impact of hydrogen was minimal. For the ratio of 25/75, the weight loss varied from 7.42 g to 7.57g. For the ratio of 50/50, the weight loss increased from 7.50 to 7.76g. The weight loss obtained with a higher hydrogen ratio (i.e. 75/25) varied from 7.57 to 7.82g. When comparing the weight loss obtained in the reductions using biochar only at 1200°C and the weight loss obtained in hydrogen presence at 1200°C, the weight loss recorded is almost the same. This implies that biochar and hydrogen had the same impact on the reduction at 1200°C.

3.2 Reduction in hydrogen presence at 1300°C

The weight loss at different H₂/Ar volume ratios at 1300°C is recorded in **Table 2** and trend shown in **Figure 2**.

Table 2 Recorded weight loss (g) at different H₂/Ar volume ratios at 1300°C

Time (min)	H ₂ /Ar (volume percentage) ratio		
	25/75	50/50	75/25
30	7.44	7.50	7.59
60	7.45	7.56	7.78
120	7.58	7.76	7.89

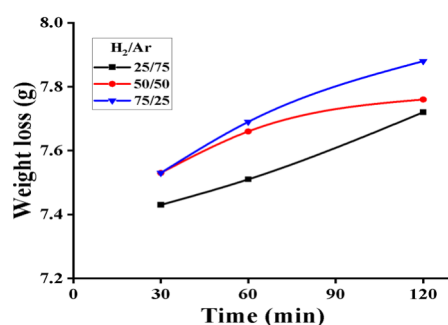


Figure 2 Weigh loss measured at different times at 1300°C

Figure 2 depicts the weight loss recorded during the reduction. On 25/75 gas ratio increased from 7.44 to 7.58g with increasing time from 30 to 120 minutes while for 50/50 gas and 75/25 ratios the recorded increases in weight were 7.50 to 7.76g and from 7.57 to 7.89g respectively. The variation of H₂/Ar ratio had no major impact on the reduction behavior.

3.3 Reduction in hydrogen presence at 1400°C

The weight loss at different H₂/Ar volume ratios at 1400°C is recorded in **Table 3** and trend shown in **Figure 3**.

Table 3 Recorded weight loss (g) at different H₂/Ar volume ratios at 1400°C

Time (min)	H ₂ /Ar (volume percentage) ratio		
	25/75	50/50	75/25
30	7.44	7.57	7.66
60	7.51	7.59	7.79
120	7.57	7.90	7.92

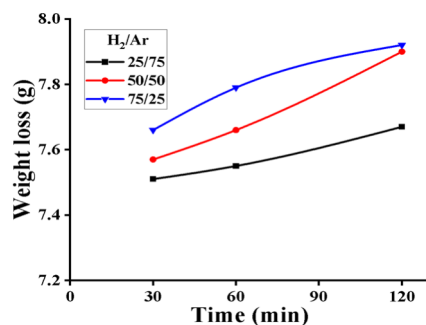


Figure 3 Weigh loss measured at different times at 1400°C

Figure 3 depicts the weight loss recorded during the reduction. On 25/75 gas ratio increased from 7.44 to 7.66g with increasing time from 30 to 120 minutes while for 50/50 gas and 75/25 ratios the recorded increases in weight were 7.51 to 7.79g and from 7.57 to 7.92g respectively. The variation of H₂/Ar ratio had no major impact on the reduction behavior. To observe the reduction behavior in the reduction using biochar only, a mixture manganese ore, fluxing agent, and the stoichiometric amount of biochar calculated by mass balance (2.5 g) was heated up to 1200,1300, and 1400°C, under argon gas as carrier gas. The reduction was evaluated based on weight loss. **Figure 4** depicts the weight loss recorded in the reductions in the reduction using biochar.

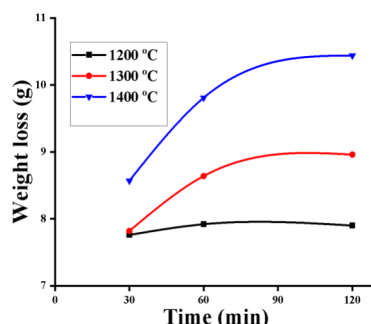


Figure 4 Recorded weight loss in the reduction using biochar at 1200,1300 and 1400°C

As seen in **Figure 4**, the weight loss recorded at 1200°C was 7.56, 7.92 and 7.94 g for reduction time of 30,60 and 120 minutes respectively. At this stage, the weight loss is mainly attributed to the reduction of higher manganese oxide to MnO, and reduction of the Iron contained in the ore. The weight loss recorded at 1300°C was 7.82, 8.64 and 8.96 for reduction time of 30,60 and 120 minutes respectively. At 1400°C, the weight loss recorded were 8.57, 9.81, and 10.44g for 30,60 and 120 minutes of reduction. The difference in weight loss at 1300 and 1400°C can be explained by the impact of reduction in temperature and holding time. The weight loss increased with increasing temperature and reduction time. The effect of biochar content on the reduction extent was studied at 1500 °C. 10, 20 and 30% excess of the stoichiometric amount of biochar was added to the charge and the weight loss behavior was observed. The recorded weight loss is plotted in **Figure 5**.

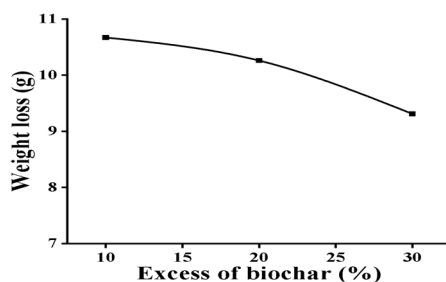


Figure 5 Recorded weight loss in the reduction using 10, 20 and 30 % of biochar excess at 1500 °C.

The observations made from **Figure 5** reveal that the biochar amount influenced the reduction extent. Increasing 10% biochar excess to the charge material led to weight loss of 10.6 g. Increasing to 20% slightly decreased the weight loss to 10.26g. Increasing the biochar up to 30% excess resulted in a lower reduction extent. The distinct difference between the reduction behavior with the variation of biochar content could be explained by the increasing ash content from the biochar. The ash content and its chemical composition have a great influence on the reduction mechanism. Any change in feed material affects the slag formation and slag properties which in turn influences the productivity and product quality. As seen in **Figure 5**, the increase in biochar content caused a decrease in weight loss, therefore on the reduction extent. The weight loss recorded with the reduction with 10% was 10.6g. When the biochar increased to 20%, the weight loss decreased down to 10.26 g and the weight loss with 30% was 9.31 g. This is presumably due to the higher amount of slag that

had formed. It is established that the extend of slag formation and slag chemical composition determine the reduction extent and reduction rate, consequently Mn recovery. The silicates barriers have been assumed to block the progression of MnO reduction leading to the formation of manganese silicates. This is presumably due to the increase in slag mass because of Mn reporting to the slag instead of metal. The mass of slag after reduction was calculated by mass balance and presented in **Table 3**.

Table 3 Calculated mass of slag for the reduction with excess of biochar at 1500 °C

Biochar excess (%)	Mass slag
10	15.25
20	16.30
30	18.69

The calculated reduction of MnO from the slag in hydrogen presence is presented in **Figure 6** below.

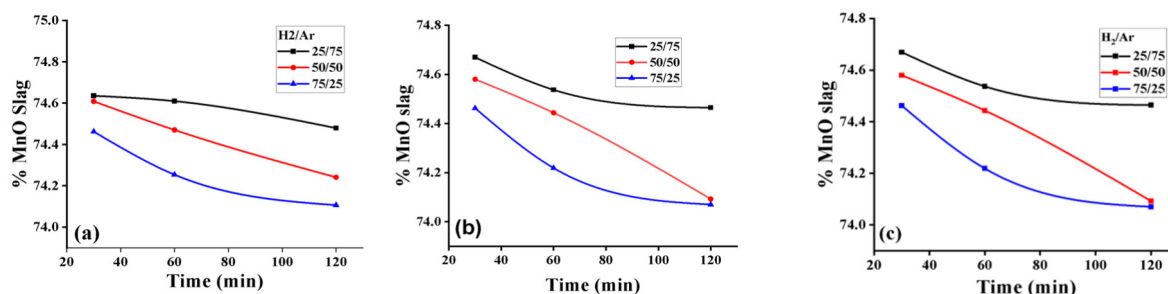


Figure 6 Calculated % MnO in the slag for reductions in presence of hydrogen

These results confirm that no reduction beyond the formation of MnO had taken place. Both the temperature and gas atmosphere did not have an impact on the reduction rate. Although the reduction did not go to completion, the reduction in 75/25 had the highest rate at all temperatures. This is due to the possible manganese silicates barriers that enrobe the MnO particles inhibiting a further reduction.

Figure 7 depicts the calculated MnO in the slag for reductions with hydrogen in presence of biochar.

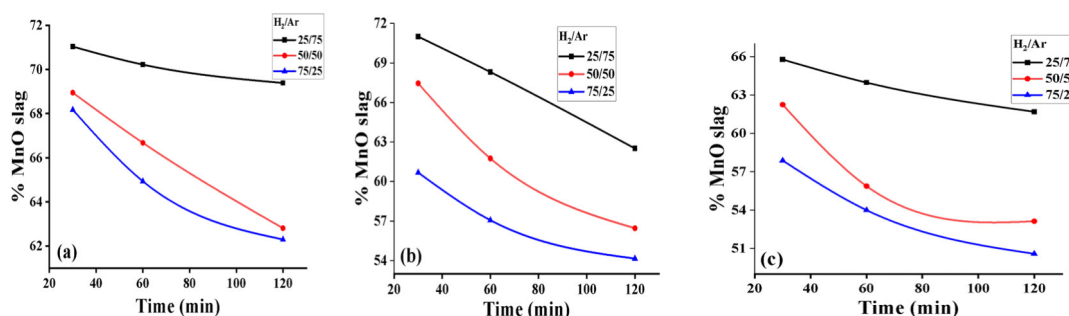


Figure 7 Calculated % MnO in the slag for reductions in presence of hydrogen and biochar

As observed in **Figure 7**, the samples reduced using biochar in hydrogen presence experienced a faster reduction rate compared to the ones in the two previous reduction conditions. At 1200°C, within 30 minutes, with a hydrogen ratio of 25/75 a higher reduction could be achieved as compared to the reductions achieved at 1200°C using biochar only. Increasing the hydrogen ratio to 50/50 accelerated the reduction rate. Further increase in hydrogen ratio caused the reduction to be faster. This fact is attributed to the higher reduction

conditions. The sample in 75/25 experienced a slightly higher reduction rate. Increasing temperatures resulted in higher reduction rate as well. The highest reduction rate and extent were obtained at 1400°C. The rate of MnO reduction from the slag increased significantly with both the increase of hydrogen ratio and temperature. These results indicate that the reduction rate was higher in a hydrogen-containing atmosphere. As expected, the reduction rate increased with increasing hydrogen ratio. This showed how strongly the reduction was affected by both the hydrogen presence and temperature. Additionally, the presence of hydrogen played a crucial role in kinetic reduction. The reduction was significantly faster in reduction in hydrogen presence than the reductions using biochar. It could be observed from **Figures 5 and 6** that the reduction rate and extent were higher in the reduction in presence of hydrogen than the reductions using biochar only. These results obtained indicate that the reduction rate was affected by both the hydrogen ratio and temperature and that the reduction rate was the highest in the presence of hydrogen and biochar. The higher rate of reduction of manganese oxide in hydrogen was attributed to the higher reducing atmosphere, ensuring low oxygen pressure in the furnace.

4. CONCLUSION

The recorded weight loss was the highest in the reduction using biochar in hydrogen presence. At 1200 °C , within 120 minutes of reduction a weight loss of 8.45, 9.12, and 9.57 g respectively while the weight loss recorded at 1200 °C in the reductions using biochar only was 7.94 g. At 1400 °C, in the reduction using biochar in hydrogen presence, the weight loss obtained were 10.21, 10.67, and 11.1 g respectively. The weight loss obtained at 1500 °C in the reduction with excess of biochar were 10.67, 10.26 and 9.31 g for 10,20 and 30 % biochar excess respectively. Addition up to 30% biochar excess was found to give significantly lower reduction extent.

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