

Prereduction Behavior of Manganese Ores With Solid Carbon and in CO/CO₂ Gas Atmosphere



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The prereduction reactions in the submerged arc furnace (SAF) are highly decisive of the total carbon, and energy consumption of the ferromanganese process. Therefore, understanding the dependency of prereduction behavior on ore characteristics and furnace conditions is of paramount importance. Prereduction behavior of Comilog, Nchwani and UMK ores with solid carbon was studied in an open 75 kVA induction furnace set up simulating the conditions of an industrial SAF. In addition, the ores were thermogravimetrically studied with non-isothermal heating to 1000 °C in a flowing 70/30 CO/CO₂ atmosphere. Gasification of carbon according to Boudouard reaction was considered significant for carbonate ores in induction furnace setup. UMK had a greater extent of prereduction compared to Nchwani which is low in carbonates and Comilog which is known to have a higher CO reactivity at similar CO contents. TGA rate curves shows that prereduction of UMK ore occurred with two major distinctive steps. The first one was a combination of prereduction reactions and decomposition of carbonates with a peak temperature of 700 °C, and the second peak was the decomposition of calcite at 900 °C. The O/Mn ratio for UMK shows that prereduction is already completed prior to the second decomposition peak at 900 °C. In addition to prereduction reactions, Nchwani is also characterized by an endothermic step which is decomposition of carbonates at 900 °C. Comilog ore produced the most fines followed by Nchwani and lastly UMK on decrepitation.

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I. INTRODUCTION

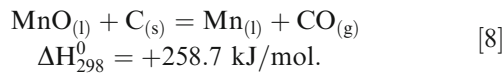
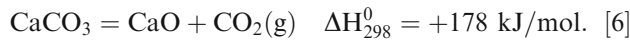
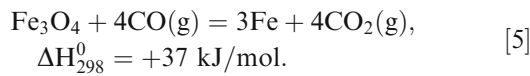
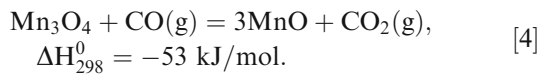
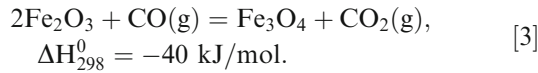
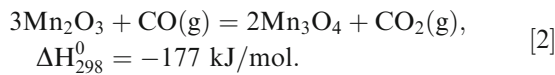
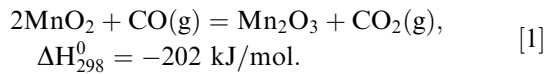
FERROMANGANESE (FeMn) alloys are mainly produced in the submerged arc furnace (SAF) with a constant supply of raw materials such as manganese ore, sinter, metallurgical coke, and flux blended in predetermined ratios^[1]. The FeMn production process is energy intensive with requirements ranging between 2.0 and 3.5 MWh per tonne alloy produced.^[1–4] Energy for the process is supplied by conversion of electrical energy into heat at the electrode tip through resistive heating of the coke bed to attain smelting temperatures. A temperature gradient develops in the furnace through heat exchange between descending burden materials and hot

ascending CO gas generated from the smelting reactions. The furnace is typically divided into two main zones namely the prereduction zone (200 °C to 1200 °C) and the coke bed zone (1200 °C to 1600 °C). Initially, iron oxides and higher manganese oxides (MnO₂, Mn₂O₃ and Mn₃O₄) contained in manganese ores are prereduced in the prereduction zone by CO gas to metallic Fe and MnO. Subsequently, the MnO is reduced in the coke bed zone from liquid slag to FeMn metal by means of solid carbon.^[1,5] The typical ferromanganese process reactions and their corresponding standard reaction enthalpies calculated using HSC Chemistry® software^[6] are presented as follows:

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The solid–gas prereduction reactions [1] through [5] are mostly exothermic (apart from reaction [5]) and produce CO₂. Carbonates in the charge mixture typically consist of Ca, Mg and Mn bearing carbonates or dolomite which decompose to produce CO₂. The resultant CO₂ gas from prereduction of Mn₃O₄ and decomposition of carbonates, will react with solid carbon according to the highly endothermic Boudouard reaction (reaction [7]) at temperatures greater than 800 °C, thereby increasing the consumption of energy and carbon. In the coke bed zone, the energy requirements and necessary quantity of carbon to produce FeMn alloy by direct reduction (reaction [8]) of the prereduced ore is fixed for a specific alloy composition. As such, the total carbon and energy consumption is highly dependent on the extent of gaseous reduction of higher manganese oxides in the prereduction zone and the extent of the Boudouard reaction. Therefore, the gas–solid reactions in the prereduction zone are to a large extent decisive for the variations of both coke and energy in ferromanganese production.^[7] This will also affect the total CO₂ emissions from the process.

Characteristics of the prereduction process differ and are significantly dependent on the ore type used. This is mainly because manganese ores used by industry in the production of FeMn alloys have different origins and therefore differ in mineralogy, chemical and physical

properties. Typically, metallurgical grade ores contain more than 35 pct Mn and literature^[8–14] covers properties of ores with Comilog, CVRD, Groote Eylandt, Wessels and Mamatwan type ores as examples. Several studies^[10,11,15–22] have been conducted on the prereduction of manganese ores by either CO gas or solid carbon.

Kor^[15] studied the rate of reduction of Mn₃O₄ by CO and carbonaceous reductants namely; coconut charcoal, coke and pure graphite in the temperature range 900 °C to 1200 °C. The rate of reduction in CO was determined to be fast and the overall rate of reduction by a carbonaceous reductant was influenced by the oxidation of the carbon by CO₂. The oxidation of carbon by CO₂ was found to be significantly pronounced when the reductant was either carbon or coke and in addition, catalyzed by Mn₃O₄. Halim *et al.*^[16] studied the prereduction reactions for a 57.2 pct MnO₂ ore in a rotary kiln at 800 °C to 1100 °C. They used large sample sizes (3 kg) with particle sizes (100 to 400 μm) mixed with Pet Coke. The coke (carbon) was mixed at 1.25 times the stoichiometric ratio for reducing iron and manganese oxides. The crucible was kept in an inert atmosphere of argon during the experiment. Micro TGA was also used to measure weight loss for 1 g of pelletized samples, also mixed with coke. The gas emissions were measured in a different experiment with 1 g of pelletized samples heated isothermally in a horizontal tube furnace. With these experiments they concluded that the prereduction of manganese ores takes place by gaseous reduction mechanism and Boudouard reaction as the rate controlling step. Turkova *et al.*^[17] studied correlation between CO-reactivity and porosity for three different manganese ores, CVRD, Assmang (Nchwanning) and Gabonese (Comilog). They used 200 ± 30 g samples heated in a vertical tube furnace with a heating rate of 10 °C/min. They used a gas composition of 70/30 CO/CO₂ with a flow rate of 4 L/min. The ores were heated to three different max temperatures of 400 °C, 800 °C and 1100 °C. They found that ores with higher initial porosity will have a higher CO-reactivity, and that for Assmang (Nchwanning), a low porosity ore, an agglomerate with higher porosity will give a higher CO-reactivity. In addition, porosity increase below 400 °C was reported to be caused by the removal of bound water and in the temperature range 400 °C to 800 °C, the porosity increase was an effect of the prereduction of higher manganese oxides, swelling of the particle due to heating, and decomposition of carbonates. In another study, De Jesus and Tangstad^[18] investigated the CO reactivity for lump manganese ore and briquettes at 1100 °C. A macro TGA was used with a gas composition of 70/30 CO/CO₂ and heating rate of 10 °C/min. The lumpy ore was in the size range of 9 to 15 mm, while the briquettes were made of – 250 μm fines mixed with either molasses or clay. They concluded porosity was the biggest factor in CO reactivity, with molasses in briquettes decomposing at lower temperatures causing pores to form which resulted in the highest reactivity. Recently, extensive work on the reduction of Comilog and Nchwanning ores in CO/CO₂ atmospheres and the analysis of the reaction rate of these ores has been carried out by Larssen *et al.*^[11,19] They obtained

thermogravimetric data for the reduction of Comilog and Nchwaning ores in CO/CO₂ atmosphere were temperature, particle size and CO-concentration were investigated variables. It was reported that an increasing partial pressure of CO in CO/CO₂ atmosphere promoted the reaction rate with an order of 0.7 and 1.5 for Comilog and Nchwaning ore, respectively. Activation energies of 17 kJ/mol and 63 kJ/mol were estimated for Comilog and Nchwaning ore, respectively. Carbonates in Nchwaning were found to decompose at temperature range 800 °C to 1000 °C and in addition, decreasing particle size promoted reaction rate for both ores.

Since the prereduction reactions are highly decisive for the total carbon, and energy consumption of the ferromanganese process, understanding the dependency of prereduction behavior on ore characteristics and furnace conditions is of paramount importance. This paper elucidates on the prereduction behavior of manganese ores with focus on Comilog an oxidized ore, Nchwaning a semi-oxidized ore and UMK a carbonate ore.

II. EXPERIMENTAL

Laboratory scale experiments were performed to investigate the prereduction behavior of three different ores. Two different types of experiments were performed, namely induction furnace simulating an industrial SAF and small scale thermogravimetric experiments.

A. Characterization of Raw Materials and Prereduced Products

The manganese ores investigated were UMK, Nchwaning and Comilog ores. Comilog exhibit high level of microporosity and is mainly composed of pyrolusite (β -MnO₂), nsutite ((Mn⁴⁺)_(1-x)(Mn²⁺)O_(2-2x)(OH)_{2x} ($x = 0.06$ to 0.07)) and cryptomelane (K(Mn⁴⁺₇Mn³⁺)O₁₆) minerals. UMK and Nchwaning contains both braunite-I ((Mn²⁺, Mn³⁺)₆(SiO₄)O₈) and braunite-II (Ca(Mn³⁺, Fe³⁺)₆(SiO₄)O₈) minerals, Nchwaning contains more bixbyite ((Mn³⁺, Fe³⁺)₂O₃) and hematite (Fe₂O₃) and less carbonate minerals compared to UMK ore.^[12] Characterization of ores and products of prereduction was for porosity and chemical compositions. Techniques used for characterization include pycnometry, X-ray fluorescence (XRF), permanganometric titration, thermogravimetric and combustion-IR methods. Elemental analysis (Mn, Fe, Si, Al, Ca, Mg, P, S, Ti, K and Ba) was measured with X-Ray fluorescence (XRF) fused bead technique by employing a Bruker AXS S4 Pioneer X-Ray fluorescence spectrometer (Billerica, US). Mn and Fe were given as total contents of the ores and other elements were converted into concentrations of their corresponding oxides, *i.e.*, SiO₂, Al₂O₃, CaO, MgO, TiO₂, K₂O and BaO in accordance with the stable oxides' forms with a specific oxidation degree. The oxygen level (O/Mn ratio) of manganese ores and prereduced products was determined by permanganometric titration (ASTM

465-11:2017), in which excess oxygen above MnO is expressed as MnO₂. The analysis of carbon concentration was done with a LECO (Combustion-IR) instrument, and the measured concentration of carbon was converted to CO₂ concentration according to the stoichiometry, assuming that all carbon in the ore is in the form of CO₂. Loss on ignition (LOI) was measured to a constant weight at 950 °C in air, thermogravimetrically. It is assumed that during the analysis, all carbonates are fully decomposed, water is evaporated, while the stable forms of manganese and iron are Mn₃O₄ and Fe₂O₃, respectively. The porosity of the solids ((1-(Apparent density/Absolute density)) was determined from the measurement of the absolute density (particle density) with Accupyc 1330 helium pycnometer and the measurement of the bulk density (apparent density) using a GeoPyc 1360 pycnometer. Prior to chemical analysis and experimental runs, the ores were dried at 100 °C for 24 hour to remove free water. Table I shows the chemical composition of the raw materials.

B. Induction Furnace Experiments

The extent of prereduction of the ores was investigated by simulating an industrial HCFEMn furnace in a 75-kVA open induction furnace. A temperature gradient develops during induction coil heating, with the highest temperature at the bottom of the furnace and decreasing temperature towards the furnace top. The raw materials in each experiment were stratified as layers into the graphite crucible of 150 mm outer diameter, 115 mm inner diameter, 400 mm outer height and approximately 380 mm inner depth and two setups were used. The first setup consisted of a 100 mm coke layer in the bottom of the crucible working as the coke bed in industrial furnace, a 200 mm ore layer placed on top of the coke bed and lastly, a 50 mm coke layer on the top of the ore working as insulation and inhibits charge re-oxidation. In the second setup, the 200 mm ore layer was replaced by a mixture of 90 wt pct ore + 10 wt pct coke reductant. A sketch of the induction furnace and graphite crucible containing the raw materials in the first setup and temperature gradients at coke bed temperatures of 1200 °C, 1300 °C and 1400 °C are as shown in Figures 1(a) and (b).

The furnace crucible was heated at 25 °C/min from 25 to target temperatures of 1200 °C, 1300 °C and 1400 °C on top of the coke bed. During heating, the temperature is held for 30 minutes at 1200 °C to ensure sufficient prereduction prior to coke bed reduction reactions at higher temperatures. Final target temperatures were held constant for 60 minutes on top of the coke bed. Two type C tungsten/rhenium thermocouples encapsulated by alumina and graphite insulation tubes as shown in Figure 1(a) were used to measure the control and variable temperatures. The control thermocouple was located at the top of the coke bed and gave the reference temperature measurement. Likewise, the variable thermocouple was initially positioned on top of the coke bed and was used to measure temperatures at 20 mm interval distances away from the coke bed up to the

top of the charge whilst maintaining a constant coke bed temperature. A constant temperature at each 20 mm interval position within the charge material was established by holding the variable TC for 2 minutes. Figure 1(b) show a typical temperature gradient at different coke bed temperatures. At the end of each experiment the furnace was shut down and the crucible was cooled for 24 hours. After cooling the crucible, samples were excavated manually from the same levels where the temperatures were measured, while the material in-between the temperature measurement points were discarded. A level then corresponds to the particles excavated at a given height inside the crucible. The collected samples were taken for chemical analysis and porosity measurements.

C. TGA Experiments

The prereduction of the UMK, Nchwani and Comilog ores was investigated quantitatively by the thermogravimetric (TGA) technique. Total weight loss of the ore during prereduction was measured as a function of heating rate. The use of a TGA was meant to simulate the prereduction zone in an industrial ferromanganese furnace, with a constant supply of reducing gas CO/CO₂. Ore particles in the size range 10 to 12.5 mm were subjected to different heating rates and a peak temperature of 1000 °C in a 70/30 CO/CO₂ atmosphere. In the industrial furnace, most of the heat is developed around the electrode thereby giving a higher heating rate for particles close to the electrode, and lower heating rate for particles close to the furnace lining. To study the effect of heating rate in the furnace it was decided to use three different heating rates chosen as, 3 °C/min, closer to the furnace lining; 6 °C/min, between electrode and furnace lining; and 9 °C/min, close to the electrode.

An Entech VTF 80/15 vertical resistance tube furnace was used for the solid–gas reactions study. Ores occupying 80 mm height of the crucible were placed in a gas-tight stainless-steel double-wall crucible (L/Ø = 450/58 mm). The crucible was suspended from a scale (Mettler Toledo PR2003DR, Switzerland, 10 mg), with flexible gas inlet and outlet hoses connected at the top. The crucible was freely suspended, while the position of the furnace was adjustable vertically along a rail. The crucible was inside the furnace hot zone during the heating, while at the cooling stage the furnace was moved down. Furnace heating was regulated by an Eurotherm PID controller measured with a calibrated S-type thermocouple (Furnace Temperature), while charge temperature was measured with a K-type thermocouple (Crucible Temperature) sheathed in an alumina tube positioned in the center of the charge. The gases used in the experiments had a purity for CO, CO₂ and Ar, of 99.97, 99.9992 and 99.999 vol pct, respectively. The gas flow in all experiments was regulated at 4 L/min 70/30 CO/CO₂ by mass flow controllers (Bronkhorst High-Tech El-flow, Netherlands). The furnace was programmed to heat the sample from ambient temperature until 1000 °C at the given heating rates and the charge was then cooled under Ar flow to avoid

reoxidation of the prereduced samples. In addition, the weight of the solid charge was measured with an external scale Ohaus Pioneer PA4202 (US) before and after the prereduction to confirm the net weight loss acquired from the TGA data. The sensitivity of the external scale was ± 0.01 g. After the experiments, prereduced samples were sieved through a sieving stack consisting of 10, 6.7, 4.75, 3.35, 1.6 and 0.5 mm sieves to determine ore decrepitation. From the sieved materials, prereduced ore samples were taken for chemical analysis. The decomposition of carbonates was investigated using the same experimental procedure at heating rate of 9 °C/min with experiments ending at 700, 800 and 900 °C for UMK ore and 900 °C for Nchwani.

Oxides of manganese and iron display a wide range of solid solutions. Iron oxide (FeO) and co-existing MnO produced in prereduction has been observed by several researchers to dissolve in each other at high temperatures, forming FeO–MnO solutions.^[11,21,24] Larssen *et al.*^[11] studied the reduction of manganese ores in 80/20 CO/CO₂ atmospheres utilizing a thermogravimetric furnace up to 1000 °C. The morphological observations in these studies^[11,21] were in agreement with reduction of iron oxides ending with wüstite (FeO), which is stabilized by manganese in the monoxide phase. As such, the theoretical net weight loss of the ores during prereduction was estimated based on the chemical composition of the ore and corresponding equilibrium phases *i.e.*, MnO and FeO at 1000 °C in the CO-containing gas atmosphere. The chemical composition of the ores in Table I, shows that Comilog has a high oxidation level (O/Mn ratio) equal to 1.93 (≈ MnO₂), whereas Nchwani and UMK are semi oxidized ores (predominantly Mn₂O₃) with oxygen level to 1.47 and 1.45, respectively. Similar oxygen levels have been reported in previous studies.^[10,19,20] Fe concentration in manganese ores as measured by XRF was converted to Fe₂O₃, assuming that it is present in the ore as Fe(III). On complete prereduction, Fe concentration was converted to FeO, assuming that it is present there as Fe(II). The theoretical weight loss was calculated using LOI, O/Mn ratio, and Fe content of the ores, while accounting for the decomposition of carbonates as shown by Eq. [9]. The water content was calculated by subtracting the CO₂ content given in the chemical analysis and calculated weight loss change from MnO_x to Mn₂O₃ from the measured LOI. Table II shows the calculated theoretical weight loss for the ores.

$$\begin{aligned} & \text{Theoretical weight loss (wt pct)} \\ &= \text{wt pct}(\text{MnO}_x \rightarrow \text{MnO}) + \text{wt pct}(\text{Fe}_2\text{O}_3 \\ &\rightarrow \text{FeO}) + \text{wt pct CO}_2 \\ &+ \text{wt pct H}_2\text{O}(\text{chemically bound water}) \quad [9] \end{aligned}$$

The experimental data acquired from the macro thermogravimetric setup are reported in the form of weight change curves (wt pct) and its first derivative, the reaction rate (wt pct/s) as a function of temperature and time. To analyze the contribution to the overall weight loss of prereduction reactions, decomposition of carbonates and water evaporation, Fityk^[25] was used to decompose the rate curves into these

Table I. Chemical Composition of Raw Materials (wt pct) (Size Fraction 9.15 to 16 mm)

	MnO ₂	Mn _{tot}	Fe _{tot}	SiO ₂	Al ₂ O ₃	K ₂ O	CaO	MgO	CO ₂	Fix C	LOI	O/Mn ratio
Comilog ore	79.6	51.2	2.9	3.3	5.8	0.7	0.4	0.1	—	—	12.6	1.93
Nchwanning	36.9	46.5	9.04	4.2	0.38	0.10	7.4	1.4	4.45	—	6.49	1.47
UMK ore	26.52	38.2	4.67	6.54	0.74	0.08	13.3	3.17	15.9	—	16.7	1.45
Polish coke	—	—	—	5.05	3.31	0.27	0.34	0.21	—	88.4	—	—

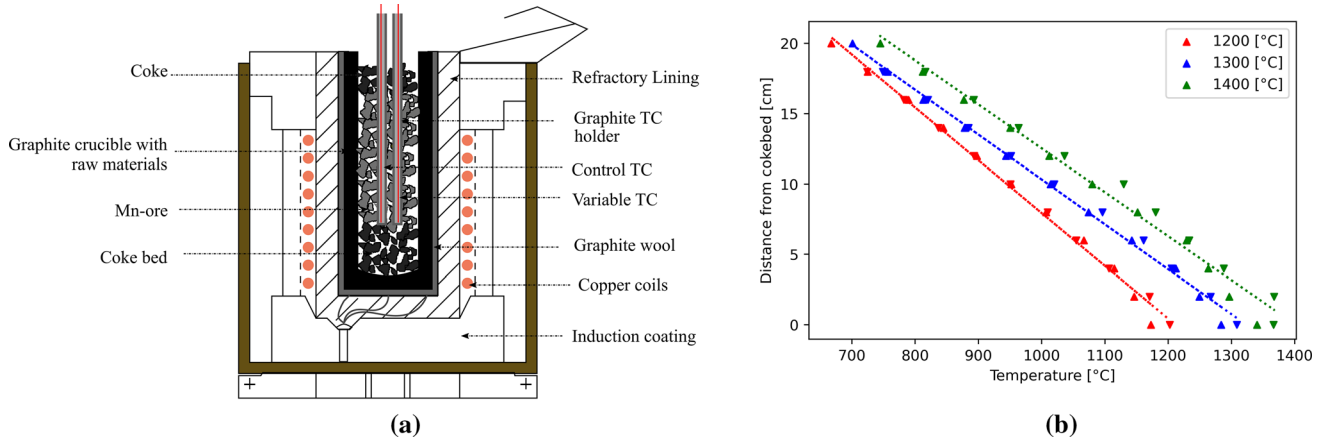


Fig. 1—Schematic of the furnace set up (a) and temperature gradient (b). “(a) reprinted with permission from Ref. [23]”.

Table II. Calculated Theoretical Weight Loss from Ores (wt pct)

	Comilog	Nchwanning	UMK
Mn prereduction (MnO _x to MnO)	14.0	6.84	4.24
Fe-prereduction (Fe ₂ O ₃ to FeO)	0.50	1.05	0.65
Carbonate decomposition	0.11	4.45	16.0
Water evaporation	3.80	—	—
Total	18.4	12.3	20.9

constituents. Fityk is a general purpose peak fitting program, which was used to analyze isothermal TGA data where reaction models are fitted to the experimental data and the model giving the best fit is assumed to be representative. The rate curves were automatically described using Gaussian curves, with the only limitation of no negative curves. The curves were checked by integrating the assumed contribution and verifying it against expected weight loss presented in Table II. The weight loss based on gas measurements only considers weight loss from reaction changing the CO/CO₂ ratio, meaning only decomposition and prereduction. One prereduction reaction removes one mole of oxygen while producing one mole of CO₂, whereas decomposition reaction removes one mole of CO₂. Therefore, considering the molecular weights, the CO₂ from decomposition reactions weighs 2.75 times more than oxygen removal from prereduction reactions. As such, for the rate curves analysis, the carbonate decomposition contribution was multiplied by the CO₂ factor of 2.75.

III. RESULTS AND DISCUSSIONS

A. Prereduction Behavior in Induction Furnace

1. *Extent of prereduction of manganese ores*
 Experiments were conducted in a setup that simulates the industrial furnace process with temperatures on top of the coke bed held at 1200 °C, 1300 °C and 1400 °C and ores were unmixed and mixed with carbon on parallel studies. Figure 2 shows the extent of prereduction of Comilog, Nchwanning and UMK ores measured as the variation of O/Mn ratio as a function of temperature from samples excavated from the induction furnace. For ores not mixed with coke, UMK prereduces completely *i.e.*, reaches O/Mn ratio equal to 1.0 at temperatures lower than both Nchwanning and Comilog. Nchwanning and Comilog reaches an O/Mn ratio of 1 at around 950 °C, and UMK at 100 °C lower temperature. As such, UMK shows the highest extent of prereduction of the three ores. The variation of O/Mn ratio for excavations from experiments of ores mixed with coke show an increased extent of prereduction for all ores.

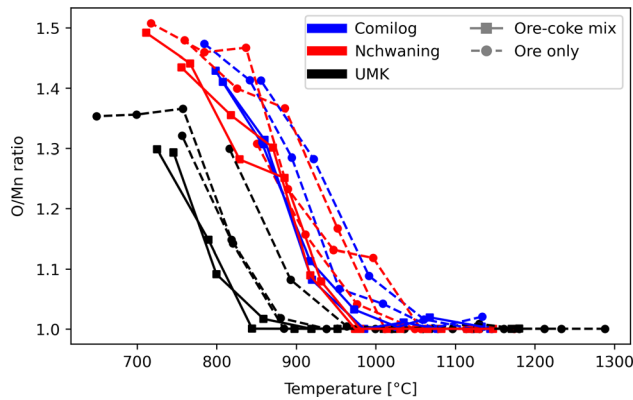


Fig. 2—Extent of prereduction of manganese ores as a function of temperature.

The prereduction of ores is affected by CO concentration in the reducing gas atmosphere. Several studies^[10,11,19,26,27] have reported an increased reduction rate of manganese ores with increasing CO concentration in CO–CO₂ atmosphere. The concentration of CO in the reducing gas atmosphere is generated from the metal producing reaction (reaction [8]) and/or the oxidation of C by CO₂. In the induction furnace set up, no significant metal producing reaction was expected for Comilog, Nchwaniang and UMK since the highest temperature peak of 1400 °C is below smelting temperatures of these ores.^[28–30] Hence, less CO is produced from the metal producing reaction compared to pilot or industrial furnaces. In comparison to Nchwaniang, the higher extent of prereduction in UMK is mainly because UMK contains a higher CO₂ content as shown in Table I, and will release more CO₂ during heating which oxidizes C thereby producing CO for prereduction of manganese oxides. The reason for the poor extent of prereduction for Comilog is mainly due to a lack of CO. Since Comilog is not a carbonate ore, the lack of CO is due to the less CO₂ produced that can react according to the Boudouard reaction and produce CO. The increased extent of prereduction when ores are mixed with solid carbon is due to increased oxidation of C by CO₂ in the presence of coke, thereby increasing the rate of reduction by CO. Gasification of carbon in coke has been previously reported to be catalyzed by Mn₃O₄ and determines the overall rate of reduction.^[15]

2. Porosity development and decomposition of carbonates

The porosity results shown in Figure 3 are for excavated ores, which were unmixed and mixed with coke and their corresponding residual carbonate content (given as CO₂ content) as a function of temperature. The trendlines were calculated using a Lowess filter with a smoothing parameter of 0.35. It can be mentioned that the porosity is measured for single particles, and hence it is expected a large variation as the properties from particle to particle may be quite large.

Porosity development during heating and reduction shows that ore particles become more porous with increase in temperature as shown in Figure 3. This is in agreement with previous findings.^[17,31] The peak porosity of Comilog and Nchwaniang during reduction is around 800 °C to 1000 °C, whereas for UMK it is at 800 °C to 900 °C. Upon reaching a peak porosity, a downward trend for the porosity measurements with further increase in temperature is observed for UMK ore. This decrease in porosity is assumed to be due to the observed sintering of the particles. The presence of coke is expected to increase the porosity at lower temperatures, because of better prereduction, but the effect is unnoticeable considering the heterogeneity of the ores.

The carbonates present in the ores decompose endothermically. Several studies^[10,32,33] have shown that the decomposition of carbonates is highly dependent on temperature and CO₂ content in the reducing atmosphere, with increasing temperature and lowering the partial pressure of CO₂ resulting in a greater extent of decomposition. The remaining CO₂ content in the samples analyzed as a function of temperature is shown in Figure 3. It can be seen in seen that almost no CO₂ content was observed from Comilog ore (Figure 3(a)), since the ore does not contain carbonate minerals and the analyzed CO₂ could be from coke dust contaminating the ore particles. UMK ore (Figure 3(c)), shows a clear trend of decrease in CO₂ content due to carbonate decomposition with increase in temperature up to 900 °C, beyond which carbonate decomposition is complete. This trend is also observed in Nchwaniang ore, with some outliers since the initial content in Nchwaniang is around 4.45 wt pct. Minerals distribution in Nchwaniang ore is heterogeneous and the ore is in general characterized by very low porosity.^[22,34] Therefore, the high carbonate content in some particles at elevated temperatures, as seen in Figure 3(b) could be pockets of undecomposed carbonates resulting from this heterogeneity. The rapid increase in porosity for UMK is believed to be due to decomposition of carbonates leaving voids in the ore particles.

B. Thermogravimetric Experiments

1. Prereduction behavior in 70/30 CO/CO₂ atmosphere

The experimental weight loss data acquired from the TGA setup are reported and utilized in calculation of change in O/Mn ratio and its first derivative as reaction rate (wt pct/s) all as functions of temperature. The variation of weight loss with temperature for non-isothermal reduction of Comilog, Nchwaniang and UMK is shown in Figure 4(a). The corresponding O/Mn ratio calculated through the mass loss as a function of temperature is shown in Figure 4(b). The mass loss follows the increase in sample temperature. Comilog ore which has a higher initial O/Mn ratio of 1.93 forms a “Z-shape” in the weight loss vs temperature curve. This is due to exothermic reduction reactions, which cause the temperature to increase above the programmed temperature and is characteristic of MnO₂-ores.^[17,19] Some deviation is observed in Figure 4(a), where the “Z-shape” curve for Comilog ore at 6 °C/min reaches a

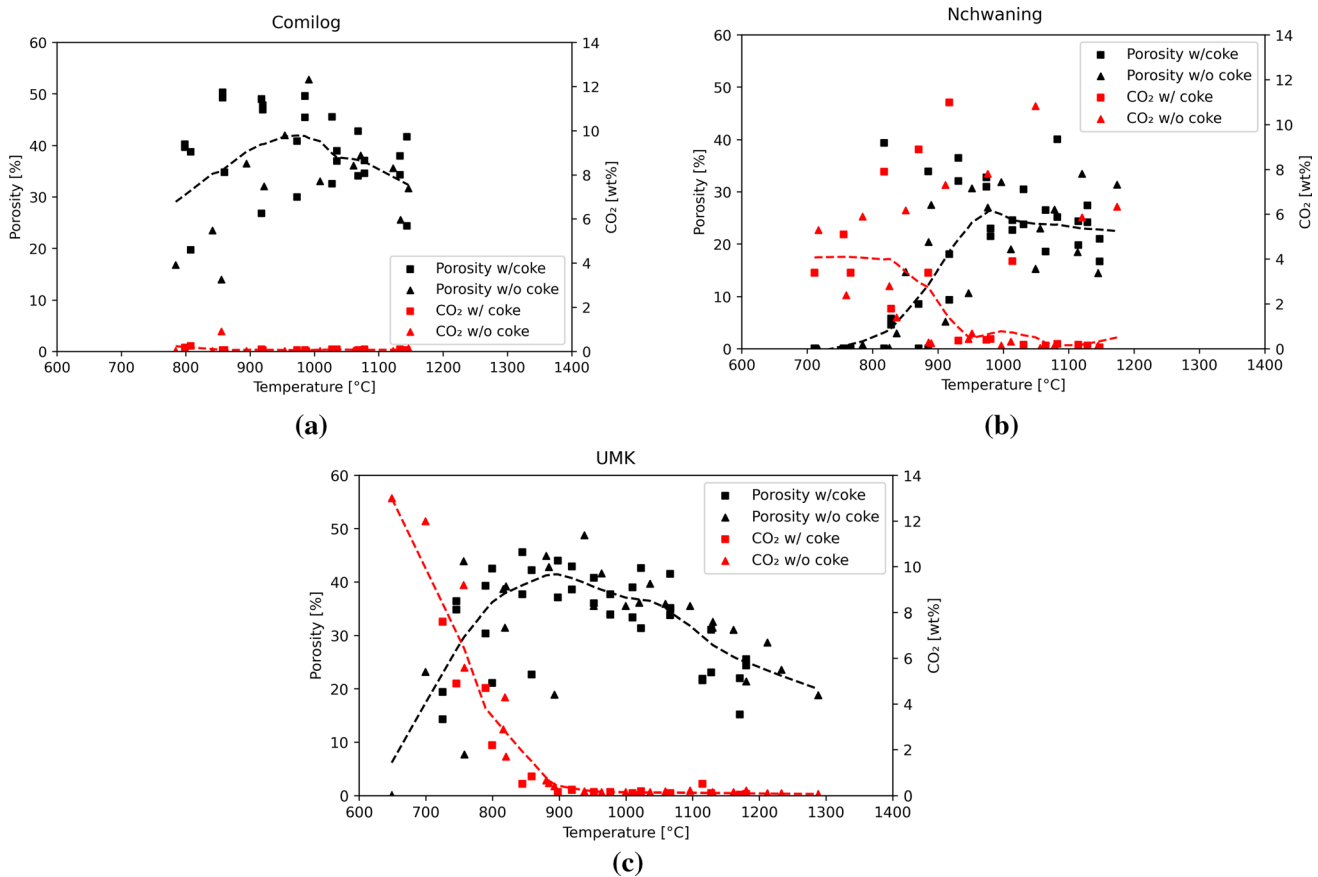


Fig. 3—The development of porosity and decomposition of carbonates as a function of temperature for (a) Comilog, (b) Nchwani and (c) UMK ores.

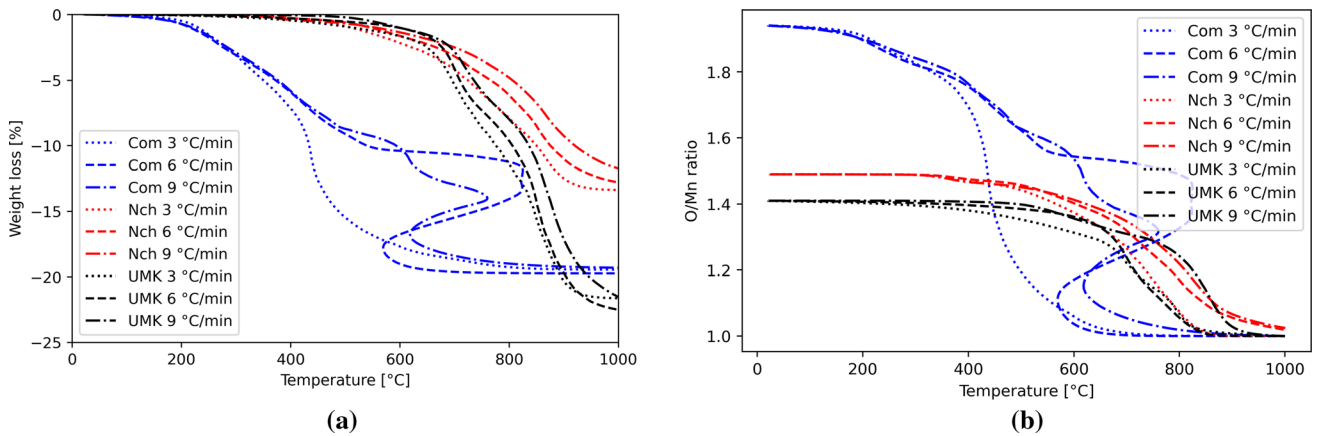


Fig. 4—(a) Weight loss (pct) as a function of temperature and (b) O/Mn ratio as a function of temperature for Comilog, Nchwani and UMK ores (10 to 12.5 mm particles). The TGA and calculated O/Mn curves are at heating rates of 3, 6 and 9 °C/min all at 70 pct CO and 30 pct CO₂.

higher temperature than that at 9 °C/min. At 9 °C/min the exothermic reactions initiate at lower temperatures compared to 6 °C/min, thus more MnO₂ has been consumed and this results in a lower exothermic peak temperature. Nchwani and UMK are Mn₂O₃ based ores and their prereduction starts from an initial O/Mn ratio of 1.47 and 1.45, respectively. Figure 4(a) shows that UMK has the highest weight loss followed by

Comilog and lastly, Nchwani. This trend is in accordance with theoretical weight loss shown in Table II. A greater part of the weight loss from UMK is from carbonate decomposition, which is approximately 4 times the weight loss contribution from prereduction as shown in Table II, whereas in Comilog its mainly from prereduction reactions and evaporation as it contains higher manganese oxides MnO₂ and

around 3.8 wt pct water content. Nchwani is an Mn_2O_3 ore, with lower carbonate content compared to UMK has weight loss contribution from prereduction and carbonate decomposition.

The very exothermic reactions observed when prereducing Comilog ore occurs very close to 500 °C at heating rates 6 °C/min and 9 °C/min as seen in Figure 4. This exothermic peak rapidly increases the temperature close to or exceeding 800 °C. At a heating rate of 3 °C, the exothermic peak is absent as the furnace is able to tune the temperature with less exothermic reactions per minute. Weight loss in Comilog ore starts at approximately 200 °C and Comilog ore has an O/Mn ratio very close to 1 at 800 °C. Between 600 °C and 800 °C, one can see that the lower heating rate gives a lower O/Mn ratio at a given temperature. Nchwani ore shows a clear distinction of the effect of heating rate on prereduction, with a lower heating rate of 3 °C/min giving rise to a higher extent of prereduction. The prereduction of Nchwani ore commences at about 350 °C and the prereduction is complete by 1000 °C. On the other hand, the prereduction of UMK ore commences at slightly higher temperature at 500 °C compared to Nchwani ore and is completely prereduced by 900 °C. The corresponding reaction rate (wt pct/s) curves as a function of temperature for all the three heating rate scenarios in the studied ores is shown in Figure 5. In general, the reaction rate is highly

influenced by heating rate, with decreasing heating rate resulting in longer time at each temperature. The rate curves for Comilog ore in Figure 5(a) shows that at 6 °C/min, the exothermic peak reaches a higher temperature compared to 9 °C/min heating rate. The rate curves in Figure 5(b) for Nchwani ore are characterized by the highest peak occurring at about 900 °C. The lower peaks at temperatures less than 900 °C become less pronounced with decreasing rate. As shown in Figure 5(c), the prereduction of UMK ore occurred with two major distinctive steps, the first one mostly occurring at about 700 °C, and the second one at the higher temperature 900 °C. It is also observed that the peaks in UMK reduce in size with decreasing heating rate, due to the longer time at each temperature.

An interesting phenomenon that could affect the TGA weight loss data and subsequently the rate curves, is carbon deposition. This may be difficult to detect from weight behavior when prereduction reactions occur simultaneously. According to thermodynamics, the Boudouard ($CO_2 + C = 2CO$) reaction is shifted to the left below 700 °C resulting in carbon deposition, whereas at higher temperatures it will proceed to the right. A high CO/CO_2 ratio enhances carbon deposition. Larsen^[22] conducted experiments with quartz in 80/20 CO/CO_2 atmospheres and found that carbon deposition was initiated at temperatures close to 400 °C and continued with increase in temperatures. At

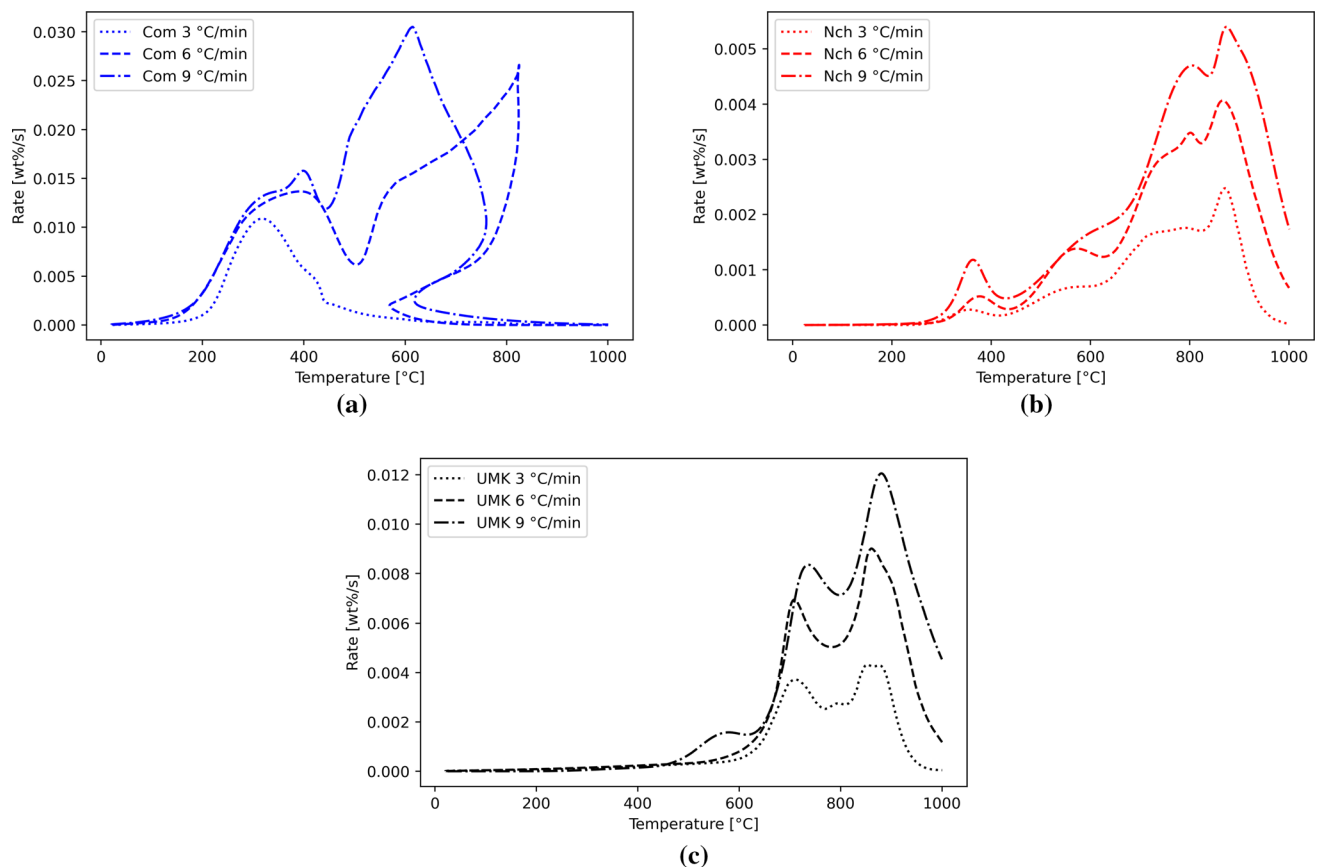


Fig. 5—Variation of rate (wt pct/sec) with temperature for Comilog, Nchwani and UMK ores (10 to 12.5 mm), heated at 3, 6 and 9 °C/min in a 70 pct CO and 30 CO_2 atmosphere.

temperatures above 780 °C gasification of the deposited carbon was observed. As such, it is believed that the initial peaks observed in the reaction rate curves for mostly Nchwanning ore and UMK ore, which increase with increasing heating rate, as shown in Figures 5(b) and (c) are due to carbonate decomposition. Prereduction reactions in Comilog ore start at relatively low temperatures as shown by the weight loss curve in Figure 4(a). This causes CO to be consumed at low temperatures, thus the driving force for the carbon deposition is lower in this case. Therefore, it is believed that prereduction of Comilog ore is not affected by carbon deposition. No carbon was observed in the reduced samples in all experiments; hence any deposited carbon had been gasified during the experiments. However, gasification of carbon is expected to occur simultaneously as the higher reduction rates in these experiments and would be obscured by the reduction reactions.

Evaluation of the reactions occurring at the distinctive peaks in Nchwanning and UMK was done by conducting non-isothermal experiments at 9 °C/min in 70/30 CO/CO₂ gas atmosphere, with final temperatures at the peak regions. The final temperatures were 700, 800 and 900 °C for UMK whereas for Nchwanning the experiment was ended at 900 °C. The chemical composition of samples from these experiments in addition to the initial experiments are shown in Table III. The chemical composition shows significant decrease in carbonate content for Nchwanning and UMK at the investigated peak temperatures. Therefore, the percentage carbonate decomposed from Nchwanning and UMK was calculated from initial values and the results are shown in Figure 6. These results show that the described distinctive peaks in UMK and Nchwanning are mainly due to decomposition of carbonates in addition to prereduction reactions.

2. Analysis of the constituents of TGA rate curves

The change of mass loss during TGA experiments corresponds to removal of oxygen from higher manganese oxides and iron oxides *i.e.*, prereduction reactions, decomposition of carbonates and water evaporation. As such, there are several reactions involved and it is not straightforward to isolate effects of these individual reaction components. Therefore, to establish the contributions of these components, Fityk^[25] a general purpose peak or model fitting software was used to decompose the rate curves.

The constituents contributing to the overall rate of weight loss in Comilog ore are water evaporation and prereduction reactions shown in Figure 7, at different heating rates. Temperature profiles are indicated on the secondary axis as a function of time. When looking at the decomposed rate curves for 3 °C/min, the water evaporation happens virtually at the same time as the main reduction rate peak. Considering all the heating

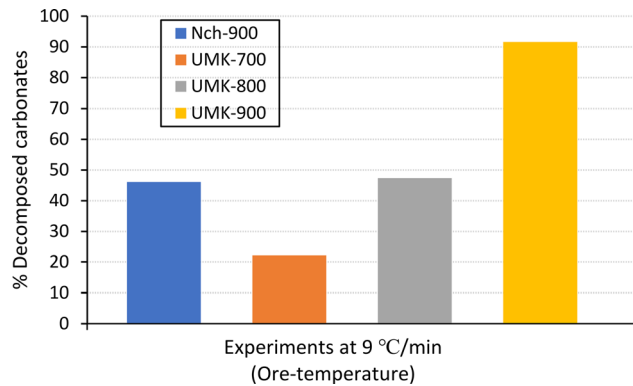


Fig. 6—Fraction of carbonates decomposed in Nchwanning and UMK as a function of temperature.

Table III. Chemical Analysis of Comilog, Nchwanning and UMK Samples Exposed to Non-isothermal Reduction

Ore	Temp. (°C)	Heating Rate (°C/min)	Fe, tot	Mn, tot	MnO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	CO ₂	Ratio
			(wt pct)									
Com	1000	3	2.28	66.5	3.79	2.97	5.13	0.11	0.12	1.05	0.11	1.04
	1000	6	3.00	64.0	5.22	3.30	6.82	0.10	0.12	1.00	0.10	1.05
	1000	9	2.99	65.2	5.64	3.91	5.15	0.11	0.04	0.97	0.11	1.05
Nch	1000	3	11.5	52.9	0.05	4.61	0.53	7.86	1.19	0.05	0.20	1.00
	1000	6	11.4	49.4	0.05	7.41	0.42	8.49	1.97	0.06	0.37	1.00
	1000	9	12.6	51.7	0.05	3.62	0.40	7.35	1.15	0.11	0.22	1.00
UMK	900	9	9.69	49.4	6.55	4.10	0.57	9.06	1.92	0.10	2.4	1.08
	1000	3	14.1	41.4	0.05	7.17	0.49	16.1	3.20	0.15	0.11	1.00
	1000	6	10.0	42.3	0.05	6.82	0.53	19.7	3.56	0.11	0.22	1.00
	1000	9	10.9	42.0	0.05	6.95	0.29	17.9	3.35	0.08	0.29	1.00
	700	9	5.08	36.4	16.4	6.79	0.47	16.0	3.11	0.19	13.0	1.29
	800	9	4.60	43.8	13.7	7.03	0.46	15.1	2.79	0.10	8.8	1.20
	900	9	13.1	39.7	0.05	6.55	0.37	16.3	3.65	0.13	1.4	1.00

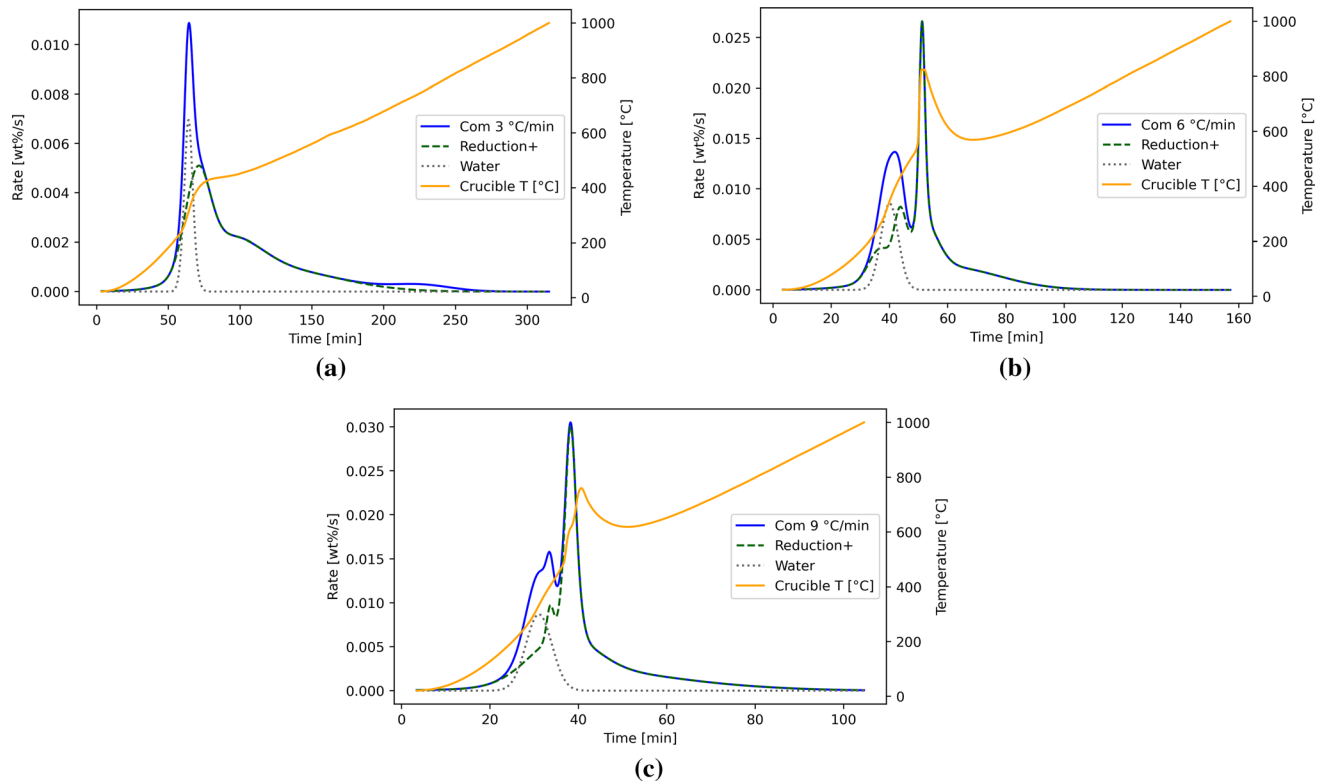


Fig. 7—Contribution of various ore constituents to the overall rate of prereduction for Comilog ore heated at (a) 3 °C/min, (b) 6 °C/min and 9 °C/min in a 70/30 CO/CO₂ atmosphere.

rates, integration of the water loss curves gives total weight of 3.24, 3.88 and 3.84 wt pct at heating rates of 3, 6, 9 °C/min, respectively. These values show a high accuracy in relation to 3.8 wt pct water content in the ore as presented in Table II. The temperature range for evaporation is 200 to 300 °C, which is in agreement with previously reported evaporation temperature range.^[22] At 6 and 9 °C/min, the reduction reaction can be seen starting at low temperatures and the crucible temperature increases in accordance with exothermic reactions, but it is not until the water is completely evaporated that the main bulk of the reaction occurs, giving a very exothermic peak.

The constituents contributing to the overall rate of weight loss in Nchwani ore are decomposition of carbonates and prereduction reactions shown in Figure 8, at different heating rates. Temperature profile indicated on the secondary axis as a function of time show an endothermic dip in the sample temperature at 900 °C, which corresponds to where the carbonate contribution peaks are. The expected weight loss from decomposition of carbonates is 4.45 wt pct as presented in Table II. Integration of the rate curves of the carbonate contribution gives total weight loss of 4.21, 3.91 and 3.47 wt pct at heating rates of 3, 6, 9 °C/min, respectively. Therefore, the weight loss due to carbonate contribution decreases with increasing heating rates.

The majority of the reduction, and exothermic reactions, occur at temperatures below 800 °C as shown by reduction constituents.

Figure 9 shows the contributions of decomposition of carbonates and prereduction reactions to the overall rate of weight loss in UMK ore and their changes with heating rate. Temperature profiles for UMK indicated on the secondary axis as a function of time show two endothermic dips in the sample temperature at 700 °C and 900 °C. The height of the first peak at 700 °C is shown to decrease with increasing heating rate and is attributed to both prereduction and decomposition of carbonates. As previously shown in Figure 6, about 20 wt pct carbonates are decomposed at this first peak, and the O/Mn ratio is 1.29 as presented in Table III. Therefore, in the first peak reduction reactions happen in parallel with the carbonate decomposition reaction. On the other hand, the height of the second peak at 900 °C appears to be unaffected by the heating rate. At this peak, a greater proportion of carbonates is decomposed as shown in Figure 6 and the prereduction reactions are complete as O/Mn ratio is 1.0 as shown in Table III. The curves in Figure 9 reveal that UMK is fully reduced by 900 °C and the carbonates decompose in two steps and this is supported by the chemical analysis in Table III and variation of the decomposition of carbonates with temperature shown in Figure 6.

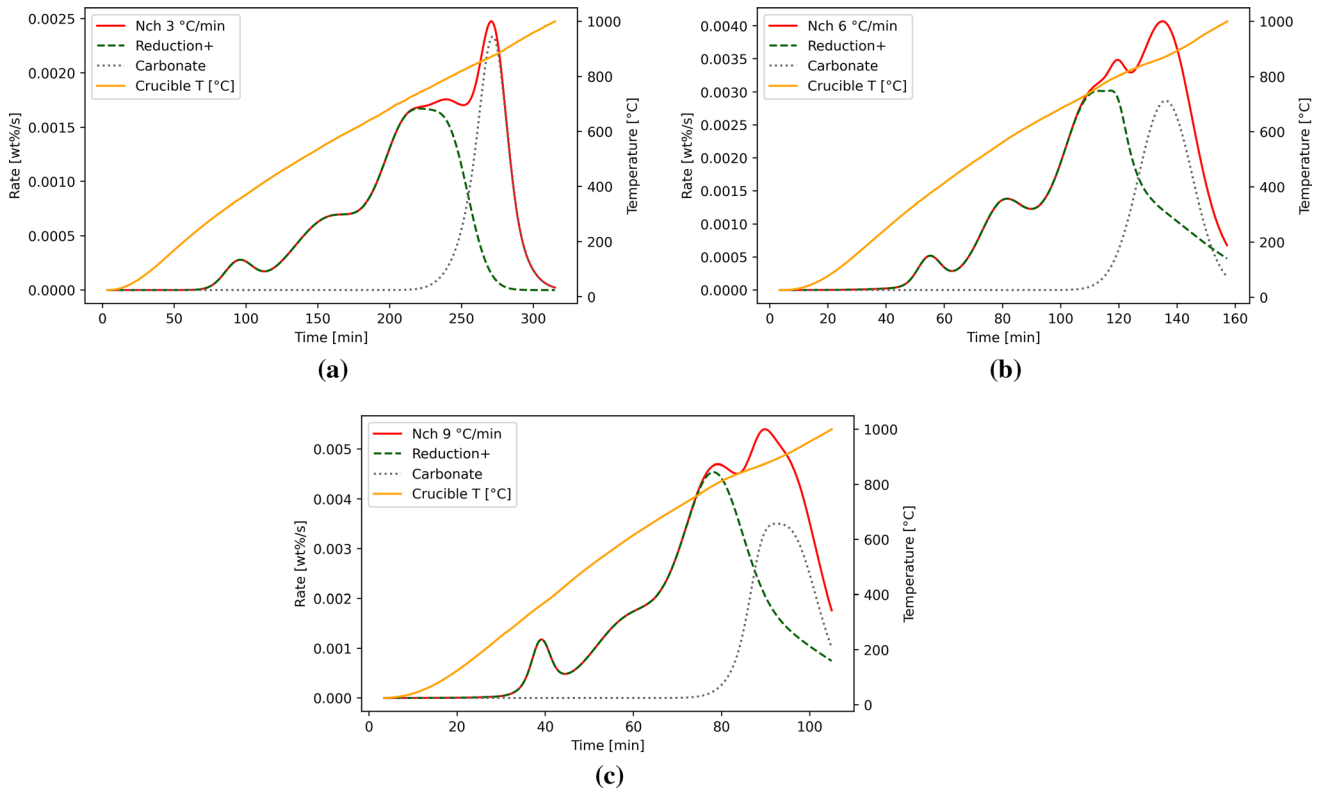


Fig. 8—Contribution of various ore constituents to the overall rate of pre-reduction for Nchwanging ore heated at (a) 3 °C/min, (b) 6 °C/min and 9 °C/min in a 70/30 CO/CO₂ atmosphere.

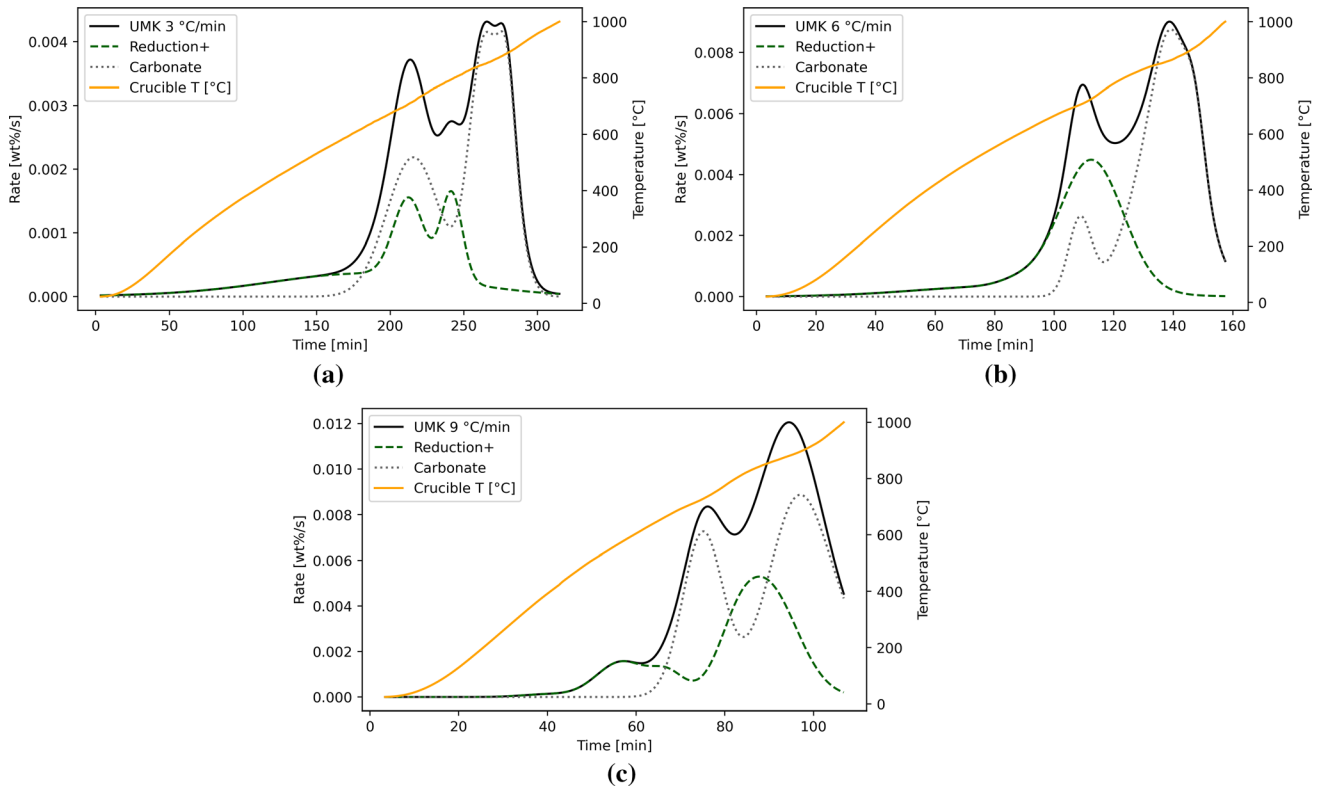


Fig. 9—Contribution of various ore constituents to the overall rate of pre-reduction for UMK ore heated at (a) 3 °C/min, (b) 6 °C/min and 9 °C/min in a 70/30 CO/CO₂ atmosphere.

Based on the chemical analysis of UMK ore in Table I, the carbonates are assumed to be dolomitic and previous studies^[32,33] have shown dolomite to decompose in two distinct steps with temperature zones depending on the type of mineral existing around it. Integration of the rate curves of the carbonate contribution gives total weight loss of 14.7, 14.0 and 13.8 wt pct at heating rates of 3, 6, 9 °C/min, respectively. As seen from Table II reduction of iron and manganese oxides in UMK ore is expected to contribute about 5 wt pct and decomposition of carbonates about 16 wt pct to the overall weight loss. The curves presented have been verified to match the total weight loss expected from their constituents and the slight variations could be attributed to heterogeneity of ores and uncertainty in chemical analysis. In conclusion, the two endothermic peaks observed in the rate of weight loss curves in UMK are essentially due to decarbonation of dolomite and reduction reactions for the first peak and mainly decarbonization of calcite in the second peak.

3. Decrepiation of ores

Figure 10 shows the particle size distribution for Comilog, Nchwanning and UMK ores heated to 1000 °C in 70/30 CO/CO₂.

The Nchwanning ore particle size distribution curve has a similar shape as the UMK ore compared to the Comilog ore curve when heated in CO/CO₂. However, in the finer size fractions below 4.75 mm Nchwanning ore generates more fines compared to UMK ore. The distribution below 10 mm is shallow for Nchwanning ore, meaning that the particles are distributed more equally between the finer mesh sizes. This signifies that when Nchwanning ore decrepitates it produces more fines than medium sized particles whereas when UMK ore decrepitates it tends to crack into larger particles, as opposed to generating fines. There is no apparent correlation between heating rate and decrepitation for Nchwanning ore. The effect of heating rate on decrepitation on UMK ore shows that an increase in heating rate results in increased decrepitation. On the contrary, Comilog ore shows that increase in heating rate results in decreased decrepitation. Though there is a difference on the effect of heating rate on decrepitation when comparing UMK ore and Comilog ore, the significance of heating rate on decrepitation of UMK ore is not high. From Figure 10, the fraction of particles with size range lower than 10 mm are 75 to 90 pct, 35 to 42 pct and 48 to 60 pct for Comilog, Nchwanning and UMK ores, respectively. There is a significant difference in size distribution for all the three ores in CO/CO₂, which

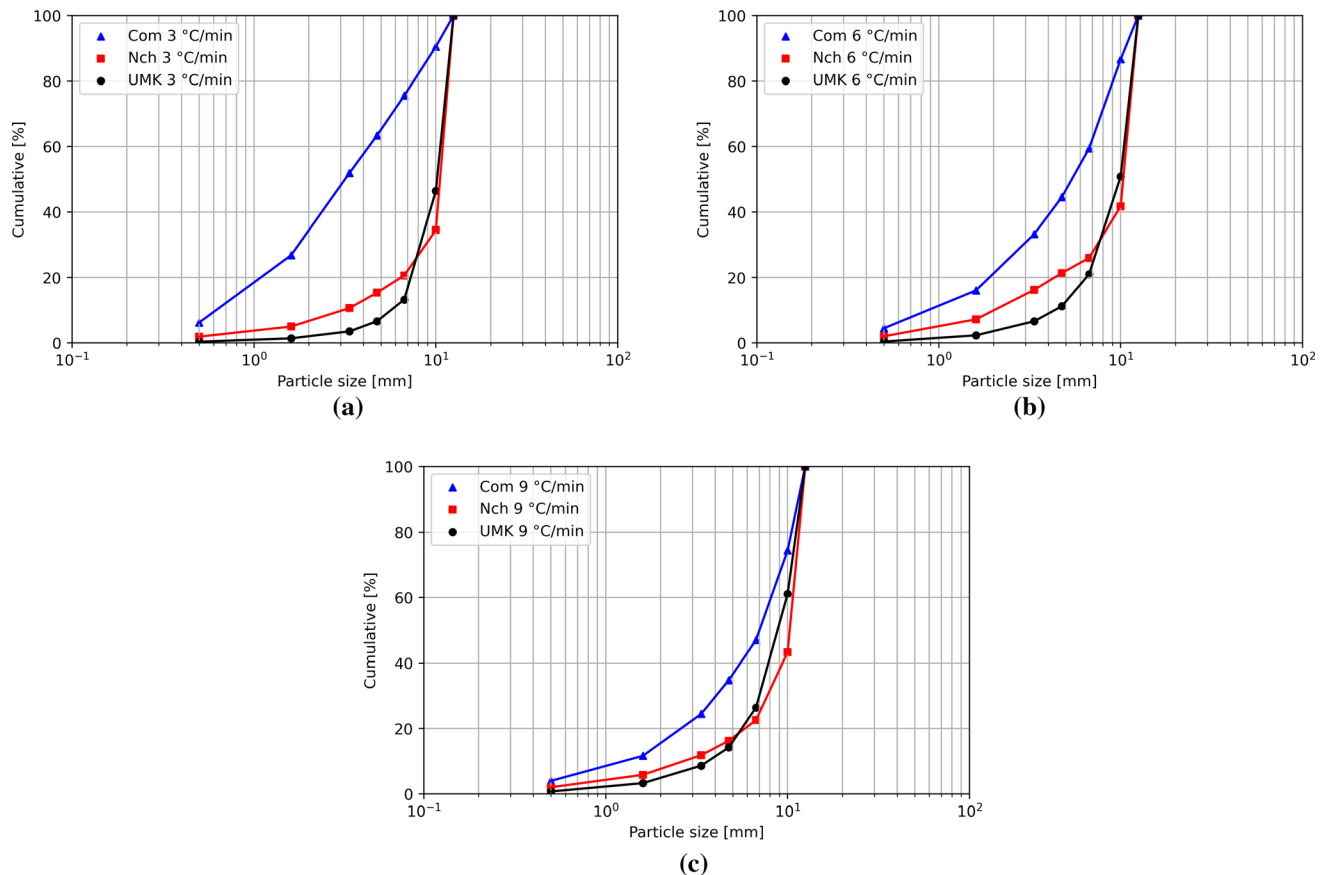


Fig. 10—Cumulative particle size distribution for Comilog, Nchwanning and UMK ores heated at (a) 3 °C/min, (b) 6 °C/min and 9 °C/min in a 70/30 CO/CO₂ atmosphere.

shows that Comilog ore produces the most fines followed by Nchwaning ore and lastly UMK ore. Higher decrepitation of Comilog in comparison to other ores is in agreement with previous investigations.^[22,31] Comilog ore has been reported to have lower mechanical strength and high initial porosity in the range 30 to 50 pct and Nchwaning ore is characterized by a higher mechanical strength and very low porosity (0 to 1 pct).^[34] As such Comilog is expected to decrepitate the most. Larssen^[22] measured the decrepitation of Comilog and Nchwaning ores, and showed the same correlation between lower heating rates and an increase in decrepitation for Comilog ore. In another study, Biørnstad^[31] studied the decrepitation for UMK, Nchwaning and Comilog and showed that Nchwaning decrepitates more than UMK, which is contrary to findings in this work, however they are both in the same area.

IV. CONCLUSIONS

From the obtained results it can be concluded that:

- (1) The decomposition of carbonates lead to better prereduction in the induction furnace experiments, due to the CO produced in the Boudouard reaction. This is the reason why UMK ore has a better prereduction compared to Nchwaning ores which is low in carbonates and Comilog ore which is known to have a higher CO reactivity at similar CO contents. Prereduction of ores mixed with solid carbon resulted in improved prereduction compared to ore only in induction furnace experiments.
- (2) Analysis of the rate curves from TGA shows that decomposition of carbonates in UMK ore is a two-step process with peak temperatures at 700 °C and 900 °C whereas for Nchwaning ore, it is a single step with peak temperature at 900 °C. The first endothermic peak in UMK ore is a combination of decomposition of carbonates and prereduction reactions whereas the second peak is mainly carbonate decomposition and O/Mn ratio is 1.0 showing that prereduction of higher manganese oxides is complete prior to second decomposition reaction. For Nchwaning, the endothermic peak is mainly decomposition of carbonates and prereduction reaction is almost complete with an O/Mn ratio of 1.08.
- (3) Comilog ore produces most fines followed by Nchwaning and lastly UMK on decrepitation.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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