Report

Prereduction of Mn-ores

Overview of work performed at SINTEF/NTNU

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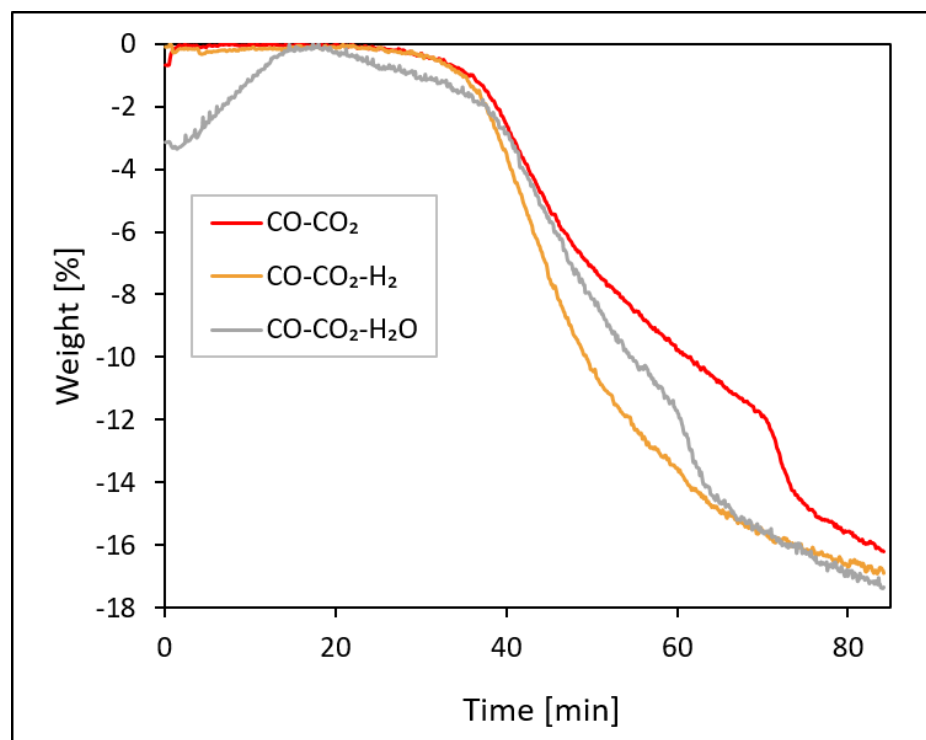
SINTEF Industry
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ABSTRACT

Throughout the years, the prereduction behaviour of manganese ores have been investigated at NTNU and SINTEF in several projects. This report aims to summarize results from the different studies and discuss the correlation or deviation between them. This report includes TGA behaviour, chemical analyses, decrepitation, and rate equations used to describe the reduction behaviour. Comilog- and Nchwaning*-ore has been the main focus in the majority of the studies. As such, a chapter regarding the characterization work of these ores is also included.

*Nchwaning-ore has been referred to as Assmang-ore in certain studies. As Assmang is the producer, and Nchwaning is the name of the ore, Nchwaning will be used throughout this report.

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1 Executive summary

Throughout the years, the prereduction behaviour of manganese ores have been investigated at NTNU and SINTEF through numerous projects. This report aims to summarize the findings from the different studies and discusses the correlation or deviations between them. While this report focuses on the experimental results, it is suggested that a part 2 will be constructed, where the focus will be on the effect of the ores in industrial operation through e.g. mass and energy balances.

The report is written based on results obtained in the following projects:

Project (duration)	Researchers/reported by	Focus	Evaluated ores
H2020 PreMa (2018-2022)	MSc-thesis Biørnstad[1] (2019-2020)	Decrepitation in air vs CO-CO_2, effect of quartz	Comilog, Nchwaning, UMK
FME HighEFF (2016-2024)	PhD-thesis Larssen[2] (2017-2020)	Factors affecting prereduction rate (gas composition, particle size)	Comilog, Nchwaning
SFI Metal Production (2015-2023)	Ngoy[3] (2017-2018)	Effect of $p(O_2)$ Influence of $H_2(g)$	Comilog, Nchwaning
KPN GasFerrosil (2012-2016)	Tangstad[4] (2017)	Effect of $p(O_2)$ Influence of $H_2(g)$ Porosity and decrepitation	Comilog (ore and sinter), Nchwaning, Groote Eylandt
KPN ROMA (2007-2013)	Turkova et al.[5] (2014)	Determine O/Mn-ratio at 800°C (and its correlation to porosity)	Ores, sinter and pellets of: Comilog, Nchwaning, CVRD
Unpublished work (2014)	Tangstad & Ringdalen	Chemical analysis and porosity measurements	Comilog (ore and sinter), Nchwaning, BHP
Internal report	Lobo[6] (2015)	Water-gas-shift reaction	Precalcined Nchwaning (ore and pellets)
Reactivity and tumbler test (project code 102001895-1)	Thomassen[7] (2014)	O/Mn-ratio at 800°C Decrepitation	Comilog (ore and sinter) Nchwaning
Project code 80562721	Thomassen & Tangstad (2012) (work included in Gasferrosil-report[4])	Reduction in CO-CO_2-H_2 (influence of $H_2(g)$)	Comilog (ore and sinter) Nchwaning
PhD-project	PhD-thesis Ishak[8] (2002)	Mn_3O_4-reduction and Boudouard reaction	Precalcined Comilog
Funded by Prosmat program by NRC	PhD-thesis Berg[9] (1998)	Influence of mineral on reduction behaviour	Precalcined Groote Eylandt (BHP), precalcined Wessels, precalcined Namibian ore
Funded by Prosmat program by NRC	MSc-thesis Beck[10] (1998)	Effect of $H_2(g)$ Particle size	Precalcined Comilog
Various student work and internal reports (1979-1998)	Reported by Tangstad et al.[11] (2001)	CO-reactivity	BHP, Mamatwan, Ghana carb. Termco sinter, Comilog, Wessel, Nchwaning, Gloria

All studies have been considered and evaluated even if they are not heavily mentioned throughout the report. This generally applies to the earliest studies, as the research has been continued and further improved in more recent investigations. These studies also utilized precalcined ore, which have shown to show highly dissimilar reduction behaviour compared to prereduced ores.

Comilog- and/or Nchwaning-ore has been the utilized material in the majority of the available studies. Nchwaning-ore is sometimes referred to as Assmang-ore in Norwegian studies. As Assmang is the name of the producer, and not the ore, Nchwaning will be used throughout this report.

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There are currently ongoing activities at SINTEF/NTNU on the prereduction behaviour of manganese ores, where the results are yet to be published. This report may be further updated when more results are made available.

Ongoing activities where results are not yet public:
- PREMA (2018-2022)
  - o PhD-student Tichaona Mukono: excavations from prereduction zone in pilot experiments. Aims to compare behaviour of pretreated and untreated manganese materials.
  - o Postdoc Dmitry Sukhomlinov: Nchwaning, Comilog, and UMK ore reduced in Disvadri furnace.
  - o Experiments by SINTEF (Main responsible: Jonas Einan Gjøvik): Comilog, Nchwaning, and UMK ore reduced in Entech furnace.
- Reduced CO_2 (2018-2022)
  - o PhD-student Trygve Schanche: isothermal reduction of Comilog and Nchwaning ore in CO-CO_2 atmosphere in Disvadri, in addition to the effect of hydrogen.

Highlights from the report:

Manganese ores differ in both chemical and physical properties. Due to these differences, the ores will behave differently when heated. Furthermore, they will respond differently to changes in the experimental conditions, e.g. particle size and atmosphere. As such, the reader is referred to the chapters in the report dedicated to the different ores for a full description of the results for the individual ore. Some more general statements of the main findings will be presented in this summary.

Some of the main findings in the studies are:
- The prereduction of manganese ores is governed by kinetics rather than thermodynamics. The kinetics are highly influenced by the ores' physical characteristics.
- Comilog ore is homogeneous and its TGA-behaviour is easily reproduced. Nchwaning-ore is more heterogeneous, where the TGA-behaviour shows lower reproducibility, particularly for larger particles (<15 mm).
- Strong correlation between weight loss and O/Mn-ratio during heating for both Comilog- and Nchwaning-ore. Lower correlation for Nchwaning due to its heterogeneity.
- Reduction of high-oxygen ores (x in $MnO_x \approx 2$) produce large amounts of reaction heat, causing the sample temperature to deviate strongly from linear heating rates. This is not observed for ores with lower oxygen level (x in $MnO_x \approx 1.5$).
  - o When ore is heated together with inert material (quartz), the temperature increase due to exothermic reduction for high-oxygen ores is lower. This decreases the reduction rate of smaller particles (3-4 mm). Larger particles (11-15 mm) were overall slightly affected.
- An oxygen level (O/Mn-ratio) of $1.5 \approx Mn_2O_3$ is obtained when ores are heated in non-reducing atmospheres at temperatures 600-1000°C. This implies that semi-oxidized ores remain at its initial oxygen level at this temperature range. Decomposition of MnO_2 to Mn_2O_3 occurred rapidly at 580°C for Comilog ore in both the Disvadri-furnace and the Entech-furnace.
- In reducing atmospheres, most ores obtain a full prereduction to MnO at 1000°C. Large ore sizes (< 15 mm) may not be fully reduced at this temperature.
- Pretreated ores (e.g. by calcination) display highly dissimilar reduction behaviour compared to untreated ores. In general, a considerably slower reduction rate is observed. It is believed that calcination densifies the particles.
- No evidence of a topochemical (shrinking core) mechanism has been observed for Comilog- or Nchwaning-ore. It has been observed for precalcined ores, however this is believed to be related to the densification of the ores during calcination.

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- No difference in reduction behaviour of different minerals of similar oxidation state has been observed. This implies that the reduction of bixbyite, braunite I and braunite II in Nchwaning may be viewed simultaneously as the reduction of Mn_2O_3-oxides. Similarly, all Mn^{4+}-minerals in Comilog ore can be viewed simultaneously. Any potential influence of the mineral is overshadowed by other factors in the evaluated investigations.

The reduction rate of manganese ores is generally promoted by the following:
- Increasing temperature
- Decreasing ore particle size
- Increasing ore porosity
- Increasing %CO in CO-CO_2 atmosphere
- Presence of hydrogen gas. Hydrogen-gas also promotes carbon deposition
- Presence of water vapor (reacting according to water-gas shift reaction which produces $H_2(g)$)

The factors are listed in arbitrary order. The influence of the mentioned factors on the reaction rate varies for different ores.

Findings on decrepitation:
- All manganese ores are subjected to decrepitation during heating.
- High-oxygen ores (Comilog ore) are more subjected to decrepitation compared to lower level oxygen ores (e.g. Nchwaning).
- Decrepitation is largely a function of the reduction extent. This may explain the why high-oxygen ores decrepitates to a higher extent compared to lower oxygen ores. It could also be partly related to the porosity, where high-oxygen ores are generally more porous compared to lower oxygen level ores.
- Disintegration is not largely affected by thermal stresses resulting from temperature gradients. Rather, the disintegration has been observed to increase with a decreasing heating rate. Furthermore, experiments conducted with quartz and Comilog ore showed that the decrepitation was of similar extent as for Comilog ore without quartz, in spite of the exothermic temperature peak being supressed.

2 Introduction

Ferromanganese alloys are produced from raw materials such as manganese ore, metallurgical coke and flux, and quartz (for SiMn). The materials are premixed in proper ratios and fed to the top of the furnace. The interior of a ferromanganese furnace may be divided into two main zones, i.e. the prereduction zone and the coke-bed zone, as shown in Figure 2.1. Prior to slag formation, i.e. while the materials are in solid state, they are said to be in the prereduction zone. As they descend through this zone, they will react with the ascending furnace gas. Manganese oxides are reduced to MnO while the ores are in solid state, and this gives rise to the name prereduction zone. The coke-bed zone is the lower part of the furnace, close to the electrode tips. In this zone, all raw materials, except for coke, has melted and formed a slag phase. The slag reacts with the solid carbon to form the alloy. These reactions also produce CO(g), which ascends to the prereduction zone and functions as a reductant. The energy consumption and gas production in the coke-bed zone is largely fixed, which implies that variations in energy and raw material efficiency arise from the behaviour in the prereduction zone.
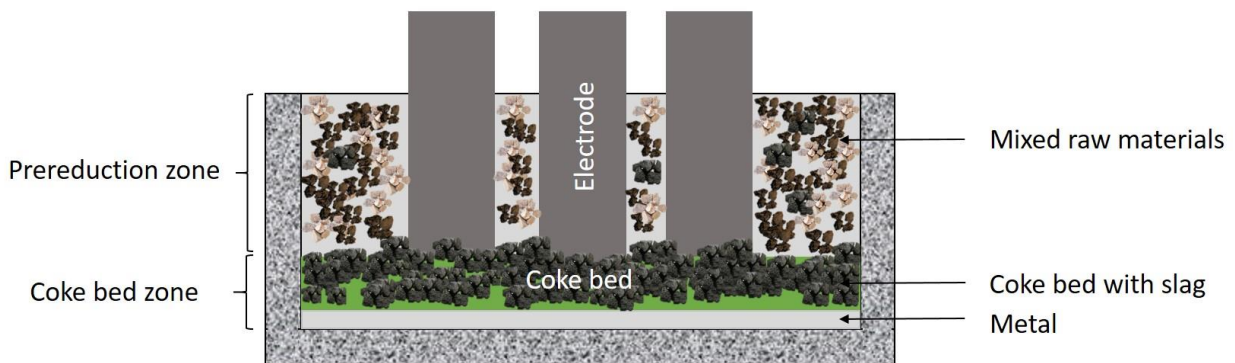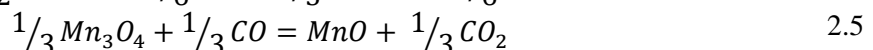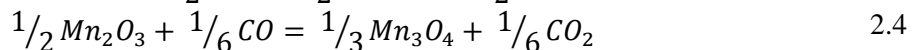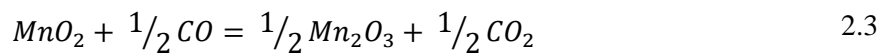

Figure 2.1: Illustration of SAF furnace used for production of manganese ferroalloys[2].

Several different reactions occur in the prereduction zone. Firstly, the charge surface temperature should be higher than 100°C, which implies that any present surface moisture in the ores will evaporate(reaction 2.1). The water vapor may further react according to the water-gas shift reaction(reaction 2.2).

$$H_2O = H_2O(g) \qquad\qquad 2.1$$
$$H_2O(g) + CO(g) = H_2(g) + CO_2(g) \qquad\qquad 2.2$$
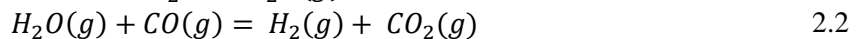
It is mentioned that certain ores also contain some chemically bound moisture, which is another source of water vapor to the system. Chemically bound moisture has been found to be expelled at temperature range 200-400°C. This implies that water vapor, and potentially hydrogen, is not present in the furnace at temperatures exceeding 400°C. As such, the effect on ore reduction is likely low. Increasing content of surface moisture increases the energy consumption, and the potential occurrence will change the off-gas composition, affecting its chemical energy.

The main characteristic of the prereduction zone is the stepwise reduction of higher manganese oxides to MnO, according to reaction 2.3-2.5. These reactions are highly exothermic, thus heating the charge material. The kinetics of the reactions will be dependent on the characteristics of the specific ore.

$$MnO_2 + {}^1\!/_2\,CO = {}^1\!/_2\,Mn_2O_3 + {}^1\!/_2\,CO_2 \qquad\qquad 2.3$$
$$ {}^1\!/_2\,Mn_2O_3 + {}^1\!/_6\,CO = {}^1\!/_3\,Mn_3O_4 + {}^1\!/_6\,CO_2 \qquad\qquad 2.4$$
$$ {}^1\!/_3\,Mn_3O_4 + {}^1\!/_3\,CO = MnO + {}^1\!/_3\,CO_2 \qquad\qquad 2.5$$

When the temperature exceeds 800°C, the Boudouard reaction may have significant rates. The Boudouard reaction is the reaction between solid carbon and CO_2 to form two moles of CO-gas, as shown in 2.6. As such, the extent at which this reaction occur, will be dependent on the amount of CO_2 present at temperatures exceeding 800°C. The Boudouard reaction is carbon consuming, highly exothermic, and also gas producing, which means that it is beneficial for the furnace efficiency that this reaction is minimized.
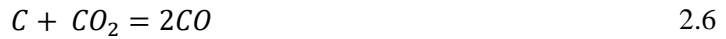
$$C + CO_2 = 2CO \tag{2.6}$$

Figure 2.2 shows the stability regions for Mn-oxides and Fe-oxides, where the systems have been superimposed. The theoretical oxygen pressure obtained by selected CO-concentrations in CO-CO_2 atmosphere is included in the figure. The stability of manganese oxides present in the ores will be determined by temperature and the oxygen pressure. From thermodynamic values from the HSC database, MnO_2 decompose at approximately 486°C at an oxygen pressure of 1 atm, whereas Mn_2O_3 decomposes at 729°C. The equilibrium constant (CO_2/CO ratio) for the reduction of Mn_3O_4 to MnO is $1.1 \cdot 10^4$ at 800°C, however laboratory studies show that the majority of the reduction of manganese ore occurs at temperatures exceeding 800°C for several types of ores. Hence, it is clear that the reduction of manganese ores is governed by kinetics rather than thermodynamics. This is also supported by industrial data reporting carbon consumption and CO/CO_2 ratio in the off-gas.
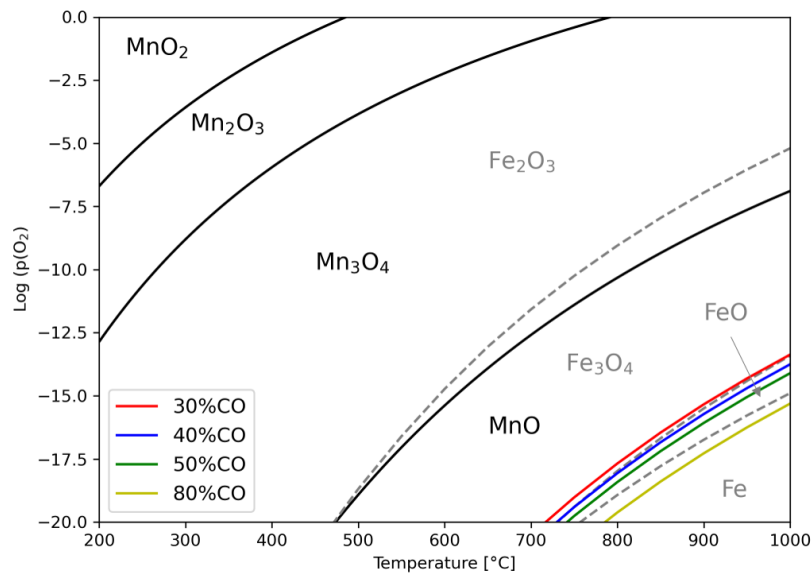

Figure 2.2: Stability diagram for Mn-O and Fe-O system superimposed[2]

The effect of the prereduction zone on the furnace efficiency is described by two main ore parameters:
- The oxygen level, which states the extent to which the exothermic reduction reactions occur. An ore with a higher oxygen level will produce more exothermic heat, which lowers the electrical energy requirement of the overall process.
- The CO-reactivity, which states the kinetics of the reaction between the solid ore and the furnace gas. A higher CO-reactivity implies that a higher reduction extent is obtained at 800°C, which in turn implies a smaller extent of the Boudouard reaction.

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2.1 Work included/considered in the report

Throughout the years, the prereduction behaviour of manganese ores have been thoroughly investigated at NTNU and SINTEF through numerous projects. This report aims to summarize the results from the different studies. While this report focuses on the experimental results, it is suggested that a part 2 will be constructed, where the focus will be on the effect of the ores in industrial operation through e.g. mass and energy balances. The report is written based on results obtained in the following projects:

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Various student work and internal reports (1979-1998)	Reported by Tangstad et al.[11] (2001)	CO-reactivity	BHP, Mamatwan, Ghana carb. Termco sinter, Comilog, Wessel, Nchwaning, Gloria

Some of the earliest studies will not be heavily mentioned in this report, as the research has been continued and further improved in more recent investigations. Further, studies using precalcined ores will not be largely covered, as it has been shown that the calcination alters the characteristics of the ore, leading to highly dissimilar reduction behaviour compared to the untreated ores.

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3 Characterization of ores

This chapter summarizes work performed in the characterization of various commercial manganese ores, mainly Comilog-ore and Nchwaning-ore, as these are the utilized sample materials in the majority of the prereduction studies. As such, this chapter may be viewed as theoretical background to the reduction studies that will be presented in subsequent chapter.

Commercial manganese ores can roughly be divided into three main categories, i.e. high oxygen ores, medium-oxygen ores, and carbonate ores. High-oxygen ores have oxygen levels (O/Mn-ratio) close to that of MnO_2. These ores have only small concentrations of iron oxides, and insignificant concentrations of carbonates. Medium-oxygen ores have an oxygen level (O/Mn-ratio) close to that of Mn_2O_3. The ores have significant amounts of iron oxides and may have smaller amounts of carbonate. Carbonate ores are characterized by their high content of carbonates, where a significant amount of the manganese also exist in carbonate form. Examples of chemical characteristics of the categories are presented in Table 3.1.

Table 3.1: Main categories of commercial manganese ores with examples of O/Mn-ratios, iron and carbonate contents.

Category	Ores	O/Mn ratio	Iron-content [wt%]	Carbonate content represented as wt%CO_2
High oxygen ores	Comilog BHP CVRD	≈ 2 (MnO_2)	1-4[12]	0[12]
Medium-oxygen ores	Nchwaning Wessels	≈ 1.5 (Mn_2O_3)	6-10[12]	2-4[12]
Carbonate ores	Gloria UMK Mamatwan	≈ 1.5 (Mn_2O_3)	5[13]	15-17[13]

While the ores may be categorized according to some parameters regarding chemical composition, ores within the same category may be composed of different minerals, and further have varying physical characteristics. It is mentioned that the characterization of manganese ores is not a straight-forward procedure. A great number of minerals constitutes the ores, where both highly similar composition of several minerals and cation substitution complicates the characterization process. Furthermore, the ores are heterogeneous and include geometric effects, such as porosity and cracks. Research also shows that several of the minerals existing in manganese ores are frequently intergrown. Overall, chemical analysis, XRD, and SEM should be used simultaneously to properly characterize manganese ores.

3.1 Comilog ore

Comilog ore is a high-oxygen ore, which is relatively homogeneous in terms of chemical composition. This is seen in Table 3.2, which shows the chemical composition reported in various studies. The mineralogy of Comilog ore has been reported in a few studies, where the results are presented in Table 3.3. It is found that the main minerals are cryptomelane, pyrolusite and nsutite. Nsutite does not exhibit a defined crystal structure, which complicates a Rietveld analysis to obtain quantified mineralogy. The abundance of nsusite, and thus other species, can be obtained through peak-shape fitting, which leads to semi-quantitative results. This was performed by Sørensen[14]. Both pyrolusite, cryptomelane, nsutite, ramsdellite, and lithiophorite are MnO_2-minerals. The amount of chemically bound moisture was quantified by Larssen[2], and was determined to be

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approximately 5 wt%. This value correlates with the amount reported by Tangstad et al.[12] and Ngoy[3]. Of the mentioned identified Comilog minerals, nsutite and lithiophorite contain hydroxides.

Table 3.2: Chemical composition of Comilog ore in various size fractions.

	0.50-1.36 mm[2]	3.33-4.00 mm[2]	10-15 mm[5]	11.20-15.00 mm[2]	10-13.2 mm[1]
Mn tot	48.4	51.4	51.7	51.0	51.2
MnO_2	71.7	76.6	78.2	76.4	75.9
Fe tot	3.5	2.8	1.3	3.1	2.9
SiO_2	5.6	3.5	4.4	3.5	3.5
Al_2O_3	6.6	5.6	5.3	5.6	5.8
CaO	0.1	0.1	0.1	0.1	0.1
MgO	0.2	0.2	0.1	0.1	0.1
TiO_2	0.2	0.1	–	0.1	0.1
P	0.1	0.1	–	0.1	0.1
S	0.0	0.0	–	0.0	0.0
K_2O	1.1	1.1	0.8	0.7	0.8
BaO	0.2	0.2	–	0.3	0.3
CO_2	0.2	0.2	0.1	0.1	-
H_2O			8.7		
H_2O(surface)	0.4	0.6		0.2	
H_2O(bound)	5.0	5.0		5.0	

Table 3.3: Reported mineralogy for Comilog ore.

	Cryptomelane, KMn_8O_{16}	Nsutite, $Mn(O,OH)_2$	Pyrolusite, MnO_2	Lithiophorite, $(Al,Li)MnO_2(OH)_2$	Quartz, SiO_2	Minor phases
Larssen[2]	X	X	X	X	X	Goethite, $FeO(OH)$ Ramsdellite, MnO_2 Gibbsite, $Al(OH)_3$
Tangstad[12]	X		X			
Sørensen [2], [14]	35.3	32.6	12.4	7.4	5.9	3% Goethite, $(FeO(OH)$ 1.9% Ramsdellite, MnO_2 1.5% Hematite, Fe_2O_3 <1% Gibbsite $Al(OH)_3$

Comilog is known to be a porous manganese ore. The porosity has been observed to show large variations between different particles, as can be seen in Figure 3.1. Considering the values presented in Figure 3.1, Comilog ore has an average initial porosity of 19.8%. The large variance in porosity may be linked to the large variance in microstructures observed by Larssen[2]. An illustration of the variance in microstructures is seen in Figure 3.2A, which shows several 0.50-1.36 mm particles in backscatter imaging at low resolution. Larssen observed similar types of microstructures in different particle size fractions, however the with higher degree of heterogeneity in larger particles. The microstructure observed in a particle of size 11.20-15.00 mm is seen in Figure 3.2B. It is seen that different mineral compositions have varying porosity. The phase region to the left appears to be relatively dense, whereas the phase region to the right shows both smaller and larger sized pores. As minerals are not evenly distributed between different particles, the particles can have a porosity dependent on the mineral composition.
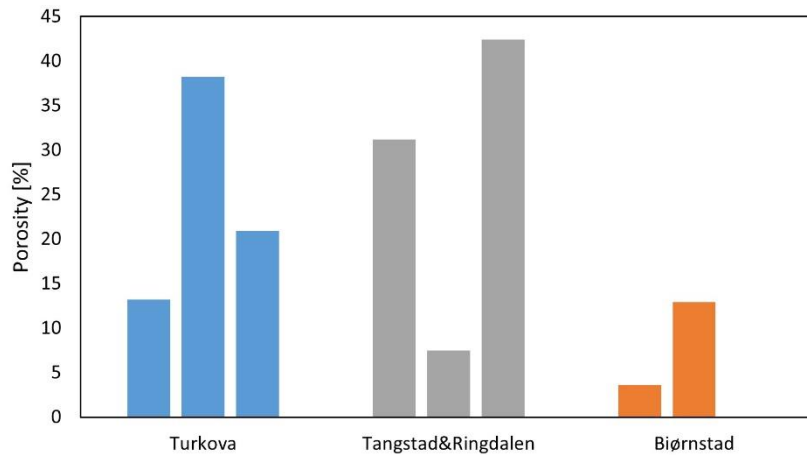
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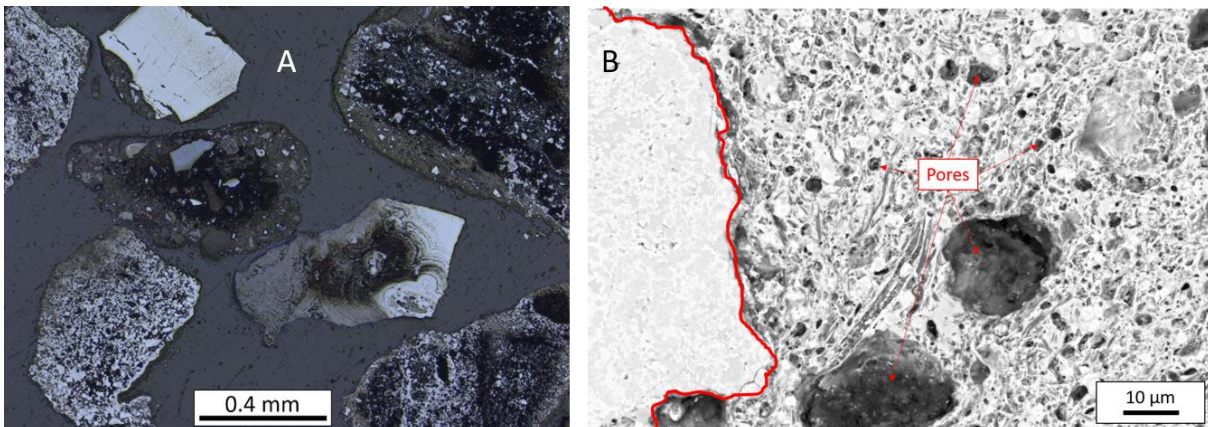**Figure 3.1: Porosity of Comilog ore reported by Turkova[5], Tangstad & Ringdalen (unreported work), and Biørnstad[1].**

Figure 3.2: Comilog ore particles of size 0.50-1.36 mm (A) and close-up of 11.20-15.00 mm particle (B) as obtained by backscatter imaging[2].

3.2 Nchwaning ore

Nchwaning is a medium-oxygen ore, where the overall O/Mn-ratio is close to 1.5 ($\approx$ Mn_2O_3). In addition, it contains considerable amounts of iron, and smaller amounts of carbonate. It does not contain any significant amounts of chemically bound moisture. Compared to Comilog ore, Nchwaning ore is more heterogeneous. Chemical analysis presented by various investigators of similar particle size fractions is shown in Table 3.4. Some variation is seen in the total manganese and iron content, where a higher manganese content correlates to a lower iron content, and vice versa. Some variations are also seen in the silicon and calcium content.

    The various Mn_2O_3-oxides constituting Nchwaning ore has been found to be bixbyite (Mn_2O_3), braunite (Mn_7SiO_{12}), and braunite II ($CaMn_{14}SiO_{24}$). The iron exists mainly as hematite (Fe_2O_3), but

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may also be found in solid solution in the Mn-bearing minerals. The carbonate is mainly calcite, but may also contain some magnesium. Reported mineralogy is shown in

Table 3.5. Bixbyite, braunite and braunite II have highly overlapping XRD spectrums, which implies that it is difficult to obtain a representative quantification of the three through Rietveld analysis. Larssen[2] obtained major amounts of bixbyite and minor amounts of braunite I and II through XRD, however SEM/EDS indicated that only minor concentrations of bixbyite are found. Similar disagreement between XRD- and SEM-analyses were also obseved by Sørensen[15] when analysing Wessels ore.

Table 3.4: Chemical analysis of Nchwaning ore.

	11.2-15 mm Larssen[2]	10-13.2 mm Biiørnstad[1]	9.5-13.2 mm Gasferrosil[4]	9.52-16 mm Ngoy[3]
Mn tot	46.5	51.3	47.5	48.5
MnO_2	34.2	36.7	34.9	40.2
Fe tot	10.0	6.4	8.6	8.1
Fe_2O_3	14.3	9.2	12.3	11.6
SiO_2	6.7	8.5	4.3	5.7
Al_2O_3	0.5		0.2	0.6
CaO	5.9	5.5	7.8	6.7
MgO	1.0	0.1	0.8	1.2
TiO_2	0.0	0.0	0.0	0.0
P	0.0	0.01	0.0	0.0
S	0.1	0.03	0.1	
K_2O	0.0	0.0	0.0	0.1
BaO	0.4	0.1	0.3	0.4
CO_2	3.0	3.1	4.1	4.0
H_2O			0.0	
H_2O(surface)			0.0	
H_2O(bound)			0.0	

Table 3.5: Reported mineralogy of Nchwaning ore.

	Bixbyite, Mn_2O_3	Braunite, Mn_7SiO_{12}	Braunite II, $CaMn_{14}SiO_{24}$	Hematite, Fe_2O_3	Carbonate, $(Ca,Mg)CO_3$	Minor phases
Larssen[2]	60	-	8	13	9	1% Hausmannite, (Mn_3O_4) 6% Manganite, $MnO(OH)$
Visser et al.[13]	5-11	39-50	9-24	6-10	10-11	2-9% Hausmannite, Mn_3O_4 1-4% Barite, $BaSO_4$ 2-4% Manganite, $MnO(OH)$ 1-5% Marokite, $CaMn_3O_4$

Two main categories of microstructures were observed by Larssen[2], as shown in Figure 3.3. One of the structures (shown to the left) contained carbonate (dark grey) in coexistence with braunite, relatively homogeneous distributed throughout the particles. The other type of structure (right) showed a relatively homogeneous structure composed of braunite II. It was however seen that the concentrations of calcium and silicon varied throughout.
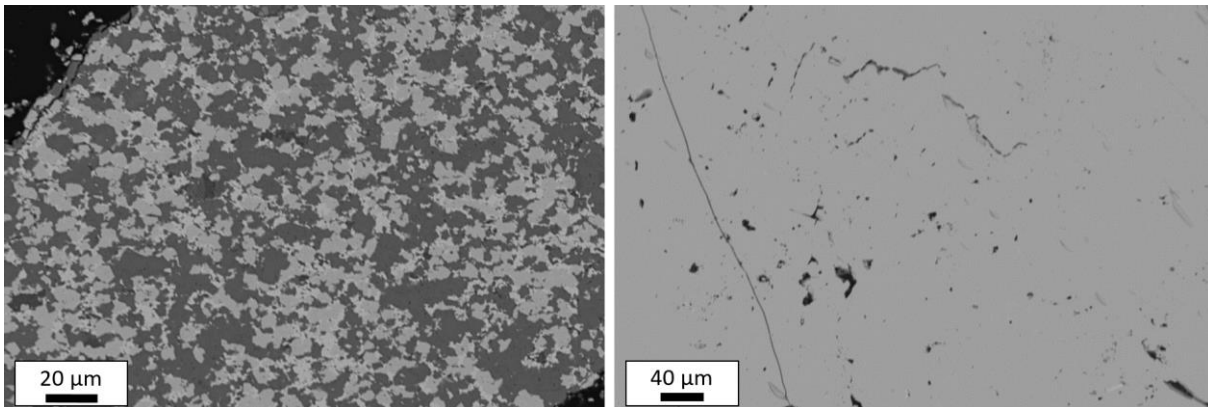
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Figure 3.3: Two main types of microstructures observed in Nchwaning ore[2]. Left: dark grey is carbonate phase, whereas bright phase is braunite. Right: braunite II.

Different types of Nchwaning-ore particles

Some researchers[2], [5] have observed that reduced Nchwaning ore particles have a varying visual appearance, where some particles appear black and others appear green. The visual appearance, as imaged by Larssen[2], is shown in Figure 3.4. Chemical analysis showed that the green particle contained 3 times the amount of SiO_2 of that in the black particle and 1.9 times the amount of CaO. Further, barium, sulphur and phosphorous were 15.9, 5.4, and 3.4 times the amount in the black particle. It was found that while the green particle had obtained a reduction of 78.9% (O/Mn = 1.10), the black particle obtained 73.7% (O/Mn = 1.12).

Turkova[5] determined the porosity of three black appearing particles and three green particles, where the results are shown in Table 3.6. While large variation is observed, the black/dark particles generally have a lower porosity compared to the green particles. This could explain the lower reduction extent obtained in the dark particles. As seen in Figure 3.4, the dark/black particles analysed by Larssen were subjected to decrepitation, while the green particle remained intact. This could explain why the difference in reduction extent is relatively small.
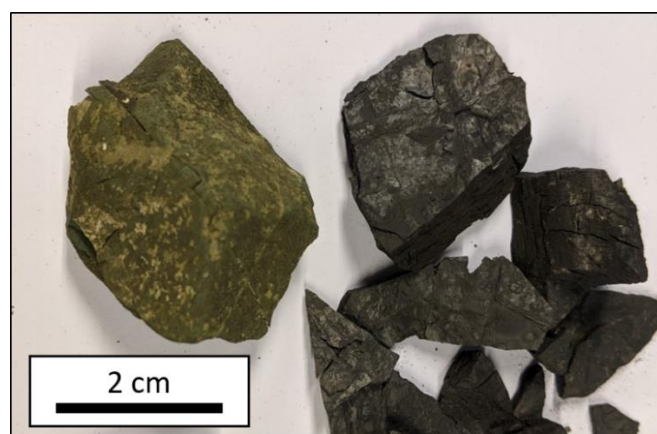

Figure 3.4: Nchwaning ore particles subjected to non-isothermal reduction, where some reduced particles appear black and others appear green[2].

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Table 3.6: Porosities for black and green Nchwaning ore particles after reduction (9°C/min) in CO-CO₂ up to 1000°C[5].

	Particle 1	Particle 2	Particle 3	Average
Dark particles	19.4	7.2	2.3	9.6
Green particles	33.3	14.3	34.3	27.3

The observations indicate that the green particles of a given particle size reduce faster compared to black appearing particles. However, the black particles could be more subjected to decrepitation due to lower porosity, which promotes the reduction rate.

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4 Reduction studies

The present chapter discusses and summarizes results obtained from reduction studies of manganese ores at SINTEF/NTNU, where section 3.1 describes the equipment and investigation methods utilized. The majority of the studies have used Comilog- and/or Nchwaning-ore as sample material. As such, section 3.2 and section 3.3 are dedicated to these respective ores, whereas section 3.3 presents results of other commercial ores.

4.1 Methods

Equipment

As this report aims to present an overview of the various studies conducted in relation to prereduction of manganese ores, the studies include certain dissimilar experimental conditions. The majority of the studies included in this summary was conducted in the DisVaDri furnace, which is a SINTEF furnace located at the facilities shared by SINTEF and NTNU at Gløshaugen. It is a thermogravimetric furnace connected to an off-gas analyzer, which continuously measures the CO and CO_2 concentrations in the crucible outlet. The gas is premixed and preheated in the crucible walls before being introduced to the sample from beneath it, from which it continues to ascend the crucible. It has been observed that the mass balance of the Disvadri furnace is subjected to drifting, which implies that the weight loss data is not always representative for ore reduction, particularly in the initial stages of the experiments.

Some experiments have been conducted in the Entech furnace. The construction is somewhat similar to the Disvadri furnace, as the gas is introduced from the lower parts and ascends through the crucible chamber. The gas exits the crucible at the top, from which a part stream may be collected for analysis of CO and CO_2 concentrations. The Disvadri furnace handles sample sizes up to 200 g, whereas the Entech furnace has a limitation of 2 kg. As such, results from these two furnaces may be used to evaluate the upscaling of the experimental procedure. The similarities and dissimilarities between the two furnaces are summarized in Table 4.1. Schematics of the two furnaces may be found in appendix.

Table 4.1: Specifics of Disvadri and Entech furnace set up.

	Disvadri	Entech
Max. sample size	200 g	2 kg
TGA	X	-
Off-gas analysis	X	X
Temperature measurements	Center of sample	Center of sample Outer region of sample
Gas flow	Ascending in crucible	Ascending in crucible

Procedure

The studies have been performed with various sample sizes, particle size fractions, at different heating programs and temperature, as well as in varying gas composition. The information that is relevant will be presented consecutively, however some additional information is found in the appendix. The "standard"/most commonly used procedure to investigate the CO-reactivity of manganese ores is non-isothermal experiments of heating rate 10°C/min at temperature range 25-1100°C using 9-15 mm particles.

Something worth noting is that the temperature behaviour during the experiments will be affected by the ongoing reduction reactions. Due to high oxygen level and fast reaction rates, the temperatures of Comilog ore will show a considerable positive deviation to the prescribed temperature program. Ores with lower oxygen level, close to that of Mn_2O_3, will generally follow the prescribed heating program. An example of the sample temperatures obtained for Nchwaning- and Comilog-ore, respectively, is shown in Figure 4.1.
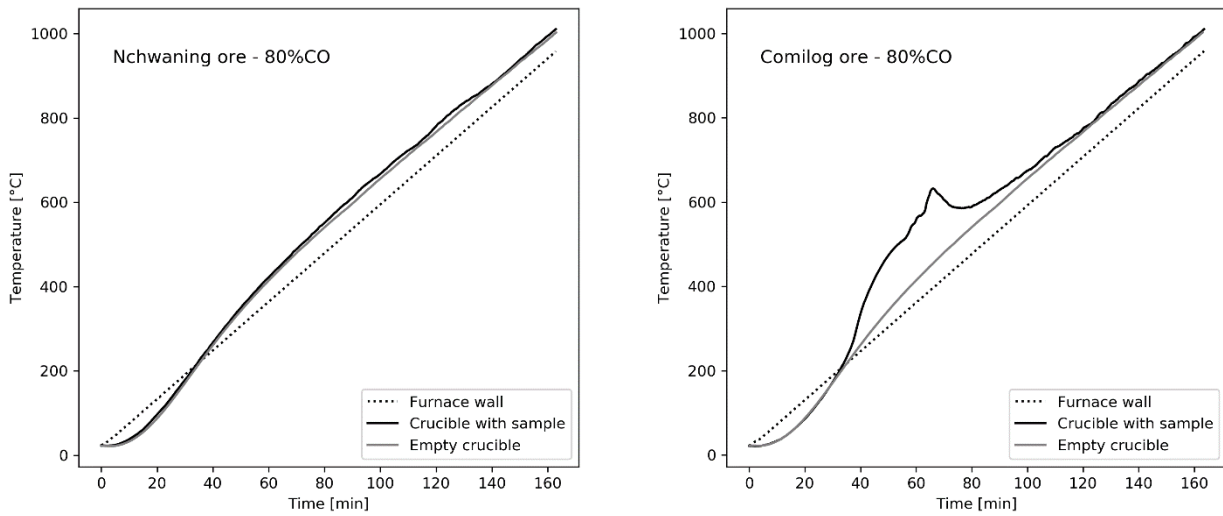
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Figure 4.1: Temperature behaviour during heating of Nchwaning- and Comilog-ore, respectively, in CO-CO₂ atmosphere[2].

Decrepitation

Manganese ores will disintegrate during heating. Decrepitation and disintegration is normally investigated using a thermal abrasion test. Reduced samples are then tumbled in a Hannover drum before the size distribution is determined by screening the sample at various screening sizes.

More often, the size distribution is determined both before and after tumbling, giving rise to two distinct indexes. DI is defined as the amount of sample that has disintegrated during heating and reduction, whereas TI is the extent of disintegration after the heated and reduced sample has been tumbled in a Hannover drum.

The indexes used to evaluate disintegration is thus:
DI = weight% of sample < x mm (decrepitation index)
TI = weight% of sample < x mm (tumbler index)

Different limits of sample size defining the indexes have been used. Biørnstad[1] used DI3.35 and TI.3.35, where the indexes then state the amount of sample that has disintegrated to a size smaller than 3.35 mm.

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4.2 Studies on Comilog ore in CO-CO₂ atmosphere

4.2.1 Reaction steps

Comilog ore is largely composed of various MnO_2-minerals, where a few minerals contain chemically bound moisture. The reaction rate behaviour observed during heating depends on the particle size and the heating rate, where separate reaction steps are observed for larger particle sizes and lower heating rates. Smaller particles and higher heating rates correlate to a rapid temperature increase, resulting in an apparent single reaction rate step.

When heating 11-15 mm particles at 6°C/min in CO-CO₂ atmosphere, the chemically bound moisture was expelled from the ore at temperatures between 200-400°C[2]. This was determined from the comparison of the reaction rate behaviour determined from the mass balance recordings and the rate behaviour from the off-gas analysis. The removal of moisture gives a weight loss registered by the mass-balance, however it is not registered by the off-gas analyzer as the moisture is condensed and collected in a container prior to the off-gas analyzer. The results are seen in Figure 4.2A, where the data is valid for ore in size 11.20-15.00 mm heated in 50%CO-50%CO₂ at 6°C/min up to 1000°C. Ngoy[3] observed a 5 wt% weight loss during heating of Comilog ore (9.5-16 mm particles) in 100% CO₂ at 6°C/min at temperatures up to 500°C. Chemical analysis showed that no reduction of Mn-oxides had occurred, implying that the weight loss may be attributed to the chemically bound moisture. The weight loss behaviour is presented in Figure 4.2B. Hence, it is shown that chemically bound moisture is removed from the ore at temperatures below 500°C.
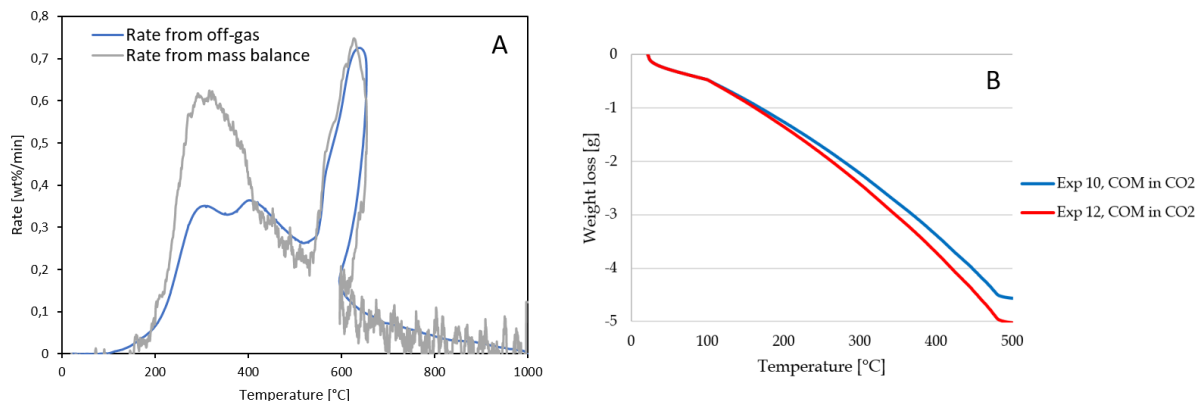

Figure 4.2: A[2]: comparison of reaction rate from mass balance values and off-gas behaviour, respectively, during heating of Comilog ore in 11.20-15.00 mm particles in 50%CO-50%CO₂ at 6°C/min. Difference between the curves are attributed to the removal of chemically bound moisture as this is detected by the mass balance, but not by the off-gas analysis. B[3]: Weight loss as a function of sample temperature during heating of Comilog ore (9.5-16 mm) in 100% CO₂ at 6°C/min. No reduction of Mn-oxides had occurred at 500°C, implying that the weight loss is from chemically bound moisture. Initial sample size was 100 g.

Comilog is nearly fully composed of MnO_2-minerals. As such, the weight loss will be a direct reflection of the changing oxidation level of manganese (x in MnOx). The total weight loss and the analysed x in MnOx from different studies is shown in Figure 4.3. The relation starts at an off-set of approximately 4-5 wt% weight loss, which is the weight loss due to evaporation of chemically bound moisture.
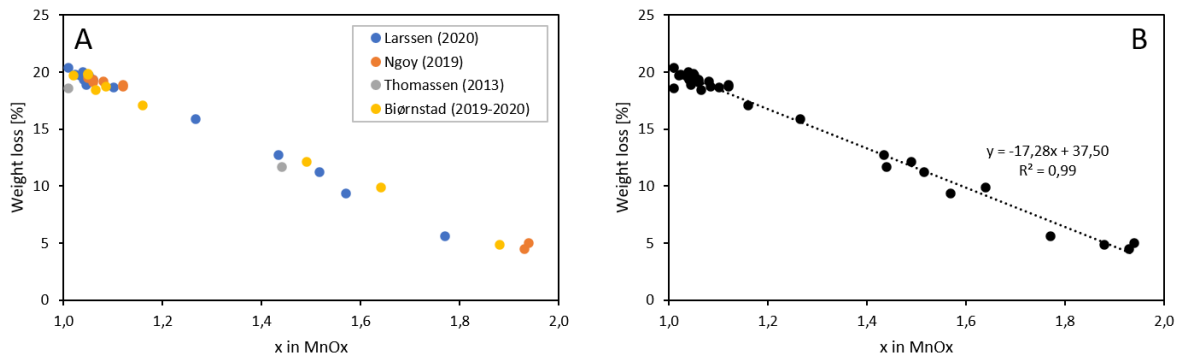
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Figure 4.3: Weight loss after reduction experiment as a function of x in MnOx (analysed by tititrmetric analysis). A: shows results from the different studies[1]–[3], [7], whereas B shows the overall trend found from all values.

The reaction rate behaviour of Comilog ore of particle size larger than 11.2 mm heated in the Disvadri-furnace in reducing atmosphere display several peaks, indicating that the reduction proceeds through several steps. Two main peaks were observed, as can be seen in Figure 4.4. The MnO_2-oxides in Comilog ore could potentially reduce to MnO through the intermediate oxidation states Mn_2O_3 and Mn_3O_4. However, according to Larssen[2], when the reduction of Comilog ore is initiated, the MnO_2 proceeds to MnO in an apparent single step. This means that the reduction rate of the intermediate oxides is considered fast compared to that of MnO_2. This correlates to step 1 and 2 in Figure 4.4. A small decrease in the reaction rate giving a local minimum is observed between step 1 and 2, at approximately 42 minutes process time. This is suggested to be due to the slightly higher temperature required to initiate the reduction of Mn_3O_4 to MnO compared to MnO_2 to Mn_3O_4. The decrease is relatively small and step 1 and 2 may thus be combined to express the overall reduction of MnO_2 to MnO. Step 1 and 2 showed similar extent of overlap for both larger particle sizes and lower heating rates.

It was observed that when the temperature reached approximately 580°C, a rapid decomposition of any present MnO_2 occurred. This correlates well with the thermodynamic decomposition temperature of MnO_2. This was confirmed by the reduction behaviour obtained at various heating rates, which is shown in Figure 4.5. It is seen that all three heating rates experience a rapid weight loss at similar temperature, i.e. ca. 580°C. At a heating rate of 3°C/min, nearly all MnO_2 is reduced prior to the decomposition temperature. Similar reduction behaviour was also seen in the Gasferrosil-project, where Comilog ore of size 10-15 mm was heated at 10°C in 70%CO-30%CO_2[4].

In the experimental work presented by Ngoy[3], the ore (10-15 mm) was heated in CO_2 up to 500°C, at which the reducing gas of composition 70%CO-30%CO_2 was introduced. As the required temperature for initiation of Comilog ore reduction is significantly lower than 500°C, the ore obtained a fast rate when the reducing gas mixture was introduced. Due to this, an overall single step reduction was observed in the experiments presented by Ngoy.

Results from Larssen[2] and Ishak[8] suggests that the reduction of Comilog ore does not follow a shrinking core mechanism.
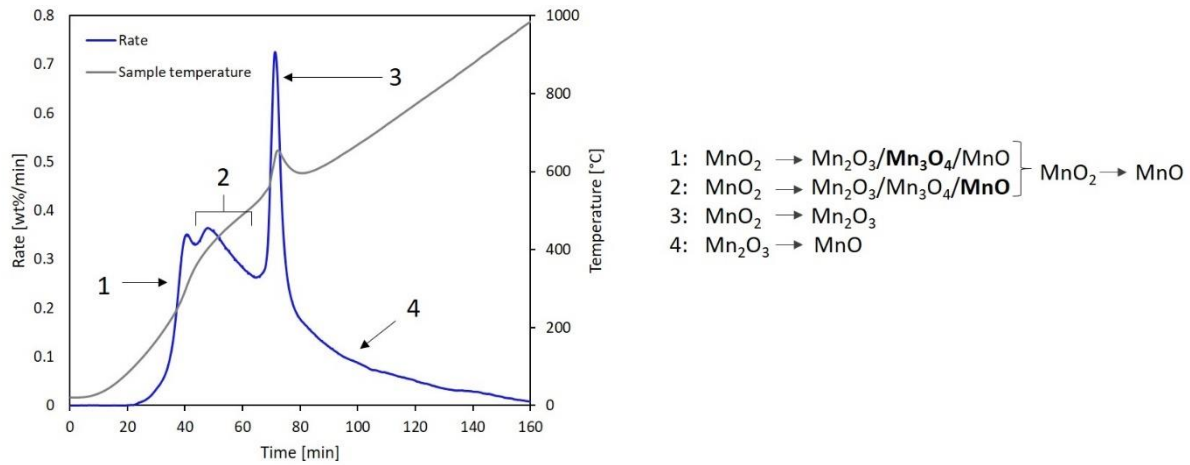
Figure 4.4: Reaction steps observed during heating (6°C/min) of Comilog ore (11.20-15.00 mm) in 50%CO-50%CO₂[2].
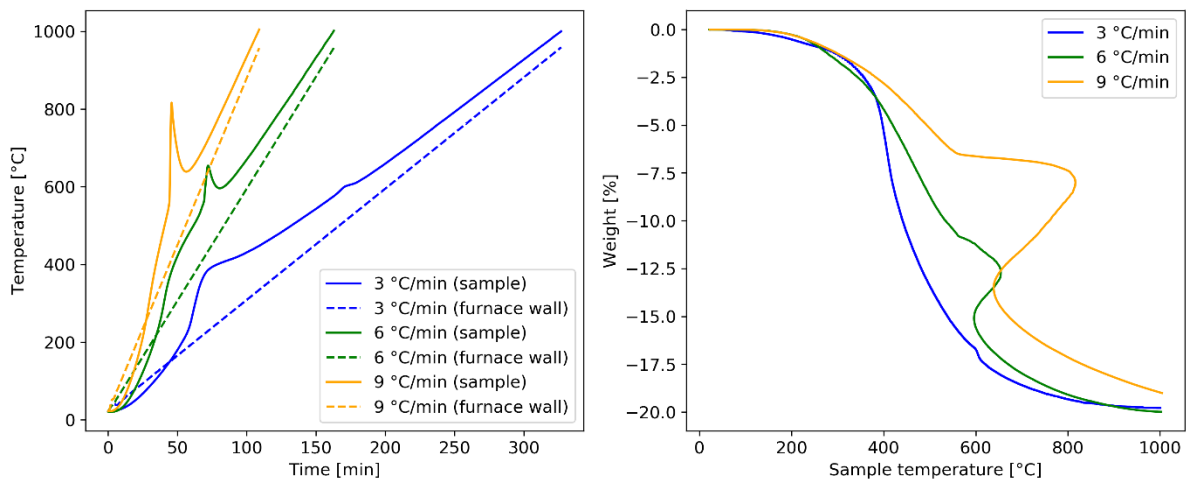

Figure 4.5: Comilog ore (11.20-15.00 mm) heated in 50%CO-50%CO₂ at 3°C/min, 6°C/min, and 9°C/min. Temperature behaviour shown in figure to the left, and weight as a function of sample temperature to the right. Rapid decomposition of any present MnO₂ occurs at c. 580°C at all three heating rates[2].

Reproducibility

Comilog is a homogeneous ore in terms of chemical composition, as the majority of the ore is MnO_2-minerals. It has been seen that the distribution of minerals is not homogeneous, and varying microstructures and porosities has been observed. In spite of this, the reduction behaviour of Comilog ore has been found to be highly reproducible, also in small sample sizes. The reproducibility can be seen in Figure 4.6 for 75 g of sample in size 3.3-4.0 mm heated at 6°C/min in CO-CO_2 up to various target temperatures.

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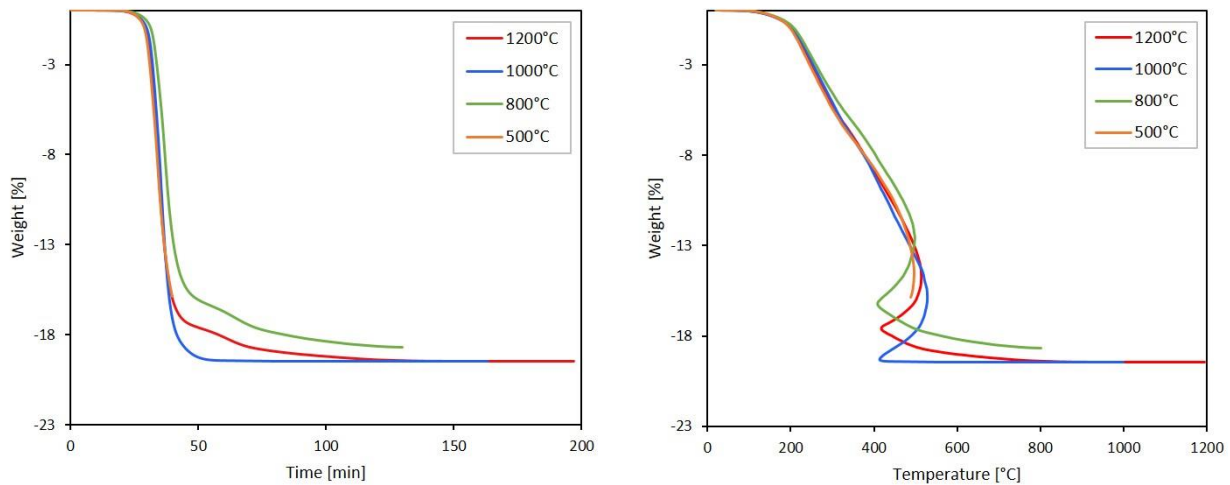
Figure 4.6: Example of reproducibility of Comilog ore shown by 75 g sample sizes of 3-4 mm particles in 50%CO-50%CO$_2$ heated at 6°C/min[2].

4.2.2 Effect of gas composition and flow

A varying concentration of CO in CO-CO$_2$ atmosphere has been investigated in several different projects. This has been done by varying the gas composition by two different approaches. Some studies have been performed by keeping the CO gas flow constant and varying the composition by adjusting the CO$_2$ gas flow. The other approach has been to keep the total gas flow constant and rather vary the gas flow of both CO and CO$_2$ accordingly.

The most recent investigation is the Ph.D thesis of Larssen[2]. CO-concentrations of 30, 40, 50, and 80% were evaluated, where the total gas flow was kept total at 4 L/min. The experiments were conducted with a sample size of 75 g heated at 6°C/min. The reduction rate was affected by the varying CO/CO$_2$ ratio, where the results for 11.2-15.0 mm particles are shown in Figure 4.7. Apparent rate constants showed that the reaction rate was proportional to the inlet partial pressure of CO of order 0.7. The decomposition of MnO$_2$ at ca. 580°C is independent of the gas composition.

As the CO-concentration was varied by increasing the gas flow of CO, it is possible that the increase in reaction rate is due to the increased gas flow rather than the increased partial pressure. However, the recorded CO-concentrations in the off-gas indicated sufficient supply of CO throughout the reduction, as shown in Figure 4.8. The exception is the experiment conducted in 30%CO which reaches a minimum of 1.5% CO in the off-gas at the rapid decomposition of MnO$_2$ at 580°C. The effect of this CO-depletion on the reduction rate is assumed to be low, both due to that the CO-levels stabilize towards the inlet values quite fast, and also as the decomposition rate is not largely affected by the gas composition.

The experimental work presented by Tangstad[4] was conducted with a heating rate of 9°C/min and a sample size of 150 g. The CO-gas flow was kept constant at 2 L/min, where the composition was varied by the gas flow of CO$_2$. The reduction rate in CO-CO$_2$ was observed to be unaffected by the presence of CO$_2$ up to 30%. It is possible that this is due to that the CO-gas flow of 2 L/min was insufficient for the rapid reduction that occurred. A heating rate of 9°C/min was utilized, which leads to a faster rate compared to the data presented in Figure 4.7 and Figure 4.8. In addition, the sample size was 2.5-3.0 times larger, which naturally leads to a considerably larger consumption of CO at a given time and temperature.
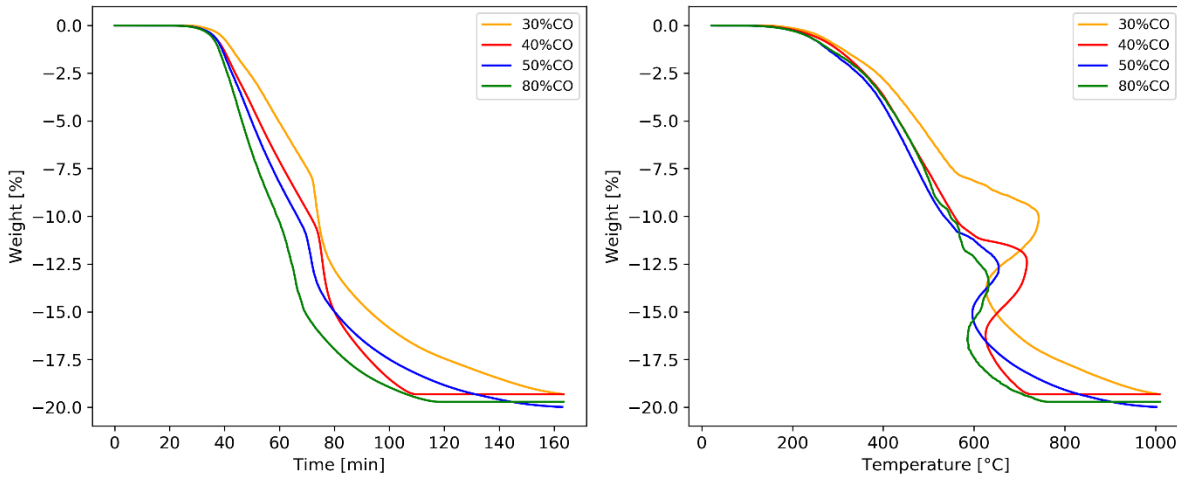
Figure 4.7: Comilog ore reduced in various CO-concentrations in CO-CO₂ atmosphere where total gas flow was kept constant[2].
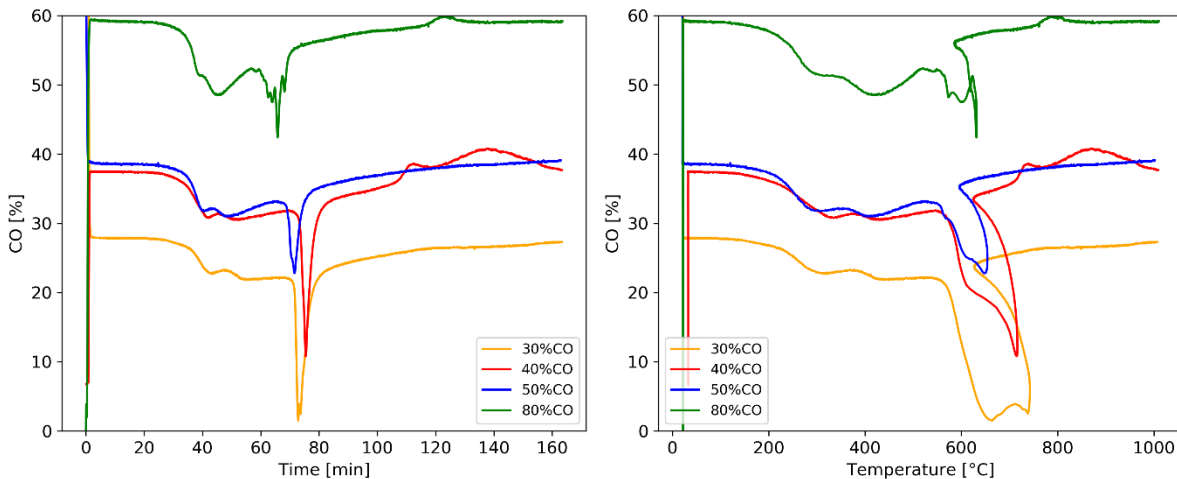

Figure 4.8: Concentration of CO measured by off-gas analyser during reduction of Comilog ore in CO-CO₂ atmosphere with various CO-concentrations, where total gas flow was kept constant at 4L/min[2].

The work by Ngoy[3] was a continuation of the work presented by Tangstad, implying that most of the experimental conditions were unchanged. The work was performed for both Comilog ore, Nchwaning ore and Comilog sinter, where a weight increase was observed for the two latter materials by Tangstad at low temperatures. This was suspected to be related to carbon deposition. To avoid this problem, Ngoy heated the ore in pure CO_2 up to 500°C, at which the CO-CO₂ atmosphere was introduced. Furthermore, Ngoy utilized a lower heating rate compared to Tangstad, i.e. 6°C/min compared to 10°C/min. The CO-gas flow was kept constant at 2 L/min, where the composition was varied by varying the CO₂-gas flow. The ore was heated in CO₂ at temperatures 25-500°C, at which the reducing gas was introduced. Ngoy observed no difference between samples reduced in 50%CO and 70% CO. From an inspection of the off-gas measurements during the experiments, it was clear that the limiting factor was the supply of CO to the system, as can be seen in Figure 4.9.

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As a sidenote, it is believed that the weight increase in the initial stages observed in Gasferrosil presented by Tangstad[4] was not merely due to carbon deposition, but partly or fully related to drifting of the mass balance, which has later been observed by others[2].
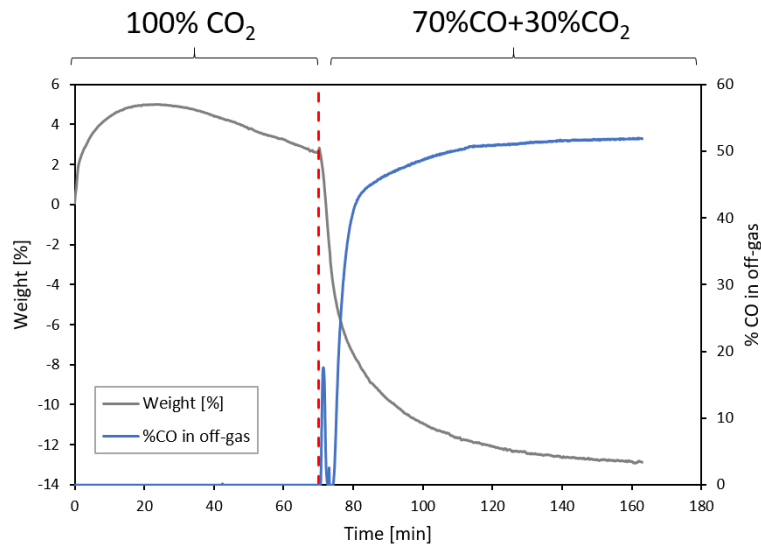

Figure 4.9: Weight recording and CO-concentration measured in off-gas as a function of time for the reduction of Comilog ore[3].

4.2.3 Effect of particle size

The reduction of Comilog ore is promoted by a decreasing ore particle size. It is mainly the Ph.D thesis of Larssen[2], and the project- and Master's work of Biørnstad[1] that have evaluated different particle sizes, where the former utilized the Disvadri furnace and the latter the Entech furnace. Ishak[8] also evaluated two different particle sizes, however the experiments were conducted with ore particles precalcined to Mn_3O_4 prior to reduction in $CO-CO_2$ atmosphere. It was seen that precalcining leads to a considerably different reduction behaviour compared to prereduced samples.

The effect of particle size fraction obtained by Larssen[2] in 50%CO-50%CO$_2$ is shown in Figure 4.10. It is clear that the reduction of Comilog ore is dependent on the initial ore size. From evaluation of the apparent rate constants, Larssen found that the reduction rate was proportional to the inverse average particle size, i.e. rate α $(1/r_p)$.

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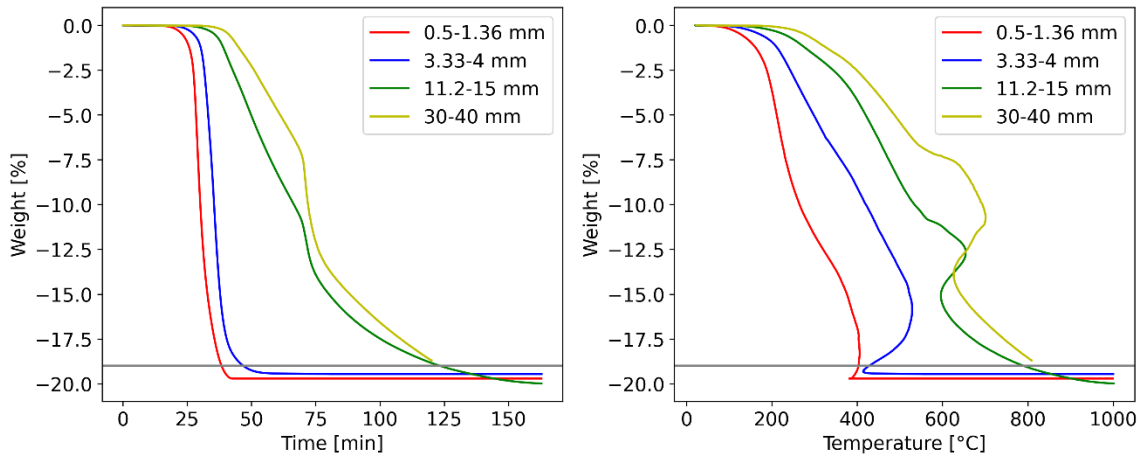**Figure 4.10: Weight as a function of time and temperature, respectively, for Comilog ore in various size fractions at 6°C/min in 50%CO-50%CO$_2$[2]**.

Analysed x in MnOx as a function of furnace temperature from the experiments presented by Biørnstad[1] is shown in Figure 4.11.
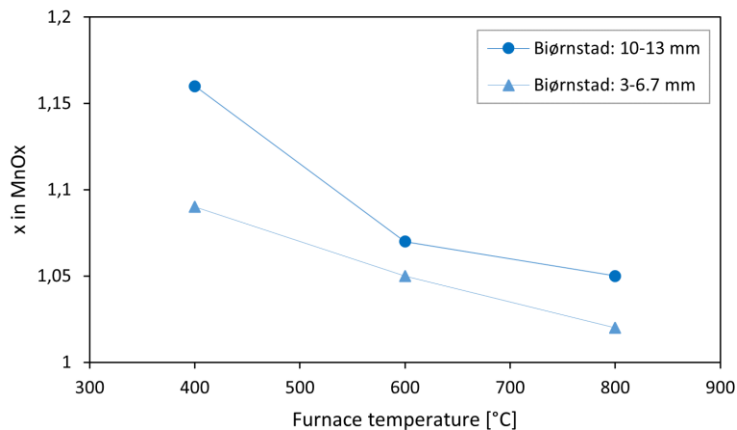

Figure 4.11: Oxidation level of manganese (x in MnOx) from titrimetric analysis as a function of furnace temperature from Biørnstad[1]. Results obtained using Entech-furnace.

4.2.4 Temperature behaviour

Comilog is a high oxygen ore, where the reduction of MnO$_2$ to MnO obtains a high reduction rate. This leads to considerable heat production during the prereduction, causing the sample temperature to exhibit a positive deviation relative to the gas temperature during reduction. The sample temperature at various experimental conditions obtained from experiments in the Disvadri furnace by Larssen[2] is shown in Figure 4.12. All data was obtained in CO-CO$_2$ atmosphere heated at 6°C/min. The magnitude and duration of the positive deviation has been observed to be close related to the reaction rate. As such, the temperature increase for smaller particle sizes show a single peak, whereas the larger particles (>11.2 mm) show two distinct steps, correlating to the reaction steps presented in Figure 4.4.
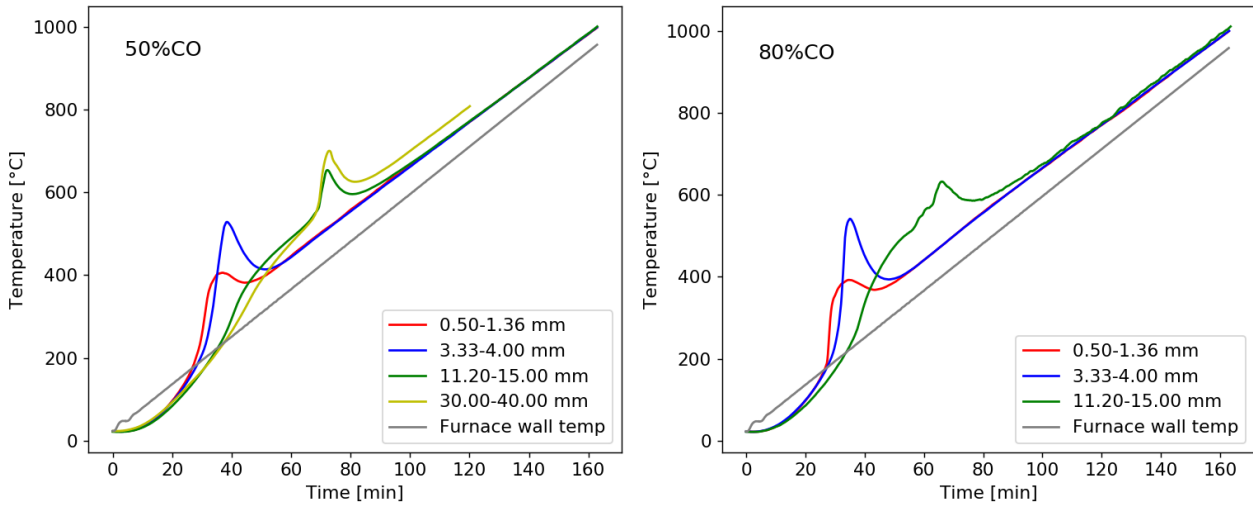
Figure 4.12: Temperature measurements during heating of Comilog ore in CO-CO$_2$ atmosphere at 6°C/min (Disvadri furnace)[2].

The Entech furnace allows for temperature measurements both in the center of the sample, as well as the outer region of the sample. This enables an estimation of the temperature gradient in a Comilog ore cluster. Figure 4.13 shows the temperature measured at the sample edge and center, respectively, during heating of Comilog ore in 70%CO-30%CO$_2$ at 3°C/min using the Entech furnace. These values were presented by Biørnstad in his specialization project[1]. It is seen that the temperature increases more rapidly in the outer regions of the sample in the early part of the experiment, as expected. A higher maximum temperature is also obtained in the center, at 845°C compared to 668°C obtained in the outer region. While the temperatures measured in the center shows a relatively symmetrical temperature peak, the temperatures measured in the edge detects the occurrence of two distinct reaction steps. The temperature increases at a given rate up to 58 minutes process time correlating to 480°C. At this time, a shift in the heating rate is seen, and the temperature increases rapidly from 480°C up to peak of 668°C.
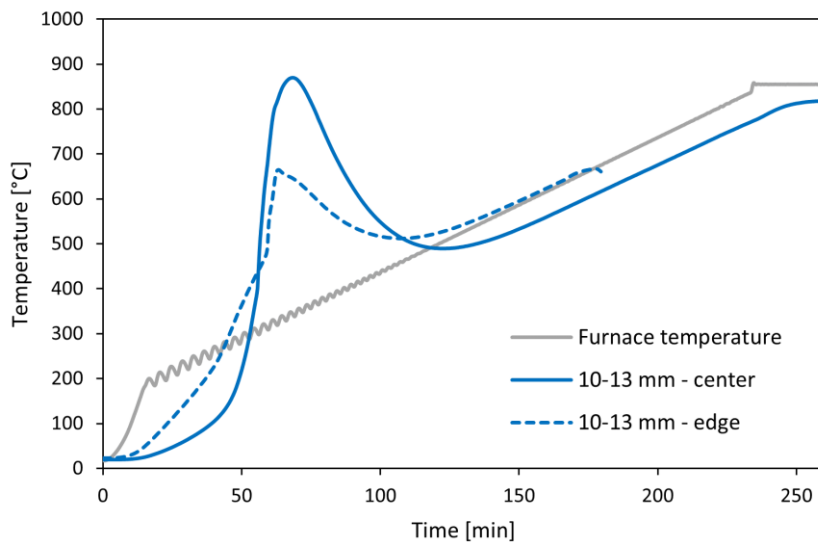

Figure 4.13: Temperatures measured in Entech furnace during heating of Comilog ore in 70%CO-30%CO$_2$ at 3°C/min[1].

Similar behaviour is observed in the Entech and Disvadri furnace, however dissimilar temperatures are recorded at the decomposition of MnO_2.

When the ore descends in the prereduction zone, it is mixed with the remaining raw materials, such as coke and quartz. The presence of these materials may affect the temperature development of the charge. The effect of inert materials on the temperature development was investigated by both Larssen and Biørnstad. Larssen evaluated 3.33-4.00 mm or 11.20-15.00 mm ore particles heated with quartz in a 1:1 or 1:3 weight ratio, respectively. Changes were observed in the temperature development for both particle sizes, where the temperature increase measured by the thermocouple submerged in the same overall decreased with an increasing content of quartz. The presence of quartz had a large effect on the reduction behaviour of small particle sizes (3.33-4 mm), whereas larger particles (11.2-15.0 mm) were merely slightly affected.
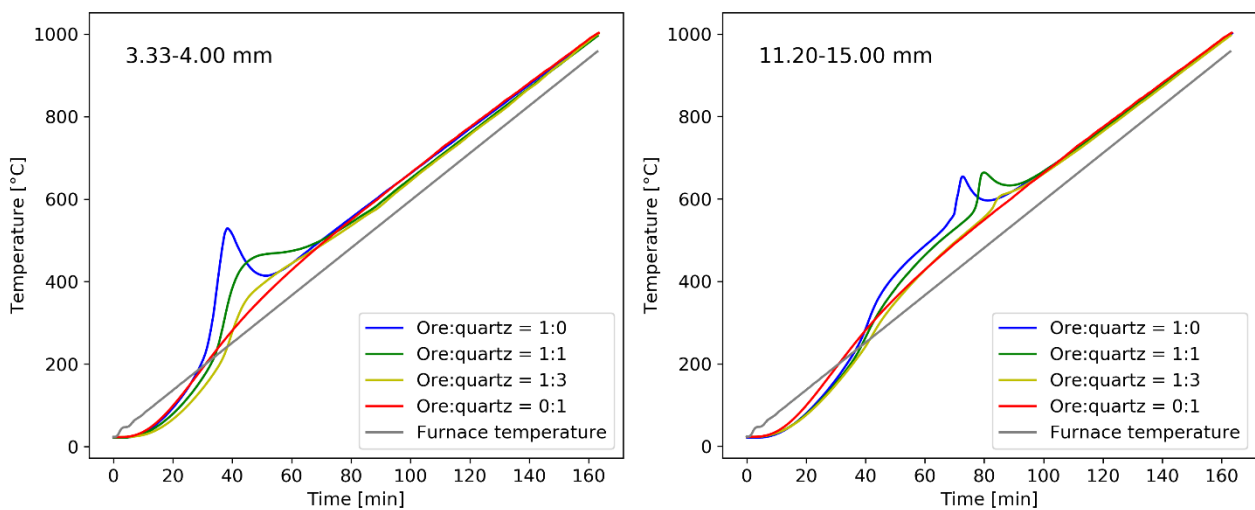

Figure 4.14: Temperature measured in sample center during experiments with Comilog ore mixed with various weight ratios of inert material (quartz)[2].

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4.2.5 Porosity and decrepitation

Porosity tests of single particles subjected to similar experimental conditions show large variance in porosity values. This is illustrated in Figure 4.15, which shows the porosity values reported by Turkova[5] and Biørnstad[1]. It is seen that the average porosity increases with temperature (or reduction extent).

The amount of sample larger than 3.33 mm, after heating in CO-CO_2 atmosphere is shown as a function of x in MnOx in Figure 4.16. The figure includes data from Larssen[2], Biørnstad[1], and Thomassen[7], all which were obtained from an initial particle size fraction of 10-15 mm. The work by Larssen and Thomassen was obtained using the Disvadri-furnace, whereas the work presented by Biørnstad is from the Entech-furnace. A clear correlation between the reduction extent (oxidation level of manganese) and the extent of disintegration is observed. This implies that it is not the rapid decomposition of MnO_2 at 580-600°C that is the main responsible factor in decrepitation. Rather, this implies that the decrepitation may not be attributed to a specific reaction. Furthermore, both Larssen and Biørnstad observed disintegration of similar magnitude in Comilog ore samples compared to a mixture of Comilog ore and quartz, even though the presence of quartz suppressed the exothermic peak.
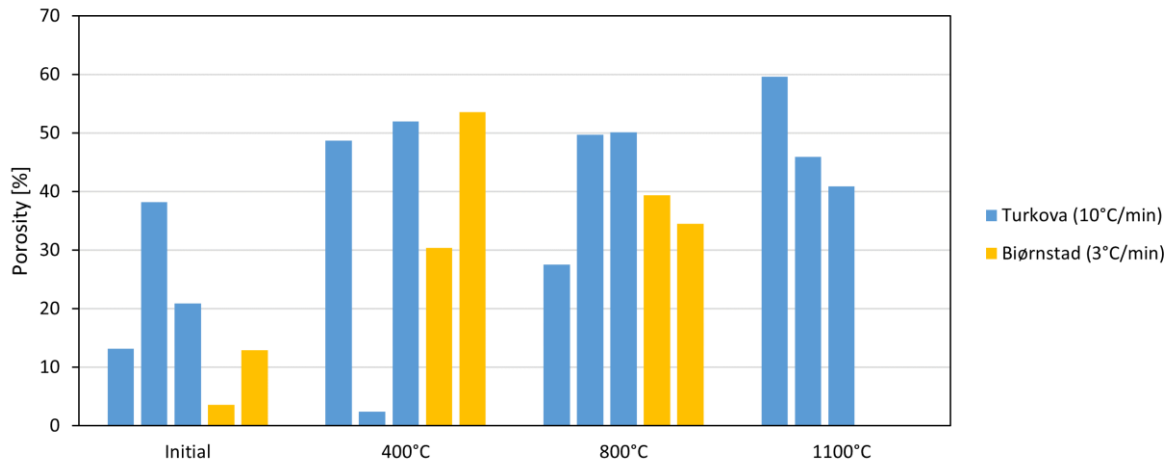
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Figure 4.15: Porosity of Comilog ore at various target temperatures after heating in 70%CO-30%CO$_2$ (initial particle size 10-15 mm). Results by Turkova[5] was obtained using Disvadri-furnace, whereas Biørnstad[1] utilized the Entech-furnace

Furthermore, the results show that the decrepitation is a function of the heating rate, where a faster heating rate correlates to lower disintegration. A clear distinction between the decrepitation extent obtained at 3°C/min, 6°C/min, and 9°C/min is seen. This is the opposite of what would be expected in terms of thermal stresses experienced by the ore. It is possible that this effect is not attributed to the heating rate itself, but rather the effect that a varying heating rate has on the gas composition the ore is exposed to during reduction. A higher heating rate correlates to a larger consumption of the available CO, which in turn leads to a higher CO$_2$ partial pressure during reduction. Several studies have indicated that porosity and surface area of manganese ore particles are largely affected by the atmosphere in which they have been heated, where heating in reducing atmosphere correlates to a considerably larger porosity and surface area compared to heating in inert atmosphere. Another potential explanation is that the ore is more susceptible towards decrepitation when the reduction proceeds at lower temperatures.

The data obtained at 3°C/min in the Disvadri and Entech furnace, respectively, show high correlation. This may indicate that the extent of disintegration is not a function of the sample size, as 75g was evaluated in the Disvadri furnace by Larssen, whereas 2 kg was evaluated by Biørnstad in the Entech furnace.

The decrepitation will alter the effective particle size of the ore as it descends in the industrial furnace. As the extent of disintegration is found to be dependent on the heating rate, the disintegration will depend on the location of the ore in the furnace. According to Pochart et al.[16], the heating rate in an industrial furnace varies between 2-8°C/min, where the rate is higher close to the electrodes. This indicates that the decrepitation is more severe in the outer regions of an industrial furnace.

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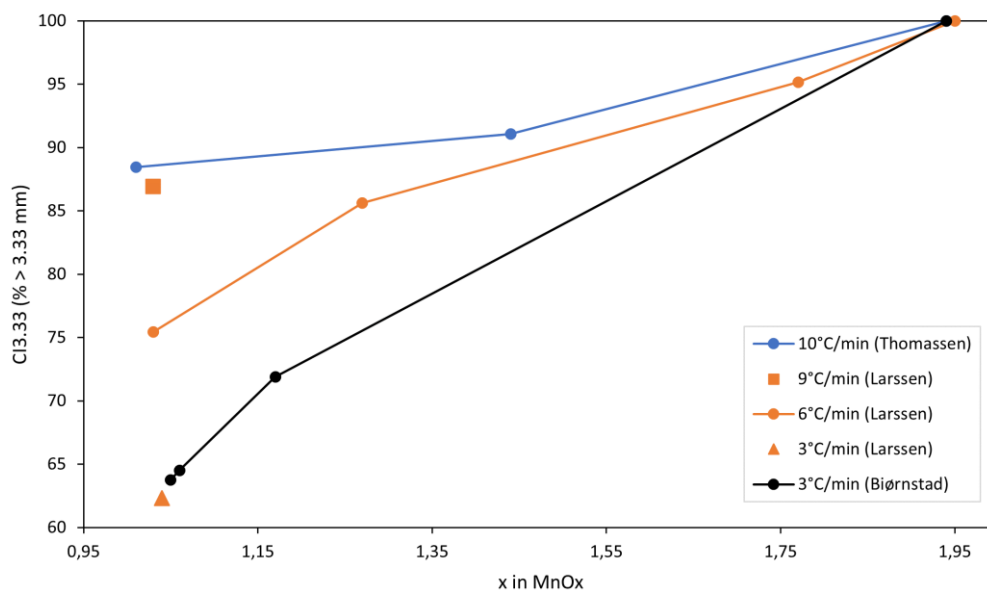
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Figure 4.16: Amount of sample of size larger than 3.35 mm after heating in CO-CO₂ atmosphere as a function of oxidation level of manganese (x in MnOx) from the results presented by Thomassen[7], Larssen[2], and Biørnstad[1]. Initial particle size fraction was 10-15 mm for all experiments. Thomassen and Larssen utilized the Disvadri-furnace, whereas Biørnstad used the Entech-furnace.

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4.3 Studies on Nchwaning ore in CO-CO$_2$

4.3.1 Reaction steps

Investigations of Nchwaning ore has revealed that the prereduction behaviour is subjected to significant variations. As such, the reaction steps and reproducibility are discussed simultaneously.

Nchwaning ore is largely composed of Mn_2O_3-minerals, however it also contains significant amounts of hematite and smaller amounts of calcite:

- The majority of the weight loss observed during reduction of Nchwaning ore is due to reduction of Mn_2O_3-oxides reducing ultimately to MnO. This reduction may theoretically proceed through the stable oxidation state of hausmannite (Mn_3O_4), however Larssen[2] did not detect this compound at any state by XRD during reduction at temperature range 25-1000°C. This indicates that any formed Mn_3O_4 will rapidly reduce further to MnO upon formation.
- The hematite present in Nchwaning could theoretically reduce to metallic iron through intermediate states Fe_3O_4 and FeO. No studies on the prereduction of Nchwaning ore (at temperatures up to 1000°C) have observed the formation of metallic iron, showing that the reduction of hematite subsides with the formation of wüstite (FeO). Further, no observations have been done by XRD of the intermediate oxidation state of magnetite (Fe_3O_4). Hence, this could indicate that hematite will reduce to wüstite in an overall single step.
- Carbonates (mainly calcite) decompose at temperatures close to 900°C regardless of particle size and atmosphere.

As such, the prereduction of Nchwaning ore involves three main reactions: Mn_2O_3-oxides to MnO, Fe_2O_3 to FeO, and $CaCO_3$ to CaO. While the decomposition of calcite appears to be purely temperature dependent, the reduction of manganese and iron oxides are affected by parameters such as particle size and gas composition. The reduction of manganese and iron oxides occur at overlapping temperature ranges. Merely small differences were observed in the reaction rate behaviour when decreasing the heating rate from 6°C/min to 3°C/min[2].

Nchwaning ore displays significant heterogeneity of large enough extent to cause variation in parallels of sample sizes of 75-100 g. This is mainly observed for larger particle sizes (> 10 mm), whereas smaller particle sizes (< 4 mm) have shown to be highly reproducible in the same sample mass size.

Potential explanations for the observed variation may be:

1. Difference in bixbyite/braunite/braunite II distributions, where the mentioned minerals show dissimilar reduction behaviour
2. The variation may be due to a variation in microstructure giving rise to e.g.,varying porosity
3. Varying chemical composition: Varying Mn/Fe-ratio or varying total amount of (Mn+Fe)

Regarding point 1, there is no evidence showing that the trivalent Mn-minerals in Nchwaning show dissimilar reduction behaviour. In his PhD-study, Berg[9] aimed to investigate the minerals influence on the reduction behaviour by evaluating single particles isothermally in CO-CO$_2$ atmosphere. Large variation was observed, however it appeared to be non-related to the mineralogy of the particles. As such, this is not believed to be the main reason for the variation observed in Nchwaning ore.

Regarding point 2, results from GasFerrosil[4] indicate that the O/Mn ratio obtained at 800°C for various ores is closely linked to the initial porosity of the manganese material. As this indicates that the reduction behaviour of a given ore is largely determined by its physical characteristics, it is possible that Nchwaning ore shows large variation in its porosity, causing the variation in repeated runs. The larger variation for larger particle sizes could be explained by the lower number of particles evaluated in each run, or it is also possible that smaller particles show less variation in porosity compared to larger particles.

In concern of point 3, the weight loss as a function of x in MnOx is plotted in Figure 4.17. While there is a clear correlation between the changing O/Mn ratio and the total obtained weight loss, it is seen that several samples show deviation from a linear trend. Of the samples obtaining a complete prereduction of manganese

oxides to MnO (x in MnOx = 1), it can be seen that the total weight loss shows variation between 9-13 wt%. Parts of this variation is attributed to a varying decomposition of calcite, as some values are obtained at 800°C (calcite intact) and others at 1000°C (calcite decomposed). It may also partially be explained by a varying content of manganese and iron, as was seen in Table 3.4, leading to a varying weight loss at total prereduction.
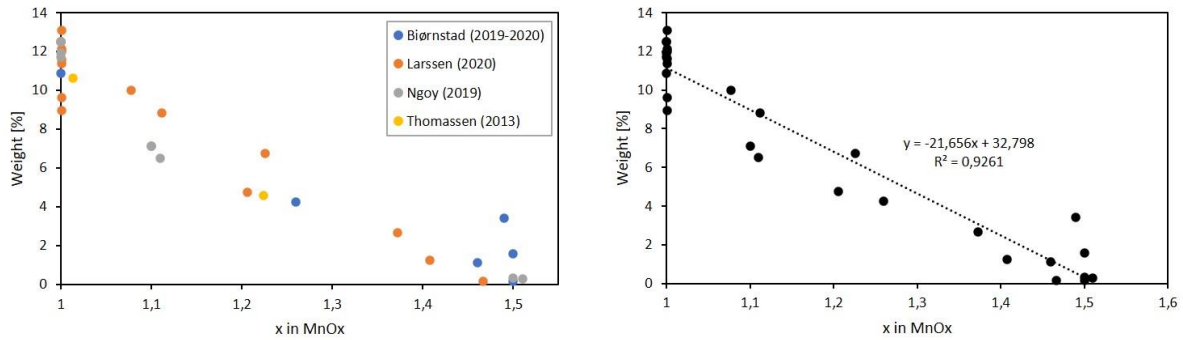

Figure 4.17: Weight loss after reduction experiment as a function of x in MnOx (analysed by tititrmetric analysis). A: shows results from the different studies[1]–[3], [7], whereas B shows the overall trend found from all values.

Figure 4.17 shows the weight loss obtained at a given reduction extent for manganese oxides for a varying Mn/Fe-ratio in the evaluated ore. It is indicated that with an increasing Mn/Fe-ratio, a higher weight loss is obtained at a given reduction degree of Mn-oxides to MnO. This is a clear contributor to the deviation from a full linear correlation between weight loss and x in MnOx for Nchwaning ore. Figure 4.19 shows the weight loss as a function of the O/Mn-ratio where the Mn/Fe-ratio obtained from chemical analysis is marked for each point. From this it is indicated that the variation may not be fully explained by a varying Mn/Fe ratio.
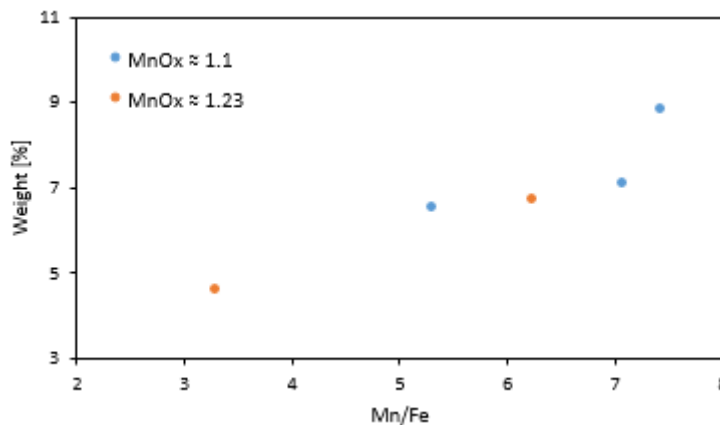

Figure 4.18: Weight loss at given O/Mn-ratio for varying Mn/Fe-ratio in ore. Values from Larssen[2], Thomassen[7], and Ngoy[3].

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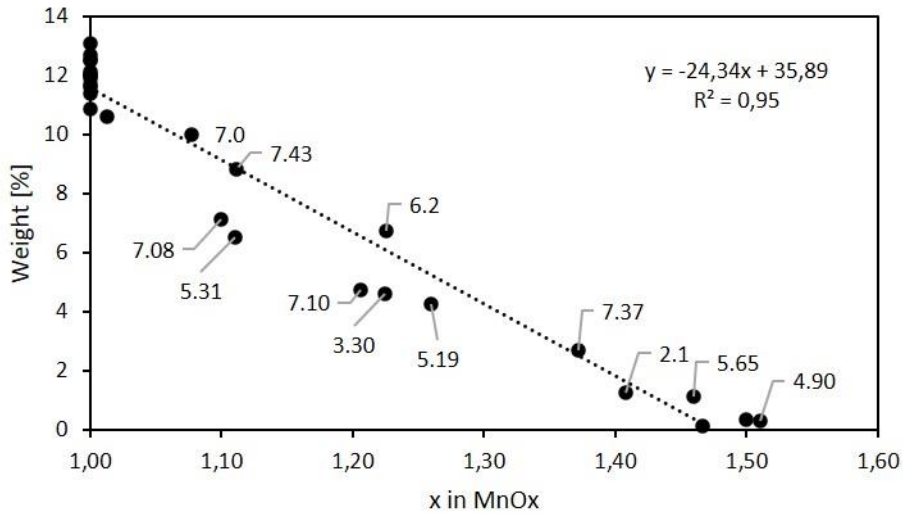REPORT NO.
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Figure 4.19: Weight loss as a function of x in MnOx (O/Mn ratio) with the correlating Mn/Fe-ratio from chemical analysis for Nchwaning ore subjected to non-isothermal reduction in CO-CO₂ atmosphere. Same values as presented in Figure 4.17.

The reaction steps identified by Larssen[2] for non-isothermal reduction in CO-CO₂ atmosphere are shown in Figure 4.20. Due to lower oxygen level and lower reaction rate, the temperature development during reduction of Nchwaning ore is insignificantly affected by any heat production accompanying the exothermic reactions. The figure shows the reaction rate for particle size 3.33-4.00 mm. Several stages in the reaction rate were observed. It was suggested by Larssen that the Mn-oxide reduction was initiated prior to the Fe-oxide reduction. The reaction steps showed increasing degree of overlap with increasing particle size. Particles larger than 11 mm show an overall single step, where the rate is slow in the initial stages. A small extent of both left and right shifted Boudouard reaction was observed during reduction of Nchwaning ore. The effect of carbon deposition is marked as reaction 1 in the figure.
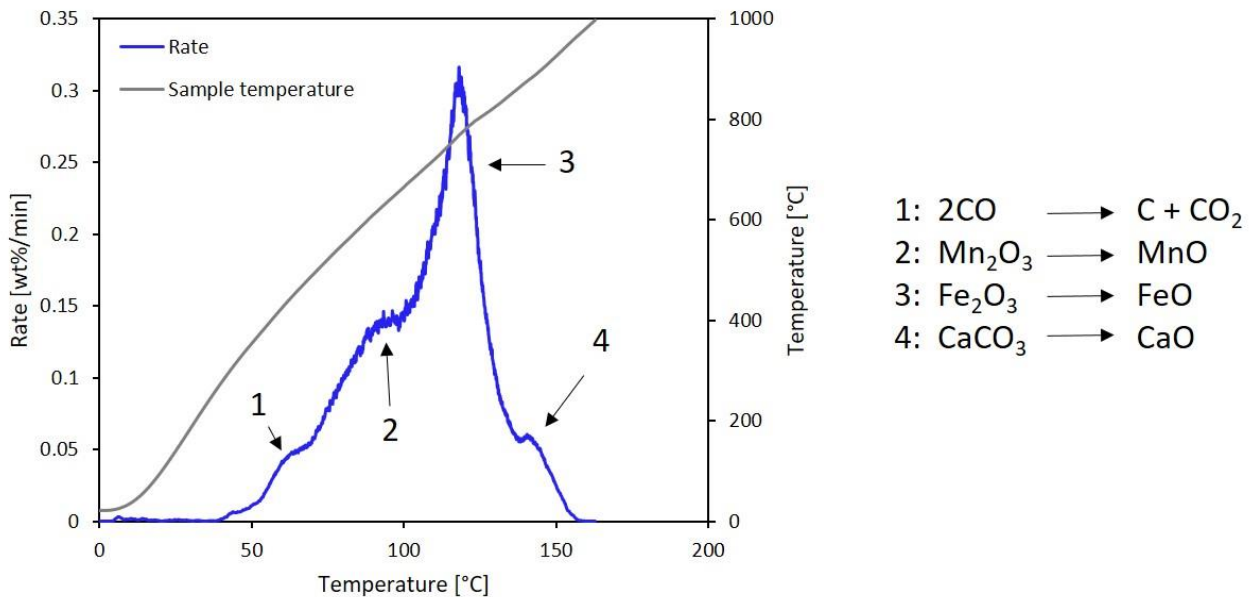

Figure 4.20: Reaction steps during heating of Nchwaning ore in CO-CO₂ atmosphere[2].

Larssen[2] investigated the microstructure development in partially reduced samples. Different types of structures were observed, however no indications of a topochemical mechanism were observed. Berg[9] observed the formation of a product layer in partially reduced samples subjected to isothermal reduction in CO-CO_2 atmosphere. It is however believed that the product layer is a result of the pre-calcination that the ore samples were subjected to before reduction. The formation of more dense particles during calcination has also been observed by others.

4.3.2 Effect of gas composition and flow

A varying CO-concentration in CO-CO_2 atmosphere has been investigated in several different projects. This has been done by different approaches:
- Total gas flow constant: CO/CO_2 varied by varying both gas flows
- Flow of CO constant: CO/CO_2 varied by varying flow of CO_2

In the Gasferrosil-project[4], Nchwaning ore was reduced in CO (2L/min) and CO-CO_2 (2 L/min+0.85 L/min), where a highly similar normalized weight loss behaviour was observed in both. This can be seen in Figure 4.21, comparing experiment 1 and experiment 4. While both experiments obtained a complete reduction of higher manganese oxides to MnO, the chemical analysis showed that the sample from experiment 1 contained 6% less manganese compared to the sample of experiment 4. Thus, it is possible that the promoting effect obtained in experiment 1 compared to 4 due to lower oxygen pressure is balances out by a decreasing effect of lower Mn-content.

Ngoy[3] also evaluated two different CO/CO_2 compositions by varying the gas flow of CO_2. Merely a small difference was observed during reduction in 50%CO-50%CO_2 compared to 70%CO-30%CO_2, as can be seen in Figure 4.22 by the reaction rate (wt%/min). The reduction appears to be initiated at similar process time, however a higher maximum rate is obtained with increasing oxygen pressure.

Larssen[2] observed a promoting effect by increasing CO/CO_2-ratio. The effect was quantified and estimated to be of order 1-2, with an average of all parallels of 1.5.
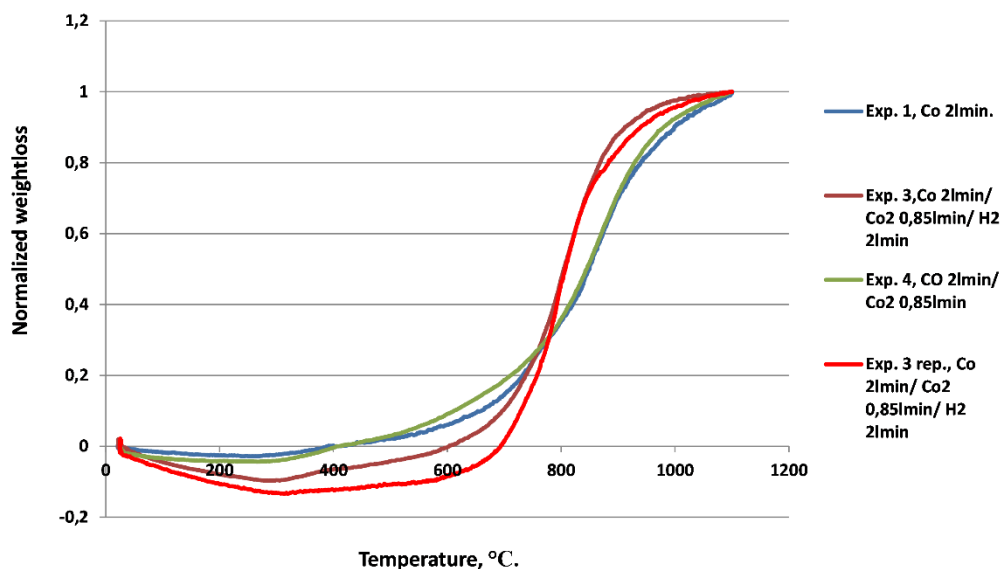

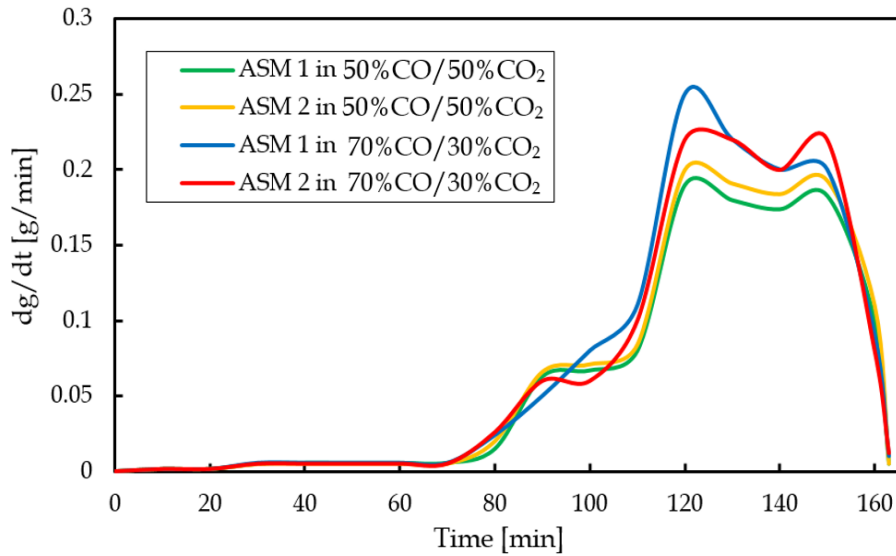**Figure 4.21: Normalized weight loss as a function of time for reduction of Nchwaning ore (Gasferrosil)[4].**

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Figure 4.22: Reaction rate (wt%/min) for two different CO-CO₂ atmospheres during reduction of Nchwaning ore[3].

4.3.3 Effect of particle size

Of studies evaluating a varying particle size of Nchwaning ore during reduction, the findings agree that the reaction rate is promoted by a decreasing average particle size. Larssen evaluated three different particle sizes in 80%CO-20%CO₂, and four particle sizes in 50%CO-50%CO₂. The weight reduction behaviour of the latter atmosphere is shown in Figure 4.23, which shows that a faster reduction is obtained with decreasing particle size. The relation between the reaction rate and the particle size was estimated by the apparent rate constants, where the obtained relations are shown in Figure 4.24. While the results are influenced by the natural variation, the reaction rate is estimated to be proportional to the inverse particle size, i.e. rate α ($1/r_p$).
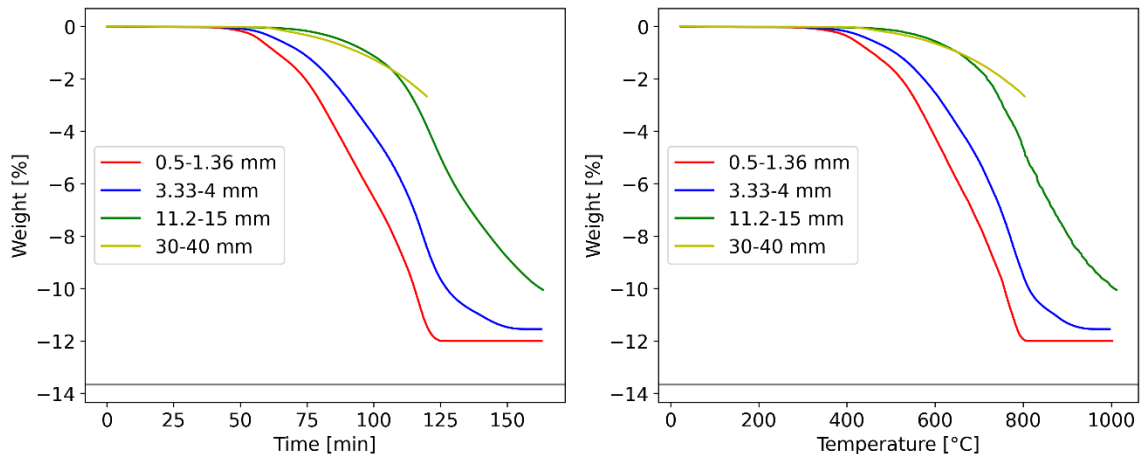

Figure 4.23: Weight as a function of time and temperature, respectively, for Nchwaning ore in various size fractions at 6°C/min in 50%CO-50%CO₂[2].
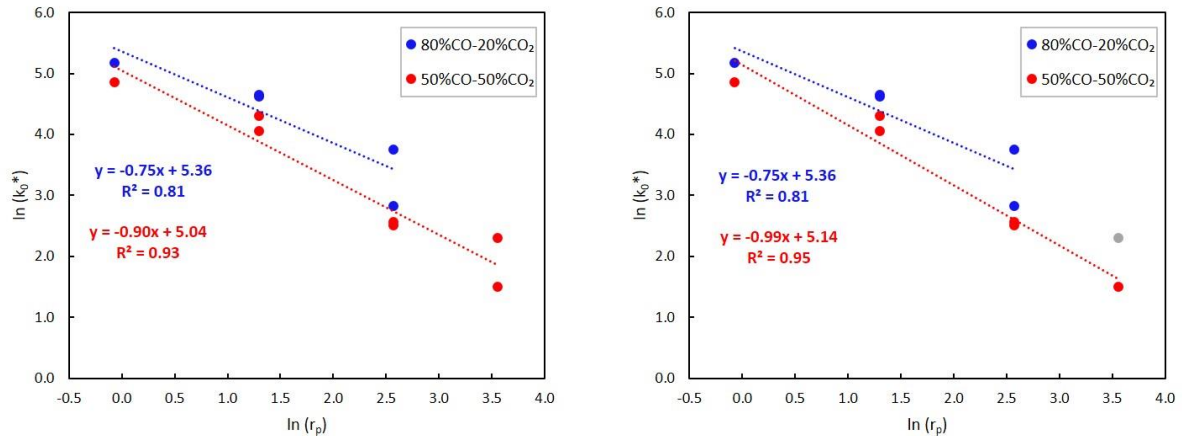
Figure 4.24: Apparent rate constants as a function of average particle size of Nchwaning ore during reduction (6°C/min) in CO-CO$_2$ atmosphere. Relation between particle size and reaction rate deduced from slope of linear regression[2]

Biørnstad[1] evaluated particle size 3-6.7 mm and 10-13 mm of Nchwaning ore, reduced non-isothermally in 70%CO-30%CO$_2$. The results were evaluated by analysed oxygen level of manganese (x in MnOx) after heating to 400°C, 600°C, and 800°C. No TGA curves were presented, implying that the effect of particle size on the reaction rate cannot be quantified. Nonetheless, the O/Mn analyses showed that a decreasing particle size promoted the reduction, as seen by the values obtained at 600°C in Table 4.2.

Table 4.2: x in MnOx (O/Mn ratio) in Nchwaning ore samples heated at 3°C/min up to 400°C, 600°C, and 800°C in 70%CO-30%CO$_2$[1]

	3-6.7 mm	10-13 mm
400°C	1.46	1.46
600°C	1.17	1.26
800°C	1.00	1.00

4.3.4 Porosity and decrepitation

Of 5 different particles analysed by Turkova[5] and Biørnstad[1], an initial porosity of 0-0.1 was obtained for untreated Nchwaning ore for all particles. The initial porosities, and the porosities analysed in samples reduced non-isothermally up to 400°C and 800°C, are shown in Figure 4.25. It is clear that the average porosity increases with increasing reduction extent, however the variation between different particles is high. At 800°C, some particles have a porosity exceeding 20%, whereas a porosity of 1% is also seen for one of the particles.
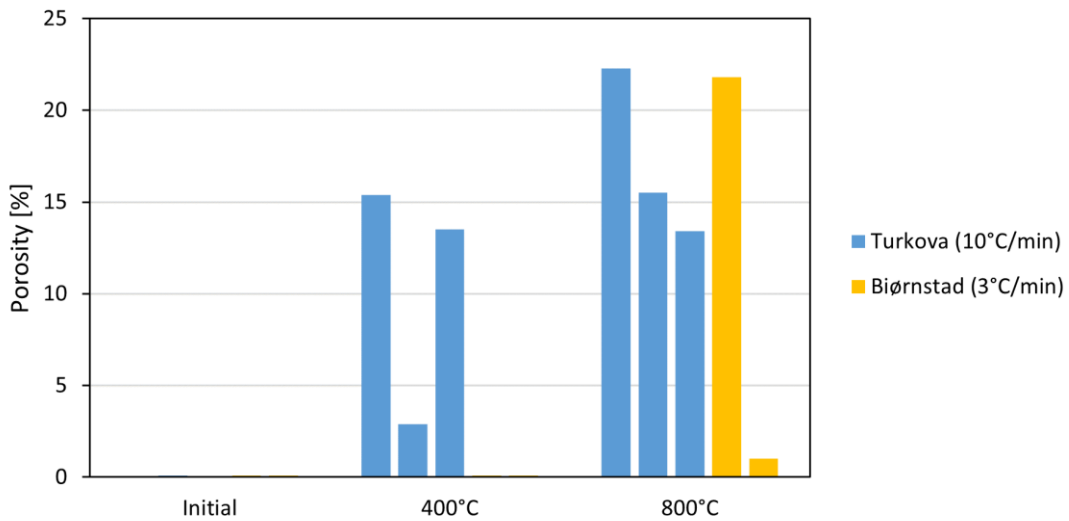
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Figure 4.25: Porosities reported by Turkova[5] and Biørnstad[1] of Nchwaning ore particles unreduced, and heated in CO-CO₂ up to 400°C and 800°C. Initial porosities were 0.

Nchwaning ore shows a low extent of decrepitation compared to many different ores, such as Comilog ore. This is often said to be due to the low porosity giving a high mechanical strength. However, it is seen that the decrepitation shows a strong correlation to the reduction extent. This is seen in Figure 4.26 from the results obtained by Biørnstad[1] and Thomassen[7]. The lower decrepitation extent of Nchwaning ore may thus potentially be correlated to the lower oxygen level of Nchwaning ore ($\approx Mn_2O_3$) compared to Comilog ($\approx MnO_2$). Similar to Comilog ore, the decrepitation of Nchwaning also appear to be influenced by the heating rate, where a lower rate correlates to a higher extent of disintegration.
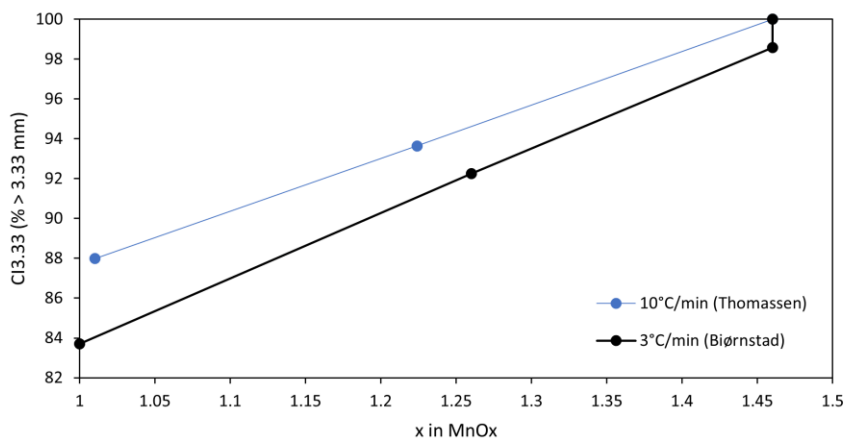

Figure 4.26: CI3.33 (amount of sample of size larger than 3.33 mm after reduction) as a function of O/Mn ratio for Nchwaning ore reported by Thomassen(Disvadri furnace)[7] and Biørnstad(Entech-furnace)[1]

4.4 Other atmospheres

The majority of the prereduction investigations have been performed in CO-CO$_2$ atmosphere, as these are the main components of the industrial furnace gas. A few studies have evaluated the influence of hydrogen (and water vapor), and the reduction in inert atmosphere. This section presents results from these studies.

4.4.1 Hydrogen and/or water vapor

The reduction behaviour of manganese ores in hydrogen is of interest as:
- Raw materials, mainly manganese ore, contain certain amounts of moisture when fed to the industrial furnace, which could be surface moisture or chemically bound in the material. This moisture will evaporate at low temperatures, and could potentially react according to the water-gas shift reaction to produce hydrogen. Experiments have been conducted to investigate the effect of this water and/or hydrogen.
- The potential use of hydrogen as the reducing agent in the prereduction zone rather than CO(g). This would be applicable by the use of a pretreatment/prereduction unit, where the atmosphere can be manually determined.

The amount of surface moisture retained in the ore will largely be a function of the materials' initial porosity. As such, Comilog ore may contain considerable amounts, whereas Nchwaning ore will contain insignificant amounts. Larssen[2] evaluated the reduction of wet and dry, respectively, Comilog ore in CO-CO$_2$ atmosphere. The ore was soaked in water prior to reduction, allowing approximately 4 wt% moisture to retain in the pores and cavities. It was seen that the reduction was initiated at a higher process time for the wet ore compared to the dry, as the initial energy was used to evaporate the water rather than increase the temperature of the ore. The lower reduction in the initial stages leads to a larger extent of the rapid decomposition of MnO$_2$ at 580°C, as more MnO$_2$ remains at this threshold temperature. This can be seen in Figure 4.27. As such, the surface moisture will lead to an increased energy consumption linearly dependent on the amount of moisture, however it will not lead to a varying extent of the Boudouard reaction, as the wet and dry ore have obtained similar reduction extents at temperatures exceeding 580°C.
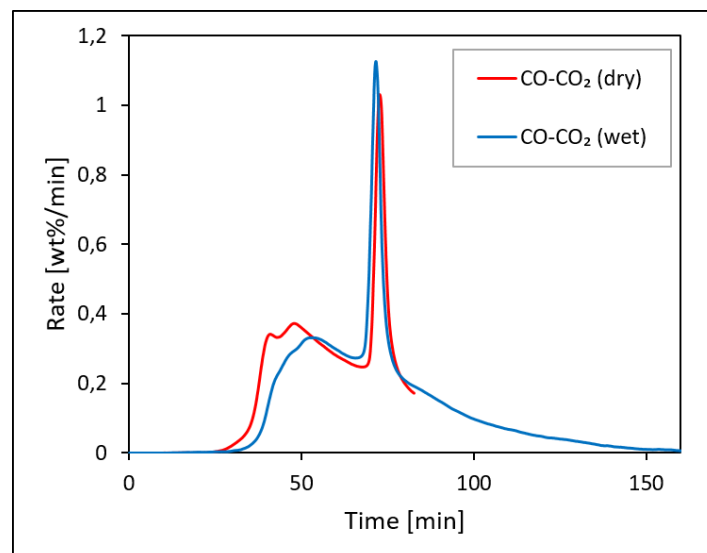

Figure 4.27: Wet and dry Comilog ore reduced in CO-CO$_2$ atmosphere. Reduction initiated at higher process time for wet ore[2].

The effect of water vapor has also been investigated by introducing water vapor in the gas phase by Larssen[2] (for Comilog and Nchwaning) and Lobo[6] (for precalcined Nchwaning ore and pellets). The results obtained by Larssen are shown in Figure 4.28, showing Comilog ore reduced non-isothermally in CO-CO$_2$, CO-CO$_2$-

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H_2O, and CO-CO_2-H_2 where all atmospheres correlate to similar theoretical oxygen pressure. It is seen that the atmosphere containing water vapor shows intermediate behaviour compared to CO-CO_2 and CO-CO_2-H_2. This indicates that the water vapor reacts according to the water gas shift reaction, producing hydrogen, however the reaction is not at equilibrium.
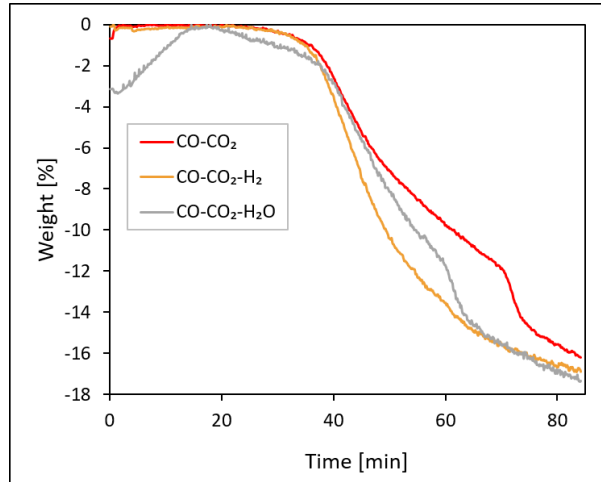

Figure 4.28: Comilog ore reduced in various atmospheres correlating to similar theoretical oxygen pressure[2].

All studies at NTNU/SINTEF evaluating the effect of hydrogen have shown that hydrogen promotes the reduction rate of manganese ores[2]–[4], [6], [10, p. 2], [17], [18]. It has been observed that the presence of hydrogen has a larger effect on the reaction rate compared to a lower oxygen pressure[2], [3]. Hydrogen has also been observed to promote carbon deposition at low temperatures[2]. At low oxygen pressures, the carbon deposition is significant, and potentially gives a prohibiting effect of on the ore reduction. This is mainly considerable for ores of lower oxygen level, as the reduction is initiated at higher temperatures. As such, the effect of hydrogen is less clear for Nchwaning ore.

While water vapor and hydrogen promotes the reduction rate of manganese ores, these gas species will likely not be present at the temperature ranges in an industrial furnace where the majority of the ore reduction occurs. As such, it is likely that the main effect of the present moisture is an increased energy consumption, as well as influencing the off-gas composition.

4.4.2 Air, argon, CO_2

Few studies have been performed evaluating the reduction/decomposition behaviour of manganese ores in inert atmospheres, such as argon or CO_2. This has been done in the PREMA project, however the results are not yet available.

When heated in a non-reducing atmosphere, the ores will decompose. It is believed that the behaviour of the ores in air may be comparable to the behaviour obtained in argon or CO_2. A comparison of the behaviour of Comilog ore in argon and CO-CO_2, respectively, is shown in Figure 4.29. It is seen that at temperatures up to 1000°C, a 50% reduction in oxygen level is obtained. This implies that the MnO_2-oxides have decomposed to Mn_2O_3.
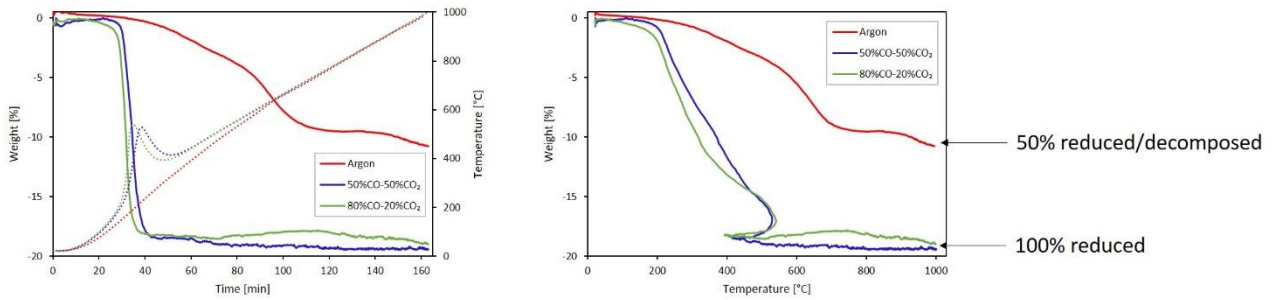
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Figure 4.29: Comilog ore heated in CO-CO$_2$ or argon at 6°C/min up to 1000°C[2].

According to the analyses by Biørnstad[1], an oxygen level of Mn$_2$O$_3$ is obtained when the ores are heated in air at temperatures up to 800°C, as seen in Table 4.3.

Table 4.3: Chemical analysis from experiments conducted by Biørnstad[1]. Manganese ores heated in air or 70%CO-30%CO$_2$ at 3°C/min

Ore	Target temperature [°C]	x in MnOx	
		Air	CO-CO$_2$
Nchwaning	400	1.49	1.46
	600	1.50	1.26
	800	1.51	1.00
Comilog	400	1.88	
	600	1.64	
	800	1.49	
UMK	400	1.46	
	600	1.46	
	800	1.51	

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5 Overview of commercial ores

Comilog- and Nchwaning-ore has been the investigated material in the majority of the studies. However, other commercial ores have also been investigated, including BHP (Groote Eylandt), Mamatwan, UMK, Gloria, and CVRD. Turkova[5] investigated pellets and sinters of several of the mentioned ores. The investigations of these ores were largely limited to their obtained O/Mn ratio at 800°C after non-isothermal reduction in CO-CO_2 atmosphere.

The oxygen level of manganese (O/Mn ratio) obtained at 800°C after reduction in CO-CO_2 atmosphere is shown in Figure 5.1 as a function of the ores' initial porosity. It is evident that the prereduction of manganese ores are highly dependent on the physical characteristics of the ores, mainly expressed through the porosity. The porosity was determined for three ore particles, and the average of these values were used in Figure 5.1. It is mentioned that the individual porosities showed large variations.
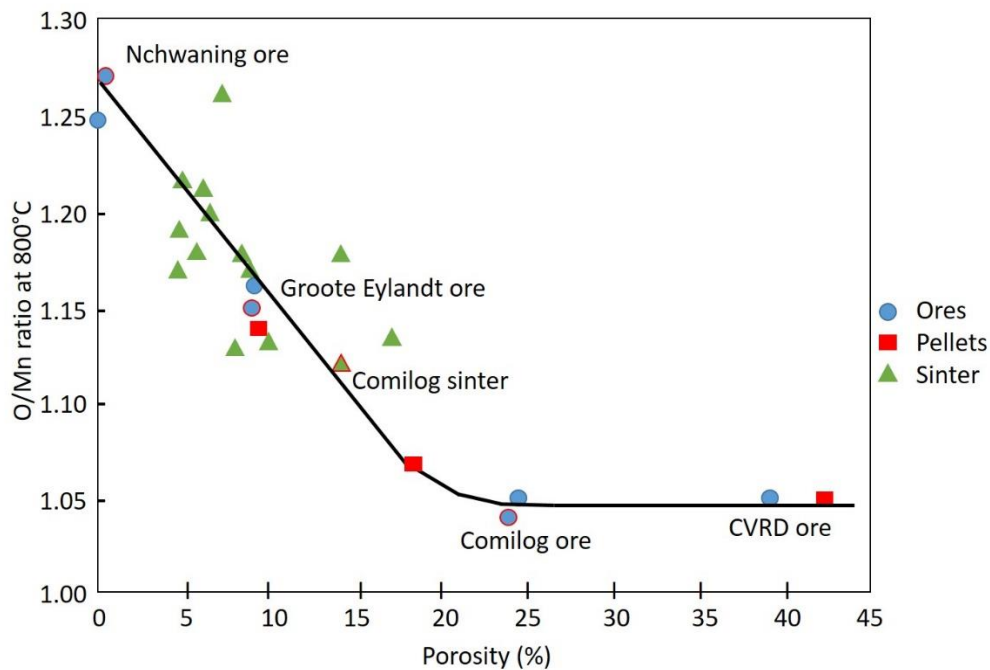

Figure 5.1: O/Mn ratio obtained at 800°C after heating in 70%CO-30%CO_2 as a function of initial porosity by Turkova[5] and values further obtained through the GasFerrosil-project[4] (marked with red edge).

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6 Reaction rate analysis

It is recognized that kinetic parameters determined for the reduction behaviour of manganese ores is dependent on the ore characteristics, the preparation of the material, and the experimental procedures. Different approaches and models have been used to mathematically express the reduction behaviour. The reduction of manganese ores involves multistep and parallel reaction schemes, where the involved reactions are dependent on the given ore. In addition, ores with a high oxygen level will lead to extensive heat production, which gives rise to irregular temperature development. As such, a mathematical description of the prereduction of manganese ores is a complex affair.

To simplify the system, Berg[9] and Ishak[8] precalcined manganese ores to decompose any higher manganese oxides to Mn_3O_4. Berg utilized the shrinking core model as a reaction front was observed in the partially reduced samples. The reaction front is believed to have been formed due to the calcination of the ores prior to the reduction experiments, hence not being representative of the ore reduction in an industrial furnace. Furthermore, while the shrinking core model successfully described a few experiments, the model was unsatisfactory for the majority of the results. Ishak[8] utilized both the shrinking core model and the grain model to analyse the isothermal reduction behaviour of precalcined Comilog ore. It has been shown that the reduction behaviour is highly influenced by any pretreatment of the ores, where precalcined ores show a considerably slower reaction rate compared to prereduced ores. The obtained kinetic values showed large variations, e.g. activation energies between 12-230 kJ/mol reported by Ishak.

A simple equation was used by Larssen[2] to describe the reduction of Comilog- and Nchwaning-ore as observed in the Disvadri furnace. The ores were not subjected to any pretreatment prior to reduction. The equation was constructed based on the obtained relations between the reaction rate and the particle size and partial pressure of CO, respectively. The reduction behaviour was normalized to a conversion extent (0-1) and the reduction was expressed as a single step. For Comilog ore, this implies that the rapid decomposition of any present MnO_2 at 580°C was not included. For Nchwaning ore, this implies that the reduction of Fe-oxides is assumed to occur at a similar rate as the Mn-oxides. The equation is presented in equation 6.1, and the parameters used in the equation is shown in Table 6.1.

$$\frac{dX}{dt} = k(T(t)) \cdot \frac{1}{r_p} \cdot p_{CO}^m \cdot (1 - X) \qquad 6.1$$

Where dX/dt is the reaction rate, k is the Arrhenius rate constant (equation 6.2), rp is the average ore size, pCO is the inlet partial pressure of CO and X is the conversion/reduction extent.

$$k = k_0 \cdot e^{-E_a/RT} \qquad 6.2$$

Table 6.1: Parameters used in equation 6.1 and 6.2 for Comilog and Nchwaning ore, respectively.

	Comilog	Nchwaning
Ea [kJ/mol]	17	63
k_0 [cm/min·atm]	0.53	60.4
m (in p_{CO}^m)	0.7	1.5

A reasonable agreement was found between the equation values and the experimental behaviour for varying heating rates, varying particle sizes, and varying inlet partial pressure of CO in CO-CO_2 atmosphere. It is

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mentioned that the driving force is expressed through the inlet partial pressure of CO. As the CO/CO_2 ratio will vary during the reduction depending on the reaction rates, the model should be further refined to include the varying CO-concentration. Examples of the correlation between the equation and the experimental behaviour is shown for Comilog ore in Table 6.1.
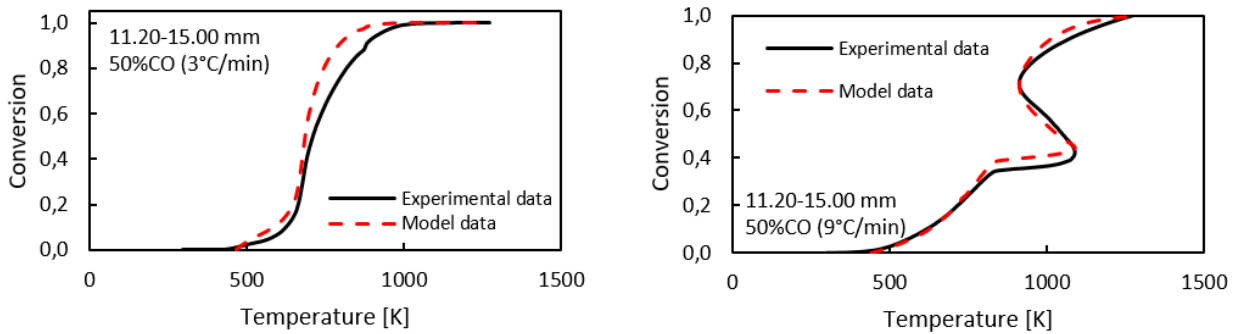

Figure 6.1: Reduction of Comilog ore expressed as conversion from 0 to 1 as described by equation 7.1 compared to experimental values[2].

The correlation between the equation and data obtained at larger scale, i.e. the Entech furnace, should be evaluated. This will be done when more of the data acquired in the PREMA-project will be made available, as these experiments includes an off-gas analysis, which can be used to express the reduction behaviour. At present stage, the equation was tried towards a temperature profile presented by Biørnstad[1] for Nchwaning ore. The sample size used by Biørnstad was 2 kg, compared to 75 g used by Larssen.

The correlation between the curve obtained by the equation and the O/Mn ratios obtained through chemical analysis is shown in Figure 6.2. At 600°C, the deviation between the model and chemical analysis is approximately 20%. It is mentioned that Biørnstad subjected the samples to an isothermal holding period after target temperature was reached. As such, the model prediction and the chemical analyses are not directly comparable. This will likely explain the observed deviation in the figure.
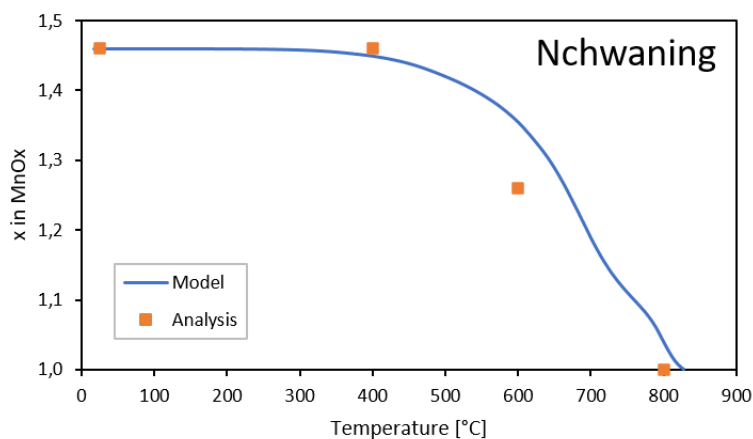

Figure 6.2: Equation 6.1 used for time and temperature profile obtained by Biørnstad for the reduction of Nchwaning ore in Entech furnace[1].

7 Concluding remarks

This report has aimed to evaluate and summarize information on the prereduction behaviour of manganese ores at NTNU and SINTEF during the last decades. The report is limited to the information that is publicly available. There are currently several ongoing projects researching these topics, where information is still confidential. This includes work done in PREMA (except that obtained by Master student Biørnstad), as well as a PhD student in Reduced CO_2.

[1] O. Biørnstad, "Decrepitation of Comilog, Assmang and UMK manganese ores during prereduction," MSc thesis, NTNU, 2020.

[2] T. A. Larssen, "Prereduction of Comilog- and Nchwaning-ore," Dr. Ing Thesis, NTNU, 2020.

[3] D. Ngoy, "Pre-reduction of manganese ores with CO and H_2 gas," NTNU, Internal report, 2019.

[4] M. Tangstad, "Summary of prereduction experiments in the Disvadri furnaces with industrial materials in Gasferrosil v.2," NTNU, Internal report, 2017.

[5] K. Turkova, D. Slizovskiy, and M. Tangstad, "CO reactivity and porosity of manganese materials," *ISIJ international*, vol. 54, no. 6, pp. 1204–1208, 2014.

[6] S. Lobo, "Reduction of manganese ores using CO, H_2, CO_2 and H_2O blends," Unpublished work, 2015.

[7] Thomassen, "Reactivity and tumbler test," 102001895–1, Mar. 2014.

[8] R. J. Ishak, "Reaction Kinetics for Reduction of Manganese Ore with Carbon Monoxide in the Presence of Carbon," Dr. Ing thesis, NTNU, 2002.

[9] K. L. Berg, "Gaseous Reduction of Manganese Ores," Dr. Ing. Thesis, The Norwegian University of Science and Technology, 1998.

[10] T. Beck, "Forreduksjon av manganmalm med H2/CO blandinger," NTNU, Internal report, 1998.

[11] M. Tangstad, S. Wasbø, and R. Tronstad, "Kinetics of the Pre-reduction of Manganese Ores," in *Conference proceedings, Infacon IX (Quebec)*, 2001, pp. 202–207.

[12] M. Tangstad, P. Calvert, H. Brun, and A. G. Lindseth, "Use of comilog ore in ferromanganese production," in *Proceedings: Tenth International Ferroalloys Congress*, 2004, vol. 1, p. 4.

[13] M. Visser, H. Smith, E. Ringdalen, and M. Tangstad, "Properties of Nchwaning and Gloria ore in the production of Mn ferro-alloys," Kazakhstan, Jun. 2013.

[14] B. Sorensen, S. Gaal, E. Ringdalen, M. Tangstad, R. Kononov, and O. Ostrovski, "Phase compositions of manganese ores and their change in the process of calcination," *International Journal of Mineral Processing*, vol. 94, no. 3–4, pp. 101–110, 2010.

[15] B. E. Sørensen, "Mineral quantification of Manganese ores," NTNU, 2010.

[16] G. Pochart, L. Joncourt, N. Touchard, and C. Perdon, "Metallurgical benefit of reactive high grade ore in manganese alloys manufacturing," *World*, vol. 800, no. 1000, Art. no. 1000, 2007.

[17] T. Beck, "Forreduksjon av Comilog manganmalm med H2 og CO gass," Internal report, 1998.

[18] T. Beck, "Kinetikk og mekanisme ved reduksjon av manganmalm," MSc thesis, NTNU, 1998.

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