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DEVELOPMENT OF THE TECHNOLOGY OF FERRONICKEL PRODUCTION IN UKRAINE

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ABSTRACT

The paper summarizes the results of numerous works performed by the employees of the Pobuzky Ferronickel Plant, the Department of Electrometallurgy of the USU of Science and Technology (Dnipro), RPC “Technosplav” under the leadership of Mykhailo Hasyk, academician of NASU. A technology of low iron recovery has been implemented at the plant, which allows producing high-percentage black ferronickel, containing 30–50 % Ni, and almost hundredth fractions of carbon and silicon, directly in electric furnaces. The thermodynamic features of out-of-furnace ladle desulfurization of ferronickel with soda are considered. A complex technology has been developed and implemented, which involves mixing black ferronickel with a reduced silicon and carbon content (up to 0.01 %) and a high nickel content (over 50 %) produced in one furnace with an alloy from another furnace with a low nickel concentration (10–17 %) and a high concentration of silicon and carbon, which are so necessary for desulfurization with soda in a ladle. The developed and proposed technological schemes for the enrichment of electric furnace slags using the “wet” technology and refining slags using the “dry” technology make it possible to recycle about 1,200 tons of nickel per year, or to extract 31.6 % and 94.65 % of nickel from the slags, respectively.

KEYWORDS: Pobuzky Ferronickel Plant, cinder, black ferronickel, ladle desulfurization, refining, slag enrichment

INTRODUCTION

Pobuzky Ferronickel Plant (PFP), which in 2022 celebrated its half a century jubilee, was put into operation for processing low-quality (up to 1 % Ni) local iron-silicon nickel ores of Kapitanivka deposit (Ukraine, Kirovohrad region). Ferronickel produced at the Plant, was characterized by an increased content of impurities (Si, Cr and C) in the black metal. So, silicon content in ferronickel in some melts was higher than nickel content, reaching the values of 6–8 % [1]. More over, the need to use fluxing additives, led to higher power consumption, increase of the amount of slag and respective nickel losses [2, 3]. After PFP restart (2001), it became possible to fundamentally change the approach to ferronickel production, which corresponds to current market requirements to nickel-containing products. The base of this concept was application of imported ore rich in nickel, and transition to melting of commercial ferronickel with up to 25 % nickel content [4, 5]. The ore was supplied from

New Caledonia and Indonesia. In connection with the fact that Indonesia stopped ore export from the beginning of 2014, PFP switched over to Guatemalan ore, which is characterized by higher content of nickel and magnesium oxide (Table 1), compared to ore from Kapitanivka deposit [5], on the base of which the Plant was designed and operated till 2006.

Over the long period of operation, the Plant developed and introduced many innovations into production [6–11], that ensured the high production efficiency. The most significant of them are energy carriers for cinder preparation in tubular rotary furnaces (TRF) from fuel oil through natural gas to pulverized coal fuel (PCF), ore predrying (from 35–38 to 20–23 %) of moisture for PCF, granulation of commercial ferronickel, installation of ore-recovery furnace (RVP1) of HATCH Company, Canada, that allows increase the capacity of the used furnace power, and lining service life due to its damping.

Recently, the technology of low iron recovery (TLIR) has been introduced at the plant, which allows

Table 1. Chemical composition of ores from different deposits, wt. %

Deposit	Ni	Fe	SiO ₂	CaO	MgO	Cr ₂ O ₃	Al ₂ O ₃
Kapitanivka (Ukraine) (1972–2001 pp.)	0.8	16	38.5	17	4.8	3.5	2.9
New Caledonia (2001–2006 pp.)	2.22	14.89	38.77	1.11	20.60	1.66	1.74
Indonesia (2006–2012 pp.)	2.08	12.62	42.95	1.05	21.45	1.18	1.91
Guatemala (TLRI) (2013–2016 pp.)	1.88	15.66	34.8	1.23	22.0	0.98	2.7

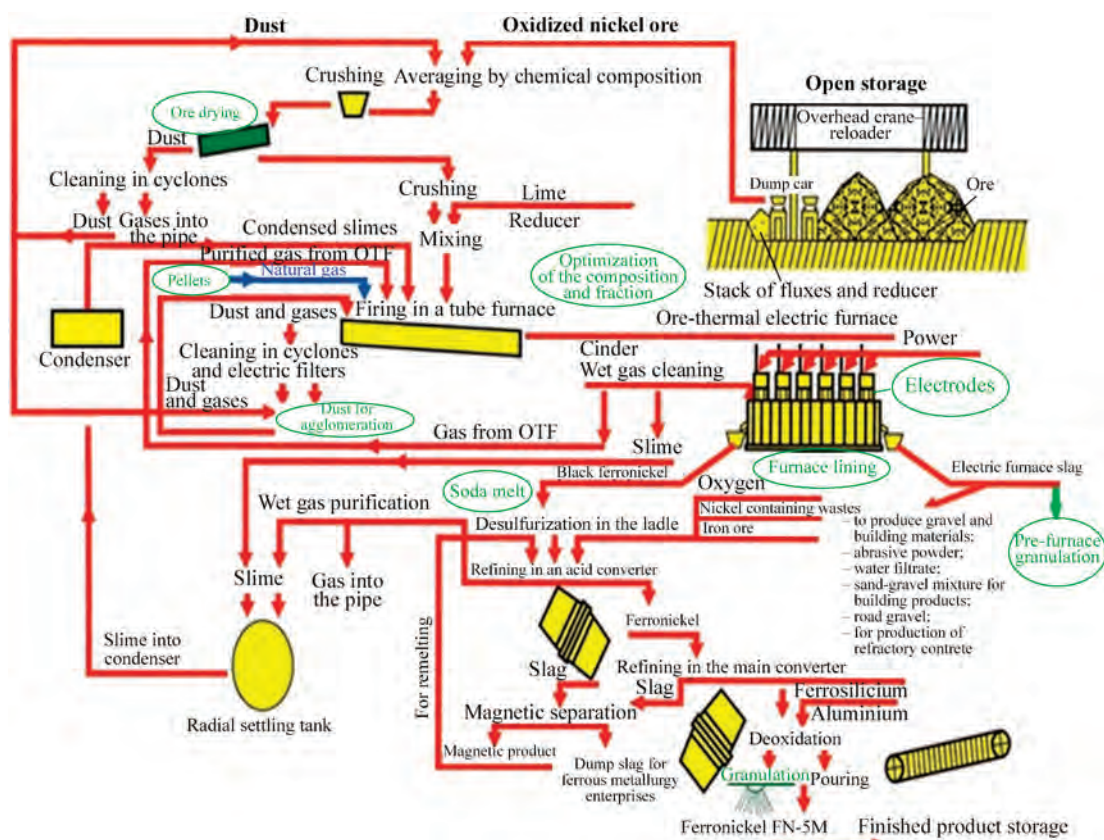


Figure 1. Acting technology scheme of ferronickel production at PFP [12]

producing directly in electric furnaces a high-percent-age black nickel, containing 30–50 % Ni and practically hundredth fractions of carbon and silicon (0.02 and 0.01 %, respectively), which influence desulfurization of black ferronickel with soda in the ladle.

The technology scheme of ferronickel production in electric furnaces includes the following stages [12, 13] (Figure 1): preparation and averaging of nickel-containing ore in an open storage; ore drying, charge material dosing and roasting of the charge, consisting of ore, limestone, anthracite and back dust, in tubular rotary furnaces; electric melting of black ferronickel in ore-thermal furnaces (RTP-1 and RPT-2) using hot charge (cinder) from tubular rotary furnaces, refining of a mixture of black ferronickel from two furnaces by the methods of out-of-furnace desulfurization of the melt in the ladle with soda ash or soda melt; successive refining of black ferronickel from silicon, chromium, carbon, sulfur and phosphorus in converters with acid and basic lining with upper oxygen blowing (duplex-process); pouring refined ferronickel in conveyor-type filling machines or water granulation; release and granulation of electric furnace slag, which is disposed as construction gravel and abrasive materials.

Charge for firing in drum furnaces consists of the following components: 1 t of dry ore; 352 kg of limestone; 106 kg of anthracite coal and 5 kg of back dust. The furnace diameter is 3 m and length is 75 m. The firing zone in the furnace is 9–12 m. The fuel used is

pulverized coal fuel (PCF) [14, 15]. The flame temperature reaches 1200 °C, and the charge is heated to not more than 850 °C, to avoid overheating and formation of ring deposits. The furnaces operate on counterflow principle. The duration of material staying in TRF is 1.5–2.0 h.

The process of firing in tubular rotary furnaces is divided into three zones: drying; heating; and firing. In the drying zone, starting from the loading end of the furnace, the raw material is heated up to 120 °C with removal of free (hygroscopic) moisture. In the heating zone the raw material is heated up to 700–800 °C with partial removal of crystallization moisture, present in the composition of mineral compounds. In the firing zone the raw material is heated up to 900–1000 °C. This process is accompanied by decomposition and partial reduction of nonferrous metal oxides, and higher iron oxides to oxide and removal of crystallization moisture.

During firing the temperature should be in the range of 950–1000 °C, evolving gases temperature should be not lower than 420 °C, the amount of gases released from TRF is up to 55000 m³/h. The gas composition here changes in the following ranges, %: CO₂ — 5–15, O₂ — 2–5; CO — absent; N₂ — balance.

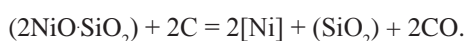
Reduction electric melt of nickel ore to produce ferronickel consists of 65–85 % slag from the loaded cinder and 10–18 % of black ferronickel.

Two ore-smelting (three-phase, six-electrode) AC electric furnaces of installed power of 48 MV.A are operating at Pobuzky Ferronickel Plant. Electrode diameter is 1200 mm, distance between electrode axes is 3200 mm; electrodes are located vertically, suspended from three hydraulic cylinders, which ensure electrode travel (along the vertical) of 1400 mm. The electrodes are continuous self-sintering.

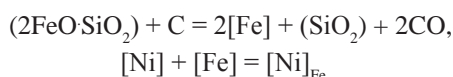
Electric melting is performed using cinder with 600–700 °C temperature of the following composition, %: 0.7–0.9 Ni; 0.03–0.05 Co; 15–18 Fe; 45–36 SiO₂; 16–20 CaO; 4–6 MgO. Cinder reduction proceeds due to the use of carbon of anthracite of AC grade or culm of ASh grade, thermal coal and silicon-carbide material [15].

During reduction melting, iron and nickel pass from the oxide melt into metal phase. Part of the nickel oxides interacts with silica from silicates of 2 (Fe, Ni)O·SiO₂ type and forms nickel silicates [16, 17].

In Ni–O–Si system one compound 2NiO·SiO₂, nickel orthosilicate, is crystallized, which at the temperature of about 750 °C can be reduced with carbon by the following reaction



At 900–1100 °C CO₂ content in the gas phase is equal to 60–75 %. Nickel dissolution in iron occurs by the following reactions

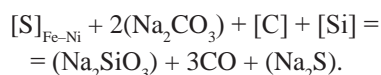


and it promotes process recovery. Phosphorus and sulfur easily transform into the metal phase — ferronickel.

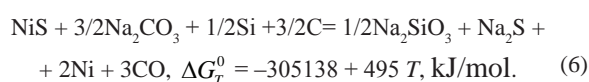
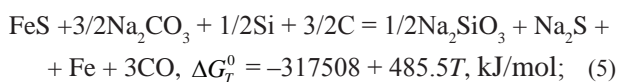
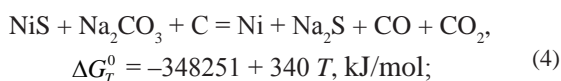
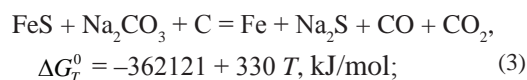
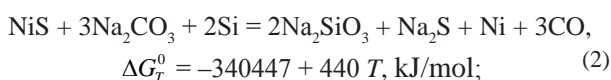
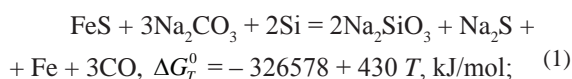
Special attention should be given to silicon and carbon content, the concentration of which determines the metal temperature and solubility of the latter in it. Silicon has the strongest influence on carbon solubility in black ferronickel. Increase of silicon content lowers the equilibrium concentration of carbon dissolved in black ferronickel.

Optimal silicon content in black ferronickel is 3–4 % [7]. Here, the process of out-of-furnace desulfurization is more complete. Lowering of silicon content impairs the indices of further ferronickel refining process. Higher silicon content leads to the need to increase the consumption of cooling additives during conversion.

As black ferronickel contains a large amount of sulfur, which enters the melt with carbon reducing agent and ore, it is subjected to out-of-furnace ladle desulfurization with soda (sodium carbonate) [13, 17, 18]. It yields ferronickel corresponding to FN-6 grade by its composition, which is used in foundry. The process of sulfur removal can be generalized by the following reaction:



Temperature dependencies of Gibbs free energies of the possible reactions of sulfur interaction with soda are given below:



Analysis of the derived results shows that compared to carbon, silicon has a thermodynamically more effective influence on desulfurization in the system (Figure 2), although some production specialists note that it is exactly carbon, which has the strongest influence on desulfurization process, that is probably related to the kinetic parameters of the process – influence of the gas phase (CO content) on reagent stirring and increase of their contact surface.

Equilibrium phase distribution in 0.5FeS + 0.5NiS + 3Na₂CO₃ system was determined using HSC Chemistry 6.0 Program data base, which was developed by the specialists of Research Center of Outotec Company.

The process of intensive desulfurization of nickel sulfide starts at the temperature of 500 °C and is over at approximately 1000 °C, and that of iron sulfide – at 750 and 1250–1350 °C, respectively. Degree of nickel desulfurization with soda is equal to 94–96 %, that of iron is 60 %, and with process temperature increase above 1350 °C its resulfurization is possible.

Equilibrium phase distribution in the complex system of FeS–NiS–Na₂CO₃–C–Si allowed determination of the optimal temperature mode of ladle desulfurization of ferronickel with soda, which is in the range of 1300–1350 °C.

During ferronickel desulfurization (0.13–0.40 % S) in the ladle with soda (consumption of 4–5 % of the metal weight) the degree of desulfurization is equal to 50–60 %, and the minimal sulfur content at the level of 0.048 % is reached in practice. To ensure the high

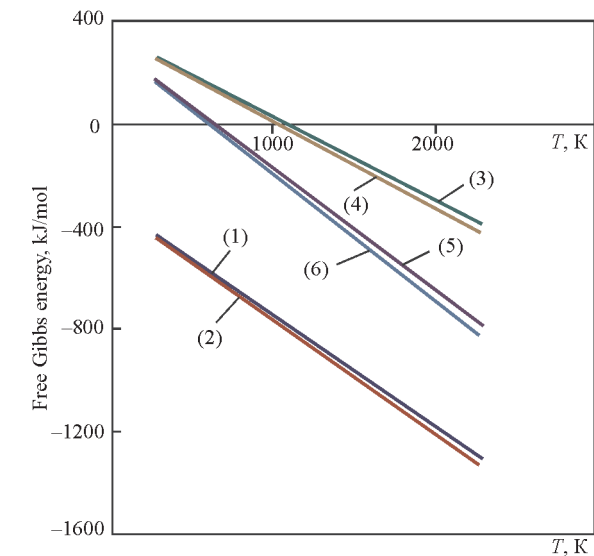


Figure 2. Free Gibbs energy for possible reactions (1)–(6) of sulfur interaction with soda

efficiency of desulfurization with soda in the ladle, it is necessary to eliminate the possibility of electric furnace slag ingress at metal release, as soda interaction with silicon dioxide and Na_2SiO_3 formation lead to its considerable losses that requires repeated metal processing by this scheme after loading the soda slag.

Chemical composition of black ferronickel, depending on the quality of nickel-containing raw materials from different deposits, is given in Table 2.

After commissioning of RTP-1 of HATCH Company, Canada, and introduction of the technology of low iron reduction (TLIR), it became possible to produce ferronickel, which contains only hundredth fractions of a percent of silicon and carbon that eliminates the possibility of its out-of-furnace refining with soda. Here, sulfur content increased two times, and was equal to 0.2–0.5 %, and electrode mass consumption was significantly increased.

That is why, the Plant developed and introduced a comprehensive technology, which envisages mixing black ferronickel, released from RTP-1 with a lower content of silicon and carbon (to 0.01 %) and high Ni content (higher than 50 %) with an alloy from RTP-2 with a low concentration of nickel (10–17 %) and high concentration of silicon and carbon, so necessary for soda desulfurization in the ladle.

Mixing allowed returning to project technology – out-of-furnace desulfurization with calcinated soda in

a ladle and finishing metal in the ladle. At present the technology of low reduction of iron has been mastered at Pobuzky Ferronickel Plant in RTP-1. Here, nickel content in black ferronickel increased up to 50 %, and silicon and carbon content was equal to only 0.01 % that makes the process of ladle desulfurization with soda more complicated.

Soda slag, forming during out-of-furnace desulfurization, is thoroughly scraped from the metal surface in the amount of 350–600 kg with wooden scrapers into a technological bowl, specially designated for this purpose. After desulfurization before pouring into acid converter the weight of black ferronickel, remaining in the ladle, with part of the soda slag, changes in the range of 34.95–37.80 t of the following composite, %: 14.1–15.5 Ni; 0.23–0.26 Co; 3.3–3.7 Si; 0.045–0.073 S; 1.4–15 Cr; 2.4–2.6 C; 0.093–0.1 P; 0.052–0.059 Cu, the temperature of which varies in the range of 1200 to 1250 °C.

Comparative analysis of technical indices of the process of black ferronickel refining by the three schemes (Table 3) shows that the most efficient is the project technology, by which both the furnaces are operating for complete reduction. Analyzing the indices of RTP-1 and RTP-2 operation by the technology of melt mixing at release from the furnace, it should be noted that RTP-2 operates more efficiently in production of black ferronickel, as over the same operation period at Ni content of 45.22 % in the alloy in the first furnace its release is by 34 % less, than in the other furnace with 10.53 % Ni content.

Black nickel refining by the experimental technology required increasing the consumption of ferro-silicium, additionally using aluminium and lime. The melting time is increased by 26 and 40 %, respectively, compared to the mixing and project technology, and process productivity is also decreased considerably by 52.2 and 60 %, respectively.

Comparison of specific material consumption for refining and removal of 1 kg of sulfur again confirmed the higher efficiency of project scheme (Table 4), which is based on desulfurization of nickel cast iron.

Ferronickel partially cleaned from sulfur, is poured into the converter with acid fire-resistant lining and it is subjected to oxygen blowing to remove silicon and chromium [19].

Table 2. Chemical composition of black ferronickel, melted using raw materials from different deposits, wt. %

Deposit	Ni	Si	Cr	C	S	P
Ukraine	7.86	4.79	2.80	3.50	0.35	0.012
New Caledonia	16.89	1.93	1.29	2.84	0.30	0.020
Indonesia	18.51	4.02	1.53	2.55	0.26	0.0313
Guatemala (old technology)	13.41	3.41	2.11	2.79	0.17	0.053
Guatemala (TLIR)	37.30	0.01	0.04	0.03	0.48	0.064

Table 3. Technical indices of out-of-furnace desulfurization of black ferronickel by different technology schemes

Parameter	Technology schemes			
	Experimental (01.11.2020– 09.02.2021)	Mixing		Project
		RTP-1	RTP-2	
Black ferronickel, t	3341.6	1022.1	5889.25	10525
Nickel, t	1406.8	462.55	619.6	1418
Ni content, %	42.1	45.22	10.53	13.48
S content, t	0.283	0.36	0.089	0.298
CaCo ₃ consumption, t	48.0	805.5		305
FeSi consumption, t	70.0	18.56		48.15
Soda consumption, t	87.17	73.85		117.7
Al consumption, t	13.75	–		–
Lime consumption, t	239.0	–		Fe ore 79
Melting time, h	2.15	1.7		0.70/0.84
O ₂ blowing, min	20.6	21.64		8.12/15.21
O ₂ flow rate, nm ³	228630	194402/286645		320058/107991
Produced				
Commercial FeNi, t	2600	5920		9130
Nickel, t	1521	1119.6		1584
Ni content, %	54.53	18.9		17.4
Ni removal, %	92.4	95.9		96.6
S content, %	0.059	0.043		0.068
Slag ratio	0.60	0.40		0.26
Nickel in slag, %	0.52	0.19/0.14		0.180/0.226
Sulfur removal, t	0.792	0.635		2.516

The finished alloy is poured in conveyor machines. Product weight is 40–50 kg. Slag from the main conversion has the following composition, %: CaO — 15–20; SiO₂ — 5–10; FeO — 35–50; Ni — 0.05; Co — 0.005; Cr₂O₃ — 1–10.

Slags from acid and basic conversion are subjected to magnetic separation to extract ferronickel particles. Specific power consumption for metallurgical processing of 1 t of dry nickel-containing ore is equal to 810 kW·h/t, or 78200 kW·h per 1 t of nickel. The processes of refining black ferronickel in acid and basic converters allow producing commercial alloy, meeting the requirements of world standards.

Production of ferronickel from oxidized nickel ores is based on application of raw materials, where nickel content is practically not higher than 2.5 %, so that the process is characterized by a large volume of slag, the ratio of which is 6–10 units, and it is the highest in ferroalloy electrothermy.

The most important aspect of recycling ferroalloy slags is their separation into the oxide and metal phases, the content of which is higher than 10 % in some cases.

Nowadays different methods of separation of the metal and oxide components of the slags are applied in the world practice, starting from manual selection up to modern X-ray radiometric separation, although technologies based on gravity and magnetic processes became the most widely accepted.

Based on the results of studying the samples of electric furnace and refining slags from ferronickel production using oxidized nickel ore from the Guatemala deposit, the method of X-ray spectral microanalysis (XSMA) analysis performed in Selmi PEM-1061 unit was applied to determine that the main amount of nickel is concentrated in metal phase shot of different shape in compounds with iron and sulfur, the concentration of which is up to 70 % in some cases. No nickel was found in the oxide phase of the slags, and it is probably contained in microshot.

Table 4. Material consumption for refining and desulfurization of black ferronickel, kg/kg of sulfur

Material	FeNi production schemes		
	Experimental	Mixing	Project
Soda ash	110	116	44
Limestone	61	267	121
Ferrosilicium	88.4	29.2	19.14
Aluminium	17.4	–	–
Lime	301	–	–
Oxygen, nm ³	288	757	170

The studied high-manganese (31.5–34.7 % MgO) acid ($\text{CaO} + \text{MgO}_2/\text{SiO}_2 = 0.72\text{--}0.74$) electric furnace granulated slags from ferronickel production, containing up to 0.31 % Ni, are represented by 0.5–5.0 mm fraction by more than 95 %, and refining highly basic ($(\text{CaO} + \text{MgO})/\text{SiO}_2$ higher than 3.0), which are self-disintegrating, with nickel concentration from 9.3 up to 10.95 %, are represented by less than 0,5 mm fraction practically by 40 %.

Based on investigation of the features of initial raw material and its movement in the working zones of separation units, a new method was developed for ferroalloy slag enrichment, both by gravity separation method, and by wet method using an upgraded magnetic separator, adapted to the characteristics of the initial raw material, which allowed increasing the indices of nickel extraction from electric furnace slags.

The schematic of refining slag processing (Figure 3) envisages feeding slag crushed in the ball mill, into gravity separator, where its separation into size grades takes place. The material of 0.4–1.6 and + 1.6 mm size fractions is fed to the magnetic separator,

where it is separated into the magnetic (metal) and nonmagnetic (slag) fractions.

Performed studies of slag enrichability in ferro-nickel production by the developed technology scheme allowed producing from them metal concentrate, containing 0.9–4.75 % nickel with the yield of 2–5 % of initial raw materials.

Performed studies on the classification and enrichment of the refining slags showed that slag fraction larger than + 1.6 mm contains 38 % of nickel at its yield of 10–14 %, and in the size grades from 0.16 up to 1.6 mm with the total yield of 43.6 % nickel content is equal to 21.94 %. In dump refining slags nickel content is not higher than 0.5 % that is 18.6–21.9 times lower than in the initial material.

The developed and proposed for introduction technology schemes of enrichment of electric furnace slags by the wet technology and of refining slags by the dry technology allow recycling close to 1200 t of nickel per year, or extracting 31.6 and 94.65 % nickel from the slags, respectively. At the world price of nickel of 18525 USD, formed by the end of 2021, the total cost effect will be equal to 22.23 mln USD.

Thus, the limited scope of the journal paper does not allow fully disclosing all the innovations and developments, performed by the staff of Electrometallurgy Department of the Ukrainian state University of Science and Technologies under the leadership of M.I. Gasik and introduced at the Plant with the assistance of scientific-technical staff and its management, many of whom are the graduates of this Department, which enabled the Plant to joint the TOP-5 of enterprises of the metallurgical complex of Ukraine on currency earnings, and the parameters of its electro-thermal equipment and electrotechnological modes

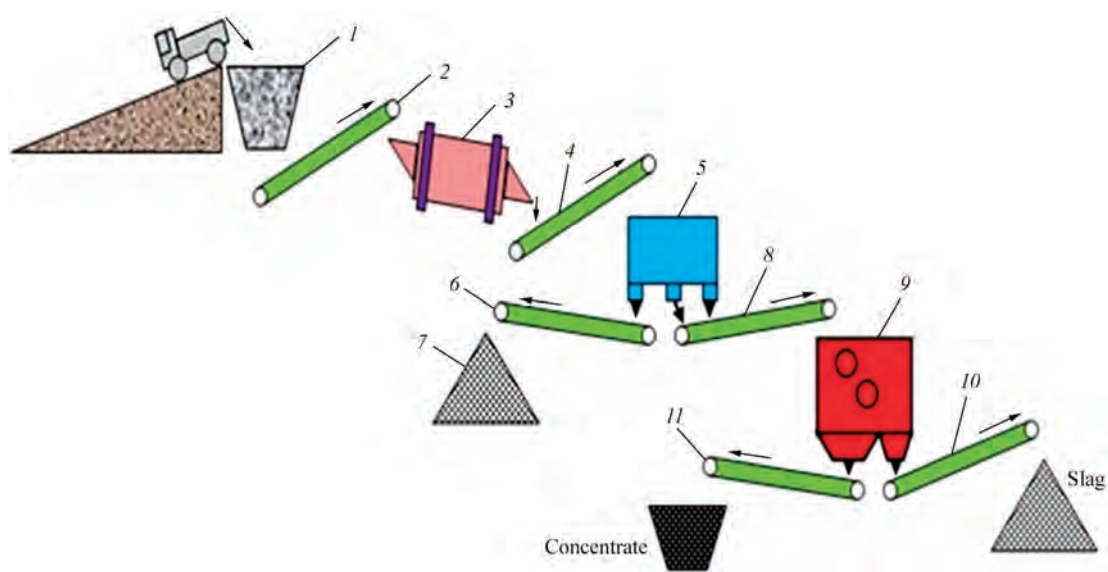


Figure 3. Technological line for processing refining slags: 1 — receiving hopper with feeder; 2, 4, 6, 8, 10, 11 — belt conveyors; 3 — ball mill; 5 — gravity separator; 7 — fraction stacking (0.16 mm); 9 — magnetic separator

of its operation were incorporated in the construction of enterprises by foreign SinoSteel Group Co (China) and Solvij (Indonesia) Companies.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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