

MANGANESE ALLOYS PRODUCTION: IMPACT OF CHEMICAL COMPOSITIONS OF RAW MATERIALS ON THE ENERGY AND MATERIALS BALANCE

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ABSTRACT

For the production of 1 ton of manganese alloys, the energy balance has been calculated for various charge mixtures. The theoretical energy consumption for some typical South African ores is calculated, and the individual contribution to the energy consumption is discussed. However, the materials and energy balances cannot easily be predicted before end product is known. Different ores with different chemical compositions, behave differently in the furnace and lead to products of different chemical compositions. In this work, the MnO in the final slag has been assumed to 20%, as the South African ores will give a high basicity slag. The mass and energy balances have shown how the composition of three different ores will affect the metal analyses, the slag/metal ratio and the energy consumption. The Mn/Fe ratio in the ore will affect the Mn/Fe ratio in the metal. The Mn content and the basicity of the ore affect the slag/metal ratio. Of the ores investigated, the most important parameter affecting the differences in energy consumption is the presence of carbonates in the ore. It has also been shown that there is a relationship between the CO/CO₂ gas ratio, specific carbon consumption and the electrical energy consumption.

KEYWORDS: Manganese ore, ferromanganese alloys, energy and materials balance.

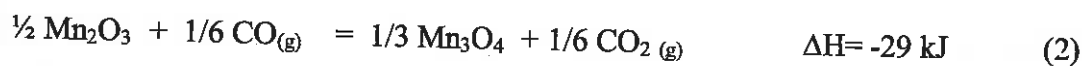
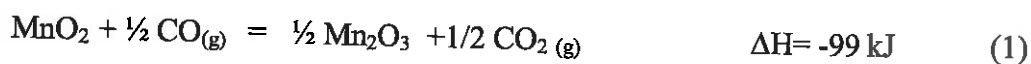
1. INTRODUCTION

During the last two decades, a considerable improvement of thermodynamics data have allowed prediction of equilibrium conditions as well as factors that affect the extend of reactions in the furnace. In addition to a large effort in determining thermodynamic data, also physiochemical data has been studied. Hence, the effect of some components of the raw material namely alumina on the slag have been investigated and have shown an influence on the viscosity which is ultimately dependent on the temperature [1], thus on the energy consumption and the slag composition.

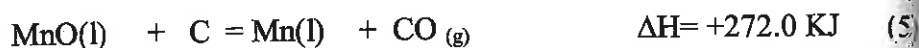
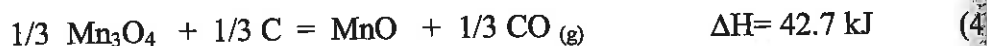
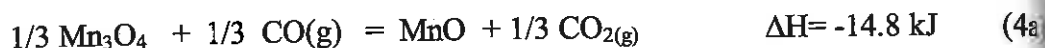
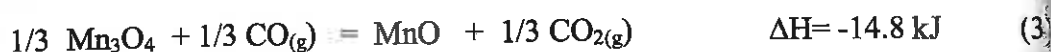
Further, a comparison between oxidized ores, semi-oxidized ores and carbonated ore was conducted and have shown that the reduction of the higher manganese oxides are all exothermic and will lead to low power consumption [2]. This means that the ore containing more carbonates would consume more power than the one containing only oxides.

A study on the degree of prereduction was conducted and was found to be dependent on the ore used and the temperature [3]. The relationship between the degree of prereduction have shown that the energy consumption decreases when the degree of prereduction increases [4].

It is important to understand that the power consumption is dependent on the energy released or consumed in different zones in the furnace. Reactions below show how higher manganese oxides of the charge are reduced to MnO and confirm that the higher the oxidation level, the lower the power consumption [4 - 6]:



MANGANESE FUNDAMENTALS



As it can easily be seen that reaction 1 to 3 are highly exothermic, thus releasing energy benefiting the process whilst reaction 5 is detrimental in terms of energy to the process. The power consumption is one key parameters to viably produce ferromanganese. From the above reference it can be seen that the chemical composition of the raw material and the extent of reaction 5, is of utmost importance when one would like to efficiently produce ferromanganese.

This paper investigates and compares theoretical mass and energy balances of different types of South African manganese ores. Manganese ores used were Nchwaneng 1 and Nchwaneng 2 and Gloria.

2. ORE PROPERTIES

2.1. Raw material

Manganese ore used in the calculation were Nchwaneng 1 and 2 and Gloria as presented in table 1 below with their chemical compositions. The basicity have been calculated according to the chemical composition based on the basicity formula $\text{Basicity} = (\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$.

Table 1: Chemical analyses of manganese ores

	Element/ Compound	Unit	Ore type		
			Ore 1	Ore 2	Ore 3
Chemical composition	Mn	wt%	46	42.5	37
	Fe	wt%	10	15.3	5.1
	SiO ₂	wt%	6.1	6.1	6.3
	CaO	wt%	6.8	5.7	15.1
	MgO	wt%	0.7	0.7	2.7
	Al ₂ O ₃	wt%	0.4	0.3	0.2
	P	wt%	0.004	0.004	0.03
	S	wt%	0.1	0.1	0.04
	Na ₂ O	wt%	0.1	0.1	-
	K ₂ O	wt%	0	0	-
	B	ppb	628	628	380
Mn/Fe	wt%/wt%	4.6	2.8	7.3	
Basicity			1.1	1.0	2.7

In this paper, all the Mn has been considered as Mn₂O₃ and all the Fe as Fe₂O₃. From the chemical analysis of the ores in table 1, it can be seen that Ore 3 has the lowest Mn content. The Mn

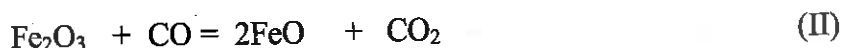
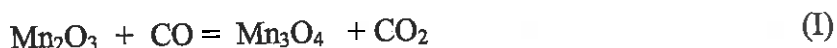
content has already been reported to have an impact on the power consumption through the change of slag/metal ratio [7]. This will be discussed in the theoretical results on the power consumption. It is important to mention two things:

- 1) The CaO and MgO are basic oxides in Ore 1 and Ore 2, whilst in the Ore 3 they are present as carbonates.
- 2) To obtain a basicity of 1.1 from the 2.7 as in table 1 above for Ore 3, theoretical amount of pure quartz was added to obtain a charge basicity of 1.1. To obtain this basicity 97.8 kg of SiO₂ per ton of Ore 3 was added.

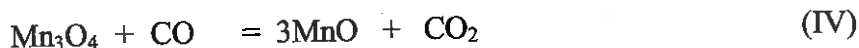
2.2. Zone Limitations and assumptions in the furnace

The furnace has been subdivided into three zones with the following temperatures:

Zone 1: In the upper zone the raw materials enter the zone at 25°C and leave the zone at 700°C. The following reactions will occur:

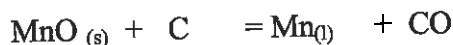


Zone 2: In the middle Zone the materials will be heated from 700°C to 1100°C. In this zone it is assumed that nothing melts and that the ores are still in solid state. The reactions are as follows:



The degree of prereduction can be calculated according to Tangstad et al [4]. But in this paper, in the base case, it was assumed that 50% of CO₂ produced in this zone will react according to reaction (VI).

Zone 3: In the Lower zone the material is heated from 1100°C to 1500°C. In the reduction zone the following reactions occur:



In addition in zone 3, the melting of the oxides and the metallic iron will occur. To calculate the enthalpy of the molten slag, the heat of solution would not be neglected given that the slag is a mixture of oxides in which activities have been found to depart from ideality [8]. In this paper the estimation on enthalpy of molten slag was done based on the assumptions of Turkdogan (1983). According to Turkdogan, the heat of formation and heat capacity of many slag systems have very similar values and similar temperature dependence. For that reason, based on the similarity of the heat capacities and on similar heats of formation at 298 K, the enthalpy of molten slag at 1773K was estimated in J/g-atom. The value was obtained from Pyrometallurgy course by Professor P.C Pharois, UP (2007). Knowing the number of mol atoms of each slag compound, the total number

of mol-atoms of the slag was calculated. The enthalpy of the molten slag was then the enthalpy of molten slag subtracted from the sum of enthalpy of each solid compound in the slag at 1773 K.

The metal and slag composition were calculated assuming that all iron from the ore was collected in the metal and that Si in metal was fixed to 0.06%. In addition, and maybe most important, as the basicity is in the area of one, the MnO content in the slag is assumed to be 20 %.

3. RESULTS AND DISCUSSIONS

3.1. Mass Balance

The resulting slag and metal tapped is shown in table 2 and 3. The MnO in the slag was considered 20 % for the three ores, value taken from industrial data [9].

The Mn in the alloy was obtained by difference between the Mn from the ore and the one reported in the slag.

The carbon content in the alloy was calculated using the Li and Morris (1997) interaction parameters by assuming to be at saturation, therefore the activity of C would be 1 [10] whilst Fe was obtained by difference. The unreducible oxides reported all to the slag. SiO₂ was calculated knowing the amount in the Si content in the ore and assumed to be 0.06 % in the metal.

Table 2: Slag composition

Compounds	Ore 1	Ore 2	Ore 3
MnO	20	20	20
MgO	4	4.4	6.4
CaO	39	35.8	35.6
SiO ₂	34.6	37.9	37.6
Al ₂ O ₃	2.3	1.9	0.5
<i>Basicity</i> (MgO+ CaO)/ (SiO ₂ +Al ₂ O ₃)	1.2	1	1.1

Table 3: Metal composition

Elements (Wt%)	Ore 1	Ore 2	Ore 3
Mn	75.1	67.03	79.1
Fe	17.3	25.6	13.3
Si	0.06	0.06	0.06
C	7.5	7.3	7.6
<i>Slag/Metal ratio</i>	0.30	0.27	1.10
<i>Mn/Fe ratio in alloy</i>	4.3	2.6	5.9

From the data obtained in table 2 and 3, one can see the following results:

1) The Mn/Fe ratio calculated from the ore, is shown in table 1 Ore 2 had the lowest (2.8) ratio whilst the same ratio in the metal was of 2.6, still the lowest from the three alloys produced as indicated in table 3. The typical Mn/Fe ratio in the metal is 78/15, this means that ore (1,2) and Ore 3 should to be mixed with high Mn/Fe ore. This can explain the reason why the iron content is high and a low C content compared to Ore 1 and Ore 3. The more iron the lower the carbon content.

2) From table 3, it is shown that the slag/metal ratio with Gloria is the highest. This is mainly due to quartz that has been added to decrease the basicity, thus increasing the slag/metal ratio. In

In addition, the manganese content in the ore is lower, and hence the high unreducible amount of oxides, which also will give a higher slag/metal ratio. If the Gloria ore was mixed with a high Mn, high acid ore like Groote Eylandt or Comilog, this would give a much lower slag/metal ratio. The (1,2) slag/metal ratios were in the same low range around 0.3. Previously reported slag/metal ratio for high basicity slag operation is higher, and this is due to several reasons. First, usually a mix of various ores is used, and hence Ore (1,2) ore is mixed with Ore 3, a higher slag/metal ratio would be expected. Also, if acid fluxes are used to lower the basicity a bit below 1, this would increase the slag/metal ratio. At last, metal loss in the slag would increase the apparent slag/metal ratio. 5% metal loss to the slag would increase a slag/metal ratio from 0.34 to an apparent slag/metal ratio of 0.41.

2. Energy consumption

The energy consumptions per zone in the furnace for the different manganese ores used are presented in table 4 with a degree of prereduction of 50% whilst the change of energy consumption against degree of prereduction is presented in table 5.

Table 4: Energy consumption per zone for different manganese ore

ZONE (Energy consumption kwh/t metal)	Manganese ore		
	Ore 1	Ore 2	Ore 3
Upper	81	86	328
Middle	230	246	864
Lower	1111	992	986
Total Energy consumption/t metal	1422	1324	2177
Total Energy consumption (if 20% loss)/ t metal	1778	1656	2723
Assumed Degree of prereduction	50	50	50

Table 5: Energy consumption versus degree of prereduction for different manganese ore

Degree of prereduction	Energy consumption kWh/ t metal metal		
	Ore 1	Ore 2	Ore 3
20	1924	1819	3001
30	1875	1764	2908
50	1778	1656	2723

It is shown from table 4 that the energy consumption from upper zone to the lower zone increases for Ore 1 and 2, but for Ore 3 the increase in the second zone increased quite considerably in the middle zone. This can be attributed to the presence of carbonates. It is important to state the following:

The values in table 4 were obtained under conditions that the upper zone and middle zone are not adiabatic, thus there was no thermal equilibrium. However, if one used the adiabatic conditions in the first zone, the temperature of the gases leaving the top zone would be lower than the assumed 700°C. In the mid zone there is a huge energy shortage. If one assumes that no electric energy is developed in this zone, this shortage could be covered by evaporation in the high temperature zone and condensation in the mid zone of species like Mn and K gas. This could also create a narrow mid zone, and hence that the heat transfer would go through diffusion and convection from the high temperature zone. This has also been seen in previous calculations Tangstad (2007).

The energy consumption is low because the off-gas has been considered leaving the furnace at low temperature of 25°C whilst if the off-gas were considered leaving the furnace at about 500°C, the energy consumption would have been higher than the one obtained in table 4. In practice they leave at around 500°C and for each 100°C, 70kWh that must be added. This accounts for about 330 kWh extra. Also, if some metal is lost to the slag, the energy consumption will increase by the same percentage. Together this could be in the area of 500 kWh.

Table 5 shows the energy consumption per ton of metal produced against the degree of prereduction. It can be seen that the energy consumption decreased when the degree of prereduction increased. This can be attributed to the fact that the lower the degree of prereduction, the more CO₂ available from the Boudouard reaction which is endothermic.

4. CONCLUSIONS

The energy consumption per ton of metal produced was found to be dependent on the chemical composition of the ore. For three manganese ores, all Mn₂O₃ ores, used in this paper and considered to be at the same degree of prereduction, the carbonates ore namely Ore 3 has a energy consumption higher than the Ores 1 and 2 which contain no carbonate. Also, the energy consumption was increasing with the decrease of the degree of prereduction for the three manganese ore. This is due to more CO₂ available for the Boudouard reaction when the degree of prereduction decreases. The Boudouard reaction is endothermic, this explains the increase in energy demand within the furnace. In addition to the above, the upper zone and the middle zone were not adiabatic as the temperatures were slightly higher than what they should be.

The overall energy consumption looked slightly lower than the values obtain practically in the plants. This could be due to the assumptions that the gases were leaving at around room temperature whilst in practice they leave at around 500°C and for each 100°C, there is 70kWh that must be added. If this is considered, the energy consumption can increase and might be close to industrial values.

It was found that Ore 2 that had the lowest Mn/Fe ratio, had the lowest C content in the metal produced compared to Ore 1 and Ore 3 which had a relatively high Mn/Fe ratio.

In addition, Ore 3 had the highest slag/metal ratio which explained the high amount of slag produced per ton of metal. This was attributed to the quartz added to modify the basicity to the same range as the Ores 1 and 2 as well as a relatively low Mn content in the ore.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- [1] K. Tang and S.Olsen: "The Effect of alumina in ferromanganese slag", INFACON XI pp. 235- 243.
- [2] G. Pochart, L. Joncourt, N. Touchard and C. Perdon: "Metallurgical benefit of reactive high grade ore in manganese alloys manufacturing", INFACON XI pp.217- 230.
- [3] M. Kumar, S. Ranganathan and S.N. Sinha: "Kinetics of Reduction of different manganese ores", INFACON XI, pp. 241- 246.
- [4] R. Ishak and M. Tangstad: "Degree of prereduction without coke consumption in industrial furnaces", INFACON XI, pp. 268- 280.
- [5] M. Tangstad: "School Manganese Ferroalloy Production", 12-13 June 2012, Misty Hills.

- Muldersdrift, Johannesburg, South Africa.
- [6] Production of Manganese Ferroalloys, 2007, S.E. Olsen, M. Tangstad and T. Lindstad, ISBN 978-82-519-2191-6, pp. 16.
- [7] Tangstad, P. Calvert, H. Brun and A.G. Lindseth: "Use of Comilog ore in ferromanganese production", INFACON X, 1-4 February 2004, Cape Town South Africa, pp. 213-222.
- [8] P.C. Pistorius: Pyrometallurgy Courses, NPM700 (2007); University of Pretoria, pp. 16.
- [9] H. Lagendijk, B. Xakalashé, T. Ligege, P. Ntikang and K. Bisaka: "Comparing Manganese FerroAlloy Smelting in Pilot-Scale AC and DC Submerged-Arc Furnace; The Twelfth International Ferroalloys Congress, pp. 497-507, June 6, 2010; Helsinki, Finland.
- [10] H. Li and A. Morris: "Evaluation of unified interaction parameter model parameters for calculating activities of ferromanganese alloys: Mn-Fe-C, Mn-Fe-Si, Mn-C-Si and Mn-Fe-C-Si systems, Metallurgical and Materials Transactions B, August 1997, Volume 28, Issue 4, pp. 553-562.