

Conference Paper

Manganese Ferroalloys of Russia

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Abstract

Manganese is an important strategic metal. The main consumer of manganese is iron and steel industry. Due to its importance in steel manufacturing, manganese has the first position among ferroalloys. The world output of manganese ferroalloys is around 1% of the total steel output. After the USSR collapsed, Russia has been left without manganese ore reserves. At present, Russia uses an imported ore to smelt only high-carbon ferromanganese and iron-silicon-manganese alloy in limited quantity. Mineral reserves of manganese ores in Russia is quite large: manganese ore reserves averages 230,000 metric tons (around 2% of the world reserves) and estimated resources – more than one billion tons. The quality of the Russian ores is lower than the one from the other main producing countries. The average content of manganese in the Russian ores fluctuates from 9 to 23%. Domestic ores contain high quantity of harmful impurities, first of all phosphorus (0.2–0.8%). The mineral reserves of manganese ores in Russia is based on carbonate ores with a share of over 77%. A problem to advance the establishment of domestic manganese mining base is an extremely important issue from the perspective of economic security. A string of questions ought to be addressed concerning the concentration of lean manganese ores, development of effective technologies to smelt manganese ferroalloys from the concentrates obtained after the concentration and creation of improved techniques to dephosphorize manganese concentrates. While producing manganese ferroalloys from ore to finished alloy, about 50% of the manganese extracted from strata is wasted in the form of by-products such as concentration sludges, slags, residue of small fractions of raw materials and finished products, sludges of smelting processes and dusts. In case of the by-products processing and following usage, it would be possible not only to reduce consumption of raw materials but also to increase manufacturing effectiveness and to minimize environmental impact.

Keywords: ferromanganese, dephosphorization, ore, reserves

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1. Introduction

Manganese is an important strategic metal. The main consumer of manganese is iron and steel industry. By its importance for steel manufacturing, manganese has the first

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position among ferroalloys. Over 90% of manganese is used at steel smelting as a deoxidizing, desulfurizing and alloying agent. In average, 9–10 kg of manganese is utilized to produce a ton of steel [1]. As an alloying element, manganese is contained in many types of steel: 0.4–0.8% of Mn in unalloyed steels, 12–30% of Mn in high-alloyed steels (heatproof, heat-resistant, stainless, non-magnetic, Hatfield steels), 4–17% of Mn in austenitic iron. Basically, not a single type of steel is smelted without manganese.

In metallurgical industry manganese is used in the form of ferroalloys: high-carbon ferromanganese, iron-silicon-manganese alloy, medium- and low-carbon ferromanganese (refined ferromanganese) and metallic manganese. Ferroalloys containing hard-reducible elements were firstly produced only by the crucible method [2]. In the early ninetieth century, the crucible method was also used to produce medium- and low-carbon ferroalloys and low-carbon ferromanganese above all. The main problems of the crucible manufacturing were high costs and low performance. For that reason, high-carbon ferromanganese was produced exceptionally with use of blast-furnaces since 1880s. In the twentieth century, when electric power became cheaper, manganese ferroalloys were started to be smelted mainly in electric furnaces – ore-thermal and refining ones.

The production of manganese ferroalloys strongly depend on the production of steel – the output of steel increases simultaneously with the output of manganese ferroalloys. The world output of manganese ferroalloys is around 1% of the total steel output.

Nikopolskoe (Ukraine), Chiaturskoe (Georgia) and Dzhezdinskoe (Kazakhstan) fields formed the basis of the manganese ore industry in USSR. Annually, 20 million tons of raw ore were mined at these fields; the average content of manganese in the ore was 20%. The ore gave up to 2 million tons of manganese ferroalloys smelted mainly at Nikopolsky (Ukraine), Zaporozhsky (Ukraine), Zestafonsky (Georgia) and Aksussky (Kazakhstan) ferroalloy factories. When the USSR has collapsed, Russia has lost manganese ore reserves. At present, Russia uses imported ore to smelt high-carbon ferromanganese (Kosaya Gora Iron Works, Satkinsky Iron Smelting Plant and Chelyabinsk Electrometallurgical Plant) and iron-silicon-manganese alloy (Chelyabinsk Electrometallurgical Plant) in limited quantity [3, 4].

Mineral reserves of manganese ores in Russia is quite large: manganese ore reserves averages 230 million tons (around 2% of the world reserves) and estimated resources – more than one billion tons (Table 1) [5].

The quality of the Russian ores is lower than the one for the other main producing countries. The average content of manganese in the foreign ores fluctuates from 40 to 45%, while in the Russian ones – 9 to 23%, with an exception for a single field with a

TABLE 1: Resources and reserves of manganese ores in the Russian Federation as of 2014/01/01 [5].

Estimated resources	P ₁	P ₂	P ₃
Quantity, billion tons	241.57	254	507
Reserves	Explored (A+B+C ₁)		Preliminary estimated (C ₂)
Quantity, metric tons	137,807		92,352

value of 31%. At the same time, the domestic ores contain high quantity of harmful impurities, first of all phosphorus (0.2–0.8%), and then iron and silica. The mineral reserves of manganese ores localized in Russia are huge; the quantity of only P₁ resources is commensurable with the total reserves. However, the content of manganese in the estimated resources, as well as in the total reserves, is modest and varies in the range of 9–20% (Figure 1).

The largest manganese ore field in Russia is Usinskoe (Kemerovo region, West-Siberian area). It is situated in the central part of Kuznetsky Alatau, 90 km from Mezhdurechensk. Its depths include more than a half of the manganese reserves in Russia. The field is characterized by massive reserves of lean carbonate ores with an average manganese content of 19.6%. The ore-bearing mass is composed of manganese limestones accommodating rhodochrosite and mangano calcite ores. Rhodochrosite ores contain 24.2% of Mn, 6.06% of Fe, 0.176% of P, 14.6% of SiO₂, 11.3% of CaO and 25.2% of loss-on-ignition. Mangano calcite ores contain 14.5% of Mn, 5.8% of Fe, 0.18% of P, 18.6% of SiO₂, 17.9% of CaO and 24.6% of loss-on-ignition. The field has a crust of weathering within which oxidized ores have formed, containing 26.7% of Mn, 8.5% of Fe and 0.27% of P.

One more large-scale manganese ore field is Porozhinskoe (Turukhansky area, the Krasnoyarsky territory, East-Siberian area). It is located in the north of the Yenisey area, 600 km north of the city of Krasnoyarsk. The field includes 12.8% of the Russian manganese reserves. The ores of the Porozhinskoe field are pure and have a high level of phosphorus, 0.3-0.8%, sometimes up to 7%). The average chemical composition of oxidized ores: 18.28% of Mn, 6.84% of Fe, 0.52% of P, 33.1% of SiO₂, 3% of CaO and 10.2% of Al₂O₃. The average chemical composition of carbonate ores: 16.75% of Mn, 3.13% of Fe and 0.52% of P.

A group of nine fields containing 15 of the total Russian reserves is explored in the Sverdlovsk region. Ore bodies are formed preliminary by carbonate ores that are difficult for concentration. The ores contain 20–22.5% of manganese and a quite high concentration of silica.

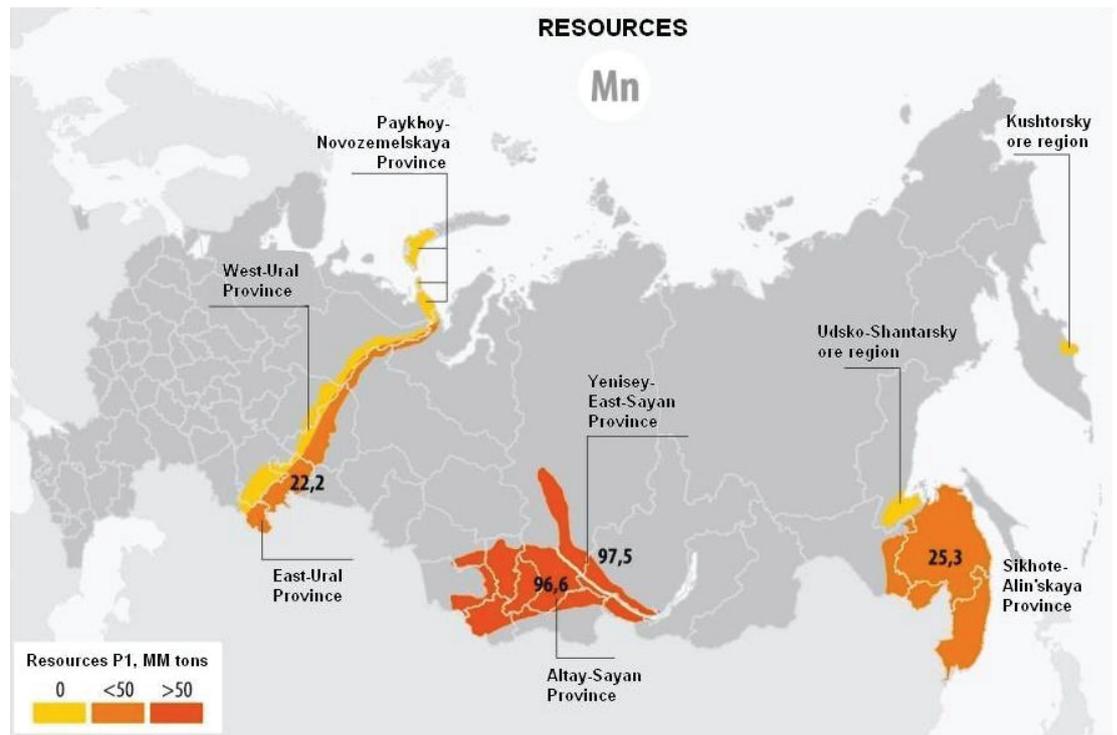


Figure 1: Resource potential of manganese-bearing provinces and ore regions in the Russian Federation, P₁, million tons.

Medium-sized Yuzhno-Khinganskoe field with iron-manganese ores (Jewish autonomous region, Malo-Khingansky ore region) holds 3.9% of the reserves in Russia. The ores of the field are of the oxide-carbonate type and contain on average 20.9% of manganese.

The highest average manganese content of 31% has Parnokskoe iron-manganese field (Komi Republic, Northern Ural). The field reserve ratio in the summarized manganese ore reserves does not exceed 2%. The following ores are distinguished at the field: oxidized (lean and rich), rich mixed (semi-oxidized), carbonate (carbonate-silicate) and oxide-carbonate ones. The content of manganese fluctuates from 20 to 57%, iron – 1.5–10%, phosphorus – 0.02–0.2%, silica – 2.2–30%.

Thus, the mineral reserves of manganese ores in Russia is based on carbonate ores with a share of over 77%. The data concerning the main fields of manganese ores in Russia are given in the Table 2 [5].

The federal register of mineral resources counts 21 deposits of manganese ores including 4 deposits of iron-manganese concretions on the shelf of the Gulf of Finland, the Baltic Sea (Figure 2). 13 of them are located in a distributed subsoil fund. The fields in unallocated subsoil fund are small by quantity of resources and contain low-grade ores [5].

TABLE 2: Main fields of manganese ores in Russia.

Field	Ore type	Ore reserves, m.t.		Part in reserves, %	Average content of Mn, %	Production in 2013, m.t.
		A+B+C ₁	C ₂			
Usinskoe	Carbonate	64,231	57,454	52.9	19.72	0
	Oxidized	5,847	164	2.6	25.57	0
Porozhinskoe	Oxidized	15,696	136,767	12.8	18.85	0
Yuzhno-Khinganskoe	Oxidized Mixed	127	0	0.06	18.09	0
	Oxidized	6,009	2093	3.5	20.88	20
	Oxygenized	285	381	0.3	21.09	0
Parnokskoe	Carbonate	786	221	0.4	30.47	0
	Oxidized	779	224	0.4	31.62	0

In Russia, manganese ores are mined sporadically (Figure 3) [5]. It is caused by the fact that the quality of ores at Russian fields is significantly lower than in the majority of commodity-dependent countries. The demands of Russian ferroalloy factories, producing manganese ferroalloys, for manganese ores and concentrates are satisfied by their import (Figure 4) [5]. The import rate increased from 270 thousand tons./year in 1996 to 1020 thousands of tons /year in 2014. The cost of manganese ore import reaches 142 million USD per year [4]. Manganese raw materials are mainly imported from South Africa and Kazakhstan, and also from Gabon, Brazil and Bulgaria. In the period of time from 2013 to 2016, the total cost of imported manganese ores to Russia was 562 million USD [6]. The structure of the import during those years is shown in the Table 3.

TABLE 3: The structure of manganese ore import to Russia from 2013 to 2016.

Country	Ore mass, m.t.	Ore cost, million USD	Share of total import, %	Content of Mn in ore, %
South Africa	1,800	240	45.6	38–51
Kazakhstan	1,600	208	39.5	20–40
Gabon	210	27.8	5.3	45–51
Brazil	130	17.8	3.4	43–50
Bulgaria	100	12.8	2.4	10–30

The annual output of high-carbon ferromanganese in Russia tends to increase – from 46.5 metric tons in 1997 (25% of the consumption rate) to 180.6 metric tons in 2013 (approximately equals to the consumption rate) [4]. In general, the consumption of high-carbon ferromanganese is 190–250 m.t./year. The output of iron-silicon-manganese alloy also tends to increase – from 50 metric tons in 1997 (20% of the consumption rate) to 230.5 metric tons in 2016 (52% of the consumption rate) [4]. The annual output of

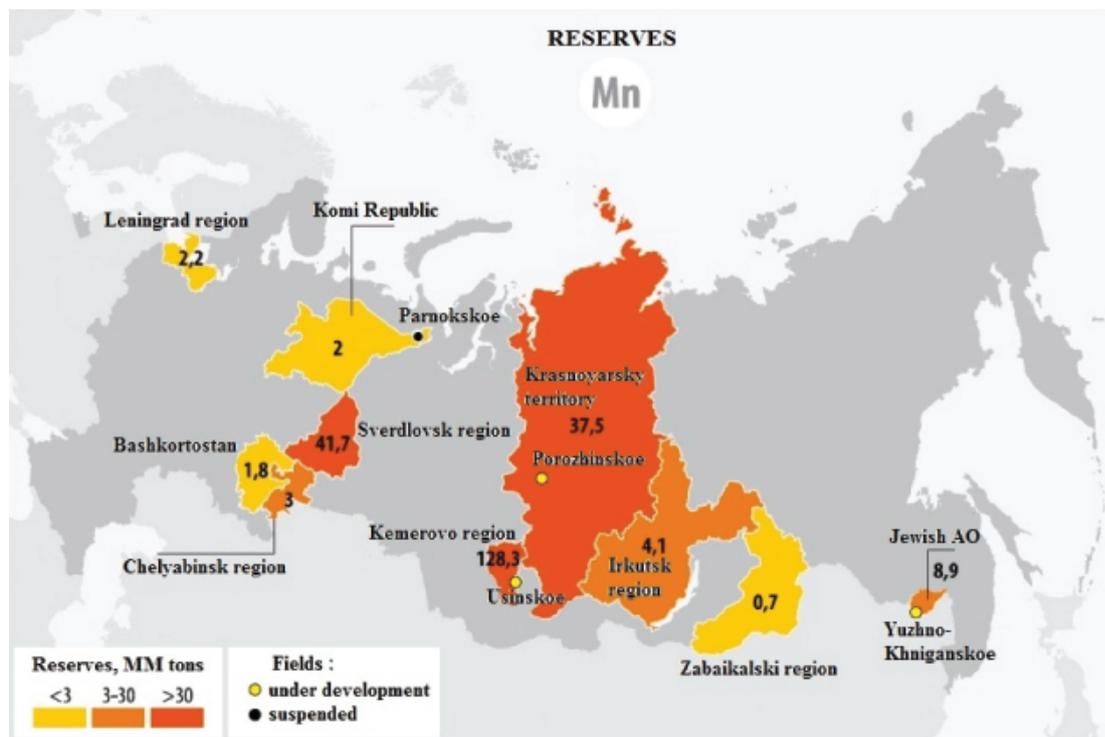


Figure 2: Main fields of manganese ores and their distribution by reserves in the region of the Russian Federation, billion tons.

manganese ferroalloys in 2013 was 334 metric tons and, for the first time, exceeded their import – 216 metric tons (Figure 5) [5].

In the past decades, it is clear that the consumption of high-carbon ferromanganese tends to decrease and iron-silicon-manganese alloy, refined ferromanganese and metallic manganese – tends to increase. The consumption of iron-silicon-manganese alloy (50-60 of the consumption rate) is balanced by the import from Ukraine (up to 175 thousands of tons) and Kazakhstan (up to 162 thousands of tons). Overall, the import rate reaches 245 thousands of tons./year [4]. Primarily, Russia imports metallic manganese, low-carbon and medium-carbon ferromanganese from Ukraine and electrolytic manganese – from China. The demands of Russian metallurgical enterprises for metallic manganese reached 60 thousands of tons in 2011 [7].

A problem to advance the establishment of domestic manganese mining base is an extremely important issue from the perspective of economic security. So far, despite the fact that manganese belongs to the group of natural resources with a strategic meaning, Russia has to import good-quality manganese ore, manganese ferroalloys, metallic manganese, manganese dioxide and potassium permanganate. It is necessary not only to increase the melting output of high-carbon ferromanganese and iron-manganese-silicon alloy, including by involving domestic manganese ores in the production, but

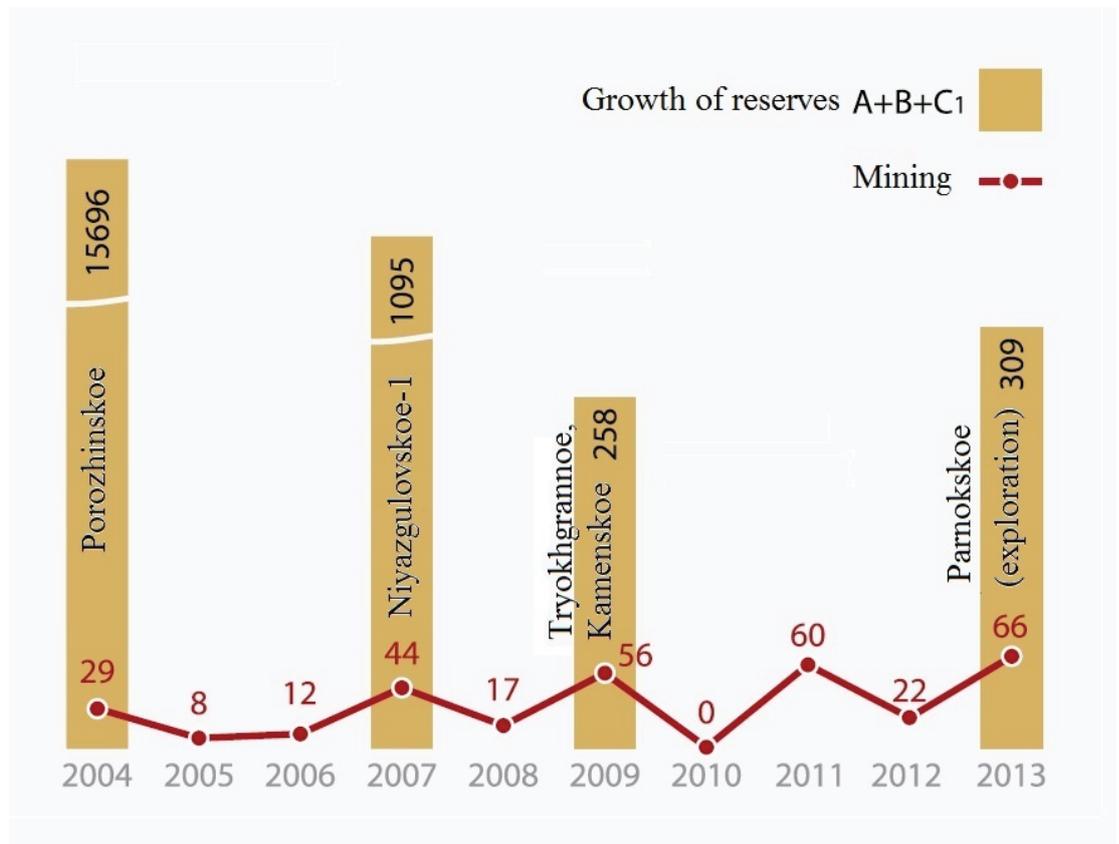


Figure 3: Dynamics of manganese ores mining and growth of their explored reserves in 2004–2013, thousands of tons.

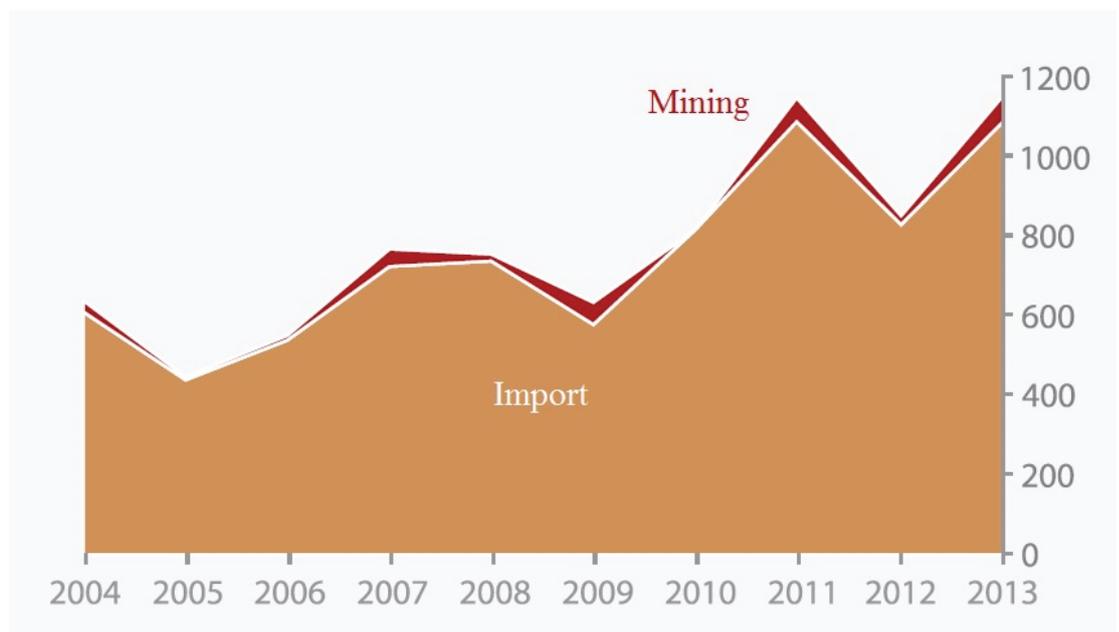


Figure 4: Dynamics of raw ore mining and marketable import of manganese ores in 2004–2013, thousands of tons.

also to organize manufacturing of refined ferromanganese and metallic manganese in Russia.

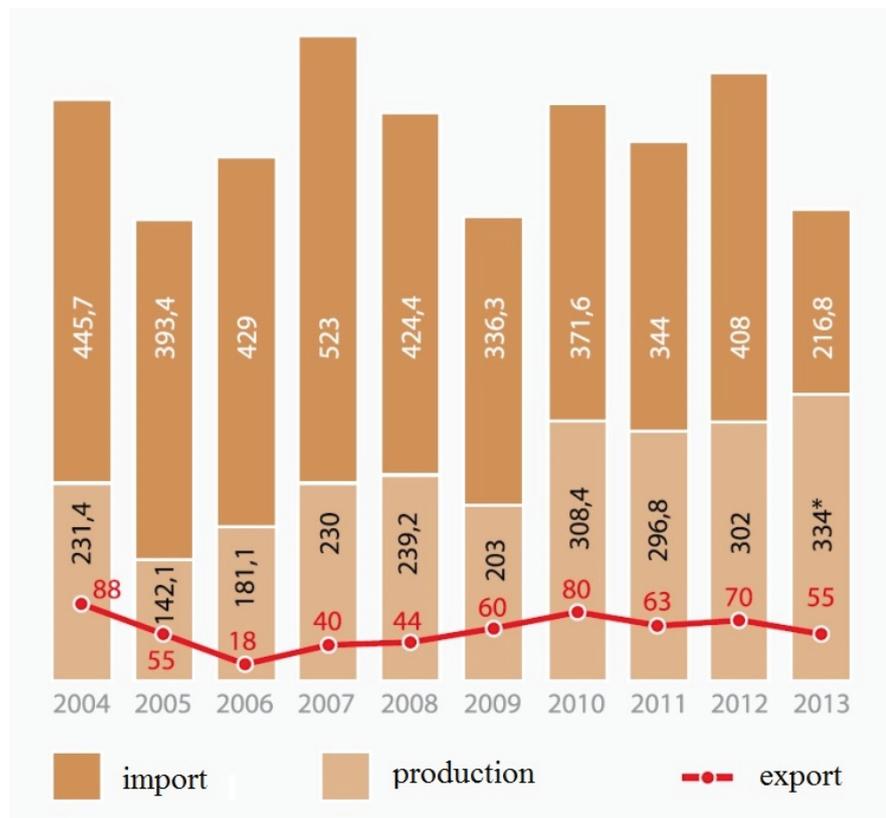


Figure 5: Dynamics of production, import and export of high-carbon ferromanganese and iron-siliconmanganese alloy in 2004–2013, thousands of tons.

A string of questions ought to be addressed concerning concentration of lean manganese ores, development of effective technologies to smelt manganese ferroalloys from the concentrates obtained after the concentration and creation of improved techniques for dephosphorization of manganese concentrates.

The situation with import-dependence of the Russian metallurgy on manganese products remains tense. Main directions to solve this problem are:

- involving domestic manganese ores in industrial production;
- development of effective technologies for dephosphorization of manganese-containing products;
- involving man-made wastes of ferroalloy production such as concentration sludges, furnace slag and gas purification dusts in recycling.

The simplest solution of how to involve domestic manganese ores in the production is additional charging of imported rich low-phosphorus ores with the domestic ones while smelting ferroalloys since the domestic ores are lean and with high-phosphorus content. Nevertheless, strategically and economically, it is essential to develop effective manufacturing schemes which allow smelting standard manganese ferroalloys with use

of domestic ores only. Investigations to create the technological schemes of manganese resources development in Russia are ongoing.

Among the explored domestic manganese deposits, the Usinskoe field is the most perspective. The ores of the field have a relatively low content of manganese (15–25%) and high content of phosphorus (0.2–0.3%). A perspective technological scheme is developed to concentrate the ores of Usinskoe with use of X-ray radiometric separation (XRRS) [8]. This scheme allows obtaining concentrates with a composition detailed in the Table 4.

TABLE 4: Chemical composition of the concentrates, % [8].

Components	Concentrate							
	Carbonate					Oxide		
	I grade (XRRS)	II grade (XRRS)	Jigging			Coarse (washing)	Jigging	
	20–100 mm	20–100 mm	10–20 mm	4–10 mm	0–4 mm	10–80 mm	4–10 mm	0–4 mm
Mn	36.00	25.20	24.00	23.50	23.30	35.83	35.00	34.20
P	0.16	0.15	0.14	0.14	0.14	0.216	0.220	0.230
Fe	3.20	3.30	3.60	5.00	5.00	11.07	10.90	10.54
SiO ₂	9.49	13.32	13.87	14.17	14.29	12.72	13.20	13.60
CaO	7.44	14.95	15.70	16.03	16.17	2.36	2.36	2.40
MgO	1.76	2.85	2.99	3.05	3.08	1.52	1.51	1.48
Al ₂ O ₃	1.18	1.40	1.47	1.50	1.52	1.84	1.89	1.99
S	0.80	0.90	0.90	0.96	0.96	0.08	0.09	0.09
Loss on ignition	26.58	27.20	26.30	25.95	25.73	7.72	9.49	10.70

A technological scheme is suggested to produce all range of manganese ferroalloys from the concentrates obtained by dressing of manganese ores of Usinskoe with use of X-ray radiometric separation (Figure 6) [9, 10].

Domestic manganese ores, as it was mentioned above, contain a high level of phosphorus, 0.2–0.8%. The key indicator for manganese ores and concentrates is a phosphorus module (P/Mn), which must be ≤ 0.003 . To smelt standard manganese ferroalloys with a defined content of phosphorus, manganese-containing materials have to be dephosphorized.

There are plenty approaches to dephosphorize manganese-containing products: hydrometallurgical, chemical and pyrometallurgical [11, 12]. Among the hydrometallurgical ones, the most well-developed and well-established are soda [12] and hausmannite [13] methods.

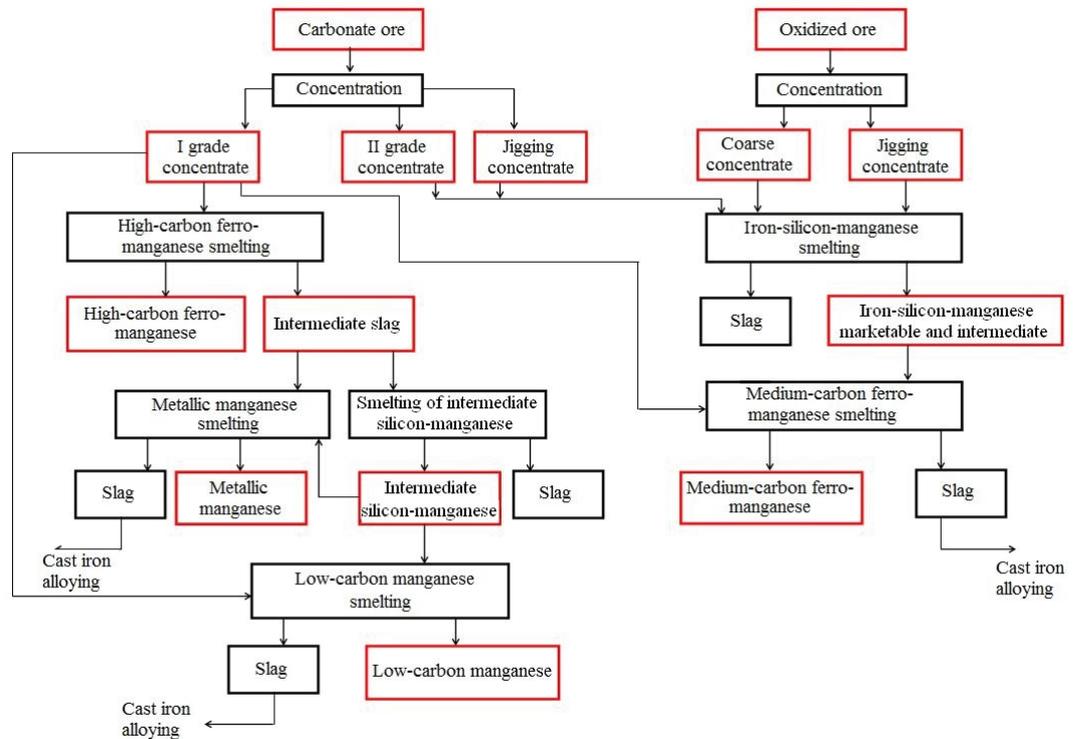


Figure 6: A technological scheme for smelting manganese ferroalloys from the ores of the Usinskoe field.

The soda method is based on roasting of manganese-containing materials with sodium carbonate followed by leaching of phosphorus and, partially, silica. In this way, it is possible to improve the quality of manganese concentrates by content of phosphorus and silica; however, the method can be used for marketable concentrates only since the content of manganese during the processing remains almost at the same level.

The point of the hausmannite method is that hausmannite Mn_3O_4 obtained after roasting of manganese concentrate has low solubility in diluted acids. The method is designed for application to dephosphorization of carbonate manganese ores. The disadvantage of the hausmannite method is that the nitric solutions formed at leaching of roasted concentrates have to be neutralized in some way, and this issue remains unresolved.

Among all chemical approaches, a dithionate method has passed industrial tests [14]. The point of the method is that leaching of manganese is carried out by using Sulphur dioxide SO_2 in the medium of calcium dithionate CaS_2O_6 . The main advantage of the method is that the method makes it possible to dephosphorize marketable ores along with products with low content of manganese such as low-grade ores, dump sludges from ore gravity concentration, slags and other substandard materials. The resulting concentrate contains 55–62% of Mn, 0.010–0.017% of P, 1–2% of Fe, 1.5–2.5% of SiO_2 , 6–8% of CaO and 2–4% of S. The extraction rate of manganese equals to 90–95%. A

high content of sulfur in the concentrate is not an obstacle to smelt high-grade manganese ferroalloys due to the fact that sulfur is limitedly soluble in manganese and its alloys [15]. The dithionate method is the only method which allows obtaining high-grade concentrates rich in manganese from low-grade high-phosphorus products.

At the Marganets ore mining and processing enterprise (Marganets, Ukraine) an experimental-industrial complex has been built for dressing and dephosphorizing dump sludges with use of the dithionate method with a performance of 25 metric tons of concentrate per year. The complex was launched in 1986. The concentrate produced at the complex was successfully used to smelt manganese ferroalloys in industrial environments [16].

Since 1950s, another method of dephosphorization was adopted and implemented in industrial scale – the electrometallurgical method [17]. The idea of the method is to selectively reduce phosphorus and iron from melted manganese ores and concentrates by direct carbon reduction and to transfer them to a minor associated metal. To do this, manganese ores and concentrates are melted in a furnace with a limited addition of coke precisely calculated for reduction of phosphorus and iron. Although the quantity of carbon in a charge is limited, a partial reduction of manganese occurs despite the fact that manganese has a greater affinity for oxygen than phosphorus and iron. Losses of manganese contained in the starting charge with a minor associated metal reach up to 15–20%, which is a significant disadvantage of the described method.

The methods described above do not solve the problem of dephosphorization of manganese-containing products. The development of effective techniques to dephosphorize manganese-containing products remains a matter of primary importance, first of all, because of the issue of involving domestic manganese ores with a high content of phosphorus in manufacturing.

There are ongoing researches on developing a new way to dephosphorize manganese-containing products, where phosphorus in oxide melt is reduced by gaseous carbon monoxide [18]. To dephosphorize melts of manganese ores and concentrates, this method proposes that phosphorus in oxide melt is reduced not by solid carbon but by gaseous carbon monoxide (CO) blown through the manganese-containing oxide melt. The reduced gaseous phosphorus P_2 is released with waste gases.

As a result of blowing of carbon monoxide through the manganese-containing oxide melt, a dephosphorized product is obtained. If the starting manganese ore or concentrate contains 0.2–0.3% of P, then the resulting product will contain 0.01–0.03% of P [19]. The value of phosphorus module (P/Mn) decreases 5–10 times in comparison

with the starting product; the degree of dephosphorization equals to 80–90%. The method of dephosphorization of manganese-containing products by carbon monoxide, in comparison with the method where solid carbon is used, not only eliminates losses of manganese with a minor associated metal but also optimizes the process of manganese ferroalloys smelting.

While producing manganese ferroalloys from ore to finished alloy, about 50% of the manganese extracted from strata is wasted in the form of by-products such as concentration sludges, slags, residue of small fractions of raw materials and finished products, sludges of smelting processes and dusts. In case of the by-products processing and following usage, it would be possible not only to reduce consuming of raw materials but also to increase manufacturing effectiveness and to minimize environmental impact. As a consequence, it will reduce both the expenses of enterprises on emission fees and recycling of wastes and government expenses related to environmental measures [20].

The involvement of manufacturing wastes in technological processes of ferroalloy production will lower the metallurgical value of ore component of the charge. Therefore, the rational application of the described approach has to be based on a reliable metallurgical evaluation of the utilized ore and man-made materials and resulting charge. The main principles to work with man-made wastes have to be:

- maximum trapping and collecting man-made wastes (sludges, slags and dusts);
- obtaining reliable information about the physical-chemical characteristics of the wastes such as chemical and fraction composition, moisture content, etc.;
- determining a rational way to involve each technological material in the production.

Additional extraction of manganese from man-made wastes and enhancement of technological processes of manganese ferroalloys smelting are the way to rise the throughout extraction of manganese [21, 22]. With dump sludges of manganese ore concentration processes up to 20% of manganese contained in ore is wasted. For example, at the Nikolskoe field concentration sludges are dumped into ravines creating “sludge ponds”. Nowadays, these ponds contain more than 100 billion tons of sludges containing at least 10,000 metric tons of manganese. Recent dump sludges contain 10–14% of Mn and old “ponds” – 17–20%. The most perspective idea for extraction of manganese from sludges is to use the dithionate method of concentration and dephosphorization of manganese-containing products [14].

At smelting of refined ferromanganese and metallic manganese a significant quantity of manganese is wasted with dump sludges. The extraction rate of manganese in these

processes does not exceed 65–70%. One of the possible ways to extract manganese from slag may be a process of manganese reduction through interaction of the slag with a metallic melt containing elements with a great affinity for oxygen. In the capacity of metallic melt to carry out such a process, cast iron can be considered as it contains carbon having a greater affinity for oxygen than manganese. A method of alloying cast iron by manganese contained in the slag of smelting processes of refined ferromanganese and metallic manganese has been developed [23]. The point of the method is that cast iron is poured from a blast-furnace into a ladle, the bottom of which is covered by a dump slag reasoning from the needed content of manganese in cast iron. In doing so, additional manganese-containing materials for a charge are not required. The conducted researches have shown that up to 75% of manganese contained in the slag is reduced by cast iron [24].

As a new type of manganese raw materials, concretions may be considered [25]. In the water area of the Gulf of Finland (the Baltic Sea, Leningrad region) in the unified field of iron-manganese concretions, four of their compact deposits are registered. The total reserves of these nominal deposits equal to around 1% of the total manganese ore reserves. The concretions are located at the depth of 30 to 70 meters, in contrast with ocean concretions located at the depth of at least 4 kilometers. The concentration of manganese in concretions depends on their granulometric composition. A considerable part of manganese (17–25%) is concentrated in the concretions with a diameter of 5 mm and higher. Concretions with smaller diameters concentrate manganese at the level of 5–8 mass %. On average, the concretions have a high content of phosphorus – up to 2%. The dithionate method is considered as the most rational method for dressing concretions [14]. Using the method, it will be possible to obtain a high-grade concentrate with a high content of (55–62%) and low content of phosphorus (0.010–0.017%).

As it was described above, by using the dithionate method, it is possible to obtain high-grade concentrates from low-grade and substandard manganese-containing products such as concretions, lean ores, dump sludges and others. Having this kind of concentrate allows producing all range of standard manganese ferroalloys from the domestic manganese ores.

According to the current technology, high-carbon ferromanganese is produced by using carbothermal process [1]. To smelt this alloy from the domestic concentrates poor in manganese and rich in phosphorus, the issue of producing alloys with standard phosphorus content can be resolved by additional charging of ordinary concentrates with the “dithionate” ones. It will allow smelting high-carbon ferromanganese with use of an

effective flux-free method in obtaining the standard alloy and low-phosphorus intermediate slag.

According to the current technology, the iron-silicon-manganese alloy is produced with use of the carbothermal process [26]. To smelt this alloy from the domestic concentrates poor in manganese and rich in phosphorus, the issue of producing alloys with standard phosphorus content can be resolved by additional charging of ordinary concentrates with the intermediate slag from flux-free smelting of high-carbon ferromanganese.

According to the current technology, refined ferromanganese and metallic manganese are smelted using silicothermal method (period process) [26]. These alloys can be smelted from the charge the ore part of which consists of the intermediate slag from flux-free smelting of high-carbon ferromanganese or the dithionate concentrate, or their mixture.

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