

THE CHALLENGES IN THE HIGH CARBON FERROMANGANESE INDUSTRY AND PROSPECTS

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Abstract

The production of High carbon ferromanganese industry worldwide is facing gigantic challenges due an ever-increasing production cost that is mainly due to the yearly increase of electricity and the depletion of metallurgical coke. The power supply in some part of the world has become a challenge therefore impacting the productivity and slowing the growth of economies. Due to the depletion of metallurgical coke, alternative carbonaceous materials that would efficiently sustain the carbothermic reduction. The current paper depicts some of the challenges and presents some prospects and directions that are being tried as rescue measures. A number of laboratory bench-scale results are presented and enjoy being of good prospects.

Keywords: Metallurgy, High carbon ferromanganese, challenges, prospects

1. INTRODUCTION

Magnese is one of the required additives in the form of ferroalloys to enhance steel properties. From the worldwide production of manganese, 90% is consumed in the steel industry. High carbon ferromanganese, refined ferromanganese, low carbon ferromanganese and silicomanganese are the four major groups of alloys marketed manganese alloys. The industrial practice for the production of manganese ferroalloys is based on carbothermic reduction of manganese oxides. Another process using aluminum to reduce manganese oxides was also developed [1]. Electric furnaces and Blast furnaces are used [2]. The heating process of the former is based on electrical energy and the reduction using coke as reducing agent. The later uses coke for supplying heat requirements and as reducing agent. The disadvantage remains with high coke consumption and high MnO content in the slag and the manganese reporting in the off-gases. Although it has been widely reported that electric furnaces present many advantages such as high yield of manganese from the manganese ore, consumption of carbon considerably reduced compared to Blast furnaces, ability to produced different types of alloys, it remains a great question to find a solution to is the increasing cost of production due to the ever-increasing cost of energy.

1.1. Manganese deposits

Several manganese deposits are found in different countries worldwide with different mineralogical compositions. The deposits are located in the Kalahari Manganese Field (KMF). Two types of ores are found with one rich in carbonates and the other bearing predominantly braunite [3,4]. The manganese ore in Australia is rich in pyrolusite and cryptomelane [5], but some other are rich in psilomelane and hollandite with sometimes high in barium [6]. The Gabonese deposit to the Australian manganese deposit. The difference between the two is that the porosity is higher for the Gabonese deposit. The brazilian deposit is mainly composed of cryptomelane, todorokite and pyrolusite. China has the largest mine output averaging 22% containing high phosphorus and iron [7]. Kazakhstan and Ukraine have low grade compsed mainly by carbonates. Georgia has also low grade material while India has medium grade material in addition to low grade. The composition of the manganese ore plays a vital role during the carbothermic reduction of manganese [8]. To improve the

recovery and the efficiency in energy consumption, a blend of manganese ores is applied when both electric and Blast furnaces are used.

Figure 1 below depicts the percentages of different ferroalloys produced by region.

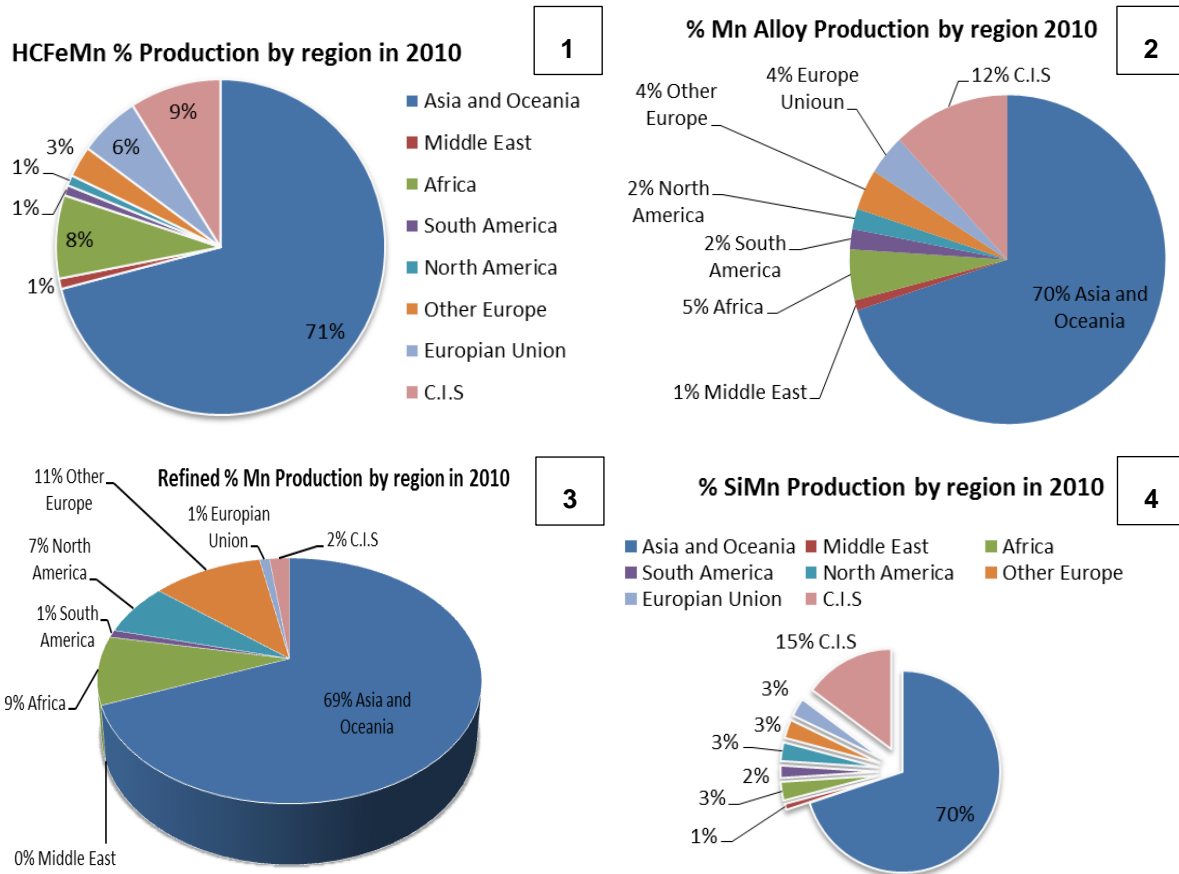


Figure 1 Percentage production of various ferroalloys by region in 2010 [2]

1.2. Carbon materials

Coal remains the main source of carbon. In submerged arc furnaces, coal cannot be used directly as reductant due to safety and environmental reasons. In order to select the reducing agent, a variety of considerations have to be taken into account namely availability, cost, process requirements, products requirements and gas emissions. The smelting productivity, reduction process and efficiency are affected by the physical properties of the carbonaceous materials [10]. The energy consumption, the amount of reductants to use and the product quality are influenced by the chemical composition of the reductant used. The freight cost for charcoal is high because of its low weight. The freight price is based on the volume than the weight. The ferrosilicon industry has chosen the use of charcoal more advantageous due to low ash content. However, in the manganese industry, the use of charcoal is not easy. The leaning toward charcoal will make this commodity scarce, therefore new challenges are on the card. Also, with the metallurgical coke being now at high demand due to high outputs in the iron and steel industry, the scarcity of both metallurgical coke and charcoal pushes the manganese industry into looking at new materials and processing, ways of decreasing energy consumption, developing new technologies to tackle environmental challenges that affect the profit margins in the manganese industry.

2. CHALLENGES IN THE MANGANESE INDUSTRY

2.1. Challenges due to mineralogical composition of the manganese ore

Reactions 25°C	kmol		MJ	kWh	Σ kWh
Drying					
$H_2O_{(l)} = H_2O_{(g)}$	11.00		484	134	
$H_2O + CO = H_2 + CO_2$	1.50		4	1	135
Pre-reduction and calcination					
$C + CO_2 = 2CO$	8.00		1379	383	383
$CaCO_3 = CaO + CO_2$	2.20		392	109	
$MgCO_3 = MgO + CO_2$	1.36		141	39	148
$Fe_3O_4 + 4CO = 3Fe + 4CO_2$	0.83		-31	-9	
$MnO_2 + CO = MnO + CO_2$	9.50		-1407	-391	
$Mn_3O_4 + CO = 3MnO + CO_2$	2.69		-137	-38	-438
Final reduction					
$MnO + C = Mn + CO$	14.4		3955	1099	
$SiO_2 + 2C = Si + 2CO$	0.014		9.7	2.7	
$C \rightarrow Mn_7C_3^*$	5.8		-211	-59	1043
Total heat of reaction (25°C)					1271
Product enthalpies (25 - T°C)	kmol	kg	MJ	kWh	Σ kWh
Metal 1500°C (s → l)					
Mn 79.0 %	14.4	790	1138	316	
Fe 14.0 %	2.5	140	177	50	
C 7.0 %	5.8	70	371	103	469
		1000			
Slag 1500°C (s → l)					
MnO 34.6 %	3.19	226	392	109	
SiO ₂ 26.5 %	2.88	173	316	88	
Al ₂ O ₃ 11.5 %	0.74	75	217	60	
CaO 18.8 %	2.19	123	339	94	
MgO 8.6 %	1.39	56	194	54	405
		653			
Off-gas 200°C					
CO	13.40		69	19	
CO ₂	12.57		90	25	
H ₂ O	9.5		57	16	
H ₂	1.5		8	2	62
Total product enthalpies (25 - T°C)					936
PROCESS total					2207

Figure 2 Typical example of mass and energy balance during high carbon ferromanganese [12]

The composition of raw material is a key player in the production of high carbon ferromanganese. Amongst other parameters are the Mn/Fe ratio. The challenge that Mn/Fe in a manganese ore is that low Mn/Fe ratio leads to high coke consumption and high electrodes consumptions with low manganese recovery [11]. The moisture content, state of oxidation of manganese in the ore, any carbonates present in the manganese ore influence the mass and energy balances. Water evaporation, carbonates decomposition are high energy consuming steps in the production of high carbon ferromanganese while the presence of high manganese oxides in the ore is beneficial to the energy consumption because reduction of higher oxides is highly

exothermic. A typical example of the energy balance and mass balance based on the mineralogy of the ore is presented in **Figure 2** below. It transpires that water evaporation alone is 6% of the energy consumption whereas carbonates decomposition amounts to 7% of the energy consumption. Moisture removal might be controlled same way for different manganese ores, but carbonates decomposition depends on the mineralogy of the ore. Further, it is noted that the presence of MnO_2 in the ore has a positive contributing factor to the overall energy consumption. However, if one assumes that the manganese ore does not contain MnO_2 but Mn_2O_3 , the impact of the absence of MnO_2 reduction to Mn_2O_3 is that the energy consumption will increase considerably. The consequence is the cost of production increases especially for electric furnaces due to ever-increasing electricity price. This constitutes a great challenge because the composition of the ore is critical not only on the quality of the products, but on the cost of the process due to energy consumption. Reactions are grouped in exothermic and endothermic. Exothermic reactions are essentially reduction of MnO_2 to Mn_2O_3 , reduction of Mn_2O_3 to Mn_3O_4 , reduction of Mn_3O_4 to MnO , reduction of Fe_3O_4 to Fe , $C = C$ (dissolution of carbon into the molten metal) while Endothermic reactions are $MgCO_3$ decomposition to MgO and CO_2 , water evaporation, $CaCO_3$ decomposition to CaO and CO_2 , Boudouard reaction ($C + CO_2 = 2CO$), reduction of MnO to Mn (highly endothermic) and partial reduction of SiO_2 to Si (reports to the metal). Furthermore, the quality of the burden is another factor is challenging. The permeability of the bed, when not well managed lead to poor gas circulation. This is governed by the composition of the feed. In case, sinters were made out of a manganese ore which contains carbonates, it may, after a certain time of storage encounter desagregation due to possibly occluded gas during sintering which took place while calcining was also taking place. Occluded gas may also, if no desintegration took place before feeding the furnace, be liberated during reduction due to high temperature and lead to desintegration, therefore decrease the permeability of the bed.

2.2. Challenges due to gas emissions

Emissions emanating from off-gas are complicated to solve compared to those from dusts emissions. Two to three-stages wet scrubbers are used to collect uncombusted CO gas for closed manganese alloys furnaces [13-15]. Although nowadays most of the air pollution problems are solved satisfactorily, the main challenges remain with water pollution. The presence of heavy metals, polycyclic Aromatic Hydrocarbons (PAC), suspended solids and possibly dissolved cyanides is the major challenge. Additionally, the CO/CO_2 ratio in the off-gas is important since it has a tremendous influence on the water pH value. This implies that the variation of reducing conditions has an impact on the acidity of water. Further, the presence of mercury in the off-gas is detrimental to the environment, therefore a number of processes for mercury removal have been required with new technologies being developed.

3. NEW DIRECTIONS AND PROSPECTS

In order to draw new directions a number of steps can be considered. Testing different new raw materials, testing new reductants that would improve the environmental impact of the ferromanganese industry, Development of new technologies: new reactors for ferroalloy production and energy, introduction of artificial intelligence to improve the prediction and monitoring of processes, vaste campaign of recrutement of scientists to refelect on the future without coke and coal can be envisaged to find new and efficient direction.

4. SOME INDICATIONS ON NEW MATERIAL

A number of focused investigations on the use of new material are ongoing. Fuel biobased have been tested to replace coke breeze in the iron ore sintering process. This has been driven by reports that the reactivity of biobased fuels is considerably higher than that of coke breeze due mainly to their higher porosity and surface area [16]. Partial replacement of coke breeze during ironmaking in the Balst furnace in the sintering section has been found successful [16]. Some studies on the possible use of biomass using the South African manganese ores were conducted and as preliminary results were generated. The use of raw macadamia nut

shells for the reduction of manganese ore has been tested. It was found that macadamia nut shells have great potentials of replacing the conventional reductants used so far. The separation of slag from the metal remains a challenging factor and needs improvement [17]. Pam Kernel Shells were also tested as a replacement of coke. Results have shown good prospect. The extraction of manganese amounted to close to 50% whereas it was around 45% when charcoal was used [18]. The prospect of replacing current generic reducing agents is considerable coupled with further detailed investigations on sizes and possible improvements of the raw materials used as coke replacement. Their impact on the recovery and the quality of end products needs thorough research and possibly innovation technology should accompany the walk on the new road. Not only that new carbonaceous materials should only be used as reductants, but test their contribution toward energy consumption as well.

5. CONCLUSION

Current challenges that the manganese industry is faced with, a new dynamic, trials and errors can be permitted to find new ways and innovative solutions to metallurgical coke replacement, reducing agents consumption with impact on energy consumption. Organizing discussion and research groups around these topics would considerably contribute to accelerating findings to these major challenges that the manganese industry encounter today the paper must contain conclusion. The conclusion should summarize the findings and explain the implications of the paper. Conclusion contains no new data or findings.

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