WASTES GENERATION AND USE IN FERROALLOY PRODUCTION*

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About 94% of ferroalloys in Russia are smelted in submerged electric arc furnaces (SAF) using a carbothermic technology. Sufficient amounts of technogeneous wastes are generated even at the stage of mining and production of concentrates from ores (quartzite, chromite and manganese ores, coals, lime et al.) before smelting.

Wastes generation in ferroalloy industry leads to formation of slags, dusts, sludge and ferroalloy gas. Volumes of these products depend on charge materials and production technology at the ferroalloy works, but slags are quantitatively the main “disposable” product.

Chromium ferroalloys in Russian Federation are produced at JSC “Chelyabinsk electrometallurgical works” (JSC “Chemk”), JSC “Serov ferroalloy plant” (JSC “SFAP”) and JSC “Klyuchevsky ferroalloy plant” (JSC “KZF”). Manganese ferroalloy producers in Russia are JSC “Chemk”, JSC “Satka pig-iron smelting works” (JSC “SHPZ”) and JSC “Kosaya Gora Iron Works” (JSC “KGIW”). Production of silicon ferroalloys concentrated at JSC “Kuznetsk ferroalloy works” (JSC “KFW”), JSC “Chemk”, JSC “SFAP” and “Bratsk ferroalloy works” (JSC “Mechel”).

Technology of carbothermic reduction in SAF for high-carbon ferrochrome and ferrochromium-silicon differs from the point of view of wastes generation. Typical slag-to-metal ratio for high-carbon ferrochrome production varies from 1.0 to 1.9 and depends mainly on concentration of Cr_2O_3 in chromites. Slag is formed from magnesia-alumina gangue of chromium ores and silica-containing flux (quartzite, slags of silicon ferroalloys).

Production of ferrochromium-silicon using a two-stage technology requires production of high-carbon ferrochrome from chromites and carbonatious reductant at the 1st stage and ferrochrome-silicon from ferrochrome, quartzite and reductant at the 2nd stage, where slag-to-metal ratio amounts to 0,02-0,06.

Quantity of slag, generated at production of bulk chromium ferroalloys can be estimated on the basis of average slag-to-metal ratio of 1.5.

Production of high-carbon ferromanganese in SAF and blast-furnaces using a flux method also depends on quality of manganese ores and concentrates, and slag-to-metal ratio varies from 0.6 to 1.22 (average 0.9). Peculiarity of high-carbon ferromanganese smelting is in maintaining of slag basicity at the level of 1.1 – 1.5 by addition of fluxing materials (lime or dolomite).

Slag-to-metal ratio for silicon and ferrosilicon production varies from 0.05 to 0.10 and depends on the alloy type.

Data on slag generation and production volumes of ferroalloys in Russia are given in table 1.

Table 1: Ferroalloy production and slag generation volumes in Russia, t/year

Alloy type	Ferroalloy production, thsd. t	Slag-to-metal ratio (average)	Amount of slag, thsd. t
Silicon and ferrosolicon	566.4	0.1	56.64
Ferrochromium and ferrochromium-silicon	354.0	1.5	531.00
Ferromanganese and silicomanganese	188.8	0.9	169.92
Total	1109.2	-	757.56

Slags of bulk ferroalloys production processes do not subject to self-desintegration after crystallization, so lump slags do not require stabilization and use of special equipment for fine materials processing.

Typical chemical composition of slags, dusts and sludge of chromium, manganese and silicon ferroalloys production [2-10] is given in Table 2-4.

As a rule, high-carbon ferrochrome and ferrochromium-silicon are produced in the same melting shop and dust collection is organized simultaneously from different furnaces without separation of different types. Dusts from ferrochromium-silicon furnaces differ from those smelting high-carbon ferrochrome mainly by concentration of silica.

Work with fine materials is far more difficult than with lump slags. Utilization of waste gases requires construction of additional installations and units for implementation of continual process.

One of the problems of dust collection from waste gases is a difference in design of submerged electric arc furnaces (SAF): open, semi-closed, closed-top and sealed type.

Table 2: Chemical composition of slag and dust of ferrosilicon production

Material	Content, % wt.										
	SiO_2	SiO_2 amorphous	CaO	Al_2O_3	MgO	SiC	Metal[*]	Fe_2O_3	Na_2O	K_2O	C
Ferrosilicon slag	32	-	18	16	0.8	15	15-25	-	-	-	-
Microsilica (furnace dust)	-	85-98	0.1-1.0	0.1-1.5	0.2-2.0	-	-	0.1-3.0	0.1-1.0	0.2-3.0	0.2-3.0

[*] Corresponds to chemical composition of smelted ferroalloy grade

Table 3: Chemical composition of slags and dusts of chromium ferroalloys production

Material	Content, % wt.							
	Cr_2O_3	MgO	Al_2O_3	SiO_2	CaO	FeO	C	SiC
Ferrochromium-silicon slag [*]	3.5	8	13	45	0.5	0.2	-	3
High-carbon ferrochrome slag	4.3	44.2	17.3	29.8	2.5	0.8	-	-
Gas-cleaning dust (bag filters)	20.1	35.8	6.1	13.4	0.8	6.3	4	-
Gas-cleaning dust (cyclones)	43.1	20.8	6.9	9.3	1	11.1	6.2	-

[*] Additionally contains ~30 % wt. of metal (composition, %: 13 Si_{metal}, 9 Cr_{metal}, 4 Fe_{metal}, 4 C)

Table 4 Chemical composition of slags and dusts of manganese ferroalloys production

Material	Content, % wt.											
	MnO	$Fe_{общ}$	P[*]	CaO	MgO	SiO_2	Al_2O_3	S	Na_2O+ K_2O	ZnO	п.п.п.	C
High-carbon ferromanganese (blast-furnace)												
Slag	16.5	0.65	0.01-0.4	41.0	6.5	32.0	7.5	1.1	0.65	0.02	-	-
Dust	16.5	2.05	0.1-0.25	28.5	6.5	26.5	7.5	1.1	0.85	0.16	-	8.0
Slurry / Gas-cleaning dust (2nd stage of cleaning)	17.0	4.50	0.1-0.3	14.5	6.0	20.0	7.5	1.0	1.50	0.50	70-85[**] /11-13	21.5
High-carbon ferromanganese and silicomanganese (SAF)												
Silicomanganese slag	14.2-16.8	0.15-0.20	0.012-0.014	17-18	4.5-5.5	49.0-50.0	7.0-8.0	0.8-1.3	3.3-4.5	-	-	0.2-0.4
High-carbon ferromanganese slag	15.5-18.1	0.10-0.15	0.08-0.11	35-38	3.0-4.0	34.0-36.0	4.0-5.0	0.5-0.8	2.4-3.5	-	-	0.2-0.4
Gas-cleaning dust	20.7-25.8	1.4-1.9	0.15-0.25	5.0-7.0	1.5-2.5	18.0-21.0	1.5-2.5	0.3-0.5	4.5-8.0	0.5-2.0	27.0-37.0	5.0-10.0

[*] Depends on phosphorus content in manganese raw materials

[**] Above 100%

It is undoubtedly that the use of closed-top and sealed furnaces provides the most effective dust collection from waste gases without air dilution. Nevertheless, units and technologies for collection of toxic manganese dusts from SAF producing high-carbon ferromanganese and silicomanganese have a broad distribution [11]. These technologies provide dry gas cleaning up to 8-11 mg/m^3 of residual dust concentration when content of dust in gas before cleaning is ~1.15 g/m^3, so bag filters efficiency exceeds 99%.

Use of top-closed and sealed furnaces for manganese and chromium ferroalloys production is rational since it is related with decrease in oxygen partial pressure under the furnace roof and promotes less oxidation of dust particles and less generation of toxic chemical compounds with Fe, Mn and Cr [12].

Volumes of dust collection in Russian ferroalloy industry are estimated on the basis of industrial data on dust generation and collection. So, blast-furnace ferromanganese production generates dust and sludge approximately 10 and 100 kg/t of alloy, respectively. High-carbon ferrochromium production in SAF generates ~50/150 kg of dust per 1 t of alloy, and silicon alloys (depends on alloy grade) 60-150 kg/t. Calculated figures on dust generation in Russian ferroalloy industry are given in table 5. Collected dust of high-carbon ferrochromium production have fine particle size (see Table 6 and 7) and alike slags of this alloy have high heat resistance and can be applied in refractories [13].

Table 5: Dust and sludge generation at Russian ferroalloys industry

Alloy type	Ferroalloys production volume, thsd. t/year	Dusts		Sludge		Total, t/year
		yield, kg/t	total, t/year	yield, kg/	total, t/year	
Siliceous	566.4	120	67968	н.д.	н.д.	67968
Chromite	354.0	150	53100	н.д.	н.д.	53100
Manganese	188.8	10	1888	100	18880	20768
Total	1109.2		122956		18880	141836

Table 6: Granulometric composition of gas cleaning dust at high-carbon ferrochromium production, % wt.

Dust type	Fraction yield, mm						
	>2.5	1.6-2.5	1.0-1.6	0.4-1.0	0.16-0.4	0.063-0.16	<0.063
Cyclone	0.28	0.25	0.42	13.37	17.27	39.74	28.67
Bag filter	-	0.003	0.015	0.51	5.99	46.76	46.62

Table 7: Granulometric composition of dust (bag filters) at SAF production of high-carbon ferromanganese and silicomanganese, % wt.

Fraction yield, μm		
<1	*10-40*	*>40*
49	39	12

There are different ways for recycling of manganese dusts. One of the most advanced and environmentally friendly way is arranged in Japan [15], where manganese dust is used in production of manganese-ore pellets. These pellets are charged into SAF after preheating and prereduction in rotary kiln with waste gases. One of the examples of wastes recycling at the post-soviet space is the use of waste slags, dusts and sludge in manganese ferroalloys industry and production of electrosmelted fluxes at Nikopol ferroalloy plant where technogeneous materials are added into agglomerate charge [16]. Though the solution leads to increased dust generation in agglomeration process and requires additional control of dusts and gases generation and propagation in atmosphere [17].

Recycling of gas cleaning dust (20-43% Cr_2O_3) at chromium ferroalloys production can be arranged in the form of additions to chromite pellets and as a charge component at smelting of metal product of slag separation [18].

Dry gas cleaning systems are very effective from the point of view of dust collection for manganese and chromium ferroalloys production [11].

Ferrosilicon slags are completely recycled in SAF as a flux for high-carbon ferrochromium and charge-chrome.

Slags of ferrochrome and ferromanganese require sophisticated separation schemes due to weak magnetic properties of metal fines and can hardly be separated from slag by magnetic separation (in contrast to metal fines in steelmaking industry). Separation complex for ferroalloy slags often includes jigging machines, classifiers and other special equipment.

Peculiar property of high-carbon ferrochromium slags is a comparatively high melting temperature (heat resistance) which allows using them in refractories industry for production of fire-bricks and tapping hole mix. These materials are in demand at the same plants where they are generated [13].

One of the ways of recycling of manganese ferroalloys slags is a production of high-quality cast products with high performance characteristics from hot liquid slags for civil and industrial engineering [19].

A special attention should be paid to wastes of chrome- and manganese ores extraction and concentration processes as these tailings make a sufficient part from the volumes of crude ores. This type of materials are often of equal or higher quality by their chemical composition if compared with technogeneous wastes of ferroalloys smelting process and, in some cases, are better than crude ores before concentration.

In the world ferroalloy industry one can find a trend for development of environmentally friendly wasteless complex technologies, where by-products are considered as additional raw materials for ferroalloy industry and analogous areas.

A good example of complex use of chromium ores is a strategy of ferroalloy producers in South African Republic where ores of Bushveld mining deposit are separated after extraction and concentration into several products. Use of these materials in ferroalloy industry varies due to chemical composition and fraction and includes smelting of both lump ores (6-150 mm and 6-25 mm) and pellets (made from fines –6 mm, with or without reductant) of different types (including Outotec process on steel belt) in SAF. Fine fractions of chromites (gravitational concentrate) can be smelted in DC electric furnaces without palletizing or sintering and with comparatively cheap coal instead of coke as a reductant. So, this technology and general approach includes alternative technological processes, furnaces and auxiliary equipment that makes national ferroalloy industry more flexible.

Peculiarities of Russian ores deposits are represented mainly by poor manganese ores and chromites and economic security issues require new sophisticated solutions for complex technological wasteless schemes. Metallurgical estimation of poor domestic chromites and manganese ores, concentrates and technogeneous raw materials (slags, dusts and sludge, tailings) is a key element, along with technical and economic estimation of a process. Availability of industrial equipment is a basis of flexibility and competitiveness of national ferroalloy industry.

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