TECHNICAL DEVELOPMENT OF FERROSILICON MANGANESE PRODUCTION IN ORE-SMELTING ELECTRIC FURNACES WITH USING OF MANGANESE MAGNESIA AGGLOMERATE

[1] V.S. Kutsin, [1] V.I. Olshanskiy, [1] U.B. Dedov, [1] I. Philipov, [2] M.I. Gasik, [2] M.M. Gasik, [2] A.N. Ovcharuk, [2] O.I. Polyakov

[1]Public Limited Company “Nikopol Ferroalloy Plant”
53200, Ukraine, Nikopol, Dnepropetrovs`k obl, Electrometalurgov str, 310, e-mail: 01@nzf.com.ua
[2]National Metallurgical Academy of Ukraine 49600, Ukraine, Dnepropetrovsk, Gagarina str, 4,
e-mail: tehnosplavy@ua.fm

ABSTRACT

In the report it is analyzed the results of the industrial development of innovative technology of ferrosilicon manganese production in PLC "Nikopol Ferroalloy Plant" conditions with the use of manganese magnesia agglomerate which has been produced by agglofactory of the plant from the domestic enriched manganese ore of the Nikopol’s deposits and dumping magnesium-silicate slag which have been received by smelting of ferronickel at Pobuzhsky Ferronickel Plant.

In the report outlines the main provisions of the current PLC “NFP” technology of production of ferrosilicon manganese MnC17 in the РПЗ-63 furnace. The starting manganese ore raw material for production of manganese ferroalloys are Nikopol oxide, mixed oxide-carbonate and carbonate concentrates which are supplied to the plant by Marganetskiy and Ordzhonikidze Mining and Processing Plants of Prindeproviya. It is shown that the potential reserves of the further enhance of the technical and economic indicators of ferrosilicon manganese smelting is concluded in the selection of evidence-based effective slag melting mode by optimizing of the content in the furnace slag of the magnesium oxide and, respectively, reasonable its basicity. To achieve this by using Nikopol manganese ore is impossible due to the small content of the magnesium oxides. Because of the deficit and high cost of standard magnesium-containing materials the use of it in the industrial scales appeared to be economically unreasonable. That is why, instead of the magnesium-contained materials it is used the dump magnesium-silicate slag smelting of ferronickel at Pobuzhsky Ferronickel Plant, which have been produced with the use of imported nickel ore that holds magnesium-silicate gangue. In the report it is shown the main stages of the researches and mastering of the technology of ferrosilicon manganese smelting with the use of manganese magnesia agglomerate.

KEYWORDS: *Ferrosilicon manganese production, manganese magnesia agglomerate, magnesium-silicate slag smelting of ferronickel.*

In the general structure of manganese ferroalloys, smelted on the domestic and foreign plants, the most large-capacity is ferrosilicon manganese (DSTU 3548-97). As a complex deoxidizer and alloying ferroalloy the ferrosilicon manganese is widely used in steel production in oxygen converters, electric arc furnaces. The need of the world steel industry in ferrosilicon manganese increases almost proportionally to the growth of steel production. Steel production all over the world in 2011 compared to 2010 increased by 93 million tons and reached 1 billion 510 million tons. According to the forecast the production of steel in 2030 will reach 1 billion 776 million tons, including the 655 million tons produced in China, 470 million tons produced in North America, 282 million produced in European Union, 120 million tons produced in South America, 86 million tons produced in Russia, 164 million tons produced in other countries. So despite the economic crisis, the periodic ups and downs, the volume of steel production by 2030 will increase, which will require a definite increase the production of manganese ferroalloys and, above all, ferrosilicon manganese.

In 2011, the smelting of manganese ferroalloy on the ferroalloy plants in Ukraine reached 1036.76 thousand tons, including 770,56 thousand tones produced on PJV "NFP". Along with the application on the domestic market, the Ukrainian manganese ferroalloys are exported to over 30 countries all over the world.

It is known [1] that smelting of the manganese characterized by the high specific power consumption. The installed electric power of the ore-smelting electric furnace on the PJV "NFP" for smelting ferrosilicon manganese and high-carbon ferromanganese (DSTU 3547-97) is 63 MB·A (furnaces types: ore-smelting square closed type furnace -63, ore-smelting square hermetic type furnace - 63) and 75 MB·A (ore-smelting square closed type furnace - 75). In combination with other electric consumers the installed electric capacity of PJV "NFP" is 1366 MB·A, which is 10% of Dnieper Power System power generation, or 2.5% of the total consumed electrical energy of the whole Ukraine.

In recent ten years, as the result of held at PJV "NFP" scientifically-based works on the improvement of existing technologies of agglomeration and smelting of manganese ferroalloys developed and implemented innovative processes and technological equipment, a number of economical questions were solved as well, which will significantly improve the technical and economic indexes of manganese ferroalloys production. However, the structural components of the prime cost of high-carbon ferromanganese and ferrosilicon manganese need the further reduce the specific expenses of manganese ore raw materials and energy due to the continuous increase of its costs.

THEORETICAL BACKGROUND OF INNOVATIVE TECHNOLOGIES OF FERROSILICON MANGANESE SMELTING ON MAGNESIA SLAG

Physical and chemical process ferrosilicon manganese smelting according to the current technology based on the reduction of manganese and silicon from its oxides manganese agglomerate and quartzite by the solid carbon. An applied manganese agglomerate (47% MnO, 28% SiO_2, 8,5% CaO, 3% FeO, 2,9% Al_2O_3) characterized by the low magnesium oxide (2,2% MgO) content, and therefore the ferrosilicon manganese of the furnace slag not fully meet the requirements of an effective continuum carbon reduction process because of the relatively low melting temperature and high electrical conductivity [2]. The chemical process of obtaining the ferrosilicon manganese in general can be represented by the scheme of participated charge components and received products by smelting

$$2(\mathrm{Mn, Fe})\ \mathrm{Al_2O_3, CaO, SiO_2 - SiO_2 - (1+x) - C} \rightarrow [\mathrm{Mn\text{-}Fe\text{-}Si\text{-}C_x}] +$$

$$+ (\mathrm{SiO_2\text{-}CaO\text{-}MgO\text{-}(Al_2O_3 - MgO + MnO) + CO}$$

Theoretical temperatures of beginning the reduction process of Mn and Si from the pure oxides MnO and SiO_2 (condition $\left(\alpha_{MnO}=\alpha_{SiO_2}=1\right)$ according to the reactions

$$2\mathrm{MnO} + 2\mathrm{C} = 2\mathrm{Mn} + 2\mathrm{CO} \qquad \Delta G_T^0 = 580590 - 346{,}4T, \ \ \mathrm{J/mol}$$

$$\mathrm{SiO_2} + 2\mathrm{C} = \mathrm{Si} + 2\mathrm{CO} \qquad \Delta G_T^0 = 669390 - 359{,}07T, \ \ \mathrm{J/mol}$$

respectively equal to 1675K (1402° C) and 1942 K (1669°C).

However, the reduction of the elements from its oxides with the help of carbon always accompanied by the formation of not pure manganese and silicon, but its carbides according to its reactions:

$$MnO + (1 + x) C = MnC_x + CO \qquad \Delta G^0_T(MnC_x) = 193293 - 123{,}0\,T, \quad J/mol$$

$$SiO_2 + 3C = SiC + 2CO \qquad \Delta G^0_T(SiC) = 555615 - 322\ T, \quad J/mol$$

At lower temperatures 1595K (1325°C) and 1724K (1451°C).

In the case of a joint reduction of manganese and silicon, the silicon carbide thermodynamically not stable and reacts with manganese carbide according to the reaction:

$$2MnC_x + SiC \rightarrow [2Mn - Si - C_x] + C_{\text{гроф}}$$

Interaction of MnC_x and SiC according to the present scheme of the chemical reaction with an increase of silicon content in the ferrosilicon manganese (DSTU 3548 - 97) from 10% to 35%, the solubility of carbon in the alloy reduce from 3.5% to 0.5%, respectively, because the thermodynamic strength of manganese silicide significantly higher of its carbides. The higher the concentration of silicon in ferrosilicon manganise, the higher the temperature of the process and more specific power consumption. On mutually approved technological positions of the producersof ferrosilicon manganese and its consumers the most needed on the domestic and international markets is a ferrosilicon manganese, grade: MnC17 (≤ 65% Mn, 15 ... 20% Si ≤ 2,5% C). According to the existing technology of ferrosilicon manganese smelting at PJV “NFP”, ZFP and StakhPF the beneficial use of manganese from the charge, consisting of manganese magnesite sinter (2,5% MgO), quartzite and coxitis is $\eta_{Mn} \leq 87\%$ and $\eta_{Si} \leq 44\%$, which is close to the data of foreign factories which produce the ferrosilicon manganese. Thus it was reached the lowest specific energy consumption 3150-3950 kW·h/t. The common task during the production of ferrosilicon manganese is the development of the innovative prevailing technological scheme, which provides increase of the useful output of manganese and silicon from the charge in the ferrosilicon manganese and decrease of power consumption.

The searching laboratory and pilot-scale experiments have shown that one of the ways of increasing the efficiency of production of the ferrosilicon manganese is the work of the furnaces on the magnesia furnace slag [3].

In the current report it was found that the liquidus temperature T_L of the manganese agglomerate according to the chemical composition is described by the following equation

$$T_L(^\circ C) = 47\left(\frac{\%MgO}{\%CaO}\right) + 27\left(\frac{\%CaO}{\%Al_2O_3}\right) - 10{,}7(\%MnO) + 1952$$

With the increasing of the ratio of % MgO / % CaO liquidus temperature rises (infusibility) of the agglomerates and therefore, the temperature of furnace slag during the smelting of the ferrosilicon manganese. According to our researches the liquidus temperature of the furnace slag is also greatly depends on the content of MgO, relationship of (% CaO) / (% Al_2O_3) and (% MnO) / (% SiO_2), and this relationship is represented by the next equation

$$T_L(^\circ C) = 7{,}84(\%MgO) + 60(\%CaO/\%Al_2O_3) - 175(\%MnO/\%\ SiO_2) + 1443$$

It is important to note that with the increasing of the MgO content in the slag the distribution ratio of manganese L_{Mn} between ferromanganese and furnace slag is also increase [4].

$$L_{Mn} = \frac{[\%Mn]}{(\%Mn)} = 0{,}568(\%MgO) - 0{,}699, \qquad (r = 0{,}93)$$

Thus, the data of preliminary experiments confirmed the main points of research on increasing of the useful extracting of manganese into the ferrosilicon manganese with increasing of the MgO content in the furnace slag [5].

THE RESULTS OF EXPERIMENTAL – INDUSTRIAL ASSIMILATION OF THE DEVELOPED TECHNOLOGY OF FERROSILICON MANGANESE SMELTING

In earlier works, carried out by the Nikopol Ferroalloy Plant specialists together with scientists from the Electrometallurgy Department of Dnepropetrovsk Metallurgy Institute regarding the increasing the content of MgO in the furnace slag during the smelting of ferrosilicon manganese were used a number of MgO-containing materials: magnesite calcined powder, dumping material of chromite ore enrichment from Donetsk ore-dressing plant, dumping slag of high-carbon ferrochrome smelting from the Aktubinsk Ferroalloy Plant (now "Kazchrome" Ltd.) characterized by the high content of MgO. The novelty and industrial utility of the developed during the last years technological options ferrosilicon manganese, MnC17 grade, smelting using the above mentioned MgO-containing materials confirmed by the data of the experimental industrial melting.

However, due to the lack and high cost of standard quality magnesite powder, high content of chromium oxide in the dump materials of the chromite ore and slag of carbon ferrochrome smelting enrichment, results of the experiments could not be implemented in the industrial scale.

Indicated in the current paper, a large-scale industrial assimilation of the cut-through technology scheme and processes of producing the manganese magnesia agglomerate and smelting, with the use of which, the ferrosilicon manganese MnC17 conducted from March to May 2012. In the production of manganese magnesia agglomerate into the experimental campaign has been used 9,000 tons of magnesium-silicate dump slag of ferronickel rich smelting (15-20% Ni) at «Pobuzhskiy ferronickel plant" (Kirovohrad region), with chemical composition, mass. %: 30,1 MgO, 54,1 SiO_2, 7,5 FeO, 4,7 CaO, 2,1 Al_2O_3 and 0,8 Cr_2O_3.

Manganese magnesia agglomerate AMHB-2M [6, 7] was carried out in agglomerate workshop of NFP on agglomerate machines AKM-105 and used as part of the charge during the smelting of ferrosilicon manganese MnC17 in the ore-smelting electric arc ore-smelting square closed type furnace -63 and ore-smelting square hermetic type furnace -63 with the unit capacity of 63 MB·A.

Summary data about the composition of agglomerate charge and chemical composition of the agglomerates, which were received during each of the five periods of the experimental campaign of assimilation and implementation of cut-through technological scheme and process are shown in table 1.

During the smelting of ferrosilicon manganese MnC17 in the base period it is used the agglomerate AMHB -2 with the chemical composition (% wt.): 47,4 Mn: 28,5 SiO_2; 8,5 CaO; 2,2 MgO; 2,3 Fe; 0,17 P and in experimental period it was used the manganese agglomerate AMHB-2M. To correct the manganese content in the charge and base furnace slag it was used, in some periods, rich imported manganese ore (Gana KK28) and first grade manganese concentrate.

A summary data of the specific consumption of charging components in the smelting of ferrosilicon manganese in each of the five periods are shown in table 2.

Data on changes in the manganese content in the furnace (dump) slag of ferrosilicon manganese MnC17 smelting, the coefficient of useful extraction of manganese and silicon from the charge into the ferrosilicon manganese and multiplication factor of dump slag are given in table 3.

Table 1: Specific consumption of charge materials and chemical compounds of the received manganese magnesium agglomerate by periods of sintering of the agglomerates and smelting of ferrosilicon manganese

Description	Period of agglomerate production AMHB-2M				
	I	II	III	IV	V
Charge materials	**Specific consumption, kg/t agglomerate**				
Manganese concentrates:					
1 grade	172	113	-	-	-
1 grade OOKNF	185	127	122	184	241
2 grade OOHF	657	475	498	312	605
1 grade Oxid. consentration	-	315	410	479	17
1B grade OONF	-	-	-	41	165
Ferronickel slag	151	142	143	132	121
PShSh	50	52	46	32	2
Total manganese raw material	1215	1224	1219	1180	1151
Chemical compound of agglomerate	**mole fraction of component, %**				
Mn	36,4	38,4	38,1	39,1	38,9
SiO_2	28,9	27,4	27,3	26,2	26,2
CaO	5,2	4,9	4,8	4,7	5,1
MgO	7,0	5,9	5,8	5,9	5,5
Fe	3,2	3,1	3,1	3,2	2,9
P	0,16	0,16	0,16	0,16	0,7

The total quantity of ferrosilicon manganese smelted during the experimental period was 24,879 tons. Analysis of Table 3 data shows that, for the all periods of ferrosilicon manganese smelting with the use of agglomerate AMHB-2M the useful extraction of manganese from the charging manganese content component into the alloy increased from 87.6% in the baseline period to 88,7-92,7% during the experimental period. At the same time, respectively, the extraction of silicon rose from 44.1% in the baseline period to 46,1-49,5 during the test period.

Table 2: Specific consumption of charging components and power during the smelting of ferrosilicon manganese in the base and experimental periods

Description	Period of ferrosilicon manganese smelting					
	Base period	Experimental periods				
		I	II	III	IV	V
AMHB-2M	-	1354,1	1405,9	1362,6	1349,5	1441,2
AMHB-2	1231,8	-	-	-	-	-
AMHB-2P	165,2	-	-	-	-	-
Gana KK28	170,1	178,9	49,5	-	-	-
1 grade carbon concentration	-	-	52,8	121,4	118	95,6
coke	390,2	399,1	367,8	394,0	357,5	369,8
quartzite	332	217,1	243,3	257,8	244,2	245,2
Fe-ore	67,5	41,8	39,1	113,3	90	53,7
Electricity, kW·h/b.t.	3949,6	4061,1	39,0	3931	3872	3902

Relationship of the manganese extraction coefficient η_{Mn} and silicon η_{Si} on a baseline and experimental periods of ferrosilicon manganese smelting are well illustrated by the data presented in figure1.

Table 3: Comparative chemical analysis of slag of smelting ferrosilicon manganese with the use of the basic and experimental manganese agglomerate and indices of manganese and silicon extraction from the charge in ferrosilicon manganese

Indicator name	Period of ferrosilicon manganese smelting					
	Base period	Experimental periods				
		I	II	III	IV	V
Smelting of ferrosilicon manganese in the period, the basic t	7559,7	4136,5	5675,5	3563,5	6629,0	4875,0
Chemical composition of slag, %						
Mn	11,2	8,8	9,7	8,6	9,2	9,5
SiO_2	50,0	50,1	49,6	49,9	48,8	49,5
CaO	18,1	14,4	14,1	15,2	15,5	15,9
MgO	6,7	11,8	10,5	10,4	9,9	8,8
Al_2O_3	8,1	7,8	78	8,6	8,5	8,4
Slag multiplication factor	1,51	1,53	1,42	1,28	1,32	1,39
Extraction Mn, %	87,6	88,7	91,0	90,4	92,7	88,33
Extraction Si, %	44,1	46,1	47,5	46,5	49,5	47,5

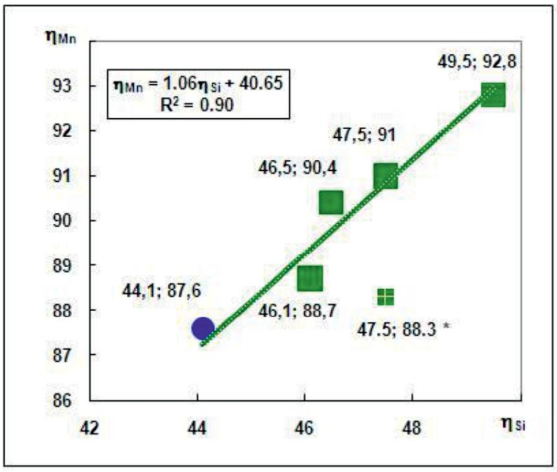

Figure 1: Relationship of silicon and manganese extraction coefficient during the ferrosilicon manganese smelting on magnesia slag using magnesia agglomerate AMNV-2M

* Decreased value η_{Mn} due to the decrease of MgO in the slag to 5.5%

The table 2 shows that the smelting of ferrosilicon manganese MnC17 (0.6% P) using the agglomerate AMHB-2M accompanied by a reduction of the specific consumption of quartzite (74,2-114,9 kg/t). During the experimental campaign smelting of ferrosilicon manganese MnC17 confirmed that the specific energy consumption in the first place, as it is known, depends from the content of manganese in the agglomerate and the charge for the smelting of ferrosilicon manganese. So in the first period of research campaign during reducing the content of manganese in the agglomerate AMHB-2M to 36.4% and in the given charge to 35.2% (against 38.2% in the baseline period) the specific energy consumption has increased by 111.5 kW·h/t, with an increase of the given manganese charge by 36,8-37,7% the specific energy consumption decreased by 18.6 ... 107.6 kW·h/t.

The determinate contribution of the use of manganese magnesia agglomerate in the increase of technical and economic indicators of ferrosilicon manganese smelting is confirmed by analysis of experimental data of the fifth period of the campaign. By reducing the specific consumption of magnesium-silicate slag in the composition of agglomerate charge to 121 kg/t, and hence, the content of MgO in the dump slag of ferrosilicon manganese to 8.8% the coefficient of useful manganese extraction has decreased to 88.3%.

Thus, the results of the 90-day campaign on assimilation of the technology of ferrosilicon manganese smelting on magnesium slag, using the manganese agglomerate with a high content of MgO allowed to confirm the evidence of theoretical studies [5, 7], to develop an effective cut-through technological scheme which includes the processes of production of manganese magnesia agglomerate and smelting of ferrosilicon manganese with its use [8, 9].

SUMMARY

1. It was analyzed the thermodynamics of reactions of separate and common recovery of manganese and silicon from its carbon oxides in relation to high-temperature conditions of ferrosilicon manganese smelting process. The attention was put and proved that the increase in temperature in the baths f ore-smelting furnaces can be achieved by raising the "smelting" temperature of manganese agglomerate during the increase in its content of the magnesium oxide.

2. It was developed, industrially assimilated and implemented the technology of production of manganese magnesia agglomerate AMHB-2M with the use in the agglomerate charge magnesium silicate dump slag (30% MgO, 50% SiO_2, 4,6% CaO and 2,5% Al_2O_3) smelting of rich ferronickel (18 - 20% Ni) at «Pobuzhsky ferronickel plant". The novelty and industrial utility of the developed technology are protected by a patent of Ukraine No.: 99087 A.

3. It was developed, industrially assimilated and implemented the technology of smelting in the super-power ore-smeltig electric furnaces ore-smelting square closed type furnace -63 and ore-smelting square hermetic type furnace-63 of ferrosilicon manganese MnC17 on stable magnesium slag (9,9-11,8% MgO, 48,8-50,1% SiO_2, 8,6 -9,9% Mn).

4. According to the result of a pilot campaign (March-May 2012) production of agglomerate AMHB-2M and smelting of ferrosilicon manganese MnC17 with the use of this agglomerate it was achieved a significant improvement in the technical and economic indicators: reduced specific energy consumption by 64 kW·h/t, manganese raw materials by 39 kg/t, coxitis by 12 kg/t and quartzite by 39 kg/t. Thus, it was achieved an increase coefficient of manganese extraction from the charge from 87.6% (basic technology) up to 88,7-91,0% (experimental technology) and silicon from 44.1% up to 46,1-49,5%.

5. During the large-scale experimental campaign settled new relationships of manganese and silicon extraction coefficient, depending on the ratio of charge components and chemical compositions of slag, which should be theoretical explained and pilot tested to identify the conditions for the further reduction of the specific energy consumption.

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