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Effect of Raw Materials on Temperature Development during Prereduction of Comilog and Nchwaning Manganese Ores

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Abstract: The effect of raw materials on the temperature development and prereduction behavior of Comilog and Nchwaning manganese ores (3.33–4.00 mm or 11.20–15.00 mm) were investigated in a CO-CO_2 atmosphere. Experiments were conducted at a heating rate of 6 °C/min from room temperature to 1000 °C where the ore was mixed with inert material (quartz) in various ratios. A similar heating program gave dissimilar temperature development for Comilog and Nchwaning ores due to differences in oxygen levels and reduction rates. The temperature development, and thus reduction rate, decreased with the increasing amount of inert material in the mix for Comilog ore in size 3.33–4.00 mm. The peak reaction rates observed during reduction were 2.4 wt%/min, 1.0 wt%/min, and 0.8 wt%/min for an ore:quartz weight ratio of 1:0, 1:1, and 1:3, respectively. For Comilog ore in size 11.20–15.00 mm, and Nchwaning ore in both sizes, the temperature development and reduction rates were slightly or insignificantly affected. It was suggested that the effect was low for reactions under a diffusion-controlled kinetic regime.

Keywords: manganese ores; prereduction; gas-solid reactions; ferromanganese production

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1. Introduction

In the production of ferromanganese alloys, manganese ore and potentially sinter are fed to the electric furnace together with other raw materials, such as coke, flux, and quartz. Coke is required as a reducing agent for all types of ferromanganese alloys, whereas potential flux and quartz additions depend on the ore type used and the target alloy composition. The raw materials are mixed in proper weight ratios prior to entering the furnace by the use of silos, automatic transport systems, and weighing devices [1]. The furnace process is often viewed as two distinct zones, namely, the prereduction zone and the coke bed zone. The raw materials will descend through the prereduction zone in solid state, where several reactions occur between the ascending furnace gas and the descending raw materials that have a substantial effect on the overall energy efficiency and gas emissions of the process. The ores contain higher manganese oxides (MnO_x, $x > 1$) that will reduce to MnO in the prereduction zone according to Equations (1)–(3). These reactions are highly exothermic, where the amount of evolved heat depends on the oxygen level of the ore. The oxygen level in the ore is determined by the minerals constituting the ore, which could be MnO_2-types (O/Mn = 2) as in Comilog ore, or Mn_2O_3-types (O/Mn = 1.5) as in Nchwaning ore. This implies that a high oxygen level will minimize the electrical energy requirement of the furnace. The ore reactions further influence the energy efficiency, and gas production, by determining the occurrence of the Boudouard reaction. The Boudouard reaction ($C + CO_2 = 2CO$), being both carbon-consuming and highly endothermic, gains significant reaction rates at temperatures exceeding 800 °C in an industrial furnace, where its reaction extent is limited by the available CO_2. As such, the reaction temperatures and rates of the ore reduction reactions producing this CO_2 is of high importance.

$$\mathrm{MnO_2} + \frac{1}{2}\mathrm{CO(g)} = \frac{1}{2}\mathrm{Mn_2O_3} + \frac{1}{2}\mathrm{CO_2(g)} \qquad \Delta H^0_{298} = -101\ \mathrm{k/mol} \tag{1}$$

$$\frac{1}{2}\mathrm{Mn_2O_3} + \frac{1}{6}\mathrm{CO(g)} = \frac{1}{3}\mathrm{Mn_3O_4} + \frac{1}{6}\mathrm{CO_2(g)} \qquad \Delta H^0_{298} = -29\ \mathrm{kJ/mol} \tag{2}$$

$$\frac{1}{3}\mathrm{Mn_3O_4} + \frac{1}{3}\mathrm{CO(g)} = \mathrm{MnO} + \frac{1}{3}\mathrm{CO_2(g)} \qquad \Delta H^0_{298} = -17\ \mathrm{kJ/mol} \tag{3}$$

Due to the large impact on energy consumption and climate gas emissions, numerous studies have been carried out to elucidate the prereduction behavior of various commercial manganese ores. The typical investigation method involves thermal treatment while monitoring the reaction rates through mass loss and/or changes in off-gas composition. The consensus of these studies is that the reactions are kinetically controlled, and the reduction behavior is highly dependent on the characteristics of the ore. This is also observed in industrial operation [2,3]. The rates have been observed to be influenced by parameters such as particle size, reducing agent, gas composition, heating rate, and temperature [3–6].

From laboratory-scale experiments, highly oxidized ores have been observed to produce a considerable amount of heat, elevating the temperature in the ore drastically, thus affecting the reduction rate at the specific time [5]. As such, an increased reaction rate will lead to an increased temperature, which in turn promotes the reaction rate. The ore is mixed with the remaining raw materials in the charge mixture when it enters the furnace. While these materials do not participate in any chemical reactions at low temperatures ($T < 800$ °C), it is reasonable to assume that they will absorb some of the heat released from the ore reduction, and thus affect the temperature and ultimately the prereduction rates of the manganese ores. Information available on the heat transfer interaction between the raw materials during prereduction is scarce; however, some work has been published on the thermophysical properties of the various raw materials used in ferromanganese production. Ksiazek et al. [7] showed that the thermal diffusivity of manganese ores is dependent on temperature, mineralogy and porosity, and furthermore, that quartz exhibits a higher thermal diffusivity than manganese ores.

This paper presents the investigation of the influence of inert materials on the temperature development during manganese ore prereduction by the mixing of manganese ore and quartz at various ratios.

2. Materials and Methods

The evaluated manganese ores were Comilog and Nchwaning that had been dried at 105 °C for 24 h before being crushed and sieved into size fractions of 3.33–4.00 mm and 11.2–15.0 mm. The chemical composition was determined by X-ray fluorescence, except for the MnO_2, CO_2, H_2O and LOI content. MnO_2 was determined by titration (ASTM 465-11:2017), whereas H_2O and LOI were determined by thermogravimetry. Eltra (combustion-IR) was used to determine amount of carbon, which was recalculated to CO_2. The amount of chemically bound moisture in the ores was estimated by heating approximately 10 g of a sample in a muffle furnace at 950 °C for 12 h. It was assumed that the potential weight loss experienced by the sample included moisture, volatiles, and potential partial decomposition of manganese oxides. The latter was determined by titration according to the aforementioned procedure.

Comilog ore is a high oxygen ore, where the majority of the manganese is present as MnO_2. It has a low content of iron and some chemically bound moisture. Nchwaning ore is a medium oxygen ore, where the %MnO_2 correlates to an O/Mn close to 1.5, i.e., that of Mn_2O_3. The chemical composition of the ores is shown in Table 1.

Table 1. Chemical composition of Comilog and Nchwaning ores.

		Comilog		**Nchwaning**	
		3.33–4.00 mm	**11.20–15.00 mm**	**3.33–4.00 mm**	**11.20–15.00 mm**
Mn	TOT	51.4	51.0	46.5	46.4
Fe	TOT	2.8	3.1	9.5	10.0
LOI (950 °C)	%	12.5	13.0	4.0	4.0
MnO_2	%	76.6	76.4	34.2	34.6
MnO	%	3.8	3.5	32.2	31.6
Fe_2O_3	%	4.0	4.4	13.6	13.4
SiO_2	%	3.5	3.5	6.2	6.7
Al_2O_3	%	5.6	5.6	0.5	0.5
CaO	%	0.1	0.1	6.3	5.9
MgO	%	0.2	0.1	1.1	1.0
P	%	0.1	0.1	0.0	0.0
S	%	0.0	0.0	0.2	0.1
TiO_2	%	0.1	0.1	0.0	0.0
K_2O	%	1.1	0.7	0.0	0.0
BaO	%	0.2	0.3	0.5	0.4
CO_2	%	0.2	0.1	3.2	3.0
H_2O (free)	%	0.6	0.2	0.0	<0.1
H_2O (bound)	%	5.7	5.7	0	0

Nchwaning and Comilog manganese ores, respectively, and quartz in various ratios were investigated in CO-CO_2 atmosphere under a non-isothermal temperature regime. It is assumed that quartz behaves as an inert material in the temperature range used in this investigation, where its only effect is that it absorbs the heat developed by the chemical reactions. Quartz of size 6.3–8 mm was used in all experiments. Experiments were conducted with ore (Comilog or Nchwaning) and quartz in weight ratios of 1:0, 1:1, and 1:3. An overview of the conducted experiments is shown in Table 2.

Table 2. Overview of experiments conducted by mixing ratios of raw materials, that is ore:quartz ratios. (x) indicates number of replicas.

Materials	**Mixing Ratio by Weight**
Comilog (3.33–4.00 mm): quartz	1:0 1:1 1:3
Comilog (11.20–15.00 mm): quartz	1:0 1:1 1:3 (2)
Nchwaning (3.33–4.00 mm): quartz	1:0 1:1 1:3
Nchwaning (11.20–15.00 mm): quartz	1:0 1:1 (3) 1:3 (2)

A vertical retort tube furnace connected to a thermobalance and off-gas analyzer was used for the experiments. The sample is located in the lower parts of the crucible, placed on top of a grid. The gas inlet is at the top of the crucible, from where the gas moves through the double walls, ensuring preheating before meeting the sample from beneath. The gas ascends in the crucible and exits from the top into a gas-analyzer (NDIR). An illustration of the different components of the furnace set up is shown in Figure 1. Two thermocouples are used in the setup, where the power control is connected to the thermocouple located in the furnace wall. A second thermocouple is placed inside the crucible, adjusted so that the hot junction is in the center of the sample. There is a known difference between the two thermocouples, as seen in Figure 2, which is accounted for in the temperature programs, ensuring that the sample reaches the target temperature. Furthermore, the temperatures measured in the sample will reveal potential temperature changes for strongly endothermic or exothermic reactions. Figure 2 shows the difference in sample temperature during the heating of a medium oxygen ore (Nchwaning ore) and a high oxygen ore (Comilog ore) in a $CO\text{-}CO_2$ atmosphere. The former shows a temperature development highly similar to that of the empty crucible, whereas the latter shows a strong positive deviation in the sample temperature during ongoing reduction.

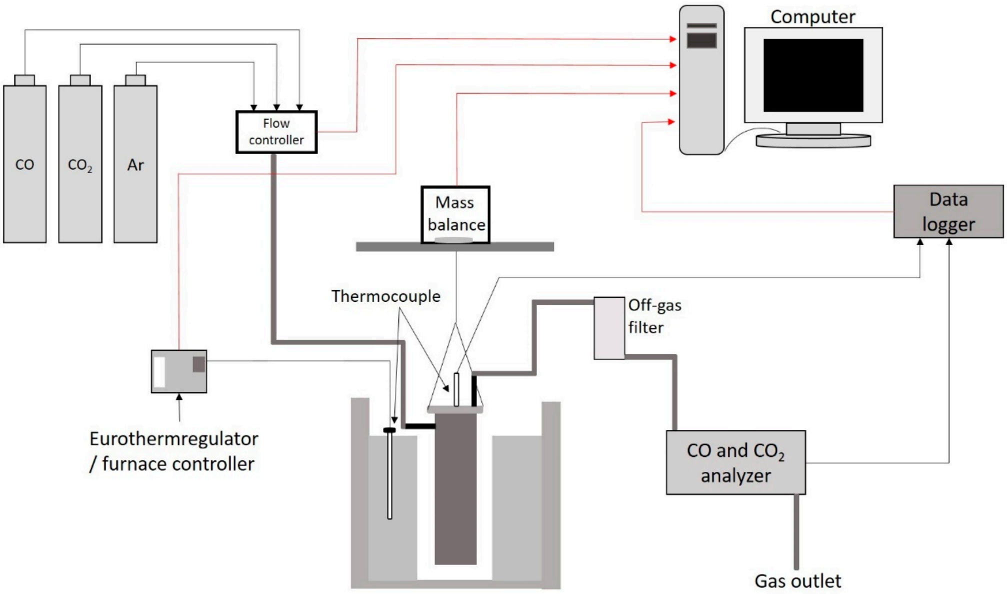

Figure 1. Illustration of furnace set up.

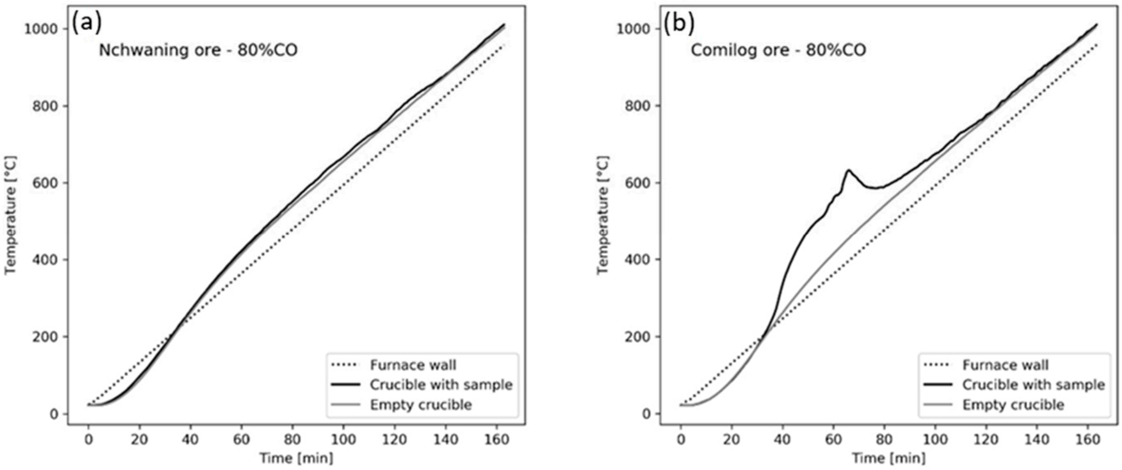

Figure 2. Example of temperature measurements in the furnace set up for (**a**) Nchwaning ore (medium oxygen ore) and (**b**) Comilog ore (high oxygen ore).

All experiments were conducted with a heating rate of 6 °C/min from room temperature to 1000 °C in a gas atmosphere consisting of 50%CO and 50% CO_2 at a total flow rate of 4 L/min. At target temperature, the atmosphere was replaced by a flow of 1 L/min of argon.

3. Results

3.1. Comilog Ore

The temperature development during the heating of Comilog ore mixed with quartz in various weight ratios is shown in Figure 3. A clear effect of the exothermic prereduction reactions is seen. A generally lower temperature is observed with the increasing amount of quartz in the charge. For 3.33–4.00 mm particles, the maximum temperature obtained during the exothermic peak at the 30–40 min process time decreases with the increasing amount of quartz in the crucible. At the 11.2–15.0 mm size, a highly similar temperature development is seen for single ore and the 1:1 mixing ratio of ore and quartz, where the difference lies in the position of the exothermic peak seen at approximately 500 °C being observed at a later process time in the presence of quartz.

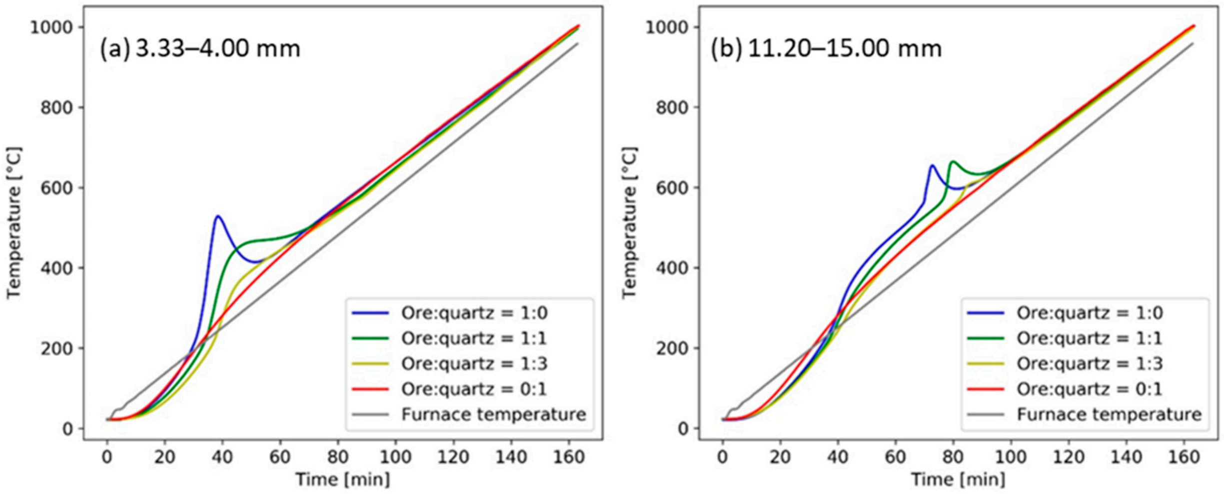

Figure 3. Temperature as a function of time for Comilog ore in size fractions of (**a**) 3.33–4.00 mm and (**b**) 11.20–15.00 mm, mixed with quartz in varying ratios.

The weight during prereduction of Comilog ore in size 3.33–4.00 mm is shown as a function of time and temperature in Figure 4. The reaction rate calculated from the weight change at 2 min intervals is shown in Figure 5. Most of the reduction is completed in the experiment where only ore is used before the reduction is initiated in the samples mixed with quartz, as seen in Figure 4a. As such, the presence of inert material leads to a lower sample temperature and thus decreases the rate. As a function of temperature, the weight loss behavior is more similar, as the temperature is a result of the reaction rate. Figure 5 shows that the maximum reaction rate is twice as high with no quartz present. No large difference is seen between the 1:1 and 1:3 weight mixing ratios of ore and quartz, respectively.

The weight and correlating weight change rate for 11.2–15.0 mm Comilog ore particles are shown in Figures 6 and 7, respectively. The weight reduction behavior is highly similar for all experiments, indicating no large effect by the presence of inert material. The characteristic exothermic peak at 550 °C is observed for all mixing ratios, although at varying magnitude. The maximum is observed at the 1:1 ore mixing ratio, whereas the lowest is observed at the 1:3 mixing ratio.

The chemical composition and oxygen level of the reduced ore were analyzed, and the obtained values are shown in Table 3. The analyzed oxidation levels (O/Mn-ratio) show that all experiments lead to a similar reduction extent at 1000 °C, where values in the range of 1.04–1.06 were found. As the weight was stable prior to the termination of the experiments, it is assumed that all experiments lead to a complete prereduction to MnO, i.e., O/Mn = 1.00. The deviation from this may be due to inaccuracy in analyses, or due to potential reoxidation occurring when the ore was exposed to air.

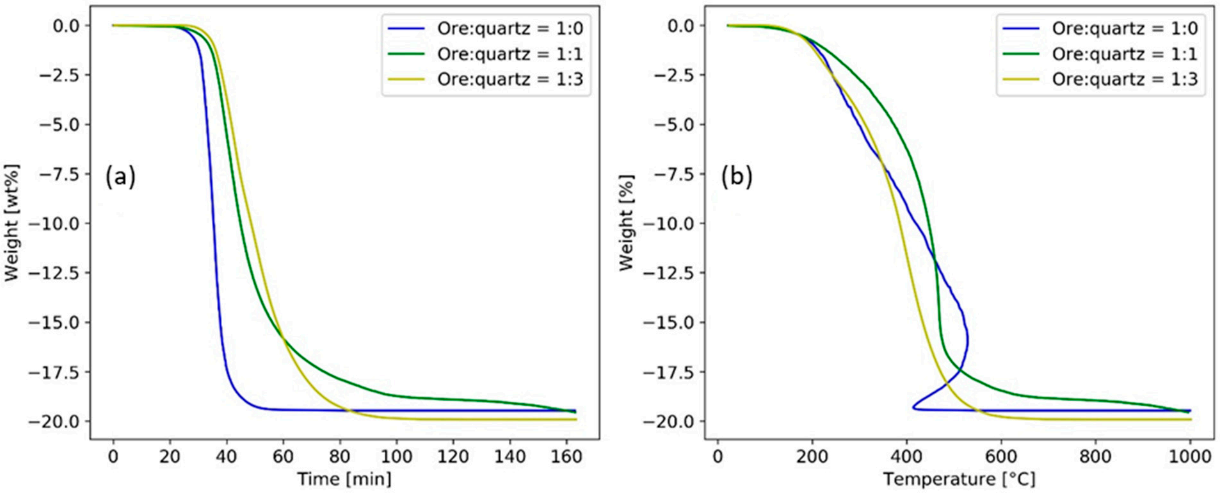

Figure 4. Weight as a function of (**a**) time and (**b**) temperature for Comilog ore in size 3.33–4.00 mm, mixed with quartz in varying ratios.

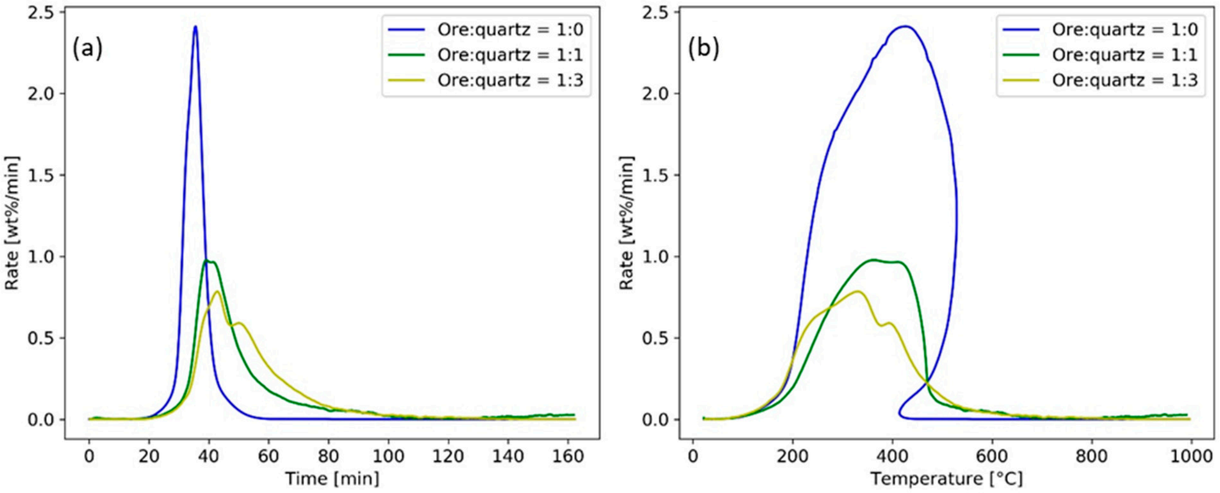

Figure 5. Reaction rate [wt%] calculated from the weight at 2 min time intervals as a function of (**a**) time and (**b**) temperature for Comilog ore in size 3.33–4.00 mm, mixed with quartz in varying ratios.

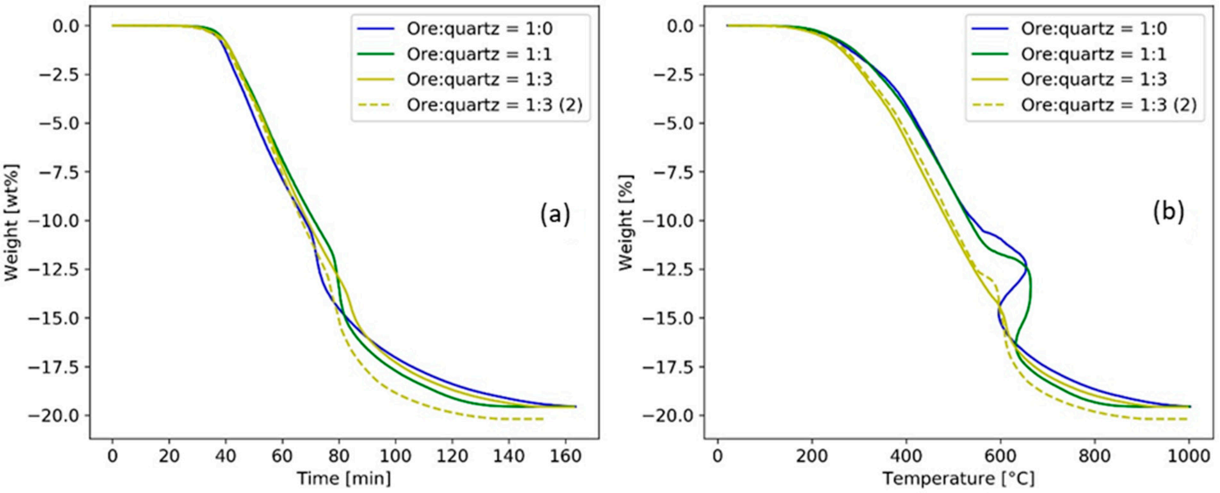

Figure 6. Weight as a function of (**a**) time and (**b**) temperature for Comilog ore in size 11.20–15.00 mm, mixed with quartz in varying ratios.

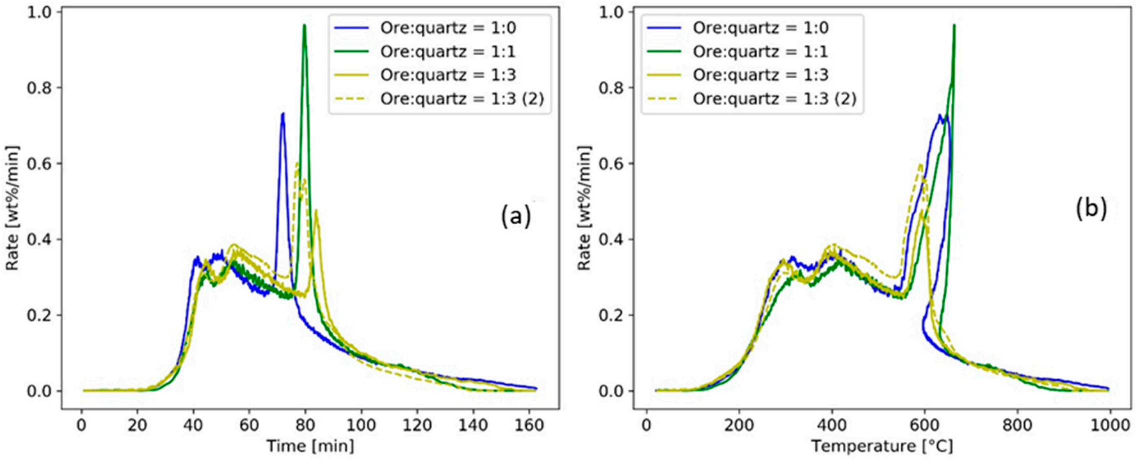

Figure 7. Reaction rate [wt%] calculated from the weight at 2 min intervals as a function of (**a**) time and (**b**) temperature for Comilog ore in size 11.20–15.00 mm, mixed with quartz in varying ratios.

Table 3. Chemical analysis of Comilog ore mixed with varying ratios of quartz reduced in 50% CO–50% CO_2 at 6 °C/min up to 1000 °C.

Size [mm]	Ore:Quartz	Temperature [°C]	Fe, tot	Mn, tot	MnO_2	MnO	SiO_2	Al_2O_3	K_2O	O/Mn
3.33–4.00	1:0	1000	2.2	62.4	4.0	77.3	4.3	6.5	1.4	1.04
3.33–4.00	1:1	1000	3.8	61.6	4.3	76.0	3.8	6.5	1.3	1.04
3.33–4.00	1:3	1000	3.6	62.1	4.7	76.3	4.0	6.2	1.2	1.05
11.2–15.0	1:0	1000	3.1	62.9	3.9	78.1	4.2	7.4	1.1	1.04
11.2–15.0	1:1	1000	3.0	60.3	4.2	74.4	6.8	7.0	1.2	1.04
11.2–15.0	1:3	1000	2.7	64.2	5.8	78.2	2.9	6.1	0.8	1.06

3.2. Nchwaning Ore

The temperature measurements during the heating of Nchwaning ore and quartz are shown in Figure 8. Nchwaning ore has a lower initial oxygen level compared to Comilog ore, leading to a more stable temperature increase. The temperature development shows a highly similar behavior for all experiments conducted with Nchwaning ore, both with and without the addition of quartz. A slightly higher temperature is obtained for the experiment conducted without any quartz addition at evaluated process times.

Figure 9 shows the weight reduction behavior as a function of time and temperature, respectively. Figure 10 shows the corresponding reaction rate, calculated from the change in weight at every 2 min process time interval (rolling average). It was observed that all trends observed at smaller time frames were preserved at the 2 min interval. The weight reduction behavior confirms that the samples have been exposed to highly similar temperature developments, as the weight reduction curves overlap to a large extent. A slightly higher weight loss is obtained at a given process time for the experiment conducted without quartz, according to the slightly higher temperature experienced by the sample. The same observations are made from the reaction rate behavior seen in Figure 10.

Figures 11 and 12 show the weight and corresponding rate, respectively, as a function of time and temperature. A highly similar weight reduction is observed for all evaluated mixtures, i.e., no significant effect of the presence of inert material was seen at this particle size either.

The reduced samples were analyzed for chemical composition and oxygen level of manganese (O/Mn), and the values are shown in Table 4. All experiments conducted with an ore of size 3.33–4.00 mm have obtained a complete prereduction of higher manganese oxides to MnO, i.e., O/Mn = 1.00. For the larger ore particles, i.e., 11.2–15.0 mm, O/Mn ratios of 1.00–1.08 are seen, where the highest level is seen for the ore heated without any quartz addition. One can, however, also see that the samples show relatively large spread in the Mn/Fe ratios.

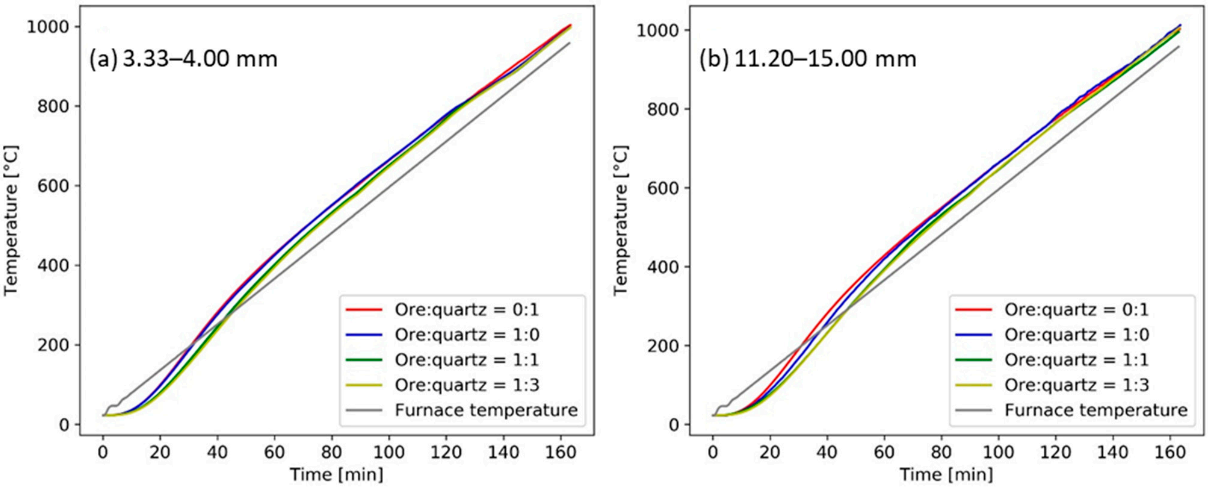

Figure 8. Temperature as a function of time for Nchwaning ore in size fractions of (**a**) 3.33–4.00 mm and (**b**) 11.20–15.00 mm, mixed with quartz in varying ratios.

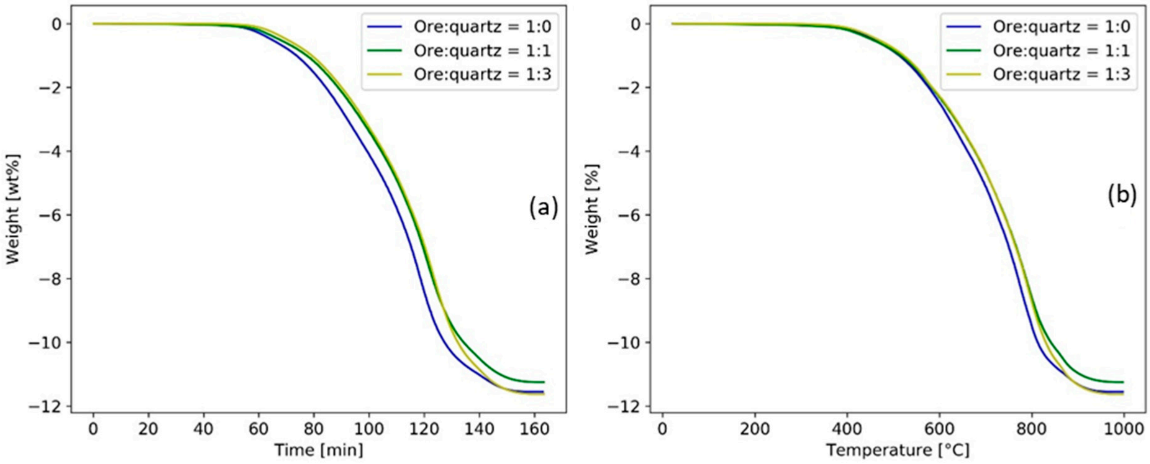

Figure 9. Weight as a function of (**a**) time and (**b**) temperature for Nchwaning ore in size 3.33–4.00 mm, mixed with quartz in varying ratios.

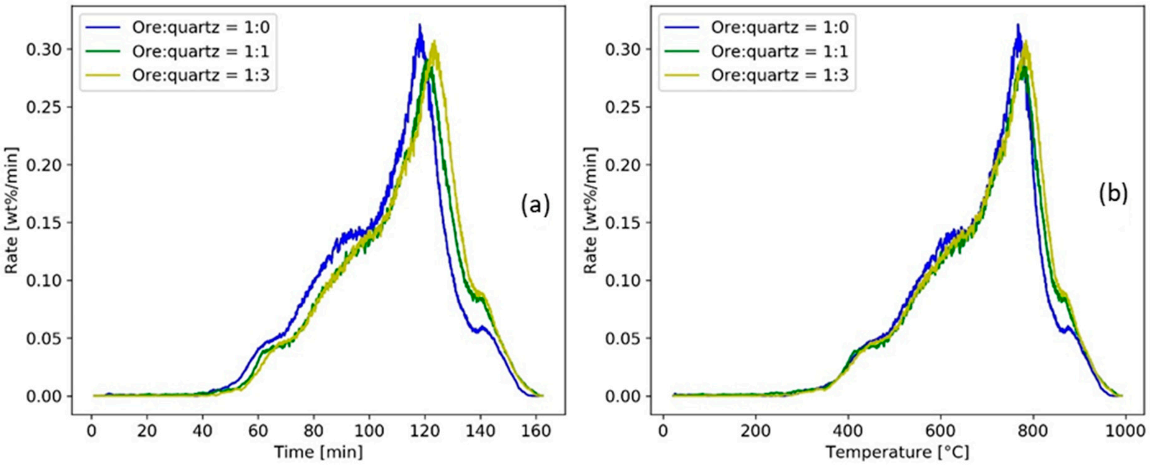

Figure 10. Reaction rate [wt%/min] as a function of (**a**) time and (**b**) temperature for Nchwaning ore in size 3.33–4.00 mm, mixed with quartz in varying ratios.

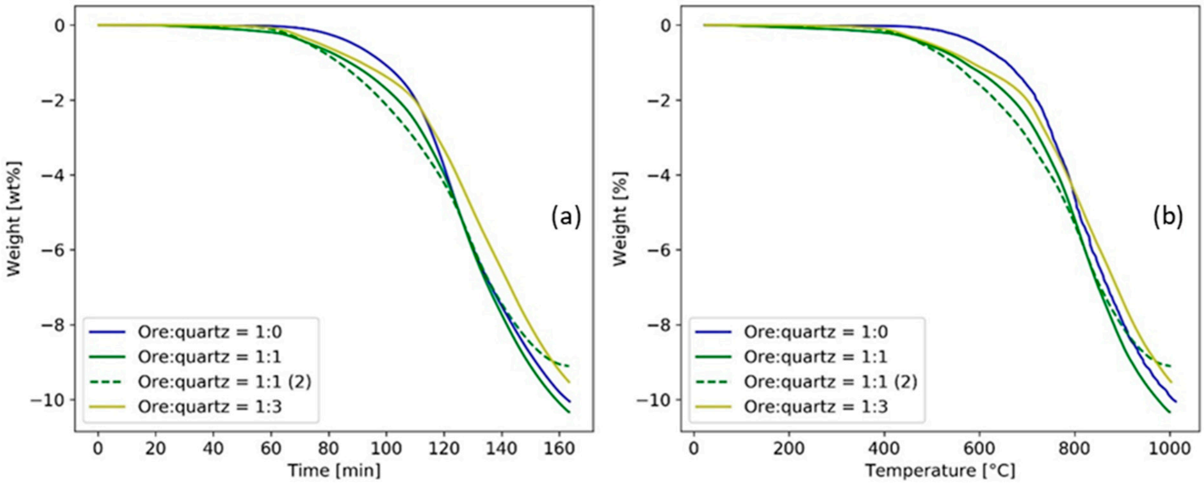

Figure 11. Weight as a function of (**a**) time and (**b**) temperature for Nchwaning ore in size 11.20–15.00, mixed with quartz in varying ratios.

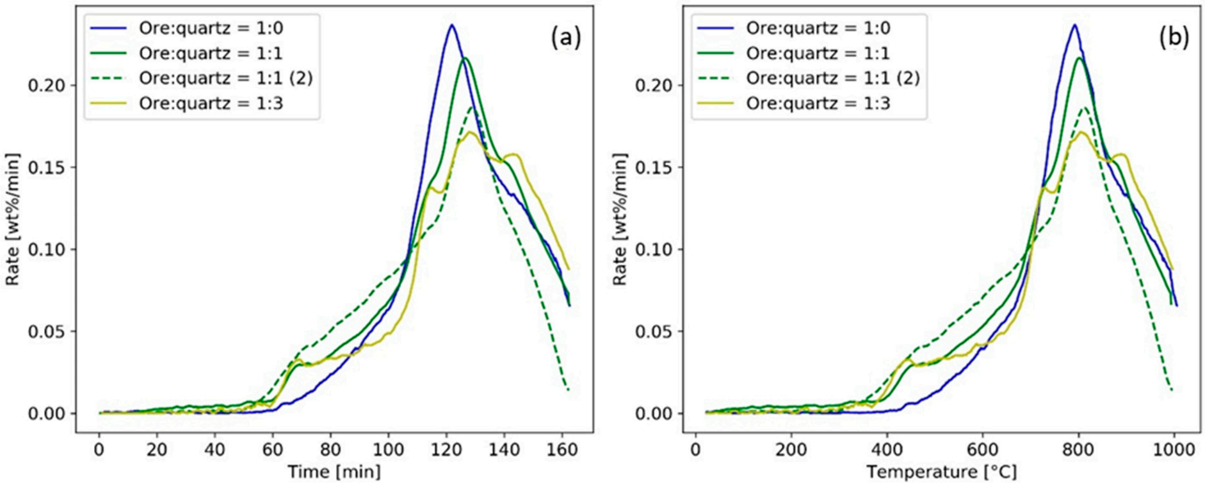

Figure 12. Reaction rate [wt%/min] as a function of (**a**) time and (**b**) temperature for Nchwaning ore in size 11.20–15.00 mm, mixed with quartz in varying ratios.

Table 4. Chemical composition of Nchwaning ore reduced while mixed with inert material (quartz). All experiments conducted at 6 °C/min up to 1000 °C in 50% CO–50% CO_2.

Size [mm]	Ore:Quartz	Temperature [°C]	Fe, tot	Mn, tot	MnO_2	MnO	SiO_2	CaO	MgO	CO_2	O/Mn
3.33–4.00	1:0	1000	11.6	52.0	0.05	67.1	6.9	6.8	1.1	NA	1.00
3.33–4.00	1:1	1000	12.5	50.4	0.0	65.1	6.8	6.7	1.1	0.4	1.00
3.33–4.00	1:3	1000	12.3	48.7	0.0	62.9	8.9	7.0	1.1	0.2	1.00
11.2–15.0	1:0	1000	7.6	53.1	6.5	63.3	7.6	7.8	1.4	0.2	1.08
11.2–15.0	1:1	1000	11.3	50.2	0.2	64.7	5.5	7.6	2.1	0.2	1.00
11.2–15.0	1:3	1000	9.4	52.6	3.1	65.4	5.8	7.7	1.2	0.2	1.04

4. Discussion

Comilog ore and Nchwaning ore differ in both chemical and physical properties and as such, show dissimilar behavior during heating in reducing atmosphere. A recent study showed that the MnO_2-oxides in Comilog ore reduce in a single step to MnO at temperatures below 550 °C, where a rapid decomposition of the remaining MnO_2 to Mn_2O_3 occurs, ultimately followed by a reduction of Mn_2O_3 to MnO [8]. The results obtained in this study are consistent with the previously reported findings for Comilog ore, as the smaller-sized particles that obtained a complete prereduction at a temperature below 550 °C showed a single-step reaction rate, whereas the larger-sized particles (11.2–15.0 mm) showed a clear shift in the reaction rate at 550 °C. Prereduction of Nchwaning ore involves the reduction of Mn_2O_3-oxides to MnO, reduction of Fe_2O_3-oxides to FeO/Fe, and decomposition of the smaller amount of carbonate present in the ore. It has been reported that the manganese and iron oxides in Nchwaning ore reduce at highly overlapping temperature ranges, initiated at temperatures exceeding 400 °C, and the decomposition of carbonate, reported to be mainly calcite, occurs at temperatures exceeding 800 °C [8]. Previously reported findings are in accordance with the prereduction behavior observed in the present study.

Similar heating programs lead to dissimilar temperature development for Comilog and Nchwaning ores due to differences in oxygen levels and reduction rates. Comilog ore is a high oxygen ore experiencing fast reduction rates. This produces a considerable amount of heat, causing the temperature in the ore to increase. Nchwaning ore has a lower oxygen level, which, in combination with lower reduction rates, leads to a temperature increase consistent with the applied heating rate. The relation between the sample temperature and the reduction rate for Comilog ore is shown in Figure 13. The temperature increase is initiated at a slightly higher process time compared to the reaction rate, in line with the sample temperature being a result of the reaction rate. The mixing of ore with quartz decreased the sample temperature, and thus the reduction rate of the ore, during reduction of smaller-sized (3.33–4.00 mm) Comilog ore, while larger particles appeared to be insignificantly affected. An explanation for this may be that the reduction of larger particles is more governed by diffusion, which has a low dependency on temperature. Smaller particles experience less diffusional resistance, leading to a chemical-reaction-controlled mechanism, which is more sensitive towards temperature. This would further be in line with the observations that Nchwaning ore was affected by the presence of inert material (quartz) to a low or insignificant extent in both evaluated particle sizes, as Nchwaning ore has been reported to exhibit a low porosity [5,9,10], suggesting a diffusion-controlled reduction.

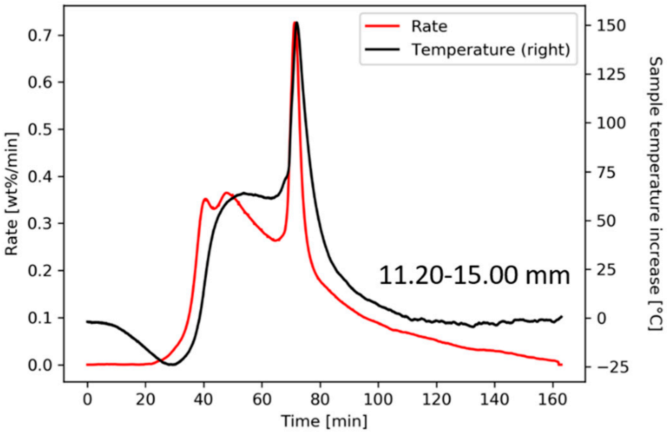

Figure 13. Reaction rate [wt%/min] and temperature increase in sample relative to furnace temperature for Comilog ore in size 11.20–15.00 mm, reduced in 50% CO–50% CO_2.

A mathematical description of the prereduction of manganese ores, particularly high oxygen ores, requires a relation between the reaction extent and the temperature. A complete heat balance is complex, as the temperature is affected by the thermal radiation heat, the convective heat transfer between the gas and solid phase, and the reaction heat from the ore and other raw materials. In addition, there are heat losses in the system to consider. In the current study, the contribution to the temperature development from the reaction heat and interaction between raw materials was assessed. The heat generated by the prereduction reactions can be analytically estimated by the use of Equation (4), where

ΔH_{rx} is the reaction enthalpy, m is the sample mass [g], Cp is the heat capacity [J/K·g] and ΔT is the temperature change experienced by the sample in Kelvin.

$$\Delta H_{rx} = m \cdot Cp \cdot \Delta T_{rx} \tag{4}$$

Experimental results obtained in this study were used for the sample mass. Previously reported experimental results by Ksiazek et al. [7] were used for the heat capacities of Comilog and Nchwaning ores. The reported heat capacities were relatively similar for Comilog and Nchwaning ores, were temperature dependent, and showed a decreasing trend with increasing temperature. The largest difference was seen at temperatures of 600–800 °C due to the decomposition of MnO_2 to Mn_2O_3 in Comilog ore, where the reported heat capacities were 0.72 J/K·g and 0.95 J/K·g for Comilog and Nchwaning, respectively, at 700 °C. The reaction enthalpies were calculated based on information found in a previous study regarding the reaction steps observed during non-isothermal reduction of Comilog and Nchwaning ores, respectively, in a CO-CO_2 atmosphere [8]. This implies that the reduction of smaller-sized Comilog ore particles (3.33–4.00 mm) was estimated by the overall reaction of MnO_2 to MnO. For the larger-sized Comilog ore particles, the overall reduction of MnO_2 to MnO was used to evaluate development at temperatures below the exothermic peak; the exothermic peak was described by reduction of MnO_2 to Mn_2O_3, whereas the reduction after peak position was described by Mn_2O_3 to MnO. For Nchwaning ore, the reaction enthalpy was calculated for the reduction of Mn_2O_3 to MnO in a single step for both particle sizes. The temperature contribution from the remaining factors was accounted for by utilizing the temperature development recorded during the heating of quartz (assumed inert). Hence, the overall temperature development was calculated according to Equation (5), where T_{quartz} is the temperature development for quartz and ΔH_{rx} was calculated from Equation (4).

$$T = T_{quartz} + \Delta T_{rx} \tag{5}$$

The calculated temperatures of the sample due to the heat of exothermic reduction are presented together with the temperatures measured by the thermocouple in Figures 14 and 15 for sizes 3.33–4.00 mm and 11.20–15.00 mm, respectively. The calculated temperatures correlate well with the measured temperatures, showing that Nchwaning ore follows the gas temperature during reduction. Furthermore, there is a reasonable agreement between measured and calculated temperatures for Comilog ore, where the temperature increase calculated from the reaction enthalpy and reaction rates shows the same trends as the measured temperature. Nonetheless, the calculated temperature is generally lower than the measured. The magnitude of the exothermic peak was calculated to be 150 °C and 50 °C for sizes 3.33–4.00 mm and 11.2–15.0 mm, respectively. The measured peak heights were 263 °C and 151 °C, i.e., a relative increase of 75% and 205% to the calculated values. In addition to the lower peak height, the width of the exothermic peak was narrower in the calculated temperature. The calculation approach evaluates the temperature by viewing the mass as a single particle and provides an estimate for the average temperature increase of the sample. As such, it does not account for the fact that the mass consists of smaller-sized ore particles forming a cluster. A significant temperature gradient has previously been reported for Comilog ore, where a considerably higher temperature has been measured in the center of the ore cluster compared to the outer areas during prereduction [11]. Hence, it is likely that the differences in the measured and calculated temperature originates from heat transfer effects encountered in clusters, as the temperature measurements from the laboratory-scale experiments in this study are valid for the center of the sample.

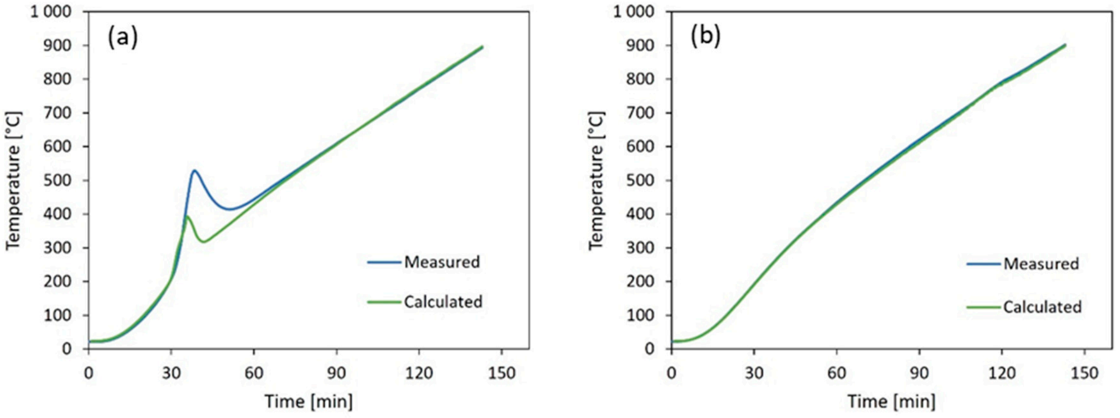

Figure 14. Measured temperature and temperature calculated using reaction enthalpies for (**a**) Comilog ore and (**b**) Nchwaning ore in size 3.33–4.00 mm with no quartz present.

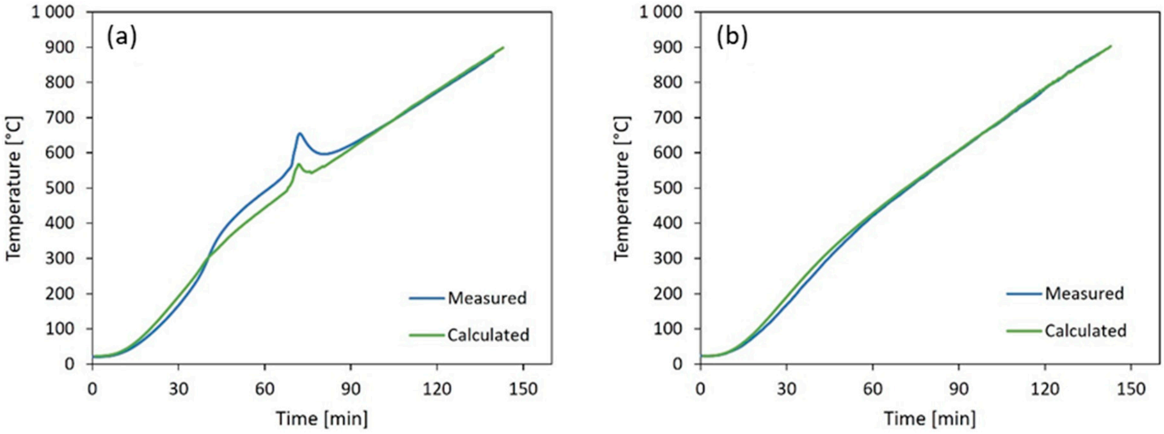

Figure 15. Measured temperature and temperature calculated using reaction enthalpies for (**a**) Comilog ore and (**b**) Nchwaning ore in size 11.20–15.00 mm with no quartz present.

While a significant temperature increase and temperature peak are often seen in laboratory scale prereduction of high oxygen ores, it is not clear to which extent this may occur in the industrial furnace. An indication can be obtained by using Equations (4) and (5) to calculate industrial charge mixtures. The chosen mixtures were 50%Comilog-50%Nchwaning and 75%Comilog-25%Nchwaning, respectively, with metallurgical coke as reductant. Both mixtures were evaluated at a basicity ($(CaO + MgO)/SiO_2$) of 1. This implied that smaller amounts of limestone were added to the 75%Comilog-25%Nchwaning mixture. As an estimation for the heat capacity of coke and limestone, values for carbon and calcite retrieved from the HSC Chemistry 10 database were used. The resulting temperature development is shown in Figure 16, where Figure 16a shows the temperature resulting from the chemical reactions and Figure 16b shows the overall temperature development. The calculated magnitudes of the exothermic peak were 12 °C and 17 °C for ore size 11.2–15.0 mm in 50–50 mixing ratio and 75–25 mixing ratio of Comilog and Nchwaning ores, respectively, whereas 36 °C and 55 °C were calculated for ore size 3.3–4.0 mm. These temperature increases appear to be too low to cause any local sintering; however, there might be local extreme points, potentially promoted by local uneven distribution of charge components. Furthermore, the experiments in this study were conducted at a heating rate of 6 °C/min. According to Pochart et al. [6], the heating rates encountered in industrial operation range from 2 °C/min to 8 °C/min, where the rate decreases with increasing distance from the electrode. It has previously been shown that the magnitude of the exothermic peak is dependent on the heating rate, where a higher heating rate leads to an increased peak temperature. This may suggest that local extreme temperatures are more likely to occur closer to the electrode.

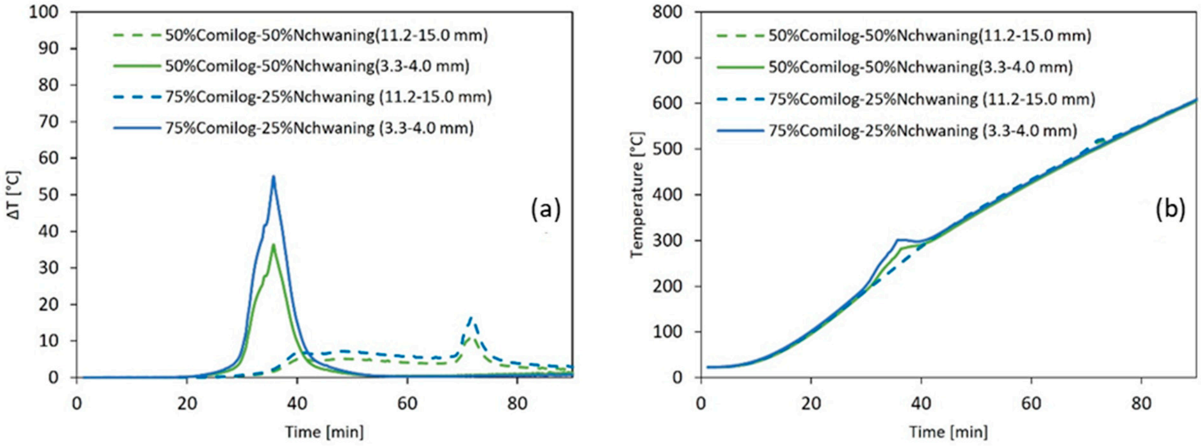

Figure 16. (**a**) Calculated change in temperature for example charge mixtures and (**b**) overall calculated temperature development for example charge mixtures.

5. Conclusions

Thermogravimetric data were obtained for the prereduction of Comilog and Nchwaning ores in a CO-CO_2 atmosphere, where the ore was mixed with various amounts of inert material (quartz), to evaluate the effect of raw materials on the temperature development and prereduction behavior. The prereduction of Nchwaning ore was, to a low extent, affected by the presence of inert material (quartz) both in small (3.33–4.00 mm) and large (11.2–15.0 mm) particle sizes. Large Comilog ore particles were also only slightly affected, whereas a significant effect was seen for small Comilog particles. It is believed that the influence is related to the extent at which the reduction rate is governed by diffusion resistance, where increased diffusion resistance implies a lower temperature sensitivity.

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