# Pre-reduction Behaviour of Manganese Ores in $H_2$ and CO Containing Gases

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This paper presents results of a study conducted on the pre-reduction of Assmang and Comilog ores with gases of CO+CO $_2$  and CO+H $_2$ +CO $_2$  up to 1 000°C. Non-isothermal experiments were carried out in a vertical thermogravimetric tube furnace. Four different gas mixtures were considered. That is, gas mixtures of 50%CO/50%CO $_2$ , 41%CO/18%H $_2$ /41%CO $_2$  and gas mixtures of 70%CO/30%CO $_2$ , 41%CO/41%H $_2$ /18%CO $_2$  whose CO/CO $_2$  ratio is respectively of 1/1 and 2.3/1. The ore and reduced samples were characterized by X-ray fluorescence technique followed by a scanning electron microscopy analysis. The extent of reduction was considered based on the recorded weight loss together with the chemical analyses done on the processed samples. It was found that for the same oxygen pressure, the highest reduction rate was achieved when hydrogen was present in the gas mixture. Results also showed that when the oxygen pressure of the gas mixture was lower, the reduction rate was the highest as expected.

KEY WORDS: pre-reduction; higher oxides of manganese; reduction rate.

# 1. Introduction

With an estimated world production of 17 million tons in 2018,<sup>1)</sup> manganese ores have been widely used in many fields, such as the steel industry and in medicine. Most of manganese alloys produced globally is used in the steel industry,<sup>2–7)</sup> while only about 6% of manganese ore is worldwide used to produce special metallurgical and chemical products. Management of the energy consumption in manganese alloys has become of primary importance to ensure the competitiveness of the industry as well as the minimization of environmental impacts, such as the greenhouse gas emissions.

The conventional method for industrially producing manganese ferroalloys involves the smelting of raw materials, *i.e.* manganese ores, flux agents and metallurgical coke as reducing agent in blast or electric arc furnaces where the pre-reduction of higher manganese oxides is customary done by means of CO gas generated in the high temperature zone of the furnace.<sup>8–12)</sup> Two reaction zones are distinguished in the submerged arc furnace, the pre-reduction zone where the present study is focused and the coke bed zone. Manganese bearing minerals containing higher manganese oxides, namely MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> are found in the pre-reduction zone and are reduced to MnO in solid state in the presence of CO. Their pre-reduction proceeds *via* the following reactions:

$$2 \operatorname{MnO}_{2(s)} + \operatorname{CO}_{(g)} = \operatorname{Mn}_2 \operatorname{O}_{3(s)} + \operatorname{CO}_{2(g)}, \dots \dots \dots \dots (1)$$

$$3\ Mn_2O_{3(s)}+CO_{(g)}=2\ Mn_3O_{4(s)}+CO_{2(g)},\ ........(2)$$

$$Mn_3O_{4(s)} + CO_{(g)} = 3 MnO_{(s)} + CO_{2(g)}, \dots (3)$$

It is well known that the reduction of higher manganese oxides is exothermic and release energy. <sup>9,13,14)</sup> However, if the Mn<sub>3</sub>O<sub>4</sub> reactivity of the raw material is slow, this oxide will still be present even at temperatures (above 800°C) where the Boudouard reaction is significant in the furnace. Thus, the reduction mechanism for Mn<sub>3</sub>O<sub>4</sub> will be reduced as follow:

$$Mn_3O_{4(s)} + CO_{(g)} = 3 MnO_{(s)} + CO_{2(g)}, \dots (4)$$

$$C_{(s)} + CO_{2(g)} = 2 CO_{(g)}, \dots (5)$$

$$Mn_3O_{4(s)} + C_{(s)} = 3 MnO_{(s)} + CO_{(g)}, .....(6)$$

This overall reaction (6) is endothermic and therefore increases the consumption of energy and carbon during the process

Hydrogen gas can also be used to reduce higher manganese oxides, according to the following reactions:

$$2 \text{ MnO}_{2(s)} + H_{2(g)} = \text{Mn}_2 O_{3(s)} + H_2 O_{(g)}$$
 ......(7)

$$3 Mn_2O_{3(s)} + H_{2(g)} = 2Mn_3O_{4(s)} + H_2O_{(g)}$$
 ......(8)

$$Mn_3O_{4(s)} + H_{2(g)} = 3MnO_{(s)} + H_2O_{(g)}$$
 .....(9)



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Various studies conducted on the reduction of manganese ores have demonstrated that CO and H<sub>2</sub> alone are unable to reduce MnO in the solid state under normal working conditions. <sup>2,3,8,15–19)</sup> The total reduction down to Mn metal must hence be performed with solid carbon.

The metal is produced by reactions that take place in the coke bed zone and one of the reaction products is CO gas which is then utilized in the pre-reduction zone, making the whole process a source of CO<sub>2</sub> emission. <sup>11,21)</sup> The reduction of MnO to Mn metal is given by the following reaction:

$$MnO_{(s)} + C_{(s)} = Mn_{(l)} + CO_{(g)}$$
 .....(10)

Iron is a typical constituent of manganese ores, therefore all the higher iron oxides present in the ore will be completely reduced to its metallic form<sup>9)</sup> according to the overall reaction (11)

$$Fe_2O_{3(s)} + 3CO_{(g)} = 2Fe_{(s)} + 3CO_{2(g)}$$
 ......(11)

It is important to point out that the use of CO gas as direct reductant for manganese ores lies in the need to remove the product gas, CO<sub>2</sub>. This has been considered by most researchers as they agree on the fact that the rate of reduction for the higher manganese oxides (MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>) is a process that is mix-controlled by the chemical reaction and diffusion of CO<sub>2</sub> through the product layer.<sup>22)</sup>

Thus, before producing the alloy itself, manganese ores are first subjected to the pre-reduction step of all higher manganese oxides to the formation of MnO. This step is important since it directly affects the energy and carbon consumption of the overall process. 5,11,23,24)

Ishak and Tangstad investigated the degree of pre-reduction without coke consumption of different manganese ores in CO gas. 11) It has been found that the coke and energy consumptions decrease at higher degree of pre-reduction. This was illustrated with manganese ores such as Comilog and BHP for their high CO reactivity as well as their high oxygen content.

The pre-reduction of manganese ores and manganese oxide using hydrogen gas has also been studied. Ostrovski and colleagues have investigated the non-isothermal reduction of  $MnO_2$  in a gas mixture of  $Ar-H_2$  with 20 vol% $H_2$  and 80 vol%Ar from 200 to 900°C, they found that the reduction of pure  $MnO_2$  started at 305–320°C and complete reduction of  $MnO_2$  to MnO was achieved at 610–620°C with no further reduction with further increase in temperature. <sup>8)</sup> This was however done powder and not on particles.

The reduction kinetics of a synthetic manganese dioxide by hydrogen has been investigated by Barner and Mantell. <sup>14)</sup> This reduction was studied in the temperature range of 200 to 500°C at different hydrogen partial pressures. Particles of size ranging from 0.07 to 0.21 mm as well as compressed pellets of 1.5 g were reduced respectively in 100%H<sub>2</sub>, 24.9%H<sub>2</sub>/75.1%He and 9.7%H<sub>2</sub>/91.3%He. It was found that below 250°C a product of approximately 90% of Mn<sub>3</sub>O<sub>4</sub>

could be obtained. They also reported that the reduction kinetics of a Belgian Congo pyrolusite ore was considerably faster than the synthetic sample.

Elliott and colleagues<sup>4)</sup> reported in their recent review experimental observations from an investigation conducted on a low-grade manganese ore using hydrogen as reducing agent in the temperature range of 800 to 950°C that an increase in H<sub>2</sub> partial pressure and temperature improved the reduction rate. No reduction beyond the formation of MnO was observed. In the same review, another investigation conducted on high manganese containing iron ores stated that all the higher manganese oxides were reduced to MnO.

The present experimental study focused on the pre-reduction kinetics of Assmang and Comilog ores in non-isothermal conditions by gaseous CO-rich mixtures. Influence of H<sub>2</sub> on the reaction mechanism, rate and extent of reduction as well as its impact on the carbon and energy consumption were investigated too. Thus, the results acquired in this work are aiming to increase the basic knowledge of manganese ores pre-reduction by complex gas mixtures containing CO-CO<sub>2</sub>-H<sub>2</sub>.

# 2. Experimental

#### 2.1. Material Characterisations

The manganese ores investigated are South African Assmang ore and Comilog ore from Gabon. The lumpy materials were crushed to a size ranging from 9.52 to 16 mm. The chemical analyses of the raw materials (and pre-reduced samples) were done using the Bruker AXS S4 Pioneer X-Ray fluorescence spectrometer allowing direct elemental analysis which thereafter is converted to oxides. The concentration of MnO<sub>2</sub> in the sample was analysed by using a modified standard test method for determination of manganese (IV) by redox titrimetry ASTM E465-11, test method with sodium oxalate. The loss on ignition of the sample was determined by heating up the sample to 950°C in an oven and holding it for one hour at that temperature. The chemical analyses of the ores studied are given in **Table 1** below:

Based on the chemical composition of the starting materials, Assmang ore has a calculated MnOx of 1.56 and therefore considered to be predominantly constituted by

Table 2. Calculated mass loss for Assmang and Comilog ores.

Material	Asm Ore	Com Ore
Weight in (g)	100	100
Weight loss drying (g)	0.03	0.47
Weight loss L.O.I (g)	3.97	12.2
Weight loss Mn <sub>3</sub> O <sub>4</sub> to MnO (g)	4.68	5.27
Weight loss Fe <sub>2</sub> O <sub>3</sub> reduction to Fe (g)	3.48	0.72
Weight change (g)	12.1	18.2
Weight change (%)	12.1	18.2

Table 1. Chemical composition of ores measured by XRF (wt%).

	Mn <sub>tot</sub>	MnO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	BaO	H <sub>2</sub> O	L.O.I	[MnOx]
ASM	48.5	40.2	29.8	11.6	4.98	0.02	0.55	1.16	6.69	0.42	0.03	3.97	1.56
COM	51.8	76.7	4.27	2.39	5.69	0.10	5.44	0.08	0.19	0.19	0.47	12.2	1.94

Mn<sub>2</sub>O<sub>3</sub>. On the other hand, Comilog ore shows a x equals to 1.94 which is assumed to be mostly constituted by MnO<sub>2</sub>. This is also confirmed by previous mineralogical analyses conducted by Visser and colleagues.<sup>3)</sup>

The calculated mass loss corresponding to complete pre-reduction was based on the following assumptions: all higher iron oxides will be reduced to metallic iron, all higher manganese oxides will be reduced to MnO. All carbonates will be decomposed, the water will be evaporated. The L.O.I is assumed to be the total loss down to Mn<sub>3</sub>O<sub>4</sub>.

It should be noted that for each experiment the sample was measured before and after reduction.

### 2.2. Experimental Set Up

To initiate the reduction, the reducing gas CO/CO<sub>2</sub> or CO/H<sub>2</sub>/CO<sub>2</sub> was blown through the charge at a constant flow rate until the set temperature was reached, the charge was then cooled in argon atmosphere to avoid the re-oxidation of the processed samples. The sample was heated with at a nominal rate of 6.8°C per minute throughout the process. The following table below summarizes the experimental conditions in all experiments. Notice that all experiments have replicas.

From this table it can be seen that all experiments have been done in such a way that from room temperature up to  $500^{\circ}$ C the gas atmosphere inside the furnace was 100%CO<sub>2</sub> and from  $500^{\circ}$ C to  $1~000^{\circ}$ C the different gas mixtures were used. This to the ends of preventing the carbon deposition that could occur as a result of the reverse Boudouard reaction up to  $500^{\circ}$ C when  $H_2$  is used. It is also important to notice that the reduction process is a non-isothermal process, this to simulate the industrial pre-reduction process.

**Figure 1** shows different oxygen pressures according to each gas mixtures used during experiments. The reduction process has been carried out in a vertical thermogravimetric tube furnace that can record the weight change in the course of the experiment. Its maximum temperature is 1 250°C. The figure below shows the schematic of the crucible as well as the balance set up:

During the reduction process, the reducing gas is blown into the crucible from the top into the double-walled crucible wall to be heated before it enters the charge from the bottom, see Fig. 2(A). During the experiments, a computer connected to the furnace records automatically the weight change, time, crucible temperature as well as the gas flow.

#### 3. Results and Discusion

When plotting reduction curves, it was assumed that any loss of weight is counted negative while any gain of weight is positive, whereas the reduction rate curves calculated by differential of the mass loss curves.

# 3.1. Reduction of Assmang Ore in Different Gas Mixtures

**Figures 3** and **4** show the mass loss of Assmang ore as function of temperature and time achieved at 1 000°C respectively in various gas mixtures, with the horizontal dotted line representing the calculated theoretical mass loss. The first part of each reduction curve is flat within the

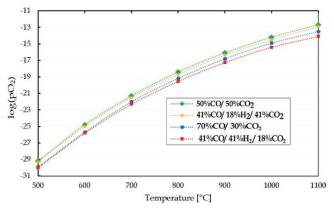


Fig. 1. The logarithm of partial pressure of O<sub>2</sub> for various gas mixtures, 50%CO/50%CO<sub>2</sub> and 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>, 70%CO/30%CO<sub>2</sub> and 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub> used during experiments (HSC9). (Online version in color.)

**Table 3.** Overview of gas atmospheres, temperatures and ores used.

Exp1, Exp3 Exp2, Exp4	25–500°C 0.85CO <sub>2</sub> 0.85CO <sub>2</sub>	500-1 000°C 2CO+0.85CO <sub>2</sub>	1 000–25°C 1 Ar	Ore ASM
Exp2, Exp4	-	2CO+0.85CO <sub>2</sub>	1 Ar	ASM
1 / 1	0.85CO <sub>2</sub>			ASIVI
F 5 F 7	0.02002	$2\mathrm{CO} + 0.85\mathrm{CO}_2$	1 Ar	COM
Exp5, Exp7	$0.85\mathrm{CO}_2$	$2\text{CO} + 0.85\text{CO}_2 + 2\text{H}_2$	1 Ar	ASM
Exp6, Exp8	$0.85\mathrm{CO}_2$	$2\text{CO} + 0.85\text{CO}_2 + 2\text{H}_2$	1 Ar	COM
Exp9, Exp11	$0.85\mathrm{CO}_2$	$2\text{CO} + 2\text{CO}_2$	1 Ar	ASM
Exp10, Exp12	$0.85\mathrm{CO}_2$	$2\text{CO} + 2\text{CO}_2$	1 Ar	COM
Exp13, Exp15	$0.85\mathrm{CO}_2$	$2\text{CO} + 2\text{CO}_2 + 0.85\text{H}_2$	1 Ar	ASM
Exp14, Exp16	$0.85\mathrm{CO}_2$	$2\text{CO} + 2\text{CO}_2 + 0.85\text{H}_2$	1 Ar	COM
	25-500°C	500-800°C	800–25°C	
Exp3a	0.85CO <sub>2</sub>	2CO+0.85CO <sub>2</sub>	1 Ar	ASM
Exp2a	$0.85\mathrm{CO}_2$	$2\mathrm{CO} + 0.85\mathrm{CO}_2$	1 Ar	COM
Expla	$0.85\mathrm{CO}_2$	$2\text{CO} + 2\text{CO}_2$	1 Ar	ASM
Exp4a	$0.85\mathrm{CO}_2$	$2\text{CO} + 0.85\text{CO}_2 + 2\text{H}_2$	1 Ar	COM
	Exp9, Exp11 Exp10, Exp12 Exp13, Exp15 Exp14, Exp16  Exp3a Exp2a Exp1a	Exp6, Exp8	Exp6, Exp8	Exp6, Exp8         0.85CO2         2CO+0.85CO2+2H2         1 Ar           Exp9, Exp11         0.85CO2         2CO+2CO2         1 Ar           Exp10, Exp12         0.85CO2         2CO+2CO2         1 Ar           Exp13, Exp15         0.85CO2         2CO+2CO2+0.85H2         1 Ar           Exp14, Exp16         0.85CO2         2CO+2CO2+0.85H2         1 Ar           Exp3a         0.85CO2         2CO+0.85CO2         1 Ar           Exp2a         0.85CO2         2CO+0.85CO2         1 Ar           Exp1a         0.85CO2         2CO+0.85CO2         1 Ar           Exp1a         0.85CO2         2CO+2CO2         1 Ar

region from room temperature to 500°C because within this temperature range only evaporation of the water content and insignificant thermal decomposition of manganese dioxide occur as the theory stipulates. <sup>4,8)</sup> In the course of reduction above 500°C, the ore shows a similar behaviour in different gas mixtures, which is the increase in mass loss with the increase of temperature. Figures 3 and 4 indicate also that the highest mass loss was achieved for the gas mixtures with 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. At the end of the experiments conducted up to 1 000°C all samples are reduced to MnO with the exemption of experiment 13, which contains a very small amount of Mn<sub>3</sub>O<sub>4</sub> expressed as MnO<sub>2</sub> (see chemical analyses). This is shown in the chemical analyses of the

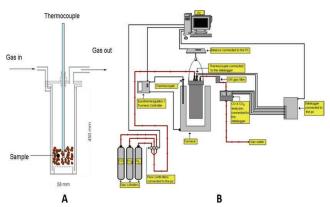


Fig. 2. Schematic drawing of (A) the crucible including thermocouple, gas flow, and charge and (B) the thermobalance setup. (Online version in color.)

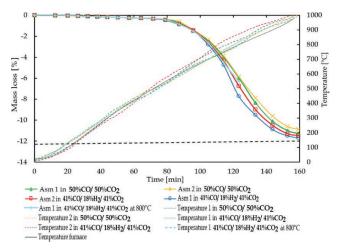
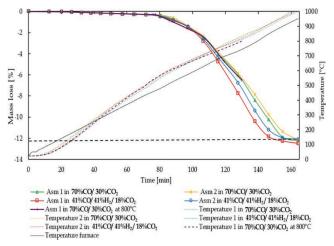


Fig. 3. Mass loss curves of Assmang ore as function of temperature in 50%CO/50%CO<sub>2</sub> vs 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>. (Online version in color.)

reduced samples which are given in Tables 4 and 5.

Tables 4 and 5 show the chemical analyses of Assmang ore reduced up to 1 000°C and 800°C respectively in gas mixtures of 50%CO/50%CO<sub>2</sub>, 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub> and 70%CO/30%CO<sub>2</sub>, 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. The content of MnO<sub>2</sub> in these samples shows that all the higher manganese oxides had been reduced to MnO regardless of the gas mixture composition. This means that with or without hydrogen in the reducing gas mixture, the reduction was complete at 1 000°C.

Figures 5 and 6 show the reduction rate of Assmang ore in gas mixtures containing 50%CO/50%CO<sub>2</sub>, 41%CO/ 18%H<sub>2</sub>/41%CO<sub>2</sub> and 70%CO/30%CO<sub>2</sub>, 41%CO/41%H<sub>2</sub>/ 18%CO<sub>2</sub> respectively. The real temperature in the sample is also shown. It can be mentioned that the temperatures will also be affected by the exothermic reactions. It can be observed from Figs. 5 and 6 that the reduction rate was faster in the gas mixture with hydrogen than without it. For all experiments conducted the 73rd minute of the reduction process corresponds to the time when the reducing gas is introduced into the furnace. It was found that at 120th minute which is half the reduction time for the gas mixtures containing 50%CO/50%CO<sub>2</sub> and 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>, the amount of the removable oxygen reduced was 41% and 51.2% respectively. The difference is accounted for hydrogen which was present in one of the gas mixtures. The same observation was made when looking at Fig. 6, the presence of hydrogen in the gas mixture improved the reduction rate, with respectively 44% and 56% of the removable oxygen reduced by the gas mixture without and with hydrogen in it. This fact



**Fig. 4.** Mass loss curves of Assmang ore as function of temperature in 70%CO/30%CO<sub>2</sub> vs 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. (Online version in color.)

**Table 4.** Analyses of reduced samples for experiments 9, 11 and 1a in 50%CO/50%CO<sub>2</sub> and experiments 13 and 15 in 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub> gases.

		T [°C]	Mn <sub>tot</sub>	MnO <sub>2</sub>	MnO	Fe <sub>tot</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	[MnOx]
	Exp 9	1 000	54.2	< 0.05	70.0	7.62	6.10	0.54	1.40	7.83	1.00
ASM	Exp 11	1 000	55.1	< 0.05	71.1	7.16	5.79	0.54	0.89	8.32	1.00
	Exp 1a	800	50.7	6.87	60.0	9.54	6.05	0.86	0.82	6.66	1.11
ACM	Exp 13	1 000	53.2	2.76	68.7	7.94	5.33	0.53	1.03	8.39	1.04
ASM	Exp 15	1 000	52.9	< 0.05	68.3	8.25	6.38	0.89	1.81	8.82	1.00

Table 5. Analyses of reduced samples for experiments 1, 3 and 3a in 70%CO/30%CO<sub>2</sub> and experiments 5 and 7 in 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub> gases.

		T [°C]	Mn <sub>tot</sub>	MnO <sub>2</sub>	MnO	Fe <sub>tot</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	[MnOx]
	Exp 1	1 000	53.7	< 0.05	69.3	8.67	6.36	0.47	1.02	8.46	1.00
ASM	Exp 3	1 000	52.3	< 0.05	67.5	8.56	7.05	0.49	2.05	8.68	1.00
	Exp 3a	800	51.3	7.52	60.1	9.20	5.85	0.66	1.12	6.84	1.11
A CN (	Exp 5	1 000	53.4	< 0.05	68.9	9.68	5.79	0.94	1.34	6.83	1.00
ASM	Exp 7	1 000	50.2	< 0.05	64.8	9.85	4.04	0.81	1.83	10.6	1.00

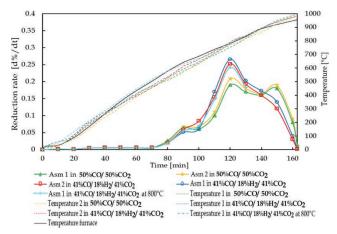
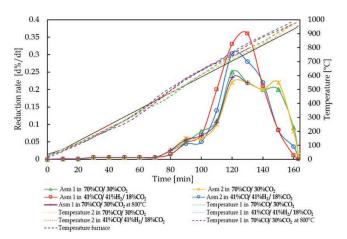


Fig. 5. Reduction rate of Assmang ore as a function of time and temperature in 50%CO/50%CO<sub>2</sub> and 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>. (Online version in color.)



**Fig. 6.** Reduction rate of Assmang ore as a function of time and temperature in 70%CO/30%CO<sub>2</sub> 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. (Online version in color.)

indicates clearly how in the similar oxygen partial pressure hydrogen affects the reduction rate and is in agreement with the findings of De Bruijn and colleagues<sup>15)</sup> and Kononov and colleagues<sup>22)</sup> who conclued that the presence of hydrogen in the gas mixture during the gaseous reduction of manganese improved the reduction rate. It can also be seen that the reduction rate increases with about 20% when the oxygen pressure is reduced with a factor of 10 as seen in Figs. 5 versus 6.

# 3.2. Reduction of Comilog Ore in Different Gas Mixtures

**Figures 7** and **8** show the mass loss behavior of Comilog ore as function of temperature and time achieved at specific

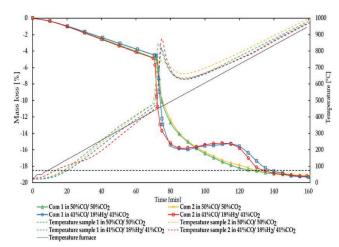


Fig. 7. Mass loss curves of Comilog ore as function of temperature in 50%CO/50%CO<sub>2</sub> vs 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>. (Online version in color.)

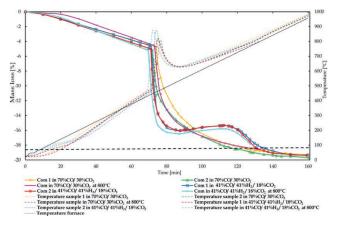


Fig. 8. Mass loss curves of Comilog ore as function of temperature in 70%CO/30%CO<sub>2</sub> vs 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. (Online version in color.)

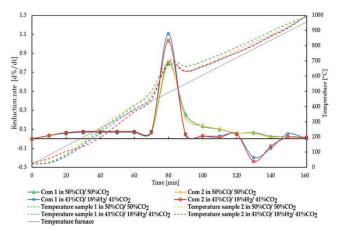
temperatures 1 000°C and 800°C in various gas mixtures. It can be observed that the recorded mass loss falls in the expected area of 18.2%. However, Comilog ore presents curves whose shape are quite particular in that the temperature inside the crucible increased significantly in a short period of time instantly when the reducing gas was introduced into the furnace as a result of its exothermic nature. However, experiments conducted with reducing gas mixtures containing hydrogen revealed an increase in weight from 90th minute to about 115th minute, this is due to the carbon precipitation which is in turn consumed as the reduction continued taking place. The chemical compositions of the reduced samples are listed in **Tables 6** and **7**:

**Table 6.** Analyses of reduced samples for experiments 10 and 12 in 50%CO/50%CO<sub>2</sub> and experiments 14 and 16 in 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub> gases.

		T [°C]	Mn <sub>tot</sub>	MnO <sub>2</sub>	MnO	Fe <sub>tot</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	[MnOx]
COM	Exp 10	1 000	66.4	5.53	81.2	2.95	5.07	4.75	0.09	0.08	1.06
COM	Exp 12	1 000	65.6	5.01	80.6	3.11	5.30	4.81	0.06	0.16	1.06
COM	Exp 14	1 000	65.2	4.73	80.3	2.85	5.94	5.36	0.11	0.14	1.06
COM	Exp 16	1 000	66.2	5.22	81.0	2.79	5.14	5.36 5.11	0.08	0.12	1.06

**Table 7.** Analyses of reduced samples for experiments 2,4 and 2a in 70%CO/30%CO<sub>2</sub> and experiments 6,8 and 4a in 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub> gases.

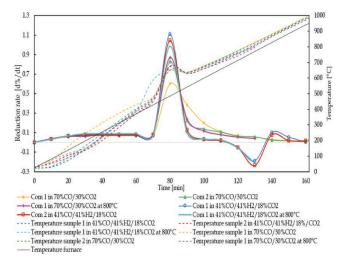
		T [°C]	$Mn_{\text{tot}}$	$MnO_2$	MnO	$Fe_{tot} \\$	$SiO_2$	$Al_2O_3$	MgO	CaO	[MnOx]
	Exp 2	1 000	67.5	7.27	81.2	2.95	4.66	5.08	0.09	0.08	1.08
COM	Exp 4	1 000	65.3	4.56	80.6	3.24	4.30	5.81	0.06	0.16	1.05
	Exp 2a	800	64.8	10.2	75.2	2.57	3.53	4.83	0.02	0.40	1.12
	Exp 6	1 000	61.9	3.26	78.9	2.85	5.94	7.18	0.36	0.17	1.04
COM	Exp 8	1 000	63.1	2.98	80.6	3.06	5.08	6.07	0.29	0.10	1.04
	Exp 4a	800	63.7	9.96	74.1	2.72	4.92	6.34	0.05	0.08	1.12



**Fig. 9.** Reduction rate of Comilog ore as a function of temperature in 50%CO/50%CO<sub>2</sub> and 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub>. (Online version in color.)

Tables 6 and 7 show the chemical composition of reduced Comilog ore in different gas mixtures. The MnO<sub>2</sub> content of the samples means that the reduction of manganese oxides was not complete even though the recorded mass loss curves and the net mass loss indicates a full reduction. As industrial materials are used, and can be somewhat inhomogeneous, one will however expect some deviation on the total mass loss.

**Figures 9** and **10** show the reduction rate of Comilog ore for gas mixtures containing 50%CO/50%CO<sub>2</sub>, 41%CO/18%H<sub>2</sub>/41%CO<sub>2</sub> and 70%CO/30%CO<sub>2</sub>, 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub> respectively. It can be seen that the reduction rate with hydrogen in the gas mixture is higher in the very first stage of reduction when the reducing gase is introduced into the furnace and after approximately 20 min of reduction the most part of the higher manganese oxides is reduced. One can also point out that with hydrogen present in the reducing gas, the reduction rate is the highest. Moreover, as previously stated when the oxygen pressure of the reducing gas is lower, the reduction rate is higher. This fact agrees with the work of Yastreboff and colleagues, <sup>25)</sup> they concluded that the reduction rate of MnO reduction in



**Fig. 10.** Reduction rate of Comilog ore as a function of temperature in 70%CO/30%CO<sub>2</sub> and 41%CO/41%H<sub>2</sub>/18%CO<sub>2</sub>. (Online version in color.)

Ar–CO gas increased with decreasing CO partial pressure. The reason why the reduction rate reached negative values is the evidence of carbon precipitation mentioned earlier on.

With the aim to investigate the carbon consumption, some experiments were conducted and were intentionally stopped at 800°C. This temperature is important from an industrial viewpoint, because in this condition the Boudouard reaction becomes favourable in the presence of carbon causing its consumption in industrial furnaces employed for ferromanganese production. Any oxygen left at about 800°C will react with coke increasing the energy and carbon consumption as a result.

Though Comilog is reduced much faster than Assmang ore, fact observed by Larssen and colleagues, <sup>26)</sup> this is mainly due to their respective properties such as chemical composition, porosity <sup>16,18,25,27–30)</sup> *etc.*, they are both on the same oxygen level at 800°C as summarized in **Table 8**. This is however not in agreement with previous studies that have shown a higher reduction rate up to 800°C for

**Table 8.** Calculated carbon consumption per ton of manganese ore in Boudouard zone based on the oxygen content left at 800°C.

Material	Mn (tot) kmoles	Gas composition	X value in MnO <sub>x</sub> at 800°C	$T_1$	T <sub>2</sub>	C consumption kg/ton of Mn ore
ASM	0.0	$2CO + 0.85CO_2$	X=1.11	73	130	11.62
ASIVI	8.8	$2\text{CO} + 2\text{CO}_2 + 0.85\text{H}_2$	X=1.11	73	128	11.62
COM	0.4	2CO+0.85CO <sub>2</sub>	X=1.12	74	132	13.54
	9.4	2CO+0.85CO <sub>2</sub> +2H <sub>2</sub>	X = 1.12	73	127	13.54

Comilog versus Assmang ore. 9,11,13,16) Another interesting thing is also that H<sub>2</sub> in the gas will increase the reduction rate in the area of 20-30%. As these reactions are exothermic a higher reduction rate will heat the charge and hence obtain a higher temperature. For the H<sub>2</sub> gas mixture 800°C will hence be obtained at lower time, or industrially higher up in the furnace. At 800°C, the total extent of reduction will hence be the same as seen on the chemical analyses in Table 7. This will also give the same carbon consumption per ton of metal or quite similar carbon consumption given in extra kg C per ton of ore, depending on the Mn content in the ore. In a submerged arc furnace, one may hence postulate that H<sub>2</sub> present will shift the 800°C isotherm higher up in the furnace, as the reduction will occur higher up in the furnace. If H<sub>2</sub> is used in e.g. the pre-heating unit, one may expect around 20% higher reduction rate, also a totally higher reduction extent as the time will be of the same order.

With  $T_1$  and  $T_2$  the time when the gas mixture is introduced into the furnace and the time when the reduction is stopped respectively.

# 4. Conclusion

This study had a focus on the impact of hydrogen addition to the gas mixture CO/CO<sub>2</sub> during the pre-reduction of manganese ores. Assmang and Comilog ores have been reduced under CO/CO<sub>2</sub> and CO/H<sub>2</sub>/CO<sub>2</sub> gases. Experiments have been carried out in such a way that from room temperature up to 500°C the ambient gas is composed of CO<sub>2</sub> only in order to avoid any carbon deposition.

It was found that, although the degree of reduction seemed to be about the same for all different gas mixtures, the reduction rate was strongly affected by the presence of hydrogen in the reducing gas. The reduction rate was higher and faster when hydrogen was present in the reducing gas than when it was not.

Results showed also that the reduction rate was the highest when the oxygen partial pressure of the gas mixture was the lowest.

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# **REFERENCES**

- U. S. Geological Survey: Mineral Commodity Summaries, U. S. Government Publishing Office, Virginia, (2018), 104. https://doi.org/10.3133/70194932
- A. Cheraghi, H. Yoozbashizadeh and J. Safarian: Miner. Process. Extr. Metall. Rev., 41 (2019), 198. https://doi.org/10.1080/08827508. 2019.1604523
- S. Gaal, D. Lou, S. Wasbø, B. Ravary and M. Tangstad: Proc. 11th Int. Ferroalloys Cong., INFACON 11, (New Delhi), Indian Ferro Alloy Producers' Association (IFAPA), Mumbai, (2007), 247.
- R. Elliott, K. Coley, S. Mostaghel and M. Barati: *Miner., JOM*, 70 (2018), 680. https://doi.org/10.1007/s11837-018-2769-4
- M. Visser, H. Smith, E. Ringdalen and M. Tangstad: Proc. 13th Int. Ferroalloys Cong., INFACON 13, (Almaty), International Committee on Ferro-Alloys (ICFA), Johannesbrug, (2013), 553.
   L. Deng, B. Qu, S.-j. Su, S.-L. Ding and W.-Y. Sun: *J. Chem. Eng.*
- L. Deng, B. Qu, S.-j. Su, S.-L. Ding and W.-Y. Sun: *J. Chem. Eng. Jpn.*, **50** (2017), 892. https://doi.org/10.1252/jcej.16we377
   M. Postle, T. Nwaogu, S. Upson, C. Clark and A. Heinevetter: Man-
- M. Postle, T. Nwaogu, S. Upson, C. Clark and A. Heinevetter: Manganese, The Global Picture- A Socio Economic Assessment, Risk & Policy Analysts, (2015), https://www.rpaltd.co.uk, (accessed 2018-04-17).
- R. Kononov, O. Ostrovski and S. Ganguly: Proc. 11th Int. Ferroalloys Congr., INFACON 11, (New Dehli), Indian Ferro Alloy Producers' Association (IFAPA), Mumbai, (2007), 258.
- M. Tangstad, M. Sibony, S. Wasbø and R. Tronstad: Proc. 9th Int. Ferroalloys Cong., INFACON 9, (Quebec City), Ferroalloys Association, Washington, DC. (2001), 202.
- tion, Washington, DC, (2001), 202.

  10) D. Y. Kim, I. H. Jeong and S. M. Jung: *Ironmaking Steelmaking*, **43** (2016), 526. https://doi.org/10.1080/03019233.2015.1114307
- R. Ishak and M. Tangstad: Proc. 11th Int. Ferroalloys Congr., INFACON 11, (New Dehli), Indian Ferro Alloy Producers' Association (IFAPA), Mumbai, (2007), 268.
- M. Eissa, H. El-Faramawy, A. Ahmed, S. Nabil and H. Halfa: J. Miner. Mater. Charact. Eng., 11 (2012), 1. https://doi.org/10.4236/jmmce.2012.111001
- M. Tangstad, P. Calvert, H. Brun and A. Lindseth: Proc. 10th Int. Ferroalloys Cong., INFACON 10, (Cape Town), The Southern African Institute of Mining and Metallurgy (SAIMM), Johannesbrug, (2004), 213.
- H. E. Barner and C. L. Mantell: *Ind. Eng. Chem. Process Des. Dev.*, 7 (1968), 285. https://doi.org/10.1021/i260026a023
- T. J. W. De Bruijn, T. H. Soerawidjaja, W. A. De Jong, and P. J. Van Den Berg: *Chem. Eng. Sci.*, 35 (1980), 1591.
- K. Turkova, D. Slizovskiy and M. Tangstad: *ISIJ Int.*, **54** (2014), 1204. http://doi.org/10.2355/isijinternational.54.1204
- M. Tangstad, D. Leroy and E. Ringdalen: Proc. 12th Int. Ferroalloys Cong., INFACON 12, (Helsinki), International Committee on Ferro-Alloys (ICFA), Johannesbrug, (2010), 457.
  B. Sorensen, S. Gaal, M. Tangstad, E. Ringdalen, R. Kononov
- B. Sorensen, S. Gaal, M. Tangstad, E. Ringdalen, R. Kononov and O. Ostrovski: Proc. 12th Int. Ferroalloys Cong., INFACON 12, (Helsinki), International Committee on Ferro-Alloys (ICFA), Johannesbrug, (2010), 439.
- O. Ostrovski, S. E. Olsen, M. Tangstad and M. Yastreboff: Can. Metall. Q., 41 (2002), 309. https://doi.org/10.1179/cmq.2002.41.3.309
- 20) D. P. Crawford, P. L. J. Mayfield, A. D. Brent and A. H. Olsen: Proc. 7th Int. Ferroalloys Congr., INFACON 7, (Trondheim), The Norwegian Ferroalloy Producers Research Organization, Trondheim, (1995), 239.
- S. E. Olsen, M. Tangstad and T. Lindstad: Production of Manganese Ferroalloys, SINTEF and Tapir Academic Press, Trondheim, (2007), 217.
- R. Kononov, O. Ostrovski and S. Ganguly: ISIJ Int., 49 (2009), 1107. https://doi.org/10.2355/isijinternational.49.1107
- C. H. Eom and D. J. Min: Met. Mater. Int., 22 (2016), 129. https://doi.org/10.1007/s12540-015-5419-1
- 24) R. Kononov, O. Ostrovski and S. Ganguly: *Metall. Mater. Trans. B*, 39 (2008), 662. https://doi.org/10.1007/s11663-008-9191-1
- M. Yastreboff, O. Ostrovski and S. Ganguly: ISIJ Int., 43 (2003), 161. https://doi.org/10.2355/isijinternational.43.161
- 26) T. A. Larssen, M. Tangstad and I. T. Kero: The Minerals, Metals & Materials Series, Extraction 2018, Springer, Cham, (2018), 1093. https://doi.org/10.1007/978-3-319-95022-8\_88
- T. Yagihashi, K. Asada, K. Atarashiya, S. Ichinohe and H. Hanada: *Tetsu-to-Hagané Overseas*, 4 (1964), 11. https://doi.org/10.2355/ isijintoverseas.4.1 11
- Y. Fujii, Y. Nakai, Y. Uchida and Y. Miki: ISIJ Int., 57 (2017), 609. https://doi.org/10.2355/isijinternational.ISIJINT-2016-568
- K. N. Swamy, D. G. C. Robertson, P. Calvert and D. Kozak: Proc. 9th Int. Ferroalloys Congr., INFACON 9, (Quebec City), Ferroalloys Association, Washington, DC, (2001), 293.
- M. Ksiazek, M. Tangstad and E. Ringdalen: Proc. Southern African Pyrometallurgy Int. Conf., (Johannesburg), Southern African Institute of Mining and Metallurgy, Johannesburg, (2011), 345.