

Use of H₂ in Mn-ferroalloy production

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Keywords: Mn-ferroalloy process, Hydrogen, prereduction

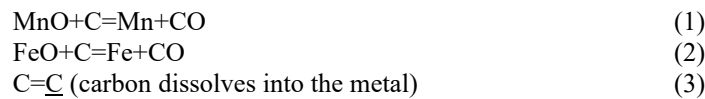
Abstract

The use of H₂ as a reductant in the iron and steel industry is an obvious choice towards carbon neutrality. For pyrometallurgical processes like Mn and Si, H₂ cannot be the only solution, as the stability of the oxides of these elements are higher compared to Fe. H₂ can however be used in the Mn-process together with other low CO₂ emission mitigations. In the Mn-ferroalloy process H₂ can be used to reduce higher manganese oxides to MnO, and the last part of the reduction to metallic Mn can be done with biocarbon or with electrolysis. In studies from NTNU, the reduction of higher manganese oxides to MnO has been investigated with pure H₂ or with CO/H₂ mixtures. It is shown that the H₂ containing gases will give higher reduction rate compared to CO/CO₂ gases with the same reduction potential. The reduction rate will be increased in the order of 20-100%, and H₂ has a larger impact on reduction rate for high oxygen pressures. In H₂ gas it is seen that the final degree of reduction is higher than using CO gas, and this is believed to be due to the formation of metallic iron. The reduction rate in H₂ gases varies for various ores, and as for CO containing gases, the reduction rate of Comilog ore is faster than the Nchwaning ore, and activation energies of 23 kJ/mol versus 68 kJ/mol is respectively found for isothermal experiments in CO, H₂, CO₂ gases.

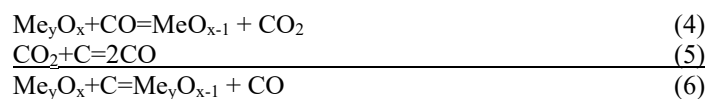
1 INTRODUCTION

Mn ferroalloys are mainly produced in Submerged Arc Furnaces (SAF) as many other ferroalloys. The most typical geometry is the circular furnace with 3 Søderberg electrodes. In the lower part of the furnace the electrical energy is provided by the electrodes, and here the temperature is 1400-1600 °C. At these temperatures the oxide materials are melted and reduced to metal, before it is drained from the furnace as metal and slag¹. The slag/metal ratio is typically in the area of 0.5-1. The raw material mix, containing Mn-sources, fluxes and carbon materials, are being fed to the charge by gravity at the top of the furnace, where the temperature is at its lowest, in the area of 200-600 °C. As slag and metal are being tapped from the furnace the rest of the material in the furnace will descend while heated by the gas coming from the high temperature zone. The high temperature zone is called the coke-bed (1400-1600 °C), due to a stagnant layer of carbon materials, while the low temperature zone (200-1400 °C) is called the pre-reduction zone.

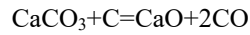
In the high temperature zone, the following carbon consuming reactions occur in the metal producing reactions during High Carbon FeMn (HC FeMn) production²:



Analysing the CO₂ emission, one can start to discuss the total carbon consumption per ton of metal produced. The typical composition of HC FeMn is 76-79%Mn, 7%C and the rest being iron. As shown in Table 1, this requires 273 kg carbon, however only 203 kg will go the gas phase as CO, and the rest will dissolve in the metal. There is however also some carbon consumption in the prereduction zone. The higher Mn- and Fe-oxides is reduced with CO gas to CO₂ (Rx.4) and if this reaction happens above about 800 °C, the CO₂ will subsequently react with the carbon materials according to the Boudouard reaction (Rx.5), and the sum of these two reactions (Rx.6) will consume carbon^{2,3}.



CO₂ from the decomposition of carbonates may also react according to the Boudouard reaction (Rx.5), and hence the total reaction will be according to Rx.7:



(7)

Based on industrial operation over 5 years and 4 different furnaces³, it has been seen that the CO₂ from the reduction of MnO₂, Mn₂O₃ and Fe₂O₃ with CO gas, will not react with solid carbon, and hence the total oxygen content of the charge mix will not affect the total carbon consumption. The CO₂ from Mn₃O₄ and Fe₃O₄ to MnO and FeO, as well as the CO₂ from the decomposition of lime (CaCO₃), may or may not react with carbon to CO gas. If none of this CO₂ is reacting with C, it has been defined as 100% degree of prereduction, and if all of this CO₂ reacts C it has been defined as 0% degree of prereduction. Industrially, it was seen that the typical degree of prereduction was changing between 0% to 60%. The degree of prereduction is determined by type and size of Mn-sources as well as furnace operation.

So far we have discussed the carbon consumption, as it is proportional with the final CO₂ emissions (with the exemption of the carbon dissolved in the metal). This is always the case for open furnaces where all CO gas will burn on the charge top. There are however some notes that must be included on this issue. For closed furnaces, the off gas will be a mixture of CO and CO₂ gas. If the gas is flared, again the carbon consumption will be proportional with the C consumption. As the off gas from Mn-alloy production may contain high amounts of CO (50-90%), this gas may be sold to other users of CO as e.g., fuel. When this gas is burned to CO₂ and emitted, the total amount of CO₂ emissions will again be proportional with the original carbon consumption. This CO₂ may however be reported as a part of the customers CO₂ emissions and not the metal producer. From an environmental point of view, the total CO₂ emission will still be proportional with the carbon consumption in the metal producing furnace, and the goal is to reduce this to a minimum.

In Table 1 the carbon consumption needed in the HC FeMn is shown. In the high temperature zone 273kg of carbon per ton of metal is required, however 70kg of these will be dissolved in the metal and hence 203 kg C or 743kg CO₂ will be emitted from the reactions in this zone. If no prereduction is occurring, the additional carbon consumption in the prereduction zone is 81 kg C, that is 341kg CO₂, will be emitted. This means that with these operating conditions, 31% of the CO₂ emitted from the furnace will come from the prereduction zone.

Table 1. Example of carbon consumption and subsequently CO₂ emission producing a metal with 79%Mn, a slag/metal ratio of 0.7, 40% MnO in the slag, 100kg lime/ton metal and 0% prereduction.

		kg C	kg CO ₂
790 kg Mn	MnO+C=Mn+CO	173	633
140 kg Fe	FeO+C=Fe+CO	30	110
70kg C	C dissolved in metal	70	0
C in cokebed zone		273	743
s/m=0,7, 40%MnO	Mn ₃ O ₄ +C=3MnO+CO	59	217
	Fe ₃ O ₄ +C=3FeO+CO	10	37
100kg CaCO ₃ /ton metal	CaCO ₃ +C=CaO+2CO	12	88
0% degree of prereduction		81	341
Total		354	1084

One of the strategies to reduce the CO₂ emissions in today's processes is to increase the degree of prereduction in the furnace, that is to reduce the extent of the Boudouard reaction, and hence reduce the total carbon and energy consumption. Figure 1 shows the carbon consumption and the CO₂ emission for the same charge as shown in Table 1 as a function of degree of prereduction. As previously noted, the highest degree of prereduction seen industrially was in the area of 60%, and this would reduce the CO₂ emissions to 870 kg CO₂, that is 19% reduction. To obtain such numbers, the operation is optimal under today's conditions. The main factor for this to happen is first and foremost, good raw materials. If the raw materials could be developed further to obtain 100% degree of prereduction, a total reduction of 31% CO₂ emission compared to 0% prereduction could be obtained.

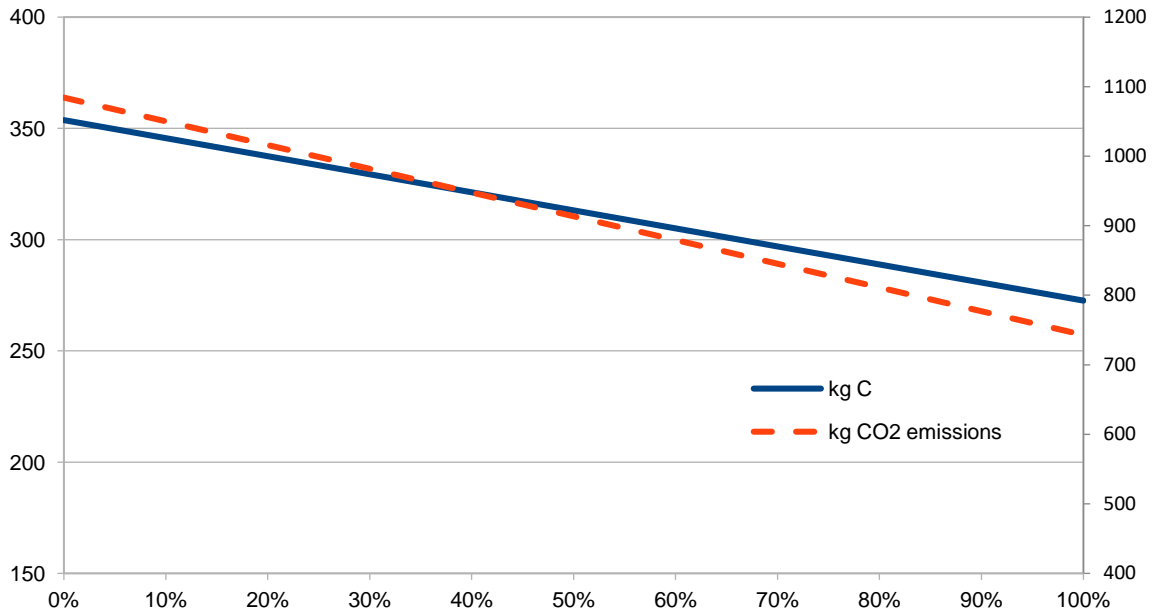


Figure 1 . C consumption and subsequently CO₂ emissions for a given charge (slag/metal ratio=0.7, %MnO in slag=40%, 100kg CaCO₃ per ton metal, all Mn-sources are MnO₂, Mn₂O₃ or Mn₃O₄).

One of the discussed paths to reduce CO₂ emissions is to use H₂ instead of solid carbon. MnO is a stable oxide and cannot be reduced with H₂, only with C as shown in reaction 1. FeO and the higher manganese oxides can however be reduced with H₂ according to reaction 8 and 9 as seen in Figure 2.

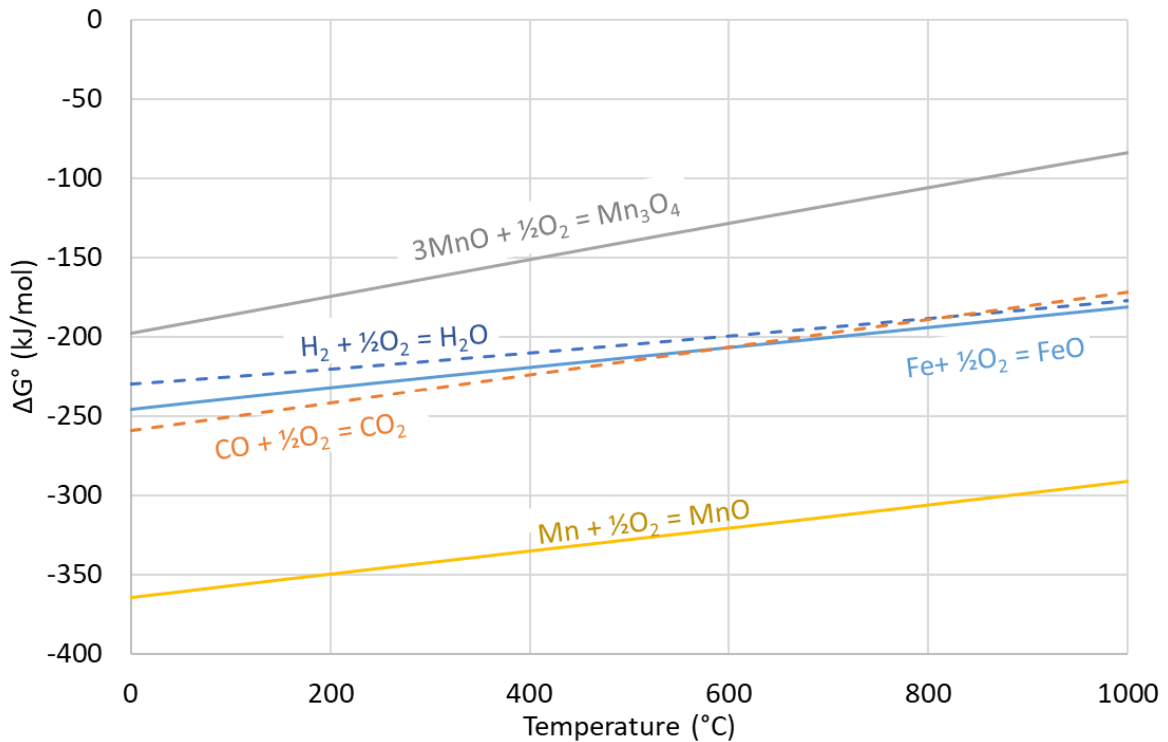
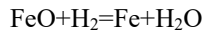


Figure 2. Ellingham diagram of Mn- and iron-oxides compared to H₂/H₂O and CO/CO₂ gases (calculated from HSC Chemistry10).



(8)



(9)

In a process where the reactions of the prereduction zone could be separated from the high temperature cokebed zone, e.g. in a prereduction unit, H_2 could be used to reduce the higher manganese oxides and the FeO without any Boudouard reaction. A more possible scenario is to operate a prereduction unit with no solid carbon, and hence both the CO from the furnace and/or additional H_2 may be used. In both cases, the total emitted CO_2 would now be down to 633 kg CO_2 per ton of metal produced (or 743 kg CO_2 if the iron is reduced to metallic iron in the prereduction unit). The conditions, which is required to reduce the ore down to MnO and Fe is investigated in a number of projects⁴⁻⁸. This paper will sum up the work done at the Norwegian University of Science and Technology within the use of H_2 as a reductant for Mn-ores.

2.1. Methods and materials

Nchwanning and Comilog ore was the raw materials used in most of the studies, in addition to one study using UMK ore. UMK is a semi-oxidized (Mn_2O_3) carbonate ore. The main minerals are braunite I ($3(\text{Mn,Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$), carbonates (calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and hausmannite (Mn_3O_4). Kutnahorite ($(\text{Ca,Mn,Mg,Fe})(\text{CO}_3)_2$), bixbyite ($(\text{Mn,Fe})_2\text{O}_3$), and hematite (Fe_2O_3) is also found but to a lesser degree.^[14] Comilog is a high oxygen ore, where the oxygen level is close to that of MnO_2 . The ore is low in iron and contains no carbonates. It contains approximately 5 wt% chemically bound moisture found in minerals such as lithiophorite and nsutite, as recently reported^{5,9,10}. Nchwanning ore is a semi-oxygen ore, where the oxygen level is close to 1.5 correlating to Mn_2O_3 . It contains insignificant amounts of chemically bound moisture but has a relatively high iron-content and smaller amounts of carbonate. The chemical analyses for the ores is given Table 2.

A TGA technique was used to investigate prereduction. The experiments were performed in an Entech VTF 80/15 vertical resistance tube furnace. The ore was placed in a high-temperature gas-tight stainless-steel (steel grade 253 MA) double-wall crucible (height 45 cm and diameter 4.8 cm). The double wall crucible ensures preheating and premixing of the gas. The gas outlet is connected to an off-gas analyser (NDIR) which determines the CO and CO_2 concentrations in the off-gas. The crucible was suspended from a balance (Mettler Toledo PR2003DR, Switzerland, 10mg) to record the weight changes during the experiment. The heating of the furnace was controlled by a Eurotherm PID controller and measured with a calibrated S-type thermocouple. A K-type thermocouple placed in an alumina tube and positioned in the middle of the charge was used to measure the charge temperature.

Flexible gas inlet and outlet pipes were connected to the top of the crucible which allowed multiple gasses to mix before entering the crucible. Each gas had its own mass flow controller (Bronkhorst F-201C). The weight of the sample before and after the experiment was recorded to confirm the net weight loss obtained from the TGA data. After the experiment was complete the sample was allowed to cool in Ar.

The chemical composition of the raw materials and the prereduced ores was examined by X-ray fluorescence (Bruker AXS S4 Pioneer X-Ray fluorescence spectrometer) using the fused bead technique. Permanganometric titration (ASTM 465-11:2017) was employed to measure the excess oxygen above MnO which is expressed as MnO_2 . The carbon concentration was analysed with a LECO (Combustion-IR) instrument and the CO_2 concentration was determined by assuming that all carbon in the ore is in the form of CO_2 .

Table 2: Chemical composition of ores (average \pm st.dev.)

	Fe, tot [wt%]	Mn, tot [wt%]	MnO_2 [wt%]	MnO [wt%]	CaO [wt%]	SiO_2 [wt%]	Al_2O_3 [wt%]	K_2O [wt%]	CO_2 [wt%]
Comilog ⁶	3.1	51.0	76.4	3.5	0.1	3.5	5.6	0.7	0.1
Comilog ¹⁰	3.6	51.4	74.3		0.1	3.3	5.1	0.8	0.15
Nchwanning ⁶	10.0	46.4	34.6	31.6	5.9	6.7	0.5	0.0	3.0
Nchwanning ⁸	8.7 \pm 2.5	48.7 \pm 3.3	38.8 \pm 2.0		5.9 \pm 0.6	4.4 \pm 0.1	0.4 \pm 0.1	0.0	2.5 \pm 0.5
UMK ¹¹	5.9	33.7	20.55		17.0	7.3	0.4	0.06	17.0

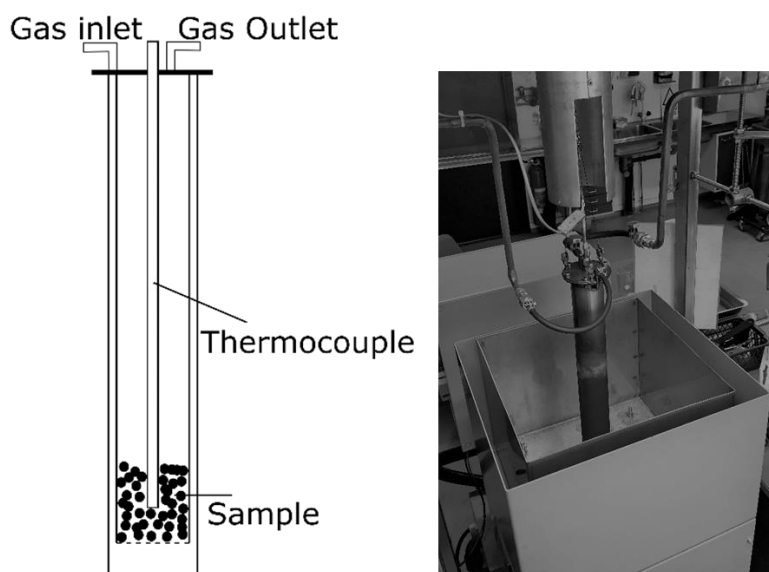


Figure 3. Sketch of the crucible used in the reduction experiments⁶.

Table 3. Experimental conditions of the studies discussed in this article.

	Lobo	Ngoy	Larssen	Davies	Schanche
Ores	Nchwaniing	Nchwaniing Comilog	Nchwaniing Comilog	UMK	Nchwaniing Comilog
	pellets	lumps	lumps	lumps	lumps
Size	10-14mm	9.5-16mm	11.2-15mm	9.5-16mm	9.2-15mm
Gas	various mixes of H ₂ , H ₂ O, CO, CO ₂	CO/CO ₂ , CO/CO ₂ H ₂	CO/CO ₂ , CO/CO ₂ H ₂ , CO/CO ₂ /H ₂ O	CO/CO ₂ , H ₂ /H ₂ O, H ₂	CO/CO ₂ , CO/CO ₂ /H ₂
	Isothermal	Non-isothermal	Non-isothermal	Isothermal*	Isothermal*
Gas flow	5l/min	2.85, 4.85l/min	4l/min	4 l/min	4l/min
Isothermal temp.	950 °C			700, 800, 900°C	605, 700, 790 °C (Nch) 365-605 °C (Com)

* Parts of the reduction will occur before isothermal temperature is reached

As seen in Table 3, the temperature profile and gas compositions vary in the different studies. For the isothermal experiments two strategies were chosen. Lobo heated the Nchwaniing pellets in Ar to the isothermal temperature. Lobo also roasted the pellets for 2 hours in 800 °C to get a good mechanical strength. It has however been seen that the heating conditions is affecting the subsequent prereduction rate¹³, and Schanche and Davies hence chose to heat the ore in the gas species used during the isothermal reduction, to simulate an industrial process. The disadvantage for this method is that some of the reduction will occur during the heating. Also in the non-isothermal experiments, where a fixed heating rate was used, two different strategies was chosen. Larssen chose to use the same gas atmosphere during the whole temperature range. It was however seen that CO would decompose to C and CO₂ at lower temperature in H₂ rich atmospheres, and hence Ngoy heated the ore to 500 °C in CO₂, before adding the reducing gas composition from 500 to 1000 °C. As seen by both Ngoy¹² and Biørnstad¹⁴, Comilog ore would then decompose from MnO to Mn₂O₃ during the heating step, while Nchwaniing would hardly change the oxidation degree.

2 RESULTS AND DISCUSSION

2.1 Reduction of Mn-ores in H₂-H₂O gases compared to CO-CO₂ gases

Figure 2 shows the reducing potential of H₂/H₂O versus CO/CO₂ gases. For the same H₂/H₂O ratio as CO/CO₂ ratio, the CO/CO₂ gas will have lower O₂-partial pressure below 800 °C and H₂/H₂O gas will have the lowest O₂-

partial pressure, and thus the highest reduction potential, above this temperature. It can also be seen that the difference in reduction potential is not very large above 800°C; at 900 °C the O₂ partial pressure for a 70/30 H₂/H₂O gas is 5.5 · 10⁻⁵ bar and for a 70/30 CO/CO₂ gas it is 6.3 · 10⁻⁵ bar. The overall picture is hence that the CO and H₂ has quite similar reduction potential in the temperature range 500-1100 °C.

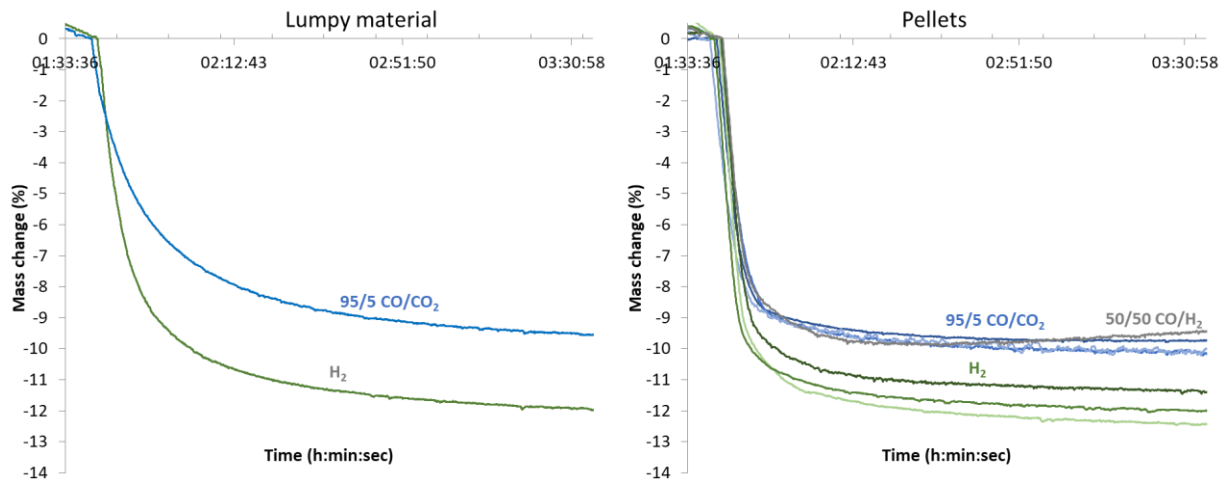


Figure 4. Comparison of reduction of lumpy material and pellets from Nchwaning ore with H₂ and 95%CO gas at 950 °C from Lobos study.

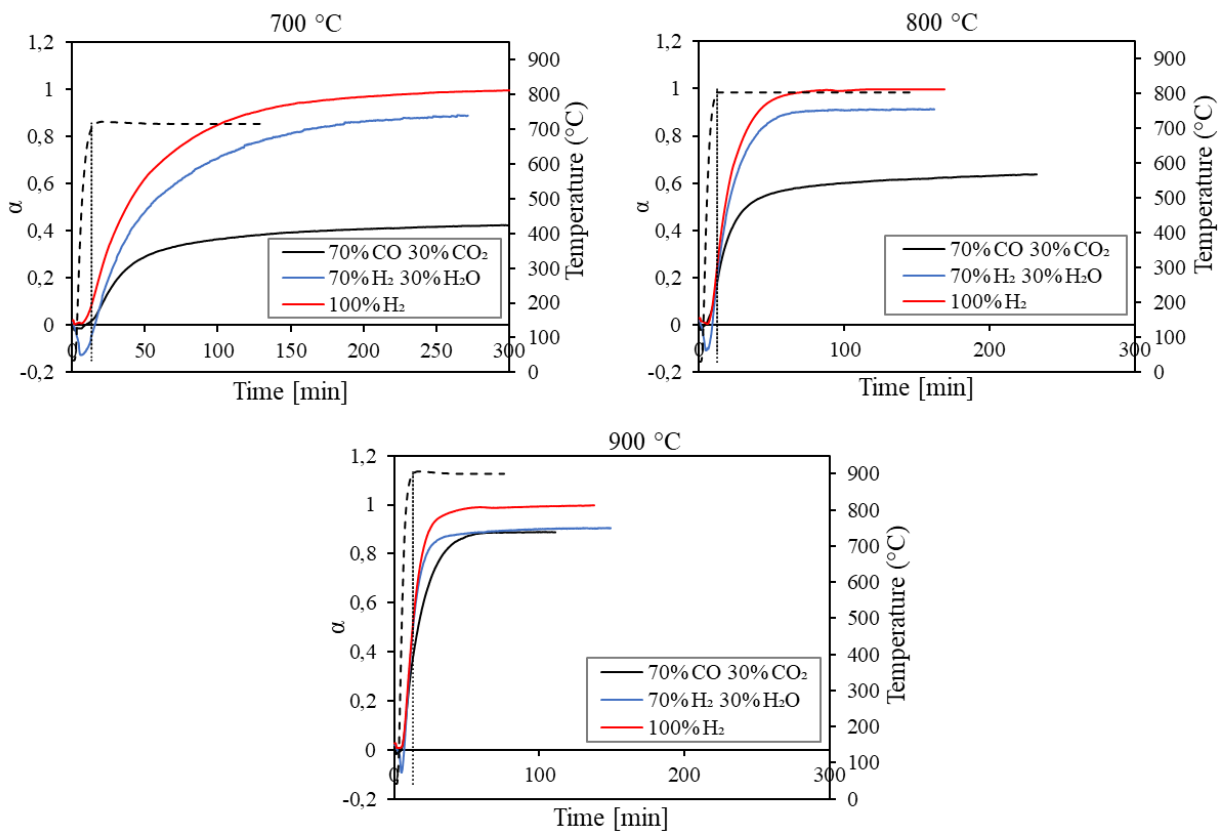


Figure 5. Extent of reduction and decomposition of carbonates in UMK ore at 700, 800 and 900 °C investigated by Davies¹¹. (Note a negative extent below 200 °C due to H₂O condensation from the H₂-H₂O gas.)

Figure 4 shows the difference between the reduction rate and the extent of the reduction in CO and the H₂ system for Nchwaning ore and Nchwaning pellets. Though the reduction potential is quite similar as discussed above, it is seen that the H₂ gas is reducing the ore to a higher extent than the CO gas. If however a mixture of H₂ and CO is used, the extent of the reduction will be in the same area as the CO gas. The higher extent of reduction is also

seen by Davies¹¹ as shown in Figure 4 when reducing the UMK carbonate ore. At 700 and 800 °C in CO-CO₂ gas, the carbonates are not yet decomposed as seen in Figure 6 which explains the lower extent of mass loss at these temperatures. At 900 °C, where all the carbonates are decomposed, the extent of reduction is higher in H₂ compared to H₂/H₂O and CO/CO₂ mixtures, which can be explained by the increased reduction potential in the H₂ gas as shown in Figure 7. H₂ gas will at equilibrium condition reduce some iron to metallic state, while the Mn will be in the (Mn,Fe)O phase. The 70/30 H₂/H₂O and CO/CO₂ gas will be at the boundary line between the metallic Fe and FeO line. According to the XRD as shown in Figure 8, it verifies that metallic Fe is produced in H₂ gas. In the mixed gases the metallic phase was not found. The difference in α when all FeO is reduced to Fe is 7% and hence it seems like most of the FeO is reduced to metallic state. Going back to the study of Lobo in Figure 4 again, the difference between H₂ and CO cannot be explained by the difference in reduction potential, as the equilibrium state at this temperature and gas composition will now be metallic for both gas mixtures. Metallic iron was found by XRD for both gas mixtures, however for the H₂ gas experiments the monoxide was MnO and for the CO gas it was (Mn,Fe)O. This also indicate that it is the difference in the iron reduction that separates the extent of reduction.

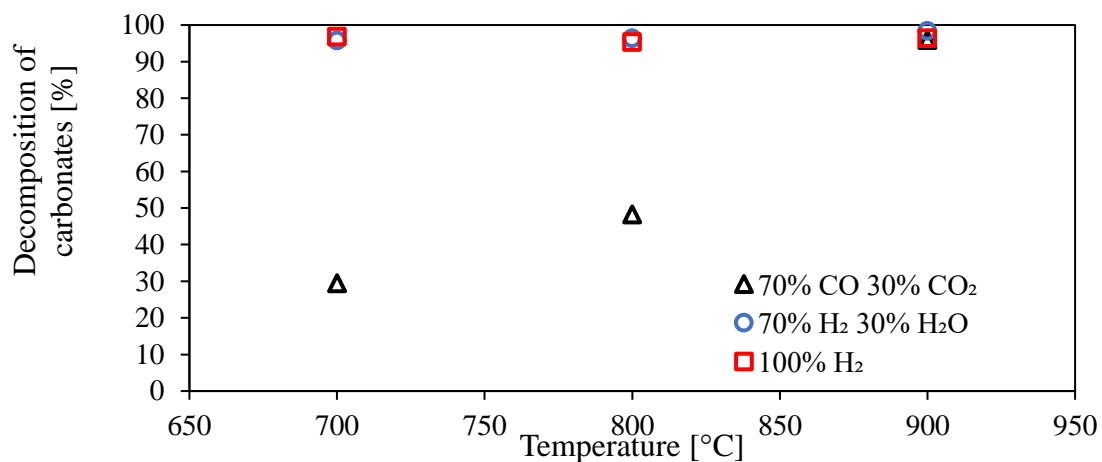


Figure 6. Fraction of the total wt.% of carbonates decomposed in UMK ore as a function of temperature.¹¹

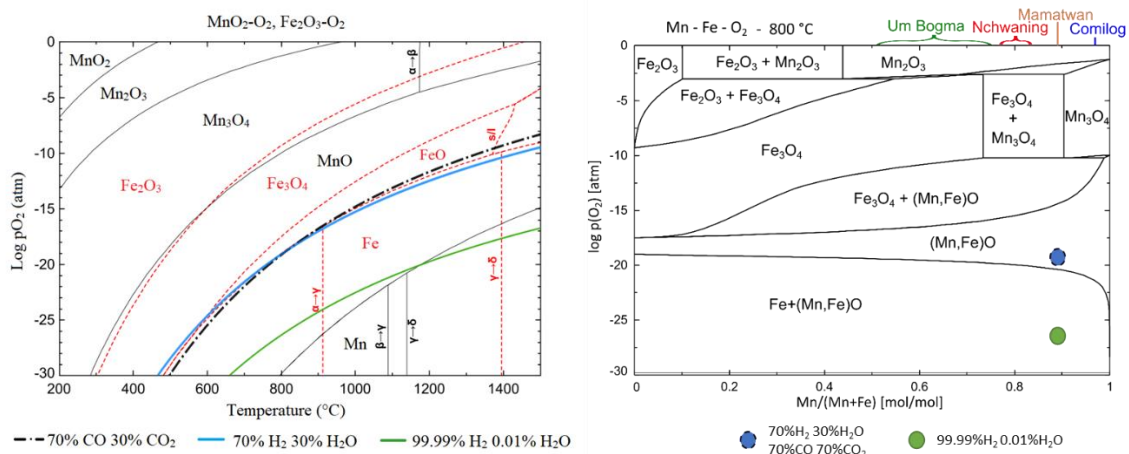


Figure 7. The Fe-O and Mn-O stability diagrams show the stable phases with varying oxygen partial pressure and temperature calculated by Factsage and HSC chemistry. Left show the superimposed Fe-O and Mn-O diagram, and right shows solid solution Fe-Mn-O diagram^{10,11}.

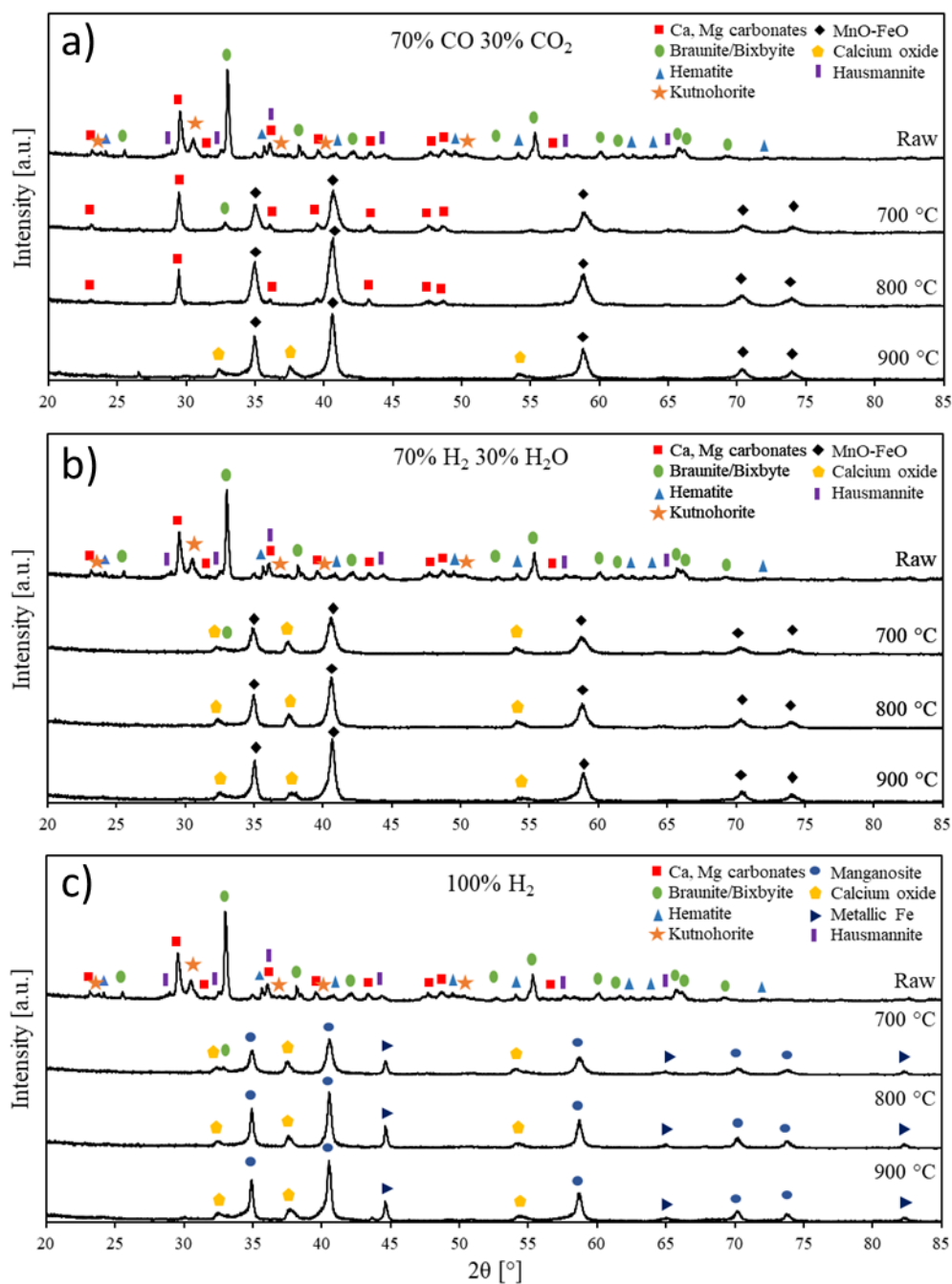


Figure 8. XRD results of the ore and pre-reduced in 70% CO 30% CO₂ (a), 70% H₂ 30% H₂O (b), and 100% H₂ (c) at 700, 800, and 900 °C. Chemical formula of compounds: calcite (CaCO₃); magnesium carbonate (MgCO₃); braunite (3(Mn,Fe)₂O₃·MnSiO₃); bixbyite ((Mn,Fe)₂O₃); hematite (Fe₂O₃); kutnohorite ((Ca,Mn,Mg,Fe)(CO₃)₂); manganosite (MnO); calcium oxide (CaO); hausmannite (Mn₃O₄).¹¹

2.2 Reduction of Mn-ores in H₂-H₂O-CO-CO₂ gases

Ngoy¹² investigated CO-CO₂-H₂ mixtures and compared it with CO-CO₂ mixtures with the same partial pressure of O₂ when in equilibrium, that is the same reduction potential. The samples were heated to 500 °C in CO₂ before the reducing gas was added. Both Comilog and Nchwaning ore was investigated with two oxygen partial pressures. The mass loss is shown in Figure 9. It is seen that the rate is higher in the H₂ containing gases in the low O₂ containing gases, that is Figure 9 a) and c). At higher oxygen pressures, Figure 9 b) and c) the H₂ containing gas reduces the Comilog ore faster. For the Nchwaning ore, the H₂ gas starts the reduction a bit later, however the rate is faster when it has started. This experiment may be an outlier as it does not fit the results in the later work done. In the H₂-containing gas experiments, carbon deposition was seen both visually after the experiment, and

on the weight curve, as shown by the increasing weight for Comilog ore. If carbon deposition occurred during the whole reduction path, it means that the H₂ containing gases will reduce the ore faster than the graph shows.

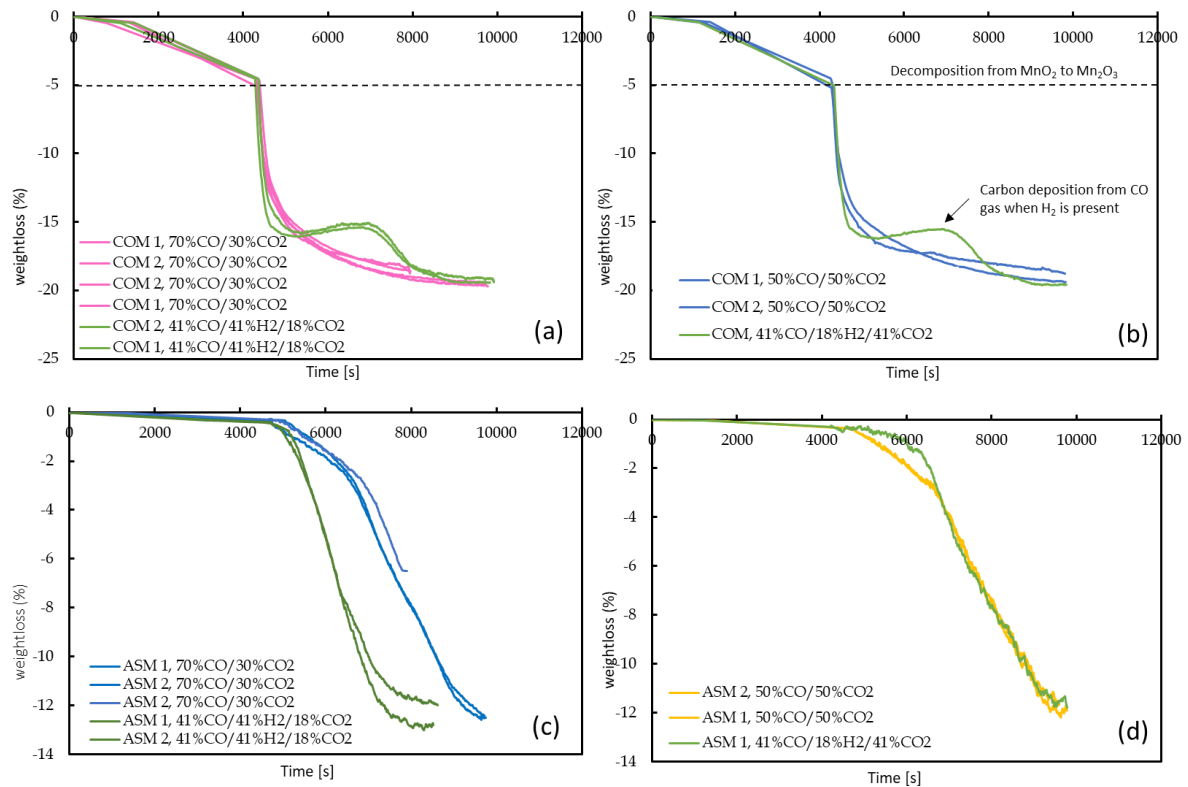


Figure 9. Comparison of mass loss for H₂ containing and H₂ free gas for Comilog (a and b) and Nchwaning ores (c and d). a9 and c) have the same low oxygen pressure and (b) and d) has a higher oxygen pressure in the gas. (Note: In c) the two H₂ containing gas experiments have been shifted in time, to start the reduction at the same time as the H₂ free gases in c).¹²

Larssen⁶ investigated the prerduction of Comilog ore with increasing temperature for two oxygen partial pressures, with and without H₂, as seen in Figure 10. Both for the high oxygen partial pressures experiments, the 50/50% CO/CO₂ and 44/12/44% CO/H₂/CO₂ experiments, and the low oxygen partial pressure experiments, the 80/20% CO/CO₂ and 70/12/18% CO/H₂/CO₂ experiments, the hydrogen has a strong effect on the reduction rate. It was also noted that the C content after the experiments was above 1% for the H₂ containing gas and about 0.2-0.3 in the CO-CO₂ experiments, which again means that carbon was deposited during the experiments, and hence that the real weight loss from the reduction was even higher. In the low oxygen partial pressure experiment, one did not experience the typical temperature peak from high oxygen ores just below 600 °C, where the remaining MnO₂ would decompose to Mn₂O₃⁵. This is explained by the fast reduction due to the low oxygen partial pressure and H₂ being present.

Similar experiments were performed using Nchwaning ore, however they were influenced by carbon deposition⁶. For both oxygen partial pressures, the carbon deposition was initiated above 400 °C. This correlates well with previous reports where carbon deposition is initiated at 400°C for this type of system, and the deposition extent is promoted by an increased CO-concentration in the CO-CO₂ atmosphere⁹. The carbon deposition also increased with increased H₂ pressure as seen by Ngoy et al.¹². Compared to Nchwaning ore, Comilog ore produce more CO₂ during the reduction with CO gas, and carbon deposition occur to a lesser extent.

Schanche^{8,10} investigated the isothermal prerduction for Nchwaning and Comilog ore with and without H₂ present in CO/CO₂ gases as seen in Figure 11 and

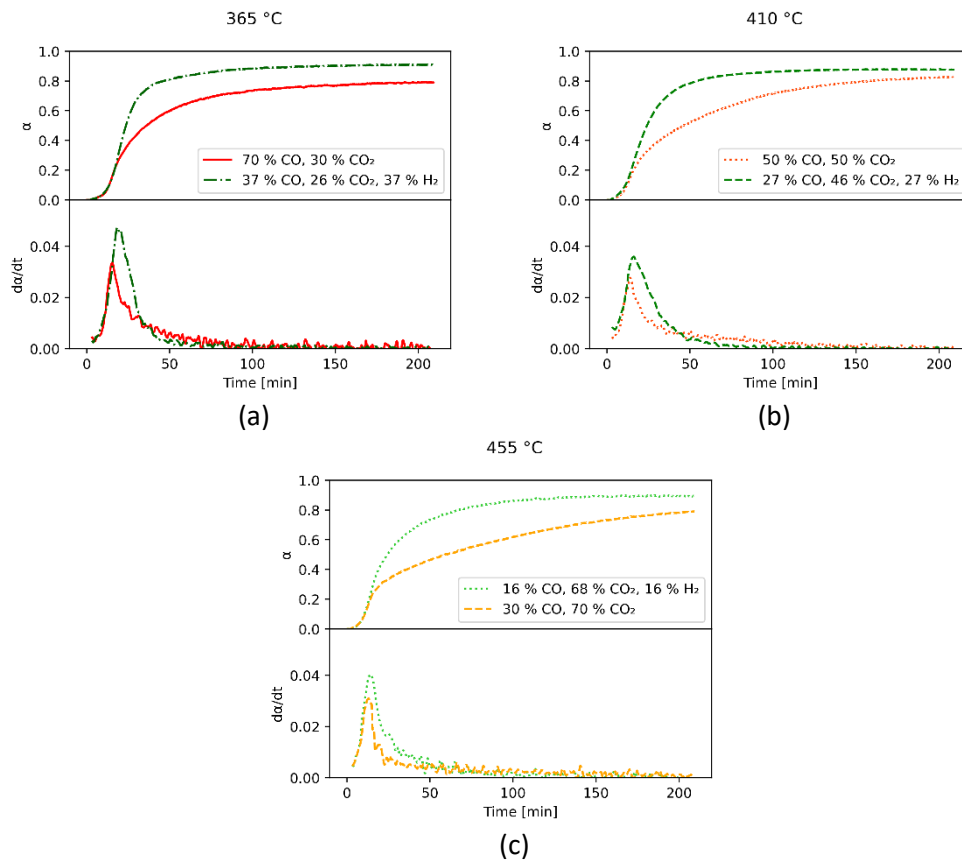


Figure 12. As for previous studies the H₂ added to the CO/CO₂ gases increased the reduction rate, mainly in the area of 30-50%, with the exemption of high oxygen gas mixture and Nchwanging ore, where the H₂ in the gas mixture more than doubled the rate. Ngoy also found in his study that the H₂ in the gas increased the rate with 20-40%.

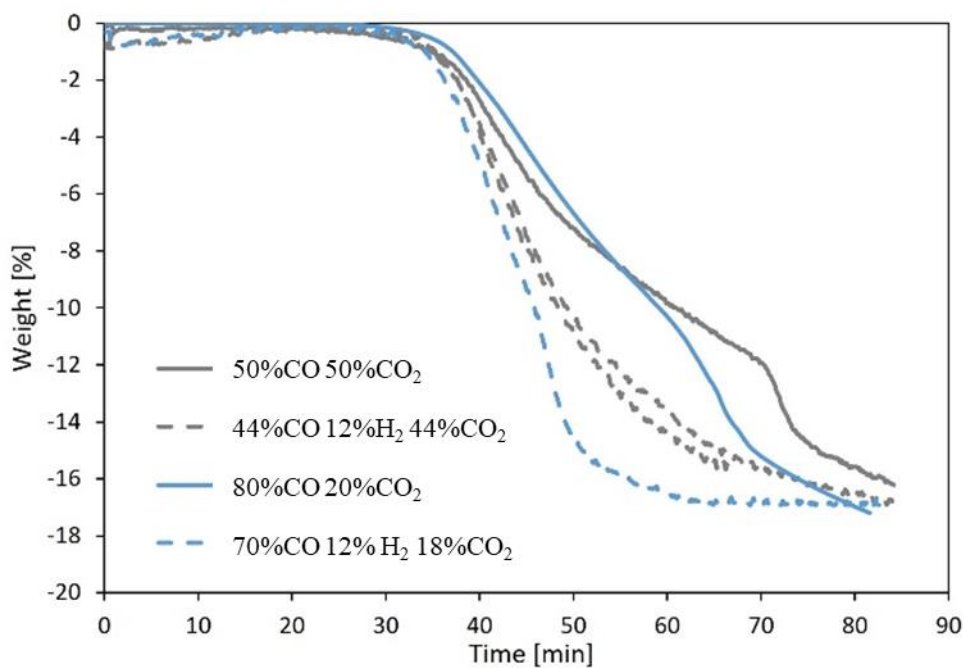


Figure 10. Weight loss for non-isothermal reduction of Comilog with H_2 containing and H_2 -free gas composition, where the grey lines have high oxygen pressure, and the blue lines have low oxygen pressure⁶.

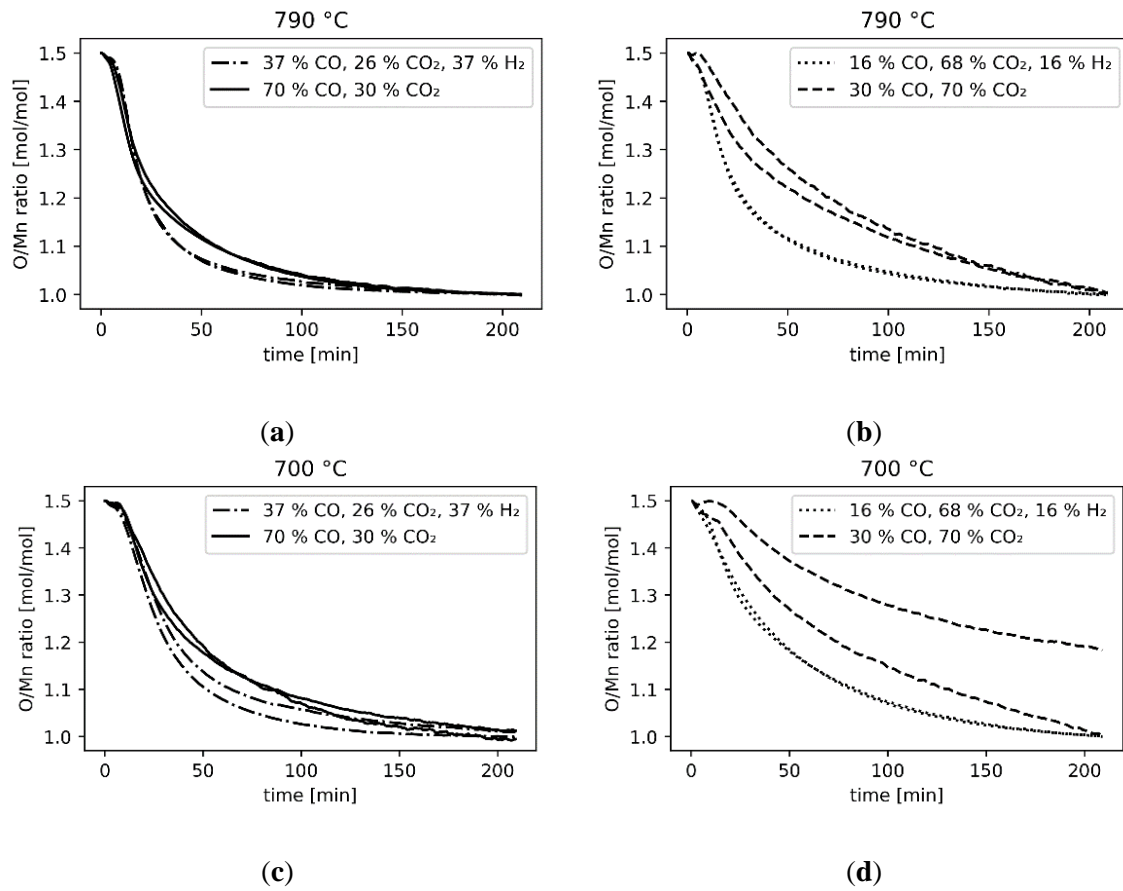
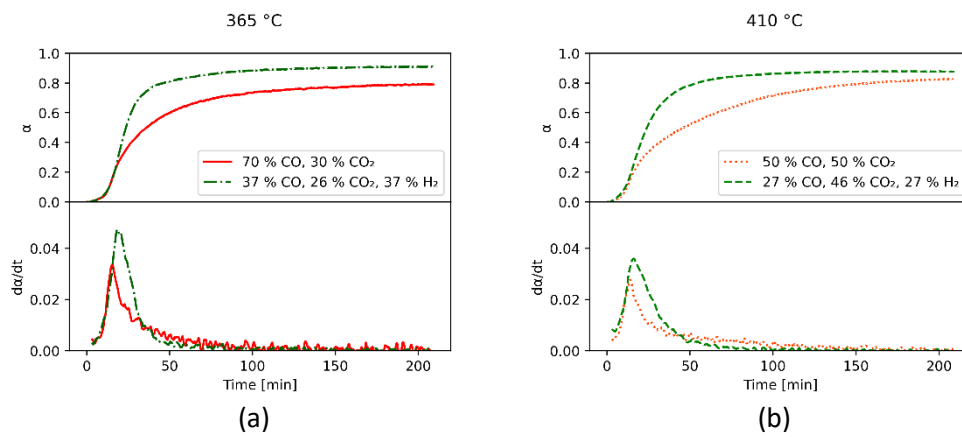


Figure 11. The effect of hydrogen at constant oxygen partial pressure at 790 °C for (a) low p_{O_2} , and (b) high p_{O_2} (Nchwaning ore)¹⁰.



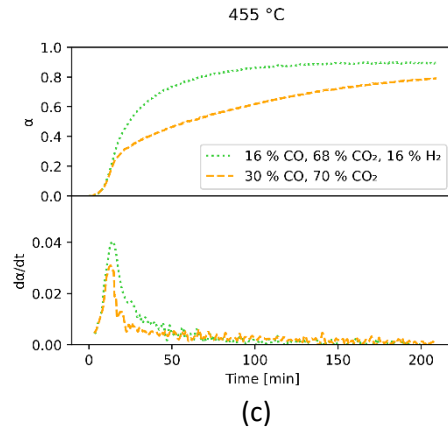


Figure 12 The fractional conversion curves for Comilog ore; (a) - hydrogen free gas mixtures at 410 °C, (b) - hydrogen containing gas mixtures at 410 °C, (c) - low pO_2 at 365 °C, (d) - medium pO_2 at 410 °C, (e) - high pO_2 at 455 °C¹⁰.

The reduction rate can be assumed to be a function of the reduction potential, temperature and the extent of the reaction as well as the presence of H_2 in the reduction gas. Based on this, Schanche¹⁰ modelled the reaction rate according to the following equation.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = k_0 \exp\left(-\frac{E_a}{RT(t)}\right)(1-\alpha)^x. \quad (10)$$

To find the dependency of the gas composition the logarithm of k_0 is plotted as a function of $\ln(1-CO_2)$. The parameters m and k are determined based on the slope and y-intercept of the linear regression between the points as shown in

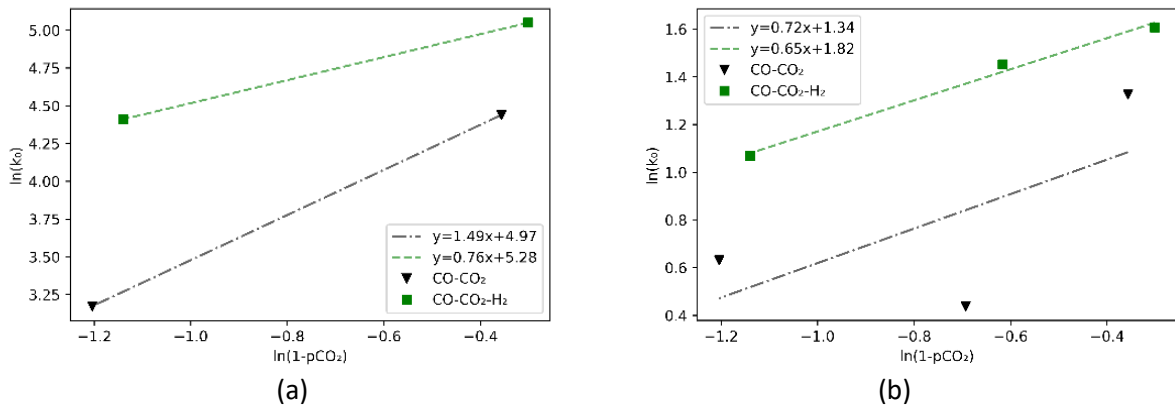


Figure 13. Based on the correlation, the total equation describing the reaction rate is given in equation (10).

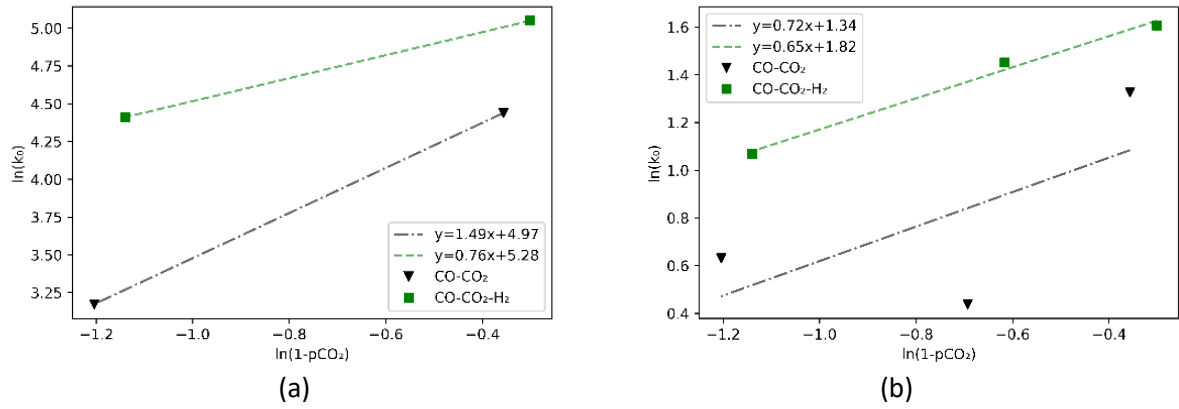


Figure 13: The dependency of reaction rate on gas composition for (a): Nchwani ore and (b): Comilog ore ¹⁰.

$$\frac{d\alpha}{dt} = k \exp\left(-\frac{E_a}{RT(t)}\right) (1-\alpha)^x p_{(1-CO_2)}^m \quad (11)$$

Table 4 contains the kinetic parameters in Schanches work¹⁰. The determined kinetic parameters can be used for reduction of Nchwani and Comilog ore in CO/CO₂ gas mixtures and in CO/CO₂ gas mixtures containing hydrogen where the H₂/CO ratio is 1.

Table 4. Values obtained from modelling of Nchwani and Comilog ore using equation 11. Numbers in parenthesis are excluding the medium pO₂¹⁰

Parameter		Nchwani		Comilog	
		CO/CO ₂	CO/CO ₂ /H ₂	CO/CO ₂	CO/CO ₂ /H ₂
k	Rate constant	75.9	69.4	3.82 (5.05)	6.18
Ea	Activation energy	68.1	68.1	23.2	23.2
x	Reaction order	2	2	2	2
m	Order of 1-CO ₂	1.21	0.38	0.72 (0.82)	0.65

There are a couple of issues when doing experiments with CO-H₂-CO₂ gases assuming the same O₂ partial pressure, that is having the same reduction potential. The first issue is that the same O₂ partial pressure has been calculated based on an assumption that the water-gas-shift (WGS) reaction, reaction (12), is in thermodynamic equilibrium.



It is reported that ^{6,10} the WGS reaction is in equilibrium above 500 °C as seen in Figure 14. As the total amount of oxygen is the same, that is the $\frac{CO+H_2}{CO_2+H_2O}$ ratio is constant in the gas, the reduction potential of the gas is quite constant even if the WGS reaction is not in equilibrium. The second, and more serious issue, is that C is being deposited according to the reverse reaction (5) ($2CO = C + CO_2$), especially when H₂ is present. This could be due to the WGS reaction which will give a higher CO/CO₂-ratio when H₂ is added. On a microscale it could also be due to the reactions (13) and (14), even though the equilibrium CH₄ partial pressure is $5 \cdot 10^{-5} \text{ bar}$ at 800 °C for a 60/20/20 CO/H₂/CO₂ gas. The carbon deposition is determined by kinetics rather than the thermodynamics, and the CH₄ may decompose faster than the reaction rate of the reverse reaction 5 ($2CO = C + CO_2$).



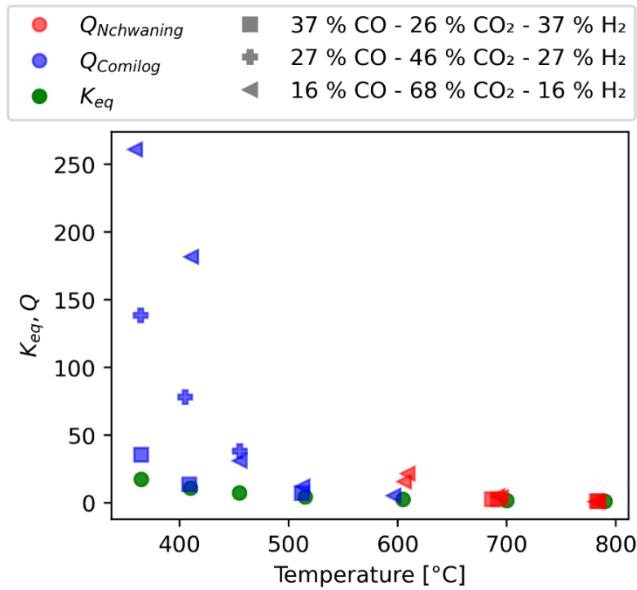


Figure 14. Shows the reaction quotients (Q) from the final gas composition of the hydrogen containing experiments and the equilibrium constant, K_{eq} , from the water gas shift reaction, as a function of temperature. The equilibrium constants were calculated using HSC Chemistry¹⁰.

To summarize the impact of H_2 in CO/CO₂ mixtures, it is generally seen that H_2 will increase the reduction rate for the same reduction potential, that is the same or similar O_2 partial pressure. This is believed to be due to the mass transfer in the gas phase. As seen in Figure 15, the diffusion coefficient of H_2 in CO₂ is many times higher than the diffusion coefficient of CO in CO₂ and may hence explain the increased reaction rate. It has been shown in all the discussed studies that the pre-reduction of Mn-ores are not in equilibrium and hence the increased mass transfer with H_2 will increase the reaction rate.

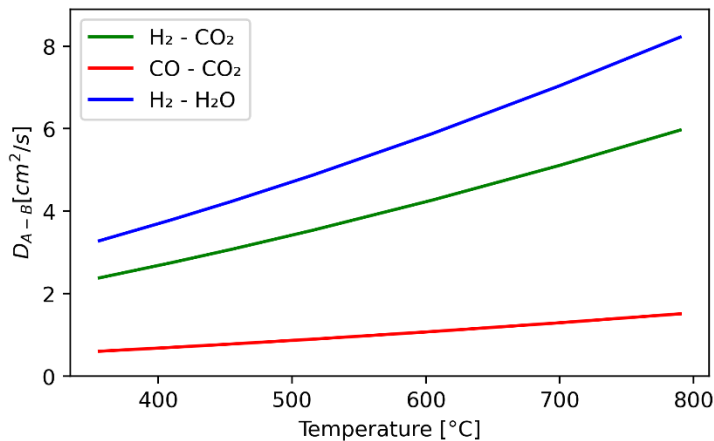


Figure 15. The calculated binary diffusion coefficients for H_2-H_2O , H_2-CO_2 and $CO-CO_2$ ¹⁰

As a final short-point it can be mentioned that the decrepitation during reduction in H_2 containing gases has not changed compared to H_2 free gases¹⁰.

3 CONCLUSION

Today, solid carbon is used to partly pre-reduce the Mn-ores in the production of Mn-ferroalloys. The solid carbon can be substituted with H_2 and hence reduce the environmental footprint. In 4 studies it is shown that the H_2 containing gases will give higher reduction rate compared to CO/CO₂ gases with the same reduction potential. The reduction rate will be increased in the order of 20-100%, where H_2 has a larger impact on reduction rate for high oxygen pressures. In H_2 gas it is seen that the final degree of reduction is higher than using CO gas, and this

is believed to be due to the formation of metallic iron. The reduction rate in H₂ gases varies for various ores, and as for CO containing gases, the reduction rate of Comilog ore is faster than the Nchwaning ore, and activation energies of 23 kJ/mol versus 68 kJ/mol is respectively found for isothermal experiments. For the carbonate UMK ore, the presence of CO₂ in the gas, reduces the decomposition rate of the carbonate.

4 Acknowledgement

The Norwegian Research Council and the Norwegian ferroalloy industry is acknowledged through the SFI Metal production (237738), the Thanos project (309475), the Reduced CO₂-project (280968), FME High Eff (257632) and Gasferrosil (224950). Stephen Lobo is acknowledged for agreeing to include unpublished work regarding prereduction of Mn-ores.

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