

# Extent of Ore Prereduction in Pilot-scale Production of High Carbon Ferromanganese

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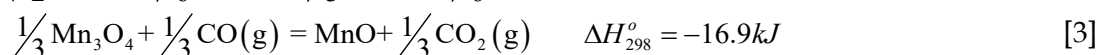
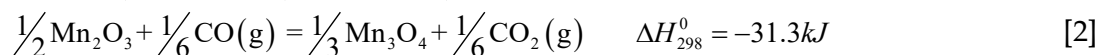
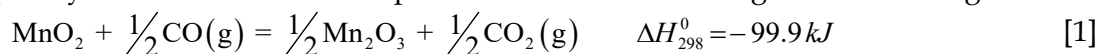
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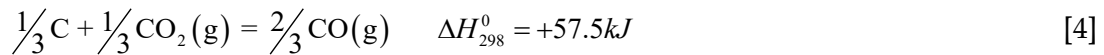
**Abstract** – Three pilot-scale experiments have been conducted at SINTEF/NTNU in a 440 kVA AC electric furnace to demonstrate the process operation, energy requirements and CO<sub>2</sub> emissions in the production of high carbon ferromanganese alloys. Comilog, UMK and Nchwanging (Assmang) ores blended with other materials, such as sinter and flux, thus achieving different charge mixtures have been utilized in the experiments. In the prereduction zone, higher manganese oxides in the ore are reduced to MnO through solid-gas exothermic reactions and at a temperature around 800°C, the unwanted endothermic Boudouard reaction is also active. As such, the total coke and energy consumption is highly dependent on if the prereduction occurs by CO gas or solid C. The pilot furnace has been excavated after each experiment and the extent of prereduction of the ore has been investigated by collecting samples from specific regions in the prereduction zone. In addition, material, and energy balance calculations for the three pilot experiments have been calculated using HSC Chemistry software. The HSC material and energy balance calculations have shown that the slag/alloy ratios, metal analyses, carbon consumption and the overall energy consumption are mainly affected by the composition of the charge mixtures. The relationship between the specific carbon consumption, the off-gas CO<sub>2</sub>/(CO<sub>2</sub>+CO) ratio and energy consumption to produce 1 tonne of HCFeMn alloy is discussed for the three different pilot-scale scenarios.

## INTRODUCTION

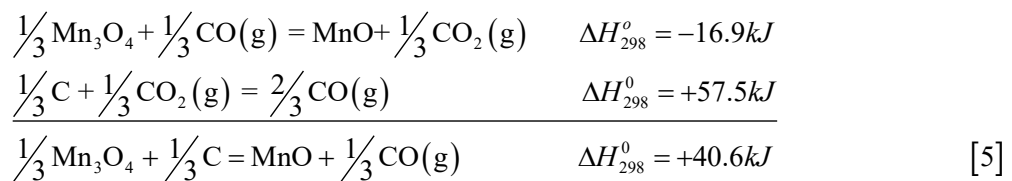
High carbon ferromanganese alloys (HCFeMn) are mainly used as alloying constituents for steel production. Production of HCFeMn is energy-intensive with energy requirements ranging between 2.0 and 3.5MWh per ton alloy (Eissa *et al.*, 2012; Olsen, Tangstad, & Lindstad, 2007; Steenkamp, 2020). Its production is mainly through the submerged arc furnace (SAF), a shaft type furnace with a constant supply of raw materials such as manganese ore, sinter, metallurgical coke and flux premixed in required ratios. The charge mixture is fed from the top of the furnace and is gradually heated in a reducing atmosphere as it descends in the furnace and is reduced to molten metal and slag as it moves down to the furnace hearth. Heat for reduction smelting is generated by electrical energy applied to electrodes and is mainly supplied via the coke bed which builds up around the electrodes and partially through the slag and metal. The higher manganese oxides (i.e. MnO<sub>x</sub>, x>1) in the charge meet the furnace gas that contains significant amounts of CO(g) as they descend in the furnace and are hence subsequently reduced to MnO in the prereduction zone according to the following reactions:



The solid-gas prereduction reactions are all exothermic and as such, the higher oxidation level of manganese ore will give a lower energy consumption as the reactions release heat. The gaseous reduction of  $Mn_3O_4$  by CO is the final prereduction step and at temperatures above  $800^\circ C$ , the unwanted Boudouard reaction is highly active:



Ideally, it is desirable that higher manganese oxides are reduced in solid-state to MnO below  $800^\circ C$  where the endothermic Boudouard reaction is insignificant. If the prereduction is not completed at temperatures below  $800^\circ C$ , the prereduction of  $Mn_3O_4$  will be carried out at higher temperatures through the highly endothermic reaction path as follows:



The prereduction of manganese oxides is highly dependent on ore CO gas reactivity, which as stated by Turkova *et al.*, (2014) has been defined as the ability of higher manganese oxides to be reduced to MnO by CO gas at temperatures below the temperature where the Boudouard reaction is active. An ore with low CO gas reactivity renders the reduction of  $Mn_3O_4$  to occur at higher temperatures and the resultant  $CO_2$  gas will react according to the Boudouard reaction [4] and the overall reaction becomes the endothermic reaction [5]. As such, this will increase the overall carbon consumption, energy consumption and decreases the  $CO_2/CO$  gas ratio in the off-gas.

The MnO from the prereduction zone is reduced by carbon to manganese metal at high temperatures ( $1400 - 1600^\circ C$ ) in the cokebed zone. In this zone, the necessary quantity of carbon to produce manganese by direct reduction of the prereduced ore is fixed for a given metal composition (Olsen *et al.*, 2007). However, the total carbon consumption is highly dependent on the extent of gaseous reduction of higher manganese oxides in the prereduction zone and the extent of the Boudouard reaction. Hence, the gas-solid reactions are to a large extent decisive for the total consumption of both coke and energy in ferromanganese production (Ishak & Tangstad, 2007). The extent of ore prereduction i.e. gas-solid reactions is influenced by factors such as the ability of oxygen above MnO in the ore to react with CO to produce MnO and  $CO_2$ ; reactivity of the coke in the burden mix; porosity of the ore material and the depth of the burden mix, which is influenced by furnace design, among other factors.

Several studies (de Jesus & Tangstad, 2020; Larssen, 2020; Larssen, Tangstad, & Kero, 2018; Swamy *et al.*, 2001; Tangstad *et al.*, 2004; Turkova *et al.*, 2014) have been reported on the prereduction behavior of manganese ores and their implications on the Boudouard reaction, off-gas composition, carbon and energy consumption. The prereduction behavior of Comilog and Nchwanning ores as a function of particle size, gas composition and temperature has been reported in a recent PhD thesis by T. A. Larssen (2020). Comilog ore was reported to be prereduced at a lower temperature than Nchwanning ore. Experiments were conducted in a thermogravimetric set-up using two different particle size fraction of 0.5 – 1.36 mm and 3.33–4.0 mm in two different gas atmospheres of 50% CO and 80% CO and they showed that Comilog ore was completely prereduced at  $600^\circ C$ , whereas reduction of Nchwanning ore was not completed at  $800^\circ C$ . The results were highly repeatable. In addition, a lower reduction

temperature and increasing reduction rate correlated with decreasing particle size and results from these investigations indicated that the use of highly reducible ores leads to an increased indirect reduction of  $Mn_3O_4$  at temperatures below the temperatures where the Boudouard reaction is active and thus, leads to lower carbon consumption. Turkova et al., (2014) investigated the CO reactivity and porosity of Gabonese (Comilog ore), CVRD and Nchwaning (Assmang) lumpy ores and their respective sinters and pellets. It was shown that manganese ores with a higher initial porosity have higher CO reactivity and that the porosity increased with temperature and prereduction. Gabonese and CVRD ores with high initial porosity had a higher CO reactivity compared to their sinters and pellets and were highly beneficial in alleviating Boudouard reaction. On the other hand, making an agglomerate with high initial porosity from Nchwaning (Assmang) ore, which has a low initial porosity, increased the CO reactivity.

The degree of prereduction defined by Tangstad (1996) is a measure of the extent of the gas reduction of higher manganese oxides, which is reflected in the  $CO_2/(CO_2+CO)$  ratio of the off-gas and is inversely related to the coke and energy consumption. A higher degree of prereduction reflected by high gas-ratio results in lower coke and energy consumption. The purpose of this present work has been to investigate the extent of prereduction from pilot furnace experimental work through furnace digouts and determining the degree of prereduction of various charge mixtures based on HSC Chemistry 10 material and energy calculations. The relationship between the specific carbon consumption, the  $CO_2/(CO_2+CO)$  ratio and energy consumption to produce 1 tonne of HCFeMn alloy is discussed for three different pilot-scale scenarios using Comilog, Nchwaning and UMK charge mixtures.

## EXPERIMENTAL

Pilot-plant smelting test-works have been conducted at SINTEF/NTNU in a 400 kVA AC electric furnace to demonstrate the process operation, energy requirements and  $CO_2$  emissions in the production of high carbon ferromanganese alloys. Comilog, UMK and Nchwaning ores blended with other materials, such as sinter and flux, thus achieving different charge mixtures have been utilized in the experiments.

### Pilot furnace description and operation

Figure 1 shows the sketch of the pilot-scale furnace set-up and a photograph of the pilot-scale furnace in operation.

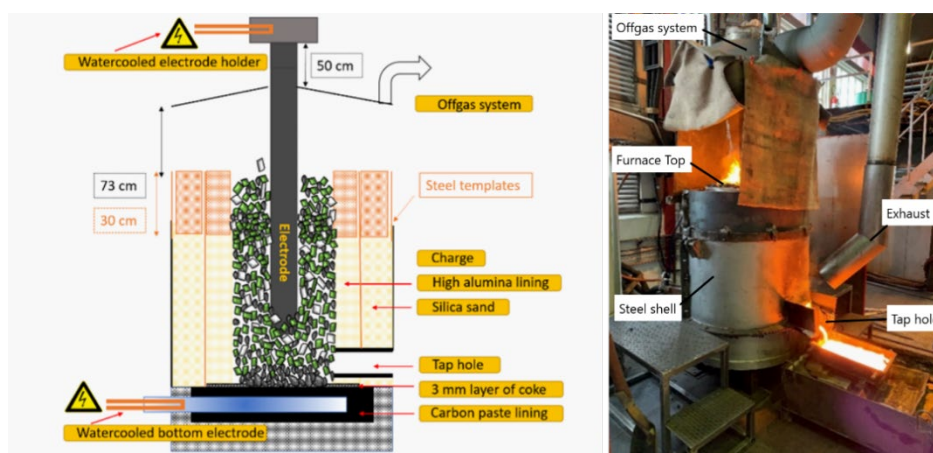


Figure 1: Sketch of pilot-scale furnace setup and a photograph of the pilot furnace in operation

The smelting furnace consists of an outer steel shell with a bottom and a top electrode. A lining is built inside the steel shell, with a 150 mm graphite electrode in the centre. The inner diameter of the furnace shell is typically around 450 mm. The gap between the high alumina lining, the inner lining, and the outer steel shell is filled with quartz sand. The inner lining is approximately 100 mm thick and typically lasts for one smelting experiment. Initially, the furnace was charged with a 10 kg coke bed placed at the bottom of the furnace and the electrode was lowered into the coke bed. The furnace was then preheated for 150 kWh before the tap hole was plugged and around 180 to 200 kg of premixed raw materials was charged in 30 kg batches into the furnace up to the rim. This charge level was kept constant throughout the experiment by manual charging. The electrode was held at a constant position of 20 cm above the bottom of the furnace during all experiments. In total, the furnace was tapped 12 times. The first tap was done when the furnace had been supplied with 150 kWh after the initial charging. Further, the furnace was tapped every 80 kWh of electrical energy consumed. The furnace was shut down 40 kWh after the last tapping and then it was cooled down for approximately 72 hours before it was excavated.

The furnace is designed so that it can be excavated by digging out the loose burden in the prereduction zone and by casting epoxy in the remaining burden in the coke bed zone. A cross-section of the cokebed furnace interior can then be cut, and core-samples can be drilled out and prepared for further investigations with electron micro-probe (EPMA). Results from the cokebed will not be included in this paper. A micro-GC off-gas sampling system was used to measure the composition of the off-gas with the sampling line located 100 mm under the top of the charge surface and 75 mm from the electrode. The process off-gas was continuously measured throughout the pilot experiment to quantify CO, CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> contents, which were used to ascertain the degree of prereduction.

## Raw Materials

The manganese sources used in these experiments were sinter, Comilog, Nchwaniing and UMK ores. UMK ore is Mamatwan type-ore which is enriched in Mn-bearing carbonates, Nchwaniing is a Wessels-type ore, which contains both braunite-I ((Mn<sup>2+</sup>,Mn<sup>3+</sup>)<sub>6</sub>(SiO<sub>4</sub>)O<sub>8</sub>) and braunite-II (Ca(Mn<sup>3+</sup>,Fe<sup>3+</sup>)<sub>6</sub>(SiO<sub>4</sub>)O<sub>8</sub>), more bixbyite ((Mn<sup>3+</sup>,Fe<sup>3+</sup>)<sub>2</sub>O<sub>3</sub>), more haematite (Fe<sub>2</sub>O<sub>3</sub>) and less carbonate compared to UMK, whereas Comilog is mineralogically dominated by pyrolusite (β-MnO<sub>2</sub>), nsutite ((Mn<sup>4+</sup>)<sub>(1-x)</sub>(Mn<sup>2+</sup>)O<sub>(2-2x)</sub>(OH)<sub>2x</sub> (x = 0.06–0.07)) and cryptomelane (K(Mn<sup>4+</sup><sub>7</sub>,Mn<sup>3+</sup>)O<sub>16</sub>) and exhibit relatively high level of microporosity (Peterson, Manuel, & Hapugoda, 2020; Steenkamp, 2020). Raw materials were chemically analysed by SINTEF Norlab using X-ray fluorescence while the MnO<sub>2</sub> amount was obtained by titration for ore and sinter. Eltra (combustion-IR) was used to determine amount of carbon, which was recalculated to CO<sub>2</sub>. Table I shows the chemical composition of the raw materials.

Table I: Chemical composition of raw materials for pilot experiments. (analysed by SINTEF Norlab)

Raw Materials	Composition (wt. %)													
	MnO <sub>2</sub>	Mn	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	CaO	MgO	BaO	P	S	CO <sub>2</sub>	Fix C
Comilog ore	79.6	51.2	2.9	3.3	5.8	-	0.7	0.4	0.1	-	0.1	-	-	-
Nchwaniing ore	37.5	45.5	9.04	4.2	0.38	-	0.10	7.4	1.4	0.6	0.03	-	3.10	-
UMK Ore	26.52	38.22	4.67	6.54	0.74	-	0.08	13.29	3.17	0.05	0.02	-	14.00	-
Sinter	19.33	57.46	3.89	6.41	7.38	-	0.78	0.12	0.04	-	0.09	-	-	-
Coke	-	-	-	5.05	3.31	0.15	0.27	0.34	0.21	0.03	-	0.52	-	88.35

The manganese ores were utilized in combination with other raw materials such as sinter, flux and coke as charge mixtures. The calculation of the charge mix relied on a set of assumptions and aimed at a certain metal and slag composition out of the furnace. The following assumptions were made:

- (i) Oxides such as  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$  and  $\text{BaO}$  will go to the slag phase.
- (ii) The slag is assumed to contain 30%  $\text{MnO}$ .
- (iii) Fe and P will end up the metal phase.
- (iv) The carbon requirement was calculated by assuming that the degree of pre-reduction was 0%. This implies that it is assumed that the final reduction step  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}$  proceeds in the active region of the Boudouard reaction. In practice, this will likely lead to an over-coked operation.

Table II shows a summary of the planned calculated experimental charge mix parameters.

Table II: Assumed or calculated charge mix parameters

Ore	Basicity (*B <sub>2</sub> )	Slag/alloy ratio	Alloy composition (wt.%)				Slag composition (wt.%)			
			Mn	Fe	C	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
			Comilog	0.82	0.69	86.4	6.6	7.0	30	17.2
UMK	0.80	0.66	83.7	9.2	7.0	30	24.0	13.8	24.4	5.8
Nchwani	0.81	0.37	76.6	16.4	7.0	30	26.3	11.3	25.0	5.4

The calculated charge mixture per pilot experiment is shown in Table III. Sinter was added to the charge mixture in all pilot experiments with the purpose of controlling the basicity for Nchwani and UMK ores and decreasing the average oxygen level of the charge for the Comilog experiment. Comilog ore is a highly reactive ore with an oxygen level around 1.98 and in order to achieve a stable operation, sinter of oxygen level 1.21 was added to the charge mixture to an oxygen level around 1.5.

Table III: Charge blend for each pilot experiment

Raw Materials	Pilot experiment charge blend (%)		
	Comilog Pilot	Nchwani Pilot	UMK Pilot
Comilog ore	29.3	-	-
UMK ore	-	-	47.0
Nchwani ore	-	66.5	-
Sinter	46.0	15.6	36.0
Coke	16.0	17.9	17.0
Limestone	8.7	-	-
Total	100	100	100
O/Mn	1.51	1.44	1.31

### Furnace digout procedure

Upon completing the pilot run, the furnace was allowed to cool down for 72 hours before excavation. The furnace excavation for the HCFMn pilot experiment may be divided into two zones namely the prereluction zone and the coke bed zone, only the prereluction zone will be described here. The top part of the furnace i.e. the prereluction zone is composed of loose solid charge materials and this zone was excavated by digging out the solid materials. The schematic illustration of the furnace digout is as shown in Figure 2. The charge mixtures fed during the furnace operation were of particles size 5 – 25mm and samples of these solid materials were taken from two regions close to the electrodes (i.e. positions B and D) and two regions close to the wall of the furnace (i.e. positions A and C) and at 100mm interval depth distances from the top of the furnace up to a depth of 600mm, as illustrated in Figure 2. The

sampling positions were selected with a rationale that samples would exhibit differences depending on the position of the sample in relation to the electrode (i.e. adjacent the electrode and towards the wall of the furnace) and depending on the level of the sample in relation to the top of the furnace.

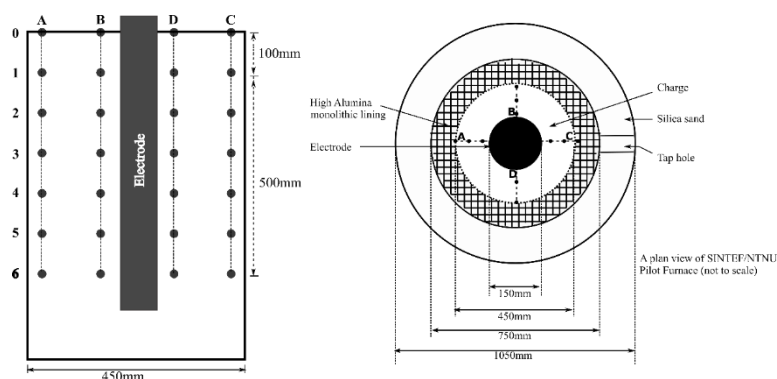


Figure 2: A schematic illustration of the sampling regions during the furnace digout and a plan view of the SINTEF/NTNU Pilot furnace

Approximately 500 – 1200g samples were sampled at each position and level. The samples were later separated into three categories, namely, coke, sinter and ore for further investigations. The ore samples from the furnace digouts were analysed by SINTEF Norlab using X-ray fluorescence while the oxygen content related to the manganese oxides, given as  $MnO_2$ , amount was obtained by titration. The obtained results were used to calculate the oxygen level of the ore samples determined as the O/Mn ratio. Charge material was observed to be sintered at a depth of 600mm and this represents the second part of the furnace i.e. the coke bed zone.

### Material and energy balance

The accounting material and energy balance calculations for the three pilot experiments were calculated in HSC Chemistry software using the actual slag and alloy chemistry established from the products tapped during the pilot experiments and the input charge blend previously shown in Table III. Table IV shows the stable slag and alloy chemistry from the three pilot experiments as measured by SINTEF Norlab.

Table IV: Summary of relevant parameters of slag and alloy chemistry used for HSC mass and energy balance calculations

%	Alloy Chemistry			%	Slag Chemistry		
	Comilog	Nchwaniq	UMK		Comilog	Nchwaniq	UMK
Mn	85.8	77.0	82.6	MnO	33.0	30.0	22.0
Fe	6.9	15.0	8.8	SiO <sub>2</sub>	20.2	24.2	24.5
Si	0.4	0.3	0.01	Al <sub>2</sub> O <sub>3</sub>	23.8	10.4	14.5
C	7.0	7.1	7.3	CaO	21.3	24.3	29.7
Mn/Fe	12.4	5	9.4	MgO	0.9	5.8	7.0

In mass balance calculations, the MnO in slag as measured in the tapped slag was fixed and the Mn in the alloy was obtained by the difference between the total Mn from the charge mixture and the one reported in the slag as MnO. The carbon content in the alloy was considered to be saturated and fixed at 7% in the alloy, whilst the total input of Fe was considered all to report to the alloy phase. The unreducible oxides reported to the slag phase and SiO<sub>2</sub> was calculated by balancing the amount of Si input from the charge mixture and Si reported in the alloy phase. A gas balance was done considering carbon from the difference between input carbon and carbon saturated in alloy reacting with total oxygen from the

reduction of reduceable oxides to form CO and CO<sub>2</sub>. The degree of prereduction for the charge mixtures was calculated at 0 and 100%. When all the Mn<sub>3</sub>O<sub>4</sub> from the reduction of higher manganese oxides is reduced at low temperatures before the Boudouard reaction is activated, the degree of prereduction was defined to be 100%. If all CO<sub>2</sub> from the reduction of Mn<sub>3</sub>O<sub>4</sub> is consumed by the Boudouard reaction, the degree of prereduction is 0%. However, the actual degree of prereduction from the charge blends was calculated from the experimental off-gas measurements. In calculating the energy balance, raw materials input temperatures were assumed to be 25°C whereas, slag and alloy were considered to be tapped at 1500°C and the off-gas was assumed to be 200°C.

## RESULTS AND DISCUSSION

### Extent of prereduction

The raw materials in the burden were observed to be loosely sintered during the digout of the prereduction zone up to a depth of about 600mm from the top of the furnace. Figure 3 shows the variation of the oxygen level i.e. O/Mn ratio of the Comilog, UMK and Nchwanging ores with furnace depth for samples collected adjacent the electrode and furnace wall.

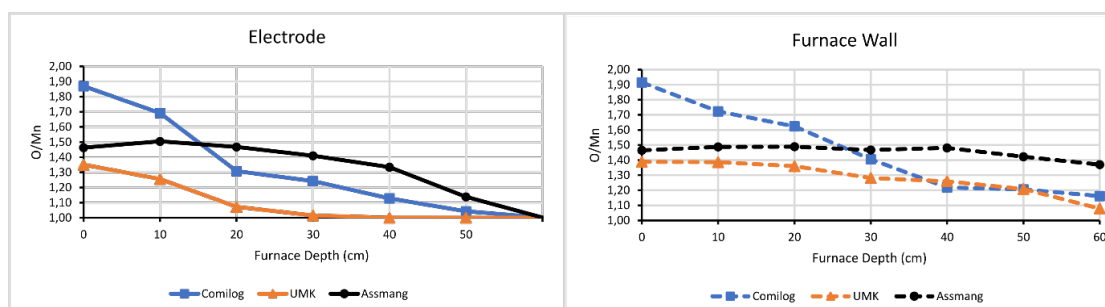


Figure 3: Variation of O/Mn ratio with furnace depth for Comilog, UMK and Nchwanging (Assmang) ores

The initial O/Mn ratios for the Comilog, UMK and Nchwanging ores were 1.98, 1.44 and 1.51, respectively. At least below 10cm from the top of the furnace, the level of oxygen i.e. O/Mn ratio remaining in the ore particles adjacent the electrode was in general lower compared to corresponding samples from the same level of the furnace close to the furnace wall. Figure 3 shows that UMK ore had the lowest O/Mn ratio with increase in depth compared to Comilog and Nchwanging, while Comilog is reduced faster than Nchwanging even though it starts at a higher oxygen content. The greater extent of prereduction adjacent the electrode compared to the furnace wall is an indication of prevailing high temperature conditions for ore materials close to the electrode. Barcza *et al.*, (1979) previously reported for their furnace digout work that raw materials descend rapidly around the electrode. Therefore, it was assumed the ore reduction followed a material distribution of 70% and 30% for material close to the electrode and furnace wall, respectively, the variation of O/Mn ratio with depth is as presented in Figure 4 for all ores.

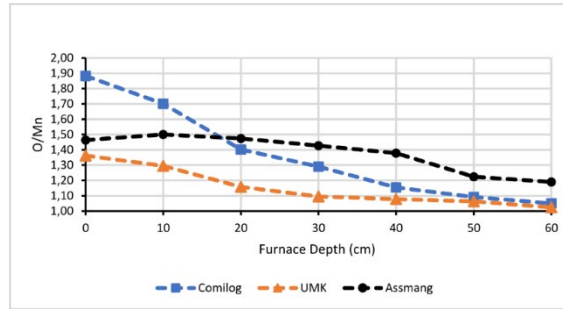


Figure 4: Variation of O/Mn ratio with depth at an electrode/furnace wall material distribution ratio of 70/30

Figure 4 indicates that UMK ore had greater extent of prereduction followed by Comilog and lastly Nchwanging. The greater extent of prereduction for Comilog compared to Nchwanging is in line with previous observations from laboratory experiments (de Jesus & Tangstad, 2020; Larssen et al., 2018; Turkova *et al.*, 2014) where Comilog ore has a high CO reactivity and initial porosity compared to Nchwanging ore. Consequently, Comilog ore should have a greater extent of prereduction and also give the lowest amount of Boudouard reaction and thus better prereduction compared to Nchwanging. Reiersen (2020), studied the extent of prereduction of manganese ores in small scale experiments and observed a high increase in porosity with increasing temperature for UMK ore resulting from its high carbonate content decomposing with increasing temperature and could be the reason for the high extent of prereduction for UMK ore.

### Mass and Energy Balance

The material balance per 100kg input material calculated in HSC Chemistry 10 is as shown in Tables V, VI and VII for the three pilot scenarios. MnO in slag was considered to be 33%, 22% and 30% for Comilog, UMK and Nchwanging blends respectively as has been determined from the slag analysis. The theoretical weights were calculated based on the known weights and analyses of input raw materials as well as the metal and slag analyses. Ideally, these weights are not the same as the tapped weight mainly because there is some metal entrapment in the slag phase and the furnace is not always 100% emptied. As such, for the mass balance of the furnace, the theoretical metal and slag weights are used. The theoretical slag/alloy ratios were calculated to be 0.74, 0.53 and 0.35 for the Comilog, UMK and Nchwanging experiments, respectively. The accounting energy balances were calculated between 0% and 100% degree of prereduction and the actual degree of prereduction for the three pilot experiments were calculated based on the CO/CO<sub>2</sub> ratio from the off-gas measurements of the last stable period towards the end of the experiments.

Table V: Calculated materials balance for pilot experiment with Comilog ore in charge blend

Raw Materials	Mass (kg)	MnO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO <sub>2</sub>	Fix C
Comilog	29.33	23.81	0.69			1.38		1.04	1.73		0.35	0.35	-	
Sinter	46.0	-	-	24.3	12.32		2.40	3.08	3.42		0.14	0.34	-	
Lime	8.67									8.67				
Coke	16.0							0.68	0.68					14.6
Sum	100	23.81	0.69	24.3	12.32	1.38	2.40	4.80	5.83	8.67	0.49	0.69	-	14.6
Kmol		0.27	0.004	0.11	0.17	0.01	0.03	0.08	0.06	0.16	0.01	0.01	-	1.22
Products	Mass (kg)	Mn	Fe	C	Si	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO	CO <sub>2</sub>	
HCFeMn	40.78	34.92	2.83	2.85	0.17									
Slag	29.99						9.90	4.43	5.83	8.67	0.49	0.69		
Gas	29.25											19.53	2.47	
Sum	100	34.92	2.83	2.85	0.17	9.90	4.43	5.83	8.67	0.49	0.69	19.53	2.47	
Kmol		0.64	0.05	0.24	0.01	0.14	0.07	0.06	0.16	0.01	0.01	0.87	0.11	
Metal Composition (mass %)					Slag composition (mass %)					Gas composition (%)				
Mn	Fe	C	Si		MnO	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O		CO	CO <sub>2</sub>	
85.6	6.9	7.0	0.4		33	14.8	28.9	1.6	19.4	2.3		88.8	11.2	



Table VI: Calculated materials balance for pilot experiment with UMK ore in charge blend

Raw Materials	Mass/ kg	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO <sub>2</sub>	Fix C
UMK ore	46.55	17.24	9.48	-	3.16	-	3.16	0.29	6.61	1.44	-	5.17	-
Sinter	36.49	-	19.25	9.77	-	2.01	2.30	2.87	-	-	0.29	-	-
Coke	16.96	-	-	-	-	-	0.86	0.58	-	-	-	-	15.52
Sum	100	17.24	28.73	9.77	3.16	2.01	6.32	3.74	6.61	1.44	0.29	5.17	15.52
Kmol		0.11	0.13	0.14	0.02	0.03	0.11	0.04	0.12	0.04	0.003	0.12	1.29
Products	Mass/ kg	Mn	Fe	C	Si	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO	CO <sub>2</sub>
HCFeMn	43.39	36.28	3.77	3.04	0.30	-	-	-	-	-	-	-	-
Slag	22.79	-	-	-	-	5.01	5.68	3.70	6.67	1.45	0.28	-	-
Gas	33.82	-	-	-	-	-	-	-	-	-	-	30.28	3.54
Sum	100	36.28	3.77	3.04	0.30	5.01	5.68	3.70	6.67	1.45	0.28	30.28	3.54
Kmol		0.66	0.07	0.25	0.01	0.07	0.10	0.04	0.12	0.04	0.003	1.08	0.08
Metal Composition (mass %)				Slag composition (mass %)						Gas composition (%)			
Mn	Fe	C	Si	MnO	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CO	CO <sub>2</sub>		
83.6	8.7	7.0	0.7	22.0	24.9	29.3	6.4	16.2	1.2	93.1	6.9		

Table VII: Table VI: Calculated materials balance for pilot experiment with Nchwanning ore in charge blend

Raw Materials	Mass (kg)	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO <sub>2</sub>	Fix C
Nchwanning	66.45	42.56	2.05	-	10.24	-	2.73	0.23	4.32	0.91	-	3.41	-
Sinter	15.61	-	8.26	4.13	-	0.92	0.92	1.15	-	-	0.23	-	-
Coke	17.94	-	-	-	-	-	0.91	0.68	-	-	-	-	16.35
Sum	100	42.56	10.31	4.13	10.24	0.92	4.56	2.06	4.32	0.91	0.23	3.41	16.35
Kmol		0.27	0.05	0.06	0.06	0.01	0.08	0.02	0.08	0.02	0.002	0.08	1.36
Products	Mass (kg)	Mn	Fe	C	Si	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	CO	CO <sub>2</sub>
HCFeMn	47.71	36.35	7.88	3.34	0.14	-	-	-	-	-	-	-	-
Slag	16.84	-	-	-	-	5.05	4.25	2.06	4.33	0.91	0.23	-	-
Gas	35.47	-	-	-	-	-	-	-	-	-	-	27.31	8.16
Sum	100	36.35	7.88	3.34	0.14	5.05	4.25	2.06	4.33	0.91	0.23	27.31	8.16
Kmol		0.66	0.14	0.28	0.01	0.07	0.07	0.02	0.08	0.02	0.002	0.98	0.19
Metal Composition (mass %)				Slag composition (mass %)						Gas composition (%)			
Mn	Fe	C	Si	MnO	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CO	CO <sub>2</sub>		
77.2	16.5	7.0	0.3	30.0	25.3	25.7	5.4	12.2	1.4	84.0	16.0		

**CO/CO<sub>2</sub> off-gas composition**

Figure 5 shows a direct comparison of CO<sub>2</sub> and CO concentrations in the off-gas, which reveals significant differences between the different ore types in charge mixtures.



Figure 5: Off-gas composition for time region 300 - 400 minutes (left) and the corresponding average values (right) for Comilog, UMK and Nchwanning (Assmang) pilot experiments

Charge mixture with Comilog ore gave the highest CO<sub>2</sub> concentrations during the experimental runs, followed by charge mixture with UMK-ore and lastly, Nchwanning ore with the lowest observed CO<sub>2</sub> concentration. The opposite trend will be observed for CO

concentrations. The mean CO/CO<sub>2</sub> composition were 55/45, 65/35 and 70/30 for the charge mixtures of Comilog, UMK and Nchwaniing, respectively. These gas measurements correlate very well with the extent of prereduction as presented in Figure 4. Nchwaniing ore had the lowest variation of O/Mn ratio with furnace depth compared to the other charge mixtures and as such, it was hence expected that a larger extent of prereduction of Nchwaniing ore occurred in the active region of the Boudouard reaction leading to a higher content of CO(g) in the off-gas.

### Carbon and energy consumption

The minimum and maximum carbon consumption for the three pilots were calculated by the raw materials in and the slag and metal composition out and are shown in Table VIII. The minimum carbon consumption is fixed for a given metal composition and was calculated at 100% degree of prereduction for the reduction of MnO and SiO<sub>2</sub> to Mn and Si in metal, respectively and carbon dissolution in the metal. Maximum carbon consumption is additionally given by the extent of the Boudouard reaction when all CO<sub>2</sub> from reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO, FeO to Fe and decomposition of carbonates is reacting with carbon according to Boudouard reaction i.e. at 0% degree of prereduction.

Table VIII: Theoretical fixed carbon requirements per ton alloy for the HCFMn grades produced from the pilot experiments and maximum carbon requirements (Calculated using HSC Chemistry 10)

Reaction	Element	Elements (Wt. %) per Pilot experiment			kg C/ton of alloy (Pilot experiment grades)		
		Comilog	UMK	Nchwaniing	Comilog	UMK	Nchwaniing
MnO+C = <u>Mn</u> +CO	Mn	85.6	83.6	77.2	187.2	182.8	168.8
Fe = <u>Fe</u>	Fe	6.9	8.7	16.5	-	-	-
SiO <sub>2</sub> +2C = <u>Si</u> +2CO	Si	0.4	0.7	0.3	3.4	6.0	2.6
C = <u>C</u>	C	7.0	7.0	7.0	70.0	70.0	70.0
<b>Total minimum theoretical carbon requirements (100 % *DPR)</b>					<b>260.6</b>	<b>258.8</b>	<b>241.4</b>
C consumed by Boudouard reaction (C+CO <sub>2</sub> =2CO) at 0% DPR					74.4	106.2	109.6
<b>Total maximum carbon consumption (0 % DPR)</b>					<b>335.0</b>	<b>365.0</b>	<b>351.0</b>

\*DPR – degree of prereduction

The relationship between the specific carbon consumption, the off-gas CO<sub>2</sub>/(CO<sub>2</sub>+CO) ratio and energy consumption to produce 1 tonne of HCFMn alloy for the three different pilot-scale scenarios are shown in Figure 6. As the CO content of the off-gas increases, the energy consumption due to the Boudouard reaction increases. The main conclusion on this part of the work shows that the lower CO<sub>2</sub> to (CO + CO<sub>2</sub>) ratio in the off-gas indicates higher CO<sub>2</sub> consumed in the Boudouard reaction and consequently higher carbon and energy consumption. This relationship is similar to what has been observed in other works (Ahmed *et al.*, 2014; Swamy *et al.*, 2001; Tangstad & Olsen, 1995).

The degree of prereduction for the three pilot scenarios in this work was calculated based on the previously stated CO/CO<sub>2</sub> gas measurements from the pilot experiments and related to the off-gas CO<sub>2</sub>/(CO<sub>2</sub>+CO) ratio as shown in Figure 6. Energy consumption and carbon consumption versus the degree of prereduction for the different charge mixtures in the pilot scenarios are summarized in Table IX. The calculated total theoretical carbon consumptions for the different charge mixtures of Comilog, UMK and Nchwaniing shown in Table IX is above their respective stoichiometric fixed amount presented in Table VIII by 12.4%, 12.8% and 28.8%, respectively. This is in agreement with 10 to 30% more carbon above the theoretical amount of fixed carbon reported by Swamy *et al.*, (2001). The degree of prereduction as shown in Table IX was highest (68%) for the charge mixture containing UMK ore, which correlates

very well with the greater extent of prereduction of UMK as has been observed from the extent of prereduction presented in Figure 4.

Table IX: Energy and carbon consumption versus degree of prereduction for different pilot scenarios

Pilot experiment	Degree of prereduction (%)	Carbon consumption (kg C/t alloy)	Energy consumption kWh/t alloy
Comilog mix	59	293	1732
UMK mix	68	292	2000
Nchwaning mix	35	311	1835

Ishak & Tangstad (2007), previously showed that for industrial furnaces the degree of prereduction varies between 10 to 40% and can be as high as 50 to 60% in very good periods. Carbonates in the burden have been reported to have a double effect, first requiring energy on the decomposition of carbonates and next to increase energy and coke consumption according to Boudouard reaction (Tangstad & Olsen, 1995). As such UMK ore, a Mamatwan type-ore, which is enriched in Mn-bearing carbonates would exhibit a high energy consumption compared to Nchwaning which contains less carbonates. Nchwaning mix was shown to have a higher carbon consumption, 311 kg C/t alloy compared to 292 kg C/t alloy for UMK mix, this is attributed to a lower degree of prereduction of 35%. The lower degree of prereduction in Nchwaning mix is expected to increase energy consumption, which cannot be seen due to the higher amount of carbonates in UMK mix. This can also be due to the slag/alloy ratio; Nchwaning (Assmang) charge mixture had a lower S/A ratio of 0.35 compared to 0.53 for UMK charge mixture, which means there is less slag produced from the Nchwaning (Assmang) charge mixture and ultimately a lower kWh/t alloy. An increase in S/A ratio by about 0.1 has been reported to increase energy consumption by about 60 – 70 kWh/t alloy produced (Olsen et al., 2007).

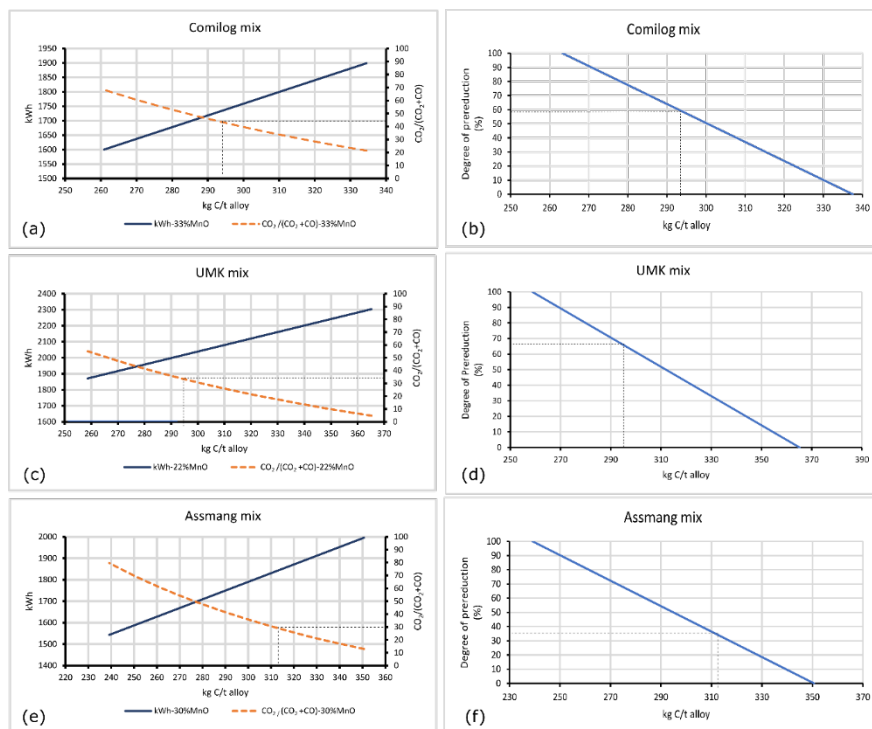


Figure 6: The relationship between energy consumption,  $\text{CO}_2/(\text{CO}_2+\text{CO})$  ratio and carbon consumption for production of 1 tonne of alloy (a, c & e) and the variation of the degree of prereduction and coke consumption (b, d & f)

Comilog charge mixture had the lowest energy consumption. Comilog is mineralogically dominated by pyrolusite, nsutite and cryptomelane and exhibit relatively high level of microporosity and its utilisation results in lower energy consumption mainly because of the higher energy from exothermic reactions (Tangstad *et al.*, 2004). Eissa *et al.*, (2012) reported in their studies on parameters affecting energy consumption in the high carbon ferromanganese process and they showed that increasing mass percent of sinter in the charge blend lowers the energy consumption. This was attributed to the decrease of the total mass of charge blend accompanied by an increased percentage of sinter in the charge blend added to obtain a higher Mn/Fe ratio. In this work, the sinter ratio of the Comilog blend was the highest of the three pilot experiments at 46%, as presented in Table III and thus, a corresponding lower energy consumption. The energy consumption for the three pilot scenarios was calculated on a dry basis. However, practically charge blends into the SAF will contain some moisture level as well as energy losses. As such assuming 80% efficiency the energy consumption will be 2165, 2500 and 2294 kWh per ton of alloy produced for the Comilog, UMK and Nchwanning charge blends.

The degree of prereduction for the three pilot scenarios calculated based on off-gas ratio,  $CO_2/(CO_2+CO)$  are reported with uncertainty. There is a need to evaluate if the total carbon balance reflects the observations from the experiment with regards to accumulated carbon in the furnace. Knowing the kg ore/ t alloy ratio based on HSC material balance and the real kg C/kg ore in the blend, the input total carbon is calculated and used to determine the carbon accumulation in the furnace in relation to the carbon consumed as estimated from the  $CO/CO_2$  in the offgas. The calculation of the carbon accumulation in the furnace was shown in Table X.

Table X: Calculation of accumulated carbon in the furnace

Charge blend	HSC	Furnace C/Ore ratio	Total C input	C consumed (based on DPR)	C accumulation in Pilot Furnace
	kg Ore/t alloy	kg C/kg ore	kg C/t alloy	kg C/t alloy	kg
Comilog mix	1847.3	0.19	359.0	293	12.24
UMK mix	1912.8	0.19	358.6	292	12.14
Nchwanning mix	1719.9	0.20	342.7	311	7.28

Table X shows that the accumulation of carbon in the pilot furnace was equal to 12.2, 12.1 and 7.3kg for the Comilog, UMK and Nchwanning charge blends, respectively. For coke with 88% Fix C and a bulk density of 590 kg/m<sup>3</sup>, this will translate to a volume of about 24, 23 and 14 litres, respectively. This can be verified by measuring the volume and size of the coke bed and the  $CO/CO_2$  gas ratio and consequently the degree of prereduction can be confirmed.

## CONCLUSIONS

The main concluding remarks from this work can be summarized as follows:

- The necessary quantity of carbon to produce manganese by direct reduction of the pre-reduced ore, varies with the alloy composition. The minimum carbon required to produce alloys with Mn/Fe ratios of 12.4, 9.6 and 4.6 from blends of Comilog, UMK and Nchwanning were 261, 259 and 239 kg C/t alloy, respectively.
- The total carbon consumption is highly dependent on the gaseous reduction of higher manganese oxides in the prereduction zone and the extent of the Boudouard reaction. Analysis of ores from the digouts have shown that most of the prereduction occurs when approaching the high temperature zone and UMK had the lowest O/Mn ratio

with depth approaching the high temperature zone followed by Comilog and lastly Nchwaning ore in their respective blends.

- The extent of the gas reduction of higher manganese oxides is reflected in the  $\text{CO}_2/(\text{CO}_2+\text{CO})$  ratio of the off-gas, a higher degree of prereduction results in a lower carbon consumption i.e. coke rate, as well as a lower energy consumption. The UMK charge blend had the highest energy consumption for a charge blend with the highest degree of prereduction and this is mainly attributed to the energy consumption through decomposition of carbonates.

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